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FEBRUARY, 1944

A II—ORGANIC CHEMISTRY

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BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

FEBRUARY, 1944.

I.—ALIPHATIC.

Isomorphous replaceability of bivalent atoms and ψ-atoms in organic compounds. A. Lüttringhaus (*Ber.*, 1940, **73**, [*B*], 1022—1023).—A reply to Bruni (A., 1943, II, 308). Valency angles are considered. R. S. C.

Behaviour of the free *n*-propyl radical. G. Semerano, L. Riccoboni, and L. Götz (*Z. Elektrochem.*, 1941, **47**, 484—486).—From the amounts of C_3H_6 and C_3H_8 produced by the thermal decomp. of $AgPr^{\alpha}$ it is concluded that ~77% of the Pr^{α} radicals initially formed disproportionate to C_3H_6 and C_3H_8 and the remainder dimerise to *n*-C_6H_{14}. J. F. H.

Optical rotation and atomic dimension. The four optically active β-halogenopentanes. D. H. Brauns (*J. Res. Nat. Bur. Stand.*, 1943, **31**, 83—106).—The enantiomorphic modifications of pentan-β-ol (I) have been prepared in the pure state and the lævorotatory isomeride has been converted into dextrorotatory β-Cl-, -Br-, and -I-derivatives. Lævorotatory β-CHMePr^{α}F is obtained from the dextrorotatory β-bromo- or -iodo-pentane and AgF. The derivatives obtained by halogenation of the alcohol with $PHal_3$ have higher [α] than those obtained by use of HHal. The purity of the Cl-, Br-, and I-derivatives is ~70—80%; the optical purity of the F-derivative, the prep. of which involves another Walden inversion, is less. The relative amounts of the isomeric modifications are determined by the purity of the alcohol obtained by hydrolysis and the relative optical rotations of the pure F-, Cl-, Br-, and I-derivatives are calc. All halogen derivatives of (I) of like configuration have the same sign of optical rotation. The difficulty of obtaining optically pure compounds on account of incomplete Walden inversion (partial racemisation) prevents an adequate check of the rule according to which for compounds in which the halogen is directly attached to the asymmetric C the differences of sp. rotations of the *d*- or *l*-compounds (Cl — F), (Br — Cl), and (I — Br) have the same numerical relation as the differences of the respective at. radii of the neutral halogen atoms. The experimental data, however, in no manner contradict the rule, the deviations which are observed being plausibly explained by the incompleteness of the Walden inversion. H. W.

Hydrogenation of the triple linking. A. L. Henne and K. W. Greenlee (*J. Amer. Chem. Soc.*, 1943, **65**, 2020—2023).—CH:CAlk in liquid NH_3 are quantitatively reduced to *trans*-olefines by Na and $(NH_4)_2SO_4$ (insol. in liquid NH_3); NH_4Cl, which is sol. in liquid NH_3, gives inefficient reduction; thus, H generated from an acetylene is more efficient than H generated from NH_4^+; the function of the NH_4 salt is to regenerate the acetylene from its Na derivative. Reduction of CAlk:CAlk′ by Na and NH_4 salts is inefficient, some H_2 escaping and an excess of Na being consumed; the Na probably adds to the C:C. Catalytic hydrogenation of acetylenes to olefines is best effected by Ni–kieselguhr in EtOH at 30—80°/3 atm.; it yields mainly *cis*-olefines (cf. Campbell *et al.*, A., 1941, II, 216; 1942, II, 71). The following are prepared: Δ^{α}-, m.p. −102·56°, b.p. 121·37°, *trans*-Δ^{β}-, f.p. −87·8°, b.p. 124·94°, *trans*-Δ^{γ}-, f.p. −110·05°, b.p. 123·29°, and *trans*-Δ^{δ}-, f.p. −93·80°, b.p. 122·37°, "*cis*"-Δ^{β}-, f.p. −100·5°, b.p. 125·62°, "*cis*"-Δ^{γ}-, f.p. −137° to −138°, b.p. 122·7°, and "cis"-Δ^{β}-*n*-octene, f.p. −120·2°, b.p. 122·8°; "*cis*"-Δ^{β}-, f.p. −141·4°, and -Δ^{γ}-*n*-hexene, f.p. −143·3°; "*cis*"-Δ^{ϵ}-*n*-decene, f.p. −112·8°. With Na and $(NH_4)_2SO_4$ in NH_3, $[CH_2]_3(C{:}CH)_2$ and $[CH_2]_3(C{:}CMe)_2$ give $\Delta^{\alpha\zeta}$-heptadiene, f.p. −129·35°, b.p. 90·01°, and impure *trans-trans*-$\Delta^{\beta\eta}$-nonadiene (I), f.p. −76·2°, b.p. 150·5°. (I), prepared by Na alone, is purer and has f.p. −72·4°, b.p. 150·3°. Catalytic hydrogenation gives impure *cis-cis*-$\Delta^{\beta\eta}$-nonadiene, a glass, b.p. 151·0°. R. S. C.

Substituted acetylenes and their derivatives. XLVI. Formaldehyde derivatives of acetylenic hydrocarbons. G. F. Hennion and E. P. Bell (*J. Amer. Chem. Soc.*, 1943, **65**, 1847—1848; cf. A., 1942, II, 327).—Adding $RCO_2{\cdot}CH_2Cl$ to finely dispersed CR:CNa (prep. *in situ* described) in C_6H_6–N_2 and then boiling gives Δ^{β}-*n*-*heptinenyl acetate* (16%), b.p. 82—83°/7 mm., *propionate* (21%), b.p. 70—71°/4 mm., and *benzoate* (10%), b.p. 160—162°/2 mm., and *n*-$C_5H_{11}{\cdot}C{:}C{\cdot}CH_2{\cdot}OAc$ (10%), b.p. 79—81°/6 mm.; coating of the CR:CNa with NaCl prevents more than initial reaction. $CH_2Cl{\cdot}OAc$ does not react with CH:CNa in Et_2O or C_6H_6; $CBu^{\alpha}{:}CNa$ cannot be obtained sufficiently fine in Et_2O to react. $CH_2Cl{\cdot}OR$ and $CBu^{\alpha}{:}C{\cdot}MgBr$ in Et_2O give Me (42%), b.p. 80—81°/29 mm., *Et* (27%), b.p. 77—78°/20 mm., and Pr^{α} Δ^{β}-*n-heptinenyl ether* (34%), b.p. 60—62°/6 mm.; $(CH_2Cl)_2O$ in presence of a little CuCl gives *di*-Δ^{β}-*n-heptinenyl ether* (21%), b.p. 140—142°/6 mm. CH_2Br_2 does not react with $CBu^{\alpha}{:}CNa$ in liquid NH_3 (gives much tar) or $CBu^{\alpha}{:}C{\cdot}MgBr$ in Et_2O. $CH_2{\cdot}SO_4$, $CBu^{\alpha}{:}C{\cdot}MgBr$, and a trace of CuCl in boiling Et_2O give $\Delta^{\epsilon\theta}$-n-*tridecadi-inene* (13%), b.p. 108—110°/8 mm. *d*, *n*, and [*M*] are given for the products. R. S. C.

Radioactive exchange and adsorption of methyl bromide with several inorganic bromides.—See A., 1944, I, 42.

βββ-Trifluoroethyl iodide. H. Gilman and R. G. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 2037—2038).—$CF_3{\cdot}CHN_2$ with HI–PhMe at −75° gives *βββ-trifluoroethyl iodide* (I) (77%), b.p. 54·5—55°/730 mm., obtained only in 4—5% yield from $CF_3{\cdot}CH_2{\cdot}OH$ by I–P. With Mg in Et_2O–N_2, (I) gives no Grignard reagent (Michler's ketone test) but instead $CH_2{:}CF_2$, b.p. 91°/740 mm. R. S. C.

Electrolysis of the nitroparaffins. R. Pearson and W. V. Evans (*Trans. Electrochem. Soc.*, 1943, **84**, *Preprint* 21, 227—231).—Electrolysis of $MeNO_2$ containing 1% of NMe_3 between Pt electrodes at 15° with c.d. 0·8—2·4 amp. per dm.² gives at the cathode NHMe·OH (oxalate, m.p. 157—158°; sulphate, m.p. 129°) in 53% yield and at the anode $NO_2{\cdot}[CH_2]_2{\cdot}OH$, b.p. 191·5°, in 25% yield, identified further by reduction to $NH_2{\cdot}[CH_2]_2{\cdot}OH$; NO, NH_2OH, and some $CH_2{:}N{\cdot}OH$ are also obtained. Under similar conditions $EtNO_2$ affords NHEt·OH (oxalate, m.p. 95—96°) in 40% yield and $NO_2{\cdot}[CHMe]_2{\cdot}OH$ in 25% yield with some NH_2OH and apparently $CHMe{:}N{\cdot}OH$. In aq. alkali NH_2OH does not result and the solution contains NO_3' but not NO_2'; O_2 is evolved at the anode. $Pr^{\beta}NO_2$ and NMe_3 give a green solution probably containing $NO{\cdot}CMe_2{\cdot}NO_2$; on electrolysis $NHPr^{\beta}{\cdot}OH$ is formed at the cathode and $COMe_2$ at the anode with a residue of high b.p. In presence of NaOH there is no production of NH_2OH but there is a 15% yield of dinitro-βγ-dimethylbutane which causes partial polarisation of the anode, at which O_2 is evolved. H. W.

Anode reactions in the electrolysis of ethyl alcohol.—See A., 1944, I, 43.

Catalytic dehydrogenation. I. Catalytic conversion of alcohols into aldehydes, paraffins, and olefines. E. J. Badin (*J. Amer. Chem. Soc.*, 1943, **65**, 1809—1813).—Catalytic changes of n-$C_xH_{2x+1}{\cdot}OH$ (x = 5, 8, 9, 10, and 16) in presence of Raney Ni at 140—275° are reported. Reactions are successively: loosening of an α-H; $R{\cdot}[CH_2]_3{\cdot}OH \rightarrow R{\cdot}[CH_2]_2{\cdot}CHO + H_2$; $R{\cdot}[CH_2]_2{\cdot}CHO \rightarrow CHR{:}CH_2 + CO + H_2$; $CHR{:}CH_2 + H_2 \rightarrow CH_2MeR$; and, slowly, $CO + 3H_2 \rightarrow CH_4 + H_2O$. At 140° only aldehyde is formed. Max. amounts of aldehyde (measured as 2 : 4-dinitrophenylhydrazone; probably present largely as acetal) are obtained at 200—215°, of CH_2MeR at 250°, and of olefine at 275°. Temp. is thus the main factor. n-*Decaldehyde*-2 : 4-*dinitrophenylhydrazone* has m.p. 104°. R. S. C.

Reaction between alcohols and metal oxides. E. Berner (5 *Nordiske Kemikermøde*, 1939, 231—232).—Anhyd. MeOH and CaO give basic Ca methoxide, of very variable composition, which reacts with more MeOH to give $Ca(OMe)_2$ and H_2O. $Sr(OMe)_2$ and $Ba(OMe)_2$ are freely sol. in MeOH at room temp.; their pptn. on heating is due to conversion into an unsolvated modification. PbO and MeOH at room temp. in sunlight or Hg-vapour light give finely-divided Pb; the reaction is quantitatively reversed in darkness. M. H. M. A.

Leaf alcohol. IV. *trans–cis* Problem of the leaf alcohol, Δ$^{\gamma}$-*n*-hexen-α-ol. S. Takei, M. Ono, and K. Sinosaki (*Ber.*, 1940, **73**, [*B*], 950—955; cf. A., 1939, III, 536).—H_2–Pd–$BaSO_4$ converts $CEt{:}C{\cdot}[CH_2]_2{\cdot}OH$ (I) in Et_2O at −18° into *trans*- (II) (96%) (3 : 5-dinitrobenzoate, m.p. 49°; allophanate, m.p. 146°; anthraquinone-2-carboxylate, m.p. 68°) but in xylene at 100° into *cis*-$CHEt{:}CH{\cdot}[CH_2]_2{\cdot}OH$ (III) (3 : 5-*dinitrobenzoate*, m.p. 28°; allophanate, m.p. 143°; anthraquinone-2-carboxylate, m.p. 50°), and in C_6H_6 at 50° into a mixture (cf. Stoll *et al.*, A., 1939, II, 2). Complete hydrogenation in Et_2O yields n-$C_6H_{13}{\cdot}OH$ (3 : 5-dinitrobenzoate, m.p. 59—60°). (II) is identical with the natural product (A., 1938, II, 345). (III) is also obtained from Et_2 sorbate by reduction by Na. The dibromide, b.p. 119—122°/6 mm. (4′-*iododi-*

phenylylurethane, m.p. 127°), of (**II**) with KOH–aq. EtOH in the cold gives $C_6H_{10}Br{\cdot}OH$, b.p. 68—69°/3 mm. (*allophanate*, m.p. 171°), and thence at the b.p. (**I**), b.p. 69—71°/16 mm. [*allophanate* (**IV**), m.p. 187°; 3 : 5-*dinitrobenzoate*, m.p. 72°; *anthraquinone-2-carboxylate*, m.p. 129°] (cf. *loc. cit.*), regenerated by distilling (**IV**) + KOH in steam and oxidised by aq. $KMnO_4$ at 70° to $EtCO_2H$.

R. S. C.

Volatile vegetable compounds. XXV. Presence of Matsutake's alcohol (Δ^{α}-*n*-octen-γ-ol) and of 3-methyl*cyclo*hexanol in oil of pennyroyal [*Mentha puleguim*, L.]. Y. R. Naves (*Helv. Chim. Acta*, 1943, **26**, 1992—2001).—Different samples of the oil of Spanish origin which contain piperitenone and *n*-octan-γ-ol also contain octenols. In one such sample *d*-*n*-octan-γ-ol, Δ^{α}-*l*-*n*-octen-γ-ol, and 3-methyl*cyclo*hexanol have been identified; other alcohols are present. dl-n-*Octan-γ-yl allophanate*, m.p. 155·5—156°, appears new. *d*-*n*-Octan-γ-yl allophanate has m.p. 182—182·5°. H. W.

Optically active phytol. P. Karrer, A. Geiger, H. Rentschler, E. Zbinden, and A. Kugler (*Helv. Chim. Acta*, 1943, **26**, 1741—1750).—Partly racemised (+)-citronellol (**I**), b.p. 106—108°/12 mm., $[\alpha]_D^{15}$ +2·9°, is hydrogenated (Pt) to (+)-dihydrocitronellol, b.p. 104—107°/12 mm., $[\alpha]_D^{15}$ +2·56°, which is converted by PBr_3 at 0° into (−)-dihydrocitronellyl bromide, b.p. 98—100°/12 mm. This is condensed with $CHAcNa{\cdot}CO_2Et$ to Et (−)-βζ-dimethyloctylacetoacetate, b.p. 155°/12 mm., ϕ −1·6°, hydrolysed by KOH–MeOH at room temp. to (+)-*hexahydro-ψ-ionone* (**II**), b.p. 122°/12 mm., $[\alpha]_D^{15}$ +0·55°, which is purified to optical homogeneity through the *semicarbazone*, m.p. 95°. (**II**) and C_2H_2 afford γηλ-*trimethyl*-Δ^{α}-*dodecinen-γ-ol*, b.p. 140—142°/13 mm., ϕ +0·82°, converted by partial hydrogenation (Pt or Pd) into γηλ-*trimethyl*-Δ^{α}-*dodecen-γ-ol*, b.p. 142—144°/13 mm., which gives successively γηλ-*trimethyl*-Δ^{β}-*dodecenyl bromide* (which could not be purified), Et γηλ-trimethyl-Δ^{β}-dodecenylacetoacetate, and (−)-ζκξ-*trimethyl*-Δ^{ϵ}-*pentadecen-β-one* (**III**), b.p. 175—178°/11 mm., ϕ_D −0·20°. Thus far the compounds contain only one asymmetric C but partial reduction of (**III**) involves the formation of a second asymmetric centre. Only one (−)-ζκξ-*trimethylpentadecan-β-one*, b.p. 168—172°/11 mm., ϕ_D −0·24°, appears to be formed as judged by the behaviour of the cryst. *semicarbazone*, m.p. 68°, $[\alpha]_D^{15}$ −0·35° in EtOH. Optical homogeneity at $C_{(\zeta)}$ is not regarded as definitely established. Addition of C_2H_2 to the ketone leads to γηλο-*tetramethyl*-Δ^{α}-*hexadecinen-γ-ol*, b.p. 159—164°/0·6 mm., ϕ_D −0·2°, transformed by partial catalytic hydrogenation into (−)-γηλο-*tetramethyl*-Δ^{α}-*hexadecen-γ-ol* [(−)-iso*phytol*], b.p. 136—141°/0·1 mm., ϕ_D −0·2°, transformed by PBr_3 into phytyl bromide, converted by KOAc in $COMe_2$ followed by hydrolysis into (−)-*phytol* (**IV**), b.p. 132°/0·02 mm., ϕ 0·18°. Since the processes involved in the production of (**IV**) are analogous to those used in the isolation of chlorophyll phytol, the optical inactivity of the latter compound is not due to racemisation during isolation. Re-examination of a phytol obtained from stinging nettles has disclosed an optical activity equal in magnitude but opposite in sign to that of (**IV**). The reality of the observation is established by ozonisation of the compound to (+)-ζκξ-trimethylpentadecan-β-one with ϕ +0·22° (synthetic ketone −0·22°). Further the ketone is oxidised (CrO_3) to (+)-γηλ-trimethyltridecoic acid, ϕ +0·2—0·24°. An optically active, dextrorotatory phytol, therefore, is sometimes found in the plant of which (**IV**) may be the optical antipode. Previous observations of optically inactive phytol in plants are due to the natural occurrence of both *d*- and *r*-phytol. H. W.

Vitamin-A_2. P. Karrer and E. Bretscher (*Helv. Chim. Acta*, 1943, **26**, 1758—1778).—The unsaponifiable matter of winter trout-liver oil is largely freed from sterols by freezing and purified by repeated chromatography over $Ca(OH)_2$ followed by distillation in a cathode-ray vac. The best specimens of vitamin-A_2 thus obtained still contain ~2—3% of -*A* as judged by the yield of geronic acid after ozonisation. This result invalidates the formulæ for -A_2 proposed by Gillam *et al.* (A., 1938, III, 315) and by Gray (A., 1942, II, 185). The isolation of $COMe_2$ and CH_2O by the ozonisation of -A_2 indicates that it may be a mixture of isomerides,
$CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}[CMe{:}CH{\cdot}CH{:}CH]_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}OH$ and
$CH_2{:}CMe{\cdot}[CH_2]_2{\cdot}[CMe{:}CH{\cdot}CH{:}CH]_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}OH$, similar to that occurring in natural citronellal. It is, however, possible that the production of CH_2O is due to an isomerisation within the mol. under the action of O_3 since -*A* gives the product in smaller amount than -A_2 and nearly equal amounts are derived from carotene and lycopene; in these cases it is undoubtedly due to subsidiary reactions or isomerisations. The constitution of -A_2 is confirmed by its hydrogenation to dihydrophytol, isolated as the allophanate, m.p. 73°. The purest specimens of -A_2 have ~1/10th of the physiological activity of -*A*; this is due in part to the presence of -*A*, but it appears that the rat has a limited capacity to cyclise -A_2 to -*A*. H. W.

Derivatives of α-bromo-β-methyl-*n*-valeric acid. C. D. Hurd and F. W. Cashion (*J. Amer. Chem. Soc.*, 1943, **65**, 2037).—$CHMeEt{\cdot}CH_2{\cdot}CO_2H$ with red P–Br at 95° gives *α-bromo-β-methyl-n-valeryl bromide* (54%), b.p. 98—100°/23 mm., and thence the *amide*, m.p. 104°, *anilide*, m.p. 84°, and *p-toluidide*, m.p. 105°.

R. S. C.

Course of autoxidation reactions in polyisoprenes and allied compounds. VII. Rearrangement of double linkings during autoxidation. E. H. Farmer, H. P. Koch, and D. A. Sutton (*J.C.S.*, 1943, 541—547; cf. A., 1943, II, 151).—Et linolenate (**I**) and Me docosahexaenoate (**II**), both showing unsaturation of the methylene interrupted type, ·C:C·C·C:C·C·C:C·, are shown by spectrographic measurements to develop conjugated-diene and -triene unsaturation during incorporation of mol. O_2. (**II**) is obtained from glycerides of cod-liver oil, which are converted by MeOH–HCl into Me esters, the C_{23} ester fraction is separated by mol. distillation at <115°, and after rapid hydrolysis with KOH–MeOH, the K soaps are converted through the free acid into Li soaps, and the purified, more sol., Li soap yields the free acid and thence (**II**), which is purified by mol. distillation in N_2 or high vac.; the yellow colour developed in O_2 is removed by chromatographic treatment (Al_2O_3) in purified N_2. (**I**) absorbs 1·1% of O_2 in 24 hr., 3·7% in 48 hr., and 12% in 110 hr.; (**II**) absorbs 6·3% in 72 hr., and a second sample, 7·2% in 24 hr. Extent of double linking displacement is correlated with degree of peroxidation. After incorporation of 1 mol. of O_2, rearrangement of double linkings in (**I**) has progressed to a stage at which ~28·5% of ester contains 2 double linkings in conjugation, and 4·5% has 3 conjugated. (**II**) exhibits a similar rearrangement, as shown by the development of intense absorption in the originally feeble absorbing regions of 2340 and 2700 A. (cf. Triebs, A., 1942, II, 392). Squalene (rectified by mol. distillation at <112°, and purified by chromatographic treatment in N_2) and rubber (purified by fractional dissolution of crêpe rubber in petroleum–$COMe_2$ in N_2) show another type of unsaturation, ·C:C·C·C:C·C·C:C·C·C:C·, and do not develop conjugated units. No representative increase in absorption of light is noted. Such small increases observed in the spectra of squalene or two of its oxidation products are probably due to small degrees of conjugation or to formation of peroxide groups. Apart from an induction period (no O_2 is absorbed in 2 days, but 8·7% is absorbed in 10 days), the result of oxidising (**I**) at room temp. in complete darkness is the same with regard to efficiency of peroxide formation and extent of double linking rearrangement as that observed in summer daylight. Mechanisms of autoxidative reactions are discussed. A. T. P.

Configurative relation between optically active lactic acid and α-hydroxybutyric acid. A. Fredga, M. Tenow, and I. Billström (*Arkiv Kemi, Min., Geol.*, 1943, **16**, **A**, No. 21, 10 pp.).—*r*- (**I**), through the brucine salt, gives (−)-α-hydroxybutyric acid (**II**), m.p. 55—55·5°, $[\alpha]_D^{25}$ −2·5° in H_2O, −4·1° in $COMe_2$, +1·7° in AcOH, +6·8° in $CHCl_3$. (**I**)–aq. NaOH–CS_2, then EtBr, afford *ethylcarbothiolon-α-hydroxybutyric acid*, $SEt{\cdot}CS{\cdot}O{\cdot}CHEt{\cdot}CO_2Et$ (**III**), m.p. 58—59°, resolved into the (+)- (**IV**), m.p. 31·5—32° (*cinchonidine salt*, $+H_2O$), and (−)-*acid*, m.p. 30·5—31·5° (*brucine salt*, $+3H_2O$). The (+)-acid, also obtained from (−)-(**I**), shows vals. of $[\alpha]_D^{25}$ +39·2° in C_6H_6, +14·5° in $CHCl_3$, +6° in AcOH, which are similar to those of $SEt{\cdot}CS{\cdot}O{\cdot}CHMe{\cdot}CO_2H$ (**V**). M.p. curves of (+)- and (−)-(**II**) or (**III**), *r*-(**III**) and *r*-(**II**), (+)-(**III**) and (+)-(**V**) (eutectic) are shown. The 1 : 1 mol. compound, indicated from the curve derived from (+)-(**III**) and (−)-(**V**), gives a continuous m.p. curve with *r*-(**V**), but with *r*-(**III**) affords a eutectic. The steric series (**II**), (**IV**), (+)-(**V**), (+)-$OH{\cdot}CHMe{\cdot}CO_2H$ is deduced.

A. T. P.

Irreversible transformation of dehydroascorbic acid.—See A., 1944, III, 127.

Rearrangement of allyl-type esters of β-keto-acids. W. Kimel and A. C. Cope (*J. Amer. Chem. Soc.*, 1943, **65**, 1992—1998).—$CH_3Ac{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2$ (**I**) and its derivatives at 250° give $Ac{\cdot}[CH_2]_2{\cdot}CH{:}CH_2$ etc. and CO_2, reaction proceeding by chelation, migration of allyl etc. to the CH_2 of $CO{\cdot}CH_2{\cdot}CO$ with inversion, shift of the ethylenic linking, and finally loss of CO_2. Similar reactions with $CH_2Bz{\cdot}CO{\cdot}O{\cdot}CHR{\cdot}CH{:}CHR'$ (R and R′ = H or Me) occur even more readily, owing to the superior activating effect of Bz on CH_2. Formation of $Ac{\cdot}[CH_2]_2{\cdot}CH{:}CHPh$ (**II**) or $CH_2Ac{\cdot}CHPh{\cdot}CH{:}CH_2$ (**III**) from $CH_2Ac{\cdot}CO_2Et$ and $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ (Carroll, A., 1941, II, 310) occurs by re-esterification in presence of the alkaline catalyst, followed by an allylic shift of Ph and the ethylenic linking. $CH_3Ac{\cdot}CO_2Me$ and $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ give (**I**) (71%), but the reaction fails with analogous alcohols. The alcohols with diketen and 0·01 mol. of NaOAlk at 0—25° give *β-methylallyl* (**IV**) (85%), b.p. 95—97°/18 mm., *crotyl* (**V**) (83%), b.p. 100—102°/16 mm., Δ^{γ}-*β-butenyl* (**VI**) (89%), b.p. 92—93°/18 mm., *cinnamyl* (**VII**) (69%), b.p. 101—104°/0·025 mm., *α-phenylpropenyl* (**VIII**) (70%), b.p. 77°/0·002 mm., *linalyl* (**IX**) (61%), b.p. 71—74°/0·006 mm., and *geranyl* (**X**) (77%), b.p. 79—80°/0·006 mm., *acetoacetate*. (**X**) contains some neryl ester (disclosing itself by variation of *n*); hydrogenation of (**X**) gives only tetrahydrogeraniol. At the b.p., (**I**) gives $CH_3{:}CH{\cdot}CH_2{\cdot}OH$, $COMe_2$, dehydroacetic acid, and only 5·5% of $COMe{\cdot}[CH_2]_2{\cdot}CH{:}CH_2$ (**XI**), but in Ph_2O at 185—200° gives 31% of (**XI**). In Ph_2O at 200—215° (**IV**) gives *β-methyl*-Δ^{α}-*hexen-ε-one* (26%), b.p. 148—149° (*semicarbazone*, m.p. 136·5—137·5°) (also obtained from $CH_2{:}CMe{\cdot}CH_2Cl$ and $CHAcNa{\cdot}CO_2Et$), (**V**) at 190—220° gives $COMe{\cdot}CH_2{\cdot}CHMe{\cdot}CH{:}CH_2$ (37%), and (**VI**) at 185—200° gives $COMe{\cdot}[CH_2]_2{\cdot}CH{:}CHMe$ (80%), b.p. 151—153° {semicarbazone, m.p. 104·5—105·5° (lit. 97°); with O_3–C_5H_{12} and then H_2O_2 gives

MeCHO and COMe·[CH_2]$_2$·CO_2H}. At 250° (**VII**) (no solvent) gives (**III**) (74%), b.p. 85—86°/1 mm. [2 : 4-dinitrophenylhydrazone, m.p. 102—103° (lit., 101—102°)], (**VIII**) at 200—240° gives (**II**) (88%), b.p. 97—99°/0·3 mm. [2 : 4-dinitrophenylhydrazone, m.p. 143·5—145° (lit. 145—146·5°); semicarbazone, m.p. 130·5—131° (lit., 132°)]; geranylacetone, b.p. 101·5—103°/2·5 mm. [semicarbazone, m.p. 94·5—96° (lit. 96°)], is obtained (78%) from (**IX**) at 170—235° or (23%) from (**X**) at 220—230°. CH_2Bz·CO_2Et, ROH, and NaOR give *crotyl* (31%), b.p. 112—114°/0·20 mm., and Δ^{γ}-*β-butenyl benzoylacetate* (65%), b.p. 110°/0·5 mm., which at 240—250° give *Ph β-methyl-*Δ^{γ}*-butenyl* (76%), b.p. 98—100°/2·1 mm. (*semicarbazone*, m.p. 176—177·5°; with O_3–C_5H_{12} at −5° and then H_2O–Zn dust–quinol–$AgNO_3$ gives CH_2O and with H_2–Pd–C–EtOH gives COPh·CH_2·CHMeEt), and Δ^{γ}-n-*pentenyl ketone* (83%), m.p. 23°, b.p. 96—97°/9 mm. (*semicarbazone*, m.p. 129—130°; with O_3 gives MeCHO and with H_2–Pd–C gives *n*-C_6H_{13}Ph), respectively. In the pyrolyses yields of CO_2 considerably exceed those of the ketones. R. S. C.

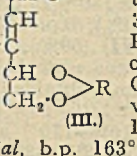
Carboxyphenylhydrazones in the identification of carbonyl compounds. S. Veibel [with A. Blaaberg and H. H. Stevns] (5 *Nordiske Kemikermode*, 1939, 223—225; cf. A., 1939, II, 133).—*p*-SO_3H·C_6H_4·NH·NH_2 is unsuitable for the identification of CO compounds owing to its poor solubility. *o*- (**I**) is as suitable as *p*-CO_2H·C_6H_4·NH·NH_2 (**II**) for this purpose; both react normally with α- and γ-CO-acids, but with β-CO-acids (**I**) reacts normally whilst (**II**) yields pyrazolones. (**II**) reacts normally with CH_2Ac_2 whilst (**I**) gives an unidentified substance sol. in acids and pptd. by alkalis. M. H. M. A.

Methanetri-β-propionic acid. V. Prelog and K. Balenović (*Ber.*, 1940, **73**, [*B*], 875—877).—CH([CH_2]$_2$·Br)$_3$ is converted by the protracted action of KCN in boiling aq. EtOH into *αε-dicyano-γ-β′-cyanoethylpentane*, m.p. 83°, hydrolysed by boiling aq. H_2SO_4 (1 : 1) to *methanetri-β-propionic acid* [*γ-β′-carboxyethylpentane-αε-dicarboxylic acid*] (**I**), m.p. 108·5—109°. The corresponding Et_3 ester, b.p. 163°/0·06 mm., is condensed by Na in PhMe at 115—120° to *β-4-keto-3-carbethoxy*cyclo*hexylpropionic acid*, m.p. 101°; alkaline hydrolysis affords the free *keto-acid*, decomp. ~80°, which at 100°/0·05 mm. yields β-4-keto*cyclo*hexylpropionic acid, m.p. 69—70° (hydrate, m.p. 55°; 2 : 4-dinitrophenylhydrazone, new m.p. 156°), also obtained by heating (**I**) with Ac_2O (cf. Harris *et al.*, A., 1938, II, 332). H. W.

Hydroxyl-ion-catalysed aldol condensation of benzaldehyde with methyl ethyl ketone and acetone.—See A., 1944, I, 42.

α-Keto-β-hydroxybutyric acid. E. Hoff-Jørgensen (5 *Nordiske Kemikermode*, 1939, 251—252).—CHMeBr·CO·CN (from EtCO·CN with Br–AcOH) is heated with aq. $Pb(OAc)_2$ for 30 min. at 70°, $PbBr_2$ filtered off and all Pb removed with H_2S, and the solution evaporated 4—5 times, with H_2O addition, at 50° to give n-*α-keto-β-hydroxybutyramide*, m.p. 214°, which is converted via the *Me* ester, liquid, and the *Ba* salt into the corresponding *acid* (**I**). (**I**) reduces Fehling's solution and is decarboxylated at pH >7, but is stable in acid solution. M. H. M. A.

Stabilisation of keto-compounds by acetalisation. M. Kühn (*J. pr. Chem.*, 1940, [ii], **156**, 103—149; cf. Salmi, A., 1938, II, 427).—Stabilisation of CO-compounds as acetals, which because of their tendency to form peroxides may be useful as polymerisation catalysts, is studied. Cyclic acetals are obtained from various CORR′ and a glycol in C_6H_6 or C_2HCl_3 using an acid catalyst (*e.g.*, $PhSO_3H$); the H_2O formed in the reaction is removed by distillation. Thus, saturated α-, β-, γ-, and δ-CO-acids (as esters) all give 5- and 6-membered ring ketals; the ring is completely stable to alkali and is hydrolysed by dil. HCl only at >50°. Reaction does not occur with ketones containing C:C αβ to the CO (*e.g.*, CHR:CAc·CO_2Et; R = Ph, 2-furyl) or with compounds which can enolise to produce C:C·CO· (*e.g.*, $CHAc_2$·CO_2Et; CN·CHPh·COMe). CEt_2Ac·CO_2Et does not react. *cyclo*Hexanone (**I**), glycerol, and a trace of $PhSO_3H$ in boiling C_6H_6 thus give cyclo*hexanone γ*(or *β*)*-hydroxy-αβ*(or *αγ*)*-propylene ketal* (64%), b.p. 133—135°/15 mm. [*chloroacetate*, b.p. 170—174°/15 mm., with NEt_2·[CH_2]$_2$·OH in EtOH affords the 1 : 1 additive *compound*, m.p. 196° (decomp.)], ultra-violet irradiation of which causes strong peroxide formation. CH_2Cl·[CH_2]$_2$·OH with camphor (in C_6H_6 + $PhSO_3H$) and COPhMe (in PhMe + H_2SO_4) gives the *γ-chloro-αβ-propylene ketals*, b.p. 146°/17 mm. and 138—140°/15 mm., respectively. $(CH_2·OH)_2$ and COPh·CH_2Cl in C_6H_6 + $PhSO_3H$ afford the *ethylene ketal* (95%), b.p. 144—146°/15 mm., m.p. 67°, the Cl of which is stable to EtOH–NaOH and to CHNaAc·CO_2Et or OMe·[CH_2]$_2$·O·[CH_2]$_2$·ONa in PhMe; it slowly forms a Grignard reagent. COPh·$CHCl_2$ does not similarly react but *ethylene ketals* of the following are prepared: COPh·CH_2Br, b.p. 154°/17 mm., m.p. 60—61° (no reaction with MeOH–NaOMe at 70°/10 hr.), COMe·CH_2Br, b.p. 76—78°/16 mm., $CO(CH_2Br)_2$, b.p. 113°/16 mm., COMe·CH_2Cl, b.p. 62—64°/18 mm., and $CO(CH_2Cl)_2$, b.p. 105°/12 mm. CH_2:CH·COMe (**II**), $(CH_2·OH)_2$, and C_6H_6 + $PhSO_3H$ give a mixture of probably (COMe·[CH_2]$_2$·O·CH_2)$_2$ and its diketal; COMe·[CH_2]$_2$·Cl [from (**II**) and HCl in C_6H_6] gives an impure product [from which the ketal of (**II**) could not be obtained by treatment with alkali] and COPh·[CH_2]$_2$·Cl affords a polymerisation product. CHPh:CH·COPh and CHR:CH·COMe (R = Ph, 2-furyl) did not react (cf. above). Glucose and (**I**) in C_6H_6–BuOH–$PhSO_3H$ give 1 : 2 : 5 : 6-*di*cyclo*hexylidene*-3 : 4-*anhydroglucofuranose* (**III**) (R = *cyclo*hexylidene), b.p. 193—195°/0·5 mm.; phenylglucosazone similarly affords a *product* containing 80% of the 3 : 4 : 5 : 6-*di*cyclo*hexylidene* ether. 3 : 4 : 5 : 6-*Di*iso*propylideneglucosazone* (from $COMe_2$ + $PhSO_3H$) is a resin. NEt_2·[CH_2]$_3$·COMe (as hydrochloride which is dried by C_6H_6) does not react with CH_2R·OH (R = Me, Pr, Bu, C_7H_{15}) and H_2SO_4 in various hydrocarbons but gives the *ethylene*, b.p. 116°/15 mm., and *γ*(or *β*)*-hydroxy-αβ*(or *αγ*)*-propylene ketal*, b.p. 163°/15 mm. NEt_2·[CH_2]$_2$·COMe affords the *ethylene*, b.p. 93—94°/13 mm., 208°/760 mm. (the wax-like quaternary *salt* with $C_{12}H_{25}$Br is an emulsifying agent for oils), *αγ-butylene*, b.p. 112—113°/13 mm., and *γ*(or *β*)*-hydroxy-αβ*(or *αγ*)*-propylene ketal*, b.p. 145—150°/12 mm. Me *β-N-cyclo*hexyl-*N*-ethylaminoethyl ketone (from C_6H_{11}·NHEt,HCl, CH_2O, and $COMe_2$) and 2-*N-cyclo*hexyl-*N*-methylaminomethyl*cyclo*hexanone [from (**I**), *cyclo*hexylamine hydrochloride, and CH_2O] give *ethylene ketals*, b.p. 166°/14 mm. and 190—192°/14 mm., respectively. *NN*-Di-(*γ*-keto-Δ^{δ}-pentenyl)*cyclo*hexylamine [from *cyclo*hexylamine sulphate, (**II**), and $(CH_2O)_x$ in AcOH] does not react with $(CH_2·OH)_2$ in C_6H_6 + $PhSO_3H$; diacetonamine similarly decomposes but diacetone-ethylamine and Me *β-cyclo*hexylaminoethyl ketone [from *cyclo*hexylamine and (**II**)] form *ethylene ketals*, b.p. 84—86°/14 mm. and 162—163°/18 mm., respectively. The *hydroxypropylene ketal* obtained from glycerol and mixed COPh·CH_2·NMe_2RCl (R = C_{10}—C_{20} alkyl) forms a frothy aq. solution which emulsifies oils.


(III.)

CH_2Ac·CO_2Et (**IV**) does not react with [CH_2]$_4$(OH)$_2$ or various CH_2R·OH in C_6H_6 + $PhSO_3H$ or PhMe + H_2SO_4; its ethylene ketal (**V**) (*loc. cit.*) is hydrolysed by 5N-aq. EtOH–NaOH to CH_2Ac·CO_2H ethylene ketal (readily sol. in H_2O), which can be esterified to (**V**) (46% yield). The *αγ*-butylene ketal of (**IV**) is similarly hydrolysed. (**IV**) also yields the *γ*(or *β*)*-hydroxy-αβ*(or *αγ*)*-propylene*, b.p. 145°/14 mm., and *γ-chloro-αβ-propylene ketal* (**VI**), b.p. 132°/13 mm. Boiling MeOH–NaOMe converts (**VI**) into the not quite pure *αβ-allene ketal* (**VII**), b.p. 118—120°/13 mm.; MeOH–NaOPh gives (**VII**) (42%) and the *γ-phenoxy-αβ-propylene ketal* (48%), b.p. 198°/11 mm., and Na *p-iso*octylphenoxide in PhMe affords the γ-p-iso*octylphenoxy-αβ-propylene ketal*. *Et dodecylacetoacetate*, b.p. 168—170°/0·5 mm., gives the *ethylene ketal*, b.p. 184—186°/0·5 mm. (corresponding *acid*, m.p. 63°). *Ethylene ketals* of the following are prepared: $CO(CH_2·CO_2Et)_2$, b.p. 162—164°/25 mm., CH_2Ph·CHAc·CO_2Et, b.p. 178—179°/11 mm., Et_2 α-acetylglutarate, b.p. 180—182°/24 mm., Me Et(α) α-acetylglutarate, b.p. 168—170°/15 mm. (*γ-chloro-αβ-propylene ketal*, b.p. 209—210°/17 mm.), Et γ-acetylbutyrate, b.p. 135—136°/17 mm., Et lævulate, b.p. 110—112°/15 mm., $AcCO_2$Et, b.p. 80—81°/15 mm., Et and Bu α-formylphenylacetate, b.p. 172—174°/15 mm. and 212—214°/20 mm., respectively, Et γ-ketobutylmalonate, b.p. 162—164°/14 mm., Et δ-keto-α-cyanohexoate, b.p. 168—170°/14 mm., and Et_2 α-acetylsuccinate, b.p. 162°/14 mm. Et phenacylacetoacetate and $(CH_2·OH)_2$ (2 mols.) in PhMe + $PhSO_3H$ give the *di*(*ethylene ketal*), b.p. 174—178°/0·5 mm., m.p. 62—64° (free *acid*, m.p. 150—151°), and Et 2-phenyl-5-methylfuran-3-carboxylate (free acid, m.p. 179—181°). 2-Chloro*cyclo*hexanone and CHNaAc·CO_2Et in PhMe followed by $(CH_2·OH)_2$–$PhSO_3H$ give *Et* 1-*methyl*-3 : 4 : 5 : 6-*tetrahydrocoumarone*-2-*carboxylate*, b.p. 143—144°/13 mm. (free *acid*, m.p. 161°). $CH_2(CHAc·CO_2Et)_2$ affords the *di*(*ethylene ketal*), b.p. 214—218°/20 mm. H. B.

Deuterium as indicator in keto–enolic tautomerism. A. Tananger (5 *Nordiske Kemikermøde*, 1939, 229—230).—The type of di-enolisation in diketo-compounds is studied by introducing D into an active CH_2 group and measuring the rate of enolisation and the distribution of D in the dienol. M. H. M. A.

Behaviour of trimethylamine, trimethylammino-sulphur trioxide, and trimethylamine oxide towards sulphur dioxide.—See A., 1944, I, 16.

Additive compounds of trimethylamine with boron fluoride and its methyl derivatives.—See A., 1944, I, 44.

Interaction of higher α-chloroparaffins with ammonia, primary, *sec.*, and *tert.* amines. O. Westphal and D. Jerchel (*Ber.*, 1940, **73**, [*B*], 1002—1011).—RCl (R = *n*-alkyl here and below) with 1 : 1 liquid NH_3–EtOH give mainly NHR_2 with smaller amounts of NH_2R and NR_3; the amount of NR_3 decreases with the size of R. Thus, *n*-C_8H_{17}Cl (**I**) at 140° gives *n*-C_8H_{17}·NH_2 (11·4%), b.p. 76—78°/12 mm., $(n\text{-}C_8H_{17})_2$NH (~40%), m.p. 35°, b.p. 142—147°/3 mm., and *tri-n-octylamine* (~22%), b.p. 183—185·5°/3 mm. *n*-$C_{12}H_{25}$Cl (**II**) at 170° gives $(n\text{-}C_{12}H_{25})_2$NH (**III**) (81%), m.p. 57—58° (lit. 55—56°) [hydrochloride, dimorphic (transition point ~72°), m.p. ~200° (decomp.)], but at 110° gives *n*-$C_{12}H_{25}$·NH_2 (**IV**) (16%) [*hydrochloride*, m.p. 183—186° (decomp.)] and (**III**) (64%). H_2–Ni–Co–Cu at 100°/~100 atm. reduces *n*-$C_{11}H_{23}$·CN in MeOH–H_2O (150 : 80 ml.) to (**IV**) but in 96% EtOH to (**III**). *n*-$C_{16}H_{33}$Cl (**V**) at 170° gives

much (n-$C_{18}H_{33})_2NH$ and 24% of n-$C_{18}H_{33}$·NH_2 (*hydrochloride*, m.p. 178°). In EtOH at 175° (**II**) and (**IV**) give 47% of pure (**III**). With NH_2Me in a little EtOH, RCl gives NHMeR and $NMeR_2$ (only with lower alkyl), but, if R = $C_{\leq 6}$, no $NMeR_3Cl$. Thus, $Bu^{\alpha}Cl$ at 100—110° gives *methyldi-n-butylamine* (69%), b.p. 53·5—54°/11 mm., and some $NHMeBu^{\alpha}$. n-$C_5H_{13}Cl$ at 100° gives much NHMe·C_5H_{13}-n and 40% of (n-$C_6H_{13})_2NMe$, b.p. 118°/12 mm. At 140° (**I**) gives n-C_8H_{17}·NHMe (24%) and *methyldi-n-octylamine* (30%), b.p. 143—145°/3 mm. At 160° (**II**) gives n-$C_{12}H_{25}$·NHMe (**VI**) (59%), b.p. 108—110°/1·5 mm. (*hydrochloride*, m.p. 181—184°), and *methyldi-n-dodecylamine* (37%), m.p. 15—16°, b.p. 201°/1·5 mm. [obtained in 51% yield from (**II**) and (**VI**) in EtOH at 160°]. At 140—150° (**V**) gives n-$C_{16}H_{33}$·NHMe (15%) (*hydrochloride*, m.p. 169—170°) and (n-$C_{16}H_{33})_2NMe$ (68%), m.p. 36—37° (lit. 34—35°), b.p. 269—271°/1 mm. With *sec.* amines RCl in MeOH or EtOH (not C_6H_6 or light petroleum) gives, usually, good yields of *tert.* base. *E.g.*, $NHEt_2$ with (**I**) at 160° gives *diethyl-n-octylamine*, b.p. 112—113°/12 mm., and with (**II**) at 140° gives *diethyl-n-dodecylamine* (86%; in absence of EtOH), b.p. 122—124°/2 mm. (*hydrochloride*, m.p. 119·5°). $NH(CH_2Ph)_2$ and (**II**) at 150° give *dibenzyl-n-dodcecylamine* (75%), b.p. 219—220°/2 mm. (hydrochloride, m.p. 101°). $NHMe_2$ and (**V**) at 140° give *dimethyl-n-hexadecylamine* (82·5%), b.p. 138°/1 mm. (hydrochloride, m.p. 198°). Higher alkyl chlorides and *tert.* amines react with difficulty in EtOH and not at all in other solvents or alone. NMe_2·CH_2Ph (**VI**) and (**I**) in a little EtOH at 105° (24 hr.) give *benzyldimethyl-n-octylammonium chloride* (~90%), f.p. ~0°. NMe_3 and (**II**)–EtOH at 80—90° give *trimethyl-n-dodecylammonium chloride* (75—80%), m.p. ~37°. (**VI**) and (**II**)–EtOH at 90° (45 hr.) give *benzyldimethyl-n-dodecylammonium chloride* (~100%), an oil. NMe_3 and (**II**)–EtOH at 180° (18 hr.) give n-$C_{12}H_{25}$·NMe_2 (*hydrochloride*, m.p. ~132°). NMe_3 and (**V**)–EtOH at 100—105° (12—16 hr.) give n-$C_{16}H_{33}$·NMe_3Cl, m.p. ~70° (lit. 240°). (**VI**) and (**V**)–EtOH at 90° (28 hr.) give *benzyldimethyl-n-hexadecylammonium chloride* (70%), m.p. 58°. R. S. C.

Constitution of thionylamines. K. A. Jensen (5 *Nordiske Kemikermøde*, 1939, 216—217).—The absence of *syn-* and *anti-*forms and their low dipole moments support the resonance structure: R–N=S→O ⇌ R–N←S=O. M. H. M. A.

Reaction of *d*-glucosamine with *o*-phenylenediamine. R. Lohmar and K. P. Link (*J. Biol. Chem.*, 1943, **150**, 351—352).—*d*-Glucosaminic acid and o-$C_6H_4(NH_2)_2$ (**I**) do not give a cryst. product. Direct oxidative condensation of *d*-glucosamine hydrochloride with (**I**) in presence of $Cu(OAc)_2$–aq. AcOH at 50° affords 3-(*D-arabo*-tetrahydroxybutyl)quinoxaline, m.p. 192—193° (decomp.), $[\alpha]_D^{20}$ −85·8° in 4N-HCl (tetra-acetate, m.p. 121°, $[\alpha]_D^{20}$ −29·2° in $CHCl_3$) (cf. Ohle, A., 1934, 392). A. T. P.

Amino-acids and peptides. XV. Physical properties of *l*(+)- and *d*(−)-alanine. M. S. Dunn, M. P. Stoddard, L. B. Rubin, and R. C. Bovic (*J. Biol. Chem.*, 1943, **151**, 241—258).—Benzoyl-*dl*-alanine is resolved into its optical components by successive use of strychnine and brucine in aq. solution and the optically active substances are hydrolysed by HCl. The following sp. rotations are recorded: *l*-strychnine benzoyl-*l*(+)-alanine dihydrate, $[\alpha]_D$ −10·45° in H_2O; *l*-brucine benzoyl-*d*(−)-alanine (+4·5H_2O), $[\alpha]_D$ −26·53° in H_2O; benzoyl-*l*(+)-alanine, $[\alpha]_D$ +33·4 in N-NaOH; benzoyl-*d*(−)-alanine, −32·5° in 1·05N-NaOH; *l*(+)-alanine (**I**), $[\alpha]_D^{25\cdot0}$ +13·77° ±0·02° in 6·0N-HCl; *d*(−)-alanine (**II**), $[\alpha]_D^{25}$ −13·60°±0·01° in 6N-HCl. Vals. of $[\alpha]_D^{\theta}$ (θ varied between 0·50° and 45·0°) (**I**) and (**II**) in 7·25N-, 5·97N- (c = 10, 6, or 3·5), 4·83N- (c = 2), 0·884N- (c = 8), 0·502N- (c = 4·5), and 0·228N-HCl (c = 2), and in H_2O (c = 10 or 6) are recorded. The solubilities of (**I**) and (**II**) in H_2O have been determined. The sp. rotations of (**I**) and (**II**) recorded in the literature have been evaluated by means of temp. and solute concn. factors derived from the present authors' data. H. W.

Dihydroxyacyl derivatives of β-alanine and *l*-leucine from tunny fish liver.—See A., 1944, III, 124.

Isolation of valylvaline from gramicidin hydrolysates. H. N. Christensen (*J. Biol. Chem.*, 1943, **151**, 319—324).—Valylvaline (**I**) has been isolated as the *Bz* derivative (**II**), m.p. 218°, apparently optically inactive, from hydrolysates of gramicidin (**III**) prepared by boiling this substance with 16% HCl for 6 or 24 hr. (none obtained in 2 hr.). The resulting mixture of NH_2-acids is fractionated as the Cu salts and the fraction sol. both in H_2O and in MeOH is freed from reagents and benzoylated. When completely hydrolysed (**II**) yields BzOH and 2 mols. of *dl*-valine, identified as the Ac (**IV**), m.p. 149°, and *p-toluenesulphonyl* (**V**), m.p. 170° (corr.), derivatives. In separate experiments ~90% of the N was recovered as valine hydrochloride, 80% as (**IV**), and 50% as (**V**). The implication of the presence of (**I**) in the hydrolysates of (**III**) is discussed. H. W.

Amide metabolism in etiolated seedlings. I. H. B. Vickery and G. W. Pucher (*J. Biol. Chem.*, 1943, **150**, 197—207).—See A., 1944, III, 83). Almost quant. results are obtained in Schiff's method for the prep. of aspartic acid (A., 1885, 377) if the asparagine is hydrolysed with HCl (2 mols.) for 3 hr., aq. NH_3 (1 mol.) added, followed by EtOH, and the pH then adjusted to 3·0.

Carbamic acid peptides. New type of peptide. Possible source of ammonia from proteins. A. H. Corwin and (Miss) C. I. Damerel (*J. Amer. Chem. Soc.*, 1943, **65**, 1974—1984).—NH_2·CH_2·CO_2·CH_2Ph,HCl, KCNO, and a slight excess of NaOH in H_2O at 100° (2—3 min.) give *N-carbamylglycine* CH_2Ph ester (50%), m.p. 124·5—126°, converted by CH_2Cl·COCl in boiling C_6H_6 (1 hr.) into *N-N'-chloroacetylcarbamylglycine* CH_2Ph ester (70%), m.p. 179·5—180°, which with H_2–Pd–C in MeOH–H_2O–AcOH (a little) gives *N-N'-chloroacetylcarbamylglycine* (65%), m.p. 198—200° (decomp.), also obtained (56%) from NH_2·CO·NH·CH_2·CO_2H (**I**) by CH_2Cl·COCl in dioxan (not various other solvents). The *Et* ester, m.p. 145—146°, is also prepared. NH_2·CO·NH·CHR·CO_2H and the appropriate acid halide lead similarly to *N-N'-chloroacetylcarbamyl*-dl-*alanine* (51%), m.p. 181—181·5° (decomp.), *N-N'-α-chloropropionylcarbamyl-glycine* (51%). m.p. 208·5—211° (decomp.). -dl-*alanine* (56%), m.p. 191—192·5° (decomp.), and -l-*leucine* (46%), m.p. 147—148° (remelts at 148—148·5°), *N-N'-α-bromopropionyl-* (10%), m.p. 201—204° (decomp.), and *N-N'-acetyl-carbamylglycine* (poor yield), m.p. 234—235° (decomp.). The halogenated products with liquid NH_3 in ice–$COMe_2$ give *N-N'-glycylcarbamyl-glycine* (**II**) (70%), m.p. 192·5—194°, and -dl-*alanine* (**III**) (77%), and *N-N'-alanylcarbamylglycine* (**IV**) (55%), $+H_2O$ (absorbed from air), softens 180°, m.p. 190—195° (decomp.). (**II**)—(**IV**) are amphoteric, having pK_1 ~3·34 and pK_2 ~7·6, and changes in titration curves due to CH_2O resemble those of NH_2-acids and polypeptides. The course of hydrolysis is elucidated by titration. In 0·3N-NaOH at room temp. (**II**) or (**III**) gives glycine + (**I**) or NH_2·CO·NH·CHMe·CO_2H, respectively, (**IV**) gives alanine + (**I**), and NHAc·CO·NH·CH_2·CO_2H gives AcOH + (**I**); to a slight extent, more with (**IV**) than with (**III**), decomp. occurs into NH_2·CHR·CO·NH_2 + CO_2H·NHR'·CO_2H, the amide then decomp. further with liberation of NH_3. In strong alkali, quant. yields of CO_2 and NH_3 are obtained. In 0·3N-HCl at 90—100° (**II**), (**III**), and (**IV**) give NH_2·CHR·CO_2H + NH_2·CO·NH·CHR'·CO_2H, with subsequent ring-closure of the latter product to hydantoin (**V**) or methylhydantoin (**VI**), respectively; ring-closure to (**V**) is slower than that to (**VI**) and only the latter reaction is completed under the conditions of hydrolysis. In H_2O at 90—100° NH_2·CHR·CO·NH·CO·NH·CHR'·CO_2H gives (**V**) or (**VI**) and NH_2·CHR'·CO_2H; thus (**V**) is isolated from (**II**), alanine from (**III**), and glycine and (**VI**) from (**IV**). NHAc·CO·NH·CH_2·CO_2H gives, slowly, AcOH + (**I**). In boiling 5N-HCl, (**II**) gives CO_2 (16·3%) and NH_3; thus, if ·NH·CO· units occur in polypeptides, some CO_2 and NH_3 may be formed on hydrolysis but the amount of ·NH·CO· cannot be calc. by simple stoicheiometric rules. R. S. C.

Crystalline quinine salt of pantothenic acid. Synthesis and resolution of the racemate. R. Kuhn and T. Wieland (*Ber.*, 1940, **73**, [*B*], 971—975).—COCl·$[CH_2]_2$·NH_2,HCl (prep. from the acid by PCl_5–AcCl) with CH_2Ph·OH at 70—80° give β-alanine CH_2Ph ester hydrochloride, m.p. 100—101° [derived *platinichloride*, m.p. 202—203° (block)], which with the lactone (**I**) of OH·CH_2·CMe_2·CH(OH)·CO_2H (**II**) at 100°, and then H_2–PtO_2 in AcOH or HCO_2H, gives syrupy *dl*-pantothenic acid, obtained pure by adsorption from H_2O at pH 8·5 on Al_2O_3 and elution by $Ba(OH)_2$. This acid has 2 × 10^7 Sbm units per g. (cf. A., 1943, III, 124). The derived Ba salt (pH 8·5) with quinine sulphate in H_2O gives *l*-pantothenic acid, $[\alpha]_D^{21}$ −26·7° in H_2O, $[\alpha]_D^{24}$ −56·3° in MeOH {Ba, $[\alpha]_D^{24}$ −20·4° in H_2O, and *quinine* salt, m.p. 165—167° (block), $[\alpha]_D^{24}$ −115° in H_2O}, having 4·5—5 × 10^7 Sbm units per g. and a rat dose ~15 μg. per day. With hot, aq. $Ba(OH)_2$, (**I**) gives the derived Ba salt, m.p. 220°, and thence, by quinine sulphate, the quinine salts, m.p. 182—183°, and 164—165°, of (−)- and (+)-(**II**), respectively, and thence *d*-, m.p. 82—84°, $[\alpha]_D^{20}$ +28·0°, and *l*-(**I**), m.p. 76—80°, respectively. R. S. C.

Solubilities of amides etc.—See A., 1944, II, 34.

Structure and insecticidal properties of organic compounds. N. N. Melnikov, N. D. Suchareva, and M. L. Fedder (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 610—613).—See A., 1944, III, 133. The following are described (% yields in parentheses): Pr^{α} (88), b.p. 108—110°/4 mm.; *allyl* (60), b.p. 115—117°/5 mm.; Bu^{α} (88), b.p. 114—115°/3 mm.; Bu^{β} (92), b.p. 111—113°/4 mm., and *octyl thiocyanate* (63), b.p. 185—187°/16 mm.; Pr^{α} (80), b.p. 125—127°/8 mm., *allyl* (72·5), b.p. 113—114°/5 mm., Bu^{α} (75), b.p. 137—140°/10 mm., Bu^{β} (70), b.p. 125—126°/9 mm., and *octyl α-thiocyanobutyrate* (53), b.p. 159—162°/5 mm. J. N. A.

Theory of allyl isomerisation. IV. Allyl thiocyanate → allylthiocarbimide. O. Mumm and H. Richter (*Ber.*, 1940, **73**, [*B*], 843—860; cf. A., 1939, II, 113, 478).—Further evidence is adduced in favour of the view that there is a change in position of attachment of the allyl group in all cases of allyl isomerisation in which the intermediate production of a 6-membered ring is possible even by participation of partial valencies. Technical CHMe:CH·CHO is reduced [$Al(OPr^{\beta})_3$] to CHMe:CH·CH_2·OH, converted by saturated aq. HBr at 0° into a mixture of 87% of the primary and 13% of the *sec.* bromide. Gradual addition of NH_4CNS to this material in well-cooled EtOH leads to *crotyl thiocyanate* (**I**), b.p. 40°/0·7 mm., which can be kept for a few days in the dark at 0° but soon becomes

isomerised at room temp. The presence of the identical chain in (I) and the initial material is proved by ozonisation of (I) and decomp. of the ozonide by H_2O to MeCHO, further identified by oxidation to AcOH in 77% yield [anhyd. NaOAc has m.p. 330° (corr.; block)]. Distillation under atm. pressure causes isomerisation of (I) to crotylthiocarbimide (II), b.p. 158—159°/760 mm., 50°/11·5 mm. (II) is converted by aq. NH_3 into crotylthiocarbamide, m.p. 107—108°, reduced (H_2 at room temp./15 atm., Pd–$BaSO_4$–H_2O) to *sec.*-butylthiocarbamide (III), m.p. 131—133°. Authentic material is obtained as follows: CHMeEtBr is converted by *o*-$C_6H_4(CO)_2NK$ at 210° into sec.-*butylphthalimide* (IV), m.p. 24·5—25·5°, transformed by aq. NaOH at 100° into sec.-*butylphthalamic acid* (V), m.p. 132—133°, and further hydrolysed to $CHMeEt{\cdot}NH_2$ [platinichloride, m.p. 228° (decomp.)]. The base is transformed by CS_2 in Et_2O into the *dithiocarbamate*, which with aq. $HgCl_2$ yields successively *sec.*-butylthiocarbimide, m.p. 159·5°, and (III), (II) and *o*-$C_6H_4(CO_2H)_2$ at 155° afford *crotylphthalimide* (*α-methylallylphthalimide*), m.p. 87—88°, and its unsymmetrical *isomeride*, $CO<\overset{C_6H_4}{\underset{O}{}}>C{:}N{\cdot}CHMe{\cdot}CH{:}CH_2$ (VI), m.p. 52—53°, the former of which is hydrogenated to (IV), further identified by conversion into (V). (VI) is hydrogenated (Pd–$BaSO_4$ in EtOAc) and then partly hydrolysed to sec.-*butylisophthalamic acid*, $CO_2H{\cdot}C_6H_4{\cdot}C(OH){:}N{\cdot}CHMeEt$, m.p. 101°. (II) is therefore identical with the product described by Charon (A., 1899, i, 848). The product described by Schimmel & Co. (A., 1910, i, 759) is $CHMe{:}CH{\cdot}CH_2{\cdot}NCS$. $OH{\cdot}CHEt{\cdot}CH{:}CH_2$ is converted into a mixture separated by fractional distillation into γ- and α-ethylallyl chloride. The former compound is slowly transformed by NH_4CNS in well-cooled EtOH into *γ-ethylallyl thiocyanate* (VII), b.p. 55°/1·6 mm., which becomes isomerised with separation of S in a few days at room temp. Fission of (VII) by O_3 gives EtCHO (*p*-nitrophenylhydrazone, m.p. 123—124°) and oxidative fission of the ozonide by alkaline $KMnO_4$ gives $EtCO_2H$ in nearly quant. amount. Distillation under atm. pressure isomerises (VII) to *α-ethylallylthiocarbimide*, b.p. 71°/19 mm., transformed by NH_3 in EtOH at room temp. into *α-ethylallylthiocarbamide*, m.p. 92°; this is reduced to γ-amylthiocarbamide, m.p. 78—79°. γ-Ethylallyl thiocyanate is converted similarly into the corresponding *-carbimide*, b.p. 186—188°. H. W.

Effect of molecular environment on absorption of organic compounds in solution. Compounds containing the chromophore :C·C·C:N·.—See A., 1944, I, 28.

II.—SUGARS AND GLUCOSIDES.

***d*-Ribose. Preparation of a crystalline anhydroribose.** H. Bredereck, M. Köthnig, and (Miss) E. Berger (*Ber.*, 1940, **73**, [*B*], 956–962).—$[\alpha]_D^{20}$ of *d*-ribose (I) (prep. described) in C_5H_5N at 20° changes regularly from −38·4° (after 4 min.) to −43·1° in 2 days, but const. vals. for *k* are not obtained (cf. Phelps *et al.*, A., 1934, 494). With CPh_3Cl in C_5H_5N at 37° (4 days) and then 100° (0·5 hr.), (I) gives the 5-*CPh_3 ether* (+0·5EtOH), m.p. 125°, $[\alpha]_D^3$ (in C_5H_5N) + 12·1° (4 min.) → 9·9° (12 hr.) (k = ~0·0205, const.) (reduces Fehling's solution; blue colour with $CuSO_4$–alkali), and thence (Ac_2O–C_5H_5N; room temp.) the 5-*CPh_3 ether* 1 : 2 : 3-*triacetate*, a syrup, $[\alpha]_D^{20}$ +4·9° to +5·2° in EtOH, which with HBr–AcOH at 0° gives *anhydroribose* <1, 5>, <1, 4> 2 : 3-*diacetate*, m.p. 169°, and thence *anhydroribose* <1, 5>, <1, 4>, sinters 225°, m.p. 229—230°, $[\alpha]_D^{20}$ +78·8° to +77·8° in H_2O (reduces Fehling's solution only after hydrolysis; blue colour with $CuSO_4$–alkali). R. S. C.

Carbohydrate characterisation. IV. Identification of *d*-ribose, *l*-fucose, and *d*-digitoxose as benziminazole derivatives. R. J. Dimler and K. P. Link (*J. Biol. Chem.*, 1943, **150**, 345—349; cf. A., 1942, II, 248).—*d*-Ribose and *l*-fucose are oxidised by KOI–MeOH to *d*-ribonic acid (I) (through the K salt) and *l*-fuconic acid (through the Ba salt), and condensation with *o*-$C_6H_4(NH_2)_2$–HCl–H_3PO_4 at 135° then gives d-*ribo*- (II), m.p. 190°, $[\alpha]_D^{25}$ +22·5° in N-HCl (*hydrochloride*, m.p. 196—198°; *picrate*, m.p. 185—186°) (cf. Richtmeyer *et al.*, A., 1942, II, 395), and l-*fuco-benziminazole*, m.p. 248—249°, $[\alpha]_D^{26}$ −41·2° in N-HCl [*hydrochloride*, m.p. 224—225°; *picrate*, m.p. 189—191° (also +H_2O)], respectively. K *d*-arabonate (~5%) is also formed during prep. of (I), by epimerisation, and gives insol. d-*arabobenziminazole*, m.p. 235—237°, $[\alpha]_D^{25}$ −45° in N-HCl (*picrate*, m.p. 155—156°), which is not isolated if (I) is prepared by oxidation by the Br–$Ba(OBz)_2$ method of Hudson *et al.* (A., 1929, 1043). Oxidative condensation of *d*-digitoxose in presence of $Cu(OAc)_2$,H_2O–aq. AcOH at 53° for 14 hr. yields d-*digitoxobenziminazole*, m.p. 207—209°, $[\alpha]_D^{25}$ −45·7° (hydrochloride, an oil; *picrate*, m.p. 124—127°). A. T. P.

Reaction of glucose with some amines. A. E. Mitts (*Iowa State Coll. J. Sci.*, 1943, **18**, 68—70).—NH_2R with glucose yields *glucosyl*-n-*butyl*-, m.p. 96—97°, $[\alpha]_D^{25}$ −22° to −7·8° in EtOH, *-amyl*-, m.p. 96—97°, $[\alpha]_D^{25}$ −22° to −8° in EtOH, *-heptyl*-, m.p. 97—98°, $[\alpha]_D^{25}$ −13° to −7° in EtOH, and *-dicyclohexyl-amine*, m.p. 97—98°, $[\alpha]_D^{25}$ −23·5° to −11·6° in EtOH. Cryst. compounds were not obtained from β-$C_8H_{17}{\cdot}NH_2$, $NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2$ and NH_2Pr^{β}. Also prepared were *glucosyl*-n-*octa*-, m.p. 104—105°, and *-hexa-decylamine*, m.p. 106—107°, and *diglucosylethylenediamine*, m.p. 152—153°, $[\alpha]_D^{25}$ −17° to +14·5° in EtOH. Hydrogenation (Raney Ni) of these yields N-*butyl*-, m.p. 126—127°, $[\alpha]_D^{25}$ −14° in 50% EtOH, N-*amyl*-, m.p. 129—130°, $[\alpha]_D^{26}$ −138° in 50% EtOH, N-*heptyl*-, m.p. 126—127°, $[\alpha]_D^{25}$ −14° in 50% EtOH, N-cyclo*hexyl*-, m.p. 145—146°, $[\alpha]_D^{25}$ −11° in 50% EtOH, N-*hexadecyl*-, m.p. 123—124°, and N-*octadecyl*-*d*-*glucamine*, m.p. 118—119°, and NN'-*ethylenediglucamine*, m.p. 136—137°, $[\alpha]_D^{25}$ −15·5° in 50% EtOH. F. R. G.

***d*-Fructopyranose, a sugar unfermentable by yeast.** A. Gottschalk (*Austral. J. Exp. Biol.*, 1943, **21**, 133—137; cf. Hopkins *et al.*, A., 1935, 1538).—At 0° and pH 4·3 the rate of fermentation of the β-pyranose form of *d*-fructose by suspension of baker's yeast is minute compared with that of α-*d*-glucose, is independent of the concn. of the yeast, and depends on the partial conversion of *d*-fructopyranose into *d*-fructofuranose. Hence it is the latter alone which undergoes alcoholic fermentation. At 0° and pH 3·05—5·35 the rate of mutarotation of α-*d*-glucose is < one tenth of that of β-*d*-fructopyranose: this indicates that α-*d*-glucose is fermented without first undergoing a change in mol. structure. The pH of the yeast cell is 5·9: its buffering power, which is high compared with that of serum, is chiefly due to its content of salts. W. McC.

Proportion of fructofuranose in *d*-fructose solution at equilibrium. A. Gottschalk (*Austral. J. Exp. Biol.*, 1943, **21**, 139—140).—Advantage is taken of the fact that the only fermentable component of *d*-fructose solution at equilibrium is fructofuranose, to determine the proportion of this form in the equilibrium mixture at pH 4·3. The val. is ~12% at 0° and probably 20% at 20°. W. McC.

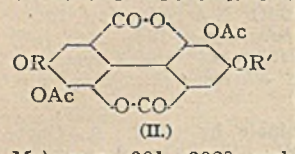
Alkaline degradation of phenyl-β-lactoside, -β-cellobioside, and -*D*-gluco-β-*D*-guloheptoside. (Miss) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1848—1854).—Phenyl-β-lactoside in boiling 2·6N-KOH ([α] −36·0° becomes −44·0°) gives, after acetylation (Ac_2O–C_5H_5N), 4-β-*D*-galactopyranosido-*D*-glucosan <1, 5>β<1, 6> hexa-acetate, m.p. 206—208°, [α] −40·8° in $CHCl_3$ (cf. Karrer *et al.*, A., 1933, 1146), converted by $Ba(OMe)_2$ into the unesterified *glucosan*, +H_2O, m.p. 128—130°, [α] −50·6° in H_2O, and anhyd., m.p. 140—144°, [α] −53·5° in H_2O (lit., an oil; does not reduce Fehling's solution), which in 2 : 1 Ac_2O–AcOH containing 2·5% (vol.) H_2SO_4 at 20° gives α-lactose octa-acetate (83%). Phenyl-β-cellobioside hepta-acetate (prep. described), m.p. 206—208° (lit. 193°), [α] −36·0° in $CHCl_3$, with $Ba(OMe)_2$ gives *phenyl-β-cellobioside*, m.p. 211—213°, [α] −59·5° in H_2O, which in 2·6N-KOH at 110—115° gives 4-β-*D*-glucopyranosido-*D*-glucosan <1, 5>β<1, 6>, m.p. 122°, [α] −75·0° in H_2O (*loc. cit.*), by way of the hexa-acetate, m.p. 145—146°, [α] −54·4° in $CHCl_3$. *D*-Gluco-β-*D*-guloheptose hexa-acetate, m.p. 134—135°, [α] +4·8° in $CHCl_3$, with HBr–AcOH at room temp. (dark) gives acetobromo-*D*-gluco-α-*D*-guloheptose (I), m.p. 111°, [α] +187° in $CHCl_3$ (cf. lit.). With PhOH and Ag_2CO_3 in C_6H_6 and then $Ba(OMe)_2$ this gives phenyl-*D*-gluco-β-*D*-guloheptoside, m.p. 168°, [α] −90·0° in H_2O (hepta-acetate, m.p. 99°, [α] +8·0° in $CHCl_3$), which in boiling 2·6N-KOH gives D-*gluco*-D-*guloheptosan* <1, 5>β<1, 6> (II), m.p. 95°, [α] +52·9° in H_2O (additive *compound* with 1 NaCl, m.p. 165—167°, [α] +48·6° in H_2O), isolated as *tetra-benzoate*, m.p. 154—155°, [α] +144·4° in $CHCl_3$, or -p-*nitrobenzoate*, m.p. 268°, [α] +218° in C_5H_5N, and converted by H_2SO_4–Ac_2O–AcOH into *D*-gluco-β- (60%) and -α-*D*-guloheptose (20%). 2·02 $NaIO_4$ are consumed by (II) with formation of 0·98 HCO_2H. In C_5H_5N, (II) gives its 2 : 3 : 7-*tri*-p-*toluenesulphonate* (III) (76%), m.p. 157°, [α] +34·6° in $CHCl_3$, and thence the 4-*acetate* 2 : 3 : 7-*tri*-p-*toluenesulphonate*, +$COMe_2$, m.p. 105° (gas), [α] +55·2° in $CHCl_3$, which with NaI in $(CH_2Ac)_2$ at 70° gives the 7-*iodide* 4-*acetate* 2 : 3-*di*-p-*toluenesulphonate* (83%), m.p. 135°, [α] −4·0° in $CHCl_3$. With $Ba(OMe)_2$ at room temp. this gives 4 : 7-*anhydro*-D-*gluco*-D-*guloheptosan* <1, 5>β<1, 6> 2 : 3-*di*-p-*toluenesulphonate* (85%), m.p. 180—182°, [α] −37·0° in $CHCl_3$, also obtained from (III) by NaI directly.

[(Miss) O. P. Hartley.] Methyl-*D*-gluco-β-*D*-guloheptoside, m.p. 167—169°, [α] −74·7° in H_2O, gives its penta-acetate, m.p. 153—154° (lit. 150°), [α] −21·3° in $CHCl_3$ (lit., −16°), also obtained from (I) by MeOH–Ag_2CO_3. Methyl-*D*-gluco-α-*D*-guloheptoside, +0·5EtOAc, hygroscopic, [α] (solvent-free) +111·3° in H_2O (penta-acetate, m.p. 174—175°, [α] +105·5° in $CHCl_3$), and *Cd* D-*gluco*-D-*idoheptonate* [d-β-*glucoheptonate*], +$CdBr_2$ + H_2O, discolours at 190°, [α] −5·7° in H_2O, are reported. [α] are $[\alpha]_D^{20}$. R. S. C.

Synthesis of the acetyl derivative of primulaveroside, the glucoside of the ordinary primrose (*Primula officinalis*). F. Mauthner (*J. pr. Chem.*, 1940, [ii], **156**, 150—153).—Gentisic acid (prep. from *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ by $K_2S_2O_8$ in aq. NaOH + $FeSO_4$ at room temp.) is methylated (Me_2SO_4, aq. NaOH) to the 5-Me ether, the Me ester, b.p. 261—262° (lit. 235—240°) (prep. by MeOH–HCl), of which with acetobromoprimverose and dry Ag_2O in quinoline gives primulaveroside hexa-acetate, m.p. 198—199°. H. B.

New hamameli-tannin. C. P. Edwards and M. Nierenstein (*Pharm. J.*, 1943, **151**, 241).—The bark of English witch-hazel

(*Hamamelis virginica*, Lin.), extracted with CCl_4 and then $CHCl_3$, yields to cold H_2O *γ-hamameli-tannin* (**I**), m.p. 217—233° (slight decomp.), and then to hot H_2O ellagitannin, m.p. 347° (decomp.), $[\alpha]_D^{21}$ +23·07° in H_2O, $[\alpha]_D^{19}$ +17·11° in EtOH. (**I**) is 3 : 4 : 5 : 1-$(OH)_3C_6H_2{\cdot}CO_2{\cdot}[C_6H_{10}O_4{\cdot}O]_2{\cdot}CO{\cdot}C_6H_2(OH)_2{\cdot}OMe$-1 : 3 : 4 : 5; with hamamelase in H_2O at 37° it yields gallic acid, the 3-Me ether thereof, and glucose; with aq. $NaHCO_3$ in air it gives a mixture, whence Ac_2O yields *ellagic acid Me₂ ether diacetate* (**II**; R = R′ = Me), m.p. 287—291°, *Me₁ ether triacetate* (**II**; R = Ac, R′ = Me), m.p. 301—302°, and *tetra-acetate* (**II**; R = R′ = Ac), m.p. 344—347°.



(II.)

R. S. C.

Two types of molecules in starch. B. Brimhall and R. M. Hixon (*Wallerstein Lab. Comm.*, 1943, **6**, 95—100).—Evidence supporting the two-component theory of starch structure is presented. Methods for separating amylose (straight chain) and amylopectin (branched chain) are outlined, and the properties of these components discussed, variations between starches of different origin being noted. I. A. P.

Starch. X. End-group determination of starch components. K. Hess and B. Krajnc (*Ber.*, 1940, **73**, [*B*], 976—979).—Erythro- and amylo-amylose (Samec *et al.*, A., 1921, i, 226) give, in end-group determinations, 4·94—5·01 and 0·46—0·50%, respectively, of tetramethylglucose, indicating 23·3—23·4 and 229—247 units per mol., respectively, whereas η in $CHCl_3$ indicates 113—129 and 213—283 units, respectively. R. S. C.

Characterisation of components of starch. J. F. Foster (*Iowa State Coll. J. Sci.*, 1943, **18**, 36—38).—Mol. wts. of various amyloses have been determined from viscosity measurements and are related to the potentials at which I is taken up. Osmotic behaviour of amylose and amylopectin has also been investigated. F. R. G.

Starch–iodine complex. R. R. Baldwin (*Iowa State Coll. J. Sci.*, 1943, **18**, 10—12).—Absorption spectra of the starch–I complex under varying conditions indicate that the I atoms have definite positions in the starch helix. From these results deductions concerning the structure of starch can be made. F. R. G.

Starch. XXV. Glycogen of native muscle. K. H. Meyer and R. Jeanloz (*Helv. Chim. Acta*, 1943, **26**, 1784—1798).—Only a part of the glycogen (**I**) of mussel muscle can be extracted with hot H_2O. The remainder is found with the coagulated proteins. This fraction can be solubilised by $CCl_3{\cdot}CH(OH)_2$ or 40% $CaCl_2$. These reagents do not hydrolyse the proteins or rupture chemical linkings between carbohydrate and protein but the glycogen remains insol. (**I**) therefore consists of parts sol. and insol. in H_2O. Sol. (**I**) after pptn. by MeOH contains 85% of pure (**I**) and proteins, the greater part of the latter being removable by pptn. with picric acid. Electrodialysis of (**I**) gives a fraction (*A*) sol. and limpid, an opaque fraction (*B*), and swollen particles (*C*). *A* and *B* can be freed from proteins by agitation with $CHCl_3$ but this method is not applicable to *C*, which is dissolved in 40% $CaCl_2$ and pptd. by I as a brown compound from which the carbohydrate is readily regenerated. There remains some (**I**) which can be solubilised with a proportion of proteins by heating with 33% $CCl_3{\cdot}CH(OH)_2$ and purified through its compound with I (fraction *D*). Even after complete purification *C* and *D* remain insol. in H_2O. (**I**), prepared by treatment with KOH at 100°, is also composed of sol. and insol. portions. P is absent from all fractions and the N content can be diminished to 0·07% by methods which do not attack chemical linkings. After dissolution in $CCl_3{\cdot}CH(OH)_2$ and pptn. by EtOH, the fractions are acetylated by Ac_2O and C_5H_5N, the difficulty increasing with the insolubility of the fraction; measurements of $\eta_{sp.}$ of these acetates in $CH_2Ph{\cdot}OH$ indicate a mol. sp. wt. $>6 \times 10^6$. Comparison of the viscosity curve of the acetates of amylopectin, amylose, and (**I**) indicates that the mol. of (**I**) is very highly branched and compact in character. The limit of degradation of *A* by β-amylase is 43—43·5% whereas the figures for *B* and *C* are 33—34% and 30—32% respectively. HCl converts (**I**) into fragments which retain their highly polymerised character. It appears therefore that the voluminous enzyme fails to penetrate the mol. of (**I**) and that certain ramifications are consequently protected. H. W.

Yeast-mannan. R. Garzuly-Janke (*J. pr. Chem.*, 1940, [ii], **156**, 45—54).—By the methods of Salkowsky (A., 1894, i, 316), Daoud *et al.* (A., 1931, 1277), and Harden *et al.* (*J.C.S.*, 1902, **81**, 1224), bakers' yeast yields mannans having $[\alpha]_D^{20}$ +90·1°, +70°, and +78°, respectively, and containing no P or N. Extraction of the yeast by H_2O at, successively, room temp., 40°, and 100° (total 100—120 hr.) gives a product containing carbohydrate 85·8—87, N 0·89—0·99, P 0·08—0·09, and ash 1·00—1·18%, and having $[\alpha]_D$ +62° to +63°. Extraction with 75% H_2SO_4 at room temp. (<24 hr.) gives a product containing carbohydrate 87·6—89·5, N 1·09—1·21, P 0·12—0·18, and ash 1·91—2·00%, and having $[\alpha]_D$ +66·8° to +67·2°. Alkali extraction thus decomposes the mannan-protein or -lipin components originally present. R. S. C.

Preparation of main valency gels by net formation from cellulose molecules in solution. R. Signer and P. von Tavel (*Helv. Chim. Acta*, 1943, **26**, 1972—1978).—Methylcellulose (**I**) of mean mol. wt. 21,000 and containing 68 free OH groups per 100 glucose residues reacts with $(COCl)_2$ (**II**) in $CHCl_3$ containing p-$C_6H_4Me{\cdot}NMe_2$ (**III**) to form a main valency gel. For every such solution a definite solidification time can be determined. It is considered that a mol. of (**II**) reacts one-sidedly with a free OH of a mol. of (**I**) to give an ester chloride; the second COCl group is unable for steric reasons to react with a further OH of the same mol. of (**I**) but speedily encounters a OH of a second mol. so that oxalic ester bridges are produced between 2 macromols. The bridge building extends to a third and to further mols. and ultimately proceeds through the whole solution. With a const. ratio of 0·5 mol. of (**II**) to 1 free OH of (**I**) increase in the amount of (**III**) diminishes the solidification time and increases the rate of gel formation. With a const. ratio of 1 mol. of (**III**) per OH the time of solidification is short with 0·5 mol. of (**II**), much greater in presence of 1 mol., whilst further increase in the proportion of (**II**) prevents gel formation. With 1 mol. of (**II**) per OH the time of solidification diminishes sharply with increasing concn. of (**III**). It appears that (**III**) also facilitates the reaction: $OR{\cdot}CO{\cdot}COCl + OR'{\cdot}CO{\cdot}COCl \rightarrow OR{\cdot}CO{\cdot}CO{\cdot}OR' + (COCl)_2$ [R and R′ are glucose residues of different mols. of (**I**)]. Simultaneous variation of (**II**) and (**III**) shows the influences which have been studied separately (see above) to be superimposed. The time of solidification increases as the concn. of (**I**) diminishes in the const. presence of 0·5 mol. of (**II**) and 2 mols. of (**III**) per OH. The transition sol → gel occurs the more rapidly as the distance between the thread mols. in the solution diminishes. In solutions with higher concn. of (**I**) solidification occurs simultaneously through the entire solution whereas in more dil. solution a solid surface layer is first produced which later extends to the lower portions. Net formation is also observed with succinyl, glutaryl, and sebacyl chlorides and partly acetylated celluloses may be used in dioxan. Withdrawal of solvent and reswelling of these systems occurs exactly as with isotropic, main valency gels. H. W.

Kinetics of oxidation of cellulose with periodic acid.—See A., 1944, I, 41.

End-group content of natural ramie. K. Hess and K. P. Jung (*Ber.*, 1940, **73**, [*B*], 980—983).—No tetramethylglucose is obtained from ramie by end-group determinations if degradation is avoided during its prep. R. S. C.

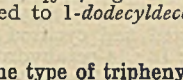
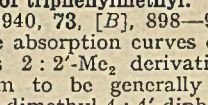
III.—HOMOCYCLIC.

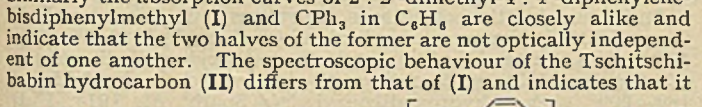
Spectral characteristics and configuration of stereoisomeric carotenoids including prolycopene and pro-γ-carotene. L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár, and L. Pauling (*J. Amer. Chem. Soc.*, 1943, **65**, 1940—1951).—Steric conditions preclude more than 5 ethylenic linkings becoming *cis* in the β-carotene series, 6 in the γ-carotene, or 7 in the lycopene series. The denomination "all-*cis*" refers to these max. Change of the all-*trans* to a one-*cis* compound shifts the absorption max. by 4—6 mμ. Pro-carotenoids have "available" one-*trans* linking, since melting and chromatography reveals compounds having max. at still shorter λ. The isomerides in the lycopene series are investigated in detail; not all have the "*cis*-peak" (A., 1944, II, 9). For lycopene in light petroleum the band at ~470 mμ. is due to the electron transition 0 → 1, corresponding to oscillation of the "unsaturation" electrons between the ends of the chain; the *cis*-peak is due to the 0 → 2 transition and oscillation between the centre and ends of the chain; the ~270 mμ. band is due to the 0 → 3 transition and oscillation between (*a*) the first and third and (*b*) second and fourth quarters of the chain. Lycopene isomerides having a vertical plane of symmetry should have an intensity at the main absorption band ≮~80% of that of the all-*trans*-compound; this is the case for several known isomerides. The *cis*-peak does not exist for compounds having a centre of symmetry; its intensity depends on the distance between the *cis*-linking and the straight line joining the two ends of the chain; it is thus a max. for the compound in which the central C:C is *cis* and the others *trans* (in the lycopene series, neolycopene-*A*). The intensity of the 0 → 3 max. ∝ approx. that of the main max. but is less for compounds which are twice bent. Further considerations allow prediction of the ease of isomerisation, *e.g.*, that the central C:C is easiest to isomerise. Equilibrium amounts of isomerides are 10^{-x}, x being the no. of *cis*-linkings, which accounts for the limited no. of isomerides isolated. R. S. C.

Physical data of alkylcyclohexanes. A. W. Schmidt and A. Grosser (*Ber.*, 1940, **73**, [*B*], 930—933).—The following -cyclo*hexanes* are obtained by hydrogenation (PtO_2 in warm AcOH) of the requisite alkylbenzenes; the process is often irregular and generally very slow, re-activation of the catalyst being frequently necessary: n-*butyl*-, b.p. 64°/12 mm.; n-*heptyl*-, b.p. 109—110°/12 mm., m.p. 41°; n-*dodecyl*-, b.p. 131—132°/0·8 mm., m.p. 12°; n-*tetradecyl*-, b.p. 155°/0·8 mm., m.p. 25°; n-*hexadecyl*-, b.p. 163—164°/1·5 mm., m.p. 32·5°. Vals. of *d*, *n*, and η are recorded. H. W.

Methylation of benzene. A. Klit (5 *Nordiske Kemikermøde*, 1939, 217—218).—MeCl and *m*-xylene ($AlCl_3$–HCl) do not give 1 : 2 : 3-$C_6H_3Me_3$ or 1 : 2 : 3 : 4-$C_6H_2Me_4$. The equilibrium mixture from *o*-xylene (I) ($AlCl_3$–HCl) does not contain (I). M. H. M. A.

Syntheses of one-, two-, and three-nuclear hydrocarbons with 22 carbon atoms. N. Turkiewicz (*Ber.*, 1940, **73**, [*B*], 861—866).—*p*-Cymene (I) and lauryl chloride are converted by $AlCl_3$ in CS_2 into *carvacryl undecyl ketone* (II), m.p. 40·5°, b.p. 168—170°/1 mm., reduced (Clemmensen) with difficulty to 2-*dodecyl*-p-*cymene*, b.p. 163—164°/1 mm. Reduction (Raney Ni–H_2 at 230—240°/148 atm.; decahydronaphthalene) of (II) affords 2-*dodecyl*-p-*menthane*, b.p. 159—160°/1 mm. Di*iso*amylacetyl chloride, (I), and $AlCl_3$ in CS_2 give *carvacryl di*isoamylmethyl *ketone*, b.p. 162°/1 mm., reduced (Raney Ni) to *α-hexahydrocarvacryl-β-di*isoamylethane [4-iso*propyl*-2-*ββ′-di*isoamylethylhexahydrotoluene], b.p. 150—152°/1 mm. (I) is converted by CH_2O and HCl in presence of anhyd. $ZnCl_2$ and $NiCl_2$ into carvacrylmethyl chloride (IV), converted by Mg and CO_2 into *αβ*-dicarvacrylethane (III), b.p. 155—156°/1 mm., and carvacrylacetic acid, m.p. 69—70°; the corresponding Et ester, b.p. 136°/2 mm., and 1-$C_{10}H_7$·MgBr afford 1-*naphthyl carvacrylmethyl ketone*, b.p. 195—198°/0·5 mm., hydrogenated at 240—260°/150 atm. in decahydronaphthalene containing Raney Ni to *α-hexahydrocarvacryl-β*-1-*decahydronaphthylethane*, b.p. 165—166°/1 mm. (III) is obtained from (IV) and Na in boiling Et_2O and is hydrogenated at 240—260°/120—160 atm. in presence of Raney Ni to *αβ-dihexahydrocarvacrylethane*, b.p. 150—154°/1 mm. 1-$C_{10}H_7$·MgBr and lauronitrile give *α-napthyl undecyl ketone*, reduced to 1-*dodecyldecahydronaphthalene*, b.p. 170—171°/1 mm. H. W.

***pp′*-Diradical of diphenyl of the type of triphenylmethyl. II.** W. Theilacker and W. Ozegowski (*Ber.*, 1940, **73**, [*B*], 898—908; cf. A., 1940, II, 270).—Comparison of the absorption curves of 4 : 4′-dihydroxydiphenylmethyldiphenyl, its 2 : 2′-Me_2 derivative, and CPh_3·OH in conc. H_2SO_4 shows them to be generally similar. Similarly the absorption curves of 2 : 2′-dimethyl-4 : 4′-diphenylenebisdiphenylmethyl (I) and CPh_3 in C_6H_6 are closely alike and indicate that the two halves of the former are not optically independent of one another. The spectroscopic behaviour of the Tschitschibabin hydrocarbon (II) differs from that of (I) and indicates that it has predominatingly the quinonoid form  whereas (I) is predominatingly the diradical,  . When exposed to air crystals of (II) give an orange-red *peroxide*, m.p. 111—112°, which immediately liberates I from acidified KI, evolves CH_4 from MgMeI, and in conc. H_2SO_4 gives the same halochromism as the carbinol. The substance has the structure



(*A*) or $[OH·O·CPh_2·C_6H_4]_2$, of which the former is considered the more probable. Passage of air through a solution of (II) in C_6H_6 or tetrahydronaphthalene causes a change of colour with gradual separation of a *peroxide*, m.p. 156—171° according to the mode of prep.; this slowly liberates I from acidified KI, evolves CH_4 from MgMeI, and in conc. H_2SO_4 gives the same halochromism as the carbinol. Analytical results indicate the formula *A* with $n > 10$. (I) and (II) behave similarly towards O_2. Since all the available evidence points against the existence of a true diradical in (II) it is doubtful whether the behaviour towards O_2 is a true criterion of diradical nature. H. W.

Reactions of tetrahydrophenanthrene. II. W. E. Bachmann and M. W. Cronyn (*J. Org. Chem.*, 1943, **8**, 456—465).—A mixture of γ-1- and -2-naphthylbutyric acid is treated with PCl_5 in C_6H_6 at room temp. and then at 100° followed by $SnCl_4$ in C_6H_6 at 5—10° and hydrolysis, thereby giving a mixture of 1- and 4-ketotetrahydrophenanthrene (85% yield), reduced to 1 : 2 : 3 : 4-tetrahydrophenanthrene (I) in 90% yield. AcCl is added to anhyd. $AlCl_3$ in CS_2 followed by $(CHCl_2)_2$; the mixture is warmed at 45—50° until the $AlCl_3$ has dissolved completely to a green solution, which is cooled to 15° and treated with (I) in CS_2; the product is hydrolysed to 9-*acetyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II), b.p. 163—166°/0·1 mm., m.p. 56·5—58°. Successive additions of AcCl in $PhNO_2$ to $AlCl_3$ at 5° and (I) in $PhNO_2$ at −14° give (II) and 7-*acetyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (III), m.p. 90·5—91·5°, reduced (Zn–Hg and HCl in boiling AcOH–PhMe) to 7-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (*picrate*, m.p. 90—91°), dehydrogenated (Pd–C at 300—320°) to 7-ethylphenanthrene, m.p. 65—66° (picrate, m.p. 93·5—94·5°). 7-*Bromoacetyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, from (III) and Br in abs. Et_2O at −15° to −5°, m.p. 115·5—116·5°, is converted by condensation with $CHNa(CO_2Et)_2$ followed by hydrolysis and decarboxylation of the product into β-1 : 2 : 3 : 4-tetrahydrophenanthryl-7-propionic acid, m.p. 155·5—157°. Addition of (I) in CS_2 to a solution of $AlCl_3$ and BzCl in the same solvent leads to 9-*benzoyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 120—121°, the *oxime*, m.p. 228—229°, of which is converted by PCl_5 in boiling C_6H_6 into 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-9-*carboxylanilide* (IV), m.p. 240—241°, also obtained from the acid chloride and NH_2Ph. Similarly (I), EtCOCl, and $AlCl_3$ in CS_2–$C_2H_2Cl_4$ afford 9-*propionyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 160—162°/0·05 mm., m.p. 43—44°, reduced (Clemmensen) to 9-*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 25—25·5° (*picrate*, m.p. 106—107°), which is dehydrogenated (Pd–C at 300—320°) to 9-propylphenanthrene, m.p. 58·5—59·5° (picrate, m.p. 95·5—96°). Dropwise addition of Br in C_6H_6 to (I) in C_6H_6 containing reduced Fe leads to 9-*bromo*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 142—145°/0·05 mm. (*picrate*, m.p. 102—103°), converted by CuCN in C_5H_5N at 215—225° into the 9-*CN*-compound, m.p. 124—125°, which is hydrolysed by protracted action of boiling KOH–MeOH to 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-9-*carboxylic acid*, m.p. 215—216° (*Me* ester, m.p. 70·5—71°). (I), paraformaldehyde, AcOH, HCl, and 85% H_3PO_4 at 80—85° yield 9-*chloromethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (V), b.p. 163—165°/0·05 mm., m.p. 60·5—61°, which in boiling aq. $COMe_2$ containing KCN passes into 1 : 2 : 3 : 4-*tetrahydrophenanthryl*-9-*acetonitrile*, m.p. 89·5—90°, hydrolysed by HCl–AcOH to the -9-*acetic acid* (VI), m.p. 153—153·5°, also obtained by hydrolysis of the -9-*acetamide*, m.p. 211·5—212·5°, obtained by the Willgerodt method from (II). Treatment of (IV) with PCl_5 in C_6H_6 and of the product with anhyd. $SnCl_2$ and dry HCl in Et_2O–$C_2H_4Cl_2$ followed by hydrolysis leads to 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-9-*aldehyde*, m.p. 128·5—129°, which condenses with $CH_2(CO_2H)_2$ in C_5H_5N at 100° to β-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-9-*acrylic acid*, m.p. 226·5—227·5°, reduced (Na–Hg) to the -9-*propionic acid*, m.p. 168—169° (*Me* ester, m.p. 49—50°), which is also obtained from (V) by aid of $CH_2(CO_2Et)_2$. The *oxime*, m.p. 157—158°, of (III) is transformed by PCl_5 in boiling C_6H_6 into 9-*acetamido*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 191—192°, hydrolysed by boiling HCl–EtOH to the 9-*amine*, m.p. 76·5—77° (*hydrochloride*, m.p. 263—264°). 7-*Acetamido*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 136—137°, and the non-cryst. 7-amine (*hydrochloride*, m.p. 238—239°) are obtained similarly from the mixture of Ac derivatives (see above). The following are obtained by similar methods: 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-7-*carboxylic acid*, m.p. 184—186° (*Me* ester, m.p. 114—115°); 1 : 2 : 3 : 4-*tetrahydrophenanthryl*-7-*acetamide*, m.p. 210—211°, and -*acetic acid*, m.p. 150—151°. (VI) is converted by $SOCl_2$ in dry Et_2O containing a little C_5H_5N at room temp. into the chloride, cyclised by $AlCl_3$ in C_6H_6 to 4-*keto*-7 : 8 : 9 : 10-*tetrahydroacephenanthrene*, m.p. 158·5—160°, which is reduced (Clemmensen) to 7 : 8 : 9 : 10-tetrahydroacephenanthrene, m.p. 89—90° (picrate, m.p. 111—112°). H. W.

1 : 2 : 9 : 10-Tetramethylanthracene. R. B. Sandin, R. Kitchen, and L. F. Fieser (*J. Amer. Chem. Soc.*, 1943, **65**, 2018—2020).—1 : 2-Dimethylanthraquinone (modified prep.), m.p. 157·5—158·5°, with MgMeI–Et_2O and then HI (50%)–HBr (*d* 1·4)–MeOH gives impure, yellow, amorphous (?) 1 : 2 : 9-trimethyl-10-iodomethylanthracene (I), which with NaOMe–MeOH at 60—70° yields (?)1 : 2 : 9-*trimethyl*-10-*methoxymethylanthracene* (II), yellow, fluorescent, m.p. 124·5—125·5° [*compound*, m.p. 142·5—143·5°, with *s*-$C_6H_3(NO_2)_3$], and (?) 9-*methoxy*-1 : 2 : 9-*trimethyl*-9 : 10-*dihydroanthracene*, non-fluorescent, colourless, m.p. 141—142° [with a drop of HCl in MeOH gives (II)]. $SnCl_2$–conc. HCl–dioxan at the b.p. reduces (I) to yellow 1 : 2 : 9 : 10-tetramethylanthracene, m.p. 52—54° after softening, which is too unstable in air to be isolated except as *picrate*, m.p. 137—138°, or *compound*, m.p. 170·5—171·5°, with *s*-$C_6H_3(NO_2)_3$. M.p. are corr. R. S. C.

Aromatic cyclodehydration. XIV. 9 : 10-Dialkylphenanthrenes. C. K. Bradsher and S. T. Amore (*J. Amer. Chem. Soc.*, 1943, **65**, 2016—2017; cf. A., 1944, II, 10).—COR_2 with *o*-C_6H_4·MgI–Et_2O and then aq. NH_4Cl gives α-2-diphenylyl*iso*propyl alcohol, m.p. 71° (lit., 75°), b.p. 145—154°/7 mm., γ-2-diphenylyl-*n*-pentan-γ-ol, b.p. 155—157°/7 mm., δ-2-*diphenylyl*-n-*heptan*-δ-*ol* (I), m.p. 68°, b.p. 182—183°/11 mm., and ε-2-diphenylyl-*n*-nonan-ε-ol, b.p. 185—192°/8 mm., dehydrated by $KHSO_4$ at 160°. to β-2-diphenylylpropylene· (71% over-all), b.p. 125—128°/7 mm., γ-2-diphenylyl-Δβ-*n*-pentene (47% over-all), b.p. 138—141°/7 mm., δ-2-diphenylyl-Δγ-*n*-heptene (71% over-all), b.p. 155—157°/8 mm., and ε-2-diphenylyl-Δδ-*n*-nonene (55% over-all), b.p. 178—179°/7 mm., respectively, containing small amounts of Ph_2. Thence BzO_2H–$CHCl_3$ at 0°, followed by boiling 34% HBr, yields 9-methyl- (40%; 68% obtained from the oxide by $KHSO_4$ at 160°), m.p. 92° (picrate, m.p. 154°), 9-*methyl*-10-*ethyl*- (54%), m.p. 85° (picrate, m.p. 150°), 9-*ethyl*-10-n-*propyl*- (44%), m.p. 69° (picrate, m.p. 117°), and 9-n-*propyl*-10-n-*butyl*-*phenanthrene* (67%), m.p. 74° (picrate, m.p. 99°), respectively. With H_2SO_4 (5 drops) in boiling AcOH (15 c.c.), (I) gives 9 : 9-*di*-n-*propylfluorene*, m.p. 37—38°. R. S. C.

Acetylation of primary aromatic amines *in vivo* and *in vitro*.—See A., 1944, III, 129.

Derivatives of 1 : 2 : 4 : 5-tetrachlorobenzene. III. Amination of 2 : 3 : 5 : 6-tetrachloro-nitrobenzene and -4-nitroaniline. A. T. Peters, F. M. Rowe, and D. M. Stead (*J.C.S.*, 1943, 576—577; cf. A., 1943, II, 323).—The NO_2 and, to a smaller extent, both Cl *o* to

it in 2 : 3 : 5 : 6 : 1-$C_6HCl_4{\cdot}NO_2$ (I) are labile. With EtOH–NH_3 at 200° for 10 hr., (I) affords 2 : 3 : 5 : 6 : 1-$C_6HCl_4{\cdot}NH_2$ (61%) and 3 : 5-*dichloro*-1-*nitro*-2 : 6-*diaminobenzene* (II) (5·6%), m.p. 172—173° [Ac_2 derivative, m.p. 315° (decomp.), darkens 295°]; 9·7% of 1 : 3 : 5 : 6 : 2-$NO_2{\cdot}C_6HCl_3{\cdot}NH_2$ is also formed, as shown by reduction with aq. EtOH–$Na_2S_2O_4$ to the diamine, and conversion by phenanthraquinone (III) in AcOH into 1 : 2 : 4-*trichloro*-5 : 6 : 9′ : 10′-*phenanthraphenazine*, m.p. 262—263°. (II) does not condense with (III); reduction and then condensation of 4 : 6 : 1 : 2 : 3-$C_6HCl_2(NH_2)_3$, m.p. 121—122° (decomp.), with (III) gives 2 : 4-*dichloro*-1-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine* (IV), m.p. 265°. 3 : 5 : 1 : 2-$C_6H_2Cl_2(NO_2)_2$ is unaltered with KNO_3–25% oleum at 130—160°. 1 : 2 : 5 : 4 : 6-$NH_2{\cdot}C_6HCl_2(NO_2)_2$, m.p. 170—171°, is reduced ($Na_2S_2O_4$) to 3 : 6 : 1 : 2 : 5-$C_6HCl_2(NH_2)_3$, converted by (III) into 1 : 4-*dichloro*-2-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine*, m.p. ~322°, isomeric with (IV). Only the two Cl atoms *o* to NO_2 in 4 : 2 : 3 : 5 : 6 : 1-$NO_2{\cdot}C_6Cl_4{\cdot}NH_2$ (V) are labile. (V) with EtOH–NH_3 at 200° for 22 hr. gives 3 : 5-*dichloro*-1-*nitro*-2 : 4 : 6-*triaminobenzene* (56%), m.p. 256—257° (decomp.) [does not condense with (III)], and a trace of 1 : 3 : 5 : 6 : 2 : 4-$NO_2{\cdot}C_6Cl_3(NH_2)_2$ as shown by reduction and conversion into 1 : 2 : 4-*trichloro*-3-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine*, m.p. >330°, darkening at 280°. A. T. P.

Action of aluminium chloride on phenol homologues. G. Baddeley (*J.C.S.*, 1943, 527—531).—PhOH (1 mol.) and $AlCl_3$ (1 mol.), warmed until evolution of HCl ceases, afford OPh·$AlCl_2$, b.p. 210°/15 mm., m.p. 183° (with H_2O gives PhOH). *p*-$C_6H_4Me{\cdot}O{\cdot}AlCl_2$ is stable at 200° for several hr., but *p*-cresol (I) and $AlCl_3$ (>1 mol.) at 130° for 2 hr. give some *m*-cresol (II). Kinetic study shows this change to be reversible and unimol. in respect of *p*-$C_6H_4Me{\cdot}O{\cdot}AlCl_2$, but bimol. in respect of the further $AlCl_3$ used. The reagent is not used up, and the unimol. velocity coeff. at a given temp. $\propto$ square root of amount of reagent present. (I) or (II) and $AlCl_3$ at 135° (34 hr.) give an equilibrium mixture containing 60·7% of (II) and 39·3% of (I). At 125°, a similar mixture results; thus the heat of isomerisation is small. *o*-Cresol (III) (1 mol.) and $AlCl_3$ (2 mols.) at 130° for 3 hr. give (III) only, but at 170° for 5 hr., intermol. change occurs and (III) [or (II) or (I)] gives PhOH + *m*-5-xylenol (IV). (IV) is also obtained from *m*-2-xylenol and $AlCl_3$ at 130—135°. *m*-4-Xylenol (at 115—120°) gives some *o*-3- and *p*-xylenol (V), but at 130—135° for 4·5 hr., (IV) is formed: (V) or *o*-4-xylenol is convertible into (IV), and (V) + (IV) are obtained from *o*-3-xylenol and $AlCl_3$ at 120—125°. Hemimellithenol is isomerised (quant.) to *iso*-ψ-cumenol by $AlCl_3$ at 100° for 10 hr. With $AlCl_3$, *p*- or *m*-$C_6H_4Et{\cdot}OH$ (at 120° or 125°, respectively) gives PhOH and 3 : 5 : 1-$C_6H_3Et_2{\cdot}OH$, also obtained from *o*-, *m*-, or *p*-$C_6H_4Et{\cdot}OH$ at 100°; C_2H_4 is probably an intermediate. 3 : 4 : 1-$C_6H_3MeEt{\cdot}OH$ (100°; 18 hr.) gives 3 : 5 : 1-$C_6H_3MeEt{\cdot}OH$. With (I), PhMe, and $AlCl_3$ at 135°, much decomp. and some demethylation occur, and PhOH + (I) are isolable. Mechanisms of interconversions are suggested. Intermol. migration is associated with a high nuclear electron availability. The sequence, C_6H_6 homologues, xylenols, cresols, PhOH, is one of decreasing electron availability (nucleophilic character) in presence of excess of $AlCl_3$. A mechanism is deduced for the Scholl reaction. A. T. P.

Action of aluminium chloride on aromatic bromo-compounds. G. Baddeley and J. Plant (*J.C.S.*, 1943, 525—527).—PhBr is a brominating agent in presence of $AlCl_3$. Thus, PhBr and $AlCl_3$ at 100° give some *p*-$C_6H_4Br_2$. *p*-Cresol (I), PhBr, and $AlCl_3$ at 100° yield small amounts of 2 : 1 : 4-$C_6H_3BrMe{\cdot}OH$ (II), C_6H_6, higher-boiling products, and unchanged materials. PhOH similarly affords high-boiling products, but no $C_6H_4Br{\cdot}OH$. *o*-, *m*-, or *p*-$C_6H_4Br{\cdot}OH$ (III) (1 mol.) and $AlCl_3$ (2 mols.) at 130° afford (III) (~70%) and PhOH (~17%), with higher-boiling products; isomerisation of the *o*- is more facile than that of the *m*-isomeride. (I) (1 mol.), (III) (1 mol.), and $AlCl_3$ (4 mols.) at 130° yield PhOH, (II), higher-boiling products, and (I) + (III). At 100° for 20 hr., 3 : 1 : 4-$C_6H_3BrMe{\cdot}OH$ (1 mol.) and $AlCl_3$ (2 mols.) give (I) (3%), (II) (60%), and 2 : 6-*dibromo*-*p*-*cresol* (IV) (3%), m.p. 109° (obtained also from 2 : 6 : 1 : 4-$C_6H_2Br_2Me{\cdot}NH_2$); at 127° for 1 hr. the respective % are 8; 67, and 6. 2 : 4 : 1-$C_6H_3BrEt{\cdot}OH$ (*p*-*nitrobenzoate*, m.p. 57°) and $AlCl_3$ at 100° afford unchanged material, *p*-$C_6H_4Et{\cdot}OH$, and 3 : 4 : 1-$C_6H_3BrEt{\cdot}OH$ (V) (*p*-*nitrobenzoate*, m.p. 108°). 4 : 2 : 1-$OMe{\cdot}C_6H_3Br{\cdot}COMe$ (*semicarbazone*, m.p. 198°) is reduced (Clemmensen) to 3 : 4 : 1-$C_6H_3BrEt{\cdot}OMe$, b.p. 123—124°/5 mm., converted by boiling HBr (*d* 1·5)–AcOH into (V). With $AlCl_3$ at 130° for 1 hr., 3 : 5 : 1 : 4-$C_6H_2Br_2Me{\cdot}OH$ gives (IV); at 100° for 24 hr., some 2 : 5-*dibromo*-*p*-*cresol* (VI), m.p. 61° [probably intermediate in forming (IV)], is obtained also. 3 : 1 : 4-$C_6H_3BrMe{\cdot}OH$ and Br–AcOH give (VI) and 2 : 3 : 5 : 1 : 4-$C_6HBr_3Me{\cdot}OH$; with Cl_2–CCl_4 at room temp., (VI) yields 3-*chloro*-2 : 5-*dibromo*-*p*-*cresol*, m.p. 95°, converted by Cl_2–CCl_4 + Fe at 70—80° into 3 : 6 : 2 : 5 : 1 : 4-$C_6Cl_2Br_2Me{\cdot}OH$, new m.p. (177—178°. 3 : 6 : 1 : 4-$C_6H_2Br_2Me{\cdot}OH$ and $AlCl_3$ at 130° give IV). With 2 : 6 : 4 : 1-$C_6H_2Br_2Et{\cdot}OH$ (*p*-*nitrobenzoate*, m.p. 93°), $AlCl_3$ at 120° causes some isomerisation to 3 : 5-*dibromo*-4-*ethylphenol*, m.p. 116—117° (convertible into 2 : 3 : 5 : 6 : 4 : 1-$C_6HBr_4Et{\cdot}OH$, m.p. 106°). 4 : 3 : 1-$C_6H_3ClBr{\cdot}OH$ is obtainable from 4 : 2 : 1-$C_6H_3ClBr{\cdot}OH$, but *o*-$C_6H_4Cl{\cdot}OH$ or 3 : 5 : 1 : 4-$C_6H_2Cl_2Me{\cdot}OH$ is not isomerised by $AlCl_3$. Br migrates to the nuclear positions of greatest electron density, as indicated by nuclear alkylation. A. T. P.

4-Diphenylyl butyrate. S. E. Hazlet and L. C. Hensley (*J. Amer. Chem. Soc.*, 1943, 65, 2041).—This *ester*, m.p. 59—60·3°, is prepared (81%) from *p*-$C_6H_4Ph{\cdot}OH$ and PrCOCl in C_5H_5N–dioxan. R. S. C.

Triterpenes. LXXXI. Synthesis of 3-hydroxy-1 : 2 : 5-trimethylnaphthalene and of 1 : 2 : 6-trimethylphenanthrene. L. Ruzicka, E. Rey, and W. J. Smith (*Helv. Chim. Acta*, 1943, 26, 2057—2065).—Successive addition of 1 : 2 : 3-$C_6H_3Me_2{\cdot}OMe$ and $(CH_2{\cdot}CO)_2O$ to $AlCl_3$ in $PhNO_2$ at 0° gives γ-*keto*-γ-4-*methoxy*-2 : 3-*dimethylphenyl*-n-*butyric acid*, m.p. 178°, reduced (Zn–Hg in AcOH–conc. HCl) to γ-4-*methoxy*-2 : 3-*dimethylphenyl*-n-*butyric acid*, m.p. 122—123°; the acid chloride ($SOCl_2$) could not be cyclised satisfactorily by $AlCl_3$ in CS_2 but the acid and P_2O_5 in boiling C_6H_6 give 1-*keto*-7-*methoxy*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (I), m.p. 78° [*semicarbazone*, m.p. 243° (decomp.)]; attempted cyclisation with 80% H_2SO_4 at 120—130° results also in hydrolysis to the 7-*OH*-compound, m.p. 203° [*semicarbazone*, m.p. 243° (decomp.)]. (I) is converted by an excess of MgMeI in Et_2O followed by treatment of the product with a little I at 140° and dehydrogenation by Se at 330° into 3-*methoxy*-1 : 2 : 5-*trimethylnaphthalene*, m.p. 106—107° [unstable picrate, m.p. 150—151·5° (decomp.)]; this is demethylated by HBr in AcOH to the 3-*OH*-compound, m.p. 140—141° (slight decomp.) (unstable picrate). 4-Methyl*cyclo*hexanone is converted by Mg β-2 : 3-dimethylphenylethyl bromide into β-1-hydroxy-4-methyl*cyclo*hexyl-α-2 : 3-dimethylphenylethane, b.p. 130—160°/0·1 mm., dehydrated and cyclised by P_2O_5 to 1 : 2 : 6-trimethyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydrophenanthrene, b.p. 117—120°/0·06 mm., which is dehydrogenated by Se at 320° to 1 : 2 : 6-*trimethylphenanthrene*, m.p. 128·5—129° (*picrate*, m.p. 167—168°). This is oxidised by CrO_3 in AcOH at room temp. to 1 : 2 : 6-*trimethylphenanthraquinone*, m.p. 207—208° (*quinoxaline* derivative, $C_{23}H_{18}N_2$, m.p. 181—182°). M.p. are corr. H. W.

Antibacterial action of stilbene derivatives. G. Brownlee, F. C. Copp, W. M. Duffin, and I. M. Tonkin (*Biochem. J.*, 1943, 37, 572—577; cf. A., 1944, III, 144).—*p*-Methoxydeoxybenzoin is reduced (Zn–Hg, aq. HCl) to *p*-methoxydibenzyl, which with MgMeI at 180—200° gives *p*-hydroxydibenzyl (cf. Späth, A., 1914, i, 1). α-Ethyldeoxybenzoin with Et_2O–MgEtBr affords α-*hydroxy*-αβ-*diethyldibenzyl* [αβ-*diphenyl*-α-*ethyl*-n-*butyl alcohol*], b.p. 182—186°/14 mm., dehydrated (PCl_3) to $(CPhEt{:})_2$, b.p. 170°/15 mm. (cf. Carlisle and Crowfoot, A., 1941, I, 103), reduced (H_2–PtO_2–$COMe_2$) to $(CHPhEt)_2$, m.p. 83—84° (lit. 88°, 92—93°). COPhEt and Al–Hg in wet Et_2O afford $(CPhEt{\cdot}OH)_2$, m.p. 135—136° (lit. 138—139°). *p*-Methoxy-αβ-diethylstilbene, m.p. 79—80° (from distillation of δ-phenyl-γ-anisylhexan-γ-ol), is reduced (H_2, Pd–C, $COMe_2$) to p-*methoxy*-αβ-*diethyldibenzyl*, m.p. 89—90°; demethylation (MgMeI) affords *p*-hydroxy-αβ-diethylstilbene, m.p. 125—127°, and p-*hydroxy*-αβ-*diethyldibenzyl*, m.p. 139—140° [*benzoate*, m.p. 110°; *O*-SO_3H-derivative (C_5H_5N salt, m.p. 195—196°)], respectively. 4-*hydroxy*-4′-*methoxy*-αβ-*diethylstilbene*, m.p. 101—102°, is obtained as a by-product during demethylation of the Me_2 ether. *p*-Nitrodeoxybenzoin and EtI in boiling EtOH–NaOEt yield p-*nitro*-α-*ethyldeoxybenzoin*, m.p. 78—80°, reduced (Fe–$FeCl_3$–H_2O–xylene) to the NH_2-compound, m.p. 128—129°, which with MgEtBr gives p-*amino*-β-*hydroxy*-αβ-*diethyldibenzyl*, m.p. 91—92°, converted by AcOH–HCl into p-*amino*-αβ-*diethylstilbene hydrochloride*, m.p. 254—255°; the corresponding *base*, m.p. 96—97°, with *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in C_5H_5N yields the *Ac* derivative, m.p. 207—208°, of p-*sulphanilamido*-αβ-*diethylstilbene*, m.p. 180—182°. 4′-Nitro-4-hydroxystilbene is reduced (EtOH–aq. NH_3–$FeSO_4$ at b.p.) to 4′-*amino*-4-*hydroxystilbene*, m.p. 270—271° (decomp.). *p*-$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ with *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ and piperidine at 140° gives 4-*hydroxy*-4′-*cyanostilbene*, m.p. 221—223°, converted (method: Ashley *et al.*, A., 1942, II, 172) into 4-*hydroxy*-4′-*amidinostilbene hydrochloride*, m.p. 316—317° (decomp.). F. O. H.

Formation of phenols by the action of hydrogen peroxide on nonphenolic, aromatic aldehydes. E. Späth, M. Pailer, and G. Gergely (*Ber.*, 1940, 73, [*B*], 935—938).—Shaking 100-vol. aq. H_2O_2 with Et_2O and drying gives 2% H_2O_2–Et_2O, whence evaporation gives ~4—6% H_2O_2–Et_2O. This reagent (1·1 mol. of H_2O_2) with ArCHO at 20° (~15 hr.), sometimes with $CHCl_3$ or more Et_2O, gives (i) 2 : 4 : 1-$(OMe)_2C_6H_3{\cdot}OH$ (26·1%) (no acid is formed), (ii) 2 : 4 : 5 : 1-$(OMe)_3C_6H_2{\cdot}OH$ (17·6%) and -$(OMe)_3C_6H_2{\cdot}CO_2H$ (trace), (iii) 3 : 4 : 6 : 1-$(OMe)_2C_6H_2Et{\cdot}OH$ (13·7) and -$(OMe)_2C_6H_2Et{\cdot}CO_2H$ (4·2%), (iv) *p*-$OMe{\cdot}C_6H_4{\cdot}OH$ (7·1) and *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ (6·5%), (v) *o*-$OMe{\cdot}C_6H_4{\cdot}OH$ (6·6) and *o*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ (4·7%), (vi) 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}OH$ (1·4) and -$(OMe)_2C_6H_3{\cdot}CO_2H$ (4·0%), and (vii) PhOH (0·7) and BzOH (8·6%). ArCHO not thus accounted for is mainly recovered unchanged. $OH{\cdot}CHAr{\cdot}O_2H$ may be intermediates. R. S. C.

Synthesis and structure of ψ-cumoquinol monoalkyl ethers. W. John and F. H. Rathmann (*Ber.*, 1940, 73, [*B*], 995—1001).—ψ-Cumoquinol, 2 : 3 : 5 : 1 : 4-$C_6HMe_3(OH)_2$ (I), with MeOH–H_2SO_4 at room temp. gives the 1-*Me ether* (II), m.p. 101°; Me_2SO_4 gives

mainly the Me_2 ether with a little (**II**). 1 : 2 : 5 : 3-$C_6H_2Me_3$·OMe (prep. by Me_2SO_4) with 1 : 2 HNO_3 (*d* 1·52)–AcOH at ~30° gives the 6-NO_2-, m.p. 107—108°, reduced by Sn–conc. HCl–EtOH to the 6-NH_2-derivative (**III**), m.p. 75° (*hydrochloride*, decomp. >230°; impure stannichloride, m.p. 213—215°), whence diazotisation in 0·5N-HCl and heating at 75° gives (**II**). In boiling 90% HCO_2H 3 : 1 : 2 : 5 : 6-OH·C_6HMe_3·NH_2 gives 6-*formamido*iso-ψ-*cumenol*, m.p. 216—219°, which with Me_2SO_4 gives the N-*CHO* derivative, m.p. 178—179°, of (**III**), hydrolysed to (**III**) by conc. HCl. 1 : 2 : 5 : 3-$C_6H_2Me_3$·OH and 1 : 4 HNO_3 (*d* 1·52)–AcOH at room temp. to 45° give the $(NO_2)_2$-derivative, m.p. 134·5° (K and Na salts; *Me*, m.p. 96°, and *Et ether*, m.p. 92°, prepared from the *Ag* salt), but no $(NO_2)_1$-derivative could be obtained. With ROH–H_2SO_4, (**I**) gives the 1-*Et*, m.p. 87—88° [*acetate* (**IV**), m.p. 57—58°; *propionate*, m.p. 40—41°], -*Pr*, m.p. 78°, -*Bu*$^{\alpha}$ (80%; 20—30% obtained by BuBr–NaOEt–EtOH), m.p. 68°, and -iso*amyl ether*, m.p. 51°. (**IV**) is physiologically inactive. R. S. C.

Constituents of red sandalwood. II. Constitution of pterostilbene. E. Späth and J. Schläger (*Ber.*, 1940, **73** [*B*], 881—884; cf. A., 1940, II, 286).—The freely sol. portion of the Et_2O extract of red sandalwood is treated with hot CCl_4. The residue after removal of the solvent is dissolved in Et_2O and fractionally extracted with aq. KOH; the alkaline extracts are acidified and extracted with Et_2O, and the residue from this extract is cryst. from Et_2O–light petroleum, thus giving *pterostilbene* [4-*hydroxy*-3′ : 5′-*dimethoxystilbene*] (**I**), m.p. 85—86°, α 0. (**I**) contains 2 OMe. It is converted by CH_2N_2 into *pterostilbene Me ether* (**II**), m.p. 56—57°. (**I**) quantitatively absorbs 1 H_2 in AcOH containing Pd sponge. Oxidation of (**I**) and (**II**) gives 3 : 5 : 1-$(OMe)_2C_6H_3$·CO_2H (**III**) and *p*-OMe·C_6H_4·CO_2H with (**III**) respectively. H. W.

Hexahydroxybenzene and its derivatives. I. E. Neifert and E. Bartow (*J. Amer. Chem. Soc.*, 1943, **65**, 1770—1772).—1 : 2 : 3 : 5 : 6 : 4-O:$C_6(OH)_4$:O is obtained (80%) from the Na_2 salt (prep. from *i*-inositol by conc. HNO_3 and then $NaHCO_3$) by 1 : 10 45% HI–37% HCl, and with 45% HI (3 pts.) in boiling EtOH (10 pts.) gives ~70% of $C_6(OH)_6$. This yields a hexa-acetate, m.p. 203°, -*propionate*, m.p. 133°, -n-, m.p. 135°, and -iso-*butyrate*, m.p. 164·5°, -n-, m.p. 103°, and -iso-*valerate*, m.p. 155°, -n-*hexoate*, m.p. 97°, -n-*octoate*, m.p. 86°, -n-*decoate*, m.p. 85°, -*chloroacetate*, m.p. 212°, -*trichloroacetate*, m.p. 245°, (decomp.), and -benzoate, m.p. 254°. In 50% EtOH it gives *compounds*, $C_6(OH)_6$,$2NH_2Ar$, in which Ar = Ph, *o*-, *m*-, and *p*-tolyl, *m*- and *p*- (not *o*-)C_6H_4Cl, and a *compound*, $C_6(OH)_6$,NH_2·C_6H_4Me-*o*. R. S. C.

Preparation of fluoreneazo-dyes. W. Bielenberg, H. Goldhahn, and H. Pluskal (*Ber.*, 1940, **73**, [*B*], 878—881).—The following 2-*fluoreneazo*-dyes are obtained by mixing equiv. amounts of 2-fluorenediazonium chloride (**I**) and the requisite phenol with at least 3 equivs. of KOAc in EtOH and purifying the product by repeated dissolution in EtOH and pptn. by H_2O: -*phenol*, m.p. 187·5—191°; -m-, -o-, and -p-*cresol*, m.p. 200°, 173—174°, and 143—144°, respectively; -*thymol*, m.p. 164—164·5°; -*guaiacol*, m.p. 145—146°; -*resorcinol*, m.p. 204—204·5°, decomp. at a slightly higher temp.; -*orcinol*, m.p. 220—221°; -m-4-*xylenol*, m.p. 179—180°; -*phloroglucinol*, softens at 215° and decomposes at a higher temp.; -*pyrogallol*, no distinct m.p. (**I**) and *o*-$C_6H_4(OH)_2$ give a product, m.p. 172—173°; an almost colourless, unidentified compound, m.p. 112—113°, is formed from *o*-$C_6H_4(OAc)_2$ but normal coupling occurs with *o*-OH·C_6H_4·OBz to the benzoate, m.p. 223°, of 2-*fluoreneazopyrocatechol*, m.p. 175°. H. W.

Lignin and related compounds. LXXII. Ultra-violet absorption spectra of compounds related to lignin.—See A., 1944, I, 28.

Constitution of the internal diazo-oxides (diazo-phenols and -naphthols). H. H. Hodgson and E. Marsden (*J. Soc. Dyers and Col.*, 1943, **59**, 271—275).—Previous views on the constitution of the diazo-oxides are reviewed and it is concluded that they are not internal cyclic oxides but resonance hybrids whereas the more stable *o*-diazosulphides are true cyclic compounds. Supporting evidence is adduced from (*a*) coupling, especially in acid solution, (*b*) replacement by H, (*c*) a new bromination reaction in which 6-nitronaphthalene-2 : 1-diazo-oxide affords 6 : 2 : 4 : 1-NO_2·$C_{10}H_4Br_2$·OH via the diazoperbromide, and (*d*) the action of $ZnCl_2$ or $SbCl_3$ in EtOH on diazo-oxides made from *p*-NH_2·C_6H_4·OH, *p*-NH_2·C_6H_4·SO_3H, 1 : 8 : 3 : 6-NH_2·$C_{10}H_4(OH)(SO_3H)_2$, 1 : 8 : 4-NH_2·$C_{10}H_5(OH)$·SO_3H, 2 : 1- and 1 : 2-NO_2·$C_{10}H_6$·NH_2, 2 : 4 : 1- and 1 : 6 : 2-$(NO_2)_2C_{10}H_5$·NH_2; these do not give isolable double salts (considered to be formed) and are recovered unchanged on dilution with H_2O when SO_3H is not present and giving *Zn* salts of the sulphonic acids. The diazo-oxides do not afford periodides with KI but either replace N_2 by I or give K salts of the diazo-oxide sulphonic acids. K. H. S.

Catalytic debenzylation. Effect of substitution on the strength of the *O*- and *N*-benzyl linkings. R. Baltzly and J. S. Buck (*J. Amer. Chem. Soc.*, 1943, **65**, 1984—1992).—The effects of substitution on catalytic debenzylation (Pd–C–H_2; usually in EtOH or MeOH) are investigated by observing the rates of hydrogenolysis of CHArR·OH and COArR etc. and by isolating the products of competitive hydrogenolysis of the hydrochlorides (bases not reduced) of CH_2Ar·NH·CH_2Ar or CH_2Ar·NMe·CH_2Ar. R = alkyl or OH-alkyl reduces the rate of reaction; R = CO·NH_2 or CO_2H prevents it; the exact effect of R = CN or Ph is uncertain, but hydrogenolysis proceeds normally. Benzoin and α-diketones are readily reduced. Reductions of C:C and CH_2·OH in CHPh:CH·CH_2·OH proceed at approx. the same rate. Substitution in Ar of OMe, OH, NH_2, Cl, NR_3Cl, or Me increases the stability. α- or β-$C_{10}H_7$·CH_2 is removed in preference to CH_2Ph, this being the only case in which the ease of removal of CH_2Ph is exceeded; its preparative usefulness is limited to special cases. Ephedrine is not reduced. Hydrogenation of COPhEt in presence of an inefficient catalyst and NH_4Cl gives 85% of CHPhEt·OH [Hartung]. *Hydrochlorides* (m.p. in parentheses) of the following are described: *o*- (123—123·5°) and *m*-methoxybenzyl- (128·5—129°), 4-diphenylylmethyl- [265° (decomp.)], and α-naphthylmethyl-methylamine (189·5—190°); 4-methoxy-3′ : 4′-methylenedioxy- (246—247°) and -4′-hydroxy-dibenzylamine (179—179·5°); 2 : 4′- (160—161°) and 3 : 4′-dimethoxy- (159—160·5°), 4-methyl- (161—162°), and 4-chloro-dibenzylmethylamine (145·5—146·5°); benzyl-α- (225°) and -β-naphthylmethylmethylamine (194—195°); α-naphthylmethyl-β-naphthylmethyl- (230·5—231°) and α-naphthylmethyl-4-diphenylylmethyl-methylamine (211·5—212°). *p*-Aminobenzylmethylamine (*dihydrochloride*, m.p. 201·5—202°), p-*aminomethylphenyltrimethylammonium chloride hydrochloride*, m.p. 223—223·5°, p-*dimethylaminodibenzylamine methochloride hydrochloride*, m.p. 164° (decomp.), p′-*benzyloxybenzylidene*-p-*methoxybenzylamine*, m.p. 82°, p-N-*acet*-N-*benzylamidomethylphenyltrimethylammonium chloride* (**I**), m.p. 130—130·5°, and 4-aminodibenzylmethylamine (*dihydrochloride*, m.p. 182·5—183°), are also described. (**I**) is prepared by the reactions: *p*-NMe_2·C_6H_4·CHO + CH_2Ph·NH_2 → *p*-NMe_2·C_6H_4·CH:N·CH_2Ph → *p*-NMe_2·C_6H_4·CH_2·NR·CH_2Ph (*A*; R = H) → (*A*; R = Ac) → *p*-NMe_3I → (**I**). R. S. C.

Action of potassium on benzpinacol in boiling ether under nitrogen. L. Anschütz and (Miss) A. Ungar (*J. pr. Chem.*, 1940, [ii], **156**, 38—44).—When K is added to $(CPh_2$·$OH)_2$ (**I**) in boiling Et_2O–N_2, change in the b.p. indicates halving of the mol. wt. within 1—2 min., followed in ≮10 min. by appearance of a blue colour due to CPh_2·OK. The first change is due to KOH present in the K decomp. (**I**) into $COPh_2$ and $CHPh_2$·OH, which later react with K to give (i) CPh_2·OK and (ii) $CHPh_2$·OK + H. Analysis (method: C., 1944, Part I) shows presence of ~80% of $CHPh_2$·OK and ~20% of CPh_2·OK, this being caused by reduction of $COPh_2$ to $CHPh_2$·OH by the liberated H. (**I**) and K react more slowly in Et_2O at room temp., in this case evolution of H_2 being visible. KOH may play a part in all formations of ketyls from pinacols. R. S. C.

Synthetic mydriatics. III. F. F. Blicke and H. M. Kaplan (*J. Amer. Chem. Soc.*, 1943, **65**, 1967—1970; cf. A., 1942, II, 237).—The following esters are prepared by heating the appropriate aminoalkyl chloride and acid in Pr$^{\beta}$OH. Mydriatic activity in 2% aq. solution is indicated by 1 poor, 2 moderate, 3 good, or 4 excellent, and anæsthetic activity by *S* slight, *G* good, or *E* excellent; absence of an entry for the salts indicates inactivity. β-Dipropyl- (*hydrochloride*, m.p. 116—118°) and β-dibutyl-aminoethyl (*hydrochloride*, m.p. 104—106°), β-piperidinoethyl (*hydrobromide*, m.p. 140—141°), γ-dibutylamino- (*hydrochloride*, m.p. 92—93°) and γ-piperidino-*n*-propyl (*hydrochloride*, m.p. 136—137°), γ-dimethylamino- [*hydrochloride*, m.p. 117—118°; *methobromide* (*S*), m.p. 145—146°], γ-diethylamino- (*G*), m.p. 66—67°, and γ-*piperidino*-ββ-*dimethyl*-n-*propyl* (*G*), m.p. 96—97°, *mandelate*; β-dimethyl- [*hydrochloride* (4, *E*), m.p. 183—185°] and β-dipropyl-aminoethyl [*hydrochloride* (*G*), m.p. 152—153°], β-diethyl- [*hydrochloride* (3, *G*), m.p. 163—164°] and β-dibutyl-amino-*n*-propyl [*hydrochloride* (*G*), m.p. 167—168°], γ-diethyl- [*hydrochloride* (4, *E*), m.p. 145—146°], γ-dipropyl- [*hydrochloride* (*G*), m.p. 158—159°], and γ-dibutyl-amino-*n*-propyl [*hydrochloride* (*G*), m.p. 114—115°; *methobromide* (*G*), m.p. 166—167°], γ-dimethyl- [*hydrochloride* (4, *E*), m.p. 169—170°; *methobromide* (4, *E*), m.p. 150—151°] and γ-diethyl-amino-ββ-dimethyl-n-propyl [hydrochloride (4, *E*), m.p. 139—140° (lit. 141—142°)] benzilate; β-diethylamino- (*hydrochloride*, m.p. 108—109°), β-dibutylamino- [*hydrochloride* (*E*), m.p. 120—121°], and β-piperidinoethyl [*hydrochloride* (*E*), m.p. 161—162°; *methobromide*, m.p. 149—150°], γ-dibutylamino- [*hydrochloride* (*G*), m.p. 93—94°] and γ-piperidino-*n*-propyl [*hydrochloride* (*S*), m.p. 130—131°], γ-dimethyl- [*hydrochloride* (3), m.p. 128—129°] and γ-diethyl-amino-ββ-dimethyl-*n*-propyl (*phosphate*, m.p. 150—151°) atrolactate; β-diethyl- [*methobromide* (2), hygroscopic, m.p. 99—101°] and β-dibutylaminoethyl (*methobromide*, m.p. 131—132°), γ-dibutylamino- (*methobromide*, m.p. 127—128°) and γ-piperidino-*n*-propyl [hydrochloride (2, *S*), m.p. 127—128° (lit. an oil)], γ-dimethyl- [*phosphate* (2), m.p. 143—144°] and γ-diethyl-amino-ββ-dimethyl-*n*-propyl [phosphate (= Syntropan) (2—3), m.p. 139—141° (lit. 138—140°)] tropate; β-diethylamino- (methobromide, an oil) and β-piperidino-ethyl (*hydrochloride*, m.p. 128—129°), γ-piperidino-*n*-propyl (*methobromide*, m.p. 116—118°), γ-dimethyl- (*methobromide*, m.p. 164—166°) and γ-diethyl-amino-ββ-dimethyl-*n*-propyl (*hydrochloride*, m.p. 99—100°) α-hydroxy-β-phenylpropionate; β-dibutyl-

amino- (*methobromide*, m.p. 129—131°) and β-piperidino-ethyl (*hydrochloride*, m.p. 102—103°; *methobromide*, m.p. 113—115°), γ-dibutylamino- (*methobromide*, m.p. 87—89°) and γ-piperidino-*n*-propyl (*hydrochloride*, m.p. 143—144°), γ-dimethyl- (*methobromide*, m.p. 117—119°) and γ-diethyl-amino-ββ-dimethyl-*n*-propyl (*hydrochloride*, m.p. 89—90°) β-hydroxy-β-phenylpropionate; β-diethylamino- [*hydrochloride* (2, *G*), m.p. 144—146°], β-dipropylamino- [*hydrochloride* (*E*), m.p. 115—116°], and β-piperidino-ethyl [*hydrochloride* (*G*), m.p. 169—171°], γ-diethylamino- [*hydrochloride* (*G*), m.p. 143—145°] and γ-piperidino-*n*-propyl [*hydrochloride* (*E*), m.p. 127—128°], and γ-dimethylamino-ββ-dimethyl-*n*-propyl [*hydrochloride* (*E*), m.p. 136—138°] β-hydroxy-ββ-diphenylpropionate. Generalities noted include the frequent but not universal concurrence of mydriatic and anæsthetic activity, irregularities among homologues, the general activity of benzilates, and the lack of or slight anæsthetic activity of tropates. $CH_2Ph{\cdot}CH(OEt)_2$, b.p. 114—120°/15 mm., is obtained (70%) from $CH_2Ph{\cdot}MgCl$ and $CH(OEt)_3$ in Et_2O and with, successively, 10% H_2SO_4, $NaHSO_3$, KCN, and 18% HCl gives $CH_2Ph{\cdot}CH(OH){\cdot}CO_2H$. β-Piperidinoethyl chloride, b.p. 69°/12 mm. [hydrochloride, m.p. 229—230° (lit., 208°, 231°)], $NBu_2{\cdot}CHMe{\cdot}CH_2Cl$, b.p. 116—120°/29 mm., $NPr_2{\cdot}[CH_2]_3{\cdot}Cl$, b.p. 99—102°, $NBu_2{\cdot}[CH_2]_3{\cdot}Cl$ (*aurichloride*, m.p. 143—146°), and $NMe_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2Cl$, b.p. 44—49°/14 mm., are also described. R. S. C.

Rearrangement of allyl groups in three-carbon systems. III. Nitriles and an acid. D. E. White and A. C. Cope (*J. Amer. Chem. Soc.*, 1943, **65**, 1999—2004; cf. A., 1941, II, 279).—$C{\cdot}C{\cdot}CRR'{\cdot}CH_2{\cdot}CH{:}CH_2$ (R and R′ = CN or CO_2Et) rearranges at 135—200°, with inversion, to $CH_2{:}CH{\cdot}CH_2{\cdot}CH{\cdot}C{:}CRR'$. *cyclo*Hexylidenephenylacetonitrile (**I**) (modified prep.), b.p. 173—174°/10 mm., with $NaNH_2$ in liquid NH_3 gives the Na derivative, which with $CH_2{:}CH{\cdot}CH_2Br$ (**II**) in boiling Et_2O gives α-Δ¹-cyclo*hexenyl*-α-*phenyl*-Δ^γ^-*pentenonitrile* (**III**) (77%), b.p. 106—109°/0·001 mm., hydrogenation of which proceeds in two stages, giving, best with Raney Ni in EtOAc at ~200°/~130 atm., *acet*-β-Δ¹-cyclo*hexenyl*-β-*phenyl*-n-*amylamide* (**IV**) (45%), m.p. 141·5—143°. With PrᵅI instead of (**II**) in C_6H_6, (**I**) gives α-Δ¹-cyclo*hexenyl*-α-*phenyl*-n-*valeronitrile*, b.p. 147—148°/1·5 mm., hydrogenated as above to (**IV**) (53%), m.p. 140·5—142° (proof of structure). $CH_2Ph{\cdot}CN$ with $NaNH_2$–NH_3 and then *cyclo*hexyl bromide in C_6H_6 gives *cyclo*hexylphenylacetonitrile (72%), m.p. 55—55·5° (lit., 56°, 60°), b.p. 165—167°/9 mm., which by propylation as above gives α-*cyclo*hexyl-α-phenyl-*n*-valeronitrile (70%), b.p. 155—158°/3·5 mm., and thence by hydrogenation as above *acet*-β-cyclo*hexyl*-β-*phenyl*-n-*amylamide* (48%), m.p. 129—130°. At 220° in N_2, (**III**) gives 2-*allyl*cyclo*hexylidenephenylacetonitrile* (**V**) (85%), b.p. 160—162°/2 mm., the structure of which is proved as follows. (**V**) absorbs 0·996 H_2 rapidly and then slowly a further quantity. Distillation of (**V**) from KOH in aq. $(OH{\cdot}[CH_2]_2)_2O$ (**VI**) gives NH_3, $CH_2Ph{\cdot}CO_2H$ (73%), and 2-allyl*cyclo*hexanone (**VII**) (43% isolated as 2 : 4-*dinitrophenylhydrazone*, m.p. 145—146°). CHPhNa·CN and (**VII**) in boiling PhMe give 28% of (**V**) (possibly a slightly different mixture of geometrical isomerides). Heating $CN{\cdot}CH_2{\cdot}CO_2H$, *cyclo*hexanone, and NH_4OAc in C_6H_6 with removal of H_2O gives *cyclo*hexylidenecyanoacetic acid, which is decarboxylated at 130—140°/50—70 mm. to Δ¹-*cyclo*hexenylacetonitrile (79%), b.p. 99°/15 mm. This is converted by $NaNH_2$–NH_3 and then (**II**)–Et_2O at, successively, −40°, room temp., and the b.p. into α-Δ¹-cyclo*hexenyl*-Δ^γ^-n-*pentenonitrile* (**VIII**) (19%), b.p. 85—87°/1·5 mm., α-Δ¹-*cyclohexenyl*-α-*allyl*-Δ^γ^-n-*pentenonitrile* (**IX**) (40%), b.p. 107—108·5°/1·5 mm., and a *substance*, $C_{22}H_{30}N_2$, m.p. 105—106°. At 185° in N_2, (**VIII**) gives 2-*allyl*cyclo*hexylideneacetonitrile*, fractions, b.p. 121—122°/10 mm. and 122—123°/10 mm., converted by KOH as above, with much hydrolysis, into small amounts of (**VII**) and AcOH. At 175° (**IX**) gives α-2-*allyl*cyclo*hexylidene*-Δ^γ^-n-*pentenonitrile* (78%), b.p. 117—119°/2 mm., cleaved as above into (**VII**) (poor yield). Alkylation of $CH_2{:}CH{\cdot}CH_2{\cdot}CN$ as above gives α-*vinyl*-α-*allyl*-Δ^γ^-n-*pentenonitrile* (**X**) (31%), b.p. 103—104°/35 mm., which at 180° in N_2 yields α-*allyl*-Δ^αε^-*heptadienonitrile* (62%), b.p. 95—96°/13 mm., whence O_3 in EtOAc and then aq. H_2O_2 at 100° yields $(CH_2{\cdot}CO_2H)_2$. Distilling H_2O from $COEt_2$–$CN{\cdot}CH_2{\cdot}CO_2H$–$NH_4OAc$–AcOH–$C_6H_6$ and heating the product at 140—145°/40—60 mm. gives β-*ethyl*-Δ^β^-n-*pentenonitrile* (72%), b.p. 104—105°/72 mm., which by alkylation gives β-*ethylidene*-α-*allyl*-n-*valeronitrile* (38%), b.p. 69—70°/2 mm. At 195° (N_2), this gives γ-*methyl*-β-*ethyl*-Δ^αε^-*heptadienonitrile* (70%), b.p. 100—101°/11 mm., whence O_3 gives $COEt{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, also obtained by ozonising $COEt{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2$ in EtOAc. With KOH–(**VI**)–H_2O, (**X**) gives α-*vinyl*-α-*allyl*-Δ^γ^-n-*pentenoic acid* (54%), b.p. 108—110°/2·5 mm., rearranged at 185° (N_2) into α-*allyl*-Δ^αε^-n-*heptadienoic acid* (61%), b.p. 116—118°/1·5 mm. [with O_3 gives $(CH_2{\cdot}CO_2H)_2$]. R. S. C.

Oxidation of *o*-cresol to salicylic acid by alkali fusion. D. E. Bland (*J. Proc. Austral. Chem. Inst.*, 1943, **10**, 239—242).—Under the most favourable conditions, the method of Lock *et al.* (A., 1939, II, 113) gives ↛~31% of o-$OH{\cdot}C_6H_4{\cdot}CO_2H$. Yields of 29—39% are obtained from a dry, intimate mixture of *o*-cresol and NaOH (3 parts) at 250°/3 hr. A. T. P.

Photochemical dimerisation of *trans*-cinnamic acid. H. I. Bernstein and W. C. Quimby (*J. Amer. Chem. Soc.*, 1943, **65**, 1845—1846).—Rapidly pptd. or commercial *trans*-$CHPh{:}CH{\cdot}CO_2H$ gives only β-truxinic acid on exposure to sunlight, but after slow recrystallisation it gives α-truxilic acid. W. R. A.

Synthesis of 3-methylpyrogallolaldehyde [2 : 4-dihydroxy-3-methoxybenzaldehyde]. F. Mauthner (*J. pr. Chem.*, 1940, [ii], **156**, 154—156).—The fraction, b.p. 145—155°/12 mm., of the mixture obtained from 1 : 2 : 3-$C_6H_3(OH)_3$ (100 g.) in EtOH (200 c.c.), MeI (80 g.), and KOH (29·4 g.) in EtOH (150 c.c.) after 10 hr. at the b.p., is treated with boiling AcCl and the product fractionated. Fractional crystallisation of the material, b.p. 160—180°/12 mm., from EtOH gives 1 : 2 : 3- and 2 : 1 : 3-$OMe{\cdot}C_6H_3(OAc)_2$, m.p. 51—54° (more sol.). Hydrolysis (dil. NaOH) then affords a poor yield of 2 : 1 : 3-$OMe{\cdot}C_6H_3(OH)_2$, m.p. 85—87°, converted by $Zn(CN)_2$–Et_2O–HCl into 2 : 4-*dihydroxy*-3-*methoxybenzaldehyde*, m.p. 83—84° (p-*nitrophenylhydrazone*, decomp. 250°). H. B.

Stabilisation of keto-compounds by acetalisation.—See A., 1944, II, 33.

***cis*- and *trans*-8-Methyl-1-hydrindanone.** W. E. Bachmann and S. Kushner (*J. Amer. Chem. Soc.*, 1943, **65**, 1963—1967).—Et 1-hydroxy-2-carbethoxy-2-methyl*cyclo*hexylacetate (prep. improved to give 88% yield; cf. Chuang *et al.*, A., 1935, 859), b.p. 173—177°/18 mm., with $SOCl_2$–C_5H_5N and then KOH–MeOH gives 2-carboxy-2-methyl*cyclo*hexylideneacetic (**I**), m.p. 101·8—103·5°, and 2-*carboxy*-2-*methyl*-Δ⁶-cyclo*hexenylacetic acid* (**II**), m.p. 170·5—170·8° [? a stereoisomeride of (**I**)]. H_2–PtO_2 converts (**II**) in AcOH into *cis*-2-carboxy-2-methyl*cyclo*hexylacetic acid (**III**), m.p. 161·5—163° (A., 1943, II, 372, m.p.163—164°), but (**I**) gives also a small amount of the *trans*-acid (**IV**), m.p. 173—174°. Treating crude (**III**) with CH_2N_2 and then NaOH–H_2O–MeOH gives *cis*-2-carbomethoxy-2-methyl*cyclo*hexylacetic acid, m.p. 54·5—60° (Chuang *et al.*, *loc. cit.*), which with $SOCl_2$ and a little C_5H_5N in C_6H_6 at 40° and then CH_2N_2–C_6H_6–Et_2O gives a diazo-ketone, converted by Ag_2O–MeOH into Me *cis*-β-2-carbomethoxy-2-methyl*cyclo*hexylpropionate, a syrup. Cyclisation by NaOMe–C_6H_6 and subsequent treatment with boiling HCl–AcOH–H_2O yields *cis*-8-methyl-1-hydrindanone, m.p. 38·2—39·5°, b.p. 121—123°/45—47 mm. (*oxime*, m.p. 85·5—87°). Hydrogenation (Raney Ni; 125—150°/1800—2000 lb.; H_2O) of K H 1-methyl-Δ²-*cyclo*hexene-1 : 2-dicarboxylate gives *trans*-1-methyl-*cyclo*hexane-1 : 2-dicarboxylic acid, m.p. 214—214·3° (lit. 210°), which yields, as above, trans-2-*carbomethoxy*-2-*methyl*cyclo*hexane*-1-*carboxylic acid*, m.p. 90—91·5° after softening. With $(COCl)_2$ in C_6H_6 this gives the acid chloride, which with, successively, CH_2N_2, Ag_2O–MeOH, and KOH–MeOH–H_2O yields (**IV**), m.p. 175—177·8°, which is converted, as above, into trans-8-*methyl*-1-*hydrindanone*, b.p. 108—109°/20 mm. [*semicarbazone*, m.p. 234° (bath preheated to 190°); *oxime*, m.p. 113—115·5°]. R. S. C.

Relationship between anti-mitotic action and constitution in colchicine derivatives. H. Lettré and H. Fernholz (*Z. physiol. Chem.*, 1943, **278**, 175—200; see also A., 1944, III, 92).—Colchiceine (in $CHCl_3$) and the diazoalkane (in Et_2O) give the amorphous *methyl*-, melts from ~130° (probably not identical with colchicine), *ethyl*-, melts from ~110°, *n*-propyl-, melts from 98°, and *n*-butyl-colchiceine, melts from 90°. p-*Anisyl* 3 : 4 : 5-*trimethoxystyryl ketone*, m.p. 134° [from 3 : 4 : 5 : 1-$(OMe)_3C_6H_2{\cdot}CHO$ (**I**) and *p*-$OMe{\cdot}C_6H_4{\cdot}COMe$ in EtOH + MeOH–NaOMe], is reduced (H_2, Pt-black, AcOH) to the β-3 : 4 : 5-trimethoxyphenylethyl ketone, m.p. 98°, the oxime, m.p. 102°, of which is reduced (Na–Hg, EtOH–AcOH) to α-*p*-anisyl-γ-3 : 4 : 5-trimethoxyphenylpropylamine (*Ac* derivative, m.p. 88°). *Ph* 3 : 4 : 5-*trimethoxystyryl ketone*, m.p. 137°, similarly leads to α-phenyl-γ-3 : 4 : 5-trimethoxyphenylpropylamine (*Ac* derivative, m.p. 137—138°). N-*Acetyl*-α-p-*anisyl*-, m.p. 112°, and -α-*phenyl*-γ-3 : 4-*dimethoxyphenyl*-, m.p. 122°, -α-*phenyl*-γ-p-*anisyl*-, m.p. 117°, -γ-*phenyl*-α-p-*anisyl*-, m.p. 115—117°, -αγ-*di*-p-*anisyl*-, m.p. 114°, and -αγ-*diphenyl-propylamine*, m.p. 88—89°, are similarly obtained. N-*Acetyl*-α-p-*anisylethylamine*, m.p. 74—75°, and the Ac, m.p. 91—92° (lit. 93—94°), *propionyl*, m.p. 79°, *n*-*butyryl*, m.p. 80—81°, and iso*valeryl* derivative, m.p. 104°, of 3 : 4 : 5 : 1-$(OMe)_3C_6H_2{\cdot}[CH_2]_2{\cdot}NH_2$ (mescaline) are described. 7-Nitro-4′-methoxystilbene is reduced (Zn dust, EtOH–AcOH) to the corresponding oxime, which with H_2–PtO_2–EtOH–$H_2C_2O_4$ gives α-phenyl-β-p-anisylethylamine (as *oxalate*, m.p. 197°; *Ac* derivative, m.p. 150°). 7-Nitro-3′ : 4′-di- and -3′ : 4′ : 5′-tri-methoxystilbene similarly afford α-phenyl-β-3 : 4-di- and -3 : 4 : 5-tri-methoxyphenylethylamine (*Ac* derivatives, m.p. 143—144° and 153—154°, respectively). *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}NO_2$ and (**I**) in EtOH–NH_2Me give 7-*nitro*-4 : 3′ : 4′ : 5′-*tetramethoxystilbene*, m.p. 137°. H. B.

New preparation of hydroxy-aromatic ketone. I. Monoketones. S. S. Israelstam and H. Stephen. **II. Diketones.** S. S. Israelstam (*J. S. African Chem. Inst.*, 1943, **26**, 41—48, 49—53).—I. A trace of conc. H_2SO_4 is added to an equimol. mixture of Ac_2O and a phenol containing two or more OH groups in the *meta* position; there is an immediate rise in temp. of ~60°, after which the mixture is heated at 130° for 15 min.; the product is boiled with H_2SO_4–EtOH to hydrolyse any *O*-Ac derivative. Thus are obtained: 2 : 4 : 1-

$(OH)_2C_6H_3$·COMe, m.p. 146°; 2 : 4 : 1-$(OH)_2C_6H_3$·COEt, m.p. 99°; 2 : 4 : 1-$(OH)_2C_6H_3$·COPr^a, m.p. 69°, and its 4-Me, m.p. 32·5°, and 2-Me, m.p. 69°, ethers; 2 : 4 : 1-$(OH)_2C_6H_3$·COPh, m.p. 144°; 2 : 4 : 1-$(OH)_2C_6H_3$·CH_2Bz, m.p. 114—115°; 2 : 4 : 6 : 1-$(OH)_3C_6H_2$·COMe, m.p. 213—214°; 2 : 4 : 6 : 1-$(OH)_3C_6H_2$·COEt, m.p. 170—171°; 2 : 3 : 4 : 1-$(OH)_3C_6H_2$·COMe, m.p. 169—170; 2 : 3 : 4 : 1-$(OH)_3C_6H_2$·COEt, m.p. 126—127°; 2 : 6 : 4 : 1-$(OH)_2C_6H_2$Me·COMe, m.p. 146°; 2 : 6-*dihydroxy*-4-*methylpropiophenone* (+H_2O), m.p. 129° (6-*Me ether*, m.p. 75°); 2-*hydroxy*-6-*methoxy*-4-*methylacetophenone*, m.p. 81°; 2 : 4 : 6 : 1-$(OH)_2C_6H_2$Me·COEt, m.p. 122°. The "phloracetophenone" of Hoesch (A., 1915, i, 820) is the corresponding ketimine sulphate.

II. Increase in the relative proportions of acid anhydride and conc. H_2SO_4 results in the introduction of two acyl groups. Thus resorcinol affords a mixture of 2 : 4-, m.p. 92°, and 4 : 6-diacetylresorcinol, m.p. 182° (*Me$_2$ ether*, m.p. 171°); similar mixtures are obtained from resorcinol, AcCl, and conc. H_2SO_4 and from *m*-$C_6H_4(OAc)_2$ and hot conc. H_2SO_4. 4 : 6- and 2 : 4-Dipropionylresorcinol, m.p. 125° and 81°, respectively, are obtained similarly. All the following diketones give a red colour with $FeCl_3$ in EtOH: *diacetylphloroglucinol*, m.p. 153°; *dipropionylphloroglucinol*, m.p. 137—138°; 4 : 6-diacetylpyrogallol, m.p. 188° (diacetate, m.p. 218°); 4 : 6-*dipropionylpyrogallol*, m.p. 186°. H. W.

Biochemistry of the lower fungi. VI. Synthesis of fumigatin. T. Posternak and H. W. Ruelius (*Helv. Chim. Acta*, 1943, **26**, 2045—2049).—3 : 5 : 4 : 1-$(OH)_2C_6H_2$(OMe)·CHO is hydrogenated in abs. EtOH containing PtO_2 to 3 : 5-*dihydroxy*-4-*methoxybenzyl alcohol* (**I**), m.p. 177—178°, or in glacial AcOH containing Pd-black to 3 : 5-*dihydroxy*-4-*methoxytoluene* (**II**), m.p. 135—136°, also obtained under these conditions from (**I**). (**II**) is converted by amyl nitrite through the K salt into 2-*nitroso*-3 : 5-*dihydroxy*-4-*methoxytoluene*, m.p. 118° (decomp.), reduced catalytically or by $Na_2S_2O_4$ to the unstable amine which is immediately oxidised to fumigatin [3-hydroxy-4-methoxy-2 : 5-toluquinone], m.p. 113—113·5°. H. W.

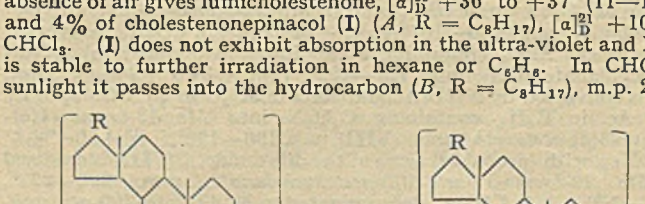
Biochemistry of the lower fungi. V. New syntheses of phœnicin and *iso*phœnicin. T. Posternak, H. W. Ruelius, and J. Tcherniak (*Helv. Chim. Acta*, 1943, **26**, 2031—2044).—4 : 1 : 3 : 5-NO_2·$C_6H_2Me(OH)_2$ is converted by Me_2SO_4 and NaOH into 4-*nitro*-3 : 5-*dimethoxytoluene*, m.p. 147—147·5°, reduced (H_2–PtO_2–abs. EtOH) to the 4-NH_2-compound, m.p. 64—65° (*H sulphate*), whence the 4-*I*-compound, m.p. 96—97°. This is transformed by activated Cu (Adams) at 170—210° into 2 : 6 : 2′ : 6′-*tetramethoxy*-4 : 4′-*dimethyldiphenyl*, m.p. 145—146°, which with HNO_3 (*d* 1·4) in Ac_2O at −10° affords 3 : 3′-*dinitro*-2 : 6 : 2′ : 6′-*tetramethoxy*-4 : 4-*dimethyldiphenyl*, m.p. 197—198°, reduced to the 3 : 3′-$(NH_2)_2$-compound, m.p. 168° or (+$2H_2O$) m.p. 132—134° (evolution of steam) and, after resolidification, m.p. 168°; this can be diazotised normally with production of relatively very stable salts. It is oxidised by $Na_2Cr_2O_7$ and H_2SO_4 to 2 : 2′-*dimethoxy*-4 : 4′-*dimethyldiphenyl*-3 : 6 : 3′ : 6′-*diquinone* (*phoenicin Me$_2$ ether*), m.p. 131—132°, identical with the compound obtained from phoenicin (**I**), Ag_2O, and MeI and hydrolysed to (**I**) by 2% Na_2CO_3 at 100°. 4-Iodotoluquinone is converted by Thiele's reagent at room temp. into a mixture of 4-iodo-2 : 3 : 5- (**II**), m.p. 154—155°, and 4-*iodo*-2 : 5 : 6-*triacetoxytoluene* (**III**), m.p. 117—118°, which retains a trace of (**II**). (**II**) is transformed by activated Cu into leucophœnicin hexa-acetate (**IV**), m.p. 200—201°. Leuco*iso*phœnicin hexa-acetate, m.p. 178—181°, is obtained similarly from (**III**) or better, together with (**IV**), from an equimol. mixture of (**II**) and (**III**). (**II**) is partly hydrolysed by HCl–MeOH to 4-*iodohydroxydiacetoxytoluene* (**V**), m.p. 173—175°; partial hydrolysis followed by methylation (CH_2N_2) leads to 4-*iododiacetoxymethoxytoluene* (**VI**), m.p. 164° [also obtained by methylation (CH_2N_2 in Et_2O) of (**V**)], and 4-*iodoacetoxydimethoxytoluene*, m.p. 82—84°. (**VI**) is converted by activated Cu into *tetra-acetoxydimethoxy*-4 : 4′-*dimethyldiphenyl*, m.p. 171° (also an unstable form, m.p. 149°), which is converted by hydrolysis followed by oxidation by $FeCl_3$ into (**I**). Partial hydrolysis (HCl in abs. MeOH) of (**III**) gives 4-*iodohydroxydiacetoxytoluene*, m.p. 196—198°, transformed by CH_2N_2 into the corresponding *OMe*-compound, m.p. 111—113°. *Hexamethyl-leucophœnicin*, m.p. 123°, is obtained by treating leucophœnicin with Me_2SO_4 and NaOH in presence of $Na_2S_2O_4$. *Hexamethyl-leuco*iso*phœnicin*, m.p. 85—86°, is obtained analogously and is converted by HNO_3 (*d* 1·4) in Ac_2O at −10° into a $(NO_2)_2$-derivative, m.p. 154°. Leuco*iso*phœnicin is converted by boiling HBr (*d* 1·5) into *anhydroleucoisophœnicin*, m.p. 290—291° (block). H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

Oxidative degradation of neoergosteryl acetate. R. P. Jacobsen (*J. Amer. Chem. Soc.*, 1943, **65**, 1789—1792).—The acetate (**I**), m.p. 118—119°, of neoergosterol (modified prep. from bisergostatrienol in boiling *n*-C_5H_{11}·OH–N_2), m.p. 152·5—154° (lit. 151—152°), $[\alpha]_D^{19}$ −10° in $CHCl_3$, with successively OsO_4–Et_2O at room temp., aq. EtOH–Na_2SO_3, and HIO_4 in Et_2O containing a little MeOH at 15° gives α-3(β)-hydroxy-$\Delta^{5:7:9}$-œstratrien-17-ylpropionic acid (**II**), +0·5H_2O, m.p. 206·5—208·5° (Remesov, A., 1938, II, 18, m.p. 210—212°), $[\alpha]_D^{19}$ −7° in $COMe_2$ [*Me* ester (**III**), m.p. (air-dried) 173—175°, (dried at 110°/vac.) 174—176·5°], also obtained (m.p. 203·5—206°) from (**I**) by O_3 in 2 : 1 AcOH–CCl_4 in 6·5—9% yield (cf. *loc cit.*). With hot Ac_2O–C_5H_5N and then CH_2N_2, (**II**) gives its Me ester acetate (**IV**), m.p. 159·5—161·5° (*loc. cit.*, m.p. 144—145°). (**IV**) with MgPhBr–Et_2O–PhMe gives *αα-diphenyl*-β-3(β)-*acetoxy*-$\Delta^{5:7:9}$-*œstratrien*-17-*yl*-n-*propyl alcohol*, +0·5H_2O, m.p. 112—120° (effervescence), dehydrated by Ac_2O–C_5H_5N and then boiling Ac_2O (a little)–AcOH to *αα-diphenyl*-β-3(β)-*acetoxy*-$\Delta^{5:7:9}$-*œstratrien*-17-*yl*-Δ^{α}-*propene* (16%), m.p. 197—201°, $[\alpha]_D^{19}$ +171° in $CHCl_3$. With MgMeI in PhMe–Et_2O, (**III**) gives γ-3(β)-*hydroxy*-$\Delta^{5:7:9}$-*œstratrien*-17-*yl*-β-*methyl*-n-*butan*-β-*ol* (**V**), m.p. 179—183°, $[\alpha]_D^{19}$ −27° in $CHCl_3$, which with Ac_2O–C_5H_5N at room temp. gives the 3(β)-*acetate*, m.p. 127—130°. This is dehydrated by AcOH + a little Ac_2O at 150—155° (less well, Ac_2O–$ZnCl_2$ or anhyd. $H_2C_2O_4$), to γ-3(β)-*acetoxy*-$\Delta^{5:7:9}$-*œstratrien*-17-*yl*-β-*methyl*-Δ^{α}-n-*butene* (**VI**), m.p. 135—136°, $[\alpha]_D^{19}$ −14° in $CHCl_3$ [corresponding 3(β)-3′ : 5′-*dinitrobenzoate*, m.p. 252—255° (decomp.)]. With OsO_4– and then HIO_4–Et_2O, (**VI**) gives, after hydrolysis, α-3(β)-*hydroxy*-$\Delta^{5:7:9}$-*œstratrien*-17-*ylethyl Me ketone*, m.p. 177—181°, $[\alpha]_D^{19}$ −22° in $CHCl_3$ (*acetate*, m.p. 148—152°), which with MgMeI–PhMe–Et_2O gives (**V**), thus proving the structure. M.p. are corr. R. S. C.

Steroid excretion in a case of adrenocortical carcinoma. I. Isolation of a Δ^5-androstene-3(β) : 16 : 17-triol. H. Hirschmann (*J. Biol. Chem.*, 1943, **150**, 363—379).—Urine obtained from a boy with adenocarcinoma of the adrenal cortex is hydrolysed by boiling with HCl; it is extracted with Et_2O and the 17-keto-steroids in the neutral fraction are determined (method: Callow *et al.*, A., 1938, III, 905). The neutral fraction is extracted with C_6H_6 and the insol. residue affords Δ^5-*androstene*-3(β) : 16 : 17-*triol* (**I**), $C_{19}H_{30}O_3$, m.p. 267—270° (decomp.). Ac_2O–C_5H_5N at room temp. gives the *triacetate* (**II**), m.p. 189·5—191°, $[\alpha]_D^{26}$ −102° in 95% EtOH; the mother-liquors (chromatographic separation) yield a *diacetate*, m.p. 183—187°, and 3-*monoacetate* (**III**), m.p. 243—245°, both of which are hydrolysed by aq. NaOH–MeOH at room temp. to (**I**), +0·5MeOH, m.p. 266—270° (decomp.). Hydrogenation (Pd–$CaCO_3$; EtOH) of (**I**) affords *androstane*-3(β) : 16 : 17-*triol* (**IV**), m.p. 256—260° (digitonide); its *triacetate*, m.p. 175·5—176·5°, $[\alpha]_D^{26}$ −44° in 95% EtOH, is obtained by hydrogenating (**II**). (**I**) and HIO_4,$2H_2O$–aq. dioxan (in N_2) at room temp. give a *product*, m.p. 131—134°. CrO_3–AcOH at room temp. (21 hr.) convert (**IV**) into 3-ketoætio*allo*bilianic acid (**V**), m.p. 253—256°, which is also obtained from *iso*androsterone as follows: NaOMe–MeOH–PhCHO afford 16-*benzylideneandrostan*-3(β)-*ol*-17-*one*, m.p. 181·5—182·5°; its *acetate*, m.p. 237—238°, and CrO_3–AcOH at 60° yield β-3-hydroxy-ætio*allo*bilianic acid, new m.p. 254—257° (decomp.), converted by CrO_3–AcOH at room temp. into (**V**). (**III**) with successively Br–AcOH, CrO_3–AcOH at room temp., and $COMe_2$–NaI gives β-3-hydroxy-Δ^5-ætiobilienic acid, forms, m.p. 232—236° and 247—255°, or after acetylation (Ac_2O–C_5H_5N), β-3-acetoxy-Δ^5-ætiobilienic anhydride, m.p. 186—188°. (**I**) is not identical with that described by Butenandt *et al.* (A., 1939, II, 165) or Stodola *et al.* (A., 1942, II, 104), there being probably a different spatial arrangement at $C_{(16)}$ or $C_{(17)}$ (or both). (**I**) could not be extracted from the urine prior to hydrolysis. M.p. are corr. A. T. P.

Photochemical transformation of αβ-unsaturated steroid ketones under the influence of ultra-violet light. II. A. Butenandt and L. Poschmann (*Ber.*, 1940, **73**, [*B*], 893—897; cf. A., 1939, II, 328).—Exposure to ultra-violet light of cholestenone in pure hexane in absence of air gives lumicholestenone, $[\alpha]_D^{23}$ +36° to +37° (11—12%), and 4% of cholestenonepinacol (**I**) (*A*, R = C_8H_{17}), $[\alpha]_D^{21}$ +103° in $CHCl_3$. (**I**) does not exhibit absorption in the ultra-violet and hence is stable to further irradiation in hexane or C_6H_6. In $CHCl_3$ in sunlight it passes into the hydrocarbon (*B*, R = C_8H_{17}), m.p. 244—



246° (block) (slight decomp. at 170°), $[\alpha]_D^{22}$ −230° in $CHCl_3$. The change is ascribed to the catalytic influence of HCl derived from decomp. of $CHCl_3$; it also occurs in EtOH or C_6H_6 containing a trace of HCl in absence of light. Analogously, testosterone propionate (**II**) in C_6H_6–hexane (1 : 10) affords lumitestosterone propionate (**II**), m.p. 350—355°, and the *pinacol* (*A*, R = O·COEt), m.p. 223° after softening, $[\alpha]_D^{23}$ +75° in $CHCl_3$, also obtained by reduction of (**II**) by Na–Hg in 96% EtOH and dehydrated by repeated dissolution in EtOH or insolation in $CHCl_3$ to the *compound* (*B*, R = O·COEt), m.p. 275—280°, decomp. >230°, $[\alpha]_D^{23}$ −272° in $CHCl_3$. H. W.

Barbier–Wieland degradation of 3-hydroxy-12-ketocholanic acid. B. Riegel and R. B. Moffett (*J. Amer. Chem. Soc.*, 1943,

65, 1971—1973).—Steric hindrance at the 12-CO allows application of the Barbier–Wieland degradation in the 3-hydroxy-12-ketocholanic acid series. A little AcCl in MeOH at the b.p. and then room temp. or $Pr^{\beta}OH$ at room temp. converts 3-hydroxy-12-ketocholanic acid into the Me (**I**), m.p. 111·5—113·5° (lit. 110—111·5°), or *Pr*$^{\beta}$ ester, m.p. 149·5—151°, respectively. With MgPhBr in boiling Et_2O–C_6H_6 and then, best, 7·5% KOH–MeOH, (**I**) gives *diphenyl-3-hydroxy-12-ketonorcholanylcarbinol* (**II**) (32%), m.p. 215—216·5°, converted by boiling Ac_2O–AcOH into *αα-diphenyl-β-12-keto-3-acetoxybisnorchanylethylene* (**III**), m.p. 180·5—182°, which with CrO_3–AcOH–$CHCl_3$ at ~35° and then boiling aq. NaOH gives 3-hydroxy-12-ketonorcholanic acid, m.p. 248—250° (Me ester, m.p. 149·5—151°). The crude H succinate, m.p. 97—115°, of diphenyl-3 : 12-dihydroxynorcholanylcarbinol (**IV**), m.p. 114—119°, with CrO_3–aq. AcOH at room temp. and then boiling KOH–MeOH gives (**II**), m.p. 214—215°., Ac_2O–AcOH and then 10% KOH–MeOH converts (**IV**) into *αα-diphenyl-β-3 : 12-dihydroxybisnorcholanylethylene*, +0·5MeOH (retained at 78°/1 mm.), m.p. 108—110°, which with $(CH_2{\cdot}CO)_2O$ in C_5H_5N at 100° (5 min.) and then room temp. (24 hr.) gives the 3-*H succinate*, m.p. 198—201°, converted by CrO_3–AcOH–H_2O at 0—5° and then boiling KOH–MeOH into *αα-diphenyl-β-3-hydroxy-12-ketobisnorcholanylethylene*, +0·5EtOH (retained at 78°/1 mm.), m.p. 158—159° [acetate = (**III**), m.p. 181·5—182·5°]. M.p. are corr. R. S. C.

Bile acids and related substances. XXVII. α-Oxides of the two 3-hydroxy- and the 3-keto-Δ^{11}-cholenic acid. G. H. Ott and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 1799—1815).—Me 3-keto-Δ^{11}-cholenate (**I**) is hydrogenated (Raney Ni) in alkaline medium and then esterified (CH_2N_2) and acetylated to a mixture of Me 3(α)- (**II**), m.p. 119—121°, and Me 3(β)-acetoxy-Δ^{11}-cholenate (**III**), m.p. 149—151°, separated from one another by chromatography over Al_2O_3. Gradual addition of an aq. solution of NHBrAc and NaOAc,$3H_2O$ to (**II**) in $COMe_2$ at 55—30° and chromatography of the product over Al_2O_3 gives the corresponding dibromide, *Me* 11(α) : 12(α)-*oxido*-3(α)-*acetoxycholanate* (**III**), m.p. 154—155° $[\alpha]_D^{12}$ +62·0°±2° in $COMe_2$, and Me 12-keto-3(α)-acetoxy-Δ^9-cholenate (**V**), m.p. 146—148°, $[\alpha]_D^{14}$ +100·0°±2° in $COMe_2$. The formation of (**IV**) and possibly of (**V**) is due to the intervention of the Al_2O_3. Under somewhat modified conditions (**II**) is converted by NHBrAc in aq. $COMe_2$ containing NaOAc,$3H_2O$ or in C_5H_5N–C_6H_6 into *Me* 12-*bromo*-11(α)-*hydroxy*-3(α)-*acetoxycholanate* (**VI**), m.p. 201—203°, $[\alpha]_D^{17}$ +70·5°±2° in $COMe_2$. (**VI**) is unchanged by boiling C_5H_5N or by Al_2O_3 which has been washed with dil. HCl and hot MeOH and dried at 250° but converted into (**IV**) by Al_2O_3 in presence of a little C_5H_5N or by technical Al_2O_3 containing alkali. Zn dust and boiling AcOH or Zn–Cu in AcOH is without action on (**VI**). Hydrogenation at 50°/100—115 atm. in MeOH–C_5H_5N containing Raney Ni causes some formation of (**IV**). (**VI**) is oxidised by CrO_3 in AcOH–$CHCl_3$ to *Me* 12-*bromo*-11-*keto*-3(α)-*acetoxycholanate*, m.p. 183—185°, $[\alpha]_D^{15}$ +13·0°±2° in $COMe_2$, debrominated by Zn dust in warm AcOH to Me 11-keto-3(α)-acetoxycholanate, m.p. 131—133°. (**VI**) is transformed into (**IV**) by KOH–MeOH at room temp. followed by re-esterification (CH_2N_2), or by technical Al_2O_3 containing alkali. Short treatment with boiling AcOH leaves (**IV**) almost unchanged whereas longer treatment results in yellow, amorphous materials. CrO_3 in AcOH oxidises (**IV**) at room temp. to an unidentified neutral substance, m.p. 131—138°. Boiling H_2SO_4–MeOH followed by re-methylation and acetylation transforms (**IV**) into a product, m.p. 131—133°. (**IV**) is hydrogenated (120—145°/~150 atm.; Raney Ni–MeOH), then re-methylated and acetylated, to Me 11(α)-hydroxy-3(α)-acetoxycholanate, m.p. 147—149°. (**I**), NHBrAc, and NaOAc,$3H_2O$ in aq. $COMe_2$ afford *Me* 12-*bromo*-11(α)-*hydroxy*-3-*ketocholanate*, m.p. 166—167°, $[\alpha]_D^{18}$ +48·9°±2° in $COMe_2$, converted by technical Al_2O_3 containing alkali into Me 3-keto-11(α) : 12(α)-oxidocholanate (**VII**), m.p. 121—122°, $[\alpha]_D^{17}$ +34·0°±2° in $COMe_2$. (**III**) is converted by NHBrAc and NaOAc,$3H_2O$ in aq. $COMe_2$ or by NHBrAc in C_6H_6 containing C_5H_5N into *Me* 12-*bromo*-11(α)-*hydroxy*-3(β)-*acetoxycholanate* (**VIII**), m.p. 196—198°, $[\alpha]_D^{18}$ +50·4°±2° in $COMe_2$, with (probably) some of the dibromide. (**VIII**) is oxidised to *Me* 12-*bromo*-11-*keto*-3(β)-*acetoxycholanate*, m.p. 226—227°, $[\alpha]_D^{18}$ −7·3°±2° in $COMe_2$, debrominated to Me 11-keto-3(β)-acetoxycholanate, m.p. 174—175°. Technical Al_2O_3 transforms (**VIII**) into *Me* 11(α) : 12(α)-*oxido*-3(β)-*acetoxycholanate* (**IX**), m.p. 151—152°, $[\alpha]_D^{18}$ +39·9°±1° in $COMe_2$; the change is also conveniently effected by KOH–MeOH followed by methylation (CH_2N_2) and acetylation. (**IX**) is hydrolysed, esterified (CH_2N_2), and then oxidised to (**VII**), also obtained analogously from (**IV**). M.p. are corr. (block); limit of error ±2°. H. W.

Isomerisation of 17-hydroxy-20-keto-steroids. IV. Reaction of 3(β) : 17(α)-diacetoxy*allo*pregnan-20-one with magnesium methyl bromide. C. W. Shoppee and D. A. Prins (*Helv. Chim. Acta*, 1943, **26**, 2089—2095).—Addition of 3(β) : 17(α)-diacetoxy*allo*pregnan-20-one (**I**) in Et_2O-dioxan to MgMeBr in boiling Et_2O followed by treatment of the product with Ac_2O–C_5H_5N at room temp. gives unchanged material, small amounts of a substance, m.p. ~265°, 17(α) : 20-*dihydroxy*-3(β)-*acetoxy*-20-*methyl*allo*pregnane* (**II**), m.p. 168—170°, and 17*a*(β)-hydroxy-3(β)-acetoxy-17*a*-methyl-*D*-homo-androstan-17-one, m.p. 159—160°, $[\alpha]_D^{18}$ −33°±3° in $COMe_2$. Oxidation by (**II**) by CrO_3 in AcOH at room temp. and hydrolysis of the neutral portion of the product leads to *trans*-androsterone, thus affording direct proof that (**I**) belongs to the *allo*pregnane series. M.p. are corr. (block); limits of error ~±2°. H. W.

Steroids and sex hormones. LXXXVII. *allo*Pregnan-3(β)-ol-21-al-20-one and pregnan-3(β)-ol-21-al-20-one. Testalolone. L. Ruzicka, V. Prelog, and P. Wieland (*Helv. Chim. Acta*, 1943, **26**, 2050—2057).—3(β)-Acetoxyætio*allo*cholanic acid is converted through the acid chloride and diazo-ketone into 21-chloro*allo*-pregnan-3(β)-ol-20-one, m.p. 152—153°, which with hot C_5H_5N gives the *pyridinium* salt, $C_{26}H_{40}O_3NCl$, m.p. 273—274° (decomp.) (also +$1H_2O$), converted by *p*-NO·C_6H_4·NMe_2 into the nitrone, m.p. (indef.) 119—120°, which is hydrolysed by HCl to allo*pregnan*-3(β)-*ol*-21-*al*-20-*one* (**I**) [*monohydrate*, m.p. 155°, softens at 136°, $[\alpha]_D$ +92·7°±3° in C_5H_5N, giving after desiccation at 90°/high vac. a *semihydrate*, $[\alpha]_D$ +87·5°±3° in C_5H_5N; *dioxime*, m.p. 246—249° (decomp.); *Me*$_2$ *acetal*, m.p. 113—115°, $[\alpha]_D$ +111·5°±3° in $CHCl_3$]. Similarly 3(β)-acetoxyætiocholanic acid is converted into 21-*chloro-pregnan*-3(β)-*ol*-20-*one*, m.p. 184—185°, $[\alpha]_D$ +116·5°±2° in $CHCl_3$, transformed through the *pyridinium chloride*, m.p. 284° (decomp.), into *pregnan*-3(β)-*ol*-21-*al*-20-*one* (**II**) [*monohydrate*, m.p. ~143°, softens at 127°, $[\alpha]_D$ +103°±3° in C_5H_5N; *semihydrate*, m.p. 129—147° $[\alpha]_D$ +103°±3° in C_5H_5N; *dioxime*, m.p. 217—223° (decomp.); *Me*$_2$ *acetal*, m.p. 126—129°, $[\alpha]_D$ +132°±10° in $CHCl_3$]. (**I**) and (**II**) are oxidised by HIO_4 to 3(β)-hydroxyætio*allo*-, m.p. 245—247°, and 3(β)-hydroxyætio-cholanic acid, m.p. 224—225·5°, respectively and by CrO_3 in AcOH to the corresponding keto-acids. Neither (**I**) nor (**II**) is identical with testalolone (A., 1936, II, 644). M.p. are corr. H. W.

Pyridazine derivative of cholestanedione. K. Bursian (*Ber.*, 1940, **73**, [*B*], 922—923).—Contrary to Noller (A., 1940, II, 18) the pyridazine derivative (**I**) of cholestanedione is a well-defined cryst. compound. It has m.p. >200° to a brown liquid, softens and darkens at 170°. The vals. for the mol. wt. in $C_{10}H_8$, C_6H_6, PhOH, and exaltone do not reach the high data recorded by Noller but show ill-defined association varying from solvent to solvent and never indicating double the expected formula so that only the formula $C_{27}H_{44}N_2$ is possible. Solutions of (**I**) in boiling C_6H_6 are turned brown by passage of air whereas (**I**) can be subjected to protracted heating in a high vac. at ~180° without suffering change; at ~200° it melts to a brown liquid which does not form a sublimate. H. W.

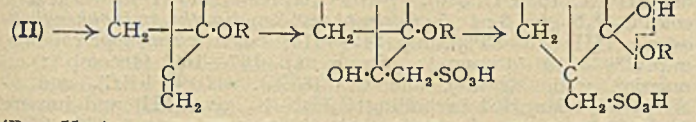
V.—TERPENES AND TRITERPENOID SAPOGENINS.

Condensation of dipentene dihydrochloride with phenol. A. Zinke and H. Hönel [with O. Benndorf, R. Dreweny, and E. Ziegler] (*J. pr. Chem.*, 1940, [ii], **156**, 97—102).—Dipentene dihydrochloride (**I**), PhOH, and a little $AlCl_3$ or $ZnCl_2$ at 40—65° give a resinous product from which CH_2Cl_2 or C_6H_6 extracts 1 : 8-*di*-p-*hydroxyphenylmenthane* (+H_2O) (**II**), m.p. 166° (*diacetate*, m.p. 122°; *dibenzoate*, m.p. 169·7°; *di*-p-*bromobenzoate*, m.p. 208·8°), which does not resinify when heated, could not be dehydrogenated, and is oxidised by HNO_3 (*d* 1·1) at 150° to picric acid. Halogenation of (**II**) gives no cryst. products. Resinous products are obtained from (**I**) and resorcinol or guaiacol; C_6H_6–$AlCl_3$ gives resin and some 1 : 8-*diphenylmenthane*, m.p. 242·5°. H. B.

Syntheses in the pinane series. G. Komppa (5 *Nordiske Kemikermøde*, 1939, 213—214).—The total synthesis of α- (**I**) and δ-pinene (**II**), starting from $R(CO_2H)_2$ (**III**) (R = $-CH<^{CH_2}_{CMe_2}>CH-$), has been accomplished in the following stages: (**III**) via the anhydride and Me H ester gave $CO_2Me{\cdot}R{\cdot}COCl$, and thence, with ZnMeI, $CO_2Me{\cdot}R{\cdot}COMe$, and then (Reformatsky) $CO_2Me{\cdot}R{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2Me$ (**IV**). H_2O was split off from (**IV**) with $SOCl_2$ to give $CO_2Me{\cdot}R{\cdot}CMe{:}CH{\cdot}CO_2Me$, catalytically hydrogenated to $CO_2H{\cdot}R{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, the Pb salt of which on dry distillation gave verbanone (**V**). Reduction of (**V**) (Na–EtOH) gave $C_8H_{14}<^{CH{\cdot}OH}_{CH_2}$, which with $SOCl_2$–C_5H_5N gave (**II**). (**V**) with $NaNH_2$–CO_2 gave $C_8H_{14}<^{CO}_{CH{\cdot}CO_2H}$, which was electrolytically reduced to $C_8H_{14}<^{CH{\cdot}OH}_{CH{\cdot}CO_2H}$, losing H_2O (Ac_2O) to yield $C_8H_{14}<^{CH}_{C{\cdot}CO_2H}$ and thence (Curtius) $C_8H_{14}<^{CH_2}_{CO}$, converted into (**I**) by known methods. (Cf. A., 1942, II, 147.) M. H. M. A.

Mechanism of the sulphonation of camphor. P. Lipp and H. Knapp (*Ber.*, 1940, **73**, [*B*], 915—921).—The (incorrect) hypothesis that the by-product (**I**) obtained by Frèrejacque (A., 1926, 1251) in the sulphonation of camphor (**II**) is a mixed anhydride of camphor-

enolsulphuric acid and AcOH suggests that Reychler's acid (**III**) is obtained according to the scheme:



(R = H, Ac, or SO_3H). In support of this hypothesis it is shown that (**III**) is obtained from 1-hydroxycamphene (**IV**) and Ac_2O–H_2SO_4 more rapidly than from (**II**). (**I**) yields AcOH but no trace of H_2SO_4 under the influence of $Ba(OH)_2$ and hence is an acetate but not a H sulphate. Further it is resistant to $KMnO_4$ in $COMe_2$, does not absorb Br in $CHCl_3$, and cannot be catalytically hydrogenated; it is therefore saturated and is not an intermediate compound in the sulphonation of (**II**). The *tert.* nature of OH in (**IV**) is established by the positive Wienhaus reaction and by the resistance of (**IV**) to the formation of a *p*-nitrobenzoate. Attempts to establish the presence of the semicyclic ethylenic linking in (**IV**) by fission with O_3 to CHO_2 and hydroxycamphenilone show that ketonisation to (**II**) takes place more rapidly than ozonisation. It is, however, readily hydrogenated giving 1-*hydroxy*iso*camphane* (**V**), m.p. 113·5—114°. Attempted methylation of (**V**) with Ag_2O and MeI leads to (**II**), the Ag_2O behaving as a dehydrogenating agent. (**V**) has the constitution assigned by Kresstinski *et al.* (A., 1937, II, 253) to their *iso*borneol. Since (**V**) has quite different properties from those of *iso*borneol, the observations of Kresstinski must be explained otherwise. H. W.

Triterpene resinols and related acids. XIV. Oxidation of acetylursolic acid. E. S. Ewen and F. S. Spring (*J.C.S.*, 1943, 523—525). —Oxidation (AcOH–H_2CrO_4) of acetylursolic acid affords *ketoacetylursolic acid* (**I**), $C_{32}H_{48}O_5$, m.p. 315—316° (decomp.), $[\alpha]_D^{20}$ +40·8° in $CHCl_3$, and a small amount of a *lactone*, $C_{32}H_{46}O_6$, m.p. 305—306° (decomp.). Similar oxidation of Et acetylursolate yields *Et ketoacetylursolate*, m.p. 210—212°, $[\alpha]_D^{20}$ +92° in $CHCl_3$, identical with that obtained from the acid and $CHMeN_2$. Quinoline and (**I**) give *nor-α-amyradienonyl acetate*, m.p. 203—205°, $[\alpha]_D^{21}$ +41° in $CHCl_3$, with loss of HCO_2H. This acetate contains the chromophoric system O:C·C:C·C:C. These transformations indicate that the CO_2H of ursolic acid is in the vicinity of the ethylenic linking. F. R. S.

VI.—HETEROCYCLIC.

Synthesis of 2-keto*cyclo*hexylsuccinic acid and related substances. III. Syntheses involving ethylene and propylene oxides. J. A. McRae, E. H. Charlesworth, F. R. Archibald, and D. S. Alexander (*Canad. J. Res.*, 1943, 21, B, 186—193).—Addition of $(CH_2)_2O$ to a well-cooled solution of $CHNa(CO_2Et)_2$ in EtOH followed by $CH_2Cl·CO_2Et$ and alkaline hydrolysis of the product gives 2-*keto-tetrahydrofuran-3-carboxylic-3-acetic acid*, m.p. 165° (*Et*$_2$ ester, b.p. 204—206°/15 mm.), which passes at 160° into 2-*ketotetrahydrofuran-3-acetic acid*, m.p. 56—58°; this is converted by NH_3–EtOH at 100° into *β-hydroxyethylsuccindiamide*, m.p. 137—139° (decomp.). Under similar conditions $Br·[CH_2]_2·CO_2Et$ affords *Et*$_2$ 2-*ketotetrahydrofuran-3-carboxylate-3-propionate*, b.p. 204—206°/15 mm.; the corresponding dicarboxylic *acid*, m.p. 125° (decomp.), is decarboxylated at 160° to 2-*ketotetrahydrofuran-3-β-propionic acid*, m.p. 51·5—53°. Analogously CH_2PhCl gives *Et* 2-*keto-3-benzyltetrahydrofuran-3-carboxylate*, b.p. 195—197°/0·5 mm., hydrolysed and then decarboxylated to 2-*keto-3-benzyltetrahydrofuran*, b.p. 165—166°/10 mm. Condensation of propylene oxide (**I**) with $CHNa(CO_2Et)_2$ and hydrolysis of the product leads to the unstable β-hydroxypropylmalonic acid (isolated as the *Ba* salt), decarboxylated at 160° to 2-keto-5-methyltetrahydrofuran [γ-valerolactone], b.p. 83—84°/12 mm.; if the Na derivative of the original condensation product is not hydrolysed by NaOH but immediately acidified the unstable γ-hydroxy-α-carbethoxyvalerolactone, b.p. 125—135°/25—40 mm. (partial decomp.), results. Successive treatments of $CHNa(CO_2Et)_2$ in EtOH with (**I**) and $Br·[CH_2]_2·CO_2Et$ followed by hydrolysis and decarboxylation of the product lead to 2-*keto-5-methyltetrahydrofuran-3-β-propionic acid*, m.p. 54—56°. H. W.

New furancarboxylic acids from glucose. T. Széki and E. László (*Ber.*, 1940, 73, [*B*], 924—929).—Glucose, $CH_2Bz·CO_2Et$, and $ZnCl_2$ in abs. EtOH give *Et* 2-*phenyl-5-αβγδ-tetrahydroxybutylfuran-3-carboxylate* (**I**), m.p. 176—177°, $[\alpha]_D^{22}$ −38·4° in AcOH, converted by Ac_2O and C_5H_5N at 0° into the *tetra-acetate*, m.p. 95°, $[\alpha]_D^{18}$ −51·2° in $CHCl_3$, and by benzoylation into an oil. Oxidation of (**I**) by $Pb(OAc)_4$ in AcOH–C_6H_6 at 0° affords *Et 5-aldehydo-2-phenylfuran-3-carboxylate* (**II**), m.p. 76°, $[\alpha]_D$ ±0° (*semicarbazone*, m.p. 170—171°; *phenylhydrazone*, m.p. 124—126°), which gives a cryst. additive product with $NaHSO_3$. (**II**) is converted by boiling 15% NaOH containing Ag_2O into 2-*phenylfuran-3-5-dicarboxylic acid*, m.p. 270—271° (decomp.) (*dichloride*, m.p. 68—72°; *diamide*, m.p. 206—208°; *dianilide*, m.p. 147—150°; *Me*$_2$ ester, m.p. 95—96°). 2-*Phenyl-5-tetrahydroxybutylfuran-3-carboxylic acid*, m.p. 195—197° (decomp.), $[\alpha]_D^{23}$ −24·6° in AcOH, is oxidised [$Pb(OAc)_4$ in C_6H_6–AcOH] to 5-*aldehydo-2-phenylfuran-3-carboxylic acid*, m.p. 145—147°, in poor yield. Similarly $CO(CH_2·CO_2Et)_2$ is condensed to *Et*$_2$ 5-*tetrahydroxybutylfuran-3-carboxylate-2-acetate* (**III**), m.p. 128—130°, $[\alpha]_D^{20}$ −14·7° in MeOH, oxidised to *Et*$_2$ 5-*aldehydofuran-3-carboxylate-2-acetate*, an oil (*semicarbazone*, m.p. 180—182°; *phenylhydrazone*, m.p. 96—97°; 3 : 5-*dinitrophenylhydrazone*, m.p. 168—170°). (**III**) is transformed by boiling alkaline $KMnO_4$ followed by MeOH into *Me*$_3$ *furan-2 : 3 : 5-tricarboxylate*, m.p. 68—73°. H. W.

Polyalkylbenzenes. XXXIII. 3 : 5 : 6-Trimethylcoumaran-2-one and its conversion into 4-hydroxy-3 : 5 : 6-trimethyl-1-*iso*propylcoumaran. L. I. Smith, J. A. King, W. I. Guss, and J. Nichols (*J. Amer. Chem. Soc.*, 1943, 65, 1594—1599; cf. A., 1943, II, 193).—2 : 3 : 5 : 1-$C_6H_2Me_3·O·CH_2·CO_2H$ (prep. from 2 : 3 : 5 : 1-$C_6H_2Me_3·OH$ by K_2CO_3–$CH_2Br·CO_2Et$–$COMe_2$ and then NaOEt–EtOH), m.p. 130—131° (lit. 128°), in H_2SO_4 at 90—95° gives 3 : 5 : 6-*trimethylcoumaran-2-one* (**I**) (86%), m.p. 90·5—91·5° [2 : 4-*dinitrophenylhydrazine* salt, m.p, 231° (decomp.), of the enolic form], converted by $ZnCl_2$–EtOH exothermally into 2-*ethoxy*-3 : 5 : 6-*trimethylcoumarone*, m.p. 86—88°. With a drop of H_2SO_4 in Ac_2O, (**I**) gives 2-*acetoxy*-3 : 5 : 6-*trimethylcoumarone*, m.p. 88—89°, which with Br–CCl_4 gives 2-*acetoxy*-3 : 5 : 6-*trimethylcoumaran-1-one*, m.p. 127·5—128·5°. With $ZnCl_2$ in boiling $COMe_2$, (**I**) gives 3 : 5 : 6-*trimethyl-1-isopropylidenecoumaran-2-one* (**II**), m.p. 90·5—91·5°, reduced by H_2–Raney Ni in EtOH at 200°/3000 lb. to 3 : 5 : 6-*trimethyl-1-isopropylcoumaran* (**III**), m.p. 38—39°, and converted by O_3 in EtBr and then H_2O_2–H_2O into 2-*hydroxy*-3 : 4 : 6-*trimethylbenzoic acid*, m.p. 181—182° (decomp.) (decarboxylated at > m.p. to 2 : 3 : 5 : 1-$C_6H_2Me_3·OH$). 2 : 3 : 4 : 5 : 1-$OH·C_6HMe_3·CO_2H$, m.p. 181° (decomp.), is obtained from 2 : 4 : 5 : 1-$C_6H_2Me_3·ONa$ and (solid) CO_2 at 250°. With Br–CCl_4, (**II**) gives HBr and 1-*bromo*-3 : 5 : 6-*trimethyl-1-α-bromoisopropylcoumaran*, m.p. 127—128° (decomp.). Br–CCl_4 converts (**III**) into 4-*bromo*-3 : 5 : 6-*trimethyl-1-isopropylcoumaran*, m.p. 65—66°, which with *cyclo*hexyl bromide and EtBr and then Mg in Et_2O gives a Mg derivative, whence O_2 yields 4-hydroxy-3 : 5 : 6-trimethyl-1-*iso*propylcoumaran, m.p. 119° (acetate, m.p. 76—77°) (cf. A., 1943, II, 240). Adding Na and then 1 : 2 : 3 : 5 : 4-$O:C_6HMe_3$ to $CH_2(COPr^a)_2$ (prep. from Pr^aCO_2Et and $COMePr^a$ by way of the Cu derivative, m.p. 145—150°), b.p. 85—86°/11 mm., in EtOH gives 4-*hydroxy*-3 : 5 : 6-*trimethyl-1-n-propylcoumarone* (16%), m.p. 88—89°, reduced by H_2–Raney Ni in EtOH at 135°/1300 lb. to the derived *coumaran*, m.p. 96—97°. R. S. C.

Reaction between quinones and metallic enolates. XVII. Dibromo-*p*-xyloquinone and sodiomalonic ester. L. I. Smith and J. Nichols (*J. Amer. Chem. Soc.*, 1943, 65, 1739—1747; cf. A., 1942, II, 267).—1 : 2 : 5 : 4-$O:C_6H_2Me_2:O$ (**I**) or 2 : 5 : 1 : 4-$C_6H_2Me_2(OH)_2$ (**II**), m.p. 208—213° (lit. 208° to 213°), with Br in AcOH at room temp. gives the red dibromoquinhydrone, converted by HNO_3 in hot EtOH into 1 : 2 : 5 : 3 : 6 : 4-$O:C_6Me_2Br_2:O$ (**III**), softens 178°, m.p. 183—184° (derived quinol, m.p. 174·5—175·5° after softening), which with $CHNa(CO_2Et)_2$ (2 mols.) in pure dioxan at room temp. gives *Et*$_2$ 5-*bromo*-3 : 6-*dimethyl*-1 : 4-*benzoquinon-2-ylmalonate* (**IV**) (83·7%; much less under other conditions), m.p. 65—66°. With $Na_2S_2O_4$–H_2O–Et_2O or H_2–PtO_2 in light petroleum this gives the derived *quinol* (**V**), softens 108°, m.p. 111—112°, which with H_2SO_4 (2 drops) in Ac_2O at room temp. gives *Et*$_2$ 6-*bromo*-2 : 5-*diacetoxy-p-3-xylylmalonate* (**VI**), m.p. 110—111°, and, when shaken in $CHCl_3$ with 75% H_2SO_4, is cyclised to give *Et* 5-*bromo-4-hydroxy*-3 : 6-*dimethylcoumaran-1-one-2-carboxylate* (**VII**) (91·2%), m.p. 117—118·5° [*acetate* (**VIII**), m.p. 120—122°]. Boiling (**IV**) with Zn in AcOH, (**VII**) in AcOH, or (**VIII**) in 1 : 1 HCl–AcOH gives 5-*bromo-4-hydroxy*-3 : 6-*dimethylcoumaran-1-one* (**IX**), m.p. 200—201° (decomp.) [*acetate*, m.p. 166—168°, obtained from (**IX**) by Ac_2O–H_2SO_4 at room temp. or (**VIII**) by boiling AcOH]. Me_2SO_4–KOH converts (**V**) in boiling MeOH into *Et* 5-*bromo-4-methoxy*-3 : 6-*dimethylcoumaran-1-one-2-carboxylate* (**X**), m.p. 96—97°, with some 5-*bromo*-1 : 4-*dimethoxy*-3 : 6-*dimethylbenzfuran-2-carboxylic acid* (**XI**), m.p. 210—211° (bath preheated at 200°) (decomp.), both [(50·8% of (**X**)] also obtained from (**VII**) by NaOH–Me_2SO_4 and both converted by boiling 70% AcOH into 5-*bromo-4-methoxy*-3 : 6-*dimethylcoumaran-1-one* (**XII**), m.p. 165—166°, unchanged by boiling KOH–EtOH–H_2O. With KOH–Me_2SO_4 in boiling MeOH, (**IX**) (81·7% yield) or (**XII**) (62·7% yield) gives 5-*bromo*-3 : 6-*dimethoxy*-p-2-*xylylacetic acid* (**XIII**), m.p. 158—159°. Me_2SO_4–KOH converts (**II**) in boiling MeOH into 2 : 5 : 1 : 4-$C_6H_2Me_2(OMe)_2$ (**XIV**), m.p. 107—108°, which with Br–AcOH gives 3-*bromo*-2 : 5-*dimethoxy*-p-*xylene* (75·8%), m.p. 57—59°, purified by chromatography and converted by HCl–CH_2O–AcOH at 60—70° into 4-*bromo*-3 : 6-*dimethoxy*-2 : 5-*dimethylbenzyl chloride* (77·8%), m.p. 94—98°, which with boiling KCN–EtOH–H_2O gives the *cyanide*, m.p. 115—116°, hydrolysed by boiling H_2SO_4–AcOH–H_2O to (**XIII**). With an excess of $CHNa(CO_2Et)_2$ in pure dioxan, (**IV**) gives 2 : 5-*dimethyl*-3 : 6-*bisdicarbethoxymethyl*-p-*benzoquinone* (**XV**) (15·7%), m.p. 74—76°, not obtained directly from (**III**) and reduced by aq. $Na_2S_2O_4$–Et_2O to the *quinol* (80%), m.p. 151—154°, which, when shaken in $CHCl_3$ with 75% H_2SO_4, gives 2 : 6-*diketo*-3 : 7-*dicarbethoxy*-4 : 8-*dimethylbenz*[1, 2-b-4 : 5-b′-]*tetrahydrodifuran* [*bis*-1′-*keto*-2′-*carbethoxy*-1′ : 2′-*dihydrofurano*-1′ : 2′-2 : 3-1″ : 2″ : 5 : 6-p-*xylene*] (**XVI**) (62·5%), m.p. 129—131°. In boiling 80% AcOH, (**XVI**) gives 2 : 6-*diketo*-4 : 8-*dimethylbenz*[1,2-b-4 : 5-b′-]*tetrahydrodifuran* [*bis*-1′-*keto*-1′ : 2′-*dihydrofurano*-1′ : 2′-2 : 3-1″ : 2″-5 : 6-p-*xylene*], decomp. 337—340°, also obtained from (**XV**) by Zn in boiling 70% AcOH and

converted by KOH–Me_2SO_4–MeOH into 2 : 5-*dimethoxy*-p-*xylylene*-3 : 6-*diacetic acid* (**XVII**) (34·6%), m.p. 267—271° (decomp.). HCl–CH_2O converts (**XIV**) into 2 : 5-*dimethoxy*-3 : 6-*di*(*chloromethyl*)-p-*xylene* (89%), m.p. 165·5—166°, which with NaCN in EtOH–$COMe_2$ gives the *dinitrile*, m.p. 207—207·5°, and thence (H_2SO_4–AcOH–H_2O) (**XVII**). With an excess of $CHNa(CO_2Et)_2$ in pure dioxan, (**I**) gives Et 4-hydroxy-3 : 6-dimethylcoumaran-1-one-2-carboxylate [and 3·8% of (**XVI**)], which is hydrolysed and decarboxylated by distillation in steam to give 4-*hydroxy*-3 : 6-*dimethylcoumaran*-1-*one* (41·5%), m.p. 214—216°. R. S. C.

Crystalline natural α- and γ-tocopherols. C. D. Robeson (*J. Amer. Chem. Soc.*, 1943, **65**, 1660).—Natural α-, m.p. 2·5—3·5° ($E^{1\%}_{1\,cm.}$ 71 at 292 mμ.) and γ-, m.p. −3° to −2° ($E^{1\%}_{1\,cm.}$ 93·2 at 298 mμ.), and synthetic α-tocopherol, m.p. ~0° ($E^{1\%}_{1\,cm.}$ 70 at 292 mμ.), are prepared. Synthetic *dl*-α-tocopherol was amorphous. R. S. C.

Derivatives of 2- and 2 : 8-substituted dibenzfurans. H. B. Willis (*Iowa State Coll. J. Sci.*, 1943, **18**, 98—101).—Dibenzfuran derivatives are discussed. New m.p. are recorded for 2-benzoyldibenzfuran (135—136°) and its oxime (182—183°). The following are stated to be new but no analyses are given: di-(2-, m.p. 201—202° and di-(3-dibenzfuryl), m.p. 245—246°: dibenzfuran-2-carboxyldiethylamide, m.p. 77—78°, and -4-carboxyldimethylamide, m.p. 116·5°, 2-benzoyldibenzfuran-*x*-carboxylic acid, m.p. 265—266° (Me ester, m.p. 189—190°), 3-nitro-2 : 8-diamino-, m.p. 210—213° (Ac_2 derivative, m.p. 322—324°), -2-β-benzamidoethyl-, m.p. 183·5—183·9°, 3-sulphanilamido- (**I**), m.p. 245° (Ac derivative, m.p. 223—224°), 4-sulphanilamido- (**II**), m.p. 195° (Ac derivative, m.p. 218°), 1 : 9(?)-bisbenzeneazo-2 : 8-dihydroxy-dibenzfuran, m.p. 155—156°; Et_2 4-, m.p. 75—76°, and Et_2 3-aminodibenzfuran-*N*-ethylmalonate, m.p. 99—100°; 2-acetoxy-1-dibenzfurancarboxylic acid, m.p. 151—152°. (**I**) and (**II**) are too insol. to be tested pharmacologically. F. R. G.

Santonin series. I. Two new desmotroposantonins and two new desmotroposantanous acids. H. Minlon, C. P. Lo, and L. J. Y. Chu (*J. Amer. Chem. Soc.*, 1943, **65**, 1780—1781).—Santonin with a drop of H_2SO_4 in cold or warm Ac_2O gives *l*-desmotroposantonin (~100%), m.p. 194—195°. *d-iso*Desmotroposantonin in dil. H_2SO_4 at 100° gives *l-desmotroposantonin* (**I**), m.p. 260—261°, $[\alpha]_D^{20}$ −106·2°, which with the *d*-isomeride gives the dl-*compound* (**II**), m.p. 231—232° (*acetate*, m.p. 182—183°). Zn in dil. AcOH reduces (**I**) to d-*desmotroposantanous acid*, m.p. 175—176°, $[\alpha]_D^{21}$ +54·0°, which with the *l*- gives the dl-*acid*, m.p. 180—181°, also obtained by reducing (**II**). Alkali-fusion converts (**I**) into the low-melting *l*-desmotroposantonin. Nomenclature of the series is revised. R. S. C.

Halogenated *m*-dioxans.—See B., 1944, II, 6.

Synthesis of a tetrahydrothiophen with substituted amino-groups in the 2- and 5-positions. G. B. Brown and G. W. Kilmer (*J. Amer. Chem. Soc.*, 1943, **65**, 1674—1675).—*cis*-Tetrahydrothiophen-2 : 5-dicarboxylic acid [prep. from *meso*-$(CH_2{\cdot}CHBr{\cdot}CO_2H)_2$], sinters 135°, m.p. 141—143° (lit. 144—145°), gives the Et_2 ester, b.p. 157°/10 mm., converted by $N_2H_4{,}H_2O$ in EtOH at ~70° into the *dihydrazide* (23%), m.p. 208—209°, which with $NaNO_2$–H_2O–HCl–Et_2O at 0° and then abs. EtOH at ~50° to the b.p. gives 2 : 5-*di*-(*carbethoxyamino*)*tetrahydrothiophen* (53%), m.p. 152—154°. In boiling N-HCl it gives much H_2S and in boiling 5% $Ba(OH)_2$ or NaOH gives 0·8 mol. of NH_3 in 30 min.; with HCl–EtOH–H_2O it gives $(CH_2{\cdot}CHO)_2$, isolated as di-*p*-nitrophenylhydrazone. R. S. C.

Relative reactivities of organometallic compounds. LI. Metallation of thianthren and dibenzo-*p*-dioxin. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1943, **65**, 1461—1464; cf. A., 1943, II, 293).—Thianthren (**I**) with $LiBu^a$ (improved prep.) in Et_2O and then solid CO_2 etc. gives *thianthren*-1-*carboxylic acid*, m.p. 217—218° [by decarboxylation gives (**I**)]. *o*-$C_6H_4Br{\cdot}SK$ with PhI and Cu-bronze in boiling xylene gives *o*-$C_6H_4Br{\cdot}SPh$ (65%), b.p. 203°/6 mm., converted by S and $AlCl_3$ into 1-*bromothianthren* (25%), m.p. 145°, which with $LiBu^a$ etc. gives (**I**) (proof of structure). With $LiBu^a$ and then $NH_2{\cdot}OMe$–Et_2O, (**I**) gives 1-*thianthrenylamine* (**II**), m.p. 139° [hydrochloride, m.p. 231° (decomp.)], which yields the N^4-*acetylsulphanilyl*, m.p. 154°, and thence the *sulphanilyl* derivative, decomp. >120°. 2-Aminothianthren yields the N^4-*acetylsulphanilyl*, m.p. 163°, and *sulphanilyl* derivative, decomp. >125°. 4-N^4-*Acetylsulphanilyl*-, m.p. 192°, amd 4-*sulphanilyl*-*amidophenoxthionin*, m.p. 168°, are also prepared. No BuSH, Bu_2S, or Bu_2S_4 is obtained from (**I**) and $LiBu^a$ if S is entirely removed from the (**I**), *e.g.*, by conc. NaOH (cf. A., 1939, II, 131; 1941, II, 54). Dibenzo-*p*-dioxin with $LiBu^a$–Et_2O gives, after carboxylation, *dicarboxylic acids*, m.p. 297—298° (20%; Me_2 ester, m.p. 142—143°) and >335° (7%; Me_2 ester, m.p. 202—204°); LiMe leads to *dibenzo*-p-*dioxin*-1-*carboxylic acid* (10%), m.p. 210° (*Me* ester, m.p. 86°). *Me* 3-*bromosalicylate*, m.p. 62°, could not be converted into dibenzo-*p*-dioxin-1 : 6-dicarboxylic acid. R. S. C.

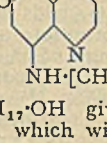
Heteropolar (XXXVI), polyarylated [compounds]. XII. Action of nitrosoaryl compounds on cyclones. Preparation of pentaphenylpyrrole. W. Dilthey, G. Hurtig, and H. Passing (*J. pr. Chem.*, 1940, [ii], **156**, 27—37).—Tetracyclone [2 : 3 : 4 : 5-tetraphenylcyclopentadienone] (**I**) reacts similarly to, but less vigorously than, phencyclone [2 : 5-diphenyl-3 : 4-2′ : 2″-diphenylene*cyclo*pentadienone] (**II**) (A., 1939, II, 326). *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and (**I**) in warm (not cold) C_5H_5N give 3 : 4 : 5 : 6-*tetraphenyl*-2-p-*dimethylaminophenyliso*-*oxazine* (**III**) (81—83%), m.p. 212—213° [colourless *monoperchlorate*, m.p. 239—240° (decomp.); *picrate*, m.p. 167—169° (decomp.); no reaction with MgMeI], and CO (83%). *cis*-$(CPhBz{\cdot})_2$ and *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2{,}HCl$ in boiling C_5H_5N–N_2 give (**III**) and impure 2 : 3 : 4 : 5-*tetraphenyl*-1-p-*dimethylaminopyrrole*, m.p. 270—273°. PhNO and (**II**), alone at 70°, or exothermally in C_5H_5N, give (i) CO (61·3%) and 9 : 10-*dibenzoylphenanthrenemonoanil* (**IV**) (57—59%), m.p. 217—218° [*perchlorate*, m.p. 297—298° (decomp.); *picrate*, m.p. 227° (decomp.)], and (ii) CO_2 (25·2%) and 1 : 2 : 5-*triphenyl*-3 : 4-*diphenylenepyrrole* (**V**) (23—25%), m.p. 351° (no salts or reaction with MgMeI). 2 : 5-Diphenyl-3 : 4-diphenylenefuran, $NH_2Ph{,}HCl$, and Al_2O_3 at 400° give (**V**). 50—70% of (**V**) is obtained by boiling (**II**) in $PhNO_2$–N_2. C_5H_5N–$C_6H_5N{,}HCl$ or AcOH hydrolyses (**IV**) to 9 : 10-dibenzoylphenanthrene (**VI**), so that condensation of (**VI**) with NH_2Ph is impossible. Dissolution of (**IV**) in C_5H_5N and addition of aq. N_2H_4 gives the azine, m.p. 335—336°, of (**VI**). H_2O_2 converts (**IV**) in warm AcOH or HCO_2H into (**VI**). H_2S converts (**IV**) in boiling C_5H_5N into (**V**). With MgPhBr in Et_2O–PhMe and then aq. NH_4Cl, (**IV**) gives 9-*benzoyl*-10-*α-hydroxybenzhydrylphenanthreneanil*, m.p. 279—280° (decomp.) [azenium *perchlorate*, m.p. 342 (decomp.), and *picrate* m.p. 233—234° (decomp.)]. PhNO and (**I**) in boiling C_5H_5N–N_2 give 1 : 2 CO_2–CO and a mixture including 1 : 2 : 3 : 4 : 5-*pentaphenylpyrrole*, m.p. 282° (no salts), also obtained (m.p. 283°) from (**I**) and boiling $PhNO_2$ or tetraphenylfuran (**VII**), $NH_2Ph{,}HCl$, and Al_2O_3 at 400°. (**VII**) does not react with *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2{,}HCl$. R. S. C.

Attempts to find new antimalarials. XVIII. D. C. Quin and (Sir) R. Robinson. **XIX.** W. L. Glen and (Sir) R. Robinson. **XX.** (Miss) J. Crum and (Sir) R. Robinson (*J.C.S.*, 1943, 555—556, 557—561, 561—565).—XVIII. Condensation of 8-amino-6-methoxyquinoline (**I**) with *o*-$C_6H_4(CO)_2N{\cdot}[CH_2]_2{\cdot}Br$ gives 8-*β-phthalimidoethyl*-6-*methoxyquinoline*, m.p. 153—155°. $OPh{\cdot}[CH_2]_3{\cdot}NH_2$ and *o*-$C_6H_4(CO)_2N{\cdot}[CH_2]_3{\cdot}Br$ in dioxan afford *phthalo*-γ-(γ′-*phenoxypropylamino*)*propylimide hydrobromide*, m.p. 184°, which with HBr yields the *phthalo*-γ-(γ′-*bromo*)-compound, m.p. 195°. This salt with (**I**) gives 8-γ-*phthalimidopropyl*-γ-*aminopropylamino*-6-*methoxyquinoline dihydrobromide*, m.p. 222—223°, which with N_2H_4 yields 8-γ-*aminopropyl*-γ-*aminopropylamino*-6-*methoxyquinoline trihydrochloride*, almost devoid of antimalarial activity; the latter was thought to be the most probable structure for R.63 (cf. Robinson, *et al.*, A., 1934, 1368). 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and $(CH_2{\cdot}NH_2)_2$ in EtOH afford 2 : 4-*dinitro*-β-*aminoethylaniline*, m.p. 54° [*hydrochloride*, m.p. 250° (decomp.)], which with $OPh{\cdot}[CH_2]_3{\cdot}Br$ and K_2CO_3 in EtOAc forms 2 : 4-*dinitro*-N-γ-*phenoxypropyl*-β-*aminoethylaniline hydrochloride*, m.p. 114°. 8-γ-Phthalimidopropylamino-6-methoxyquinoline (**II**) and *o*-$C_6H_4(CO)_2N{\cdot}[CH_2]_3{\cdot}Br$ give a mixture, from which is separated, as the hydrobromide, 8-*di*-γ-*phthalimidopropylamino*-6-*methoxyquinoline*, m.p. 166°, which with N_2H_4 yields 8-*bis*-γ-*aminopropylamino*-6-*methoxyquinoline trihydrochloride*, a weak antimalarial. 5-Chloro-8-amino-6-methoxyquinoline, m.p. 154° (lit. 150—152°), with $Cl{\cdot}[CH_2]_2{\cdot}NEt_2{,}HCl$ affords 5-*chloro*-8-β-*diethylaminoethylamino*-6-*methoxyquioline*, m.p. 76°, which has weak antimalarial properties. 2 : 5-Dichloro-7-methoxyacridine with 8-γ-aminopropylamino-6-methoxyquinoline (**III**) and PhOH gives 2-*chloro*-5-(6′-*methoxyquinolyl*-8′-γ-*aminopropylamino*)-7-*methoxyacridine*, m.p. 114° [*dihydrochloride*, m.p. 223° (decomp.)], and with (**II**), 2-*chloro*-5-γ-*phthalimidopropylamino*-(N-6′-*methoxy*-8′-*quinolyl*)-7-*methoxyacridine*, m.p. 253° (decomp.), is obtained.

XIX. New preps. of R.63 have been made, and the high antimalarial activity is confirmed. Fractionation of the *dimeconate* (+$2H_2O$), decomp. ~150—160° (corresponding *tartrate*), has afforded no specimen of higher activity and in some cases a reduction of activity has occurred in all fractions without traceable loss of material. No light has been shed on the nature of R.63 by the synthesis of various substances that might have been produced in the formation reaction. (**III**) forms a *dimeconate* (+H_2O), m.p. 165—166° (decomp.). $Br{\cdot}[CH_2]_{10}{\cdot}Br$, *o*-$C_6H_4(CO)_2NH$, and K_2CO_3 give *phthalo*-ω-*bromodecylimide* (**IV**), m.p. 57—58°, which with (**I**) affords 8-ω-*phthalimidodecylamino*-6-*methoxyquinoline*, m.p. 83—84° [*hydrochloride*, m.p. 151—153° (decomp.)], converted by N_2H_4 into the 8-ω-NH_2-compound, isolated as the *dihydrochloride*, m.p. 172° (R.95). This base with (**IV**) yields 8-ω-*aminodecyl*-ω-*aminodecylamino*-6-*methoxyquinoline*, isolated as the *meconate* (weak antimalarial). (**III**) and (**IV**) heated together, followed by treatment with N_2H_4, give 8-ω-*aminodecyl*-γ-*aminopropylamino*-6-*methoxyquinoline*, isolated as the *meconate*, m.p. 160—164°. (**III**) with $Cl{\cdot}[CH_2]_{11}{\cdot}NEt_2{,}HCl$ gives a substance(meconate, R.97, m.p. ~155°, a potent antimalarial), the salts of which could not be cryst. $CHEtCl{\cdot}[CH_2]_2{\cdot}NEt_2{,}HCl$ and (**III**) condense to a substance (meconate, R.113, decomp. 160—165°, a potent, non-toxic, antimalarial), whilst a similar substance [meconate, R.103, m.p. 150—155° (decomp.)] is obtained from (**III**) and $CHMeBr{\cdot}[CH_2]_3{\cdot}NEt_2{,}HBr$. *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and (**III**) afford 8-γ-*p*-*acetamidobenzenesulphonamidopropylamino*-6-*methoxyquinoline*, m.p. 189°.

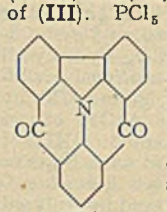
$NEt_2\cdot[CH_2]_{11}\cdot Cl,HCl$ with 5-chloro-8-amino-6-methoxyquinoline gives *5-chloro-8-ω-diethylaminoundecylamino-6-methoxyquinoline hydrochloride*, m.p. 126—128°. $Br\cdot[CH_2]_{10}\cdot CO_2Et$ and (I) lead to *8-ω-carbethoxydecylamino-6-methoxyquinoline*, m.p. 43—47°, successively converted into the *acid*, m.p. 110—111°, and *amide*, m.p. 113—114°. $Br\cdot[CH_2]_{11}\cdot CN$ and (I) give *8-ω-cyanodecylamino-6-methoxyquinoline*, m.p. 84—85°, which is converted through the imino-ether hydrochloride with EtOH–NH_3 into the *8-ω-guanyl* derivative, isolated as the *hydrochloride* ($+H_2O$), m.p. 76—77°. A similar prep. from 8-aminoquinoline affords *8-ω-cyano-*, m.p. 60—61°, and *-guanyl-decylaminoquinoline*, isolated as the *hydrochloride*, m.p. 92—93°. The appropriate reagents yield *8-γ-cyano-*, m.p. 52—53°, and *-guanyl-propylaminoquinoline* (*hydrochloride*, m.p. 152—154°). 6-Acetamidoquinaldine and $o\text{-}C_6H_4(CO)_2N\cdot[CH_2]_3\cdot Br$ give *ψ-6-acetamido-2-methyl-1-γ-phthalimidopropylquinolinium bromide*, m.p. 240—245° (decomp.), which with $p\text{-}NMe_2\cdot C_6H_4\cdot CHO$ affords *ψ-6-acetamido-2-p-dimethylaminostyryl-1-γ-phthalimidopropylquinolinium bromide*, converted by HBr into *ψ-6-amino-2-p-dimethylaminostyryl-1-γ-aminopropylquinolinium bromide hydrobromide* (no antimalarial properties, but is antiseptic and trypanocidal).

XX. A method for including *sec.*-amine end groups in the basic side-chain in antimalarials of the plasmoquin series has been devised by alkylation of (I) by means of a chlorohydrin, replacement of OH in the product by Cl, and interaction of the chloroalkylamino-compound with primary bases. The general formula of the bases is (V) and in the substances described $x = 3$. Interesting variations of antimalarial activity of the compounds are recorded. Trimethylenechlorohydrin, (I), and $C_8H_{17}\cdot OH$ give *8-γ-hydroxy-propylamino-6-methoxyquinoline*, m.p. 53°, which with $SOCl_2$ affords the *-Cl*-compound (VI), b.p. 115°/0·0001 mm., and some *bis-(8-γ-chloropropylamino-6-methoxy-5-quinolyl) sulphide*, m.p. 144° [*hydrochloride* ($+3H_2O$), m.p. 200—201°]. The latter compound with $NHEt_2$ forms the *bis-8-γ-NEt$_2$*-derivative (R.118), m.p. 85° [*hydrochloride* ($+H_2O$), m.p. 150° (decomp.)]. Condensation of (VI) with the appropriate amine affords *8-γ-methyl-* (R.105), b.p. 166°/0·5 mm. (*H oxalate*, m.p. 188°; *hydrochloride*, m.p. 218°), *-ethyl-* (R.106) [*H oxalate*, m.p. 139°; *hydrochloride* ($+H_2O$), m.p. 206°], *-propyl-* (R.119) (*hydrochloride*, m.p. 162°; *H oxalate*, m.p. 173°), *-iso-propyl-* (R.108) (*H oxalate*, m.p. 136°; *hydrochloride*, m.p. 210°), *-n-butyl-* (R.107) [*H oxalate* ($+H_2O$), m.p. 141°; *picrate*, m.p. 178°; *hydrochloride* ($+H_2O$), m.p. 180°], *-iso-butyl-* (R.110) [*H oxalate* ($+H_2O$), m.p. 218°; *hydrochloride*, m.p. 178°], *-tert.-butyl-* (R.109) (*meconate*, m.p. 188°; *hydrochloride*, m.p. 174°), *-n-heptyl-* (R.114) (*H oxalate*, m.p. 181°; *hydrochloride*, m.p. 110—112°), *-benzyl-* (R.117) [*H oxalate*, m.p. 230°; *hydrochloride* ($+0{\cdot}5H_2O$), m.p. 204°], *-cyclohexyl-* (*H oxalate*, m.p. 215°), *-furfuryl-* (R.112) [*H oxalate* ($+H_2O$), m.p. 209°; *hydrochloride* ($+EtOH$), m.p. 203°], *-diethyl-* (rhodoquin, R.116) (*dimeconate*, m.p. 178°; *hydrochloride*, m.p. 208°), and *-methylpropyl-aminopropylamino-6-methoxyquinoline* (R.123) [*meconate* ($+H_2O$), m.p. 168°; *picrate*, m.p. 152—154° (decomp.); *hydrochloride* ($+1{\cdot}5H_2O$), m.p. 180—184°]; and *8-β′-phenyliso-propyl-* (R.111) [*H oxalate* ($+H_2O$), m.p. 128°; *hydrochloride*, m.p. 127°], *-β′-aminoethyl-* (R.115) [*H oxalate*, m.p. 221°; *meconate* ($+3H_2O$), m.p. 186° (decomp.); *hydrochloride*, m.p. 244°], *-γ′-aminopropyl-* (R.120) [*H oxalate*; *hydrochloride* ($+0{\cdot}5H_2O$), m.p. 225° (decomp.)], *-δ′-amino-n-butyl-* (R.121) [*H oxalate* ($+H_2O$), m.p. 183—185°; *hydrochloride* ($+H_2O$), m.p. 210°], *-ε-amino-n-amyl-* (R.122) (*H oxalate*, m.p. 162°; *hydrochloride*, m.p. 196°), *-β-hydroxyethyl-* [*picrate*, m.p. 159° (decomp.); *hydrochloride*, m.p. 98°, remelts 154°], and *-β-hydroxyethylmethyl-γ-aminopropylamino-6-methoxyquinoline* [*meconate* ($+H_2O$), m.p. 128° (decomp.); *hydrochloride*, m.p. 212°]. R.120 is devoid of antimalarial properties, and it is now certain that R.63 owes its activity to some other constituent. F. R. S.


(V.)

Oxidations with selenium dioxide. W. Borsche and H. Hartmann (*Ber.*, 1940, **73**, [*B*], 839—842; cf. A., 1938, II, 202).—2-Methylpyridine is oxidised by SeO_2 in boiling EtOAc to small amounts of pyridine-2-aldehyde (phenylhydrazone, m.p. 178—179°; 2 : 4-*dinitrophenylhydrazone*, m.p. 239—240°) and some pyridine-2-carboxylic acid. Under similar conditions 1 : 2 : 3 : 4-tetrahydroacridine is partly oxidised to 4-keto-1 : 2 : 3 : 4-tetrahydroacridine [*dinitrophenylhydrazone*, m.p. 273—274° (decomp.), and its *hydrochloride*, decomp. 255°] but mainly dehydrogenated to acridine. Similarly the 2-Me derivative is in part oxidised to 4-keto-2-methyl-1 : 2 : 3 : 4-tetrahydroacridine (*dinitrophenylhydrazone*, decomp. 257—258°) but mainly dehydrogenated. On the other hand in so far as it reacts 7-aza-5 : 6-benzhydrindene is converted into the -hydrindone (*dinitrophenylhydrazone*, darkens and decomp. >300°). Dimethyldihydroresorcinol and SeO_2 in boiling EtOAc give anhydrodimethone selenium oxide, $CH_2{<}\overset{CO\cdot C}{CMe_2\cdot CH_2\cdot C}{>}O{<}\overset{C\cdot CO}{C\cdot CH_2\cdot CMe_2}{>}CH_2$ [*bisdinitrophenylhydrazone*, m.p. 281—282° (cf. Stamm *et al.*, A., 1933, 1314)]. Under similar conditions $\beta\text{-}C_{10}H_7\cdot OH$ affords *dihydroxydinaphthyl selenide*, m.p. 195—196°, which gives a dark green colour with $FeCl_3$, dissolves unchanged in NaOH, couples with PhN_2Cl, and yields a *dibenzoate*, m.p. 213—214°. H. W.

Relative reactivities of organo-metallic compounds. LIII. Di-metallation of 9-phenylcarbazole. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1943, **65**, 1729—1733).—9-Phenylcarbazole (I) (0·082) with LiBu^a (0·25 mol.) in Et_2O and then CO_2 gives 9-phenylcarbazole-2′-carboxylic (II) and *-2′ : 6′-dicarboxylic acid* (III) (25%), m.p. 273—274° [by decarboxylation gives 87% of (II) (cf. A., 1942, II, 122)]. CH_2N_2 gives the Me_2 ester, m.p. 156—157°, of (III). PCl_5 and then $SnCl_4$ in xylene at 0° converts (III) into *benz[ij]carbazolo[1 : 9 : 8-cdef]quinolizine-7 : 11-dione* (IV), m.p. 228—230°, which gives a *mono-oxime*, m.p. 262—264°, but does not condense with *l*-menthyl *N*-aminocarbamate. Carbazole-1-carboxylic acid, m.p. 275—276°, is obtained from Mg 9-carbazolyl bromide and CO_2 at >1 atm. in 18% yield; its Me ester, m.p. 98—100°, with $o\text{-}C_6H_4I\cdot CO_2Me$, K_2CO_3, and Cu-bronze in boiling $PhNO_2$ and then 30% KOH gives *9-phenylcarbazole-1 : 2′-dicarboxylic acid*, m.p. 231—232° (*Me$_2$* ester, m.p. 144—145°), cyclised as above into (IV) (proof of structure). Similar condensations gives *9-phenylcarbazole-2 : 2′-*, m.p. 266—267° (*Me$_2$* ester, m.p. 146—147°), *-3 : 2′-*, m.p. 246—247° (*Me$_2$* ester, m.p. 143—144°), and *-2′ : 4′-dicarboxylic acid*, m.p. 278—280° (*Me$_2$* ester, m.p. 160—161°). 1 : 3 : 2-$C_6H_3Me_2I$ (V) and boiling aq. $KMnO_4$ give 2 : 1 : 3-$C_6H_3I(CO_2H)_2$, m.p. 260° (decomp.) (lit. 205—220°, 236°). Condensation of 2 : 1 : 3-$C_6H_3I(CO_2Me)_2$ and carbazole (VI) and then hydrolysis gives only 70% of $[C_6H_3(CO_2H)_2\text{-}2 : 6]_2$, m.p. 390° (decomp.). No products are obtained by condensing (VI) with (V). The Li_2 derivative of (I) with Me_2SO_4 in Et_2O gives an inseparable mixture. Conc. HNO_3 converts (III) in AcOH at 100° into the 3 : 6-$(NO_2)_2$-derivative, m.p. >350°, which by decarboxylation gives 3 : 6-*dinitro-9-phenylcarbazole*, m.p. 298°, obtained from 3 : 6-dinitrocarbazole by PhI; HNO_3 in AcOH at room temp. gives *3-nitro-9-phenylcarbazole-2′ : 6′-dicarboxylic acid*, m.p. 282—284°, which by decarboxylation gives 3-nitro-9-phenylcarbazole and resists cyclisation. R. S. C.


(IV.)

Hydrolysis of substituted barbituric acids under pressure. H. Ruhkopf (*Ber.*, 1940, **73**, [*B*], 938—940).—H_2O at 5 atm. hydrolyses substituted barbituric acids to 1 : 1 mixtures of acyl-ureides and -amides ($+CO_2 + NH_3$), but at 10 atm. the amide is the sole product. At 5 atm. salts of strong acids favour formation of ureide, those of weak acids lead to mainly ureide, and alkalis cause further hydrolysis to the acid. *E.g.*, 5 : 5-diethylbarbituric acid in H_2O at 5 atm. gives $CHEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2$ (I) (47%) and $CHEt_2\cdot CO\cdot NH_2$ (II) (~40%), but in aq. NaCl at 3 atm. gives 80% of (I). 5 : 5-Diallylbarbituric acid in H_2O at 10 atm. gives 95% of $(CH_2{:}CH\cdot CH_2)_2CH\cdot CO\cdot NH_2$. In aq. Na_2SO_3 at 5 atm. 5-phenyl-5-ethylbarbituric acid gives 80% of $CHPhEt\cdot CO\cdot NH_2$. 1-Methyl-5 : 5-diethylbarbituric acid in H_2O at 10 atm. gives (II), CO_2, and NH_2Me. R. S. C.

Heterocyclic nitrogen compounds. Stereochemistry of tervalent nitrogen. H. H. Hatt and (Miss) E. F. H. Stevenson (*J. Amer. Chem. Soc.*, 1943, **65**, 1785—1786).—Known compounds having the ring-system of 1 : 2-trimethylenepyrazolidine (Buhle *et al.*, A., 1943, II, 207) are listed. R. S. C.

Pyrazole compounds. IV. Acylation of 3-phenyl- and 3-anilino-5-pyrazolone. A. Weissberger and H. D. Porter (*J. Amer. Chem. Soc.*, 1943, **65**, 1495—1502; cf. A., 1943, II, 280).—3-Phenyl-5-pyrazolone with Ac_2O or Ac_2O–AcOH at 100° gives 62—66% of the 1-Ac derivative (II), m.p. 127—128° (lit. 121°), and >20% of *5-acetoxy-3-phenylpyrazole* (III), m.p. 150—152° (cf. Curtius, A., 1895, i, 246; von Rothenburg, *ibid.*, 686). NaOH hydrolyses (II) and, more readily, (III) to (I). (II), but not (III), is sol. in Na_2CO_3. (II) gives a magenta dye with $p\text{-}NO\cdot C_6H_4\cdot NMe_2$ (IV) or in the film-strip test with $p\text{-}NH_2\cdot C_6H_4\cdot NMe_2$ (Fischer, *Phot. Korr.*, 1914, **51**, 19). (II) and (III) are equilibrated in boiling 66% AcOH, but C_5H_5N converts (II) irreversibly into (III); thus (III) is best prepared by treating (I) in C_5H_5N with Ac_2O at 100° or AcCl at room temp. Further treatment of (I), (II), or (III) with Ac_2O or of (III) with AcCl–C_5H_5N gives *1-acetyl-5-acetoxy-3-phenylpyrazole* (V), m.p. 84° [previously (*loc. cit.*) considered to be the 1 : 2-diacetoxypyrazolone], insol. in Na_2CO_3 but slowly hydrolysed to (I) by NaOH, to (II) by boiling piperidine–EtOH, and to (III) by hot 66% AcOH. Ac_2O and (I) give also a small amount of *1-acetyl-3-acetoxy-5-phenylpyrazole* [? 1 : 2-*diacetyl-3-phenyl-5-pyrazolone*], m.p. 75—76°, insol. in Na_2CO_3, which is also obtained from (V) by Ac_2O–AcOH, is hydrolysed by NaOH to (I) and by 66% AcOH to (III), and with hot piperidine–EtOH gives *3-hydroxy-1-acetyl-5-phenylpyrazole*, m.p. 144—146°, sol. in Na_2CO_3, hydrolysed to (I) by NaOH, and giving no dye by either test. With BzCl–C_5H_5N at 100°, (I) gives *5-benzoyloxy-3-phenylpyrazole* (VI), m.p. 170—171°, insol. in NaOH, reconverted into (I) by piperidine–EtOH and with Ac_2O at 100° or with AcCl–C_5H_5N giving *1-acetyl-5-benzoyloxy-3-phenylpyrazole*, m.p. 108—109°, which is hydrolysed to (I) by piperidine–EtOH. With BzCl in C_5H_5N, (VI) gives *1-benzoyl-5-benzoyloxy-3-phenylpyrazole* (VII), m.p. 117—118°, but in PhMe some *1-benzoyl-3-benzoyloxy-5-phenylpyrazole* (VIII), m.p. 181—182°, is also obtained; the structures assigned to (VII) and (VIII) may perhaps be reversed. (VII) and (VIII) are insol. in aq. NaOH but with NaOH–EtOH give (I);

treatment with piperidine gives erratic results; HCl in dioxan gives (VI) from (VII) or (VIII). With Ac_2O at 100° (5 min.) or Ac_2O (1 mol.)–C_5H_5N, 3-anilino-5-pyrazolone (IX) gives 3-*anilino*-1-*acetyl*-5-*pyrazolone* (X), m.p. 207—209° (decomp.), sol. in Na_2CO_3, hydrolysed to (IX) by NaOH, and giving with (IV) a magenta dye containing Ac and formed also in the film-strip test. With Ac_2O at 100° (30 min.), (IX) or (X) gives 3-*anilino*-1-*acetyl*-5-*acetoxypyrazole* (XI), m.p. 131°, insol. in Na_2CO_3 [converted by piperidine (1 mol.) or aq. AcOH into (IX)], and a small amount of 5-*anilino*-1-*acetyl*-3-*acetoxypyrazole* (XII), m.p. 108—109°, insol. in Na_2CO_3, hydrolysed by NaOH to (IX) and by piperidine to 3-*hydroxy*-5-*anilino*-1-*acetylpyrazole*, m.p. 203—205° (decomp.), sol. in Na_2CO_3, giving (IX) by NaOH, but yielding negative dye tests. Boiling AcOH causes transformation of (XI) into (XII), but (X) is unaffected. (XII) is best obtained by boiling (IX) in Ac_2O. When heated with Bz_2O or BzCl (2 mols.) + H_2O (1 mol.) in C_5H_5N, (IX) gives 3-*anilino*-5-*benzoyloxypyrazole*, m.p. 148—150°, insol. in Na_2CO_3 and hydrolysed to (IX) by piperidine; heating with BzCl–C_5H_5N in absence of H_2O gives 3-*anilino*-1-*benzoyl*-5-*pyrazolone*, m.p. 198—200° (decomp.), relatively stable to NaOH, sol. in Na_2CO_3, and giving positive dye tests; BzCl in dioxan at 100° yields 3-*anilino*-1-*benzoyl*-5-*benzoyloxypyrazole*, m.p. 132—134°, insol. in Na_2CO_3. R. S. C.

Synthesis of purine nucleosides. III. 4-Glycosidaminopyrimidines. J. Baddeley, B. Lythgoe, and A. R. Todd. **IV. 4 : 6-Diaminopyrimidine. New synthesis of pyrimidine derivatives.** G. W. Kenner, B. Lythgoe, A. R. Todd, and A. Topham (*J.C.S.*, 1943, 571—574, 574—575).—III. Direct glycosidisation of 4-aminopyrimidines is complicated since such compounds may behave as derivatives of 4-iminodihydropyrimidine. *d*-Xylose, 4 : 6-diamino-2-methylthiopyrimidine (I), and NH_4Cl in EtOH give 6-*amino*-4-d-*xylosidamino*-2-*methylthiopyrimidine* (II), m.p. 190—192° (decomp.), hydrolysed to (I), isolated as the *picrate*, m.p. 212° (decomp.). Ac_2O, AcCl, and (II) in C_5H_5N afford 6-*acetamido*-4-*triacetyl*-d-*xylosidamino*-2-*methylthiopyrimidine*, m.p. 226°, $[\alpha]_D^{18}$ +57° in C_5H_5N, which with MeOH–NaOMe yields the 6-*acetamido*-4-d-compound, m.p. 95—100°, or 192—193° (hydrated), $[\alpha]_D^{20}$ +23° in C_5H_5N. Acetylation with EtOAc–AcCl of (I) affords the *hydrochloride* (+H_2O), m.p. 213—214°, of the Ac derivative. 6-*Amino*-4-d-*mannosidamino*-2-*methylthiopyrimidine* (+1·5H_2O), m.p. 213—214° (decomp.), similarly prepared, gives rise to 6-*acetamido*-4-*tetra-acetyl*-d- (+3H_2O), m.p. 140—150°, $[\alpha]_D^{20}$ −100° in C_5H_5N, and -4-d-*mannisidamino*-2-*methylthiopyrimidine*, m.p. 242—243° (decomp.), $[\alpha]_D^{20}$ −55° in C_5H_5N. 4 : 6-Diamino-2-methylpyrimidine, *d*-xylose, EtOH, and HCl give 6-*amino*-4-d-*xylosidamino*-2-*methylpyrimidine*, m.p. 219° (decomp.), $[\alpha]_D^{20}$ +158° in H_2O (constitution proved by hydrolysis).

IV. 4 : 6-*Dichloropyrimidine*, m.p. 67·5°, prepared from the corresponding $(OH)_2$-compound and $POCl_3$–$NPhMe_2$, under pressure at 170° with NH_3–EtOH gives some 4 : 6-$(NH_2)_2$-compound (III). Small yields of (III) are also obtained from 4 : 6-diamino-2-thiolpyrimidine with NaOAc and H_2O_2, and from 6-iodo-4-aminopyrimidine with NH_3–EtOH at 180—200°. *Malondi-iminoether dihydrochloride*, obtained from $CH_2(CN)_2$ and HCl–EtOH, with cold NH_3–EtOH affords *malondiamidine dihydrochloride*, which with Na–MeOH, followed by HCO_2Et, gives (III). F. R. S.

Pyrimidines.—See B., 1944, II, 7.

Synthesis and properties of ninhydrin ureide. D. D. Van Slyke and P. B. Hamilton (*J. Biol. Chem.*, 1943, **150**, 471—476).—Ninhydrin (I) (1 mol.) and $CO(NH_2)_2$ (II) (1 mol.) combine in boiling 0·1N-H_2SO_4 to form *ninhydrin "ureide"* (III), $C_{10}H_{10}O_5N_2$, or after loss of 7·6% H_2O in vac. at 56°, $C_{10}H_8O_4N_2$, m.p. 216—217° (decomp.); there may be anhydride formation or H_2O of crystallisation. In boiling H_2O, at pH 2, (III) undergoes partial degradation or hydrolysis, with loss of CO_2 and possible decomp. to (I) + (II). (I) has a retarding effect (noted after 1 min.) on evolution of CO_2 from (II) at 100°. From the velocity of the combination of (I) and (II), conditions are defined which enable (II) to be removed from solution nearly quantitatively by formation of (III). A. T. P.

Formation and properties of azlactones obtained from vanillin substitution products. L. C. Raiford and C. H. Buurman (*J. Org. Chem.*, 1943, **8**, 466—472).—The following 2-*phenyl*-4-3′-*methoxy*-4′-*acetoxybenzylideneoxazol*-5-*ones* (azlactones) are obtained by heating the requisite substituted vanillin (I) with hippuric acid (II) and NaOAc in Ac_2O at 100°: 5′-*chloro*-, m.p. 190·5—191·5°; 6′-*chloro*-, m.p. 205—206°; 5′ : 6′-*dichloro*-, m.p. 239—240°; 5′-*bromo*-, m.p. 191—191·5°; 6′-*bromo*-, m.p. 211°; 5′ : 6′-*dibromo*-, m.p. 265°; 2′ : 5′ : 6′-*tribromo*-, m.p. 190·5—191°; 5′-*bromo*-4′-*methyl*-, m.p. 167·5—168·5°; 5′-*iodo*-, m.p. 180—181°. 2-Bromohippuric acid, m.p. 193—194°, similarly affords 2-2′-*bromophenyl*-4-3′-*methoxy*-4′-*acetoxybenzylideneoxazol*-5-*one*, m.p. 158·5—159·5°, and its 5′-, m.p. 187—188°, and 6′-*Br*-, m.p. 197—198°, 5 : 6-Br_2-, m.p. 225—226°, and 2 : 5 : 6-Br_3-, m.p. 189—191°, -derivatives. Aceturic acid yields the following 4-3′ : 4-*dimethoxybenzylidene*-2-*methylpyrazol*-5-*ones* by condensation with the appropriate vanillin derivative: 5′-*chloro*-, m.p. 203—204°; 5′-*chloro*-4′-*methyl*-, m.p. 169—170°; 5′-*bromo*-, m.p. 206—207°; 5′-*bromo*-4′-*methyl*-, m.p. 162—163°; 6′-*bromo*-, m.p. 119—120°; 5′-*iodo*-, m.p. 196—197°. Cautious heating of the azlactone (III) from (I) and (II) with ~3% KOH gives α-benzamidoferulic (α-benzamido-4-hydroxy-3-methoxycinnamic) acid, m.p. 208·5—209·5°, reconverted into (III) by Ac_2O at 100°. The following substituted 4-*hydroxy*-3-*methoxycinnamic acids* are obtained analogously: 5-*chloro*-α-*acetamido*-, m.p. 212—213°; 4-*chloro*-α-*benzamido*-, m.p. 227—228°; 5-*bromo*-α-*acetamido*-, m.p. 203—204°; 5-*bromo*-α-*benzamido*-, m.p. 229—230°; 5-*iodo*-α-*acetamido*-, m.p. 217—218°; 5-*iodo*-α-*benzamido*-, m.p. 227—228°. α-*Acetamido*- and 5-*bromo*-α-*benzamido*-3 : 4-*dimethoxycinnamic acids* have m.p. 198—199° and 201—202° respectively. *Et*, m.p. 196—197°, and *Me*, m.p. 205—206°, 5-*bromo*-α-*benzamido*-4-*hydroxy*-3-*methoxycinnamate* and *Me* 5-*bromo*-α-*benzamido*-3 : 4-*dimethoxycinnamate*, m.p. 119—121°, have been prepared. The azlactones are converted by boiling 6N-NaOH into NH_3, BzOH, and the following 4-*hydroxy*-3-*methoxyphenylpyruvic acids*: 5-*chloro*-, m.p. 228—228·5° (*oxime*, m.p. 158—159°); 5-*bromo*-, m.p. 237·5—239°/(decomp.) [*oxime*, m.p. 169° (decomp.); *semicarbazone*, m.p. 195—196°; *diacetate*, m.p. 193—194°]; 5-*iodo*-, m.p. 234—235° (*oxime*, m.p. 170—171°). 5-*Bromo*-3 : 4-*dimethoxyphenylpyruvic acid*, m.p. 175—177°, gives a *Me ether*, m.p. 162—163°. H. W.

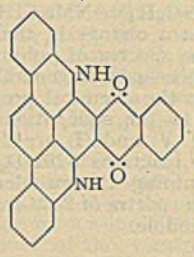
Hydroindazolone derivatives; search for new analgesics. C. W. Picard and D. E. Seymour (*Quart. J. Pharm.*, 1943, **16**, 264—269; cf. A., 1944, III, Mar.).—A simplified method for prep. of 1-phenyltetrahydroindazolone (I) consists in condensing Et *cyclo*hexanone-2-carboxylate (II) with a salt of $NHPh{\cdot}NH_2$ instead of the free base; similarly condensation of (II) with N_2H_4,H_2SO_4 in H_2O yields tetrahydroindazolone. Condensation of (I) with the appropriate alkyl halide in boiling EtOH–KOH yields 1-*phenyl*-2-n-, m.p. 65·5°, and -iso*propyl*-, m.p. 84—85°, -2-n-*butyl*-, an oil, m.p. 84°, and -iso*amyl*, an oil, and -2-*allyl*-*tetrahydroindazoline*, m.p. 65—67°. (I) with BzCl in C_5H_5N gives the 2-*Bz* derivative, m.p. 110°. Treatment of 1-phenyl-2-methyltetrahydroindazolone with $ClSO_3H$ and subsequently with NH_3 yields 2-p-*sulphonamidophenyl*-1-*methyltetrahydroindazolone*, m.p. 272—273°. 1-p-*Acetamidobenzenesulphonyl*-2-*phenyltetrahydroindazolone* has m.p. 190—191°. J. N. A.

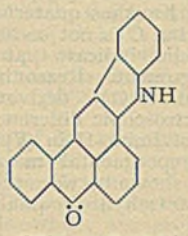
Further diacridines and diacridylium salts. K. Gleu and R. Schaarschmidt (*Ber.*, 1940, **73**, [*B*], 909—915).—Acridones (I) are reduced to " diacridines " by methods which must be adapted to the individual cases (Zn and HCl–EtOH are frequently useful) and these are readily oxidised to diacridylium nitrates by boiling dil. HNO_3. Alternatively (I) are treated with Mg+MgI_2 in boiling PhOMe; the resulting pinacols are too unstable for isolation and, after removal of the solvent with steam, the diacridylium salts are usually immediately obtained as the sparingly sol. iodides, which are readily converted into the nitrates and chlorides. The following are described: 10 : 10′-*diethyl*" *diacridine*," m.p. 275°; 10 : 10′-*diethyldiacridylium H nitrate*, $C_{30}H_{26}N_2(NO_3)_2,HNO_3,3H_2O$; 10 : 10′-*diphenyl*" *diacridine*," m.p. 342°; 10 : 10′-*diphenyldiacridylium nitrate* and *chloride*, $C_{38}H_{28}N_2Cl_2,2HCl,8H_2O$, and the *compound*, $C_{38}H_{28}N_2Cl_2,ZnCl_2,H_2O$; 10 : 10′-*dimethyldiacridylium nitrate tetra*- and *di-hydrate*. 10 : 10′-Diethyl- and -dimethyl-acridylium salts show green luminescence of about the same intensity. The chemiluminescence colour of the 10 : 10′-Ph_2 compounds in very dil. solution is pure blue comparable in shade and intensity with that of 3-aminophthalhydrazide; the fluorescence colour is pure green so that in this instance there is a distinct difference between fluorescence and chemiluminescence. Further, the chemiluminescence colour depends on the concn. whereas the fluorescence colour is not materially affected. The concn. of H_2O_2 is also significant. It appears therefore that the chemiluminescence phenomenon is more complex than assumed hitherto and that there is no general identity between fluorescence- and chemiluminescence-spectra; the identity sometimes observed is accidental. Diacridines show marked chemiluminescence in org. media in which autoxidation occurs without addition of alkali; it is best observed by addition of EtOH to a diacridine in *cyclo*hexanone. H. W.

Pyridazine derivative of cholestanedione.—See A., 1944, II, 52.

***ms*-Benzacridan derivatives.** H. Waldmann and K. G. Hindenburg [with S. Back] (*J. pr. Chem.*, 1940, [ii], **156**, 157—168).—1-Anilino-2 : 3-benzanthraquinone is converted by $AlCl_3$ (10 parts) at 150° (bath)/2 hr. or by 75% H_2SO_4 (20 parts) at 180°/8 hr. into 2 : 3-*benzcœramidonine*, m.p. 262°. 1-Amino-2 : 3-benzanthraquinone, *o*-$C_6H_4Cl{\cdot}NO_2$, K_2CO_3, $Cu(OAc)_2$, and Cu powder in boiling $PhNO_2$ give the 1-o-*nitroanilino*-, m.p. 283° [less readily obtained from 1-chloro-2 : 3-benzanthraquinone (I), *o*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, K_2CO_3, and $Cu(OAc)_2$ in $PhNO_2$], reduced (EtOH–Na_2S) to the 1-o-*aminoanilino*-derivative, m.p. 264°, which with $NaNO_2$ in aq. AcOH at −6° to 0° affords 1-1′-*benztriazolyl*-2 : 3-*benzanthraquinone*, m.p. 288° [also prepared from (I), benztriazole (II), KOAc, and $Cu(OAc)_2$ in $PhNO_2$]; this in boiling $NHPh_2$ gives 3 : 4-*phthaloyl*-ms-*benzacridan*, m.p. 289—290°. 1-o-*Chloroanilino*-2 : 3-*benzanthraquinone*, m.p. 206°, is obtained from (I), *o*-$C_6H_4Cl{\cdot}NH_2$, and NaOAc. 1 : 4-Dichloro-2 : 3-benzanthraquinone (III), (II), KOAc, and $Cu(OAc)_2$ in $PhNO_2$ at 190° (bath) give 1 : 4-*di*-1′-*benztriazolyl*-2 : 3-*benzanthraquinone*, decomp. 291° (also formed by HNO_2 on the 1 : 4-di-*o*-aminoanilino-derivative), which in boiling $NHPh_2$ affords 1 : 2-

phthaloyl-4 : 5 : 8 : 9-*dibenzo*-3 : 10-*dihydro*-3 : 10-*diazapyrene* (*A*), m.p. >400° (obtained directly if the original reaction mixture is boiled). 4-Chloro-1-hydroxy-2 : 3-benzanthraquinone, (**II**), KOAc, and $Cu(OAc)_2$ in $PhNO_2$ at 220—230° give 2-*hydroxy*-3 : 4-*phthaloyl*-ms-*benzacridan*, m.p. >310°. *ang.*-Naphthotriazole with (**I**) and (**III**) in boiling $PhNO_2$ similarly affords the *mono*-, m.p. 319° (decomp.), and *di-naphthotriazolyl* derivatives, m.p. >340°, respectively, and thence 3 : 4-*phthaloyl*-5 : 6(7 : 8)-*benzo*-ms-*benzacridan*, m.p. 290° (in boiling $NHPh_2$), and 1 : 2-*phthaloyl*-4 : 5 : 8 : 9-*di*-1′ : 2′(2′ : 1′)-*naphtho*-3 : 10-*dihydro*-3 : 10-*diazapyrene*, m.p. >400°. 3 : 4-*Phthaloyl*-6 : 7-*benzo*-ms-*benzacridan*, m.p. >320°, and 1 : 2-*phthaloyl*-4 : 5 : 8 : 9-*di*-2′ : 3′-*naphtho*-3 : 10-*dihydro*-3 : 10-*diazapyrene*, m.p. >400°, are similarly obtained directly using *lin.*-naphthotriazole. *lin.*-Naphthotriazole-4 : 9-quinone with (**I**) and (**III**) in boiling $PhNO_2$ similarly affords the *mono*-, m.p. >370°, and *di-naphthotriazolequinonyl* derivative, m.p. >400°, respectively, from which N_2 could not be eliminated. 3-Bromobenzanthrone (**IV**), *o*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, KOAc, and $Cu(OAc)_2$ in boiling $PhNO_2$ give the 3-*o*-*nitroanilino*-, m.p. 266°, reduced (EtOH–Na_2S) to the 3-*o*-*aminoanilino*-derivative, m.p. 268°. This with $NaNO_2$ in aq. AcOH at ≯−2° affords 3-1′-*benztriazolylbenzanthrone*, m.p. 306·5° [less readily obtained from (**II**) and (**IV**)], which in boiling anthracene gives the *carbazole* derivative (*B*), m.p. 348° [cautious oxidation (CrO_3, AcOH) gives anthraquinone-1-carboxylic acid]. H. B.


(*A*.)


(*B*.)

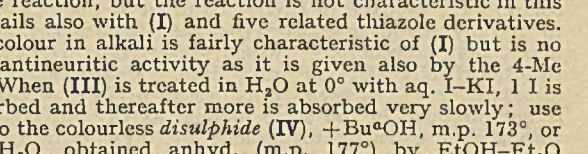
Isolation of mononucleotides after hydrolysis of ribonucleic acid by crystalline ribonuclease. H. S. Loring and F. H. Carpenter (*J. Biol. Chem.*, 1943, **150**, 381—388).—The NH_4 salt of ribonucleic acid (**I**) (yeast-nucleic acid is used) in neutral or slightly acid medium is treated with cryst. ribonucleinase (preferable to the term ribonuclease; cf. Kunitz, A., 1941, III, 47) at room temp. at pH 6·3 (decreases to 5·5). Four acids are obtained: guanylic [purified through the dibrucine salt, $+7H_2O$, sinters at 210°, decomp. 224° (immersed at 200°), and Na_3 salt, $[\alpha]_D^{23}$ −57·6° in aq. NaOH], uridylic [dibrucine salt, $+7H_2O$, $[\alpha]_D^{28}$ −54·4° in C_5H_5N; $(NH_4)_2$ salt, shrinks at 170—175°, decomp. 183° (immersed at 165°), $[\alpha]_D^{24}$ +20·0° in H_2O], cytidylic, decomp. 230°, and adenylic, $+H_2O$, decomp. 196°, $[\alpha]_D^{24}$ −38° in H_2O. These four nucleotides are not formed during fractionation processes, as they could not be obtained in experiments in which nucleic acid, in absence of enzyme, is fractionated. A. T. P.

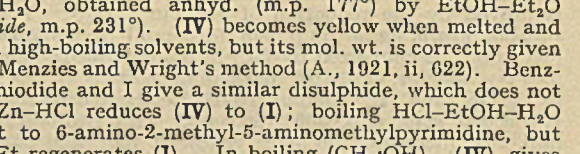
New method for isolation of crystalline adenine nucleotides. M. V. Buell (*J. Biol. Chem.*, 1943, **150**, 389—394).—The following reaction is characteristic of adenine mononucleotides and of yeast-nucleic acid (**I**): addition of solutions containing picrate + Al ions (at pH 2·4) [*e.g.*, $Al(OAc)_3$ + picric acid] affords (mainly) an Al picrate complex of the nucleotide. The method is used for the isolation of cryst. adenine nucleotide (**II**). Thus, the K acetate salt of guanine nucleotide is pptd. by 95% EtOH from a neutral solution of (**I**), previously treated with 0·3-N aq. KOH for 24 hr. at room temp. The filtrate then affords the Al picrate salt of (**II**); after dissolution in morpholine and pptn. with $COMe_2$, the salt is converted by aq. KOH + AcOH (pH 5) into (**II**), $+2H_2O$ (purified through the Pb salt). Cryst. adenylic acid (**III**) is isolated from beef heart. Enzyme action is inhibited by freezing the muscle, and proteins are removed from an aq. extract by heat-coagulation and picric acid pptn. (**III**) is obtained from the filtrate as the Hg salt, then pptd. as the Al picrate complex, and purified through the Pb salt. A. T. P.

Fluorescent irradiation products of thiazole. R. Stämpfli (*Helv. Physiol. Pharm Acta*, 1943, **1**, C54—55).—"Vitachrome" is most strongly fluorescent (deep blue) in acid solution. It is heat-stable, lowers surface tension, and is stable to long-wave ultra-violet radiation. Fluorescent substances were obtained from 2-thiol-4 : 5-dimethylthiazole, 2-thiol-4-methyl-5-acetoxyethylthiazole, Na 2-thiol-4-methylthiazolecarboxylate, and 2-thiol-4-methylthiazole; the last two prioducts show max. fluorescence at alkaline pH. Negative results were obtained with 4-methylthiazole and its nitrate, 2-amino-4-methylthiazolium nitrate, 3-benzyl-4-methyl-5-β-hydroxyethylthiazolium chloride, 3 : 4-dimethyl-5-hydroxymethylthiazolium chloride, 4-methyl-3-acetoxyethylthiazolium bromide, 4-methyl-3-diethylaminoethyl-5-hydroxyethylthiazolium chloride, 4-methylbenzylthiazolium chloride. A. S.

Conversion of 2-phenyl-4-chloromethylthiazole into 5-chloro-2-phenyl-4-hydroxymethylthiazole. E. H. Huntress and K. Pfister, tert. (*J. Amer. Chem. Soc.*, 1943, **65**, 1667—1670).—2-Phenyl-4-chloromethylthiazole (**I**) [obtained from $CO(CH_2Cl)_2$ and $PhCS{\cdot}NH_2$ with subsequent hydrolysis by conc. HCl; 71% yield], m.p. 48·2—51·2°, with boiling 0·1N-NaOH or KOAc–AcOH gives 2-*phenyl*-4-*hydroxy*- (**II**), m.p. 66—69°, and 2-*phenyl*-4-*acetoxymethylthiazole*, m.p. 42—43° [also obtained from (**II**)], respectively. CrO_3–H_2SO_4–H_2O oxidises (**II**) to 2-*phenylthiazole*-4-*carboxylic acid* (22%), m.p. 175—176·5° [*acid chloride* (**III**), m.p. 97·7—98·5°; *amide*, m.p. 143·3—143·8°]. With NaI–$COMe_2$, (**I**) gives 2-*phenyl*-4-*iodomethyl*-, m.p. 103·5—104·6°, and with NaCN–EtOH gives 2-phenyl-4-cyanomethyl-thiazole, m.p. 43·1—44·2°, b.p. 147—148°/2 mm. (lit. 180—185°/4—5 mm.), hydrolysed by boiling 6N-HCl to 2-phenyl-4-thiazolylacetic acid, m.p. 88·8—89·8° (lit. 90°) [Na salt; hydrochloride, m.p. 203·1—205·1° (gas) (lit. 206—207°)]. Boiling conc. HNO_3–H_2O (10 : 24 ml.) converts (**I**) into 5-*chloro*-2-*phenyl*-4-*hydroxymethylthiazole* (57·5%), m.p. 116·5—118° (*acetate*, m.p. 63·3—64·1°; 3 : 5-*dinitrobenzoate*, m.p. 155·1—155·3°), which with CrO_3–H_2SO_4–H_2O gives 5-*chloro*-2-*phenylthiazole*-4-*carboxylic acid* (41·6%), m.p. 198·8—199·3° (gas), also obtained in 21% yield with 2-phenylthiazole-4-carboxylic acid (54%) from (**III**) by HNO_3–H_2O. 29·2% of BzOH is obtained from (**II**) by dil. alkaline $KMnO_4$. M.p. are corr. (block). R. S. C.

Oxidation product of aneurin effective antineuritically. O. Zima and R. R. Williams (*Ber.*, 1940, **73**, [*B*], 941—949).—Triturating aneurin chloride hydrochloride (**I**) with saturated, aq. K_2CO_3 at room temp. gives the quaternary *chloride*, $C_{12}H_{17}ON_4ClS$, decomp. when heated. In NaOEt–EtOH, (**I**) gives a yellow colour and yields a yellow *Na* salt (**II**), $C_{12}H_{15}ON_4SNa$, $+3H_2O$ (lost at 78°/vac.), unstable in air. When repeatedly dissolved in EtOH and pptd. therefrom by Et_2O, this gives a colourless *Na* salt (**III**), $+4H_2O$, converted over $CaCl_2$ at room temp./vac. into a *dihydrate*, but becoming yellow at 110°. (**III**) is also obtained by adding aq. NaOH to (**I**) in H_2O at 0° and treating the product with $COMe_2$. It is probably formed by way of the quaternary hydroxide. (**II**) and (**III**) do not give a nitroprusside reaction, but the reaction is not characteristic in this series as it fails also with (**I**) and five related thiazole derivatives. The yellow colour in alkali is fairly characteristic of (**I**) but is no criterion of antineuritic activity as it is given also by the 4-Me isomeride. When (**III**) is treated in H_2O at 0° with aq. I–KI, 1 I is rapidly absorbed and thereafter more is absorbed very slowly; use of 1 I leads to the colourless *disulphide* (**IV**), $+Bu^{\alpha}OH$, m.p. 173°, or $+COMe_2 + H_2O$, obtained anhyd. (m.p. 177°) by EtOH–Et_2O (*dihydrochloride*, m.p. 231°). (**IV**) becomes yellow when melted and dissociates in high-boiling solvents, but its mol. wt. is correctly given in MeOH by Menzies and Wright's method (A., 1921, ii, 622). Benzthiazole methiodide and I give a similar disulphide, which does not dissociate. Zn–HCl reduces (**IV**) to (**I**); boiling HCl–EtOH–H_2O hydrolyses it to 6-amino-2-methyl-5-aminomethylpyrimidine, but boiling NaOEt regenerates (**I**). In boiling $(CH_2{\cdot}OH)_2$, (**IV**) gives thiochrome (**V**) and a *product* (**VI**), $C_{12}H_{16}O_2N_4S$, m.p. 233—234°, which, when kept in solution, assumes a blue fluorescence, probably by formation of (**V**). (**VI**) has ≮60—70% of the antineuritic effect (rats) of (**I**). (**I**) may be the reduced form of the natural "redox" system. R. S. C.


(III.)


(VI.)

Cyanine dyes etc.—See B., 1944, II, 7, 10.

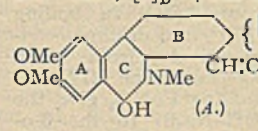
VII.—ALKALOIDS.

Constitution of yohimbine and its degradation products. B. Witkop (*Annalen*, 1943, **554**, 83—126).—It is shown that the OH group of yohimbine (**I**) is attached to $C_{(17)}$. (**I**) has m.p. 234°, new $[\alpha]_D^{20}$ +62·2° in EtOH; technical samples of its hydrochloride may contains a little *iso*yohimbine but the presence of *allo*yohimbine is excluded. Decarboxylation of yohimboaic acid (**II**) by NaOH–CaO cannot be effected at <350° and gives the ketone *yohimbone* (**III**), m.p. 307° (decomp.) [*methiodide*, m.p. ~290° (decomp.), darkens at 250°; *methochloride* ($+2H_2O$), m.p. 276° (decomp.); *hydrochloride* of 2 : 4-*dinitrophenylhydrazone*, m.p. >300°, darkens at 280°]. Rapid treatment of (**II**) with TlOH at 300°/0·1 mm. gives *deoxy-yohimbol*, m.p. 149°, $[\alpha]_D^{20}$ −24·8° in C_5H_5N (*hydrochloride*, m.p. 228°; *picrate*, m.p. 224°; *methiodide*, m.p. 198°; the *methochloride* is physiologically inactive in the frog). The mother-liquors from (**III**) contain indole and *iso*quinoline derivatives so that direct crystallisation is impossible but treatment with MeI in MeOH leads to the isolation of *yohimbol methiodide*, m.p. 282° (decomp.) (corresponding *methochloride*, m.p. 259°, softens at 245°). At 260° (**II**) evolves CO_2 but gives a non-crystallisable residue. In presence of Cu powder decarboxylation occurs at 225°, giving (**III**) in 8% yield; mol. Ag and Ag_2O are without influence. (**III**) is obtained in good yield from

(II) mixed with anthracene at 320°, and in poor yield from (II) and aq. $Ba(OH)_2$ at 280°. Slow decarboxylation of (II) with NaOH–CaO at 270—300° leads to "tetrahydroyobyrine" (IV), m.p. 166°. Dehydrogenation of (I) by $Al(OPh)_3$ and *cyclo*hexanone in xylene at 150° gives (III), $[\alpha]_D^{20}$ −105·8° in C_5H_5N (*hydrochloride*, m.p. 328°; *picrate*, m.p. 171°), similarly obtained from (II); attempts to isolate the intermediate "yohimbinone" under milder conditions were unsuccessful. (III) is dehydrogenated by black Se at 300° to tetrahydroyobyrine, m.p. 167° (hydrochloride, m.p. 236°), and yobyrine, m.p. 215° [picrate, m.p. 239° (much decomp.)], but does not appear to be affected by $Pb(OAc)_4$. *allo*Yohimboaic acid and $Al(OPh)_3$ in boiling *cyclo*hexanone–xylene afford allo*yohimbone*, m.p. 230° (decomp.) (2 : 4-*dinitrophenylhydrazone*, darkens at 250° and softens and swells at 264°), whilst under similar conditions yohimbenic acid affords *yohimbenone*, m.p. 268° (decomp.) (2 : 4-dinitrophenylhydrazone hydrochloride darkens at 260°, softens at 280°). (III), $Al(OPr^{\beta})_3$, and $Pr^{\beta}OH$ in xylene afford *yohimbol* (V), m.p. 243° (decomp.), $[\alpha]_D^{20}$ −63·4° in EtOH, −55·4° in MeOH [*hydrochloride* (+0·5H_2O), m.p. 291°, $[\alpha]_D^{20}$ −51·5° in MeOH], and epi*yohimbol* (VI), $C_{19}H_{24}ON_2$, m.p. 258°, $[\alpha]_D^{20}$ −80·1° in MeOH (*methiodide*, m.p. >300° after darkening and softening; *methochloride*, m.p. 298°); a short period of reaction favours (V) whilst with very protracted action the yield of (VI) is >50%. (IV) (*hydrochloride*, m.p 236°) is dehydrogenated by Pd sponge at 280° to 2:3′-iso*quinolyl*-3-*ethylindole*, m.p. 128° (*hydrochloride*, m.p. 212°; *methiodide*, m.p. 192°), isomeric with yobyrine (VII) [*hydrochloride*, m.p. 271° (much decomp.), softens at 240°; *picrate*, m.p. 239° (decomp.)], which remains unchanged under these conditions. (VII) is oxidised by SeO_2 in boiling xylene or, preferably, Ac_2O to *yobyrone* (VIII), $C_{19}H_{14}ON_2$, m.p. 185°, which does not react with $(NO_2)_2C_6H_3\cdot NH\cdot NH_2$ in dil. HCl. (VII) is converted by paracetaldehyde at 260° into *ethylideneyobyrine*, m.p. 298° (darkening); with p-$NO_2\cdot C_6H_4\cdot CHO$ a similar condensation occurs at 180—200° but in subsequent working up the product is converted by acid into (VIII) and o-$C_6H_3Me\cdot CO_2H$. (VII) is hydrogenated (PtO_2 in AcOH at 40°) to *hexahydroyobyrine*, m.p. 197°. *apo*Yohimbine (IX) is oxidised by $Pb(OAc)_4$ in AcOH at 40° and then hydrolysed to *tetrahydroyobyrinecarboxylic acid* (X), m.p. 286° (decomp.), $[\alpha]_D^{20}$ +217·6° in EtOH [*hydrochloride* (+2H_2O), m.p. 303° (much decomp.), $[\alpha]_D^{20}$ +307·3° in EtOH], oxidised by SeO_2 in boiling C_5H_5N to tetrahydroyobyronecarboxylic acid [*hydrochloride semihydrate*, m.p. 244° (decomp.)], which does not react with 2 : 4-$(NO_2)_2C_6H_3\cdot NH\cdot NH_2$ in dil. HCl. *Hydroxyhexahydroyobyrinecarboxylic acid* ["*tetradehydroyohimboaic acid*"] (+H_2O), m.p. 325°, is not obtained in the same manner as (X) but is best prepared through the ester hydrochloride; the presence in it of active CH_2 is proved by the reduction of SeO_2 in C_5H_5N. *Yohimboaic acid sulphate hydrochloride*, m.p. 308° (decomp.) [free *sulphate*, m.p. 289° (decomp.)], is converted by HCl in boiling MeOH followed by NH_3 into ε-*yohimbine*, m.p. 203° (darkening), softens at 195°, $[\alpha]_D^{20}$ +29·8° in C_5H_5N, and (I). Boiling KOH–MeOH hydrolyses (IX) to apo-*yohimboaic acid*, m.p. 306° (decomp.), with two *bases*, $C_{21}H_{24}O_2N_2$, m.p. 201° (decomp.), becomes yellow at 160°, and $C_{21}H_{24(26)}O_{2(3)}N_2$, m.p. 228°. In 50% of AcOH containing Pd–C under H_2 (IX) passes into α-iso*yohimbine*, m.p. 304°, $[\alpha]_D^{20}$ +53·2° in 50% AcOH, hydrolysed to α-iso*yohimboaic acid* (+1·5H_2O), m.p. 238°, and converted by NaOAc and boiling Ac_2O into (IX); oxidation (Oppenauer) of it does not give a base or CO-acid. The isolation of p-cresol by the distillation of (I) with Zn dust is described. The physiological activity of many quaternary bases of the yohimbine series is discussed. For these experiments the methiodides are frequently too sparingly sol. and must be converted into the methochlorides. apo*Yohimbine methiodide monohydrate*, effervesces at 259° after softening at 246° and becoming brown at 220°, appears new. H. W.

Constitution of derivatives of the harman series from the viewpoint of their ultra-violet spectra. F. Pruckner and B. Witkop (*Annalen*, 1943, **554**, 127—144).—Comparison of the absorption spectra of norharman (I) and yobyrine (II) leads to the conclusion that substitution in (I) at $C_{(3)}$ causes a marked diminution in the intensity in band II to an extent which exceeds the enhancement caused by addition of the extinction of the xylene residue. The spectrum of (I) and still more that of (II) is very similar to that of carbazole. The diminished height of the bands with (II) may be due to substitution as such which diminishes the symmetry of the mol. This effect is yet more prominent in the comparison of the spectra of (II) and tetrahydroyobyrinecarboxylic acid; the extinction vals. of hydroxyhexahydroyobyrinecarboxylic acid (which has nearly the same position of the bands) could not be measured. Similar results are recorded for papaverine (III)–*iso*quinoline (IV) in which substitution causes a displacement of all bands towards the red and exaltation of the extinction is caused by the addition of an aromatic ring separated by a CH_2 group; this is particularly noticeable in band II. The complete absence from the spectrum of (III) of the individual bands seen in that of (IV) is ascribed to the presence of OMe in (III). In support of this hypothesis it is observed that the individual bands of indole are absent from the spectra of 5- and 6-methoxyindole; similar observations are recorded for lepidine and p-methoxylepidine. The spectrum of harmine (V) differs considerably from that of harmaline (VI), which behaves optically more like a derivative of indole than a hydrogenated harman. Further evidence in the same direction is based on the observation that the spectrum of (VI) does not differ so greatly from that of its methiodide as do the spectra of the methiodides of (V) and (II) differ from those of the *tert.*-bases. This difference shows that (V) and (II) are closely related in spite of the differences in their spectra. The transition of (V) into the quaternary salt causes a weakening of the aromatic system similar to that caused by the change, p-toluidine → p-$C_6H_4Me\cdot NMe_3Cl$ but when N of (VI) becomes quaternary so great a change in the dihydropyridine ring C is not occasioned. The spectra of yohimbine and its methiodide indicate that caution is necessary in generalising this line of argument. Reasoning based on the chemical properties of indole and its OMe derivatives leads to the conception that the great spectroscopic differences between (V) and (I) are due to the mobility of imino-H in (V); exchange reactions with D_2O offer a possible experimental means of examining the problem. Close analogy is shown between the absorption spectra of 2 : 2′-*iso*quinolyl- and 2 : 2′-tetrahydro*iso*quinolyl-3-ethylindole. H. W.

Lycoris **alkaloids. XVI. Constitution of lycorenine.** H. Kondo and T. Ikeda (*Ber.*, 1940, **73**, [*B*], 867—874).—Lycorenine (I), m.p. 200—202°, $[\alpha]_D^{23}$ +149·33°, is *A*. Catalytic hydrogenation (Pd or PtO_2 in AcOH) of (I) gives *dihydrolycorenine*, m.p. 175—177°, or under more drastic conditions *deoxytetrahydrolycorenine*, m.p. 165—168°, with *compounds*, $C_{18}H_{23(25)}O_3N$, m.p. 120—123°, and $C_{18}H_{27}O_2N$, m.p. 165—167°. (I) is



(*A*.)

transformed by Ac_2O and fused NaOAc at 100° into a mono-, m.p. 185—187°, and a *di*-, m.p. 173—176°, *-acetyl-lycorenine*, the latter compound being produced with much the greater difficulty. *Lycorenine methiodide*, decomp. 260°, is converted by AgOH followed by distillation at 130°/vac. mainly into the amorphous α-methine base (analysed as the *methiodide*, $C_{18}H_{20}O_3NMe_2I$, decomp. 223°), with a smaller proportion of amorphous β-methine base. de-N-*Lycorenine* (II), m.p. 114·5°, is $C_{15}H_{10}O(OMe)_2$. One O is lost as H_2O in the first stage of the degradation and the residual O is present in CO and not in OH since (II) cannot be acetylated but affords an *oxime*, $C_{17}H_{16}O_2N\cdot OH$, m.p. 147—150°. The B nucleus is readily aromatised during the Hofmann degradation by the formation of a new double linking owing to loss of H_2O, and :CH·OH at $C_{(6)}$ passes into CHO whilst N is eliminated. Ozonisation of (II) leads to CH_2O, a *dialdehyde* (III), $C_{16}H_{14}O_4$, m.p. 155—157° (*disemicarbazone*, decomp. 238°), and an aldehydic *acid*, $C_{16}H_{14}O_5$, m.p. 228—230° (p-*nitrophenylhydrazone*, decomp. 276—278°), also obtained by oxidising (III) with $KMnO_4$ in $COMe_2$ at room temp., and further oxidised to a dicarboxylic *acid*, $C_{16}H_{14}O_6$, m.p. 256—257° (Me_2 ester, m.p. 135—137°). This is characterised as 3 : 4-*dimethoxydiphenyl*-6 : 3′-*dicarboxylic acid* by hydrolysis of the Me_2 ester obtained synthetically from 3 : 4 : 6 : 1-$(OMe)_2C_6H_2Br\cdot CO_2Me$, m-$C_6H_4I\cdot CO_2Me$, and Cu powder at 255—260°. CH_2O is readily obtained by the action of O_3 on (I) but the aldehydic base formed simultaneously is too unstable for further examination. Like a typical ψ-base (I) affords an *oxime hydrochloride*, decomp. 258°. H. W.

Strychnos **alkaloids. XCII. Reactions of** *N*-**methyl***sec.*-ψ-**brucine and related bases.** H. Leuchs and H. G. Boit (*Ber.*, 1940, **73**, [*B*], 885—892).—An amended method of obtaining ψ-brucine (I) is reported. The action of MeI on (I) in MeOH gives 7% of quaternary salt against 3—4% in H_2O but the quaternary salt observed previously (A., 1939, II, 349) is not encountered when (I), free from brucine, is produced. With ψ-brucine Me ether and MeI the yields of *tert.* base and quaternary salt are 39 and 61% in presence of MeOH and 60 and 40% in presence of H_2O. Reaction of (I) with Me_2SO_4 yields exclusively *tert.*-*N*-Me base. Dihydro-ψ-brucine Me ether and MeI in H_2O afford *N*-methyldihydro-ψ-brucine methiodide in 84% yield; this forms ~25% of the product from dihydro-ψ-brucine. Methylation of (I) may be expected to occur in accordance with the scheme, :C(OH)·N: → :CO·NMe· but the product does not react with $NH_2\cdot CO\cdot NH\cdot NH_2$ or with NH_2OH,HCl in C_5H_5N and $NH_2\cdot CO\cdot NH\cdot NH_2$ does not affect the quaternary methiodide or its H_2-derivative. MnO_4' oxidises (I) at 20° in $COMe_2$ but with 10 equivs. of O_2 ~40% remains unchanged and the rest is altered in an ill-defined manner. The Me base is converted by MnO_2 and SO_2 into two isomeric *sulphonic acids*, $C_{24}H_{27}O_5N_2\cdot SO_3H$, $[\alpha]_D^{20}$ −120·3°/*d* and 41°/*d* in 2 mols. of 0·1N-NaOH; the homogeneity of a third material, $[\alpha]_D^{20}$ −62·3°/*d*, is not established. With PhCHO in boiling NaOMe–MeOH it yields *benzylidene*- (II), m.p. 234—236° (vac.), reduced (Na–Hg in dil. MeOH containing a little AcOH) to *benzyl*-*N*-*methyl**sec.*-ψ-*brucine*, m.p. 195—197° (vac.) (*hydrobromide*; *perchlorate*). Hydrogenation (PtO_2 in 25% AcOH) of (II) leads to *benzyldihydro*-N-*methyl**sec.*-ψ-*brucine* [*hydrobromide* (+H_2O), m.p. 105—110° to a resin or, anhyd., m.p. 215—225° (slight decomp.); *hydrochloride*, m.p. ~100° and 215—225°]. (I) condenses with PhCHO to benzylidene-ψ-brucine, isolated as the *hydrobromide*, chars at 225°, reduced by Na–Hg in dil. MeOH to a mixture of benzyl-

ψ-brucine and -brucine hydrobromide and hydrogenated (PtO_2 in 50% AcOH) to benzyldihydro-ψ-brucine (*hydrochloride*, m.p. ~220° after softening; darkens at 190°). The *tert.* ether base obtained by the action of NaOMe or Na–Hg on *N*-methyl-ψ-brucine methiodide is hydrolysed by 12N-HCl at 100° to *N*-methyl*sec.*-ψ-brucine. The methiodide of this base is reduced by Na–Hg–H_2O to the methiodide, $C_{26}H_{36}O_5N_2$,MeI, m.p. 276—278°; other methods of treatment lead to a neutral *perchlorate*, $(C_{26}H_{34}O_5N_2)_2,HClO_4$, m.p. 102°, decomp. 112°, and a *base*, $C_{25}H_{32}O_5N_2$, m.p. 230—233° (vac.), which contains only 2 OMe and hence has suffered an Emde fission. This base absorbs 4 H when hydrogenated (PtO_2 in 0·1N-HCl) and according to conditions gives two interconvertible *salts*, $C_{25}H_{36}O_5N_2,HClO_4$, hydrated, m.p. 114—115° (decomp.), softens at 100°, anhyd. m.p. 263—269°, and $C_{25}H_{36}O_5N_2,2HClO_4$, m.p. 153—154° (decomp.); the corresponding bases are non-cryst. but another experiment gives a cryst. *base*, $C_{25}H_{34(36)}O_5N_2$, m.p. 172° in <10% yield. H. W.

Veratrine alkaloids. XIV. Correlation of the veratrine alkaloids with the solanum alkaloids. L. C. Craig and W. A. Jacobs (*Science*, 1943, **97**, 112).—5-Methyl-2-ethylpyridine (**I**) was isolated from the distillate from solanidine and Se. (**I**) is a characteristic degradation product of the veratrine alkaloids, which are probably C_{27} compounds closely related to the sterols. E. R. R.

VIII.—ORGANO-METALLIC COMPOUNDS.

Chemistry of bivalent and tervalent rhodium. V. Co-ordination complexes of rhodous halides with dialkylarsines.—See A., 1944, I, 46.

Synthetic application of *o*-β-bromoethylbenzyl bromide. II. Preparation and properties of 2-substituted 1 : 2 : 3 : 4-tetrahydro-*iso*arsinolines. III. Preparation and optical resolution of 2-phenyl-2-*p*-chlorophenacyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinolinium bromide. F. G. Holliman and F. G. Mann (*J.C.S.*, 1943, 547—550, 550—554).—II. *o*-Br·$[CH_2]_2$·C_6H_4·CH_2Br (**I**) in Et_2O with $AsPhCl_2$ and Na–EtOAc in absence of air give 2-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline* (**II**), b.p. 110—112°/0·01 mm. (*methiodide*, m.p. 136—137°), which is oxidised by HNO_3 to the oxy-compound, isolated as the *hydroxy-nitrate*, m.p. 149—150°; by Br–$CHCl_3$ to the arsine dibromide, isolated as the iso*arsinoline dichloride*, m.p. 147—149°, or as 2-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline sulphide*, m.p. 124° (by H_2S), and by chloramine-*T* to the oxy-compound, isolated as the *hydroxy-picrate*, m.p. 116—118°. $AsMeCl_2$ with (**I**) in a similar manner affords 2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline* (**III**), b.p. 131°/18 mm. (*methiodide*, m.p. 179—181°; *methopicrate*, m.p. 163—164°), which is oxidised with HNO_3 to the hydroxy-nitrate, isolated as the *hydroxy-picrate*, m.p. 164—165·5°. Cl_2 in CCl_4 converts (**III**) into 2-*methyl*-1 : 2 : 3 : 4-*terahydro*iso*arsinoline dichloride*, which at 130—140° gives MeCl and 2-*chloro*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinoline*, b.p. 157°/14 mm., unaffected by boiling C_5H_5N. 2-*Phenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinoline*, b.p. 130—160°/0·2 mm. (*methiodide*, m.p. 116—118°), can be prepared in small yield only. None of the compounds tested possesses trypanocidal or antimalarial activity.

III. *p*-C_6H_4Cl·CO·CH_2Br and (**II**) give dl-2-*phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinolinium bromide*, m.p. 190—191° (dl-*iodide*, m.p. 190·5°), which with Ag *d*-bromocamphorsulphonate yields the d-*bromocamphorsulphonate*, m.p. 119—131°, $[M]_D^{16}$ +279°. Crystallisation from C_6H_6–*cyclo*hexane affords the l-iso*arsinolinium* d-*bromocamphorsulphonate*, m.p. 236—238°, $[M]_D^{16}$ −140°, which is converted into the *picrate*, $[M]_D^{16}$ −450°, and *iodide*, m.p. 178·5—179°, $[M]_D^{16}$ −352°. The Ag *l*-salt similarly gives d-iso*arsinolinium* l-*bromocamphorsulphonate*, m.p. 236—237°, α_D^{16} +0·89°, from which the *picrate*, $[M]_D^{16}$ +457° is obtained. 2-*Phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinolinium* d-*camphorsulphonate*, m.p. 210—212°, $[M]_D^{16}$ +112°, similarly prepared, gives the *chloroplatinate*, m.p. 211—213°, and *chloroaurate*, 157—158°. The picrates and iodide are optically stable in $CHCl_3$ at room temp. These are the first arsonium salts to be obtained in optically stable forms, and the correlation of their optical and chemical stability provides strong evidence that the optical instability previously recorded for dissymmetric arsonium salts has been due to the formation of a " dissociation-equilibrium " in solution. The properties of other dissymmetric 4-covalent As compounds are discussed on this basis. All rotations are in $CHCl_3$. F. R. S.

Autoxidation of lead tri*cyclo*hexyl and its behaviour towards carbon tetrachloride. F. Hein, E. Nebe, and W. Reimann (*Z. anorg. Chem.*, 1943, **251**, 125—160).—PbR_3 (R = *cyclo*hexyl) in solution is stable towards O_2 in the dark but undergoes oxidation in light thus: $4PbR_3 + 5O_2 = PbR_2O + 2PbO + PbO_2$ + other products. The only intermediate product is $(PbR_3)_2O$. PbR_3 reacts with CCl_4 in presence of O_2 in the dark at room temp., giving PbR_3Cl, PbR_2Cl_2, $COCl_2$, CO_2, and Cl_2, and even in absence of O_2 affords PbR_3Cl, PbR_2Cl_2, and C_2Cl_6. Free CCl_3 is an intermediate product. CBr_4 and C_2Br_6 react similarly but even more energetically. Mechanisms are suggested. F. J. G.

Introduction of water-solubilising groups into some organometallic compounds. R. W. Leeper (*Iowa State Coll. J. Sci.*, 1943, **18**, 57—59).—The following were prepared: *$PbPh_3$ H maleate*, m.p. 207°, *$(PbPh_3)_2$ maleate*, sinters 198—199°, *Pb triphenyl* o-*hydroxyphenyl*, m.p. 216—218°, *$PbPh_3$ 9-phenanthryl*, m.p. 169—171°, *$PbPh_2$ di-9-phenanthryl*, m.p. 208—210°, *$PbPh_3$* 7-(1 : 2-*benzanthryl*), m.p. 295—296°, *PbPh* di*cyclohexyl chloride*, m.p. 195°, decomp. 205°, *$PbPh_2$ Et chloride*, sinters 142°, decomp. 146—147°, *Pb(C_6H_4·NO_2-m)$_2$ di-chloride*, sublimes 250°, decomp. 285—289° (*di-iodide*, decomp. 135°), *GeBu$^a_3$ iodide*, b.p. 126—128°/4 mm., *Ge tetra*-2-*furyl*, b.p. 163°/1 mm., m.p. 99—100°, *SnBu^a tri-iodide*, b.p. 154°/5 mm., *Sn di-carbethoxymethyl dibromide*, m.p. 139°. F. R. G.

Organolead compounds containing water-solubilising groups. D. S. Melstrom (*Iowa State Coll. J. Sci.*, 1943, **18**, 65—67).—RHal with $LiBu^a$ in Et_2O gives LiR which with CO_2 yields RCO_2H, the following being new: 2 : 4 : 5-*triphenylfuran*-3-, m.p. 257—258° (*Me* ester, m.p. 123·5—124°), 3 : 4 : 6-*triphenylpyridine*-2-*carboxylic acid*, m.p. 166—168° (decomp.) (*Me* ester, m.p. 117—118°) p-*carboxyphenylethyl alcohol*, m.p. 127—128°, α-p-*carboxyphenylethyl alcohol*, m.p. 138—139°. The reaction of LiR with $PbPh_3Cl$ leads to the formation of *$PbPh_3$* o- (**I**), m.p. 134—136°, m-, m.p. 113—114°, and p-*hydroxymethylphenyl* (**II**), m.p. 98—100°; *$PbPh_3$* p-β-, m.p. 87—88°, and -α-*hydroxyethylphenyl*, m.p. 68—70°. (**II**) was oxidised ($KMnO_4$) to *$PbPh_3$* p-*carboxyphenyl*, m.p. 256—258° (*Me* ester, m.p. 125—127°; *Na* and *K* salts). Similarly (**I**) produces the *anhydride* of *$PbPh_2$* o-*carboxyphenyl hydroxide*, m.p. 300—305° (with turbidity) [*chloride*, m.p. 210—220° (with turbidity) (*Me* ester, m.p. m.p. 170—171°)]. Also prepared were p-*phenylenedi*(*lead triphenyl*), m.p. 285—288° and *$PbPh_3$* o-*anisyl*, m.p. 128—129°. F. R. G.

Long-chained organometallic compounds. R. N. Meals (*Iowa State Coll. J. Sci.*, 1943, **18**, 62—64).—The following were prepared: *Hg di*-n-*dodecyl*, m.p. 44—44·5°, *-tetradecyl*, m.p. 53—54°, *-hexadecyl*, m.p. 61—62°, and *-octadecyl*, m.p. 66·5—67°; *Hg* n-*dodecyl*, m.p. 114—114·5°, *-hexadecyl*, m.p. 114—115°, and *-octadecyl chloride*, m.p. 115—116°; *Hg* n-*dodecyl*, m.p. 108—108·7°, *-tetradecyl*, m.p. 110—110·5°, *-hexadecyl*, m.p. 110·5—111·5°, and *-octadecyl bromide*, m.p. 110—111°; *Hg* n-*dodecyl*-, m.p. 91°, and *-hexadecyl iodide*, m.p. 93; *Sn tetra*-n-*dodecyl*, m.p. 15—16°, *-tetradecyl*, m.p. 33—34°, *-hexadecyl*, m.p. 41·5—42·5°, and *-octadecyl*, m.p. 47°; *Pb tetra*-n-*tetradecyl*, m.p. 31°, and *-hexadecyl*, m.p. 42°; *Sn tri*-n-*dodecyl*, m.p. 33°, *-tetradecyl*, m.p. 46—47°, *-hexadecyl*, m.p. 55·5—56·5°, and *-octadecyl chloride*, m.p. 61—62°; *Pb tri*-n-*dodecyl*, m.p. 64—65°, *-tetradecyl*, m.p. 74—75°, *-hexadecyl*, m.p. 79—80°, and *-octadecyl chloride*, m.p. 82—83°; *tri-dodecyl*-, b.p. 200°/0·009 mm., and *-tetradecyl-arsine*. F. R. G.

Organotin compounds. C. E. Arntzen (*Iowa State Coll. J. Sci.*, 1943, **18**, 6—9).—A survey. The following were prepared (Grignard): *$SnPh_3$* o-, m.p. 176—177° (decomp.), and p-*hydroxy*-, m.p. 201—203°, *$SnPh_2$* o-*hydroxy*-, m.p. 136—138°, *$SnPh_3$* o-, m.p. 158—159°, and p-*hydroxymethyl*- (**I**), m.p. 98—100°; *$SnPh_3$* o-*methoxymethyl*-, m.p. 94·5—95·5°; *$SnPh_3$* o-, m.p. 110—112°, and p-*dimethylamino-phenyl* (**II**), m.p. 132—134°. (**I**) is oxidised ($KMnO_4$) to *$SnPh_3$* p-*carboxyphenyl*, m.p. 166—168°. Coupling of (**II**) yields *$SnPh_3$* 4-*dimethylamino*-3-(4′-*nitrobenzeneazo*)*phenyl*, m.p. 190—192°. F. R. G.

Organothallium compounds. R. K. Abbott, jun. (*Iowa State Coll. J. Sci.*, 1943, **18**, 3—5).—Sol., non-toxic compounds were prepared from $TlAryl_2$ and AgX (X = solubilising acid group); *$TlPh_2$ sulphanilate*, m.p. 345° (decomp.), *Tl Me_2*, m.p. 231—233°, *Et_2* m.p. 220—221°, and *Ph_2 saccharate*, m.p. 315—320° (slight decomp.), *Tl di*-2-*pyridyl lactate*, m.p. 205—208° (decomp.). With fuming H_2SO_4 at −20° *Tl(o-$C_6H_4Me)_2Br$* yields *Tl di*-2-(4-*sulphotolyl*) *sulphate* (*Na* salt). Nitration of *$TlPh_2$·NO_3* gives *Tl di*-m-*nitrophenyl nitrate*, decomp. >300°, also obtained from *m*-$C_6H_4(NO_2)_2$ H_3BO_3, and $TlCl_3$. $TlEt_2Cl$ with NaOEt yields *$TlEt_2$ ethoxide*, b.p. 101—102°/0·1 mm., m.p. 43—45°. The following were also prepared from TlX_3 and the appropriate compounds; *Tl(C_6H_4·OH-o)$_2$ bromide*, m.p. >340°, *Tl di*-2-*pyridyl chloride*, m.p. 288—291°, *$TlCl_3$,3C_5H_5N*, m.p. 148—150°, *$TlBr_3$,3C_5H_5N*, m.p. 113—115°, *$TlCl_3$,3 2-C_5H_4BrN*, m.p. 145—146°, *$TlCl_3$,3 2-$C_5H_4(NH_2)N$,3HCl*, m.p. 121—125° (decomp.), *$TlCl_3$,cysteine,HCl*, m.p. ~350° (decomp.), *Tl [$C_6H_3(NMe)_2$-p]$_2$ bromide*, m.p. >350°, *Tl di*-p-, m.p. >330°, and *di*-o-*anisyl bromide*, m.p. >330°. *p*-Li·C_6H_4·NMe_2 with $BBu^a(OH)_2$ gives p-*dimethylaminophenylboric acid*, m.p. 243—245° (decomp.), which with $TlCl_3$ yields a purple dye. The following *Tl* salts were prepared: 2 : 4 : 6-*trinitrobenzoate*, m.p. 160—163° (decomp.); *oxalate*, m.p. 315—320° (decomp.); *naphthalene*-2-, m.p. 234—236°, *benzene*-, m.p. 185—187°, *lauryl*-, m.p. 143—145°, and p-*toluenesulphinate*, m.p. 154—156°; *phenyl*-, m.p. 200—201° (*Tl_2* salt, m.p. 317—320°), and *diphenyl-phosphonate*, m.p. 203—205°; salt of $MeNO_2$, decomp. from 160°; *salt* of $EtNO_2$, m.p. 80—82° (decomp.); *Me*, m.p. 136—140° (decomp.) *Et*, decomp. 100°, and *Bu^a sulphide*, m.p. 84—90° (decomp.); *thiophenoxide*, m.p. 258—260°, p-*thiotolyl-oxide*, m.p. 178—180°, *thio-β-naphthoxide*, m.p. 165—168°, and *terephthalate*, m.p. >340°. F. R. G.

IX.—PROTEINS.

Denaturation of tobacco mosaic virus by carbamide. I. Biochemistry. M. A. Lauffer and W. M. Stanley (*Arch. Biochem.*, 1943, **2**, 413—424; cf. A., 1939, III, 729).—Tobacco mosaic virus is transformed by 6M-$CO(NH_2)_2$ from a substance sol. in dil. aq. electrolytes into one insol. in such solvents. The denatured protein is readily sol. in 6M-, considerably less sol. in 4·5M-, and very slightly sol. in 3M-$CO(NH_2)_2$. It dissolves easily in very dil. aq. Na dodecyl sulphate and in 0·1M-NaOH, but not at all readily in 0·01M-NaOH. These changes are shown by means of osmotic pressure, high-speed quantity centrifugation, ultra-centrifugation, stream double refraction, and turbidimetric examination to be accompanied by disintegration of the high-mol. virus nucleoprotein particles into much smaller particles $\sim 10^4$ or 10^5. The nucleic acid is removed from the protein in this disintegration, and the no. of SH groups increases during denaturation. $CO(NH_2)_2$ also causes a loss of virus infectivity. Residual infectivity is always associated with remaining high-mol. nucleoprotein in cases of partial denaturation, and the sp. infectivity of this residual material is considerably < that of untreated virus. This shows that virus inactivation can occur before the virus nucleoprotein mol. is extensively disintegrated, and denaturation by $CO(NH_2)_2$ appears to involve at least two consecutive reactions. The overall denaturation process is irreversible.
J. N. A.

Effect of denaturation on sulphur content of ovalbumin and edestin. B. M. Hendrix and J. Dennis (*Arch. Biochem.*, 1943, **2**, 371—380).—Denaturation of ovalbumin with acid and alkali causes a decrease in the S content of the protein. Material rich in S is removed from the protein by these treatments, and denaturation appears to be accompanied by addition of H_2O to the protein. Alkali-denaturation of edestin resembles acid- and alkali-denaturation of albumin, whilst acid-denaturation of edestin differs from other acid- and alkali-denaturations in that no S is removed from the protein.
J. N. A.

Effect of dry grinding on properties of proteins. I. Native, denatured, and coagulated ovalbumin. H. R. Cohen (*Arch. Biochem.*, 1943, **2**, 1—8).—Dry grinding (ball mill at 100 r.p.m.) of cryst. and acid-denatured ovalbumin (I) produces insol. protein. Heat-denatured (I) gives some H_2O-sol. protein; the insol. fraction contains more S and less tyrosine and tryptophan than does cryst. (I). The rates of digestion by pepsin of the ground proteins are intermediate between those of cryst. and coagulated (I).
E. R. S.

Effect of dry grinding on properties of proteins. II. Casein. III. Gelatin. IV. Human, ox, and pig coagulated hæmoglobins. H. R. Cohen (*Arch. Biochem.*, 1943, **2**, 345—351, 353—355, 357—361).—II. When casein (I) is dry ground for 48 hr. a H_2O-sol. fraction is obtained, which contains more P and less tryptophan (II) than the unground (I); it is also attacked by rennin. The other H_2O-sol. fractions by successive 48-hr. periods of grinding all contain more P and less (II) than native (I), and they are all unaffected by rennin. There is very little difference in N content of any of the fractions. They all contain dialysable proteins, and are pptd. from aq. solution by picric, trichloroacetic, and phosphotungstic acids, $HgCl_2$, and 50% saturation with $(NH_4)_2SO_4$. They are not precipitinogenic but produce anaphylactic sensitisation in guinea-pigs. The insol. residue left after prolonged grinding is only slowly attacked by trypsin. The H_2O-sol. fractions are all digested much more readily, whilst that from the first grinding is hydrolysed at a greater rate during the first 45 hr. than is native (I). The total H_2O-sol. product is partly nutritionally deficient since it does not support growth of mice although they are maintained in good health and at relatively const. wt., whilst the insol. residue is just as effective as is unground (I). The mechanism of degradation of the protein mol. by grinding is discussed.

III. Dry grinding of gelatin converts it into a protein sol. in cold H_2O. Grinding for 7 hr. has no effect on the ability to gel, but there is a marked increase in solubility in H_2O at room temp., and the time for gelling is considerably increased. After grinding for 72 hr. the product no longer forms a gel. There is no increase in formol titration val. during grinding, which shows that there is no appreciable cleavage of peptide bonds.

IV. Dry grinding of coagulated human, ox, and pig hæmoglobins (III) produces H_2O-sol. fractions which contain varying amounts of Fe. They all give the benzidine reaction, and the fact that the hæmatin is sol. in H_2O shows that the prosthetic group is not removed from the protein constituent during grinding. The H_2O-sol. proteins contain dialysable protein; they are non-coagulable by heat and require 50% or more EtOH for pptn. They are pptd. by $HgCl_2$, picric acid, and $CCl_3{\cdot}CO_2H$, and by 50% saturation with $(NH_4)_2SO_4$. They are sol. in acids and alkalis, and do not give rise to precipitin antibodies and do not react with native (III) antisera. The N content decreases with successive fractions, and in the case of human (III) the amount of tyrosine decreases in each successive fraction, whilst with ox (III) the amount of tyrosine in each fraction is fairly const. Tryptophan is absent from the last fractions from human (III) and from one of the H_2O-sol. fractions from ox-(III). 79% of coagulated human (III) is converted into H_2O-sol. protein in 384 hr. For coagulated ox- and pig-(III) the corresponding vals. are 75% in 192 hr. and 32·5% in 96 hr. respectively. The H_2O-sol. fractions from human (III) contain at least 70% of dialysable N which shows that they are small mol. fragments. The H_2O-sol. fractions from the various (III) differ from native (III) mainly in the ultra-violet spectrum between 313 and 264 mμ. In this region there is considerably more absorption than with native (III).
J. N. A.

Methionine- and tryptophan-free casein hydrolysates. A. A. Albanese (*Science*, 1943, **98**, 46).—1 kg. of casein in refluxed for 20—23 hr. with 500 ml. of H_2SO_4 and 1 l. of H_2O, cooled to 80°, 200 ml. of 30% H_2O_2 added, and the mixture kept at room temp. for 24 hr. 2 l. of H_2O and 4 l. of 16% CaO suspension are added, and the mixture is kept overnight and filtered through a norite-precoated filter. The $CaSO_4$ is re-suspended in 2 l. of hot H_2O, filtered, and the filtrate and washings conc. in vac. at 50—60° to 2 l., neutralised with 50% H_2SO_4, and refiltered. 650 g. of tryptophan-free (not detected) and methionine-free (0·12—0·21% of the protein) hydrolysate are obtained.
E. R. R.

Etherification of hydroxyamino-acid residues in silk fibroin by dimethyl sulphate. A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1943, **37**, 538—543).—Fibroin with Me_2SO_4 and N-NaOH is *O*-methylated; the max. degree of methylation obtainable corresponds to conversion of nearly all the tyrosine residues and about half the serine residues, suggesting the presence in fibroin of two types of serine residues, differing in accessibility to methylation.
F. O. H.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin esters of mono- and di-basic aliphatic acids. H. F. Lewis, F. E. Brauns, M. A. Buchanan, and E. B. Brookbank (*Ind. Eng. Chem.*, 1943, **35**, 1113—1117).—The prep. of lignin from soda black liquor from hardwood cooks by pptn. with CO_2 is described. Lignin esters are prepared by adding the acid chloride to a solution of lignin in C_5H_5N, and isolated by pouring into ice-H_2O. The esters of 17 monobasic aliphatic acids, ranging from acetic to stearic, and of succinic, adipic, suberic, azelaic, benzoic, *p*-toluenesulphonic, and phthalic acids were prepared and their m.p. and solubility data tabulated. In esters of monobasic acids, 3, 4, or 5 acyl groups are combined with each structural unit of lignin. The m.p., which are not sharp, decrease with increasing chain length of the acid group. These esters are sol. in $COMe_2$, dioxan, C_6H_6, and EtOAc; the solubility in MeOH and EtOH decreases and in Et_2O and light petroleum increases with increasing mol. wt. of the acid radical. Esters of dibasic acids have higher m.p. and are less sol.; this is attributed to attachment of the acid mol. to two neighbouring lignin chains forming a network structure. The stearic ester has possible industrial applications as a mould lubricant for wood plastics and for incorporation in inks and paints.
R. H. F.

Purification and properties of humulon. V. Salac and J. Dyr (*Gambrinus*, 1943, **4**, 253—255).—A solution in MeOH of the residue obtained by extracting lupulin with Et_2O and evaporating the solution was freed from myricin wax, and the humulon (I) pptd. by aq. $Pb(OAc)_2$. The Pb salt of the α-bitter acid (II) was extracted with 25% H_2SO_4 + 4 vols. of Et_2O, and (I) purified by the *o*-$C_6H_4(NH_2)_2$ method, followed by pptn. of a solution in MeOH with H_2O. The crystals had m.p. 63—64°, $[\alpha]_D^{20}$ −206·24° in MeOH, −212·53° in EtOH, −190·44° in Et_2O. With solutions in C_6H_{14} $[\alpha]_D^{20}$ was ∝ the concn. Dil. aq. $FeCl_3$ gave a violet-brown and dil. aq. $CuSO_4$ an emerald-green colour with a solution of (II) in EtOH. Polarimetric determinations of (I) from different hops gave lower vals. than pptn. with $Pb(OAc)_2$.
J. G.

Relationship of lupulin to the bitter constituents of hops. V. Salac and J. Dyr (*Gambrinus*, 1943, **4**, 255—258).—Crude β-bitter acid (I), obtained as fine needles by the evaporation at 30° in CO_2 of an extract of lupulon (II) in C_5H_{12}, was dissolved in MeOH; 2 days later, two layers [a syrupy liquid containing β-soft resin (III), and a milky upper layer containing fine needles of (I)] had separated. After recrystallisation (I) had m.p. 78—81°, but (II) remained amorphous; both had [α] 0. Aq. $FeCl_3$ produced a brown and aq. $CuSO_4$ a blue-green colour with the MeOH solution. The crystals of (II) and their solutions in MeOH had no bitter taste, but (III) was very bitter. A dil. solution of lupulin in MeOH–H_2O boiled free from MeOH became very bitter owing to the rapid conversion of (II) into (III). Since [α] of hop oil is ~0, humulon can be determined polarimetrically (see above).
J. G.

Esters of penicillin.—See A., 1944, III, 141.

Purification and properties of penatin.—See A., 1944, III, 141.

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FEBRUARY, 1944.

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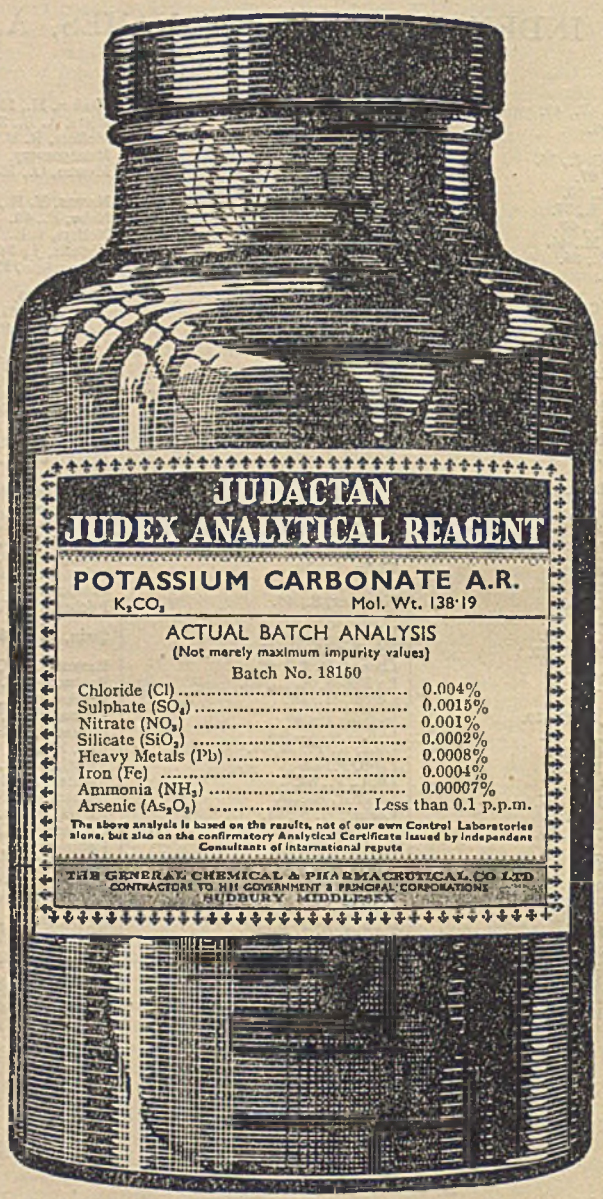

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