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DECEMBER, 1944

A II—ORGANIC CHEMISTRY

CONTENTS

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Catalytic aromatisation of branched-chain aliphatic hydrocarbons. V. I. Komarewsky and W. C. Shand (*J. Amer. Chem. Soc.*, 1944, **66**, 1118—1119).—Aliphatic hydrocarbons containing a quaternary C, which does not permit direct aromatisation, are dehydrocyclised in presence of Cr_2O_3–Al_2O_3 catalysts to aromatic hydrocarbons, indicating that isomerisation occurs during dehydrocyclisation. Dehydrocyclisation of aliphatic hydrocarbons having a structure which allows cyclisation in > one way takes place by a mechanism permitting their direct formation. W. R. A.

Properties of synthetic lubricants. I. Synthesis and properties of λ-*n*-decyldocosane. S. Klos, E. Neuman-Piljat, and S. Piljat (*J. Appl. Chem. Russ.*, 1940, **13**, 1369—1374).—λ-n-*Decyldocosane*, b.p. 233—235°/1 mm., is obtained by reduction (H_2–Ni at 240—245°) of the alcohol derived from Et laurate and *n*-$C_{10}H_{21}$·MgBr. J. J. B.

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Thermal polymerisation and cyclic dimerisation of *iso*butylene. J. B. McKinley (*Univ. Pittsburgh Bull.*, 1944, **40**, 185—194).—Polymerisation of *iso*butene at 365—430°/1280—5350 lb. per sq. in. gives a liquid (yield up to 81%) from which a cyclic dimer, 1 : 1 : 3-*trimethylcyclopentane* (I), b.p. 105·0° (yield up to 23%), is obtained on fractionation. 1-Hydroxy-1 : 3-dimethyl*cyclo*pentane (from 2-methyl*cyclo*pentanone) with dry HCl at 2° gives 1-*chloro*-1 : 3-*dimethyl*cyclo*pentane*, b.p. 33·2°/15 mm., which with $ZnMe_2$ or MgMeI yields (I) for comparison. The effect of variables on the polymerisation and its mechanism are discussed. D. G.

α-Bromo-Δ^β^-heptene. R. Delaby and J. Hubert (*Bull. Soc. chim.*, 1943, [v], **10**, 573—575; cf. A., 1937, I, 282).—On fractionating the product obtained from vinylbutylcarbinol, PBr_3, and C_5H_5N, pure $CHBu^{\alpha}$:$CH·CH_2Br$ (I) (*trans*), b.p. 73—74°/19 mm., is isolable, and fractions of b.p. ~60—63°/19 mm. contain some $CHBu^{\alpha}Br·CH$:CH_2; Raman spectra of the fractions are examined. (I) and Na–Et_2O yield Δ^{α}-tetradecadiene, b.p. 111—114°/15 mm. (liquid bromide) (cf. Prévost *et al.*, A., 1932, 40). A. T. P.

Co-polymerisation of acetylene and butylene in silent electric discharge. A. D. Petrov and D. N. Andreev (*J. Appl. Chem. Russ.*, 1940, **13**, 1341—1347).—Δ^α^-Octene and branched $C_{12}H_{26}$ to $C_{16}H_{34}$ are found in the polymerisate of Δ^α^-butene (I). Co-polymerisation of C_2H_2 and (I) gives 30% of hydrocarbons boiling at <130° and containing acetylenic hydrocarbons, and 70% of higher-boiling hydrocarbons which at 200° are transformed into a porous rubber-like mass. J. J. B.

Aliphatic nitro-compounds. XV. Nitrations with nitryl chloride. W. Steinkopf and M. Kühnel (*Ber.*, 1942, **75**, [*B*], 1323—1330).—The action of NO_2Cl on a variety of unsaturated compounds is described. C_2H_4 and NO_2Cl give only $C_2H_4Cl_2$ and NO_2. Slow addition of NO_2Cl to well-cooled CH_2:CHBr yields *α-chloro-α-bromo-β-nitroethane*, b.p. 76—77°/15 mm. (:$CHCl)_2$ at 100° yields *ααββ-trichloro-β-nitroethane*, b.p. 63°/13 mm. (yield 65%); similarly CCl_2:CHCl and C_2Cl_4 afford *αααβ-tetrachloro-*, b.p. 76°/18 mm., and *αααββ-pentachloro-*, m.p. 192° (sealed capillary), *-β-nitroethane*. Styrene affords *α-chloro-β-nitro-β-phenylethane*, b.p. 78°/13 mm., in small yield in C_6H_6 whereas in Et_2O it gives styrene *ψ*-nitrosite, m.p. 133° (lit 129°). Similarly $(CHPh:)_2$ in C_6H_6 yields *α-chloro-β-nitro-αβ-diphenylethane*, m.p. 220° (decomp.), in C_6H_6 but in Et_2O gives $(CHPhCl)_2$, m.p. 189—193°. *α-Chloro-β-nitro-β-phenylpropionic acid*, m.p. 162—163°, is formed from CHPh:CH·CO_2H and NO_2Cl in CCl_4 at 100°. CPh:CH is transformed by NO_2Cl in dry Et_2O into unstable, non-cryst. *α-chloro-β-nitro-β-phenylethylene*, which cannot be distilled unchanged under 12 mm.; in the absence of solvent the reactants explode very violently. Alternate passage of keten and NO_2Cl into well-cooled Et_2O leads to $CH_2Cl·COCl$ and small amounts of *nitroacetyl chloride*, b.p. 68°/12 mm., m.p. ~—35° (prolonged distillation easily leads to explosions); on exposure to air it is transformed into $MeNO_2$, HCl, and CO_2 and is transformed by NH_3 in Et_2O into $NO_2·CH_2·CO·NH_2$, m.p. 102—103°. C_6H_6 at 120° is converted into 1-*chloro*-2-*nitro*cyclo*hexadiene*, b.p. 21°/12 mm., m.p. ~—30°, which passes into $PhNO_2$ when exposed to air. In Et_2O *cyclo*hexene adds NO_2Cl vigorously, giving 1-*chloro*-2-*nitro*cyclo*hexane*, b.p. 122°/9 mm. $CH_2Cl·NO_2$, b.p. 122—123°, is obtained from CH_2N_2 and NO_2Cl in Et_2O at 0°. *Et chloronitroacetate*, b.p. 88°/0·04 mm., is obtained in small yield with $CH_2Cl·NO_2$ from $CHN_2·CO_2Et$ in well-cooled Et_2O. $NO_2·CH_2·CO_2K$ is smoothly transformed by Cl_2 in H_2O into *dichloronitromethane*, b.p. 106—107°. Gradual addition of saturated K_2CO_3 to a mixture of CH_2O and $CH_2Cl·NO_2$ in H_2O affords $NO_2·CHCl·CH_2·OH$, converted by PCl_5 into *αβ-dichloro-α-nitroethane*, b.p. 124°/10 mm., and by $SOCl_2$ into *di-β-chloro-β-nitroethyl sulphite*, b.p. 147°/10 mm. $CCl_3·CO_2H$ and $CH_2Cl·CN$ at 135° yield *trichloroacetylchloroacetamide*, m.p. 96°. PhOH and NO_2Cl in cold Et_2O give only *o*-$NO_2·C_6H_4·OH$ whereas at room temp. the product is 2 : 4 : 6 : 1-$NO_2·C_6H_2Cl_2·OH$. PhOMe and NO_2Cl afford a very unstable *adduct*, b.p. 32°/12 mm., which loses Cl and N, leaving PhOMe. Solid $C_{10}H_8$ reacts very vigorously with NO_2Cl, giving a mixture of 1-$C_{10}H_7Cl$ and 1-$C_{10}H_7·NO_2$. H. W.

Electrochemical oxidation of *n*-butyl alcohol.—See A., 1944, I, 289.

Preparation of silicon tetrachloride and its use as a basis for obtaining silicic acid esters.—See A., 1944, I, 291.

Action of chromia catalyst on aliphatic *iso*-alcohols and -aldehydes. V. I. Komarewsky and L. G. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 1116—1117).—At atm. pressure in presence of Cr_2O_3 *iso*-$C_5H_{11}·OH$ forms $COBu^{\beta}_2$ by a condensation–dehydrogenation (*c–d*) process. *iso*Alcohols, having an α-substituted C, give no (*c–d*) reactions but are dehydrogenated to the corresponding aldehydes which remain unaffected at even relatively high pressures. $Bu^{\beta}CHO$ at higher pressure is converted into βζ-dimethyl-Δ^γ^-heptene and at atm. pressure into $COBu^{\beta}_2$ in presence of Cr_2O_3. These results support the aldol mechanism. W. R. A.

Substituted acetylenes. XLVII. Acetylenic alcohols from αβ-unsaturated aldehydes and ketones. G. F. Hennion and D. J. Lieb (*J. Amer. Chem. Soc.*, 1944, **66**, 1289—1290; cf. A., 1944, II, 29).—1 : 2-Addition of CH:CNa to compounds containing C:C·CO (cf. Jones *et al.*, A., 1943, II, 53) occurs in Et_2O–liquid NH_3 at —60°, yielding CHMe:CH·CH(OH)·C:CH (I) (46%), b.p. 66°/20 mm., *γ-methyl-*Δ^δ^*-penten-*Δ^α^*-inen-γ-ol* (21%), b.p. 58—59°/60 mm., *γ-methyl-* (27%), b.p. 61—62°/25 mm., and *γε-dimethyl-*Δ^δ^*-n-hexen-*Δ^α^*-inen-γ-ol* (24%), b.p. 65—66°/17 mm., and *ε-phenyl-γ-methyl-*Δ^δ^*-penten-*Δ^α^*-inen-γ-ol* (20%), m.p. 50—51°, b.p. 114—116°/4 mm. With HgO and a little BF_3 in MeOH, (I) gives 2 : 5-*dimethoxy*-2 : 5-*dimethyl*-3 : 6-*dipropenyl*-1 : 4-*dioxan* (22%), m.p. 119—120°. *n* and *d* for the products are recorded. R. S. C.

[Ethylene] glycol complexes of the light transition metals. R. Gomer and G. N. Tyson, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 1331—1333).—The under-mentioned *compounds* of metal salts with $(CH_2·OH)_2$ (I) are prepared. Magnetic data, which are recorded, show that all are ionic. Colours of Co^{II} compounds are independent of the geometric form. The no. of unpaired electrons is indicated by *UE* below. $CuSO_4$,(I) and $CuSO_4$,2(I), light blue (*UE* 1); $FeSO_4$,(I), +$2H_2O$, light yellow (*UE* 4); *X*,2(I), +H_2O, where *X* = $NiSO_4$, light green (*UE* 2), $CoCl_2$, dark blue (*UE* 3), or $MnCl_2$, pale rose (*UE* 5); $FeSO_4$,3(I), light yellow (*UE* 4); $CoCl_2$,3(I), dark blue; *X*,3(I), +H_2O, where *X* = $NiSO_4$, light green (*UE* 2), $CoCl_2$, pink (*UE* 3), or $FeSO_4$, yellowish-green; $NiSO_4$,4(I), light green (*UE* 2). R. S. C.

Halogen derivatives of cineole.—See A., 1944, II, 374.

Dihydroxypropyl bismuthate, m.p. 240—245° (decomp.).—See A., 1944, III, 684.

αγ: βδ-Dimethylene- and βδ-methylene-*D-epi*rhamnitol. A. T. Ness, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **66**, 1235—1237).—αγ : βδ-Dimethylene-*D*-sorbitol with *p*-$C_6H_4Me·SO_2H$ in C_5H_5N at 0° and later 23° gives the ζ-p-*toluenesulphonate* (82%), m.p. 160—161°, $[\alpha]_D^{20}$ —10·0° in $CHCl_3$, converted by NaI in, best (90%), $COMe_2$ at 100° into the *ζ-iodide*, m.p. 177—179°, $[\alpha]_D^{20}$ —21·7° in $CHCl_3$, whence H_2–Raney Ni in aq. NaOH at slightly >1 atm. gives αγ : βδ-*dimethylene*-D-epi*rhamnitol* (I) (89%), m.p. 182—183°, $[\alpha]_D^{20}$ —40·9° in H_2O. *D-epi*Rhamnitol (prep. from methyl-β-*D-epi*rhamnoside), conc. HCl, and 37% CH_2O at room temp. (4 days) over NaOH–H_2SO_4 give (I), $[\alpha]_D^{20}$ —40·6° in H_2O. Ac_2O–

AcOH–H_2SO_4 at 0° converts (I) into *γ-acetoxymethyl-βδ-methylene*-D-epi*rhamnitol aε-diacetate* (87%), m.p. 116—117°, $[\alpha]_D^{20}$ +5·3° in $CHCl_3$, converted by NaOMe–$CHCl_3$–MeOH into *βδ-methylene*-D-epi-*rhamnitol* (100%), m.p. 176—177°, $[\alpha]_D^{20}$ −20·2° in H_2O, which is stable to aq. HIO_4 at 25° and in Ac_2O–C_5H_5N at 25° (3 days) yields the *aγε-triacetate*, m.p. 149—150°, $[\alpha]_D^{20}$ −0·6° in $CHCl_3$, −1·8° in $COMe_2$. Structures are proved by the reactions described. M.p. are corr. R. S. C.

Carbohydrate *C*-nitro-alcohols. α-Nitro-α-deoxy-*D*-mannitol. J. C. Sowden and H. O. L. Fischer (*J. Amer. Chem. Soc.*, 1944, **66**, 1312—1314).—4 : 6-Benzylideneglucose with NH_2OH–EtOH at 70° gives the *oxime* (83%), m.p. 195° (decomp.), $[\alpha]_D^{27}$ −72° in C_5H_5N, converted by Ac_2O–NaOAc at 120—125° into 4 : 6-*benzylidenegluconitrile* 2 : 3 : 5-*triacetate*, m.p. 135·5—136°, $[\alpha]_D^{25}$ +44° in $CHCl_3$, which with $MeNO_2$ and NaOMe in MeOH at ~5° (42 hr.) yields *α-nitro-δζ-benzylidene-α-deoxy*-D-*mannitol* (I) (31%), m.p. 146—147°, $[\alpha]_D^{21}$ −70·4° in H_2O (cf. Pictet *et al.*, A., 1922, i, 4), the corresponding sorbitol derivative being sol. In 0·1N-H_2SO_4 at 70° (I) gives *α-nitro-α-deoxy*-D-*mannitol* (78%), m.p. 134·5—135°, $[\alpha]_D^{19}$ −7·0° in H_2O, which gives a red colour in the Griess–Ilosvay test and reduces hot Fehling's solution. H_2–Raney Ni reduces (I) at room temp. to α-amino-δζ-benzylidene-α-deoxymannitol [*oxalate*, m.p. 208° (decomp.), $[\alpha]_D^{20}$ −37° in H_2O], whence dil. H_2SO_4 at 70° yields α-amino-α-deoxymannitol [oxalate, m.p. 183—184° (decomp.), $[\alpha]_D^{21}$ +5·0° in H_2O]. ~8% H_2SO_4 at 35—40° converts (I) into mannose, which is isolated as phenyl- or phenyl-α-methyl-hydrazone. R. S. C.

Peroxidation of ethyl ether. R. Viallard (*Bull. Soc. chim.*, 1943, [v], **10**, 512—516).—Analysis of the products formed from Et_2O and O_3 indicates the formation of dihydroperoxydiethyl oxide ozonide (I) and $O_3{:}O(CHMe{\cdot}O_2H)_2$; (I) would yield MeCHO thus: $O_3{:}O(CHMe{\cdot}O_2H)_2 \rightarrow OH{\cdot}O(:O_3){\cdot}CHMe{\cdot}O_2H + MeCHO$. A. T. P.

[Oxidation of di*iso*propyl ether.] G. Wittig (*Ber.*, 1942, **75**, [*B*], 1301).—In reply to the statement that "monomeric ketone peroxides" have not yet been discovered (Rieche *et al.*, A., 1943, II, 79) it is pointed out that monomeric fluorenone peroxide has been described by Wittig *et al.* (A., 1942, II, 49). H. W.

Acetyl phosphate : chemistry, determination, and synthesis. F. Lipmann and L. C. Tuttle (*J. Biol. Chem.*, 1944, **153**, 571—582).—The synthesis of AcH_2PO_4 (I) (cf. Lynen, A., 1943, II, 250) is simplified. $Ag_3PO_4 + 2H_3PO_4$ and AcCl–Et_2O give a product which is treated with aq. Na_2CO_3 (to pH 3—3·5); AcOH is removed by Et_2O, aq. NaOH added (to pH 7), and Na_3PO_4 frozen out and filtered off from (I) at +−5°. The Ag_2 salt is prepared (cf. *loc. cit.*), and similarly the Ag_2 salts $COEt{\cdot}O{\cdot}PO(OAg)_2$ and $COPr{\cdot}O{\cdot}PO(OAg)_2$. From $(CH_2{\cdot}COCl)_2$ and Ag_3PO_4–H_3PO_4 [removing $(CH_2{\cdot}CO_2H)_2$ by EtOAc], a mixture of succinyl phosphate (40%) and diphosphate (60%) is similarly obtained. The rate of decomp. of (I) is studied under various conditions. Max. stability is at pH 5—6. The hydrolysis of (I) by 0·5N-HCl is very greatly accelerated by $(NH_4)_6Mo_7O_{24}$; rates are identical for (I) prepared as above or from $AcCO_2H$ and *B. delbrückii* (cf. A., 1940, II, 266). Methods of determining (I), depending on MoO_4'' colorimetry and on the solubility of $AcCaPO_4$ are described (cf. C., 1945, Part 1). E. W. W.

Inhibition of catalysed oxidations by hæmins.—See A., 1944, III, 838.

Preparation of glucose 1-phosphate. J. B. Sumner and G. F. Somers (*Arch. Biochem.*, 1944, **4**, 11—13).—A modification of the procedure of Green and Stumpf (A., 1942, III, 419), in which a preliminary digestion of dextrins with pancreatic amylase is introduced, is given. E. R. S.

Action of ozone on thioethers. H. Böhme and Harriet Fischer (*Ber.*, 1942, **75**, [*B*], 1310—1311).—The sulphide, dissolved in abs. $CHCl_3$, is saturated with O_2–O_3 at 0° and the solvent is removed in vac. at room temp. or 0°. Thus are obtained: Me_2SO_2, Et_2SO_2, $(Cl{\cdot}[CH_2]_3)_2SO_2$, $PhMeSO_2$, $CH_2Ph{\cdot}SO_2Et$, and $(CH_2Ph)_2SO_2$. The isolation of $(CH_2Ph)_2SO$ by use of an insufficiency of O_3 indicates the intermediate production of sulphoxides. *CH_2Cl Et sulphoxide* has b.p. 70°/0·2 mm. H. W.

New synthesis of β-keto-esters of the type, $COR{\cdot}CH_2{\cdot}CO_2Et$. D. S. Breslow, E. Baumgarten, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 1286—1288).—Treating $CO_2Et{\cdot}CH_2{\cdot}CO_2Bu^\gamma$ (I) with Mg turnings and a little CCl_4 in boiling EtOH or with $Mg(OEt)_2$–Et_2O and then RCOCl gives $COR{\cdot}CH(CO_2Et){\cdot}CO_2Bu^\gamma$, which with a little *p*-$C_6H_4Me{\cdot}SO_3H$ in boiling C_6H_6 gives $CMe_2{:}CH_2$ and $COR{\cdot}CH_2{\cdot}CO_2Et$ (cf. A., 1944, II, 320). Decomp. of $CHBz(CO_2Et)_2$ in steam gives only a poor yield of $CH_2Bz{\cdot}CO_2Et$ (cf. Bernhard, A., 1895, i, 93) and the method is not well applicable to aliphatic compounds. Prep. of (I) in 48—55% yield from $CH_2(CO_2Et)_2$ is described. The synthesis is applied to yield $COEt{\cdot}CH_2{\cdot}CO_2Et$ (63%), Et β-keto-β-*cyclo*hexyl- (65%), b.p. 146—150°/18 mm., and -β-2-furyl-propionate (70%), b.p. 137—139°/9·5 mm., $CH_2Ph{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (47%), b.p. 154—156°/9 mm., and $CHMe{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (35%), b.p. 101—105°/15 mm. (*Cu* salt, m.p. 159°). $CHBu^\alpha(CO_2Et)_2$ yields $CO_2Et{\cdot}CHBu^\alpha{\cdot}COCl$, b.p. 90—107°/9·5 mm., and thence $CO_2Et{\cdot}CHBu^\alpha{\cdot}CO_2Bu^\gamma$, b.p. 126—128°/15 mm., which, as above, gives *Et α-benzoyl-n-hexoate*, b.p. 157—161°/5 mm. (derived *amide*, m.p. 153—154°). R. S. C.

Synthesis, some derivatives, and metabolism of αβ-diketo-octoic acid.—See A., 1944, II, 379.

Autoxidation of oxygen-active acids. VII. Action of molecular oxygen on methyl licanate. W. Treibs (*Ber.*, 1942, **75**, [*B*], 1373—1376).—The conjugated triene system of Me licanate [γ-keto-$\Delta^{9\kappa\mu}$-octatrienoate] (I) is responsible for the reaction between the ester and mol. O_2 whereas the CO group takes no direct part but merely acts as an accelerating catalyst. The course of the reaction is identical with that of elæostearic esters. (I) boils unchanged at 240—242°/20 mm. but after long heating at 280° shows signs of incipient cyclisation and simultaneous dimerisation. It can be kept unchanged for months at 20° in sealed vessels under N_2. The viscosity of (I) increases very greatly after absorption of a little O_2, showing immediate mol. enlargement. The absorption of O_2 by (I) and Me elæostearate (II) when spread on glass plates is found gravimetrically to be closely similar and different from that of esters with isolated double linkings. The autoxidative similarity of (I) and (II) is shown particularly by the alteration of *n* and *d* in the products. Similar results are obtained by periodic examination of the autoxidation products with MeMeI. Licanic acid and boiling Ac_2O give a polyfunctional material as a dry, very hard film in place of the expected acetate. H. W.

Production of succinic acid.—See B., 1944, II, 303.

Synthesis of α-bromo-aldehydes. P. Z. Bedoukian (*J. Amer. Chem. Soc.*, 1944, **66**, 1325—1327).—Converting aldehydes by boiling Ac_2O–KOAc into the enol acetates (35—80%) and adding to these in CCl_4 Br (1 mol.) and then an excess of MeOH gives $CHRBr{\cdot}CH(OMe)_2$ (75—80%), which are stable when pure but are very sensitive to acidic impurities and in hot acid (HCl or 50% citric acid) give 25—95% of $CHRBr{\cdot}CHO$. Thus are obtained the enol *acetates* of $Pr^\beta CHO$, b.p. 124—126°, *n*-$C_6H_{13}{\cdot}CHO$, b.p. 88—90°/17 mm., and PhCHO, b.p. 113—115°/10 mm., $CMe_2Br{\cdot}CHO$, b.p. 113—115° (2 : 4-*dinitrophenyldrazone*, m.p. 116°; Me_2 acetal, b.p. 52—54°/10 mm.), *n*-$C_5H_{11}{\cdot}CHBr{\cdot}CHO$, b.p. 90°/17 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 106°; *Me_2 acetal*, b.p. 117—119°/17 mm.), and *α-bromophenylacetaldehyde*, b.p. 108—109°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 139°; *Me_2 acetal*, b.p. 133—135°/10 mm.). R. S. C.

Action of ammonia on crotonaldehyde.—See A., 1944, II, 380.

Preparation of unsaturated ketones.—See B., 1944, II, 303.

Triacetone dialcohol and its dehydration products. E. E. Connolly (*J.C.S.*, 1944, 338—339).—The vac.-still residues from large-scale production of diacetone alcohol (I) contain s-*triacetone dialcohol* (*βζ-dimethylheptane-βζ-diol-δ-one*) (II) (cf. Leopold *et al.*, G.P. 481,290), m.p. 56·4°, b.p. 128°/15 mm. When distilled with syrupy H_3PO_4, (II) gives "semiphorone" (*βζ*-dimethyl-Δ^ϵ-hepten-β-ol-δ-one) (III) (cf. Grignard *et al.*, A., 1929, 396). When heated with a little conc. H_2SO_4, (II) gives phorone (IV) [H_2O which is also formed is carried away by $CHAc{:}CMe_2$ (V) derived from $CH_3Ac{\cdot}CMe_2{\cdot}OH$ in crude (II), or by excess of C_6H_6, which is added when cryst. (II) is used]. Cryst. (II) when heated under reflux with dil. H_2SO_4 gives (IV), 2 : 2 : 6 : 6-*tetramethyltetrahydro*-1 : 4-*pyrone* (VI), m.p. 12·8°, b.p. 70°/15 mm. (oxime, m.p. 101°), and (III). (VI) is dehydrated to (IV). With 2 : 4 : 1-$C_6H_3(NO_2)_2{\cdot}NH{\cdot}NH_2$, (I) and (V) give the same product, m.p. 197—198°, whilst (II), (III), and (VI) give a second product, m.p. 171—173°, different from that, m.p. 118—188·5°, obtained from (IV). E. W. W.

Reductone and vitamin-*C*. J. G. A. Griffiths (*Nature*, 1943, **152**, 163).—$(CHO)_2$ may be obtained from O_3, H_2O, and C_2H_2, and reductone from $(CHO)_2$, by irradiation with ultra-violet light. E. R. R.

New reagent for primary and *sec.* amines.—See A., 1944, II, 372.

Complex compounds of cupric azide. III. Non-electrolytes with organic bases.—See A., 1944, I, 290.

Preparation, resolution, and optical properties of β-amino-*n*-octane. F. G. Mann and J. W. G. Porter (*J.C.S.*, 1944, 456—461).—CrO_3 oxidation of *n*-octan-β-ol gives ~95% yield of $COMe{\cdot}C_6H_{13}$-*n*, the oxime of which is reduced with Na and EtOH to pure β-amino-*n*-octane in 70% yield (*Bz* derivative, m.p. 73—74°; *hydrochloride*, m.p. 91—92°; *phenylhydrazone*, b.p. 119—120°/0·05 mm.). The *l*-amine is prepared by repeated recrystallisation of the *dl*-amine H *d*-tartrate from MeOH; similarly the H *l*-tartrate gives the *d*-amine. The rotations of the pure amine and its C_6H_6 solution are similar and ⩾ that of the EtOH solution, which is unaffected by the concn. The d- and l-*amine hydrochlorides*, m.p. 90—91°, are freely sol. in ionising and in non-ionising solvents, in which they are associated. They show a pronounced "acid effect," *e.g.*, the *l*-amine hydrochloride gives strongly dextrorotatory solutions in ionising solvents, *e.g.*, H_2O, MeOH, EtOH, $HCO{\cdot}NH_2$, the rotation in EtOH being almost independent of concn.; in non-ionising solvents, as the concn. is progressively increased, the lævorotation decreases to zero, *e.g.*, in PhMe or dioxan saturated at room temp., and becomes a dextrorotation at moderately high concns., *e.g.*, in CH_2Cl_2, $C_2H_4Cl_2$, $CHCl_3$, C_6H_6. The d-*camphorsulphonate*, m.p.

162—165°, $[M]_D^{19}$ +49·5°, and d-α-*bromocamphorsulphonate*, m.p. 180—185°, of the *dl*-amine are unsuitable for resolution. H. D. W.

Production of β-aminopropionic acid.—See B., 1944, II, 303.

Hydroxyleucines. H. D. Dakin (*J. Biol. Chem.*, 1944, **154**, 549—555).—*iso*Butene oxide (excess) and NHAc·CH(CO_2Et)$_2$ in dioxan with NaOMe, followed by hydrolysis (HCl), give *γ-hydroxyleucine* (I), m.p. 226—228°, purified through the *flavianate*, m.p. 272—273°. (I) is apparently not identical with the small amount of NH_2-acid, $C_6H_{13}NO_3$, m.p. 248—250°, obtained from casein. *Glycine flavianate* has m.p. 244—245° (efferv.). F. R. S.

ε-Diethylaminoamyl β-dithiocarbamate, m.p. 136—138°.—See C., 1944, 167.

Preparation of nitrourea.—See B., 1944, II, 304.

Manufacture of cyanohydrins.—See B., 1944, II, 304.

Ethylenic nitriles; Δ^α- and Δ^β-octenonitrile. R. Delaby and J. Hubert (*Bull. Soc. chim.*, 1943, [v], **10**, 576—580).—CHBu^a:CH·CH_2Br (I) or mixtures of (I) and CHBu^{a}Br·CH:CH_2, heated slowly with CuCN to 100—105°, then at 100° for 1 hr., give trans-Δ^β-*octenonitrile* (II), b.p. 93—95°/20 mm., and some Δ^α-*octenonitrile*. Raman spectra of the various fractions are examined. Hydrogenation (Raney Ni–EtOH) of (II) gives C_8H_{17}·NH_2. (II) is transformed into cis-, b.p. 78—80°/15 mm. and trans-Δ^α-*octenonitrile* (III), b.p. 88—90°/15 mm. by adding to PhOH–Na_2CO_3 (previously heated at 150°) at 150° for 2 hr. HCl is introduced into (II) or (III) (mixture of *cis-* and *trans-*) and SH·CH_2·CO_2H in Et_2O for 5 hr. (method: Condo *et al.*, A., 1937, II, 139) to yield 40—50% of the respective *adduct*, *e.g.*, RCN → CO_2H·CH_2·S·CR:NH,HCl. The reaction is much more rapid in the cases of CHMe:CH·CN and CH_2:CH·CH_2·CN. With such nitriles, fixation of Br is the slower the greater is the mol. wt. A. T. P.

II.—SUGARS AND GLUCOSIDES.

Existence and significance of sugar–triose equilibrium. C. Enders and S. Sigurdsson (*Naturwiss.*, 1943, **31**, 92—93).—Determinations of the AcCHO contents of distillates from 0·2 and 2·0% solutions of sugars are used as basis for calculating the consts. of the thermodynamic equilibria which exist between sucrose (I), maltose, galactose, mannose, glucose, fructose (II), arabinose, and xylose, on the one hand, and the primary product of hydrolysis, a triose which readily (*e.g.*, by heating) changes into AcCHO. The vals. obtained form a series decreasing in the order named, from (I) to (II), the position of the equilibria being dependent on temp., pH, and the nature of any acid present. The existence of the triose, which is possibly a hydrated form of glyceraldehyde, provides an explanation of many problems of carbohydrate chemistry. W. McC.

Analysis of mixtures of 2 : 3 : 4 : 6-tetramethylglucose with 2 : 3 : 6-trimethyl- and dimethyl-glucoses by partition on a silica water column : small-scale method for investigating structures of glucopolysaccharides. D. J. Bell (*J.C.S.*, 1944, 473—476).—Abs. separation of 50—200 mg. of 2 : 3 : 4 : 6-tetramethyl- from 2 : 3 : 6-trimethyl-glucose (I) (1—200 mols.) and dimethylglucoses is achieved by partition of a $CHCl_3$ extract of the aq. solution on a SiO_2–H_2O column; further extraction of the aq. solution with $CHCl_3$–BuOH (9 : 1) and partition of the extract on the same column gives (I) free from dimethylglucoses, which can be eluted with $COMe_2$. High recoveries of analytically pure sugars are obtained in both separations. The method is applied to determine the average length of unit chain in methylated derivatives of cellobiose, glycogen, and whole starch. H. D. W.

Enzymically synthesised crystalline sucrose. W. Z. Hassid, M. Doudoroff, and H. A. Barker (*J. Amer. Chem. Soc.*, 1944, **66**, 1416—1419).—The phosphorylase, freed from invertase, of *Pseudomonas saccharophila* is kept with K glucose 1-phosphate, fructose, and $Ba(OAc)_2$ in H_2O at 37° and pH 6·85 for 12 hr. and then at 29° for a further 12 hr. Cooling, filtration, removal of electrolytes by chromatography and of monosaccharides by washed cells of *Torula monosa*, concn., and treatment with EtOH gives sucrose, $[\alpha]_D$ +66·5° in H_2O (cf. Doudoroff *et al.*, A., 1943, III, 599; 1944, III, 288), identified by its osazone, *X*-ray spectrum, crystallo-optical properties, hydrolysis, and by its octa-acetate, m.p. 69—70°, $[\alpha]_D$ +60° in $CHCl_3$. The synthesis supports the view that glucose exists in sucrose in the α-form. R. S. C.

Separation of methylated methylglycosides by adsorption on alumina. New method for end-group determinations in methylated polysaccharides. J. K. N. Jones (*J.C.S.*, 1944, 333—334).—Tetramethylmethylglucoside (I), mixed with excess of trimethylmethylglucoside, in Et_2O–light petroleum (also used for elution) is separated (94%) chromatographically on activated Al_2O_3, which also effects some separation between the α- and (less strongly adsorbed) β-forms. Rice starch (II) (Hirst *et al.*, A., 1939, II, 495) treated with MeOH–HCl and Ag_2CO_3 and chromatographed gives (I) and trimethyl-β-methylglucoside; the proportion of (I) in the mixed methylglucosides obtained indicates that there are 33 glucose residues in the repeating unit of (II). Banana starch (Hawkins *et al.*, A., 1940, II, 207), similarly treated, gives (I) in proportion indicating 26 residues per unit (cf *loc. cit.*), with trimethyl-β-methylglucopyranoside. Methylated damson gum hydrolysed by MeOH–HCl gives a mixture of glucosides containing a const.-boiling mixture separated chromatographically into fractions which are hydrolysed by 0·5N-HCl to 2 : 3 : 4-trimethyl-*d*-xylose and 2 : 3 : 5-trimethyl-*l*-arabofuranose; it thus contains trimethylmethyl-1-arabofuranoside and -*d*-xylopyranoside. E. W. W.

Preparation of *N*-*d*-ribityl-*o*-4-xylidine. M. Tishler, N. L. Wendler, K. Ladenburg, and J. W. Wellman (*J. Amer. Chem. Soc.*, 1944, **66**, 1328—1330).—*d*-Ribolactone, *o*-4-xylidine (I), and a trace of quinol at 100° give d-*ribono*-o-4-*xylidide*, m.p. 164—165° (slight decomp.), converted by Ac_2O–C_5H_5N at >45° into the *tetra-acetate* (II), m.p. 114—115°, $[\alpha]_D^{25}$ +16±1° in $CHCl_3$, whence PCl_5 in $CHCl_3$ at room temp. yields the *chloro-imide tetra-acetate* (III), m.p. 68—70° [reconverted into (II) by H_2O]. H_2–Pd–$BaCO_3$ or –$CaCO_3$ in EtOAc or dioxan at 50—55°/15—30 lb. reduces (III) to N-d-*ribityl*-o-4-*xylidine tetra-acetate*, m.p. 94—95° (cf. B.P. 550,169, 551,491; B., 1943, II, 107, 172), also obtained (m.p. 99—100°) by hydrogenating (Pd–C) *d*-ribonitrile tetra-acetate and (I) in MeOH–AcOH–H_2O at 5—10 lb. and hydrolysed by $Ba(OMe)_2$ or NaOMe in boiling MeOH to *N*-*d*-ribityl-*o*-4-xylidine, m.p. 142—143°. R. S. C.

Synthesis of asebotin. G. Zemplén and L. Mester (*Ber.*, 1942, **75**, [*B*], 1298—1301).—Phloracetophenone 4-Me ether and acetobromoglucose in aq. $COMe_2$ containing a small amount of NaOH give 2-*glucosidophloracetophenone 4-Me ether tetra-acetate*, m.p. 187·5°, $[\alpha]_D^{25}$ −46·3° in C_5H_5N, which is condensed with *p*-OH·C_6H_4·CHO by conc. KOH to 2-glucosidonaringenin 4′-Me ether. This is hydrogenated (Pd–C in 96% EtOH) to asebotin, m.p. 148° after softening, $[\alpha]_D^{25}$ −52·1° in 55% EtOH, −46·2° in abs. EtOH, hydrolysed by 2·5% HCl at 100° to phloretin 4′-Me ether, m.p. 158° and 167·5° (triacetate, m.p. 78—79°, softens at 76°). H. W.

Glucosides of 4-hydroxycoumarins.—See A., 1944, II, 345.

Gum tragacanth. S. P. James and F. Smith (*Biochem. J.*, 1944, **38**, *Proc.*, xix).—Gum tragacanth consists of tragacanthic acid, a neutral polysaccharide, and a sterol glucoside. Hydrolysis of methylated tragacanthic acid with MeOH–HCl yields 2 : 3 : 4-trimethyl-α-methyl-*l*-fucoside, 2 : 3 : 4-trimethyl-, and 3 : 4-dimethyl-methyl-*d*-xyloside, Me ester of 2 : 3-dimethylmethylgalactofuronoside, and methyl-β-methylgalactopyranoside. The acid is essentially a chain of galacturonic acid residues joined by 1 : 4-α linkings. Hydrolysis of the methylated polysaccharide by MeOH–HCl yields 2 : 3 : 5-trimethylmethyl-*l*-arabofuranoside; 2 : 3-dimethylmethyl-*l*-arabopyranoside, β-methyl-*l*-arabopyranoside, and a dimethylhexoside. The ease of hydrolysis and the high negative val. of [α] indicate the presence of arabinose units of the furanose type in the polysaccharide, which, however, is not a simple araban. P. G. M.

Water-soluble mannan from seeds of *Daubentonia drummondii*.—See A., 1944, III, 856.

III.—HOMOCYCLIC.

Preparation of benzene by Kolbe's synthesis. Electrolysis of *trans*-1 : 2-dihydrophthalic acid. E. A. Pasquinelli (*Anal. Asoc. Quím. Argentina*, 1943, **31**, 181—190).—Electrolysis (10 v., 5 amp.) of *trans*-1 : 2-dihydrophthalic acid yields C_6H_6. F. R. G.

Nitration of toluene. Continuous partial-pressure process using nitric acid alone.—See B., 1944, II, 301.

Nitrations with nitryl chloride.—See A., 1944, II, 357.

Hydrogen chloride as a condensing agent. J. H. Simons and H. Hart (*J. Amer. Chem. Soc.*, 1944, **66**, 1309—1312).—Anhyd. HCl resembles HF as catalyst for alkylation of aromatic hydrocarbons; it yields only *p*-compounds. PhMe with Bu^{γ}Cl, Pr^{β}Cl, or Bu^{a}Cl and HCl at 235°/200 atm. (apparatus: C, 1944, 197) gives *p*-C_6H_4MeBu^γ (88%), *p*-C_6H_4MePr^β (67%) + C_6H_3MePr$^β_2$ (16%), and *p*-C_6H_4MeBu^a (15%), respectively. C_6H_6 yields similarly at 150° PhBu^γ (45·5%) + *p*-$C_6H_4Bu^γ_2$ (24%), at 235° PhPr^β (48%) + *p*-$C_6H_4Pr^β_2$ (44%), and at 195° PhBu^a (30%) + *p*-$C_6H_4Bu^a_2$ (60%). C_6H_6, *cyclo*hexene (I), and HCl at 208° give *cyclo*hexylbenzene (37%), *cyclo*hexyl chloride (II) (27%), and some polymer. C_6H_6, AcCl, and HCl give no COPhMe, but BzCl at 200° leads to 4·4% of $COPh_2$. PhBu^γ, PhOH, and HCl do not give C_6H_6 + *p*-C_6H_4Bu^γ·OH (III). PhOH, Bu^{γ}Cl, and HCl at 75°/200 atm. give 90% of (II) but 67% is obtained by merely boiling PhOH and Bu^{γ}Cl without a catalyst; catalytic effect of HCl in the general reaction is shown by failure of PhMe and Bu^{γ}Cl to condense at 235°/575 lb. (N_2). PhOH, *tert.*-C_5H_{11}Cl, and HCl at 90—160° give 72% of *p-tert.*-C_5H_{11}·C_6H_4·OH. *iso*-C_6H_{12}, (I), and HCl at 200—220° give 30% of (II), 40% of polymer, and 4% of a saturated hydrocarbon, b.p. 195—200°. R. S. C.

Catalytic aromatisation of branched-chain aliphatic hydrocarbons.—See A., 1944, II, 357.

Thermal polymerisation and cyclic dimerisation of *iso*butylene.—See A., 1944, II, 357.

Synthesis of polyenes. IV. M. S. Kharasch, W. Nudenberg, and E. K. Fields (*J. Amer. Chem. Soc.*, 1944, **66**, 1276—1279; cf. A., 1943, II, 159).—Condensation of CH_2RHal by $NaNH_2$ in liquid NH_3 to $(CHR{:})_2$ proceeds by way of $CH_2R{\cdot}CHRHal$ and depends on R being strongly electronegative and not containing reactive substituents and on the high dielectric const. of the solvent. A detailed reaction mechanism is propounded. $CH_2Ph{\cdot}NH_2$,HCl (5%) is obtained from CH_2PhCl by KOH, NaOEt, or CHO·NHNa in liquid NH_3, or (15%) by $NaNH_2$ in Et_2O; CHO·NHNa in HCO·NH_2 gives $CHO{\cdot}N(CH_2Ph)_2$ (55%); $NaNH_2$ in light petroleum is without effect, but in liquid NH_3 gives 100% of $(CHPh{:})_2$. With $NaNH_2$ in liquid NH_3, CH_2BzBr gives $(CHBz{:})_2$ (42%), m.p. 111°; $(CH_2Br{\cdot}CH{:})_2$ gives a *polymer*, $CH_2Br{\cdot}[CH{:}CH]_2{\cdot}CH_2Br$ (100%); $CHPh{:}CH{\cdot}CH_2Cl$ gives *αζ-diphenylhexatriene* (10%), *form*, softens 150—160°, m.p. 165°, but an excess of $NaNH_2$ leads to polymeric products; $(o\text{-}CH_2Br{\cdot}C_6H_4)_2$ gives 80% of phenanthrene; CH_2PhCl + $CH_2{:}CH{\cdot}CH_2Cl$ gives $CHPh{:}CH{\cdot}CH{:}CH_2$ (14%), styrene, hexatriene, and polymers; CH_2PhCl + $CH_2{:}CMe{\cdot}CH_2Cl$ gives $CHPh{:}CMe{\cdot}CH{:}CH_2$ (23%), styrene (13%), $(CH_2{:}CMe{\cdot}CH{:})_2$ (35%), and polymers (29%); geranyl chloride gives 35% of geranylamine. 6-*Phenyl*-4-*methyl*-, m.p. 194° (decomp.) (*anhydride*, m.p. 90—91°), and 6-*phenyl*-, m.p. 200—203° (decomp.; rapid heating), -1 : 2 : 3 : 6-*tetrahydrophthalic acid* are prepared. R. S. C.

Preparation of substituted styrenes. L. A. Brooks (*J. Amer. Chem. Soc.*, 1944, **66**, 1295—1297).—*o*-$C_6H_4Cl{\cdot}CHO$ with MgMeBr–Et_2O gives α-*o*-*chlorophenylethyl alcohol* (76%), b.p. 109°/7 mm., converted by >1% of $KHSO_4$ and a little quinol at 200—210°/110—130 mm. into *o-chlorostyrene* (70%), b.p. 60—61°/4 mm. Similarly are prepared α-m-, b.p. 102—104°/3 mm., and α-p-*chlorophenyl*-, b.p. 87—89°/2 mm., α-o-, b.p. 117—118°/45 mm., α-m-, b.p. 120—121°/45 mm., and α-p-*fluorophenyl*-, b.p. 122—123°/45 mm., and α-2 : 5-*dichlorophenyl-ethyl alcohol*, m.p. 63—64°, b.p. 107—109°/2 mm., and thence *m*-, b.p. 62—63°/6 mm., and *p*-chloro-, b.p. 53—54°/3 mm., o-, b.p. 32—34°/3 mm., m-, b.p. 30—31°/4 mm., and p-*fluoro*-, b.p. 29—30°/4 mm., and 3 : 5-*dichloro-styrene*, b.p. 72—73°/2 mm. 3 : 4 : 1-$C_6H_3Cl_2{\cdot}COMe$ yields α-3 : 4-*dichlorophenylethyl alcohol* (91%), b.p. 127—128°/2 mm., and thence 3 : 4-*dichlorostyrene*, b.p. 69—70°/4 mm. The styrenes are less stable when purified. Relative stabilities of $CHAr{:}CH_2$ are $Ar = C_6H_4F > C_6H_4Cl > C_6H_3Cl_2$. R. S. C.

Reactivity of 2-chloro-3 : 5-dinitrodiphenyl. C. K. Bradsher and S. T. Amore (*J. Amer. Chem. Soc.*, 1944, **66**, 1283—1284).—1 : 2 : 3 : 5-$C_6H_2PhCl(NO_2)_2$ (I), best obtained (m.p. 115—116°; cf. Borsche *et al.*, A., 1917, i, 390) from 3 : 5 : 1 : 2-$(NO_2)_2C_6H_2Ph{\cdot}NH_2$ by $NO{\cdot}SO_3H$ and then aq. CuCl–HCl, differs from 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ owing to steric hindrance by the Ph. In boiling NaOR–ROH, (I) gives 3 : 5-*dinitro*-2-*ethoxy*- (II) (93%), m.p. 114—115°, and -2-methoxy-diphenyl, m.p. 113·5—114°, in boiling piperidine gives 3 : 5-*dinitro*-2-*piperidinodiphenyl*, m.p. 184·5—185°, and with Cu powder at 215° and then 190° gives 4 : 6 : 4′ : 6′-*tetranitro*-2 : 2′-*diphenyldiphenyl*, m.p. 248—249°. $CH_2(CO_2Et)_2$ or $CH_2Ac{\cdot}CO_2Et$ does not react with (I); $CH_2(CO_2Et)_2$ in NaOEt–EtOH gives only (II). R. S. C.

Bond system and stereochemistry of cumulenes.—See A., 1944, I, 268.

Di*cyclo*hexadienes and the strain theory.—See A., 1944, I, 267.

Aromatic cyclodehydration. XVI. Phenanthrene hydrocarbons from unsymmetrical ketones. C. K. Bradsher and S. T. Amore. **XVII. 9- and 10-Methyl-1 : 2 : 3 : 4-dibenzphenanthrene.** C. K. Bradsher and L. Rapoport (*J. Amer. Chem. Soc.*, 1944, **66**, 1280, 1281—1282; cf. A., 1944, II, 130).—XVI. *o*-$C_6H_4Ph{\cdot}MgI$ with $COR{\cdot}CH_2R'$ and then $KHSO_4$ gives α-*phenyl*-α-2-*diphenylyl*-Δ^{α}-*n*-*pentene* (65%), m.p. 78—79°, b.p. 207—208°/8 mm., and -Δ^{α}-*n*-undecene (60%), b.p. 242—254°/5 mm., β-2-diphenyl-Δ^{β}-*n*-butene (36%), b.p. 132—140°/9 mm., and -Δ^{α}-*n*-heptene (51%), b.p. 140—160°/8 mm., and thence by oxidation and cyclisation 9-*phenyl*-10-n-*propyl*- (64%), m.p. 148·5—149·5°, 9-*phenyl*-10-n-*decyl*- (39%), m.p. 99—100°, 9 : 10-dimethyl- (39%), m.p. 142·5—143° (lit. 139°) (picrate, m.p. 193—194°), and 9-*n*-amyl-phenanthrene (31%), m.p. 69—70°.

XVII. 1-Keto-4-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene and *o*-$C_6H_4Ph{\cdot}Li$ in boiling Et_2O give 4-2′-*diphenylyl*-1-*methyl*-1 : 2-*dihydronaphthalene* (64·5%), b.p. 215—218°/6—7 mm., converted by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ and then HBr–AcOH–H_2O into 9-methyl-9 : 10-dihydro-1 : 2 : 3 : 4-dibenzphenanthrene (89·5%), an oil (*picrate*, m.p. 170·5—171°), whence 30% Pd–C in CO_2 at 310—350° yields 9-*methyl*-1 : 2 : 3 : 4-*dibenzphenanthrene* (I) (64%), m.p. 150·5—151·5° (*picrate*, m.p. 207·5—208·5°). $Na_2Cr_2O_7$–AcOH oxidises (I) to 1 : 2 : 3 : 4-dibenzphenanthraquinone (proof of structure). (I) absorbs O_2 fairly rapidly in air. 1-Keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene leads similarly to 4-2′-*diphenylyl*-2-*methyl*-1 : 2-*dihydronaphthalene* (65%), m.p. 77—78°, 10-*methyl*-9 : 10-*dihydro*- (73%), m.p. 151—152° [unstable picrate, m.p. 117·5—119°; *s*-$C_6H_3(NO_2)_2$ *compound*, m.p. 138·5—139·5° after softening], and 1 *methyl*-1 : 2 : 3 : 4-*dibenzphenanthrene* (70%), m.p. 163·5—164° [unstable picrate, m.p. 150·5—151·5°; *s*-$C_6H_3(NO_2)_2$ *compound*, m.p. 161—162°]. 1-Keto-3 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene gives 4-2′-*diphenylyl*-1 : 2-*dimethyl*-1 : 2-*dihydronaphthalene*, m.p. 78—79·5°, b.p. 217—218°/8 mm., and 9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 3 : 4-dibenzphenanthrene, a resin (picrate, m.p. 154—154·5°), which is unchanged by chloranil and with Pd–C–CO_2 at 310—350° or S at 250° yields only (I). R. S. C.

Aromatic hydrocarbons. XXXIV. New synthesis of hexacene. E. Clar (*Ber.*, 1942, **75**, [*B*], 1283—1287; cf. A., 1940, II, 75).—*o*-$C_6H_4(CO)_2O$ is condensed with *o*-xylene to *o*-3 : 4-dimethylbenzoylbenzoic acid, which is oxidised by $KMnO_4$ in alkaline solution to benzophenone-2′ : 3 : 4-tricarboxylic acid. This passes at ~240° into the anhydride, m.p. 185—186° (lit. 175°), which is condensed with tetrahydronaphthalene by $AlCl_3$ in $C_2H_2Cl_4$ at 90° to *p*-*o*′-carboxybenzoyl-*o*-5 : 6 : 7 : 8-tetrahydro-2-naphthoylbenzoic acid, which could not be obtained cryst. It is reduced by Cu–Zn in alkaline solution to *p*-*o*′-carboxybenzyl-*o*-5 : 6 : 7 : 8-tetrahydronaphthyl-2-methylbenzoic acid, transformed by Zn dust, NaCl, and $ZnCl_2$ at 340° into a mixture from which 5 : 16-*dihydrohexacene* (I) is isolated by fractional sublimation in CO_2/1 mm. Its constitution is deduced from its orange-red colour, its absorption spectrum in C_6H_6, and great reactivity towards $(CH{:}CO)_2O$. In boiling xylene (I) passes into 6 : 15-*dihydrohexacene* (II), which is pale yellow in colour, reacts more difficultly with $(CH{:}CO)_2O$, and shows the absorption spectrum of a $C_{10}H_8$ and an anthracene complex united by 2 CH_2. (I) and (II) have m.p. 357—370° (vac.), ill-defined by reason of thermal transformability. Dehydrogenation of (I) or (II) gives hexacene. Pure (II) is oxidised in boiling $PhNO_2$ by SeO_2 to *hexacene*-6 : 15-*quinone*, m.p. (indef.) 295—310°, possibly containing the -5 : 16-isomeride. H. W.

Complex compounds of cupric azide. III. Non-electrolytes with organic bases.—See A., 1944, I, 290.

Photochemical investigation of dark-coloured aniline.—See A., 1944, I, 289.

Influence of alkyl groups on reaction velocities in solution. V. Formation of phenyltrialkylammonium iodides in methyl alcohol.—See A., 1944, I, 286.

Phenylthiocarbimide from phenyl azide. W. Borsche (*Ber.*, 1942, **75**, [*B*], 1312—1313).—PhN_3 and $AlCl_3$ in $PhNO_2$ give N_2 and a dark resin from which no definite compound could be isolated. In CS_2 the products are PhNCS and "phenylthiocarbimide sulphide," $CS\langle^{S-S}_{NPh}\rangle C{:}NPh$, m.p. 155°. The first products are therefore N_3 and PhN. H. W.

Preparation and properties of derivatives of sulphamide. K. W. Wheeler [with E. F. Degering] (*J. Amer. Chem. Soc.*, 1944, **66**, 1242—1243).—$SO_2(NH_2)_2$ and $CO_2H{\cdot}CH_2{\cdot}COCl$ in Et_2O give *H malonylsulphamide*, $CO_2H{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}SO_2{\cdot}NH_2$, m.p. 147° (decomp.; uncorr.), which in EtOH–H_2SO_4 gives (?) the Et ester, m.p. 84—85° (uncorr.). SO_2Cl_2 (2 mols.) and $NHMe_2$,HCl (1 mol.) at 60° give HCl and $NMe_2{\cdot}SO_2Cl$ (80%). $NAlk_2{\cdot}SO_2Cl$ with NH_2R or NHR_2 alone (exothermally) or in boiling C_6H_6 or Et_2O yields N-o-, m.p. 64·6—65·2°, and N-m-*tolyl*-, m.p. 47—48°, N-m-4-*xylyl*-, m.p. 74·7—75°, N-o-*chlorophenyl*-, m.p. 49·4—49·7°, and N-p-*anisyl*-, m.p. 56·3—56·8°, -N′N′-*diethylsulphamide*; N-*phenyl*-NN′N′-*trimethylsulphamide*, m.p. 45·5—46°, and -N′N′-*dimethyl*-N-*ethylsulphamide*, m.p. 31·5—32°; N-o-, m.p. 104·8—105·2°, and N-m-*tolyl*-, m.p. 80·5—81°, N-m-4-*xylyl*-, m.p. 132—132·5°, N-o-, m.p. 75·5—76°, N-m-, m.p. 88·2—88·7°, and N-p-*chlorophenyl*-, m.p. 56·5—57·1°, N-p-*bromophenyl*-, m.p. 78·8—79·3°, N-p-*iodophenyl*-, m.p. 83·6—84·2°, N-m-*nitrophenyl*-, m.p. 126·7—127°, N-p-*dimethylaminophenyl*-, m.p. 108·6—109·3°, N-p-*anisyl*-, m.p. 55·6—56·2°, N-p-*carbethoxyphenyl*-, m.p. 125—125·4°, N-α-, m.p. 107·3—107·7°, and N-β-*naphthyl*-, m.p. 110—110·4°, N-*pentamethylene*-, m.p. 55·5—56·2°, and N-2-*pyridyl*-, m.p. 130·7—131·2°, -N′N′-*dimethylsulphamide*. $NHPh{\cdot}SO_2{\cdot}NMe_2$ and AcCl give the N-*Ac* derivative, m.p. 92·3—92·7°. These products are more stable than $SO_2(NH_2)_2$. They are sol. without decomp. in cold, conc. H_2SO_4. Those containing at least one H attached to N are sol. in dil. alkali. With the exceptions noted, m.p. are corr. R. S. C.

***N*-Chlorocarbamic esters.** P. Chabrier (*Ann. Chim.*, 1942, [xi], **17**, 353—370).—Partly an account of work previously abstracted (A., 1943, II, 82). *NN*-Dichlorocarbamates, $NCl_2{\cdot}CO_2R$, are prepared from $NH_2{\cdot}CO_2R$, NaOCl, and aq. H_2SO_4 or AcOH; thus prepared is *β-chloroethyl* NN-*dichlorocarbamate* (I), m.p. 38°. $NCl_2{\cdot}CO_2Et$ (II) and styrene in C_6H_6 afford *Et* N-*chloro*-N-*β-chloro-β-phenylethylcarbamate*, a liquid (not distillable), reduced by $NaHSO_3$ to *Et* N-*β-chloro-β-phenylethylcarbamate*, m.p. 50°, convertible by Na_2CO_3 or $AgNO_3$ in aq. EtOH into the corresponding *β-OH*-ester, m.p. 85°, or by Zn–aq. NH_3 into $Ph{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO_2Et$. Similarly prepared are *Et* N-*chloro*-N-*β-chloro-β*-m-*anisyl*-, and -*β-methylenedioxyphenyl*-α-*methylethylcarbamate*, and *Et* N-*β-chloro-β*-m-*anisyl*- *and* -*β-methylenedioxyphenyl*-α-*methylethylcarbamate*, m.p. 76° and 114°, respectively. $NCl_2{\cdot}CO_2Me$ (III) and $(C_2H_4Cl)_2S$ in C_6H_6 give *tetrachlorodiethyl sulphide*, b.p. 115°/15 mm., which decomposes to HCl and

$CH_2Cl{\cdot}CHCl{\cdot}S{\cdot}CH{:}CHCl$. Carbazole and (**III**) in AcOH give *tetrachlorocarbazole*, m.p. 212°; $CH_2Ph{\cdot}CO{\cdot}NH_2$ in H_2O yields *phenylacetchloroamide*, m.p. 120°; 3 : 5-diketo-6-alkyl-1 : 2 : 4-triazine in alkali affords 2 : 4-*dichloro*-3 : 5-*diketo*-6-*benzyl*-, m.p. 119° (explodes at 150°), and -6-*phenylethyl*-1 : 2 : 4-*triazine*, m.p. 130° (explodes at 165°); similarly prepared is 2-*chloro*-3 : 5-*diketo*-4 : 6-*dibenzyl*-1 : 2 : 4-*triazine*, m.p. 153°; 1 : 3-*dichloro*-5 : 5-*diphenylhydantoin*, m.p. 166°, is obtained from diphenylhydantoin; indole-2-carboxylic acid or its Me ester in AcOH yields probably 2 : 3 : (?)5-*trichloro*-2 : 3-*oxido*-2 : 3-*dihydroindole*, m.p. 188° [Zn–AcOH give (?)5-*chloro*-2 : 3-*oxido*-2 : 3-*dihydroindole*, m.p. 192°], or *Me* 2 : 3 : (?)5-*trichloro*-3-*hydroxy*-2 : 3-*dihydroindole*-2-*carboxylate*, m.p. 184°, respectively. (**II**) and aq. glycine give $CH_2(NH{\cdot}CO_3Et)_2$, readily decomposed to CH_2O. $NCl_2{\cdot}CO_2R$ and $NH_2{\cdot}CO_2R$ give $NHCl{\cdot}CO_2R$, which with NaOEt–EtOH–Et_2O afford $NNaCl{\cdot}CO_2R$. *Na Et* N-*chlorocarbamate*, deflagrates at 140°, is prepared. $NNaCl{\cdot}CO_2Me$ and $AsPh_3$ in C_6H_6 give N-*triphenylarsine Me carbamate*, $CO_2Me{\cdot}N{:}AsPh_3$, m.p. 84°, readily hydrolysed to $NH_2{\cdot}CO_2Me$ and $AsPh_3O$. Also prepared (method : *loc. cit.*) are N-*carbethoxy*-N-3-*pyridylcarbamide*, m.p. 200°, N-*carbomethoxy*-, m.p. 100°, and N-*carbethoxy*-N′-*ethoxymethyl*-, m.p. 82°, N-*carbomethoxy*-, m.p. 65°, N-*carbethoxy*-, m.p. 40°, and N-*carbo*-β-*chloroethoxy*-N′-α-*ethylpropyl*-, m.p. 108·5°, and N-*carbomethoxy*-, m.p. 133·5°, and N-*carbethoxy*-N′-*benzyl*-*carbamide*, m.p. 93°. Also prepared are *ethoxymethyl*-, m.p. 132° (*CHPh:* derivative, m.p. 167°), *benzyl*-, m.p. 171° (*semicarbazones* from $COMe_2$, m.p. 151°, PhCHO, m.p. 194°, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, m.p. 192°, *p*-$C_6H_4Pr^{\beta}{\cdot}CHO$, m.p. 174°, and $CH_2Ph{\cdot}CO{\cdot}CO_2H$, m.p. 204°), and *phenyl*-*carbamylsemicarbazide* (**IV**), m.p. 228° (*semicarbazones* from $COMe_2$, m.p. 214°, PhCHO, m.p. 233°, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, m.p. 215°, and COPhMe, m.p. 212°). Prolonged action of N_2H_4 on $NHPh{\cdot}CO{\cdot}NH{\cdot}CO_2Me$ liberates NH_2Ph. Derivatives of (**IV**) are converted by Na–Hg into (probably) a *bis*(*phenylcarbamylsemicarbazide*), $(NHPh{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH)_2$, m.p. 263°, which does not combine with RCHO. $NNaCl{\cdot}CO_2Me$ and $CO_2Na{\cdot}CR{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$ in H_2O yield ketotriazoles, $CR{<}^{N{-}NH}_{NH{\cdot}CO}$.

A. T. P.

Copper complexes of sulphanilamide and sulphathiazole. W. R. Todd (*Arch. Biochem.*, 1944, **4**, 343—346).—Cryst. complexes of Cu and sulphanilamide or sulphathiazole are prepared by the action of glucose and an alkaline Cu reagent. Both complexes are stable in alkaline solution, but are insol. and unstable in org. solvents and H_2O. Mineral acid decomposes the complexes producing Cu_2O. The sulphanilamide *complex*, $(C_6H_8O_2N_2S)_2Cu_3(OH)_2$, decomp. ~200°, darkens on drying; the sulphathiazole *complex*, $(C_9H_9O_2N_3S_2)Cu$, decomp. ~300°, remains white, and can be obtained in white, yellow or orange crystals, identical microscopically.

E. R. S.

Bacterial chemotherapy. IV. Synthesis of N^1:N^4-diacylsulphanilamides. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 343—350).—Sulphanilamide or its N^4-acyl derivative with the appropriate acid chloride in C_5H_5N gives N^1-*acetyl*-, m.p. 166—169° (decomp.), N^1-n-*butyryl*-, m.p. 164—168°, N^1-n-*heptoyl*-, m.p. 148—152°, N^1-*palmityl*-, m.p. 123—126°, N^1-*stearyl*-, m.p. 127—130°, N^1-*benzoyl*-, m.p. 180—183°, N^1-*hexahydrobenzoyl*-, m.p. 185—187°, N^1-*cinnamoyl*-, m.p. 228—231°, N^1-α-*naphthoyl*-, m.p. 154—157°, N^1-m-*nitrobenzoyl*-, m.p. 173—178°, and N^1-p-*nitrobenzoyl*-N^4-*hexoyl*-, m.p. 222—230°, and N^1 : N^4-*dihexoyl*-, m.p. 164—172°, -*di*-n-*butyryl*-, m.p. 217—220°, -*di*-n-*heptoyl*-, m.p. 131—134°, -*dibenzoyl*, m.p. 239—240°, -*dihexahydrobenzoyl*-, m.p. 248—250°, -*dicinnamoyl*-, m.p. 216—218°, -*di*-p-*nitrobenzoyl*-, m.p. 251 (decomp.), and *di*-*furoylsulphanilamide*, m.p. 255° (decomp.), and N^1 : N^4-*di*-p-*nitrobenzoylsulphapyridine*, m.p. 232—234° (decomp.). The mechanism of the action of the sulphonamides is discussed.

F. R. S.

***N*-Sulphanilylcarbamides.**—See B., 1944, II, 304.

***N*^{1}-Sulphanilyl*iso*thiocarbamides.** P. C. Guha, P. L. N. Rao, and V. Mahadevan (*Current Sci.*, 1943, **12**, 325—326).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and $NH_2{\cdot}C(SR){:}NH,HCl$ (or HBr), after hydrolysis with 8—10% aq. HCl, yield N^1-*sulphanilyl*-*propyl*-, m.p. 133—134° (*Ac* derivative, m.p. 174°), -*butyl*-, m.p. 116° (*Ac* derivative, m.p. 157°), and -*allyl*-iso*thiocarbamide*, m.p. 170° (*Ac* derivative, m.p. 173—174°). The Et analogue, m.p. 155—156° (Ac derivative, m.p. 180—181°), is prepared similarly (cf. Winnek *et al.*, A., 1942, II, 400), but p-*acetamidobenzenesulphonylbenzyl*iso*thiocarbamide*, m.p. 171—173°, is hydrolysed to *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ and $CH_2Ph{\cdot}SH$.

A. T. P.

Sulphanilylguanidine.—See B., 1944, III, 237.

Guanidine derivatives.—See B., 1944, II, 305.

Preparation of *p*-substituted aromatic ethylene derivatives. R. Roleff (*Chem.-Ztg.*, 1943, **67**, 81).—Heating aromatic ketones or aldehydes with MgMeBr (prep. in Et_2O, subsequently removed) in C_6H_6 gives good yields of olefine. Details are given for $(p\text{-}NMe_2{\cdot}C_6H_4)_2C{:}CH_2$.

R. S. C.

Ethylenediamine derivatives having trypanocidal action. A. Funke, D. Bovet, and G. Montezin [with, in part, Viaud and Horclois] (*Ann. Inst. Pasteur*, 1943, **69**, 358—371).—CH_2PhCl (1 mol.; 12 g.) and $(CH_2{\cdot}NH_2)_2,H_2O$ (4 mols.) in EtOH at 120° give $CH_2Ph{\cdot}NH{\cdot}[CH_2]_2{\cdot}NH_2$ (1945 F) (6 g.), b.p. 125—130°/10 mm. (dihydrochloride, m.p. ~255°), and $(CH_2Ph{\cdot}NH{\cdot}CH_2)_2$, b.p. ~190°/10 mm. Similar preps., best at room temp., lead to N-p-*methyl*- (2156 F), b.p. 140°/13 mm. (dihydrochloride, m.p. ~205°), *N*-*p*-ethyl- (2440 RP) [*dihydrochloride*, m.p. 216—218° (decomp.)], N-p-n- (1986 F), b.p. 145—150°/8 mm., and N-p-iso-*propyl*- (**I**) (1921 F) (65—70%), b.p. 145—150°/8 mm. [*dihydrochloride*, m.p. ~235° (decomp.)], N-p-sec.-*butyl*- (2463 RP), b.p. 130—135°/1·3 mm., N-p-*benzyl*- (2160 F), b.p. 200—202°/2·5 mm. (dihydrochloride, m.p. ~230°), N-p-β-*phenylethyl*- (2162 F), b.p. 228—235°/10 mm., N-p-cyclo*pentyl*- (1971 F), b.p. 180—196°/14 mm., N-p-cyclo*hexyl*- (**II**) (1955 F), b.p. 187—190°/7 mm., N-2 : 5- (2152 F), b.p. 155—160°/16 mm. [dihydrochloride, m.p. 255° (decomp.)], and N-2 : 4-*dimethyl*- (2157 F), b.p. 150—154°/13 mm., N-2 : 4 : 6-*trimethyl*- (2163 F), b.p. 160—164°/12 mm., N-2-*methyl*-5-iso*propyl*- (1988 F), b.p. 165°/10 mm., N-4-*methoxy*-2-*methyl*-5-iso*propyl*- (1997 F), b.p. 190—195°/12 mm., N-2-nitro-4-*iso*propyl- (**III**) (2172 F) [*dihydrochloride*, m.p. ~170° (decomp.)], N-2-amino-4-*iso*propyl- (2083 F) [prep. from (**III**) by H_2–Raney Ni in aq. EtOH] [*dihydrochloride*, m.p. 220° (decomp.)], *N*-*p*-nitro- [*dihydrochloride* (2170 F), m.p. ~218°], and thence *N*-*p*-amino- [*dihydrochloride* (2075 F), m.p. 200—235°], N-p-*cyano*- (2097 F), b.p. 160—170°/1·6 mm. (*dihydrochloride*, m.p. ~260°), and N-p-*chloro*- (2115 F), b.p. 135°/2 mm., -*benzylethylenediamine*. Similarly are prepared *N*-*p*-xenylmethyl- (2462 RP) [*dihydrochloride*, m.p. ~295° (block)], N-*tetrahydro*-β-*naphthylmethyl*- (1993 F), b.p. 170—175°/0·8 mm., N-α-*naphthylmethyl*- (1990 F), b.p. 200°/14 mm., N-4-iso*propyl*-1-*naphthylmethyl*- (1999 F), b.p. 187°/6 mm., N-*citronellyl*- (2015 F), b.p. 156—160°/24 mm., and N-β-p-iso*propylphenylethyl*- (2146 F), b.p. 170°/18 mm., -*ethylenediamine*. *p*-$C_6H_4Pr^{\beta}{\cdot}CH_2Cl$ (1 mol.) and $NH_2{\cdot}[CH_2]_2{\cdot}NEt_2$ (2 mols.) give exothermally N-p-iso*propylbenzyl*-N′N′-*diethylethylenediamine* (1964 F), b.p. 155°/8 mm. The appropriate di(chloromethyl) compound leads to 2 : 5-*di*-(β-*aminoethylaminomethyl*)-p-*xylene* (2154 F), b.p. 190—192°/0·7 mm., 4 : 6-*di*-(β-*aminoethylaminomethyl*)-m-*xylene* (2158 F), b.p. 200—205°/1·52 mm., *di*-(x-β-*aminoethylaminomethylphenyl*)*methane* (2159 F), b.p. 250—260°/0·6 mm., and αβ-*di*-(x-β′-*aminoethylaminomethylphenyl*)*ethane* (2161 F), b.p. 255—268°/0·8 mm. CH_2ArCl and the appropriate diamine give δ-p-iso*propylbenzylamino*-α-*diethylamino*-n-*pentane* (1989 F) (prep. at 130°), b.p. 170—172°/8 mm. (hygroscopic dihydrochloride), 1-p-iso*propylbenzylpiperazine* (1966 F), b.p. 165°/13 mm., and N-p-iso*propylbenzylhexamethylenediamine* (1994 F), b.p. 190°/1·2 mm. Heating $OH{\cdot}CH(CH_2Cl)_2$ (1 mol.) and $CH_2Ar{\cdot}NH_2$ (4 mols.) slowly to ~150° gives αγ-*dibenzylamino*- (2079 F), b.p. 217—220°/8 mm., αγ-*di*-p-iso*propylbenzylamino*- (2080 F), and αγ-*di*-p-cyclo*hexylbenzylaminopropan*-β-*ol* (2081 F). As by-products are obtained NN′-*di*-p-n-[*dihydrochloride* (1987 F)] and NN′-*di*-p-iso-*propylbenzyl*- (1943 F), b.p. 230—240°/8 mm. (dihydrochloride), NN′-di-2 : 5-dimethylbenzyl- (2153 F), *NN*′-di-2-nitro-4-*iso*-propylbenzyl- [*dihydrochloride* (2173 F), m.p. 210° (decomp.)], *NN*′-di-*p*-nitrobenzyl- [*dihydrochloride* (2171 F), m.p. ~260° (decomp.)], NN′-*di*-p-*chlorobenzyl*- (2116 F), m.p. 120°, and *NN*′-di(tetrahydro-β-naphthylmethyl)-, b.p. 240—250°/0·8 mm. [*dihydrochloride* (2001 F)], -ethylenediamine and NN′-*di*-p-iso*propylbenzylhexamethylenediamine* (1995 F), b.p. 250—260°/2 mm. Treating (**I**) with, successively, PhCHO, Na_2CO_3–Et_2O–BzCl (later at the b.p.), and 0·1N-HCl gives N-*benzoyl*-N-p-iso*propylbenzylethylenediamine hydrochloride*, m.p. 166°. BzCl and (**I**) in C_6H_6 give the *Bz*$_2$ derivative, m.p. 121°. With $CHEt_2{\cdot}CHO$ and then $Na\text{-}C_5H_{11}{\cdot}OH$, (**I**) gives *N*-*p*-*iso*propylbenzyl-*N*′-β-ethyl-*n*-butylethylenediamine [*dihydrochloride* (1947 F), m.p. ~255° (decomp.)]. Boiling the dihydrochloride of (**II**) with $CN{\cdot}NH_2$ (? in a solvent) gives β-p-cyclo*hexylbenzylaminoethylguanidine dihydrochloride* (1968 F), cryst. For pharmacological data see A., 1944, III, 830.

R. S. C.

***p*-Diazonium tertiary amines.**—See B., 1944, II, 304.

Phenol synthesis and catalyst.—See B., 1944, II, 305.

Thymol and *iso*propyl-*m*-cresols obtained from *m*-cresol by condensation reactions. A. E. Tschitchibabin [with C. Barkovsky] (*Ann. Chim.*, 1942, [xi], **17**, 316—334).—*m*-Cresol (**I**) and $Pr^{\beta}OH$–H_3PO_4 (*d* 1·8) at 50—60° or 65—75° for 20 or 14 hr., respectively, then at 18° for 36 hr., give 1 : 4 : 3- (thymol) (**II**), 1 : 6 : 3- (*p*-thymol) (**III**), m.p. 114°, and 1 : 2 : 3-$C_6H_3MePr^{\beta}{\cdot}OH$ (*o*-thymol) (**IV**), m.p. 69° [*NO*-derivative, m.p. 178° (block)]. (**I**) and H_2SO_4 (*d* 1·84) at 120—125° for 2—3 hr., followed by $Pr^{\beta}OH$ at 70—85°, give (**III**) + (**IV**); the use of 100% H_2SO_4 or 35% oleum at ~80° yields (**II**) + (**III**); $C_6H_2MePr^{\beta}{}_2{\cdot}OH$ (**V**) are also formed. Many experiments under varying conditions are recorded. The isomerides obtained depends on the relative amounts of *m*-cresolsulphonic acids formed, the concn. of H_2SO_4, and duration of heating. (**II**) and (**III**) are isolable from (**I**)–$Pr^{\beta}OH$ and H_2SO_4–$Na_2S_2O_7$ at 60—70°. 3 : 1 : 4-$OH{\cdot}C_6H_3Me{\cdot}SO_3H$ (A., 1942, II, 223) and $Pr^{\beta}OH$–100% H_2SO_4 at 65—70° for 3·5 hr. afford 10% of (**IV**), 13% of (**III**), and (**V**); 3 : 1 : 6-$OH{\cdot}C_6H_3Me{\cdot}SO_3H$ gives 25% of (**II**), 12% of (**III**), and (**V**), and the 4 : 6-disulphonic acid yields some (**II**), (**III**), and (**IV**); in all cases, neutral products are also formed. (**I**)–$Pr^{\beta}Cl$–$AlCl_3$–$C_2H_4Cl_2$ at −11° to −13° gives (**II**), (**III**), and a little 1 : 3 : 5-

$C_6H_3MePr^{\beta}$·OH (*m*-thymol) (**VI**), m.p. 51°; (**VI**) increases in amount as the temp. of reaction rises, and is the main product at room temp. The most stable $C_6H_3MePr^{\beta}$·OH is (**VI**), which can be obtained from the other isomerides and $AlCl_3$ at 30°. (**III**) [and (**VI**)] is unchanged on heating at 350—400°, but in presence of $ZnCl_2$–fuller's earth at the same temp., conversion into (**VI**) occurs. A. T. P.

Condensation of *tert.*-butyl chloride with *m*-cresol and of *iso*propyl chloride with *m*-4-xylenol. A. Tschitchibabin and C. Barkovsky (*Ann. Chim.*, 1942, [xi], **17**, 349—352).—$Bu^{\gamma}Cl$, *m*-cresol (**I**), and $AlCl_3$ in $C_2H_4Cl_2$ at −13° (7 hr.), then at room temp. (15 hr.), yield (probably) 5-tert.-*butyl*-m-*cresol*, m.p. 50°, b.p. 128°/13 mm.; with H_3PO_4–$Bu^{\gamma}OH$, (**I**) yields 1 : 4 : 3-$C_6H_3MePr^{\beta}$·OH, m.p. 23° (cf. A., 1936, 602), and a small amount of an isomeride, probably 1 : 6 : 3-$C_6H_3MeBu^{\gamma}$·OH. *m*-4-Xylenol and $Pr^{\beta}Cl$–$AlCl_3$–$C_2H_4Cl_2$ at 9—12° give (?)5-iso*propyl*-, m.p. 46—47°, and a *diiso*propyl-m-4-*xylenol*, m.p. 99°. A. T. P.

***cyclo*Hexyl sulphite.**—See A., 1944, II, 318.

Nitration of *p*-diphenylyl acetate. S. E. Hazlet, D. A. Stauffer, L. C. Hensley, and H. O. Van Orden (*J. Amer. Chem. Soc.*, 1944, **66**, 1245—1247).—*p*-C_6H_4Ph·OAc (**I**) is more difficult to nitrate than *p*-C_6H_4Ph·OH. With conc. HNO_3 in AcOH at 100° (6 hr.) and then room temp. (2 days) it gives some 4 : 3 : 5 : 1-$OH·C_6H_2(NO_2)_2·C_6H_4·NO_2$-*p* (**II**), and other conditions usually give only (**II**). Adding (**I**) to HNO_3 (*d* 1·479) in AcOH at 100° gives (**II**) and a small amount of 4-*nitro*-4′-*acetoxydiphenyl*, m.p. 138—139°. Steric effects are responsible for these results and the difference from bromination. 3-*Nitro*-, m.p. 85—86°, 3 : 5-, m.p. 129—130°, and 3 : 4′-*dinitro*-, m.p. 137—138°, and 3 : 5 : 4′-*trinitro*-, m.p. 148—149°, -4-*acetoxydiphenyl* are obtained from the phenols by boiling Ac_2O–NaOAc. R. S. C.

Action of hydriodic acid on phenolic pinacols and pinacolins. Synthesis of œstrogenic compounds. E. Adler, H. von Euler, and G. Gie (*Arkiv Kemi, Min., Geol.*, 1944, **18**, **A**, No. 1, 21 pp.).—$[OH·C_6H_4·CMe(OH)]_2$ is converted by red P and HI (*d* 1·96) at 135—140° in presence or absence of AcOH into PhOH, meso-$\beta\gamma$-4 : 4′-*dihydroxydiphenylbutane* (**I**), m.p. 231—233° (*diacetate*, m.p. 138—140°; sparingly sol. Na salt), a *compound* (**II**), $C_{16}H_{18(16)}O_2$, m.p. 174—175° (*diacetate*, m.p. 117—118·5°; *dibenzoate*, m.p. 151—151·5°), and r-$\beta\gamma$-4 : 4′-*dihydroxydiphenylbutane* (**III**), m.p. 139—139·5° (also + $CHCl_3$) (*dibenzoate*, m.p. 144—145°). These compounds are also prepared similarly from $\gamma\gamma$-*di*-p-*hydroxyphenylbutan*-β-*one* (**IV**), m.p. 130°, which therefore represents the first step in the change. The next step is not $\gamma\gamma$-*di*-p-*hydroxyphenylbutan*-β-*ol*, m.p. 147—148° (obstinately retains solvent of crystallisation; *dibenzoate*, m.p. 163—164°), obtained by reducing (**IV**) with Na and C_5H_{11}·OH at 140°, since this does not give (**I**), (**II**), or (**III**) with P–HI. Reduction of $(p\text{-}OH·C_6H_4·CMe:)_2$ (**V**) gives mainly resin from which (**I**) can be isolated in very small amount. The smooth production of (**III**) from (**V**) and H_2–Pd in AcOH establishes the constitution of the former. $[p\text{-}OH·C_6H_4·CEt(OH)]_2$ with red P and HI affords PhOH, δ-p-*hydroxyphenylhexan*-γ-*one*, m.p. 67—68° [*monobenzoate*, m.p. 66—67°; *oxime* (? mixture of forms), m.p. 84—86°, softens at 74°], and a *substance*, $C_{18}H_{20(22)}O_2$, m.p. 226—227° (slight decomp.) (*diacetate*, m.p. 102—104°, softens at 101°). The mechanism of the reactions is discussed (see also A., 1944, III, 810). H. W.

Rearrangement of *iso*dialkylstilbœstrols to dialkylstilbœstrols.—See B., 1944, III, 216.

(A) Mechanism of the cleavage of ethers of the anisole type by Grignard mixtures. (B) Action of Grignard solutions on α-bromoketones. A. Schönberg and R. Moubasher (*J.C.S.*, 1944, 462—463).—(A) PhOMe and related substances undergo fission with Et_2O–Mg halides, resembling that with Grignard mixtures: PhOMe + $MgHal_2$ → $[MgHal·OPhMe]^+Hal^-$ → PhO·MgHal + MeHal. Et_2O–MgI_2 is more effective than Et_2O–$MgBr_2$ at 200—220°. $PhO·CH_2·CH:CH_2$ with Et_2O–$MgBr_2$ at 95° (in CO_2) similarly gives PhOH and $CH_2:CH·CH_2Br$.

(B) $COPh·CPh_2Br$ with MgI_2 (not $MgBr_2$) in boiling Et_2O, or $MgBr_2$ in warm PhOMe, gives $COPh·CHPh_2$. Analogous reactions with α-Br-ketones and Grignard mixtures is attributed to the $MgHal_2$ present. P. T. C.

Reduction by dissolving metals. I. A. J. Birch (*J.C.S.*, 1944, 431—436).—Methoxyalkyl- (*A*) and alkyl-benzenes with Na in liquid NH_3 in presence of MeOH, EtOH, or *tert.*-C_5H_{11}·OH as proton source undergo a 1 : 4-addition of 2 H [the products from (*A*) being converted into Δ²-*cyclo*hexenones with dil. acid and determined with 2 : 4 : 1-$(NO_2)_2C_6H_3·NH·NH_2$ or $NH_2·CO·NH·NH_2$]. (*A*) also give ~10% of the phenol by demethylation. α-$C_{10}H_7$·ONa with *tert.*-C_5H_{11}·OH thus gives 5 : 8-dihydro-α-naphthol, m.p. 74°; Na alone gives little reduction. β-$C_{10}H_7$·ONa gives 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 140°/13—14 mm.; in absence of alcohol some of an ar-*dihydro*-2-*methoxynaphthalene*, b.p. 145—150°/14 mm., is obtained after methylation (Me_2SO_4) of the alkali-sol. product. α-$C_{10}H_7·CO_2Na$ is readily reduced in absence of alcohol to 1 : 4-m.p. 75°, and, after treatment with 20% NaOH at 100° (bath), 3 : 4-dihydro-α-naphthoic acid, m.p. 112°.

Reducing *m*-$C_6H_4Me·OMe$ (**I**) in presence of MeOH yields 1-methyl-Δ¹-*cyclo*hexene and 3-*methyl*-2 : 5-*dihydroanisole*, b.p. 170—171°, characterised as 3-methyl-Δ²-*cyclo*hexenone [*semicarbazido*-*semicarbazone*, m.p. 210° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 173°]; in absence of MeOH ~50% of (**I**) is converted into *m*-$C_6H_4Me·ONa$. 6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene gives 2-keto-$\Delta^{1:9}$-octahydronaphthalene (MgMeI–CuBr gives *cis*-2-keto-9-methyldecahydronaphthalene), but no ketonic product was obtained from the 6-methoxy-5-methyl derivative. Amongst other compounds similarly prepared, the following are new: 2 : 6-, m.p. 210—211°, 4 : 6-, m.p. 175°, and (?) 3 : 4-*dimethyl*-Δ²-cyclo*hexenone*-*semicarbazone*, m.p. 193°; (?) 3 : 6-*dimethyl*-Δ²-cyclo*hexenone*-*semicarbazidosemicarbazone*, m.p. 214° (decomp.) and -2 : 4-*dinitrophenylhydrazone*, m.p. 134°; 6-*methyl*-Δ²-cyclo*hexenone*-2 : 4-*dinitrophenylhydrazone*, m.p. 122—126°; 5-*keto*-$\Delta^{4:9}$-*tetrahydrohydrindene*-*semicarbazone*, m.p. 228—230°, and -2 : 4-*dinitrophenylhydrazone*, m.p. 197—198°. With EtOH, reduction converts *m*-xylene into 2 : 5-dihydro-*m*-xylene (ozonolysis yielding CH_2Ac_2) [*nitrosochloride*, m.p. 123° (decomp.); *nitrolpiperidine*, m.p. 137°], *p*-xylene into (? 2 : 5-)dihydro-*p*-xylene (nitrosochloride, m.p. 98°; nitropiperidine, m.p. 133°), tetrahydronaphthalene into 1 : 2 : 3 : 4 : 5 : 8-hexahydronaphthalene (*nitrosochloride*, m.p. 91°), and *p*-cymene into a product (25—30%) containing γ-terpinene (nitrosochloride, m.p. 110°; nitrolpiperidine, m.p. 144°). A rule correlating reduction products with the position of substituents is stated. P. T. C.

Oxidation [of dienes].—See A., 1944, II, 317.

Photochemical properties of 1 : 4-dimethoxy-9 : 10-diphenylanthracene.—See A., 1944, I, 290.

Colchicine and related compounds. Synthesis of 2 : 3 : 4 : 5-, 2 : 3 : 4 : 6-, and 2 : 3 : 4 : 7-tetramethoxy-9-methylphenanthrene.—See A., 1944, II, 314.

***o*-*p*′-Nitrobenzamidophenol: a correction.** L. C. Raiford and N. N. Crounse (*J. Amer. Chem. Soc.*, 1944, **66**, 1240—1241).—*o*-$NH_2·C_6H_4·OH$ and *p*-$NO_2·C_6H_4·COCl$ (**I**) in dioxan–$NPhMe_2$ (cooling) give o-p′-*nitrobenzamidophenol* (**II**) (77%), m.p. 202—203°, converted by (**I**) in $CHCl_3$–C_5H_5N exothermally into o-p′-*nitrobenzamidophenyl* p-*nitrobenzoate* (**III**), m.p. 219°. The compound, m.p. 219—220°, supposed by Tingle *et al.* (A., 1907, i, 209) to be (**II**) was (**III**), but the mother-liquors obtained by their method contain some (**II**), m.p. 203—204°. *o*-$NH_2·C_6H_4·OMe$ and (**I**) in C_5H_5N–dioxan give o-p′-*nitrobenzamidoanisole*, m.p. 145·5—140°, also obtained from (**II**) by NaOMe–MeI–MeOH. R. S. C.

Structure and properties of azo-β-naphthol dyes. V. N. Ufimtzev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 351—353).—Absorption curves are compared for the azo- and hydrazone forms of 4 : 1-$NPh:N·C_{10}H_6·OH$ and 1-*p*-sulphobenzeneazo-β-naphthol (Na and Na_2 salt, $+2H_2O$), and 1-*m*-sulphobenzeneazo-2-naphthol-3-carboxyanilide (Na, $+H_2O$, and Na_2 salt, $+1·5H_2O$). The Na and Na_2 salts are formed in neutral aq. solution and EtOH–NaOEt, respectively; in dil. aq. or EtOH alkali the Na and Na_2 salts are in equilibrium. The difference in structure of *o*- and *p*-azonaphthol dyes is apparent from the shift of the absorption max. which occurs on salt formation and ionisation. With *p*-azo-dyes, the shift is towards the long-wave side; with *o*-azo-dyes it is to the opposite side in accordance with a chelate structure. A. T. P.

Bacterial chemotherapy. V. Synthesis of phenolic azo-dyes derived from sulphonamides. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 351—356).—The following are prepared from *p*-$NHR·SO_2·C_6H_4·N_2Cl$ and the appropriate phenol: *mono*- and *di*-p-*sulphamylbenzeneazoresorcinol*; p-*sulphamylbenzeneazo*-*thymol*, -*phloroglucinol*, -α-*naphthol*, and -3-*phenanthrol*; 2 : 4-*dihydroxy*-4′-*guanidinosulphonyl*-, -4′-2″-*pyridyl*-, -4′-2″-*thiazolyl*-, and -4′-2″-*thiazolinyl*-*sulphamylazobenzene*; 8-*hydroxy*-5-p-2′-*thiazolylsulphamylbenzeneazoquinoline*. F. R. S.

Azo-compounds from *o*-nitrothiophenol and its methyl ether. C. Simons and L. G. Ratner (*J.C.S.*, 1944, 421—422).—*o*-$NO_2·C_6H_4·SH$ (**I**) with *n*-C_5H_{11}·ONa in C_5H_{11}·OH at 130° gives Na_2 *azobenzene*-2 : 2′-*disulphinate* (**II**), which gives a pink free acid [dimorphous (probably) Me_2 esters, m.p. 135° and 195°, with CH_2N_2]. Acid or alkaline reduction of (**II**) or the Me esters failed to give *o*-$NH_2·C_6H_4·SO_2H$. *o*-$NO_2·C_6H_4·SMe$ (**III**) with C_5H_{11}·ONa similarly gives no sulphone but 2 : 2′-*di*(*methylthiol*)-*azobenzene*, m.p. 153—155°, and -*azoxybenzene*, m.p. 78—80° (separated by chromatographic analysis), with some *o*-$NH_2·C_6H_4·SMe$. Enolisation of the NO_2 group of (**I**) may occur; this cannot occur with (**III**). P. T. C.

Sulphones.—See B., 1944, III, 238.

Vinyl alcohols. XI. β-Phenyl-β-mesitylvinyl alcohol. R. C. Fuson, N. Rabjohn, and D. J. Byers. **XII. Oxidation of αα-diarylethylenes.** R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley (*J. Amer. Chem. Soc.*, 1944, **66**, 1272—1274, 1274—1276).—XI. β-*Phenyl*-β-*mesitylvinyl alcohol* (**I**) resembles $CMes_2:CH·OH$ (Mes = mesityl here and below). α-*Phenyl*-β-*mesitylethylene glycol* (cf. Weinstock, *Thesis*, 1936), m.p. 144—146°, is obtained from COPh·COMes by H_2–Cu chromite in EtOH at 150°/2200 lb. or from COPh·COMes or COMes·CHPh·OH by H_2–PtO_2;

with H_2SO_4–AcOH it gives $CH_2Mes{\cdot}COPh$ but with boiling conc. HCl–AcOH yields (I), m.p. 114—115°. (I) is unchanged at 175°, in conc. aq. NH_3 at 100° gives *di-β-phenyl-β-mesitylvinyl ether*, m.p. 172—174°, is not affected by O_2 in Et_2O or light petroleum (23 hr.), P–I, or hot KOH–MeOH, but slowly decomposes in air; with MgMeI it yields 0·87 CH_4. With HCl–EtOH or –MeOH it gives the *Et*, b.p. 169—170°/2 mm., or *Me ether*, m.p. 44—45°, b.p. 144—145°/0·1 mm. (oxidised by SeO_2 in boiling dioxan to COPh·COMes), respectively. In Ac_2O–C_5H_5N at room temp. (I) gives the *acetate* (II), m.p. 91—92°, with BzCl–C_5H_5N–$CHCl_3$ at the b.p. and then room temp. gives the *benzoate*, m.p. 117—117·5°, and with H_2–Raney Ni in EtOH at 150°/1700 lb. yields *β-phenyl-β-mesitylethyl alcohol*, b.p. 170—173°/4 mm. (*p-nitrobenzoate*, m.p. 124—125°). (I) is oxidised by O_3 in $CHCl_3$ to $CHPhMes{\cdot}CO_2H$ [also obtained similarly from (II)] and COPh·CHMes·OH, by $KMnO_4$–$COMe_2$ to a saturated *compound*, $C_{34}H_{34}O_2$, m.p. 152—153° (decomp.), by NaOCl to COPh·COMes, by H_2–Ni–NaOH–MeOH–H_2O to COPhMes, and by CrO_3 to an oil and small amounts of a *compound*, $(C_{12}H_{12}O)_x$, m.p. 204—205° (decomp.), and COPh·COMes. (I) has absorption max. at 2·76 and 2·84 μ. due to the OH.

XII. O_3 converts some sterically hindered $CAr_2{:}CH_2$ into $CAr_2{:}CH{\cdot}OH$. Thus, $CPhMes{:}CH_2$ gives (I), m.p. 114—115° (corr.), and small amounts of COPh·COMes and $CHPhMes{\cdot}CO_2H$, and *α-iso*durylstilbene gives *β-phenyl-β-isodurylvinyl alcohol* (III) (20%), m.p. 121·5—122°, and *phenyl*isodurylacetic *acid* (IV), m.p. 198—198·5°. With Ac_2O–C_5H_5N, (III) gives the *acetate*, m.p. 93—93·5°, with MgMeI gives 1 CH_4, and with H_2–Raney Ni in EtOH at 50°/1000 lb. gives *β-phenyl-β-isodurylethyl alcohol*, m.p. 72—73°. (IV) is also obtained from *iso*durene (V) by OH·CHPh·CO_2H and $SnCl_4$ or, by way of its *Et* ester, m.p. 57·5—58°, b.p. 188—189°/6 mm., by $CHPhBr{\cdot}CO_2H$ etc. O_3 converts *p*-$C_6H_4Me{\cdot}CMes{:}CH_2$ into *p-tolylmesitylacetic acid*, m.p. 211—212°, but no vinyl alcohol is obtained. $CH_2Ph{\cdot}COCl$–$AlCl_3$ converts (V) into iso*duryl* CH_2Ph *ketone*, m.p. 60·5—61° [and (?) *di*(*phenylacetyl*)iso*durene*, m.p. 137—137·5°], oxidised by SeO_2 and a little H_2O in boiling dioxan to syn- and anti-*Ph* iso*duryl diketone*, m.p. (VI) 65—66° (*oxime*, m.p. 87—87·5°) and 63—63·5° (*oxime*, m.p. 129·5—130°) or vice versa. *iso*Durylglyoxal, C_6H_6, and $AlCl_3$ at room temp. give 2 : 3 : 4 : 6-*tetramethylbenzoin*, m.p. 92—93° (*dibenzoate*, m.p. 133—135°, of the enediol), oxidised by I–NaOMe in boiling MeOH to (VI). H_2–Raney Ni in EtOH at 150—175°/2000 lb. reduces (VI) to *α-phenyl-β-isodurylethylene glycol*, m.p. 131·5—132°, whence boiling, conc. HCl–AcOH yields (III).

R. S. C.

Acyloxyaralkyl nitriles.—See B., 1944, II, 305.

Antibacterial action of derivatives and analogues of *p*-aminobenzoic acid. O. H. Johnson, D. E. Green, and R. Pauli (*J. Biol. Chem.*, 1944, **153**, 37—47).—See A., 1944, III, 830. The following are stated to be new (analyses given) but no details of prep. are recorded: 4-*amino*-2-*acetamidobenzoic acid*, m.p. 205°; p-*acetamidomethylbenzoic acid*, m.p. 191°; 2-p-*aminobenzamidothiazole*, m.p. 257—258°; p-*aminobenzoyl*-l-*glutamic acid*; 5-*nitrothiophen*-2-*carboxylamide*, m.p. 191°; 5-*aminothiophen*-2-*carboxylamide hydrochloride*; 5-*acetamido*-2-*thienyl Me ketone*, m.p. 279°; 2-*aminothiazole*-5-*carboxylic acid*, m.p. 191°. M.p. are corr.

E. C. W.

Preparation and catalytic reduction of γ-nitro-β-butyl *p*-nitrobenzoate.—See A., 1944, II, 317.

Oxidation of aromatic amino-acids, tyrosine, tryptophan, and phenylalanine. B. B. Drake and C. V. Smythe (*Arch. Biochem.*, 1944, **4**, 255—263).—Phenylalanine is not oxidised by $KMnO_4$ or cerox (Ce^{III} NH_4 sulphate). Tryptophan shows no end-point with 4 equivs. of either oxidant. Tyrosine shows an end-point with 3 equivs. of cerox; the impure oxidation product was isolated, some of its properties are described, and an oxidation mechanism is suggested.

E. R. S.

Mono-iodotyrosine. C. R. Harington and (Mrs.) R. V. Pitt Rivers (*Biochem. J.*, 1944, **38**, 320—321).—Diazotisation [$Ba(NO_2)_2$ in dil. H_2SO_4] of 3-amino-*l*-tyrosine and treatment with KI and Cu-bronze gives 3-*iodo*-l-*tyrosine*, m.p. 204—206° (decomp.), $[\alpha]_D^{20}$ −4·4° in N-HCl. 3-*Nitro*-dl-*tyrosine*, m.p. 214—215° (decomp.) (prep. from *dl*-tyrosine and dil. HNO_3 at <25°), is reduced to the NH_2-compound, m.p. 288° (decomp.), and converted into the *I*-derivative (+H_2O), m.p. 200—201° (decomp.), which appears to be identical with the compound obtained by Ludwig *et al.* (A., 1939, II, 369). That isolated by Herriott (A., 1942, III, 172) is not identical with either of the compounds.

F. R. S.

***In-vitro* formation of thyroxine from di-iodotyrosine.**—See A., 1944, III, 728.

Acetolysis of esters. S. G. Cohen (*J. Amer. Chem. Soc.*, 1944, **66**, 1395—1397).—After boiling in AcOH–Ac_2O (35 : 2 by vol.) for 20 hr. 17% of $Bu^{\gamma}OBz$ was recovered, 87% of the remainder was isolated as BzOH, but only 8·5% of $Bu^{\gamma}OAc$ was formed. After keeping for 2 days with a little *p*-$C_6H_4Me{\cdot}SO_3H$ (I) in Ac_2O–AcOH at room temp. only 25% of $Bu^{\gamma}OBz$ is recovered, and of the remainder 65% is obtained as $Bu^{\gamma}OAc$, 61% as BzOH, and 6·5% as $CMe_2{:}CH_2$; acetolysis is rapid at the b.p. (76% in 2·5 hr.) but no $Bu^{\gamma}OAc$ is obtained. With (I) in boiling Ac_2O–AcOH for 24 hr. 69·7% of $Pr^{\beta}OBz$ is unchanged and of the remainder 57% appears as BzOH and 58% as $Pr^{\beta}OAc$; EtOBz and MeOBz are substantially (88%) unchanged under these conditions and no ROAc or BzOH is obtained. $Pr^{\alpha}CO_2Et$ is unchanged by KOAc in boiling Ac_2O–AcOH, but only 55% of $CCl_3{\cdot}CO_2Bu$ is recovered after similar treatment, 65% of the remainder being obtained as BuOAc. $CCl_3{\cdot}CO_2Bu$ is unaffected by (I) in AcOH at 115°. Reaction mechanisms are discussed.

R. S. C.

Derivatives of dialkoxyphthalides. R. H. F. Manske and A. E. Ledingham (*Canad. J. Res.*, 1944, **22**, **B**, 115—124).—2 : 3 : 1-$(OMe)_2C_6H_3{\cdot}CO_2H$, HCl, and 40% CH_2O yield 3 : 4-*dimethoxy*-6-*chloromethylphthalide* (CO=2) (I), m.p. 106°, *di*-(4 : 5-*dimethoxy*-3-*carboxy*-2-*hydroxymethylbenzyl*) *ether dilactone*, m.p. 213°, and a little meconine. Reduction (Zn–HCl–EtOH) of (I) affords 3 : 4-*dimethoxy*-6-*methylphthalide*, m.p. 127°, also prepared from 2 : 3 : 5 : 1-$(OMe)_2C_6H_2Me{\cdot}CO_2H$, CH_2O, and HCl. 3 : 2 : 1-$OMe{\cdot}C_6H_3(OEt){\cdot}CO_2H$ with CH_2O–HCl yields 4-*methoxy*-3-*ethoxy*-6-*chloromethylphthalide* (II), m.p. 130°, hydrolysed (H_2O) to the 6-*OH*·CH_2 derivative, m.p. 120°, and converted by MeOH–NaCN into 4-*methoxy*-3-*ethoxy*-6-*cyanomethylphthalide*, b.p. 145°/2 mm., m.p. 132°, which is hydrolysed (NaOH) to 4-*methoxy*-3-*ethoxy*-6-*carboxymethylphthalide*, m.p. 151°. Reduction of (II) with Zn–HCl–EtOH gives 4-*methoxy*-3-*ethoxy*-6-*methylphthalide* (III), m.p. 119°. 2 : 5 : 3 : 1-OH·$C_6H_2Me(OMe){\cdot}CHO$ (IV), m.p. 77° (improved prep.; lit., an oil) (*oxime*, m.p. 165°), is methylated (Me_2SO_4–NaOH) to 2 : 3-*dimethoxy*-5-*methylbenzaldehyde*, m.p. 40° (*oxime*, m.p. 99°), which with $CH_2(CO_2H)_2$, C_5H_5N, and piperidine gives 2 : 3-*dimethoxy*-5-*methylcinnamic acid*, m.p. 188°, reduced (Na–Hg) to β-2 : 3-*dimethoxy*-5-*methylphenylpropionic acid*, m.p. 63°. 3-*Methoxy*-2-*ethoxy*-5-*methylcinnamic acid*, m.p. 168°, prepared by ethylation of (IV) followed by $CH_2(CO_2H)_2$ etc., is reduced (Na–Hg) to β-3-*methoxy*-2-*ethoxy*-5-*methylphenylpropionic acid*, m.p. 100°. Oxidation ($KMnO_4$) of 3 : 5 : 2 : 1-$OMe{\cdot}C_6H_2Me(OEt){\cdot}CHO$ gives 3-*methoxy*-2-*ethoxy*-5-*methylbenzoic acid*, m.p. 89°, which with CH_2O–HCl yields (III). Creosol acetate with $AlCl_3$ in $PhNO_2$ at 80° gives 3-*hydroxy*-4-*methoxy*-6-*methylacetophenone*, m.p. 129°, with a little of the 3 : 4-(*OH*)$_2$-derivative, m.p. 169°, both of which with Me_2SO_4–NaOH give 3 : 4-*dimethoxy*-6-*methylacetophenone*, m.p. 76°. This yields *oximino*-3 : 4-*dimethoxy*-6-*methylacetophenone*, m.p. 122°, hydrolysed (NaOH) to 3 : 4 : 6 : 1-$(OMe)_2C_6H_2Me{\cdot}CO_2H$. The following are also described; 3-*methoxy*-2-*ethoxycinnamic acid*, m.p. 152° [from the aldehyde and $CH_2(CO_2H)_2$], reduced (Na–Hg) to β-3-*methoxy*-2-*ethoxyphenylpropionic acid*, m.p. 64°; 4-*methoxy*-3-*ethoxy*-2-*methylcinnamic acid*, m.p. 186°, reduced to β-4-*methoxy*-3-*ethoxy*-2-*methylphenylpropionic acid*, m.p. 121°; 2-*methoxy*-3-*ethoxycinnamic acid*, m.p. 184°, reduced to β-2-*methoxy*-3-*ethoxyphenylpropionic acid*, m.p. 66°. 2-*Methoxy*-3-*ethoxybenzoic acid*, m.p. 64°, is prepared by oxidation of the aldehyde. M.p. are corr.

J. D. R.

Iodinated acyltaurines.—See B., 1944, III, 237.

Sulphamide-amidines. I. *p*-Sulphamylbenzamidine and related compounds. R. Delaby and J. V. Harispe (*Bull. Soc. chim.*, 1943, [v], **10**, 580—584).—*p*-$CN{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and HCl in abs. EtOH at 0° give the hydrochloride, m.p. ~174° (freshly prepared; loses HCl when kept and melts at 182—183°), of the *imino Et ether*, m.p. 157°, converted by NH_3 in abs. EtOH into p-*sulphamylbenzamidine*, m.p. 251° (*hydrochloride*, m.p. 242°).

A. T. P.

Theory of biogenesis of lichen depsides and depsidones. T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **20**, **A**, 1—14).—Lichen depsides and depsidones are considered to arise from a common source, 2 : 3 : 5 : 1-$CHO{\cdot}C_6H_2(OH)_2{\cdot}CH_2{\cdot}OH$, which originates from aldol condensation between a hexose and a biose with elimination of H_2O. Oxidation and reduction lead to various modifications of this unit and increase in the length of the side-chain arises from condensation with simple sugars and reduction. Depsides are formed by the combination of two of these units. β-Orcinol derivatives are obtained by nuclear methylation by CH_2O and this reaction in general takes place prior to depside formation, though the other possibility is not altogether excluded as far as the left half of the mol. is concerned. Depsidones come last in the evolution; they are based on depsides and require oxidation or dehydrogenation involving $C_{(5)}$ which is *para* to the activating OH. Nuclear oxidation also occurs without leading to depsidone formation; either $C_{(3)}$ or $C_{(5)}$ is involved and *meta*-depsides result. Oxidation involving the left half is also possible and is represented by diploschistesic acid. The occurrence of orcinol and psoromic acid is attributed to decarboxylation occurring in the plant.

H. W.

Preparation of homophthalyl and 4-aminohomophthalyl cyclic hydrazides. W. F. Whitmore and R. C. Cooney (*J. Amer. Chem. Soc.*, 1944, **66**, 1237—1240).—*o*-$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ (I), readily obtained in 58% yield from indene by $K_2Cr_2O_7$–H_2SO_4–H_2O at the b.p., with AcCl or, better, Ac_2O gives the anhydride (II), which with N_2H_4,H_2O in boiling EtOH yields cyclic *homophthalhydrazide* (III) (80%), m.p. 298—300°. (III) could not be obtained from the Me_2 ester or imide of (I) and the diacid chloride of (I) could not be prepared. (III) behaves as a monoenol towards aq. NaOH (phenolphthalein); it gives no Ac derivative but in boiling AcOH gives

N-*aminohomophthalimide*, m.p. 147—148° (N'-*Ac* derivative, m.p. 239—240°), which is also obtained from (II) by N_2H_4,H_2O in boiling AcOH. 2 : 4 : 1-$CO_2H{\cdot}C_6H_3(NO_2){\cdot}CH_2{\cdot}CO_2H$ [obtained from (I) by fuming HNO_3 or, better, KNO_3–H_2SO_4] in boiling AcCl gives the *anhydride* (70%), m.p. 154—155°, which with N_2H_4,H_2O in AcOH at 100° gives cyclic 4-nitrohomophthalhydrazide (70%), amorphous, m.p. 248—250° (decomp.), reduced by H_2–Raney Ni in aq. NaOH to cyclic 4-*aminohomophthalhydrazide*, m.p. 210—212° (decomp.; rapid heating) or decomp. ~200—320° (slow heating) (N^4-*Ac* derivative, m.p. >320°). With H_2O_2–NaOH the cyclic hydrazides are much less luminescent than is phthalhydrazide. R. S. C.

Nitrones. III. Condensation of 2 : 4 : 6-trinitrotoluene with arylnitroso-compounds. I. Tănăsescu and I. Nanu (*Ber.*, 1942, **75**, [*B*], 1287—1292; cf. A., 1939, II, 323).—Contrary to Radulescu *et al.* (A., 1939, II, 537), nitrones and not additive NH_2OH compounds are formed from 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ (I) and *o*-, *m*-, or *p*-$C_6H_4Me{\cdot}NO$ or *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ (II). (I) and *o*-$C_6H_4Me{\cdot}NO$ in boiling EtOH containing Na_2CO_3 or piperidine or in C_5H_5N containing I at 40—50° afford 2 : 4 : 6-*trinitrophenyl*-N-*o*-*tolylnitrone*, m.p. 147—148° (explosion), the constitution of which follows from its behaviour when heated, its partial hydrolysis by HCl to 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}CHO$ (III), and its isomerisation by AcCl in hot $COMe_2$ to 2 : 4 : 6-*trinitrobenz*-*o*-*toluidide*, m.p. 259° (decomp.) (*Ac* derivative, m.p. 200°), identical with the product obtained from 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}COCl$ and *o*-toluidine in boiling C_6H_6. 2 : 4 : 6-*Trinitrophenyl*-N-m-*tolylnitrone*, m.p. 157° (explosion), obtained similarly, is isomerised to 2 : 4 : 6-*trinitrobenz*-m-*toluidide*, m.p. 209·5° (*Ac* derivative, m.p. 185°). Similarly 2 : 4 : 6-*trinitrophenyl*-N-p-*tolylnitrone*, m.p. 151° (explosion), is isomerised to 2 : 4 : 6-*trinitrobenz*-p-*toluidide*, m.p. 217° (*Ac* derivative, m.p. 210°). With $NHPh{\cdot}NH_2$ in acid solution all these nitrones afford 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}CH{:}N{\cdot}NHPh$ in small yield. Hydrolysis is accompanied by a marked phenolic odour. (I) and (II) gives the somewhat unstable 2 : 4 : 6-trinitrophenyl-*N*-*p*-dimethylaminophenylnitrone, characterised by its tendency towards explosion and hydrolysis to (III) and *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$. H. W.

Synthesis of aromatic amino-aldehydes and amino-ketones. W. Hao-Tsing (*J. Amer. Chem. Soc.*, 1944, **66**, 1421—1422).—When NH_2Ph is gently heated with HCN–HCl–Et_2O, a brown oil is pptd., which, when further heated at 250—300° and then boiled in aq. KOH, gives *p*-$NH_2{\cdot}C_6H_4{\cdot}CHO$. NH_2Ph with MeCN–HCl–Et_2O similarly gives *p*-$NH_2{\cdot}C_6H_4{\cdot}COMe$. Reagents and conditions must be anhyd. The oily intermediates are probably $NH{:}CR{\cdot}NHPh$, rearranged by heat to *p*-$NH_2{\cdot}C_6H_4{\cdot}CR{:}NH$, which is hydrolysed by the KOH. The reaction may be general. R. S. C.

Structure of *o*-hydroxybenzaldazines. H. von Euler, E. Adler, and J. Ettlinger (*Arkiv Kemi, Min., Geol.*, 1944, **17**, **A**, No. 16, 15 pp.).—1 : 4 : 2 : 6-$OH{\cdot}C_6H_2Me(CHO)_2$ (I) and $COEt{\cdot}NH{\cdot}NH_2$ or $(CO{\cdot}NH{\cdot}NH_2)_2$ in dil. EtOH give respectively *hydroxyuvitinaldehydedi*(*propionylhydrazone*) (II), m.p. 239—241° (also +2AcOH), and amorphous polyhydroxyuvitinaldehydedi(oxalylhydrazone) (III), no definite m.p. (II) is converted readily by boiling dil. mineral acid into *hydroxyuvitinaldazine* (IV), m.p. 278—280°, best obtained by the gradual addition of $N_2H_4,2HCl$ in 50% EtOH to (I) in the same solvent. Under similar conditions (III) affords polyhydroxyuvitinaldazine (V), decomp. >360°, also obtained from (I) and N_2H_4,H_2O in EtOH or, preferably, in presence of AcOH; it has pronounced indicator properties. (IV) is sparingly sol. in dil. NaOH, freely in KOH; it cannot be methylated by CH_2N_2 or KOH–Me_2SO_4 and does not give an Ac derivative. The stability of (IV) and (V) towards dil. mineral acids suggests the possibility of a quinonoid structure, which, however, is less probable for (V). This hypothesis is strengthened by the less intense colour of *methoxyuvitinaldazine* (VI), m.p. 234—235°, and the amorphous polymethoxyuvitinaldazine (VII) obtained from methoxyavitinaldehyde and N_2H_4 in acid and neutral solution, respectively. The hydrochloride of (V) is very stable towards heat (117°/12 mm.); this property is shared to some extent by the hydrochloride of *o*-methoxybenzaldazine but not by those of (IV), (VI), (VII), salicylaldazine, and benzaldazine. Examination of the equilibrium $(CHR{:}N{\cdot})_2 + 2H_2O \rightleftharpoons 2RCHO + N_2H_4$ in presence of acid shows no difference in stability between hydroxy- and methoxy-aldazines. Since only the aldazine structure is possible for the latter compounds there appears no reason to assume a peculiar (quinoid) constitution for the former substances and the greater resistance of the azomethine group (in comparison with PhCHO) must be ascribed to steric hindrance. The most probable structure for *o*-hydroxyaldazines is the "normal" benzenoid form with co-ordinatively united bridge H. The individuality of (IV) is in harmony with the occurrence of mesomerism. *Methoxyuvitinaldehydedi*(*propionylhydrazone*) has m.p. 295°. H. W.

2 : 3 : 5 : 8-Tetramethoxy-6 : 7-dimethyl-1-naphthaldehyde. R. Adams and Z. W. Wicks (*J. Amer. Chem. Soc.*, 1944, **66**, 1315—1316).—Attempts to prepare OH-naphthaldehydes having the properties of gossypol failed. Pure *o*-xyloquinone and $[CH_2{:}C(OMe)]_2$ at 140° give 6 : 7-dimethoxy-2 : 3-dimethyl-1 : 4-naphthaquinone (I) (77—82·5%), m.p. 248—249° (lit. 241—242°), which by hydrogenation (H_2–Raney Ni; MeOH; 50°/1500 lb.) and thereafter immediate methylation (Me_2SO_4–KOH–H_2O–$Na_2S_2O_4$) yields 1 : 4 : 6 : 7-*tetramethoxy*-2 : 3-*dimethylnaphthalene* (73%), m.p. 151—152°. With $HCO{\cdot}NPhMe$ and $POCl_3$ at the b.p. this gives 2 : 3 : 5 : 8-*tetramethoxy*-6 : 7-*dimethyl*-1-*naphthaldehyde* (67%), m.p. 135—136°, which yields normally a *phenylhydrazone*, m.p. 156—157°, and *oxime*, m.p. 155—156° (with boiling Ac_2O yields 2 : 3 : 5 : 8-*tetramethoxy*-6 : 7-*dimethyl*-1-*naphthonitrile*, m.p. 122·5—123°). Reductive acetylation of (I) gives 1 : 4-*diacetoxy*-6 : 7-*dimethoxy*-2 : 3-*dimethylnaphthalene* (91%), m.p. 180·5—181°. No cryst. phenols could be obtained from the OMe-products. M.p. are corr. R. S. C.

Cinnamylideneacetone tetrabromide. P. Duquénois and Z. Sezer (*Rev. Fac. Sci. Istanbul*, 1943, **8**, **A**, 158—159).—$CHPh{:}CH{\cdot}CH{:}CH{\cdot}COMe$ and Br in Et_2O give a red oil from which *cinnamylideneacetone tetrabromide*, m.p. 173·5° (slight decomp.) (cf. Diehl *et al.*, A., 1885, 1221), is isolated by repeated crystallisation from EtOH. H. W.

Synthesis of model substances for the ligninsulphonic acids. Synthesis of α-phenylacetone-α-sulphonic acid and propioveratrone-α-sulphonic acid. A. von Wacek, K. Kratzl, and A. von Bézard (*Ber.*, 1942, **75**, [*B*], 1348—1357).—$CHPhAcBr$, from CH_2PhAc and Br in anhyd. Et_2O, is converted by KCNS in EtOH into α-thiocyano-α-phenylacetone (I), m.p. 51—52°, and by KSAc and KSBz in EtOH into α-*acetylthiol*- (II), b.p. 157—158°/12 mm., m.p. 31°, and α-*benzoylthiol*-, m.p. 58°, -α-*phenylacetone*, respectively. (II) is smoothly hydrolysed by alkali (but not by acid) to α-*thiol*-α-*phenylacetone* (III), m.p. 108—110° (*Hg* derivative, m.p. 124—126°). Chlorination of an aq. suspension of (I) gives, in proportion varying with the experimental conditions, $CHPhAcCl$, unchanged material, and an α-*thiocyano*-α-*chlorophenylacetone*, m.p. 56·5°. Similar treatment of (II) affords $CHPhAcCl$ and somewhat impure (?) αα-*dichloro*-α-*phenylacetone*, m.p. 120—125° (oxidation gives BzOH). Oxidation of (III) with NaOCl in C_6H_6–Et_2O–H_2O gives the *disulphide*, m.p. 108°, and a residue converted into an unidentified *benzylthiuronium* salt, m.p. 164°. Similar treatment of (II) appears to give no disulphide; mixtures of benzylthiuronium salts which cannot be separated are obtained. A well-stirred mixture of $CHPhAcBr$ and boiling aq. Na_2SO_3 gives *Na* α-*phenylacetone*-α-*sulphonate*, m.p. 204—206°, isolated through the *benzylthiuronium* salt, m.p. 140—141°. Similarly bromopropioveratrone affords *Na propioveratrone*-α-*sulphonate* (corresponding *benzylthiuronium* salt, m.p. 153°). H. W.

New reagent for primary and secondary amines. A. J. Birch (*J.C.S.*, 1944, 314—315).—*cyclo*Hexene nitrosochloride warmed with C_5H_5N gives 1-(2'-*oximino*cyclo*hexyl*)*pyridinium chloride* (+H_2O), m.p. 125°, which when heated in 10% Na_2CO_3 with the hydrochloride of the base gives 2-*oximino*cyclo*hexyl* derivatives (m.p. in parentheses) of the following: $NHMe_2$ (120°), NH_2Pr^{α} (72°), NH_2Bu^{α} (81°), NH_2Bu^{β} (73°), NH_2Bu^{γ} (91°), $NHEt_2$ (63°), morpholine (118°), and *n*-$C_7H_{15}{\cdot}NH_2$ (66°). The derivative from piperidine has new m.p. 116° (lit. 119°). *cyclo*Hexylamine gives 2-*oximinodi*cyclo*hexylamine*, m.p. 145°. E. W. W.

Synthesis of possible degradation products of metathebainone. II. H. L. Holmes and L. W. Trevoy (*Canad. J. Res.*, 1944, **22**, **B**, 109—114; cf. A., 1944, II, 281).—$(CH_2{\cdot}CO)_2O$ and veratrole yield (method: Fieser *et al.*, A., 1937, II, 20) β-3 : 4-*dimethoxy*- (I) and some β-4-*hydroxy*-3-*methoxy*-*benzoylpropionic acid* (II), m.p. 131—131·5°, reduced (Clemmensen) to γ-4-*hydroxy*-3-*methoxyphenylbutyric acid*, m.p. 114—116°. (II) with KOH–Et_2SO_4 gives β-3-methoxy-4-ethoxybenzoylpropionic acid, m.p. 139—140° (lit. 136—137°), the orientation of which is proved by oxidation ($KMnO_4$) of the Et ester to 3 : 4 : 1-$OMe{\cdot}C_6H_3(OEt){\cdot}CO_2H$, also prepared from vanillin. Prep. of (I) is modified to give 83%. M.p. are corr. J. D. R.

Stereochemistry of cyclanes. XII. Polybenzyl*cyclo*hexanones; isolation of four *o*-dibenzyl*cyclo*hexanones of which three are almost certainly 2 : 6-derivatives. R. Cornubert, P. Anziani, M. André, M. de Demo, and G. Morelle (*Bull. Soc. chim.*, 1943, [v], **10**, 561—565; cf. A., 1939, II, 164).—The 2 : 6-dibenzyl*cyclo*hexanone (I), new m.p. 105° (*oxime*, m.p. 123°; *semicarbazone*, m.p. 164—165°) (cf. A., 1939, II, 324), prepared by benzylation of 2-benzyl*cyclo*hexanone, could not be obtained by hydrogenating dibenzylidene*cyclo*hexanone; the latter method affords isomerides, m.p. 122° and 55°, of (I) (cf. A., 1934, 279), convertible by CH_2PhCl–$NaNH_2$–Et_2O into 2 : 2 : 6-tribenzyl-, m.p. 61—62°, and 2 : 2 : 6 : 6-tetrabenzyl-*cyclo*hexanone (II), m.p. 174°. (II) is also obtained by dibenzylating (I) or the 2 : 2-isomeride, m.p. 69—70° (cf. A., 1932, 161). (I) is not isomerised by HCl. With Na–EtOH, (I) yields probably an impure *sec.* alcohol, but with H_2–PtO_2–Et_2O it gives probably a 2 : 6-dihexahydrobenzyl*cyclo*hexanol (*phenylurethane*, m.p. 132—134°). A. T. P.

Synthesis of compounds related to santonin. (Miss) K. D. Paranjape, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 381—384).—α-(2-Hydroxy-4-formyl-3-keto*cyclo*hexyl)propiolactone, $COMe_2$, and EtOH–NaOEt give α-1-*hydroxy*-7-*keto*-$\Delta^{5:8}$-*hexahydro*-2-*naphthylpropiolactone*, m.p. 91°; $COMeEt$ similarly affords the corresponding 8-*Me* derivative, m.p. 111°. α-(2-Hydroxy-4-formyl-3-keto-4-methyl*cyclo*hexyl)propiolactone

condenses similarly with $COMe_2$ to *α-1-hydroxy-7-keto-10-methyl-*$\Delta^{5:8}$*-hexahydro-2-naphthylpropiolactone*, m.p. 141° (semicarbazone, m.p. 201°). F. R. S.

3 : 4-Benzfluorenones. I. Effect of groups on their formation and their fission with alkali. F. G. Baddar and M. Gindy (*J.C.S.*, 1944, 450—452).—Factors governing the point of cleavage of 3 : 4-benzfluorenones and mode of cyclisation of 1-phenylnaphthalene-2'-carboxylic acids are of polar, and not steric, origin. 4 : 2-$C_{10}H_6I{\cdot}OMe$ (I) and *o*-$C_6H_4I{\cdot}CO_2Me$ with Cu-bronze at 200—210° give *3-methoxy-1-phenylnaphthalene-2'-carboxylic acid*, m.p. 191—192°, cyclised (P_2O_5–C_6H_6) to *1-methoxy-3 : 4-benzfluorenone*, m.p. 148—150°, and 2-methoxy*meso*benzanthrone (little). 3 : 1 : 2-$C_6H_3I(CO_2Et)_2$ with 1-$C_{10}H_7I$ and Cu-bronze at 210° (bath) gives 1-phenylnaphthalene-2' : 3'-dicarboxylic acid, m.p. 178—179° (slow), 192—193° (rapid heating) [*Me_2* ester, m.p. 133—134°; *anhydride* (II), m.p. 179—180°]. Cyclisation of (II) (CS_2–$AlCl_3$) yields 3 : 4-*benzfluorenone-8-carboxylic acid* (III), m.p. 276—276·5° (little), and *meso*benzanthrone-8-carboxylic acid, m.p. 262—263° (lit. 254—255°) (Me ester, m.p. 173·5—174·5°). *1-Phenylnaphthalene-2 : 4'-dicarboxylic acid* (IV), m.p. 265—266° (from *p*-$C_6H_4I{\cdot}CO_2Me$ and 1 : 2-$C_{10}H_6Br{\cdot}CO_2Me$), gives on ring-closure (chloride with $AlCl_3$–CS_2) only 3 : 4-*benzfluorenone-7-carboxylic acid* (V), m.p. 323—324°. (III) with KOH at 225—230° gives *1-phenylnaphthalene-2 : 3'-dicarboxylic acid*, m.p. 255—256°, whilst (V) gives a mixture of (IV) and (probably) 1-phenylnaphthalene-2' : 4'-dicarboxylic acid. (I) is obtained (diazo-method) in poor yield from 4 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}OMe$ (*Ac* derivative, m.p. 179°); 2-hydroxy-1 : 4-naphthaquinone [which may arise from 1 : 4-$C_{10}H_6(OH)_2$] is isolable from the many by-products. *Et* 3-p-*toluenesulphonamidophthalate* has m.p. 147—148°. P. T. C.

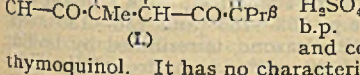
2-Methyl-2-phytyl-2 : 3-dihydro-1 : 4-naphthaquinone.—See B., 1944, III, 218.

Hydrolysis of quinoneoximes. W. T. Sumerford and D. N. Dalton (*J. Amer. Chem. Soc.*, 1944, **66**, 1330—1331).—Hydrolysis of quinone mono-oximes by Cu_2O (1 mol.) in boiling HCl–$COMe_2$–H_2O–methylcellosolve or in HCl–$COMe_2$–H_2O at room temp. gives good yields (55—92% in 9 out of 11 examples) of the parent quinone. The methods of Karrer *et al.* (A., 1939, II, 335) and Tseng *et al.* (A., 1934, 1005; 1944, II, 166) are less satisfactory. R. S. C.

Molecular compounds of the quinhydrone type in solution. L. Michaelis and S. Granick (*J. Amer. Chem. Soc.*, 1944, **66**, 1023—1030).—The absorption of light (λ 300—550 mμ.) by solutions containing mixtures of a quinone (*Q*) with a benzenoid substance (*B*) that combine to form a compound of the quinhydrone type is due almost entirely to the compound, and has been used to detect and obtain a relative measure of the extent of such combination with various pairs of components. It is assumed that the concn. *m* of the compound is always small compared with that of the components, so that the association const. $k = m/[Q][B]$ can be taken to refer to the initial concns. of *Q* and *B*. The measured optical absorption $[(I_0 - I)/I_0]$, after correction (often negligible) for the components, is divided by the known val. of $[Q][B]$ to obtain ε_{st}, which is related to the mol. extinction coeff. $\varepsilon_{mol.}$ for the compound by $\varepsilon_{st} = k\varepsilon_{mol.}$; the vals. of ε_{st} are then $\propto m$, although the abs. val. of *m* is not known. The following pairs of substances were studied in EtOH and, sometimes, in C_6H_6, light petroleum, or 0·05N-HCl: (*a*) *p*-O:C_6H_4:O (I)–quinol, (I)–resorcinol, *p*-O:C_6Cl_4:O–C_6Me_6, duroquinone–durohydroquinol; (*b*) (I)–PhOH, (I)–*p*-OH·C_6H_4·OMe; (*c*) (I)–*s*-$C_6H_3(OH)_3$; (*d*) (I)–PhOR, (I)–*p*-$C_6H_4(OR)_2$ (R = Me, Et). Combination occurs in all the mixtures, and is $\propto$ both [*Q*] and [*B*]; hence the compound formed is in every case *QB*. Since the substances in groups (*a*), (*b*), and (*c*) form solid compounds *QB*, QB_2, and Q_2B respectively, whilst those in (*d*) form no solid compounds, it appears that the structure of the compounds formed in solution differs from that of the solids. H linkings are not necessary, and the affinity of (I) for a phenol is approx. the same as for its ethers. It is suggested that combination in solution involves a planar superposition of the rings. F. L. U.

Naphthaquinone 2 : 3-oxides.—See B., 1944, II, 305.

Dithymoquinone. L. I. Smith and R. W. H. Tess (*J. Amer. Chem. Soc.*, 1944, **66**, 1323—1325).—Dithymoquinone (prep. described) is probably (I). It is unchanged by H_2SO_4 (little) in Ac_2O, by AcCl or PCl_3 at room temp., H_2SO_4–MeOH, or $FeCl_3$–EtOH at the b.p. It is resinified by HBr–AcOH and converted by $Na_2S_2O_4$ slowly into thymoquinol. It has no characteristic absorption. R. S. C.



(I.)

IV.—STEROLS AND STEROID SAPOGENINS.

Steroids and specificity of the Pettenkofer reaction. I. Qualitative studies. G. W. Kerr and W. M. Hoehn (*Arch. Biochem.*, 1944, 4, 155—158).—The Schmidt modification (A., 1942, III, 755) of Pettenkofer's reaction was applied to 43 steroids; 12 give a positive result. All steroids with OH at $C_{(7)}$, or a group easily converted into OH, give a positive result as well as Δ^3-, Δ^5-, and Δ^8-monocholenic acids and their esters. αβ-Unsaturated ketones gave a negative result. Dehydro-*trans*-androsterone gave a positive result. E. R. S.

Preparation and properties of ergosteryl iodide. A. Jendrassik (*Biochem. Z.*, 1941—1942, **311**, 402—407).—Ergosterol with I powder in a little $CHCl_3$ at room temp. gives a stable *iodide*, $C_{28}H_{44}OI_2$ ($+H_2O$), m.p. 92° (absorption max. at 370 and 298 mμ.), which has no antirachitic power (daily dose 2 μg.) even after irradiation, and is converted by Na_2S–$CHCl_3$–0·1N-HCl (little) into an I-free compound, m.p. 127° [not pptd. by digitonin; absorption max. at 275 mμ.; no antirachitic power (daily dose 2 μg.) even after irradiation]. W. McC.

Bile acid derivatives.—See B., 1944, III, 216.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Halogen derivatives of 1 : 8-cineole. R. Delaby and A. Billuart (*Bull. Soc. chim.*, 1943, [v], **10**, 567—573).—Cineole (I) is chlorinated by Cl_2–CCl_4–aq. $CaCO_3$ in sunlight or artificial light (cf. Gandini, A., 1933, 830; 1937, II, 295). Raman spectra of resulting fractions, b.p. (*a*) 118—121°, (*b*) 121—123°, (*c*) 123—125°, (*d*) 125—127°, and (*e*) 127—129°, all at 50 mm., are examined; (*a*) and (*b*) and some of (*c*) probably contain *cis*- and *trans*-2-chlorocineole, and (*d*) and (*e*) the 3-isomeride, but no definite conclusions are reached. Dehalogenation is difficult, but prolonged boiling (90 hr.) with AcOH and AgOAc or KOAc gives some OAc-derivative, b.p. 118—123°/50 mm., hydrolysed by boiling NaOH–MeOH to *cineolic alcohol*, b.p. 108—111°/9 mm. (*allophanate*, m.p. 169°; two *phenylurethanes*, m.p. 140° and 188°, corresponding probably to the *cis*- and *trans*-alcohols). (I) and Br–CCl_4–aq. $CaCO_3$ yield some cis- or/and trans-*2-bromocineole*, b.p. 93—95°/4 mm. Oxidation of *l*-pinene or *d*-α-pinene by BzO_2H–$CHCl_3$ gives the respective oxides. Similarly prepared is *αβ-oxidoheptan-γ-ol*, b.p. 86—89°/10 mm., which is hydrolysed by boiling H_2O (+HCl) to *n*-butylglycerol, m.p. 53·5°. Similarly, vinyl*iso*butylcarbinol (*allophanate*, m.p. 147·5°) affords the *oxide*, b.p. 93—97°/20 mm., hydrolysed to iso*butylglycerol*, b.p. 173—174°/16 mm. A. T. P.

Rearrangement of santenonequinone. R. N. Chakravarti (*Current Sci.*, 1944, **13**, 158).—*dl*-Santenonequinone with conc. H_2SO_4 gives 2 : 3-*dimethyl*cyclo*hexan-1-one-4-carboxylic acid* (I), m.p. 132° (*semicarbazone*, m.p. 191°), which is oxidised (HNO_3) to *α-methylbutane-αβδ-tricarboxylic acid*, m.p. 181—182°, also obtained by condensing $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ with $CO_2Et{\cdot}CHMe{\cdot}CH(CN){\cdot}CO_2Et$ followed by hydrolysis. Et αβ-dimethylacrylate with $CN{\cdot}CH_2{\cdot}CO_2Et$ and NaOEt affords a Na salt, which with $Cl{\cdot}[CH_2]_2{\cdot}COEt$ yields *Et γ-cyano-αβ-dimethylpentane-αγε-tricarboxylate*, b.p. 200—204°/6 mm. This on hydrolysis and subsequent esterification gives *Et αβ-dimethylpentane-αγε-tricarboxylate*, b.p. 178°/7 mm., which is cyclised (Na) to *Et* 2 : 3-*dimethyl*cyclo*hexan-1-one-4* : 6-*dicarboxylate*, b.p. 170°/8 mm., hydrolysed to (I). F. R. S.

Sesquiterpenes. LXIV. Addition of acetylenedicarboxylic ester, azodicarboxylic ester, and maleic anhydride to caryophyllene. P. A. Plattner and L. Werner [with, in part, N. Clauson-Kaas] (*Helv. Chim. Acta*, 1944, **27**, 1010—1016).—Adducts of the type *A* (R = $\cdot N(CO_2Et){\cdot}NH{\cdot}CO_2Et$, $\cdot C(CO_2Me){:}CH{\cdot}CO_2Me$, or $\cdot CH<\begin{matrix}CO-O\\CH_2-CO\end{matrix}>$) are described. Caryophyllene *B* (I) and $(:C{\cdot}CO_2Me)_2$ at 180° according to experimental conditions give varying amounts of polymeric compounds, possibly owing to the non-homogeneity of (I). A mixture of stereoisomerides is probably present in the monomeric condensation product, which gives the dicarboxylic *acid* (II), $C_{19}H_{26}O_4$, m.p. 122—123°, [α] +77·2° in $CHCl_3$, in only 25% yield. (II) affords a non-cryst. *Me_2* ester, b.p. 180—190°/1 mm., $[\alpha]_D$ +79·3° in $CHCl_3$, which gives a yellow colour with $C(NO_2)_4$. (II) is hydrogenated to a non-cryst. H_6-acid, the *Me_2* ester, b.p. ~180°/1 mm., α_D −11°, of which is converted by Mg, MeI, and NH_2Ph into the dianilide, m.p. 228° (vac.), $[\alpha]_D$ +39° in $COMe_2$, identical with the *trans*-tetrahydrodicarboxyanilide obtained from (I) and $(:CH{\cdot}CO)_2O$. The adducts from (I) and $(:C{\cdot}CO_2Me)_2$ or $(:CH{\cdot}CO)_2O$ therefore have the same C skeleton and must be produced by a similar reaction scheme. (I) and $(:N{\cdot}CO_2Et)_2$ react rapidly at room temp. but only ~15% of the product could be isolated as the cryst. *adduct*, $C_{21}H_{34}O_4N_2$, m.p. 139°, $[\alpha]_D$ +39° in $CHCl_3$; this evolves 2 CO_2 when hydrolysed by acid but does not yield cryst. products. The behaviour of $(:N{\cdot}CO_2Et)_2$ indicates the presence of C:C·C in (I). Unknown catalytic influences appear to affect the reaction between (I) and $(:CH{\cdot}CO)_2O$; the yield of additive product is increased by prolongation of the change and by use of an increased proportion of anhydride, but the quantities of polymeride are also thereby increased. Unchanged (I) resembles the original material in *d* and *n* but $[\alpha]_D$ is appreciably lower. Feebly dextrorotatory fractions may be obtained from it by distillation. M.p. are corr. H. W.

(A.)

Triterpenes. LXXXVIII. Friedelin and cerin. L. Ruzicka, O. Jeger, and P. Ringnes (*Helv. Chim. Acta*, 1944, **27**, 972—988; cf. Drake, A., 1936, 1386).—The presence of the group $\cdot CH_2\cdot CH_2\cdot CO\cdot CH\cdot CH<$ in friedelin (**I**) and cerin (**II**) which is now established shows that the structure of the terminal ring in these compounds differs from that of the oleanolic series. The isolation of (**I**), m.p. 248—250° (open capillary), 264—265° (vac.), $[\alpha]_D$ −27·8°, and of (**II**), m.p. 250—254° (open capillary), $[\alpha]_D$ −41·2°, from cork is described. *enol*Friedelin benzoate (**III**) has m.p. 246—249° (open capillary), 265—266° (high vac.), $[\alpha]_D$ +64·1°. (**I**) is reduced by N_2H_4,H_2O–NaOEt in EtOH at 200—220° to friedelan, m.p. 243—244°, $[\alpha]_D$ +41·8°, saturated towards $C(NO_2)_4$ and identical with the compound obtained by Clemmensen's method. Under different conditions, oxidation of (**I**) by CrO_3 in AcOH gives varied proportions of friedelonic acid (**IV**) (Me ester, m.p. 153—154·5°, $[\alpha]_D$ +11·8°) and *friedelindicarboxylic acid* (**V**), $C_{30}H_{50}O_4$, m.p. 288° (decomp.), $[\alpha]_D$ +21·4° [*Me*$_2$ ester, m.p. 174—176°, $[\alpha]_D$ +9·8°; *anhydride* (**VI**), m.p. 264—265° (decomp.), $[\alpha]_D$ +74·6°]. (**II**) is oxidised by CrO_3 (=6 O) in AcOH–CCl_4 at room temp. to (**V**) and enol*friedelandione*, $C_{30}H_{48}O_2$, m.p. 265—267°, $[\alpha]_D$ +18·5° (*acetate*, m.p. 283—285°, $[\alpha]_D$ +3°; *benzoate*, m.p. 301—303°, $[\alpha]_D$ +25·7°; *quinoxaline* derivative, m.p. 244—246°), which gives a dark brown colour with $FeCl_3$ and a feebly positive test with $C(NO_2)_4$. (**III**) is oxidised by CrO_3 in AcOH at 100° to (**IV**) and *enol*friedelandione benzoate, m.p. 302—304° (decomp.), $[\alpha]_D$ +24·1°. Thermal decomp. of (**VI**) leads to an amorphous *norfriedelanone* (**VII**) and a fraction, m.p. 231—232°, $[\alpha]_D$ −83·7°, also obtained by subliming (**VI**) at 210°/high vac., showing that CO of (**I**) lies in a terminal ring of the skeleton. SeO_2 in boiling AcOH oxidises (**VII**) to *norfriedelenone*, $C_{29}H_{46}O$, m.p. 260—261°, $[\alpha]_D$ −108°, reduced (Clemmensen) to (**VII**), whereas in dioxan at 200° the oxidation product is *norfriedelenedione* (**VIII**), $C_{29}H_{44}O_2$, m.p. 269—270°, $[\alpha]_D$ +241° (*quinoxaline* derivative, m.p. 240—240·5°), which is saturated towards $C(NO_2)_4$, does not give a colour with $FeCl_3$, cannot be acetylated, and is greatly decomposed by KOH–MeOH. (**III**) is oxidised by SeO_2 in dioxan at 170° to (**VIII**), also obtained by the similar oxidation of *enol*friedelandione benzoate. $Pb(OAc)_4$ or H_2O at 80° oxidises (**VIII**) to a *compound*, $C_{29}H_{44}O_3$, m.p. 236·5—237°, $[\alpha]_D$ −40·9°, which does not give a colour reaction with $C(NO_2)_4$ or $FeCl_3$ and is unaffected by 5% KOH–EtOH at 100°. (**VIII**) is transformed by Br in AcOH into *nordibromofriedelenone*, m.p. 197° (decomp.), $[\alpha]_D$ +63·6°, transformed by boiling KOH–MeOH to enol*norfriedelenedione*, m.p. 260—261°, $[\alpha]_D$ +179·5° [*acetate*, m.p. ~256° (decomp.), $[\alpha]_D$ +208°]. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

Saponins and sapogenins. XXV. Norechino- and *iso*norechinocystenedione. J. F. Carson, D. B. Cosulich, and C. R. Noller. **XXVI. Conversion of echinocystic acid into oleanolic acid.** D. Frazier and C. R. Noller. **XXVII. Structure of triterpenoids.** C. R. Noller (*J. Amer. Chem. Soc.*, 1944, **66**, 1265—1267, 1267—1268, 1269—1271; cf. A., 1944, II, 343).—XXV. *iso*Norechinocystenedione (**I**) is unchanged by hot Ac_2O–C_5H_5N and, except for a little tar-formation, by MeI–Ag_2O, but with boiling Ac_2O–KOAc or HCl–MeOH or –EtOH gives norechinocystenedione (**II**), m.p. 203—205°, $[\alpha]_D^{29}$ −94·2°, $[\alpha]_{5460}^{28}$ −113° in dioxan [dioxime, m.p. 246—249° (decomp.; bath preheated at 225°), $[\alpha]_D^{23}$ −127° to −128°, $[\alpha]_{5460}^{25}$ −136° in dioxan]. With BuSH–HCl (but not either alone) in hot EtOH, (**I**) gives a conjugated, isomeric *dione* (**III**), m.p. 236—242°, $[\alpha]_D^{25}$ +45·3°, $[\alpha]_{5460}^{26}$ +56·1° in $CHCl_3$ [*oxime*, m.p. 269—271° (decomp.; bath preheated at 200°), $[\alpha]_D^{25}$ −23·4° in dioxan], having absorption max. at 252 mμ. (log ε 4·10). Purification of (**II**) gives a product having a single absorption max. at 294 mμ. (log ε 1·98) (cf. A., 1939, II, 517); the impurity is not (**III**), since prolonged treatment of (**II**) with alkali yields only a small amount of (**I**). The change, (**I**) ⟷ (**II**), is thus reversible.

XXVI. Me echinocystate acetate, in which the OH β to the CO_2H is free, with $MeSO_2Cl$–C_5H_5N gives *Me echinocystate acetate methanesulphonate* (**IV**), decomp. ~165°, which with NaI in $COMe_2$ at 100° gives *Me anhydroechinocystate acetate* (**V**), m.p. 192—193°, $[\alpha]_D^{23}$ +19·5°, $[\alpha]_{5460}^{23}$ +22·2° in $CHCl_3$, hydrolysed by hot, conc. HCl–MeOH to *Me anhydroechinocystate* (**VI**), m.p. 177°, resolidifies, remelts at 192—193°, or, after drying at 110°, m.p. 192—193°, $[\alpha]_D^{23}$ +18·3°, also obtained directly from (**IV**) by MeOH at 140°. Hydrogenation (PtO_2; AcOH) of (**VI**) or (**V**) gives Me oleanolate, m.p. 199—200°, $[\alpha]_D^{25}$ +73·2°, $[\alpha]_{5460}^{26}$ +86·7° in $CHCl_3$, and the acetate thereof, m.p. 219—220°, $[\alpha]_D^{24}$ +69·7°, $[\alpha]_{5460}^{24}$ +84·7° in $CHCl_3$, respectively. Thus echinocystic acid (**VII**) differs from oleanolic acid only in containing an OH β to the CO_2H.

XXVII. Current formulæ for the triterpenoids of the β-amyrin series are inadequate for (**II**), (**VII**), and various absorption spectra. Absorption max. at 258, 248, and 241 mμ. (log ε 4·31, 4·47, and 4·42, respectively) are recorded for the Me keto-ester, $C_{31}H_{46}O_3$, derived from (**VII**). R. S. C.

VI.—HETEROCYCLIC.

Crossed Cannizzaro reactions—benzaldehyde and furfuraldehyde. S. E. Hazlet and R. B. Callison (*J. Amer. Chem. Soc.*, 1944, **66**, 1248—1250).—Shaking 1 mol. each of PhCHO and furfuraldehyde with aq. NaOH gives a ~5 : 3 mixture of $CH_2Ph\cdot OH$ and furfuryl alcohol and a mixture (~3 : 5) of BzOH and 2-furoic acid. For analysis see C., 1945, Part 1. R. S. C.

Antibacterial substance from *Aspergillus clavatus*. F. Bergel, A. L. Morrison, A. R. Moss, and H. Rinderknecht (*J.C.S.*, 1944, 415—421).—An antibacterial substance, clavatin (**I**), m.p. 109·5—110·5°, has been isolated from *A. clavatus* metabolism solution, and is identical with claviformin and most probably with patulin. Additional evidence is presented for its structure which confirms the formulæ advanced by Raistrick *et al.* (cf. A., 1944, III, 219). The results of oxidative and other degradations suggest the existence of predominant tautomeric forms such as anhydro-4-hydroxy-5-hydroxymethyl- and -5 : 6-dihydro-1 : 2-pyran-6-carboxylic acid. (**I**) is acylated and etherified under unusually mild conditions, forming a monoacetate, *monobenzoate*, m.p. 143·5—144·5°, and *Me$_2$ ether*, m.p. 69—71°; (**I**) forms an *oxime*, m.p. 152—153° (decomp.) (*monoacetate*, m.p. 82—84°). Hydrogenation (≡3—4 H_2) (H_2–Pd–C) of (**I**) in EtOH–H_2O gives a lactone (?) and other products. With HBr the crude hydrogenation product yields a small amount of a *lactone monobromide*, $C_7H_{11}O_2Br$, b.p. 175—180°/15 mm. (*piperidino hydriodide*, $C_{12}H_{22}O_2NI$, m.p. 170—171°), hydrogenated to β-(*α′-bromo*-n-*propyl*)*butyrolactone*, which affords a phenylhydrazide identical with that from β-*n*-propylbutyrolactone. Ozonolysis of (**I**) gives HCO_2H and glyoxal and traces of $H_2C_2O_4$. HCl (dry) with (**I**) in EtOH at −10° affords an oil, $C_{11}H_{17}O_3Cl$, b.p. 114—116°/0·15 mm. [2 : 4-*dinitrophenylhydrazones* (from EtOH), m.p. 168—170° (decomp.), and (from MeOH), m.p. 164—166° (decomp.) (not identical)], hydrolysed with dil. acid to 3-*chloromethylenetetrahydro-γ-pyrone*-2-*carboxylic acid*, m.p. 129—130° (2 : 4-*dinitrophenylhydrazone*, m.p. 189—190°). This acid with HI yields ε-iodo-γ-ketohexoic acid and on hydrogenation (H_2–Pd–C) gives 3-*methyltetrahydro-γ-pyrone*-2-*carboxylic acid* (S-*benzylthiuronium* salt, m.p. 149—150°; p-*phenylphenacyl* ester, m.p. 125—127°; 2 : 4-*dinitrophenylhydrazone*, m.p. 197—199°). The latter acid with HI forms *αε-di-iodo-γ-keto-β-methylhexoic acid*, m.p. 103—105°, hydrogenated to γ-keto-β-methyl-*n*-hexoic acid (S-*benzylthiuronium* salt, m.p. 144·5—145·5°). F. R. S.

Triacetone alcohol and its dehydration products.—See A., 1944, II, 360.

4-Hydroxy-3-methylcoumarin oxime, m.p. 95°.—See A., 1944, III, 717.

Optically active tocols and degradation products of phytol and phytadiene. P. Karrer, A. Kugler, and H. Simon (*Helv. Chim. Acta*, 1944, **27**, 1006—1009).—Slight dextrorotation of εη-dimethyltocol acetate in EtOH and of the εθ-compound in substance is observed but the activity of the ηθ-derivative remains uncertain; the substances are derived from natural phytol. Oxidation ($Na_2Cr_2O_7$–50% H_2SO_4) of Me δθμ-trimethyltridecyl ketone (obtained by ozonolysis of natural *d*-phytol) affords *d*-δθμ-trimethyltridecoic acid (**I**), b.p. 138—144° (bath)/high vac. (p-*bromophenacyl* ester, m.p. 53°; p-*xenylamide*, m.p. 99—100°). Phytadiene is ozonised to (**I**), CH_2O, and small amounts of MeCHO; it therefore consists mainly of $Bu^{\beta}\cdot[CH_2]_2\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_2\cdot CH{:}CMe\cdot CH{:}CH_2$, with a small proportion of $Bu^{\beta}\cdot[CH_2]_2\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CH{:}CH\cdot CMe{:}CHMe$. H. W.

Reaction between quinones and metal enolates. XIX. Structure of diduroquinone. L. I. Smith, R. W. H. Tess, and G. E. Ullyot (*J. Amer. Chem. Soc.*, 1944, **66**, 1320—1323; cf. A., 1944, II, 103).—Diduroquinone (**I**), m.p. 207·5—208°, obtained from duroquinone by a little KOH in 95% EtOH at room temp. (cf. Rugheimer *et al.*, A., 1896, i, 68), is probably 7-*hydroxy*-2 : 3 : 5 : 6 : 8 : 4a : 9a-*heptamethyl*-4a : 9a-*dihydroxanthen*-1 : 4-*quinone*. With MgMeI it gives 0·81 CH_4 and 2·05 mols. are added, but this is unreliable since its *Et ether* (prep. by EtBr–KOH in boiling EtOH), m.p. 130—131°, adds 1·84 MgMeI and gives 0·52 CH_4. With hot Ac_2O, (**I**) gives an acetate (**II**), +*x*EtOH, m.p. (dried at 100°) 132—133°. $FeCl_3$ in boiling EtOH oxidises (**I**) to 6-*hydroxy*-5-3′ : 4′ : 6′-*trimethyl*-2′ : 5′-*benzquinon*-1′-*ylmethyl*-2 : 3-*dimethyl*-5 : 6-*dihydro*-p-*benzoquinone* (**III**), m.p. ~132—138°, reduced by $Na_2S_2O_4$ to 6-*hydroxy*-5-3′ : 6′-*dihydroxy*-2′ : 4′ : 5′-*trimethylbenzyl*-2 : 3-*dimethyl*-5 : 6-*dihydro*-p-*benzoquinone* (**IV**), m.p. ~144—149°, whence H_2SO_4–MeOH at room temp. regenerates (**I**). M.p. of (**III**) and (**IV**) are approx. and variable owing either to decomp. or steric isomerism. $SOCl_2$ at the b.p. converts (**I**) into substances, m.p. 153—155° and 136—138°. (**I**) gives no oxime or dinitrophenylhydrazone, is resinified by boiling KOH–EtOH or conc. H_2SO_4 at 60—65°, is unaffected by HCl–AcOH or HBr–AcOH, and in HI–AcOH gives duroquinol, which is also obtained by H_2–Cu chromite in EtOH, Zn–AcOH, Zn–HCl, or (?) Na–Hg–EtOH (not by $Na_2S_2O_4$) and from (**III**) by Zn–AcOH. (**I**) has an absorption max. at ~290 mμ. (ε ~3000). R. S. C.

4 : 4-Dimethyl-5-ethoxymethyl-*m*-dioxan.—See B., 1944, II, 306.

Synthesis of cantharidin and deoxycantharidin. (Miss) K. D. Paranjape, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 385—388).—$(CMeAc\cdot CO_2Et)_2$ (from

CNaMeAc·CO_2Et and I in C_6H_6) with Br in CS_2–$AlCl_3$ (trace) gives *Et₂ αα′-di-(bromoacetyl)-αα′-dimethylsuccinate*, m.p. 55°, which with Ag at 120—150° gives Et_2 3 : 6-diketo-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylate (**I**) (*di-p-nitrophenylhydrazone*, m.p. 143°). Reduction (Zn–Hg) of (**I**) followed by hydrolysis and steam-distillation affords 1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylic anhydride [deoxycantharidin]. Reduction of (**I**) with $Al(OPr^{\beta})_3$ yields Et_2 3 : 6-dihydroxy-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylate (*acid*, m.p. 99°), which with conc. H_2SO_4 gives 3 : 6-oxido-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylic anhydride (separated by sublimation), identical with an authentic specimen of cantharidin. F. R. S.

Pyrrolidines and piperidines.—See B., 1944, II, 306.

Preparation of derivatives of pyrrole and pyridine by hydrogenation. H. A. Adkins, I. A. Wolff, A. Pavlic, and E. Hutchinson (*J. Amer. Chem. Soc.*, 1944, **66**, 1293—1295).—Hydrogenolysis of C–NH_2 occurs readily when β, but not when γ, to the N of pyrrole or C_5H_5N. Pyrrole with MgEtBr and then AcCl in Et_2O gives 2-acetylpyrrole, m.p. 88—89°, the oxime, m.p. 144—145°, of which with H_2–Raney Ni in dioxan or EtOH at 130°/200 atm. gives 2-α-aminoethylpyrrole (56%), which decomposes when distilled and is isolated as *Bz* derivative, m.p. 149—150°. 3-α-Oximinoethylpyridine at 100° gives similarly 3-α-aminoethylpyridine (74%), b.p. 112—113°/12 mm., 223°/740 mm. [*phenylthiocarbamide* derivative, m.p. 139—140°; picrate, m.p. 204—205°; *platinichloride*, m.p. 280° (decomp.)], and *di-(α-3-pyridylethyl)amine* (11%), b.p. 152—153°/1 mm. [*platinichloride*, m.p. 292° and 161—163°; *picrate*, m.p. 205° (decomp.)]. The *oxime*, m.p. 197—198°, of Et 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate (**I**) (prep. from CH_2Ac_2, OH·N:CAc·CO_2Et, and Zn dust in AcOH) with H_2–Rancy Ni at 130°/200 atm. gives Et 2 : 4-dimethyl-3-α-aminoethylpyrrole-5-carboxylate (80%), isolated as *Bz* derivative, m.p. 179—180°, and converted by distillation into *Et 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate*, m.p. 110·5—112°, b.p. 145—148°/3 mm. 3 : 5-Diacetyl-2 : 4-dimethylpyrrole gives the *5-mono-oxime*, m.p. 240° (decomp.), hydrogenated at 140—150° to *3-acetyl-2 : 4-dimethyl-5-ethylpyrrole* (30—36%), m.p. 159—160° (? 106—107°). Hydrogenation of (**I**) at 170° gives Et 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylate (95%). That of the *oxime*, m.p. 162—163°, of Et 5-acetyl-2 : 4-dimethylpyrrole-3-carboxylate at 130° gives *Et 2 : 4-dimethyl-5-ethylpyrrole-3-carboxylate* (94%), m.p. 106—107°. That of 3-cyanopyridine at 130° gives 3-pyridylmethylamine (42%), b.p. 112°/18 mm. [picrate, m.p. 210—211° (decomp.); dihydrochloride, m.p. 222°; *p*-nitrobenzoyl derivative, m.p. 188—189°], and *di-3-pyridylmethylamine* (48%), b.p. 147—148°/? mm. (*platinichloride*, m.p. >300°; *picrate*, m.p. 218—220°). Et β-keto-β-3-pyridylpropionate at 80° yields, by hydrogenation and dehydration, unstable Et β-3-pyridylacrylate, b.p. 136—138°/3 mm. (*hydrochloride*, m.p. 186—187°). R. S. C.

Absorption spectra of pyrrole-blue *A* and *B*.—See A., 1944, I, 265.

Chemistry of bivalent and tervalent rhodium. VI. Pyridine complexes of rhodous halides. F. P. Dwyer and R. S. Nyholm (*J. Proc. Roy. Soc. New South Wales*, 1942, **76**, 275—280).—$RhCl_3$ with KBr and C_5H_5N followed by H_3PO_2 at 100° gives *hexakis-pyridine rhodous bromide*, converted by HBr at 0° into the *bromo-pentakis* compound (*iodide*), which with aq. HBr affords *dibromo-tetrakis-pyridine rhodium*. EtOH–HBr with the latter compound yields *dibromo-hexakis-pyridine μ dibromodirhodium*, which on long boiling with EtOH–HBr is converted into a mixture of *bis-pyridinium-tetrabromo-tetrakis-pyridine μ dibromodirhodium* and *tetrakis-pyridinium-hexabromobis-pyridine dibromodirhodium* (both red-brown) and a highly H_2O-sol. compound hexakis-pyridinium-octabromodibromodirhodium. The hexakis compounds are yellow. In the chloride and iodide series certain of the compounds could not be isolated. *Hexakis-* and *chloropentakis-pyridine rhodous chloride*, *bis-pyridinium tetrachlorotetrakis-* and *tetrakis-pyridinium hexachlorobis-pyridine μ dichlorodirhodium*, and *hexakis-* and *iodopentakis-pyridine rhodous iodide* are described. F. R. S.

Co-ordination compounds derived from nicotinylacetone. F. Lions, B. S. Morris, and E. Ritchie (*J. Proc. Roy. Soc. New South Wales*, 1942, **76**, 294—303).—Nicotinylacetone (**I**) (*picrate*, m.p. 155°) forms a *methiodide*, m.p. 184°, which with NaOEt gives a *betaine*. $(CH_2{\cdot}NH_2)_2$ with (**I**) yields *ββ′-ethylenediaminobis(propenyl-3-pyridyl ketone)*, m.p. 170°. The following complexes are described: *Cu nicotinylacetonate*, chars at >320°, *bisnicotinylacetone Cu chloride*, m.p. 190°, and *sulphate* chars at ~280°, *Cu bisnicotinylacetone α-bromocamphor-π-sulphonate* (which could not be resolved), *Zn nicotinylacetonate*, chars at >300°, *bisnicotinylacetone Zn chloride*, m.p. 140°, and *sulphate*, m.p. >300°, *Zn bisnicotinylacetonate α-bromocamphor-π-sulphonate* (non-resolvable), *Ni bisnicotinylacetonate*, chars at >300°, *bisnicotinylacetone Ni chloride*, chars at >300°, and *sulphate*, *Co bisnicotinylacetonate*, *bisnicotinylacetone Co chloride*, *bisnicotinylacetone Ag nitrate*, m.p. 121°, *Fe^{III} nicotinylacetonate*, m.p. >300°, *bisnicotinylacetone Fe^{III} chloride*, m.p. >300° (mol. wt. abnormal), *trisnicotinylacetone Cr^{III} chloride* (+$4H_2O$), m.p. 105°, *Cu bisnicotinylacetonate methiodide* (+$4H_2O$), m.p. 188° [*Zn* (+$6H_2O$), m.p. 146°, and *Be* complexes, m.p. 214°], *Cu ethylenediamine bisnicotinylacetonate* (+H_2O), m.p. 167° (*dihydrochloride*, m.p. 200°), and *Zn*, m.p. 228° (*dihydrochloride*, m.p. 253°), *Ni* (+H_2O), m.p. 258° (*dihydrochloride*, m.p. 276°), and *Co* (+$6H_2O$) complexes, m.p. 165° [*dihydrochloride*, m.p. 242° (decomp.)]. F. R. S.

Pyridine-3-acetic esters and quaternary compounds.—See B., 1944, II, 306.

Biochemical and bacteriostatic actions of salicylic acid and salicylnicotinylamide. H. von Euler and B. Högberg [with H. Hasselquist] (*Arkiv Kemi, Min., Geol.*, 1944, **17**, **B**, No. 14, 8 pp.).—*Salicylnicotinylamide*, m.p. 205°, is obtained in 35% yield by the interaction of *o*-OH·C_6H_4·CO·NH_2 and nicotinyl chloride hydrochloride in C_5H_5N at 110° (see A., 1944, III, 844). H. W.

Preparation of pyridine-2 : 5-dicarboxylic acid. T. O. Soine (*J. Amer. Pharm. Assoc.*, 1944, **33**, 223—224).—Quinaldine (20 c.c.) in conc. H_2SO_4 (40 c.c.) is oxidised by cautious addition of HNO_3 (~300 c.c.) with ultimate heating to 230—240°; 7—8 hr. are required. The crude dicarboxylic acid (14·5 g.) is pptd. by addition of 50% NaOH almost to complete neutralisation and cooling to room temp. Decolorising with C and crystallising from H_2O gives the pure acid, m.p. 238° [Me_2 ester, m.p. 161—163°; diamide, m.p. 310—313° (decomp.)]. F. O. H.

Aminosulphanilamidopyridines.—See B., 1944, III, 186.

Catalytic hydrogenation of hydroxy-pyridines and -quinolines and their esters. C. J. Cavallito and T. H. Haskell (*J. Amer. Chem. Soc.*, 1944, **66**, 1166—1171).—Aroyl esters of 2- and 4-hydroxypyridine and -quinoline are more readily hydrolysed than those of the other OH-bases. The 4-acyloxy-compounds must be prepared under anhyd. conditions. The ester linkage of 2-acyloxyquinoline is weakened by 4-Me. Esters described below are prepared from ArCOCl with the OH-compound at 150° or in C_5H_5N at 100° or with the Na derivative thereof in Et_2O. Hydrogenation (Pd; dioxan or, sometimes, EtOH; 55°) of alcohols and esters of these series is reported; its course is various. 2-Hydroxypyridine gives 2-piperidone (**I**), but 3- (**II**) and 4-hydroxypyridine are unaffected. 1-Hydroxy*iso*quinoline gives 1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (**III**), m.p. 73° (lit. 71°). 3-, 5- (**IV**), 6-, 7-, and 8-Hydroxyquinolines give the corresponding hydroxy-1 : 2 : 3 : 4-tetrahydroquinolines (the 3-*OH*-compound has m.p. 93°), but 2-hydroxyquinoline gives 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline (**V**), and 4-hydroxy- (**VI**), 2-hydroxy-4-methyl- (**VII**), and 4-hydroxy-2-methylquinoline (**VIII**) are unchanged. 2-Benzoyloxypyridine, m.p. 47° (lit. 42°), gives PhMe and (**I**); *3-benzoyloxypyridine*, m.p. 51°, is unchanged; *4-benzoyloxypyridine*, m.p. 79°, gives PhMe and 4-hydroxypyridine. *2-β-Naphthoyloxypyridine*, m.p. 116°, gives 2-$C_{10}H_7$Me and (**I**). 2-p-*Benzyloxybenzoylpyridine*, m.p. 123—125°, gives *p*-cresol and (**I**). *2-3′ : 4′ : 5′-Tribenzyloxybenzoylpyridine*, m.p. 116°, gives 1 : 3 : 4 : 5-C_6H_2Me$(OH)_3$ and (**I**), but *3-3′ : 4′ : 5′-tribenzyloxybenzoylpyridine*, m.p. 120°, gives *3-3′ : 4′ : 5′-trihydroxybenzoylpyridine*, m.p. 180—185°. *2-Benzoyloxyquinoline*, m.p. 95°, gives PhMe and (**V**); *4-benzoyloxyquinoline*, m.p. 131°, gives PhMe and (**VI**); 3-, m.p. 67°, 5-, m.p. 93°, 6-, m.p. 118° (lit. 230°), and 7-benzoyloxyquinoline, m.p. 85° (lit. 88°), give the derived *benzoyloxy-1 : 2 : 3 : 4-tetrahydroquinolines*, m.p. 106°, 107°, 102°, and 117°, respectively; 8-benzoyloxyquinoline, m.p. 118°, gives *8-hydroxy-1-benzoyl-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 174°. *1-Benzoyloxyisoquinoline*, m.p. 187°, gives PhMe, (**III**), and the *2-Bz* derivative, m.p. 132°, of (**III**). *2-β-Naphthoyloxyquinoline*, m.p. 125°, gives PhMe and (**V**). *2-Benzoyloxy-4-methylquinoline*, m.p. 76°, gives PhMe and (**VII**). *2-3′ : 4′ : 5′-Tribenzyloxy-*, m.p. 117°, and *2-3′ : 4′ : 5′-triacetoxy-benzoyloxyquinoline*, m.p. 133°, give (**V**) and 1 : 3 : 4 : 5-C_6H_2Me$(OR)_3$ (R = H and Ac, respectively). *8-p-Benzyloxybenzoyloxyquinoline*, m.p. 163°, gives *8-hydroxy-1-p-hydroxybenzoyl-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 161°. *2-Hydroxy-8-benzoyloxyquinoline*, m.p. 208°, gives *2-keto-8-benzoyloxy-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 167°, also obtained with PhMe from *2 : 8-dibenzoyloxyquinoline*, m.p. 108°. *1-Benzoyl-8-benzoyloxy-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 146°, is also described. (**II**) is obtained from 3-aminopyridine by $NaNO_2$ in conc. H_2SO_4, later warm. NH_2Ph (1) and CO_2Et·CO·CH_2·CO_2Et (1 mol.) at 40—50° and then room temp. give an anil, which in mineral oil at 250° gives Et kynurenate (~60%), whence hydrolysis (4% aq. NaOH; gives the acid, m.p. 280°) and decarboxylation (mineral oil; 270°) gives (**VI**). (**IV**) is obtained from the NH_2-compound by a diazo-reaction. (**VIII**) is obtained by condensing NH_2Ph with CH_2Ac·CO_2Et and heating the product in oil at 250—260°. R. S. C.

Synthesis of oxindole. F. J. Di Carlo (*J. Amer. Chem. Soc.*, 1944, **66**, 1420).—*o*-NO_2·C_6H_4·CH_2·CO·CO_2H (prep. from *o*-C_6H_4Me·NO_2 by $Et_2C_2O_4$–NaOEt in hot EtOH and then hot aq. EtOH), m.p. 119—120°, with H_2O_2 gives *o*-NO_2·C_6H_4·CH_2·CO_2H, hydrogenation of which (AcOH; 50 lb.; PtO_2) gives oxindole (**I**) (88%) or (less PtO_2) 75% of (**I**) and some 1 : 2-dioxindole, *o*-$C_6H_4<^{CH_2}_{CO-}>$N·OH (**II**), m.p. 198—199° (*brucine* salt, m.p. 223°). (**II**) is unaffected by H_2–PtO_2; thus, the intermediate is *o*-OH·NH·C_6H_4·CH_2·CO_2H, which suffers either ring-closure to (**II**) or further hydrogenation to (**I**). R. S. C.

Dialkylaminoalkyl derivatives of substituted quinolines and quinaldines. A. M. Van Arendonk and H. A. Shonle (*J. Amer. Chem. Soc.*, 1944, **66**, 1284—1285).—4-Chloro-6-methoxyquinoline and the appropriate diamine in boiling *p*-cymene yield 4-*β-diethylaminoethylamino-*, $+H_2O$, m.p. 77—78° (hygroscopic dihydrochloride), 4-*β*-di*iso*butylaminoethylamino- (*dihydrochloride*, m.p. 250—252°), 4-*γ-diethylamino*-n-*propylamino-*, $+2H_2O$, m.p. 165—170°, 4-δ-diethylamino-α-methyl-*n*-butylamino- (dihydrochloride; picrate, m.p. 180—182°), 4-δ-*N*-methyl-*N*-butylamino-α-methyl-*n*-butylamino- (*dihydrochloride*, $+xH_2O$, m.p. 90—91°), 4-δ-*N-iso*propyl-*N-iso*butylamino-α-methyl-*n*-butylamino- (*dihydrochloride*, m.p. 157—160°), 4-δ-di*iso*butylamino-α-methyl-*n*-butylamino- (*dihydrochloride*, $+xH_2O$, m.p. 104—106°), 4-*γ-piperidino-*, m.p. 134—135°, and 4-*γ*-2′-*pipecolino*-n-*propylamino-*, m.p. 135—137°, -6-*methoxyquinoline*. Boiling 40% HBr then yields 4-*β-diethylaminoethylamino-*, m.p. 245—246°, 4-*β*-di*iso*butylaminoethylamino- (*dihydrochloride*, $+2H_2O$, m.p. 138—140°), 4-δ-diethylamino-α-methyl-*n*-butylamino- (*dihydrochloride*, m.p. 150—153°), and 4-*γ-piperidino*-n-*propylamino-*, m.p. 164—166°, -6-*hydroxyquinoline*. 4-*β-Diethylaminoethylamino-*, m.p. 145—147°, and 4-*γ*-diethylamino-*n*-propylamino- (dihydrochloride, $+2H_2O$, m.p. 125—126°) -6-methoxy-2-methylquinoline are similarly prepared. R. S. C.

Substituted quinolines. II. 2-Arylquinolines. III. 2-Arylquinolines from fluoranthene and thionaphthen. N. P. Buu-Hoï and P. Cagniant (*Rec. trav. chim.*, 1943, **62**, 713—718, 719—722).—II. Condensation in boiling alcoholic KOH of isatin (I) with the corresponding aryl Me ketone (prep. from hydrocarbon, AcCl, and $AlCl_3$) gives 2-(p-cyclo*hexylphenyl*)-, m.p. 279—280°, 2-α-*naphthyl-*, m.p. 214°, 2-*β*-naphthyl-, m.p. 240°, 2-*β-anthryl-*, m.p. 291—292° (decomp.), 2-(3′-*pyrenyl*-)-, decomp. >300°, and 2-(2′-*chrysenyl*-)-, decomp. >262°, *-cinchonic acid*. These on decarboxylation by fusion in vac. yield 2-(p-cyclo*hexylphenyl*)- (**II**), m.p. 135° (*picrate*, m.p. 162°), 2-α-*naphthyl-*, b.p. 210°/0·1 mm., m.p. 90—91° (*picrate*, m.p. 187°), 2-*β-naphthyl-*, m.p. 164° (*picrate*, m.p. 176—177°), 2-*β-anthryl-*, m.p. 180°, 2-(3′-*pyrenyl*)-, m.p. 145° (*picrate*, m.p. 260° (decomp.), and 2-(2′-*chrysenyl*)-, m.p. 185° (*picrate*, m.p. 225°), *-quinoline*. (**II**) with Se at 350° affords 2-diphenylylquinoline; 2-(5′-*acenaphthyl*)*quinoline*, m.p. 122° (*picrate*, m.p. 231—232°), is described.

III. Fluoranthene with AcCl and $AlCl_3$ in CS_2 gives 12-*acetylfluoranthene* (**III**), b.p. 210°/0·1 mm., m.p. 68° (*semicarbazone*, m.p. 240°; *oxime*, m.p. 166°, giving 12-acetamidofluoranthene by Beckmann transformation). (**III**) with (I) affords 2-(12′-*fluoranthyl*)-*cinchonic acid*, m.p. >310°, decarboxylated to 2-(12′-*fluoranthyl*)-*quinoline*, b.p. 280°/0·1 mm., m.p. 136° (*picrate*, m.p. 242°). 3-Acetylthionaphthen (modified prep.) with (I) gives 2-(3′-*thionaphthenyl*)-*cinchonic acid*, m.p. 229—230° (decomp.), and thence 2-(3′-*thionaphthenyl*)*quinoline*, b.p. 290°/15 mm., m.p. 186° (*picrate*, m.p. 201°). D. G.

Complex compounds of cupric azide. III. Non-electrolytes with organic bases.—See A., 1944, I, 290.

Hydroacridones. Synthesis and dehydrogenation. R. A. Reed (*J.C.S.*, 1944, 425—426).—*cyclo*Hexanone with *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (**I**) gives 1 : 2 : 3 : 4-tetrahydroacridone, m.p. 370° (lit. 358°), whilst with the appropriate methylanthranilic acid, 9-, m.p. 346°, 8-, m.p. 378° (*picrate*, m.p. 208—209°), 7-, m.p. 374°, 6-, m.p. 355° (*picrate*, m.p. 165—185°), and 10-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone*, m.p. 170—172° (*picrate*, m.p. 209—210°), are obtained. The methyltetrahydroacridones are dehydrogenated with Cu in air at 360° to the corresponding methylacridones. 3-Methyl*cyclo*hexanone with (**I**) affords 2-methyl-1 : 2 : 3 : 4-tetrahydroacridone [*picrate*, m.p. 212° (decomp.)] (cf. Perkin *et al.*, A., 1925, i, 64), the constitution being proved by dehydrogenation; 2-methyl*cyclo*hexanone with (**I**) yields the 1-Me compound, m.p. 305° (*picrate*, m.p. 183—184°). F. R. S.

Reaction between histidine and formaldehyde. A. Neuberger (*Biochem. J.*, 1944, **38**, 309—314).—Histidine (**I**) with 2 or more mols. of CH_2O at 37° gives 1(?1′)-*hydroxymethyl*-1′ : 2′ : 5′ : 6′-*tetrahydropyrido*-4′ : 3′-4 : 5-*glyoxaline*-6′-*carboxylic acid* ($+H_2O$), insol. in H_2O, m.p. 210—215° (decomp.), $[\alpha]_D$ −84·6° in NaOH (1·1N.), which with HCl gives CH_2O and the unmethylolated *acid* ($+2H_2O$), m.p. 277°, $[\alpha]_D$ −122·4° in N-NaOH, also obtained from (**I**) and 1 mol. of CH_2O, and decarboxylated to 1′ : 2′ : 5′ : 6′-tetrahydropyrido-4′ : 3′-4 : 5-glyoxaline, which with NaOH–BzCl affords 3 : 4-*dibenzamido*-N-*benzoyl*-1 : 2 : 5 : 6-*tetrahydropyridine*, m.p. 215°. The dissociation consts. of the two compounds have been measured and compared with those of (**I**). The kinetics of the reaction are examined and the CH_2O titration of (**I**) is discussed. F. R. S.

Glyoxalines.—See B., 1944, III, 217.

Synthesis, some derivatives, and metabolism of αγ-diketo-*n*-octoic acid. A. L. Lehninger (*J. Biol. Chem.*, 1944, **153**, 561—570).—$COMeBu^{\alpha}$ (**I**) and $Et_2C_2O_4$ in NaOEt–EtOH at the b.p., followed by H_2SO_4, give the *Et* ester (**II**), b.p. 138—139°/13 mm., of αγ-diketo-octoic acid (**III**), liquid (*Ba* salt). The structure of (**II**) is established by condensation with $NHPh{\cdot}NH_2$ to the Et ester of an acid oxidised to 1-phenylpyrazole-3 : 5-dicarboxylic acid. In 2N-NaOH at the b.p., (**III**) gives (**I**) and $H_2C_2O_4$. In EtOH with aq. $Cu(OAc)_2$, (**II**) gives a chelated *Cu* derivative, $C_{20}H_{30}O_8Cu$, m.p. 135—137°. With 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ and conc. HCl, (**II**) gives the *Et* ester, m.p. 186—187°, of 1-(2′ : 4′-*dinitrophenyl*)-5(3)-*butylpyrazole*-3(5)-*carboxylic acid*, m.p. 204° (decomp. from 185°), which is similarly obtained from (**III**). With semicarbazide hydrochloride, the Na salt (**IV**) of (**III**) gives 1-*carboxylamido*-5(3)-*butylpyrazole*-3(5)-*carboxylic acid*, decomp. from 80—82° (clear melt at 160—165°), hydrolysed by boiling H_2O to 5-*butylpyrazole*-3-*carboxylic acid*, m.p. 166—167°, also obtained from (**III**) and N_2H_4. Intestinal absorption of aq. (**IV**) by rats is small. (**IV**) does not affect the O_2 uptake of surviving rat tissue slices in PO_4'''–saline buffer, possibly owing to low diffusability, since it causes a slight increase in O_2-uptake by minced or homogenised liver. (**III**) is decarboxylated only very slowly by yeast decarboxylase, and inhibits the yeast decarboxylation of $AcCO_2H$. Hexadecan-*β*-one condenses with $Et_2C_2O_4$ to give a C_{20}-diketo-ester. E. W. W.

Production of riboflavin deficiency with phenazine analogues of riboflavin. D. W. Woolley (*J. Biol. Chem.*, 1944, **154**, 31—37).—Amino-5-ribitylamino-*o*-xylene with picryl chloride and NaOAc in aq. EtOH at room temp. gives 2′ : 4′ : 6′-*trinitro*-2-*ribitylamino*-4 : 5-*dimethyldiphenylamine*, which on boiling with NaOAc in EtOH yields 1 : 3-*dinitro*-7 : 8-*dimethyl*-5-*ribityl*-5 : 10-*dihydrophenazine*, m.p. 218—220° (decomp.), reduced (Sn–20% HCl or autoclaving in presence of reduced Fe) to the corresponding $(NH_2)_2$-compound. The diamino- and, to a smaller extent, the dinitro-phenazine derivative produce riboflavin deficiency in bacteria and mice, respectively (cf. A., 1944, III, 752). P. G. M.

***N*-Chlorocarbamic esters.**—See A., 1944, II, 364.

Guanamine derivatives.—See B., 1944, II, 249.

5-Sulphanilamidotetrazole. K. A. Jensen and O. R. Hansen (*Rec. trav. chim.*, 1943, **62**, 658—660; cf. Veldstra and Wiardi, *ibid.*, 627).—The compound, m.p. 170°, obtained from 5-aminotetrazole (**I**) and *p*-NHAc·$C_6H_4{\cdot}SO_2Cl$ (**II**) in C_5H_5N gives AcOH, *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$, $CO(NH_2)_2$, and N_3H with aq. NaOH, and is claimed to be 5-acetylsulphanilamidotetrazole (**III**). The compound, m.p. 202°, from (**I**) and (**II**) in aq. Na_2CO_3, which with aq. NaOH affords *p*-NHAc·$C_6H_4{\cdot}SO_3H$ and (**I**), is considered to be 1- or 2-acetylsulphanilyl-5-aminotetrazole. (**I**) with *p*-NHAc·$C_6H_4{\cdot}SO_2F$ in C_5H_5N does not yield (**III**). D. G.

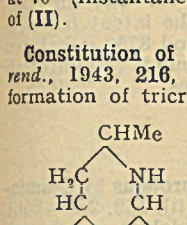
Sulphanilamide derivatives. II. 5-Sulphanilamidotetrazole. H. Veldstra and P. W. Wiardi (*Rec. trav. chim.*, 1943, **62**, 661—671).—In reply to the preceding abstract the authors claim that 5-acetylsulphanilamidotetrazole exists in three tautomeric forms. 5-Aminotetrazole (**I**) with *p*-NHAc·$C_6H_4{\cdot}SO_2Cl$ (**II**) in C_5H_5N gives tetrazoloneacetylsulphanilylimide(-5) (**III**), m.p. 166° (170° on rapid heating), which behaves like a monobasic acid on titration. In aq. Na_2CO_3 (**I**) and (**II**) yield *β*-5-acetylsulphanilamidotetrazole monohydrate (**IV**), m.p. 202° (on further purification 207°). (**III**) with aq. NaOH affords α-5-acetylsulphanilamidotetrazole monohydrate (**V**), m.p. 207°. (**IV**) and (**V**) show no depression for mixed m.p., and both react as dibasic acids, but are differentiated by electrometric titration curves and ultra-violet absorption spectra. Hydrolysis of (**IV**) and (**V**) (aq. NaOH) gives the same (mixed m.p.) 5-sulphanilamidotetrazole, m.p. 202—203°; (**III**) yields N_3H and $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CN$ (?). D. G.

(A) **Action of ammonia on crotonaldehyde.** (B) **Salts and derivatives of tricrotonylidenetetramines.** M. Delépine (*Compt. rend.*, 1943, **216**, 649—652, 697—701).—(A) At only slightly >0° $CHMe{:}CH{\cdot}CHO$ (210) and 22% aq. NH_3 (350 g.) give a syrup with only small amounts of crystal, but subsequent keeping at room temp. and then heating at 100° gives tricrotonylidenetetramine-α, $C_{12}H_{24}N_4$, $+6H_2O$ (**I**) (50—60 g.), m.p. ~70°, resolidifies, and an *isomeride*-b (**II**) (160—170 g.), (from H_2O) $+6H_2O$ or (from $COMe_2$) $+4H_2O$, m.p. ~65° (instantaneous), b.p. 150°/3 mm. (cf. Wurtz, A., 1879, 780; Combes, A., 1883, 1079). They are separated by crystallisation or by the extreme insolubility of the hydrochloride of (**I**) in HCl. Over H_2SO_4 in vac., (**I**) and (**II**) give anhyd. *forms*, m.p. 102°, and an oil, respectively, which are rapidly reconverted into hydrates in air.

(B) (**I**) and (**II**) give ppts. with Zn, Cd, Hg, Cu, Fe, Co, Al, Cr, Pb, and Sn salts. The following *salts* and *derivatives* prove the tribasicity of the compounds (cf. Kudernatsch, A., 1900, i, 337): (**I**),$2AgNO_3$,$+3H_2O$; (**II**),$2AgNO_3$,$+2H_2O$; (**I**) trihydrochloride, insol.; (**II**) dihydrochloride, sol.; 2(**I**),$3H_2SO_4$,$+12H_2O$ [the sulphate of (**II**) is a glass]; 2(**I**),$3H_2PtCl_6$,$+12H_2O$, sol.; 2(**II**),$3H_2PtCl_6$,$+12H_2O$, insol.; 2(**I**),$3H_2IrCl_6$,$+12H_2O$; trireineckates of (**I**) and (**II**); 4(**I**),$3H_3Fe(CN)_6$,$+32H_2O$, insol.; 4(**II**),$3H_4Fe(CN)_6$,$+28H_2O$; (**I**),$H_3Fe(CN)_6$,$+4H_2O$; (**II**),$H_3Fe(CN)_6$,$+H_2O$; iridi- and rhodi-cyanides isomorphous with the ferricyanides; tripicrate of (**I**) [$+4H_2O$; m.p. ~152° (block)] and of (**II**) [$+3H_2O$; m.p. 145—152° (block)]; $(NO)_3$-derivative, m.p. ~240° (block) or (in a tube) deflagrates at ~210°, of (**I**) [that of (**II**) is amorphous]; N-Cl_3-derivative, m.p. ~76° (tube) or deflagrates

at 70° (instantaneous), of (I) and amorphous, deflagrates at ~40°, of (II). R. S. C.

Constitution of tricrotonylidenetetramines. M. Delépine (*Compt. rend.*, 1943, **216**, 785—789).—A mechanism is proposed for the formation of tricrotonylidenetetramines (I) from CHMe:CH·CHO, whereby the latter (3 mols.) and NH_3 give an aminotriol, $[CHMe:CH·CH(OH)]_3N$, converted by saturation of the double linkings into an intermediate, which then loses H_2O. Oxidation of (I) (α form) (+6H_2O) with aq. $KMnO_4$–KOH at ~0° gives an anhydride (II) (trimeric) of NH_2·CHMe·CH_2·CO_2H (III), sublimes without melting, stable to boiling aq. NaOH–EtOH, and convertible by HCl at 130° for 1·2 hr. into the hydrochloride of (III); Ag_2O, followed by H_2S, then gives (III), m.p. 190°. (I) (β form) does not similarly give (III). (I), heated progressively from 160° to 250—280°, loses NH_3 and ~10% of 2-methyl-5-ethylpyridine is obtained. The α and β forms of (I) probably have the 3 Me groups in different positions. A. T. P.



(I.)

Synthesis of purine nucleosides. VII. Further observations on the synthesis of pyrimidines from esters and malondiamidine. G. A. Howard, B. Lythgoe, and A. R. Todd (*J.C.S.*, 1944, 476—477).—The pyrimidine synthesis from esters and malondiamidine (I) (cf. Kenner *et al.*, A., 1944, II, 59) has limited val. since no pyrimidine formation occurs with (I) and Et *n*-butyrate, malonate, pyruvate, and urethane, and *N*-acetyl-, phenyl-, and *NN*-dimethyl-urethane. EtOBz and (I) give 4 : 6-*diamino*-2-*phenylpyrimidine*, m.p. 195—196°; Et_2CO_3 gives 4 : 6-diamino-2-hydroxypyrimidine; $ClCO_2Et$ yields 4 : 6-*diamino*-2-*hydroxypyrimidine hydrochloride*, and $Et_2C_2O_4$, 4 : 6-*diaminopyrimidine*-2-*carboxylic acid*, m.p. >360°. NaOAc and Ac_2O convert (I) into 4 : 6-*diacetamido*-2-*methylpyrimidine* (+H_2O), m.p. 232°. F. R. S.

Bile pigments. XXXI. Intermediate products in the conversion of hæmins into bile pigments. E. Stier [with, in part, (Miss) K. Gangl] (*Z. physiol. Chem.*, 1942, **272**, 239—272).—Coproverdohæmin ester is catalytically hydrogenated (Pd in anhyd. HCO_2H at 70—75°) to coproporphyrin I Me_4 ester, identified spectroscopically; the main product is coproglaucobilin ester (I), m.p. 202°. The non-homogeneous course of the oxidation of the copro-ester pyridine-hæmochromogen (II) is shown by the isolation of (I) from the HCl–MeOH mother-liquors of hydroxycopro-ester chlorohæmin by means of Et_2O. Oxidation of (II) with H_2O_2 at 55—60° and then with O_2 followed by treatment with HCl–MeOH gives a very complex mixture of pigments which does not contain (I); a pigment is present which gives a Zn salt which is spectroscopically identical with the Zn salt of dimethoxyætioglaucobilin, but could not be isolated. Similar results are recorded with the meso-ester pyridinehæmochromogen. Successive treatments of the meso-Me_2 ester pyridine-hæmochromogen in C_5H_5N with H_2O_2 at 55—60° and BzCl, after removal of Fe by Fe(OAc)$_2$–HCl and treatment with Et_2O, gives *benzoyloxymesoporphyrin* Me_2 *ester* (III), m.p. (indef.) 197—199°, softens at 175°, which is probably a mixture of four isomerides. It is identical spectroscopically with benzoyloxycoproporphyrin. With Zn(OAc)$_2$ in boiling $COMe_2$–MeOH it affords the *complex* $C_{42}H_{44}O_6N_4Zn$, m.p. 232°. Catalytic hydrogenation in AcOH followed by re-oxidation gives only initial material whereas in hot HCO_2H mesoporphyrin and hydroxymesoporphyrin are also produced in small amount. (III) is stable towards HCl–MeOH but readily hydrolysed by NaOMe under N_2; esterification of the product with CH_2N_2 causes complete decomp. but use of HCl–MeOH leads to a hydroxymesoporphyrin Me_2 ester (IV) (not-isolated), spectroscopically identical with hydroxycoproporphyrin ester. The ethereal solution of (IV) is evaporated to dryness and the residue is treated with Fe(OAc)$_2$–NaCl at 100° for 30 sec., thus giving the hydroxymesohæmin Me_2 ester, which could not be obtained cryst.; spectroscopically it is identical with hydroxycoprohæmin ester. It is transformed by air in C_5H_5N at room temp. followed by boiling HCl–MeOH into glaucobilin ester which could not be obtained cryst. or as the Zn salt; the yield is very small and a mixture of much red-violet pigments also results. Protohæmin Me_2 ester and N_2H_4 in aq. C_5H_5N at 60° give non-cryst. *protohæmochromogen-pyridine-*Me_2*-ester*, from which Fe is removed by dissolution in AcOH–HCl (1 : 1) and which is free from meso- or hæmato-porphyrin. It is converted by the successive actions of H_2O_2 and BzCl in C_5H_5N into *benzoyloxyprotoporphyrin* Me_2 *ester*, m.p. 219°, softens at 195°, catalytically hydrogenated (Pd in dioxan) to benzoyloxymesoporphyrin Me_2 ester and hydrolysed by NaOMe in MeOH–dioxan under N_2 at 70° to *hydroxyprotoporphyrin* Me_2 *ester*, which could only be obtained in solution. It is transformed into the amorphous *hydroxyprotohæmin* Me_2 *ester* (yield 25—35%), converted by O_2 in C_5H_5N followed by HCl–MeOH into (?) tetramethylhæmatoglaucobilin, which could not be obtained cryst. in very poor yield. Rhodohæmin Me_2 ester and N_2H_4,H_2O in C_5H_5N at 80° afford rhodopyridine-hæmochromogen Me_2 ester (+2C_5H_5N), m.p. 195°, softens at 182°, transformed by H_2O_2 followed by BzCl into *benzoyloxyrhodoporphyrin* Me_2 *ester*, m.p. 205°, softens at 200°, which resembles chloroporphyrin e_4 and e_6 in spectrum. Phyllohæmin Me ester gives successively the *pyridinehæmochromogen* and *benzoyloxyphylloporphyrin Me ester*, m.p. 224° (indef.), softens at 210°, the spectrum of which is displaced somewhat towards the red in comparison with those of phyllo- and dibenzoyloxycopro-porphyrin and identical in type with that of the last substance; it is hydrolysed to *hydroxyphylloporphyrin Me ester*, sol. in Et_2O to a blue solution and giving an ill-defined spectrum. Benzoyloxycoproporphyrin ester is transformed by Fe(OAc)$_2$ and NaCl into the *chlorohæmin*, $C_{47}H_{48}O_{10}N_4ClFe$, m.p. 222°, transformed by N_2H_4,H_2O in C_5H_5N at 60° into α-*benzoyloxycopro* I *ester hæm*, m.p. 120—125°. The corresponding pyridine-hæmochromogen is converted by H_2O_2 in C_5H_5N followed by Fe(OAc)$_2$ and HCl into *dibenzoyloxycoproporphyrin* I Me_4 *ester*, m.p. 266°, softens at 200°.

Ætioxanthoporphinogen is transformed by HBr–AcOH at 140—150° into *hydroxyætioporphyrin* I, decomp. 255°. Similarly, meso-xanthoporphinogen is converted into *hydroxymesoporphyrin* IX, m.p. 255—256°, which with HCl–MeOH at room temp. yields the Me_2 ester, m.p. 171°. It is therefore possible to obtain α-hydroxy-porphyrins and bile pigments from xanthoporphinogens and hence the presence of O attached to the α-CH in the xantho-compounds is confirmed. H. W.

Helix pomatia **hæmocyanin.**—See A., 1944, III, 838.

Analgesics derived from oxazolidine-2 : 4-dione. M. A. Spielman (*J. Amer. Chem. Soc.*, 1944, **66**, 1244—1245).—Oxazolidine-2 : 4-dione with Me_2SO_4–aq. NaOH (not *p*-$C_6H_4Me·SO_3Me$) at <40° gives 3-*methyloxazolidine*-2 : 4-*dione*, m.p. 128°. 3 : 5-*Dimethyl*-, b.p. 140—144°/50 mm., 3 : 5 : 5-*trimethyl*- (I), m.p. 46°, b.p. 78—80°/5 mm., 3 : 5-*dimethyl*-5-*ethyl*-, b.p. 101—102°/11 mm., 3-*methyl*-3 : 5-*diethyl*-, b.p. 105—108°/11 mm., 3-*methyl*-3 : 5-*di*-n-*propyl*-, b.p. 100—105°/4 mm., and 5 : 5-*pentamethylene*-3-*methyl*-*oxazolidine*-2 : 4-*dione*, m.p. 95°, are similarly obtained. Use of EtI and the Ag salt in Et_2O at room temp. (3 days) gives 5 : 5-*dimethyl*-3-*ethyl*-*oxazolidine*-2 : 4-*dione*, m.p. 61°. These products are analgesic but not hypnotic, notably (I), which is comparable with aspirin and has very low toxicity. 3 : 5 : 5-Trimethylhydantoin (similarly prepared), m.p. 149°, has no pharmacological action, and 3 : 5 : 5-*trimethylthiazolidine*-2 : 4-*dione* (similarly prepared), m.p. 49—51°, is weakly hypnotic. (I) is monoacidic to NaOH (phenolphthalein), yielding this α-*hydroxyisobutyrmethylamide*, m.p. 78—79°. 5 : 5-*Pentamethyleneoxazolidine*-2 : 4-*dione*, m.p. 110—112°, is prepared from Et 1-hydroxy*cyclo*hexanecarboxylate and $NH:C(NH_2)_2$ in EtOH, subsequent hydrolysis being by hot 15% HCl. R. S. C.

Amino-alcohols. 3-Piperidyl derivatives. A. Burger, R. W. Alfriend, and A. J. Deinet (*J. Amer. Chem. Soc.*, 1944, **66**, 1327—1328).—Pyridine-3-carboxyl chloride, b.p. 75—77°/7 mm. (readily hydrolysed in moist air), with CH_2N_2–Et_2O and then 48% HBr gives cryst. 3-bromoacetylpyridine hydrobromide (82%), which with morpholine (3 mols.) in Et_2O yields 3-*morpholinoacetylpyridine* (83%), m.p. 64—68° (*dihydrochloride*, m.p. 197—198°; *dipicrate*, m.p. 158—162°). Al(OPr$^\beta$)$_3$ then yields β-morpholino-α-3-pyridylethyl alcohol (25%) (*dihydrochloride*, m.p. 211°; *dipicrate*, m.p. 166°), hydrogenated (PtO_2; EtOH) to β-morpholino-α-3-piperidylethyl alcohol (45%) (*dihydrochloride*, m.p. 256—257°). R. S. C.

Sulphonamidothiazoles.—See B., 1944, III, 218.

Methine and cyanine colouring matters.—See B., 1944, II, 308, 338.

Fluorocyanine, blue pigment from *Cypridina* **scales.**—See A., 1944, III, 745.

Resynthesis of dethiobiotin from diaminopelargonic acid. D. B. Melville (*J. Amer. Chem. Soc.*, 1944, **66**, 1422).—Passing $COCl_2$ into ζη-diamino-*n*-nonoic acid sulphate (I), micro-m.p. 245—246°, in 10% aq. Na_2CO_3 gives 66% of dethiobiotin (II), micro-m.p. 156—158°, which is fully active in promoting the growth of yeast. (I) is approx. one tenth as active as (II). R. S. C.

Structure-chemical investigations. XI. Reactive behaviour of dithioamides towards tribromotriacetylbenzene. G. Bischoff, O. Weber, and H. Erlenmeyer (*Helv. Chim. Acta*, 1944, **27**, 947—948).—$C_6Ac_3Br_3$ and PhCS·NH_2 in EtOH at 100° afford 1 : 3 : 5-*tri*-(4-*phenyl*-2-*thiazolyl*)*benzene*, m.p. 195°. Complex compounds, becoming discoloured at ~230° or ~250° (decomp.), are obtained from $C_6Ac_3Br_3$ and adip- or oxal-dithioamide. H. W.

Structure-chemical investigations. XII. Thiazole derivatives from terephthaldithioamide. H. Erlenmeyer, W. Büchler, and H. Lehr (*Helv. Chim. Acta*, 1944, **27**, 969—970).—*p*-$C_6H_4(CS·NH_2)_2$ with boiling CH_2AcCl gives 1 : 4-*di*-(4′-*methyl*-2′-*thiazolyl*)*benzene*, m.p. 166° (*picrate*, m.p. 212°), and with COPh·CH_2Br in $PhNO_2$ at 200° affords 1 : 4-*di*-(4′-*phenyl*-2′-*thiazolyl*)*benzene*, m.p. 225°. $(CO·CH_2Br)_2$ in $PhNO_2$ appears to give a complex product, m.p. >360°. H. W.

VII.—ALKALOIDS.

Cleavage of trigonelline. J. Weijlard, M. Tishler, and J. P. Messerly (*J. Amer. Chem. Soc.*, 1944, **66**, 1319—1320).—Trigonelline is unaffected by inorg. sulphides, sulphites, or thiosulphates, BrCN, HNO_2, CrO_3, HNO_3, $HClO_4$, or heating at 290°, but with conc. HCl at 250° (cf. Jahns, A., 1888, 166) or C_5H_5N,HCl at 200—204° gives 83% of nicotinic acid. Use of C_5H_5N,HCl leads also to methylpyridinium chloride. Quinoline hydrochloride is also effective. R. S. C.

Alkaloids of *Duboisia leichhardtii*. W. Mitchell (*J.C.S.*, 1944, 480—482).—*D. leichhardtii* contains *l*-hyoscyamine (1·97%), *l*-hyoscine (0·06%), *dl*-hyoscine (0·05%), norhyoscyamine (0·01%), and "*base D*" (0·06%), isolated as the *hydrobromide* (**I**), $C_{13}H_{23}O_2N$,HBr, m.p. 231° (corr.) (mixture of isomerides). iso-*Valeryltropeine hydrobromide*, m.p. 225—227° (corr.), is not identical with (**I**). Probably at least two distinct types of *Duboisia* have appeared in commerce. F. R. S.

Mode of action of quinine and quinidine. II. Synthesis of 9-hydroxy-6′-methoxyrubans. P. Rabe and W. Schuler (*Ber.*, 1943, **76**, [*B*], 318—321).—(++)(−−)-6′-Methoxyruban-9-ol (**I**) exists as hexahydrate and in *forms*, $+2H_2O$, m.p. 94—95°, and anhyd., m.p. 172°, and gives a very insol. *mono-*, $+6H_2O$, m.p. ~120°, resolidifies, remelts at ~240° (decomp.), and a more sol. *di-hydrochloride*, $+5H_2O$, m.p. ~242°, and *sulphate*, $+4·5H_2O$, m.p. 192° (decomp.). The (+−)(−+)-compound (**II**), a glass, gives a *sulphate*, $+6H_2O$, m.p. 86—87° (foams), but its hydrochloride is sol. The isomerides are thus separable. KOH converts (**II**) in boiling C_5H_{11}·OH into (**I**). Reports in the literature are confirmed that (**I**) is active in canary malaria, whereas the (++)- and (−−)-compounds are inactive. R. S. C.

Structure of a new metabolic derivative of quinine. J. Mead and J. B. Koepfli (*J. Biol. Chem.*, 1944, **154**, 507—515).—The cryst. metabolic product (**I**), m.p. 247·5—248·5°, $[\alpha]_D^{25}$ −65·5° in EtOH, derived from quinine (cf. Kelsey *et al.*, A., 1944, III, 680) is probably *l*-2′-hydroxy-6′-methoxy-3-vinylruban-9-ol. Potentiometric titration and absorption spectra for (**I**) and quinine are given. Hydrogenation (H_2–PtO_2) indicates one olefinic linking, and ozonisation affords CH_2O. (**I**) forms a *monomethiodide*, m.p. 276—277° (decomp.), and a *benzenesulphonyl* derivative, $C_{58}H_{68}O_{16}N_4S_3$, m.p. 180—181°, reconverted into (**I**) after mild acid hydrolysis. Attempts at oxidation have afforded no recognisable product. The evidence in favour of the constitution of (**I**) is discussed. M.p. are corr. F. R. S.

[**Alkaloids of**] *Mahonia nepalensis* **DC.** (*Berberis nepalensis*, **Spreng**). R. Chatterjee (*J. Amer. Pharm. Assoc.*, 1944, **33**, 210—212; cf. A., 1944, III, 856).—The root contains 0·48% of umbellatine and 0·02% of *nepratine* (**I**), $C_{19}H_{21}O_6N$, decomp. >200° without melting [*hydrochloride*; *platinichloride* (decomp. without melting)]. Colour reactions for (**I**) with alkaloidal reagents are tabulated. F. O. H.

Synthesis of *l*-roemerine. L. Marion and V. Grassie (*J. Amer. Chem. Soc.*, 1944, **66**, 1290—1292).—*o*-$C_6H_4Me·NO_2$, $Et_2C_2O_4$, and NaOEt in EtOH–Et_2O give *o*-$NO_2·C_6H_4·CH_2·CO·CO_2Et$, oxidised by H_2O_2–NaOH, later at 50°, to *o*-$NO_2·C_6H_4·CH_2·CO_2H$ (38·6%), m.p. 139—140°. The derived chloride and 3 : 4 : 1-CH_2O_2:$C_6H_3·[CH_2]_2·NH_2$ (modified prep.) give o-*nitrophenylacet-β*-3 : 4-*methylenedioxyphenylethylamide* (74·4%), m.p. 120°, converted by PCl_5 in $CHCl_3$ at room temp. into 6 : 7-*methylenedioxy*-1-o-*nitrobenzyl*-3 : 4-*dihydro*isoquinoline, m.p. 164·5°, the *methiodide*, m.p. 262°, of which with Zn dust in hot aq. HCl gives 6 : 7-*methylenedioxy*-1-o-*nitrobenzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline · *dihydrochloride* (55·4%), m.p. 283—284°. With $NaNO_2$ in 2N-H_2SO_4 at room temp. and then 100° this gives dl-*roemerine* [dl-5 : 6-*methylenedioxyaporphine*] (**I**), m.p. 85—87° (*hydrochloride*, m.p. 274°; picrate, m.p. 197°) (and a *by-product*, $C_{18}H_{19}O_3N$, m.p. 133·5°). The *methiodide*, m.p. 221°, of (**I**) with boiling KOH–MeOH gives the dl-*methine*, m.p. 81° (*methiodide*, m.p. 280°). *d*- and then *l*-tartaric acid yield successively *l*-, *forms*, m.p. 87° and (stable) 102°, $[\alpha]_D$ −79·9° in EtOH [*d*-tartrate, m.p. 264·5° (decomp.); methiodide, m.p. 224·5°], and d-*roemerine*, m.p. 102°, $[\alpha]_D$ +80·2° in EtOH [*l*-tartrate, m.p. 264·5° (decomp.); methiodide, m.p. 224·5°] (cf. A., 1940, II, 197). M.p. are corr. R. S. C.

Isolation of hypaphorine from Argentine species of *Erythrina*.—See A., 1944, III, 856.

VIII.—ORGANO-METALLIC COMPOUNDS.

Arsanilic acids.—See B., 1944, III, 186.

Some new ethyl and phenyl silicon fluorides. H. J. Emeléus and C. J. Wilkins (*J.C.S.*, 1944, 454—456).—*Ethyltri-*, b.p. −4·4°/760 mm., *diethyldi-*, b.p. 60·9°/760 mm., *phenyltri-*, b.p. 101·8°/760 mm., and *diphenyldi-fluorosilane*, b.p. 242·8°/603 mm., are prepared from ZnF_2 and the corresponding chlorides, or from HF and the oxy-compounds. Vals. of *d* and v.p. are given; the latent heats of vaporisation of the first three are 6181, 7623, and 8750 g.-cal. per mol., respectively. The resistance of the compounds to hydrolysis rises rapidly with increase in the no. of org. groups. F. R. S.

IX.—PROTEINS.

Conversion of some spheroproteins into linear proteins by deamination. III. B. Jirgensons (*J. pr. Chem.*, 1943, [ii], **162**, 224—236).—Proteins (**I**) (casein, albumin, edestin, hæmoglobin) are treated with aq. AcOH–$NaNO_2$ and the products dissolved in 0·05N-NaOH (**II**). The η of the solutions is 10—100 times that of (**I**). At low concn. (*c*), with excess of (**II**), Z_η [$= (\eta - 1)/c$] decreases with increasing *c*. With excess of (**II**), η decreases with time, but only slowly when *c* is low. All the degraded proteins have approx. equal Z_η, and behave similarly, suggesting that (**I**) have been degraded into units of approx. equal chain-length. E. W. W.

Viscosity measurements of solutions of deaminated proteins. B. Jirgensons (*J. pr. Chem.*, 1943, [ii], **162**, 237—244).—Serum-albumin and -globulin and gliadin are deaminated and η of solutions in 0·02N-NaOH determined. Z_η of the products are similar to those of other deaminated proteins (see preceding abstract). Z_η of the product of deaminating gelatin (**I**) is $< Z_\eta$ of (**I**), but approx. equals that of the other products, which have much greater aminodicarboxylic acid content. Thus Z_η depends on the unit length of the deamination products rather than on their CO_2H content. E. W. W.

Neglected constituent of proteins, α-amino-*n*-butyric acid. W. C. Tobie (*Nature*, 1943, **152**, 249).—Preliminary work suggests that α-amino-*n*-butyric acid ("quadrine") may occur widely in proteins. Prolonged acid hydrolysis liberates N from the synthetic material, and protein hydrolysis must be enzymic. The name "*iso*quadrine" is suggested for α-amino*iso*butyric acid. E. R. R.

Elucidation of structure of proteins. E. Husemann (*Chem.-Ztg.*, 1943, **67**, 24—28).—A review. W. McC.

Physical and chemical properties of casein from various animal species. E. Kovács (*Biochem. Z.*, 1940, **306**, 74—76; cf. Gróh, A., 1934, 1119).—Examination of caseins from the milk of cow, sheep, goat, horse, and ass shows that the tyrosine, tryptophan, P, and S contents, $[\alpha]_D^{20}$, and max. and min. absorption of ultra-violet light are subject to species variations of sufficient magnitude to permit identification of unmixed specimens. The magnitude is not sufficient to permit detection or determination of one casein in admixture with another or others or to detect adulteration in curds. W. McC.

Composition of casein in milk.—See A., 1944, III, 818.

Cleavability of keratins treated with hot β-naphthol by proteinases.—See A., 1944, III, 840.

Structure and reactivity of wool keratin. XIII. Keratin fibres shortened by heat.—See A., 1944, III, 818.

Chromosomin, a protein constituent of chromosomes.—See A., 1944, III, 819.

Analysis of a partial hydrolysate of gramicidin by partition chromatography with starch. R. L. M. Synge (*Biochem. J.*, 1944, **38**, 285—294).—Specimens of gramicidin (**I**) from two different sources have been compared in respect of a no. of properties and further information has been obtained about the ultimate hydrolysis products. Preliminary data are provided on the use of raw potato starch as a medium for partition chromatography of free NH_2-acids and peptides. Analysis by this method of a partial hydrolysate of (**I**) has given alanine and *l*-valylglycine, the latter in a yield embodying > half of the glycine of (**I**). The optical form of the valine residues of (**I**) is discussed in the light of new evidence and it is probable that *d*-valine residues will be discovered to be structural components of (**I**). F. R. S.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Phenol groups in lignin. K. Freudenberg and H. Walch (*Ber.*, 1943, **76**, [*B*], 305—308).—Aryl toluenesulphonates are converted by N_2H_4 into *p*-$C_6H_4Me·SO_2·NH·NH_2$ and thence into N_2H_4 *p*-toluenesulphonate, which is determined by addition of the derived acid to $CO(CH{:}CHPh)_2$. This method shows the following contents of phenolic OH in the named varieties of lignin: cuproxam- 1·5, HCl- 1·8, technical HCl-lignin 1·9, lignin of ligninsulphonic acid 2·5, and deacetylated AcOH-lignin 3·0. R. S. C.

Substance, m.p. 260—270° (acetyl derivative, m.p. 192—194°), from black currants.—See A., 1944, III, 783.

INDEX OF AUTHORS' NAMES, A II

DECEMBER, 1944.

ERRATUM.

Abstracts A II, 1944.

Col.	Lines.	
87	32–33	*For* "The ash, insol. in 2N-HCl, contains" *read* "The ash (insol. in 2N-HCl 6·6%) contains."

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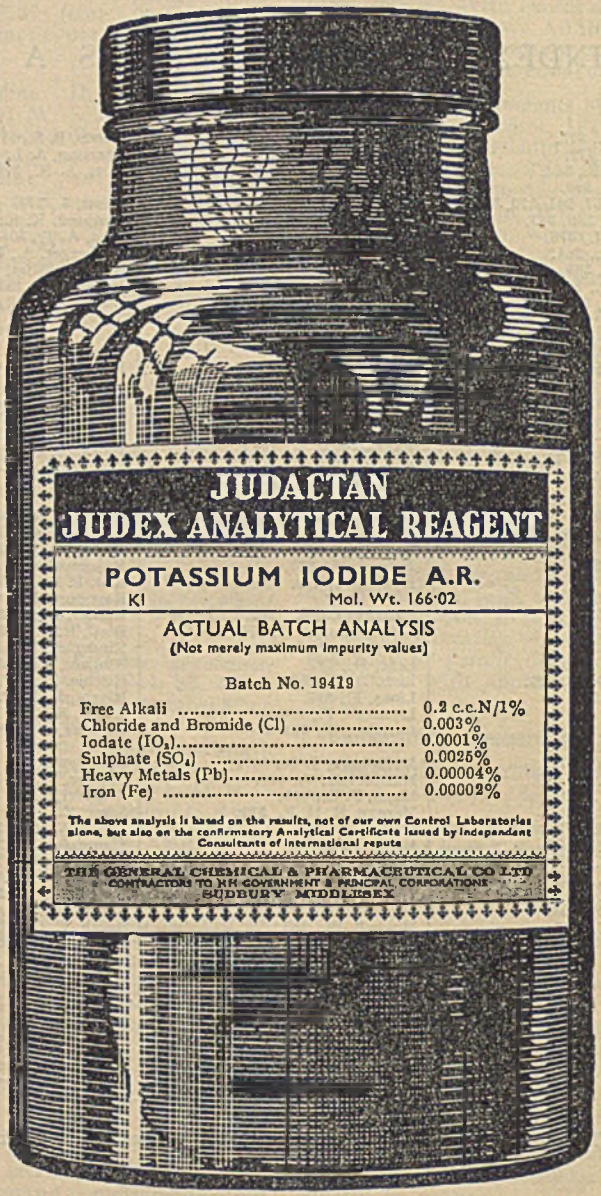

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