BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MARCH, 1941.

I.—ALIPHATIC.

Ozonisation of organic compounds. C. C. Spencer, W. I. Weaver, E. A. Oberright, H. J. Sykes, A. L. Barney, and A. L. Elder (*J. Org. Chem.*, 1940, **5**, 610—617).—Vapour-phase ozonisation of org. compounds proceeds more rapidly than ozonisation in solution owing to the greater concn. of the reactants but is applicable only to compounds with appreciable v.p. and those forming stable ozonides. The chief difficulty is caused by the ozonide mists not being easily wetted by solvents. To overcome this an electrical precipitator (described) is used. Dipentene as vapour gives a diozonide whereas in heptane a mono-ozonide is produced. Under like conditions *d*-limonene gives a di- and a mono-ozonide. Citral, ionone, *ψ*-ionone, citronellol, citronellal, terpineol, carvone, geraniol, and *iso*eugenol are not sufficiently volatile to produce appreciable amounts of ozonide. Ozonisation of pinene as vapour results in oxidation of CH_2 in the α-position to the double linking as well as in the addition of O_2 to the unsaturated linking. Complete ozonisation of $(CH_2{:}CH)_2$ (**I**) in $CHCl_3$ gives an $\alpha\beta$–$\gamma\delta$ diozonide sol. in $CHCl_3$ which cannot be readily isolated owing to its great explosiveness. $H_2C_2O_4$ separates when its solution in $CHCl_3$ is kept. Hydrolysis effected in the presence of $CHCl_3$ gives CH_2O and glyoxal. $\Delta^{\alpha\gamma}$-*Butadiene mono-ozonide* (**II**) results when O_3 is passed through (**I**) in light petroleum. The products of its hydrolysis do not appear to contain maleic anhydride as judged by attempts at its isolation through the 2 : 4-dinitrophenylhydrazone or by conversion into maleic acid. Hydrolysis yields CH_2O and acraldehyde, indicating $\alpha\gamma$ addition. Evidence of $\alpha\delta$ addition could not be found. (**II**) is relatively stable. H. W.

Hydrogenation of oxygen-containing compounds. III. Preparation of $\beta\gamma$-dimethylbutane from pinacolin. B. Moldavski and T. Nizovkina (*J. Gen. Chem. Russ.*, 1940, **10**, 653—654).—Pr^{β}_2 is obtained in 65% yield by hydrogenation of $COMeBu^{\gamma}$ (MoS_2 catalyst; 4 hr. at 340—350°). R. T.

Isomerisation of *n*-heptane and *n*-octane. A. P. Sivertzev (*J. Gen. Chem. Russ.*, 1940, **10**, 799—802).—*iso*-Octane or -heptane is obtained in ~10% yield when the *n*-hydrocarbons are passed through a porcelain tube at 450—600°. With 10% of $AlCl_3$ at 50—60° the yield is 31—37%. R. T.

Application of the xanthate method of L. A. Tschugaev to dihydric alcohols or their corresponding dibromides. V. E. Tischtschenko, V. N. Schabaschova, and N. D. Sisoeva (*J. Gen. Chem. Russ.*, 1940, **10**, 1042—1054).—$OEt{\cdot}CS_2Na$ (**I**) and *sec.-tert.*- or di-*tert.*-dibromides at 60—80° react as follows: $C_nH_{2n}Br_2 + 2$(**I**) $\rightarrow C_nH_{2n}(CS_2{\cdot}OEt)_2$ (**II**) $+2NaBr$; (**II**) $\rightarrow C_nH_{2n} + (OEt{\cdot}CS_2)_2$ (**III**); (**III**) $\rightarrow CS(OEt)_2 + COS + S$. The hydrocarbon so obtained from $CH_2Br{\cdot}CMe_2Br$ is $(CMe{:})_2$, and from $CHMeBr{\cdot}CMe_2Br$ is $CHMe{:}CMe_2$. $SK{\cdot}CO_2Et$ reacts similarly to (**I**), the products being C_nH_{2n}, KBr, and $(S{\cdot}CO_2Et)_2$. R. T.

$\alpha\alpha$-Dichlorides of the allene series. Action of phosphorus pentachloride on methyl vinyl ketone. A. N. Tschurbakov (*J. Gen. Chem. Russ.*, 1940, **10**, 977—980).—$CH_2{:}CHAc$ (**I**) and PCl_5 at 0° yield $CH_2Cl{\cdot}CH{:}CMeCl$, converted by 15% Na_2CO_3 at 100° into (**I**) and $OH{\cdot}CH_2{\cdot}CH{:}CMeCl$ (*phenylurethane*, m.p. 78·8°), which with 16% H_2SO_4 (3 hr. at 100°) also gives (**I**). R. T.

Manufacture of dihalogenobutanes.—See B., 1941, II, 32.

Preparing ethyl alcohol from ethylene of petroleum gases.—See B., 1941, II, 30.

Conjugated systems. X. Reaction of bromoprene with hypobromous acid. A. A. Petrov (*J. Gen. Chem. Russ.*, 1940, **10**, 1013—1020).—Bromoprene (**I**) and HOBr (from NHAcBr) yield $\alpha\gamma$-*dibromo*-Δ^{γ}-*buten*-β-*ol*, b.p. 91—92·5°/10 mm. (*acetate*, b.p. 99·5—100·5°), which with Br in $CHCl_3$ gives $\alpha\beta\beta\delta$-*tetrabromobutan*-γ-*ol*, m.p. 61·5—63°. This is oxidised ($Na_2Cr_2O_7$ in H_2SO_4) to $\alpha\beta\beta\delta$-*tetrabromobutan*-γ-*one*, b.p. 151—153°/10 mm. (**I**) at 150° with 60% aq. KOH yields *bromoprene oxide* (**II**), b.p. 130·5—131°, converted by 1% H_2SO_4 (3 hr. at 40°) into β-*bromo*-Δ^{α}-*butene*-$\gamma\delta$-*diol*, b.p. 120—121°/10 mm. (*diacetate*, b.p. 116—117°/10 mm.). With Br in $CHCl_3$ (**II**) gives $\alpha\beta\beta$-*tribromobutane*-$\gamma\delta$-*diol*, m.p. 121·5—123°, whilst with HBr at −5° (**II**) affords $\beta\gamma$-*dibromo*-Δ^{α}-*buten*-δ-*ol*, b.p. 99·5—101°/10 mm. (*acetate*, b.p. 108—109°/10 mm.). R. T.

Grignard synthesis of unsaturated halogeno-alcohols. G. I. Schtukin (*Bull. Sci. Univ. Kiev*, 1939, No. 4, 45—80).—$CH_2{:}CH{\cdot}CH_2{\cdot}MgBr$ and $COMe{\cdot}CH_2Cl$ or $CO(CH_2Cl)_2$ in Et_2O yield α-*chloro*-β-*methyl*- (**I**), b.p. 53°/10 mm., 159°/750 mm., or α-*chloro*-β-*chloromethyl*-Δ^{δ}-*penten*-β-*ol* (**II**), b.p. 82·5°/14 mm., 190°/750 mm. (decomp.). With $NHEt_2$ or KCN (**I**) affords α-*diethylamino*-, b.p. 158—160°/750 mm., or α-*cyano*-β-*methyl*-Δ^{δ}-*penten*-β-*ol*, b.p. 112°/17 mm.; the corresponding products from (**II**) were oils, decomp. at the b.p. R. T.

Reaction of $\beta\beta'$-dichlorodiethyl ether with dimagnesium dibromoacetylene. S. N. Popov (*J. Gen. Chem. Russ.*, 1940, **10**, 1141—1143).—$(Cl{\cdot}[CH_2]_2)_2O$ is converted into $(Br{\cdot}[CH_2]_2)O$ by the action of $(C{:}C{\cdot}MgBr)_2$ in Et_2O. R. T.

Conjugated systems. IX. Reactions of β-halogenobutadienes with alkyl hypoiodites, and the synthesis of halogeno-alkoxyprenes. A. A. Petrov (*J. Gen. Chem. Russ.*, 1940, **10**, 819—825).—The ethers $CH_2{:}CX{\cdot}CH(OR){\cdot}CH_2I$ (X = Cl, R = *Me*, b.p. 76·5—77°/10 mm., R = *Et*, b.p. 82—83°/10 mm.; X = Br, R = *Me*, b.p. 91·5—92°/10 mm., R = *Et*, b.p. 97·8°/10 mm.) are prepared from chloro- or bromo-prene, ROH, HgO, and I at room temp. With NaOH–EtOH the ethers yield $CH_2{:}CX{\cdot}C(OR){:}CH_2$, whilst with dil. H_2SO_4 the ketones $COMe{\cdot}CX{:}CH_2$ are obtained. R. T.

Structure of kephalin. E. Le B. Gray (*J. Biol. Chem.*, 1940, **136**, 167—175).—The isolation of kephalin (**I**) from brain, liver, and heart by a modification of Bloor's method (A., 1926, 752) is described. Reduction of (**I**) in AcOH–*cyclo*hexane (1 : 1) (PtO_2–H_2) gives a non-hygroscopic amorphous product, m.p. 156—162°, which differs from unreduced (**I**) only in those properties which depend on degree of unsaturation. Discrepancies between the theoretical and observed composition of (**I**) are due to the presence of a hitherto unidentified group or groups low in C and H and high in O. Cuorin is not produced during extraction of lipins but exists preformed in heart and liver (not brain). W. McC.

Manufacture of α-chloroacrylic acid esters.—See B., 1941, II, 33.

Synthesis of alkyl ethylene orthoformates. V. G. Mchitarian (*J. Gen. Chem. Russ.*, 1940, **10**, 667—669).—$(CH_2{\cdot}OH)_2$ and $CH(OEt)_3$ in presence of p-$C_6H_4Me{\cdot}SO_3H$ (**I**) (10 min. at the b.p.) yield *ethylene Et orthoformate*, $\begin{matrix}CH_2{\cdot}O\\CH_2{\cdot}O\end{matrix}\!>\!CH{\cdot}OEt$, b.p. 120—123°. With menthol or borneol and (**I**) (2 hr. at the b.p.) this gives *menthyl*, m.p. 34·2°, or *bornyl ethylene orthoformate*, b.p. 148—152°/16 mm. R. T.

Production of lævulic acid.—See B., 1941, II, 33.

Vitamin-*C* available from plant sources in Taiwan. IV. Reaction between ascorbic acid and magnesium oxide. R.

Yamato and T. Hara (*J. Agric. Chem. Soc. Japan*, 1940, **16**, 1038—1040; cf. A., 1940, III, 751).—Ascorbic acid (**I**) and 0·5 mol. of MgO in H_2O give the *salt* $(C_6H_7O_6)_2Mg$, $[\alpha]_D^{19}$ +96·5°. With 40 mols. of MgO an insol. substance is formed which yields (**I**) when treated with acid. J. N. A.

Improved preparation of *d*-galacturonic acid. W. W. Pigman (*J. Res. Nat. Bur. Stand.*, 1940, **25**, 301—303; cf. Mottern and Cole, A., 1940, III, 72).—Citrous polygalacturonide in aq. NaOH (p_H 3·7) is incubated (38°) with pectinase for 10—14 days, neutralised (H_2SO_4), and filtered. The filtrate when evaporated to a syrup and extracted with boiling MeOH gives galacturonic acid monohydrate, m.p. 109—112°, $[\alpha]_D^{20}$ +51·5°, in 74% yield. J. L. D.

Lipins of tubercle bacilli. LXII. Mycolic acid. A. Lesuk and R. J. Anderson (*J. Biol. Chem.*, 1940, **136**, 603—613; cf. A., 1939, II, 48).—Mycolic acid (**I**) with PhOH, Ac_2O, and HI (*d* 1·73) at 150° yields iodohydroxy-, reduced (Zn + AcOH–C_5H_{11}·OH) to *hydroxy-normycolic acid*, m.p. 56—58°, and a *OH-acid*, $C_{104}H_{208}O_3$ (?), m.p. 74—76°, $[\alpha]_D^{25}$ +4·03° in $CHCl_3$ (*Me* ester, m.p. 63—65°), both of which yield *n*-$C_{25}H_{51}$·CO_2H (**II**) at 250—300° (reduced pressure). With PhOH, Ac_2O, and HI (*d* 1·86) at 150° (**I**) yields *di-iodonormycolic acid*, m.p. 41—43°, reduced to *normycolic acid*, $C_{87}H_{174}O_2$, m.p. 52—54° (Me ester), which gives no volatile acid when heated. Oxidation (CrO_3 in glacial AcOH) of (**I**) yields a mixture containing *n*-$C_{17}H_{35}$·CO_2H, (**II**), and *n*-CO_2H·$[CH_2]_{16}$·CO_2H. It is concluded that (**I**) is a mixture of two acids, the principal one having two *n*-C_{26} chains with CO_2H on one. A. Li.

***α-tert.*-Butylsulphonylpropionic acid and its mono-bromo-derivative.** B. Bäcklund (*Arkiv Kemi, Min., Geol.*, 1940, **14**, A, No. 1, 25 pp.).—*α*-tert.-*Butylthiolpropionic acid*, m.p. 92° (corr.), from Buγ·OH and SH·CHMe·CO_2H in aq. HCl, gives with neutral KMnO$_4$ *α*-tert.-*butylsulphonylpropionic acid* (**I**), m.p. 139° (corr.). The bromination of (**I**) in N-HBr has been studied from 35° to 100°; 2 mols. of Br are rapidly absorbed with hydrolysis, giving Buγ·OH and SO_2H·CBrMe·CO_2H. Further absorption of Br (changes of rate at 3 and 5 mols. of Br) is due to bromination of Buγ·OH. In buffered solutions (initial p_H 3·5, final 1·7) 1 mol. of Br is added (at 35°) to give the *α-Br*-derivative (**II**), m.p. 83° (decomp.), which gives I with acid KI. (**II**) decomposes slowly at room temp., rapidly at 100°, giving SO_2 0·80, CMe_2:CH_2 0·25, tri*iso*butene 0·27, and CHMeBr·CO_2H (**III**) 0·72 mol. Hydrolysis of (**II**) by N-HBr at 35° gives Buγ·OH, (**I**), (**III**), SO_2, HBr, and H_2SO_4. M. H. M. A.

Production of formaldehyde by means of the electric arc at high and low frequencies.—See A., 1941, I, 86.

Accelerating effect of ketones on the Cannizzaro–Tischtschenko reaction. III. Action of ββ-dihydroxymethylbutan-γ-one. M. N. Tilitschenko (*J. Gen. Chem. Russ.*, 1940, **10**, 718—722; cf. A., 1939, II, 49).—CMeAc(CH_2·OH)$_2$ is a more active catalyst of the Cannizzaro reaction than is COMeEt. R. T.

Electrolytic reduction potentials of organic compounds. XXVIII. Determination of sugars by polarographic method. Determination of pentoses and pentosan. I. Tachi (*J. Agric. Chem. Soc. Japan*, 1940, **16**, 1057—1063; cf. A., 1939, I, 84).—Pentoses and pentosan are hydrolysed to furfuraldehyde (**I**), which is determined by the polarographic method. The relation between concn. and height of the reduction curve of (**I**) is very important, and when the height is determined by the so-called tangent point method, there is a linear relation. (**I**) is quantitatively formed when xylose is heated with HCl (*d* 1·06) at 160° for 2—3 hr. J. N. A.

Lecture experiment for distinguishing fructose from glucose [sucrose, lactose, or maltose]. E. W. Zmaczynski (*J. Chem. Educ.*, 1940, **17**, 399—400).—1—2 drops of aq. Pb(OAc)$_2$ and 1—2 c.c. of glycerol are added to 60—100 mg. of the sugar mixed with 10—15 mg. of S. With fructose, a black colour is obtained on heating. L. S. T.

Starch. VIII. Degradation of the constituents of starch by β-amylase. K. H. Meyer, P. Bernfeld, and J. Press (*Helv. Chim. Acta*, 1940, **23**, 1465—1476; cf. A., 1940, II, 336).—Oxidation of the aldehydic functions of starch by I followed by removal of excess of halogen leaves a residue which is normally degraded by β-amylase (**I**). They are therefore not concerned in the degradation by (**I**) which attacks the glucose residues with free OH at $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, and $C_{(6)}$. The so-called "enzymic coagulation" of amylose (**II**) is connected with the greater solubility of crude (**II**) in comparison with (**II**) of higher mol. wt. obtained by fractionation. The portions of lower mol. wt. act as protective colloids to those of higher mol. wt. and these are the portions which are preferentially attacked by (**I**). Incomplete degradation of (**II**) by (**I**) may be due to contamination of (**II**) with amylopectin (**III**), in which case the residual solution gives a red to violet colour with I or pure (**II**) may become aged during enzymic attack and a pure blue colour is then obtained with I. Provided that agency is eliminated, the graph for the degradation of (**II**) by (**I**) is rectilinear until 65% hydrolysis has occurred. This is explained by assuming the removal of a maltose residue from the end of the chain whereby a second similar group is uncovered so that the concn. of terminal groups and enzyme is const. Only when degradation verges towards complete hydrolysis of some chains is there a diminution of the no. of terminal groups with consequent deceleration of the reaction. Degradation of (**III**) by (**I**) is invariably accompanied by the production of a residual substance of high mol. wt. and is not suited to kinetic study. It is conveniently replaced by starch degraded in glycerol, with which the reaction is of zero order only until 30—40% degradation has occurred; subsequently the rate diminishes rapidly partly because fewer terminal groups are available owing to variation in the length of the chains and partly owing to branching of the chains. Fresh solutions of pure (**II**) are degraded more slowly than those of sol. starch consisting essentially of (**III**) since the latter has the larger no. of terminal groups. H. W.

***X*-Ray comparison of natural and synthetic starch.** W. T. Astbury and C. S. Hanes (*Nature*, 1940, **146**, 558).—Purified potato starch and the polysaccharide synthesised by the action of potato phosphorylase on glucose 1-phosphate give essentially the same *X*-ray powder pattern (reproduced), with that of the synthetic starch not quite so sharp. Amyloamylose pptd. by EtOH after electrophoretic separation gives a *V*-pattern photograph, whilst the synthetic starch after pptn. by EtOH gives the *B*-pattern. L. S. T.

Manufacture of dimethylamine.—See B., 1941, II, 33.

Production of amino-acids.—See B., 1941, II, 34.

Reaction of formaldehyde with amino-acids. *X*-Ray diffraction patterns. A. K. Smith, P. Handler, and J. N. Mrgudich (*J. Physical Chem.*, 1940, **44**, 874—880).—*X*-Ray diffraction patterns of CH_2O-treated histidine (**I**) show that the product is cryst. Arginine and lysine similarly treated give amorphous products. The free bases are cryst. in each case. The cryst. nature of the CH_2O–(**I**) product is increased by ageing. The other two products are unchanged after several months' ageing. C. R. H.

Identification of primary aliphatic amides as oxalates. C. A. Mackenzie and W. T. Rawles (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 737—738).—By heating the appropriate amide and $H_2C_2O_4$ in EtOAc the following *compounds* are formed: $(HCO·NH_2)_2,H_2C_2O_4$, m.p. 107·4—107·7°, $NH_2Ac,H_2C_2O_4$, m.p. 127·3°, $EtCO·NH_2,H_2C_2O_4$, m.p. 80·8—81·0°, $(PrCO·NH_2)_2,H_2C_2O_4$, m.p. 65·9—66·2°, $(BuCO·NH_2)_2,H_2C_2O_4$, m.p. 61·1—61·4°, $(C_5H_{11}·CO·NH_2)_2,H_2C_2O_4$, m.p. 71·1—71·3°. Interaction of amides and $H_2C_2O_4$ in H_2O yields only $(NH_4)HC_2O_4,H_2C_2O_4$, and Prβ·$CO·NH_2$ failed to yield a salt. J. D. R.

Preparation of nitriles.—See B., 1941, II, 34.

Reaction of magnesium *tert.*-butyl chloride with propionyl, *iso*butylacetyl, and benzoyl chloride. A. D. Petrov and N. A. Roslova (*J. Gen. Chem. Russ.*, 1940, **10**, 973—976).—EtCOCl and MgBuγCl in Et_2O yield $COEt_2$, COEtBuγ, Prα·OH, $EtCO_2H$, $EtCO_2CHEt_2$, and $EtCO_2CHEtBu^{\gamma}$. With CH_2Bu^{β}·COCl the products are *isohexyl isobutylacetate*, b.p. 170—178°, and di*iso*amyl ketone, reduced by Kishner's method to *ββ-dimethylnonane*, b.p. 177—178°. BzCl does not react with MgBuγCl at room temp., whilst in boiling xylene only tarry products are obtained. R. T.

Metallo-organic compounds. IX. Tristrimethyltin oxonium halides, $[SnMe_3]_3OX$. T. Harada (*Bull. Chem. Soc. Japan*, 1940, **15**, 455—458).—The oxonium *compounds* $(SnMe_3)_3OI$, m.p. 94°, and $(SnMe_3)_3OBr$, m.p. 88°, have been obtained by the action of $(SnMe_3)_2O$ on $SnMe_3I$ or $SnMe_3Br$ in an anhyd. solvent. F. J. G.

II.—HOMOCYCLIC.

Products of the oxidation of 1 : 1 : 4-trimethylcycloheptene. H. Barbier (*Helv. Chim. Acta*, 1940, **23**, 1477—1480; cf. A., 1940, II, 217).—Re-examination of the product of the oxidation of trimethylcycloheptene by SeO_2 confirms the formation of 2 : 5 : 5-trimethyl-Δ^2-cycloheptenone (**I**) and reveals the presence of 4 : 4-*dimethyl*-Δ^1-cyclo*hepten*-1-*aldehyde*, b.p. 76°/4 mm. The semicarbazone, m.p. 195—196° (*loc. cit.*), is separated into two portions, m.p. 177° [hydrolysed to (**I**)] and m.p. ~196—200°. The last-named, when hydrolysed and oxidised by Ag_2O, gives 4 : 4-*dimethyl*-Δ^1-cyclo*heptene*-1-*carboxylic acid*, m.p. 63—64° (p-*phenylphenacyl* ester, m.p. 73°). H. W.

Photochemical oxidation of aromatic hydrocarbons. A. A. Krasnovski (*J. Gen. Chem. Russ.*, 1940, **10**, 1094—1100).—A colorimetric method of determination of org. peroxides, depending on oxidation of Fe^{II} to Fe^{III} in presence of CNS′, is described. Oxidation of PhMe by atm. O_2 in ultra-violet light consists of two stages: $PhMe + O_2 \rightarrow PhMe_2O_2 \rightarrow PhCHO + H_2O$. With free access of O_2 the former reaction is of the zero order, and the latter of the first order. R. T.

Alkylation of aromatic hydrocarbons by means of dihalides. I. Condensation of αγ-chlorobromopropane with benzene. I. Tzukervanik and K. Jatzimirski (*J. Gen. Chem. Russ.*, 1940, **10**, 1075—1076).—C_6H_6 and $Cl{\cdot}[CH_2]_3{\cdot}Br$ at 12—13° in presence of $AlCl_3$ give chiefly $Br{\cdot}[CH_2]_3{\cdot}Ph$ (40%), with PhPr and $Ph{\cdot}[CH_2]_3{\cdot}Ph$ (**I**) as by-products. At 80—85° the chief product is (**I**) (60%), with PhPr as a by-product. R. T.

Addition of hydrogen bromide to cholesteryl bromide and the oxygen effect. Y. Urushibara, K. Nambu, and T. Ando (*Bull. Chem. Soc. Japan*, 1940, **15**, 442—448; cf. Mauthner, A., 1907, i, 921).—Cholesteryl bromide (**I**) with HBr and a trace of pyrocatechol or $FeCl_3,6H_2O$ in CCl_4, or with HBr in Et_2O, yields 3 : 5-*dibromocholestane*, m.p. 101·5° (corr.), $[\alpha]_D^{26}$ +5·36° in $CHCl_3$, which when heated in $COMe_2$ gives (**I**), and in C_5H_5N gives $\Delta^{3:5}$-cholestadiene. (**I**) with HBr and O_2 in CCl_4 yields 3 : 6-*dibromocholestane* (**II**), m.p. 154° (corr.), $[\alpha]_D^{26}$ −12·1° in $CHCl_3$, and a compound, $C_{27}H_{45}Br_3$, m.p. (impure) 84—127°, debrominated (NaI in EtOH) to (**I**). (**II**) yields with KOAc in glacial AcOH, cholesteryl acetate, and with Na + $C_5H_{11}{\cdot}OH$, cholestene. A. Li.

Reduction of nitro-compounds by means of sodium sulphide. S. Raschevskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1089—1093).—Reduction is effected via the stages: $4Na_2S + R{\cdot}NO_2 + 4H_2O \rightarrow NH_2R + Na_2S_4 + 6NaOH$ (at 50°); $3Na_2S_4 + 5R{\cdot}NO_2 + 6NaOH + 2H_2O \rightarrow 5NH_2R + 6Na_2S_2O_3$. R. T.

Substituted amides. C. V. Bowen and L. E. Smith (*J. Amer. Chem. Soc.*, 1940, **62**, 3522—3523).—The following are prepared. *Propion*-m-4-, m.p. 137—137·5°, -p-, m.p. 138°, and -m-2-*xylidide*, m.p. 115·5—116·5°, and -*xenylamide*, m.p. 176—177°. *Laur-benzylamide*, m.p. 82—82·5°, and -m-*toluidide*, m.p. 54—56°. *Palmit*-cyclo*hexylamide*, m.p. 94—95°, -*benzylamide*, m.p. 94·5—95°, -o-, m.p. 90—91°, and -m-*toluidide*, m.p. 74·5—75·5°. 2-*Furo*-cyclo*hexylamide*, m.p. 112—112·5°, -*benzylamide*, m.p. 110·5—111°, -m-4-, m.p. 104—105°, -p-, m.p. 89—90°, and -m-2-*xylidide*, m.p. 125—126°, -α-, m.p. 155—156°, and -β-*naphthylamide*, m.p. 152—153°, -2-*fluorylamide*, m.p. 201—201·5°, and -*xenylamide*, m.p. 171—172°. R. S. C.

Substituted adipanilides.—See B., 1941, II, 35.

Chemotherapeutic compounds of the streptocide series. II. M. V. Rubtzov (*J. Gen. Chem. Russ.*, 1940, **10**, 831—843).—The activity of the following compounds has been compared (figures in parentheses refer to the streptocidal activity, that of streptocide being taken as 100; compounds marked * are toxic): *p*-NHR·$C_6H_4{\cdot}SO_2{\cdot}NH_2$, where R = CH_2Ph (70), *γ-diethylaminopropyl* * (45), m.p. 140—142° (*hydrochloride*, m.p. 118—119°), γ-diethylamino-β-hydroxypropyl * (10), m.p. 112°, $CH_2{\cdot}CO_2H$ (125), m.p. 265—266° (decomp.), $CH_2{\cdot}CO{\cdot}NH_2$ (85), m.p. 203—204°, $CH_2{\cdot}SO_3Na$ (90), SO_3Na (20), H (80), *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2$ (30), and *p*-NHAc·$C_6H_4{\cdot}SO_2$ (55); *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR$, where R is CH_2Ph (65), m.p. 119—119·5° (N-*Ac* derivative, m.p. 160—161°), *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2$(33), 4-*amino*-3-*sulphophenyl*(60), *p*-$NH_2{\cdot}C_6H_4$ (100) (N-*Ac* derivative, m.p. 228—229°), pp′-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}$ (100), m.p. 268—269° (decomp.), pp′-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_6H_3(SO_3H\text{-}m)$ (25). Antipyrine and $ClSO_3H$ (5 hr. at 70—80°) yield *antipyrinesulphonyl chloride*, m.p. 185·5—187°, from which *antipyrinesulphonamide*, m.p. 220—221°, is prepared. R. T.

Isomerism of guanidines. R. P. Sieg and W. M. Dehn (*J. Amer. Chem. Soc.*, 1940, **62**, 3506—3508).—Condensation of NH_2Ar with $C(:NAr')_2$ [prep. *in situ* from $CS(NHAr')_2$ by $Pb(OH)_2$] in C_6H_6 gives only NHAr·C(:NAr′)·NHAr′ with small amounts of a carbamide and unchanged starting material. However, NAr″:C:NAr″ gives NHAr·C(:NAr′)·NHAr″ and NHAr·C(:NAr″)·NHAr′. Only one H thus migrates during the condensation. Literature data are corr. The following have been prepared, numbering being N·C(:N″)·N′. NN′-*Diphenyl*-N″-o-, m.p. 93°, -m-, m.p. 101°, and -p-, m.p. 104·5°, NN″-*diphenyl*-N′-o-, m.p. 110·5°, -m-, m.p. 92°, and -p-, m.p. 121°, N″-*phenyl*-NN′-*di*-o-, m.p. 93·5°, -m-, m.p. 92°, and -p-, m.p. 62°, N′-*phenyl*-NN″-*di*-o-, m.p. 97°, -m-, m.p. 86°, and -p-, m.p. 82·5°, NN′-*di*-o-*tolyl*-N″-m-, m.p. 88°, and -p-, m.p. 70·5°, NN″-*di*-o-*tolyl*-N′-m-, m.p. 86°, and -p-, m.p. 83°, NN′-*di*-m-*tolyl*-N″-o-, m.p. 90°, and -p-, m.p. 103°, NN″-*di*-m-*tolyl*-N′-o-, m.p. 84°, and -p-, m.p. 93°, NN′-*di*-p-*tolyl*-N″-o-, m.p. 77·5°, and -m-, m.p. 83·5°, NN″-*di*-p-*tolyl*-N′-o-, m.p. 89·5°, and -m-, m.p. 101°, -*tolylguanidine*. R. S. C.

Chemotherapeutic compounds of the streptocide series. I. Compounds containing the azo-group. O. J. Magidson and M. V. Rubtzov (*J. Gen. Chem. Russ.*, 1940, **10**, 756—768).—The following compounds have been prepared by standard reactions (figures in parentheses refer to streptocidal activity; compounds marked * are toxic): 2 : 4-diaminoazobenzene-4′-sulphonamide hydrochloride [streptocide] (100), N-(p′-2″ : 4″-*diaminobenzeneazobenzenesulphonyl*)*sulphanilamide* (55), m.p. 223—225° (decomp.), 2 : 4-*diaminoazobenzene*-3′-*sulphonamide*, m.p. 198° [*hydrochloride* (50), m.p. 219°], 6-amino-5-benzeneazoquinoline-4′-sulphonamide (100), 4-(γ-*diethylamino*-β-*hydroxypropylamino*)*azobenzene*-4′-*sulphonamide* (100), m.p. 166—167°, 4-(β-*diethylaminoethylamino*)*azobenzene*-4′-*sulphonamide* * (90), m.p. 185—186°, α-*anilino*-γ-*diethylamino*-β-*hydroxypropane*, b.p. 189—190°/12 mm., 5-benzeneazo-6-hydroxyquinoline-4′-sulphonamide (100) [hydrochloride, not melting at 290° (lit. m.p. 268°)], 1-*amino*-7-*benzeneazo*-8-*hydroxy*-3 : 6-*disulphonaphthalene*-4′-*sulphonamide* * (100) [N-*Ac* derivative (100)], 7-*benzeneazo*-1 : 3 : 6-*trisulphonaphthalene*-4′-*sulphonamide* (40), 2-amino-4-hydroxyazobenzene-4′-sulphonamide (90), 2 : 4-diamino-6-carboxyazobenzene-4′-sulphonamide * (85), 2 : 4-dihydroxyazobenzene-4′-sulphonamide * (100), 7-*benzeneazo*-1 : 8-*dihydroxy*-3 : 6-*disulphonaphthalene*-4′-*sulphonamide* (80), and 4-*amino*- (50), m.p. 225—228°, and 4-*hydroxy*-3-*carboxyazobenzene*-4′-*sulphonamide* (100). R. T.

Diazo-compounds. II. Reaction of diazo-compounds with complex heteropoly-acids. V. V. Kozlov and B. N. Archipov. **III. Complex diazo-compounds of phenylenediamines with heteropoly-acids, and certain dyes produced therefrom.** V. V. Kozlov, B. N. Archipov, and A. V. Simonovskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 685—696, 697—704).—II. The *salts* $(RN_2)_3H_4P(M_2O_7)_6$, where M is Mo or W, and $(RN_2)_4H_4Si(W_2O_7)_6$ (R = Ph, *o*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}$, *p*-$C_6H_4Me{\cdot}$, and *o*-$OMe{\cdot}C_6H_4{\cdot}$), were prepared from aq. RN_2Cl and the appropriate acids, or by diazotisation of the corresponding salts of the NH_2R. The salts are considerably more stable than are the corresponding halides. In aq. suspension they are decomposed by Cu powder, in the same way as ordinary diazonium salts.

III. The *salts* $[R(NH_2)_2]_3[H_7P(M_2O_7)_6]_2$ where M is Mo or W, and $[R(NH_2)_2]_2H_6Si(W_2O_7)_6$ (R is *m*- and *p*-C_6H_4, and 1 : 5-$C_{10}H_6$) have been prepared. Aq. suspensions of these salts when diazotised yield diazonium salts of the types $[(NH_2{\cdot}R{\cdot}N_2)_3H_4P(M_2O_7)_6]{\cdot}[H_7P(M_2O_7)_6]$ and $(NH_2{\cdot}R{\cdot}N_2)_2H_2[H_4Si(W_2O_7)_6]$, and couple with β-$C_{10}H_7{\cdot}OH$ giving the azo-dye salts $(NH_2{\cdot}R{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH)_3,H_7P(M_2O_7)_6$ and $(NH_2R{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH)_4,H_8Si(W_2O_7)_6$, from which the azo-dyes are liberated by aq. NaOH. R. T.

Preparation of alkylphenols.—See B., 1941, II, 36.

Synthesis of amylphenol.—See B., 1941, II, 30.

Oxidation of *p*-propenylphenol derivatives.—See B., 1941, II, 36.

Molecular structure in relation to œstrogenic activity. Derivatives of 4 : 4′-dihydroxydiphenylmethane. N. R. Camp-

bell (*Proc. Roy. Soc.*, 1940, **B**, **129**, 528—538).—The derivatives were prepared from the appropriate CO-compound (1 mol.), PhOH or *o*-cresol (4 mols.), and conc. (at room temp.) or dry HCl (at ~0°). The following are new: *αα-di-p-hydroxyphenyl-β-methylpropane*, m.p. 152°, *-γ-methylbutane*, m.p. 145°, *-β-ethylbutane*, m.p. 168°, *-β-n-propylpentane*, m.p. 128°, *-α-phenylpropane*, m.p. 176°, *-β-phenylethane*, m.p. 140°, and *-ββ-diphenylethane*, m.p. 236° (decomp.); *αα-di-(4-hydroxy-3-methylphenyl)-γ-methylbutane*, m.p. 124°; *ββ-di-(p-hydroxyphenyl)-hexane*, b.p. 210°/0·5 mm., and *-γ-methylpentane*, m.p. 153°; *ββ-di-(4-hydroxy-3-methylphenyl)-pentane*, m.p. 128°, *-hexane*, m.p. 104—105°, and *-γ-methylpentane*, m.p. 128°; *γγ-di-(p-hydroxyphenyl)hexane*, m.p. 155°; *γγ-di-(4-hydroxy-3-methylphenyl)-pentane*, m.p. 120°, and *-hexane*, m.p. 90°; *δδ-di-(p-hydroxyphenyl)octane*, m.p. 150°; *δδ-di-(4-hydroxy-3-methylphenyl)-heptane*, m.p. 173°, and *-octane*, m.p. 140°; *εε-di-(p-hydroxyphenyl)nonane*, m.p. 165°; *εε-di-(4-hydroxy-3-methylphenyl)nonane*, m.p. 128°; 1 : 1-*di-(p-hydroxyphenyl)-2-methyl*cyclo*hexane*, m.p. 235°, -cyclo*pentane*, m.p. 157°, *-2-methyl*cyclo*pentane*, m.p. 161°, and *-3-methyl*-cyclo*pentane*, m.p. 171°; 1 : 1-*di-(4-hydroxy-3-methylphenyl)*-cyclo*pentane*, m.p. 162°. The relationship between the determined œstrogenic activity and structure is discussed (A., 1941, III, 100). F. O. H.

Preparation of 2 : 2′-dihydroxydiphenyl.—See B., 1941, II, 36.

Preparation of multivalent iodo-compounds in the *o-*, *m-*, and *p*-iodoanisole series. R. A. Mastropaolo F. (*Anal. Asoc. Quim. Argentina*, 1940, **28**, 101—107).—*o-* and *m*-OMe·$C_6H_4ICl_2$ with aq. 40% NaOH give o- (**I**), m.p. 260—265° (decomp.) (impure), and m-*iodosoanisole*, m.p. 250—251°, respectively; the mother-liquors from (**I**) with KI afford *di-o-anisyliodinium tri-iodide*, m.p. 135—136°, converted by H_2O–Ag_2O followed by KI into *di-o-anisyliodinium iodide*, m.p. 154° (decomp.). *p*-OMe·C_6H_4·IO, *p*-OMe·C_6H_4·IO_2, and H_2O–Ag_2O followed by KI give *di-p-anisyliodinium tri-iodide*, m.p. 145°, whence the *monoiodide*, m.p. 180°. The *m*-iodinium compounds could not be prepared. F. R. G.

2 : 4-Dinitrophenyl alkyl ethers as stimulants of the metabolic rate. L. G. Wesson (*J. Amer. Chem. Soc.*, 1940, **62**, 3466—3468).—2 : 4 : 1-$(NO_2)_2C_6H_3$·OAg (prep. described) and RI at room temp., later 100° (bath), give 2 : 4-*dinitrophenyl* Pr^{α}, m.p. 30·5—31°, b.p. 172—175°/2 mm., Pr^{β} (**I**), m.p. 53·4—53·6°, b.p. 152—156°/0·75 mm. [also obtained from 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$, $Pr^{\beta}OH$, and 80% KOH], Bu^{α}, m.p. 1·5—1·8°, b.p. 178—180°/2 mm., Bu^{β}, m.p. 30·3—31·5°, b.p. 152—154°/1 mm., n-, m.p. 0—1°, b.p. 186—188°/2 mm., and iso-*amyl*, m.p. 9·5—10°, b.p. 175—178°/1 mm., n-*hexyl*, m.p. 4·2—4·6°, b.p. 202—205°/2·5 mm., and n-*heptyl*, m.p. 16·4—16·5°, b.p. 192—194°/1 mm., *ether*. These ethers increase the metabolic rate of rats more slowly than does 2 : 4 : 1-$(NO_2)_2C_6H_3$·OH (**II**). (**I**) causes evolution of only a little NH_3 due to liver damage. 70 mg. per kg. body-wt. fed to rats for 1 month increased the basal metabolic rate by 10% and after 8 months had little other effect. 1 g. per kg. body-wt. increased the basal metabolic rate of rats by 84% and caused death in 3—4 days. (**II**) is present in the bile and colon of dogs after fatal, massive doses of (**I**). R. S. C.

Di-*p*-aminophenyl sulphone. A. M. VanArendonk and E. C. Kleiderer (*J. Amer. Chem. Soc.*, 1940, **62**, 3521—3522).—Thioaniline (purified by means of the disulphate) is converted by boiling Ac_2O–AcOH and then H_2O_2–AcOH at 40—50° into $(p\text{-}NHAc\cdot C_6H_4)_2SO_2$, m.p. 275—278°, which in boiling 10% HCl gives $(p\text{-}NH_2\cdot C_6H_4)_2SO_2$, m.p. 175—176°. R. S. C.

Synthesis of vitamin-*A*. M. V. Krauze and J. M. Slobodin (*J. Gen. Chem. Russ.*, 1940, **10**, 907—912).—Axerophthol prepared from β-ionylideneacetaldehyde (**I**) and CMe_2:CH·CHO (method: Kuhn *et al.*, A., 1937, II, 288) is biologically inactive. β-Ionone and $(OEt)_2CH\cdot CH_2\cdot MgBr$ in Et_2O (4 hr. at the b.p.) give (**I**) in 50—64% yield. R. T.

Formation of insoluble digitonides of cholesterol derivatives. F. S. Spring and G. Swain (*Nature*, 1940, **146**, 718).—A *cis*-3 : 4-dihydroxy-Δ^5-cholestene monobenzoate, m.p. 153—154°, which differs from that (m.p. 209—210°) described by Rosenheim *et al.* (A., 1937, II, 191), has been isolated. It fails to give a digitonide under conditions which effect immediate pptn. of the digitonides of cholesterol (**I**) and the *cis*-diol. Hence the formation of one of the monobenzoates has been accompanied by migration of Bz from the $C_{(3)}$- to the $C_{(4)}$-OH. The introduction of a C_4-*cis*-OBz group into (**I**) prohibits the digitonin reaction. L. S. T.

Derivatives of homoanisic acid. A. Burger and S. Avakian (*J. Org. Chem.*, 1940, **5**, 606—609).—Addition of *p*-$C_6H_4Me\cdot COCl$ to CH_2N_2 in Et_2O at room temp. gives p-*anisyl CHN*$_2$ *ketone*, m.p. 90—91°, transformed by conc. aq. NH_3 and 10% $AgNO_3$ in dioxan at 60—70° into *p*-OMe·$C_6H_4\cdot CH_2\cdot CO\cdot NH_2$, m.p. 188—189°, which is hydrolysed (KOH–EtOH) to homoanisic (*p*-anisylacetic) acid (**I**), m.p. 86—87°, the overall yield being 53%. $ClSO_3H$ at −5° to 0° and then at 40° converts (**I**) into *3-chlorosulphonylhomoanisic acid*, m.p. 164—165° (yield 80·6%), reduced by Zn dust and H_2SO_4 at −5° to 80° to *3-thiol*-p-*homoanisic acid* (**II**), m.p. 83—84°. The structure of (**II**) is proved thus: 3 : 4 : 1-$NO_2\cdot C_6H_3$(OMe)·CH_2Cl is converted by KCN in EtOH containing a little KBr into *3-nitro-4-methoxyphenylacetonitrile*, m.p. 87—87·5°, which is hydrolysed (50% H_2SO_4–AcOH) to *3-nitro*-p-*homoanisic acid*, m.p. 132—133°, also prepared from (**I**) and conc. HNO_3 in glacial AcOH. This is reduced (H_2–Raney Ni–EtOH) to *3-aminohomoanisic acid*, m.p. 110—111°, converted by diazotisation and boiling with 40% H_2SO_4 into homo*iso*vanillic acid, m.p. 127—128°, and by diazotisation and treatment with alkaline Na_2S_2 into 3 : 3′-dithiohomoanisic acid, which is reduced (Zn dust and glacial AcOH at 100°) to (**II**). 1 : 3 : 2-$C_6H_3MeBr\cdot NO_2$ is oxidised by $Na_2Cr_2O_7$ and boiling dil. H_2SO_4 to 2 : 3 : 1-$NO_2\cdot C_6H_3Br\cdot CO_2H$, m.p. 250—251°. This and (**II**) are dissolved in KOH–MeOH, the solution is evaporated to dryness, and the residue is heated at 190°, thereby yielding *2′-nitro-3′-carboxy-2-methoxydiphenyl sulphide-5-acetic acid*, m.p. 232—234° (decomp.), which is reduced by $Fe(OH)_2$–aq. NH_3 to the *2′-*NH_2*-acid*, m.p. 222—224°. H. W.

Lactones related in structure to cardiac aglucones: the lactone of β-aldehydo-β-*cyclo*pentylpropionic acid. S. K. Ranganathan (*Current Sci.*, 1940, **9**, 458—459).—The method of Fried *et al.* (A., 1940, II, 312) has been applied to the prep. of β-aldehydo-β-*cyclo*pentylpropionic acid (**I**) (cf. A., 1939, II, 321). OMe·CH_2·CN and Mg *cyclo*pentyl bromide yield *cyclopentyl OMe·CH*$_2$ *ketone*, b.p. 192—194°/680 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 130°), which with Zn and $CH_2Br\cdot CO_2Et$ gives *Et β-hydroxy-γ-methoxy-β-*cyclo*pentylbutyrate*, b.p. 140°/6 mm., and this with HBr in AcOH followed by distillation yields (?) β-cyclo*pentyl-*Δ^{β}*-buteno-γ-lactone*, b.p. 155°/5 mm., which with 3% KOH–MeOH furnishes (**I**). F. R. G.

Benzyl β-dimethylamino-α-phenyl-α-ethylpropionate (hydrochloride, m.p. 167—168°).—See A., 1941, III, 128.

Stereochemical studies. XXII. Decomposition of optically active α-phenylethylthiolacetic acids. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1940, **14**, **A**, No. 2, 12 pp.).—Various routes for the transitions: CHPhMe·S·$CH_2\cdot CO_2H$ (**I**) ⇄ CHPhMe·OH (**II**) have been studied with reference to optical stability and inversion. With $CH_2Br\cdot CO_2Na$ followed by hydrolysis, (−)-(**I**) gives (+)-(**II**) (60—80% racemised); with $SH\cdot CH_2\cdot CO_2H$ this material gives inactive (**I**). (+)-(**I**) is racemised by $HgCl_2$ in N-HCl and the (**II**) formed is inactive, but the product from (−)-(**I**) and $HgSO_4$ has slight (+)-rotation. (+)-(**II**) with SO_2Cl_2 yields (−)-CHPhMeCl (**III**) (60% racemised) which is reconverted into (**I**) [still slightly (+)] by $SNa\cdot CH_2\cdot CO_2Na$. (+)-(**I**) with Br in glacial AcOH gives (−)-CHPhMeBr (**IV**), $[\alpha]_D^{20}$ −46° (calc.); this racemises very rapidly. (−)-(**III**) (NaOH) and (−)-(**IV**) (H_2O) give (+)-(**II**). The results are discussed. M. H. M. A.

Preparation of *o*-nitrobenzoic acid.—See B., 1941, II, 30.

Beckmann rearrangement of 2 : 4-dihydroxybenzhydroxamic acid derivatives. A. W. Scott and W. O. Kearse (*J. Org. Chem.*, 1940, **5**, 598—605).—2 : 4 : 1-$(OH)_2C_6H_3\cdot CO_2H$ is converted by MeOH and HCl at room temp. into the Me ester (**I**), m.p. 76° (lit. 126—128°), and by boiling $SOCl_2$ followed by ice into 2 : 4-*dihydroxybenzoyl chloride* (**II**), m.p. 142°. 2 : 4-*Dihydroxybenzhydroxamic acid* (**III**), m.p. 162°, decomp. 171° (very difficult to purify), is prepared by the successive addition of NH_2OH,HCl and (**I**) to aq. KOH at room temp. or, better, by addition of free NH_2OH to a suspension of (**II**) in light petroleum (low b.p.). Attempts to prepare the benzoate of (**III**) were unsuccessful but the *acetate*, m.p. 188° (slight decomp.), is obtained by addition of AcCl to a cooled solution of the Na salt of (**III**) in H_2O or by cautious fusion of (**III**) with Ac_2O. KOEt in abs. EtOH transforms this substance into the *K* salt, explodes at 84°, which rearranges in H_2O at 90° to 1 : 5-*dihydroxybenzoxazole* (*hydroxyoxy-*

carbonil) (**IV**), m.p. 288°. The following scheme is suggested: $(OH)_2C_6H_3\cdot C(OM):NO\cdot COR \rightarrow (OH)_2C_6H_3\cdot C(:N\cdot)\cdot O\cdot \rightarrow (OH)_2C_6H_3\cdot N:\dot{C}\cdot\dot{O} \rightarrow$ (**IV**), whereas *o*-hydroxybenzazide rearranges thus: $OH\cdot C_6H_4\cdot CON_3 \rightarrow OH\cdot C_6H_4\cdot C(:O)\cdot N< \rightarrow OH\cdot C_6H_4\cdot\dot{N}\cdot\dot{C}:O \rightarrow OH\cdot C_6H_4\cdot N:C:O$. H. W.

Preparation of thiolcarboxylic acids and their arylamides. I. V. Hopper, J. H. MacGregor, and F. J. Wilson (*J. Soc. Dyers and Col.*, 1941, **57**, 6—9).—The following arylamides are best prepared (unless stated otherwise) from the acid (1 mol.), NH_2Ar (2 mols.), and PCl_3 in C_5H_5N (cf. A., 1939, II, 505). *o*-$SH\cdot C_6H_4\cdot CO_2H$ (**I**) gives an *anilide*, m.p. 236—237°, *o*-, m.p. 217—218°, and *p-toluidide*, m.p. 230° (both prepared using P_2O_5–PhMe), *o-chloroanilide*, m.p. 218—219°, *o-anisidide*, m.p. 156—157°, *4-methoxy-2-methylanilide*, m.p. 233—234°, and *α-*, m.p. 247—248°, and *β-naphthylamide*, m.p. 167—168°. *p*-$SH\cdot C_6H_4\cdot CO_2H$ (prep. from the intermediate S_2-acid by aq. NaOH–$Na_2S_2O_4$; cf. Thompson, A., 1925, i, 815) affords an *anilide*, m.p. 263—264°, *4-methoxy-2-methylanilide*, m.p. 235—236°, and *β-naphthylamide*, m.p. 282—283°.
2:3-$SH\cdot C_{10}H_6\cdot CO_2H$ (**II**) [prep. as for (**I**); Allen *et al.*, Org. Syntheses, 1932, **12**, 76] gives an *anilide*, m.p. 285—286°, *o-*, m.p. 279—280°, and *p-toluidide*, m.p. 276—277°, *o-anisidide*, m.p. 220—221°, *α-naphthylamide*, m.p. 306—307°, and *4-chloro-2:5-dimethoxy-*, m.p. 255—256°, *4-methoxy-2-methyl-*, m.p. 264—265°, and *2-methoxy-5-diethylaminosulphonyl-anilide*, m.p. 214—215°. 1:8-$C_{10}H_6\langle^{S}_{CO}$ (**III**) is obtained in good yield from diazonaphthostyril (suspension distinctly acid to Congo-red) and Na_2S_x at +5°; 1:8-$SH\cdot C_{10}H_6\cdot CO\cdot NHAr$ could not be prepared from (**III**). Cotton yarn, impregnated with arylamides of (**I**) or (**II**) in aq. EtOH–KOH, and treated with diazotised bases, gives dyeings of biscuit, lemon, or fawn [from (**I**)] or biscuit, orange, or tan [from (**II**)], which do not possess all-round fastness properties. A. T. P.

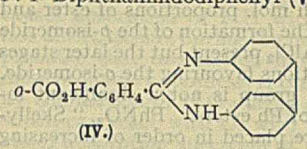
Anæsthetics of the naphthalene series. II. Esters of 4-alkylamino-1-naphthoic acids. S. I. Sergievskaja and K. P. Preobrashenskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 950—958).—1:4-$NH_2\cdot C_{10}H_6\cdot CO_2K$ and RI yield the acids 1:4-$NHR\cdot C_{10}H_6\cdot CO_2H$ [R = *Et*, m.p. 153° (decomp.), *Pr*$^{\alpha}$, m.p. 172—173°, *Bu*$^{\alpha}$, m.p. 208°, *allyl*, m.p. 151°], which are esterified in the usual way to 1:4-$NHR\cdot C_{10}H_6\cdot CO_2R'$ [R = Et, R′ = *Et*, m.p. 76—77° (*hydrochloride*, m.p. 145—146°), *Pr*$^{\alpha}$, m.p. 69° (*hydrochloride*, m.p. 143—145°), *NEt*$_2\cdot CH_2\cdot CH_2$, m.p. 188—189°; R = Pr$^{\alpha}$, R′ = *Et*, m.p. 38—39° (*hydrochloride*, m.p. 156°), *NEt*$_2\cdot CH_2\cdot CH_2$ (*hydrobromide*, m.p. 182—183°); R = Pr$^{\beta}$, R′ = *NEt*$_2\cdot CH_2\cdot CH_2$ (*hydrobromide*, m.p. 185—186°); R = Bu$^{\alpha}$, R′ = *Et*, m.p. 54° (*hydrochloride*, m.p. 143—144°), *Pr*$^{\alpha}$, m.p. 50·5° (*hydrochloride*, m.p. 114—116°), *NEt*$_2\cdot CH_2\cdot CH_2$ (*hydrobromide*, m.p. 180°); R = allyl, R′ = *Et*, m.p. 67·5° (*hydrochloride*, m.p. 147—148°, decomp.), *Pr*$^{\alpha}$, m.p. 61—62°, *NEt*$_2\cdot CH_2\cdot CH_2$ (*hydrobromide*, m.p. 191—191·5°)]. The activity of the $NEt_2\cdot CH_2\cdot CH_2$ esters is > of alkyl esters. R. T.

4-Hydroxy-3-sulphobenzoic acid. G. V. Medox and N. K. Dobrovolskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 705—706).—*p*-$OH\cdot C_6H_4\cdot CO_2H$ and 10% oleum (30 min. at 100°) afford 4:3:1-$OH\cdot C_6H_3(SO_3H)\cdot CO_2H$ in 98% yield. R. T.

Preparation of *m*-carboxybenzenesulphondichloroamide and of carboxybenzene-3:5-bis(sulphondichloroamide) from benzoic acid. O. V. Vasilevskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 683—684).—BzOH and $ClSO_3H$ yield *m*-$CO_2H\cdot C_6H_4\cdot SO_2Cl$, which with aq. NH_3 gives the sulphonamide, chlorinated to *m-carboxybenzenesulphondichloroamide*. BzOH and $ClSO_3H$ in oleum–P_2O_5 yield 1:3:5-$CO_2H\cdot C_6H_3(SO_2Cl)_2$, from which the 3:5-*disulphonamide*, m.p. 249—250°, and 3:5-*bis-(sulphondichloroamide)* are prepared as above. R. T.

Elimination of the phthalyl residue in Gabriel's synthesis [of amines]. A. A. Beer and N. K. Kotschetkov (*J. Gen. Chem. Russ.*, 1940, **10**, 714—717).—The method of Ing *et al.* (A., 1926, 1132) is preferred. R. T.

Products of condensation of phthalic anhydride with benzidine. B. A. Porai-Koschitz and P. M. Mostriukov (*J. Gen. Chem. Russ.*, 1940, **10**, 629—635).—Benzidine (**I**) and *o*-$C_6H_4(CO)_2O$ (**II**) in EtOH yield a mixture of *NN′*-4:4′-diphenylenephthalamic acid (**III**) and the substance (**IV**). (**III**) is obtained almost pure when (**I**) is added to fused (**II**), whilst (**IV**) is the sole product when (**II**) is added to fused (**I**). 4:4′-Diphthalimidodiphenyl (**V**) added to fused (**I**) yields the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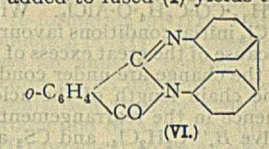

(VI.)

substance (**VI**), which regenerates (**V**) when added to fused (**II**). R. T.

Preparation of $\Delta^{9:11}$-cholenic acid. S. Bergström (*Arkiv Kemi, Min., Geol.*, 1940, **14, B**, No. 6, 2 pp.; cf. Barnett *et al.*, A., 1938, II, 497).—The semicarbazone, m.p. 227—230° (decomp.), of 12-keto-$\Delta^{9:11}$-cholenic acid with NaOEt at 200°/10 hr. gives $\Delta^{9:11}$-*cholenic acid*, m.p. 154—155° (Me ester, m.p. 85—86°). W. McC.

2:4-Dihydroxybenzaldehyde-2:4-dinitrophenylhydrazone. A. W. Scott and J. M. Burns (*J. Amer. Chem. Soc.*, 1940, **62**, 3522).—This *substance* has m.p. 286° (decomp.). R. S. C.

Sulphanilamide compounds. V. Arylidene derivatives of N^4-acetyl-N^1-*p*-aminophenylsulphanilamide and N^1-*p*-aminophenylsulphanilamide. H. G. Kolloff and J. H. Hunter (*J. Amer. Chem. Soc.*, 1940, **62**, 3355—3357; cf. A., 1940, II, 327).—*Sulphanil*-p-*aminoanilide* (**I**), m.p. 155°, or its N^4-*Ac* derivative, m.p. 230—231°, with 1 mol. of PhCHO at 140° gives *sulphanil*-p-*benzylideneaminoanilide* (**II**), m.p. 225°, and its N^4-*Ac* derivative, m.p. 206·5—207°, respectively. *Sulphanil*-p-*anisylidene-* (**III**), m.p. 204—205° (N^4-*Ac* derivative, m.p. 246·5—247·5°), *-*p-p′-*dimethylaminobenzylidene-*, m.p. 214—215° (N^4-*Ac* derivative, m.p. 242°), and *-*p-p′-*nitrobenzylidene-*, m.p. 223—224° (N^4-*Ac* derivative, m.p. 255·5—257·5°), *-aminoanilide* are similarly prepared. With 2 mols. of ArCHO, (**I**) gives N^4-p-*anisylidenesulphanil*-p-p′-*anisylidene-*, m.p. 183—184°, N^4-p-*dimethylaminobenzylidenesulphanil*-p-p′-*dimethylaminobenzylidene-*, m.p. 238·2°, and N^4-p-*nitrobenzylidenesulphanil*-p-p′-*nitrobenzylidene-*, m.p. 230°, *-aminoanilide*, but the $(CHPh:)_2$ compound could not be obtained. The structure of (**II**) and (**III**) is proved by hydrogenation (Raney Ni) in dioxan at 50—58°/3 atm. to the known *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot NH\cdot CH_2Ar$ (*loc. cit.*). R. S. C.

Orientation in the acylation of phenol and in the rearrangement of phenolic esters. A. W. Ralston, M. R. McCorkle, and S. T. Bauer (*J. Org. Chem.*, 1940, **5**, 645—659).—In the action of octoyl chloride on PhOH in presence of $AlCl_3$, the use of equimol. proportions of PhOH and $AlCl_3$ and hence of the complex $OPh\cdot AlCl_2$ (**I**) favours the production of the *o*-OH-ketone whilst if more $AlCl_3$ is used [hence if $R\cdot COCl,AlCl_3$ (**II**) is present] the *p*-isomeride is preferentially produced. If both complexes are previously formed the acyl group shows a decided preference for the *p*-position. If (**II**) reacts with (**I**) the ratio *p*/*o* is >1. The previous formation of the complexes excludes the possibility of the reaction (**II**) + PhOH → $R\cdot COCl$ + (**I**) + HCl → $OH\cdot C_6H_4\cdot COR,AlCl_3$. When this possibility is excluded the yield of *p*-isomeride is materially increased. In presence of (**I**) but not of (**II**) in $C_2H_2Cl_4$ the yield of the isomerides is independent of the temp. over the range 50—100° but *o*-orientation is abnormally favoured at 30°. Similar results are obtained at 50° and 100° when the PhOH is added to the previously-formed (**II**) but at 30° the *p*/*o* ratio differs decidedly from that at 50° and 100°. Ester formation is the predominant reaction at the lower temp. but decreases with increase in the amount of $AlCl_3$ or temp. The presence of the ester as such during the reaction cannot be assumed since it may be formed by hydrolysis of the $AlCl_3$–ester complex. Ester formation may occur: (**I**) + $R\cdot COCl \rightleftharpoons R\cdot CO_2Ph,AlCl_3$ (**III**) and (**III**) → $OH\cdot C_6H_4\cdot COR,AlCl_3$. Ester-complex formation proceeds very rapidly as compared with ketone-complex formation and if hydrolysis is effected at any intermediate point the product consists of a mixture of *o*- and *p*-OH-ketones and ester. Repetition of the work of Cox (A., 1930, 344) using Ph octoate (**IV**) with excess of $AlCl_3$ in excess of Ph_2O gives 85% of *p*-phenoxyoctophenone (**V**), 3·9% of *p*- (**VI**) and a trace of *o*-hydroxyoctophenone. The high yield of (**V**) is due to an intermol. reaction since (**VI**) is almost unaffected by treatment with 2 mols. of $AlCl_3$ in excess of Ph_2O for 6 hr. at 70°. Fries rearrangement of (**IV**) by $AlCl_3$ in $C_2H_2Cl_4$ gives a *p*/*o* ratio >1. Increase of temp. from 70° to 100° decreases the amount of ester without altering the ratio of isomerides. Increase in the amount of $AlCl_3$ increases

the *p*/*o* ratio. The rearrangement can be represented, $C_7H_{15}\cdot CO_2Ph + 2AlCl_3 \rightarrow$ (I) + (II) + HCl $\rightarrow$ $C_7H_{15}\cdot CO\cdot C_6H_4\cdot O\cdot AlCl_2$. With mol. proportions of ester and $AlCl_3$ initial conditions favour the formation of the *p*-isomeride because of the great excess of $AlCl_3$ present but the later stages of the change are under conditions favouring the *o*-isomeride. The chain length of the acid group is not a significant influence in the rearrangement of Ph esters. $PhNO_2$, "Skellysolve *B*," $C_2H_2Cl_4$, and CS_2 are placed in order of increasing *ortho*-directing influence. Under the experimental conditions rearrangement of *p*- and *o*-OH-ketones is not observed.

H. W.

4-*cyclo*Hexylbenzophenone and its oxime. R. D. Kleene (*J. Amer. Chem. Soc.*, 1940, **62**, 3523).—Phenyl*cyclo*hexane, BzCl, and $AlCl_3$ in CS_2 at room temp. and later 100° (bath) give 4-cyclo*hexylbenzophenone*, m.p. 58—60°, b.p. 195—200°/3 mm. (*oxime*, m.p. 125—127°), oxidised by $Na_2Cr_2O_7$–H_2SO_4 to *p*-$C_6H_4Bz\cdot CO_2H$.

R. S. C.

Quantitative study of the so-called "positive halogen" in ketones and esters. R. Altschul and P. D. Bartlett (*J. Org. Chem.*, 1940, **5**, 623—636).—Determinations have been made of the equilibrium const. and forward rate const. (under anti-oxidant conditions) for the debromination with HBr in glacial AcOH at 25° of CBz_3Br, $CPhBz_2Br$, CPh_2BzBr, CPh_3Br, $CHPh_2\cdot CBz_2Br$, $CMeBz_2Br$, $CHBz_2Br$, and $CBr(CO_2Et)_3$. This is regarded as typical of the so-called "positive halogen." The establishment of equilibrium in the bromination of $CHPh_2Bz$ is strongly promoted by light, indicating that there must be a peroxide-catalysed mechanism for the reverse reaction which, however, has not been detected. Peroxides are necessary to the reaction between HBr and CPh_3Br. However, compounds having Br in the α-position to :CO react with HBr at a rate which is independent of the concn. of peroxides or antioxidants (in presence of *cyclo*hexene) and is attributable to a polar mechanism, presumably the exact reversal of the bromination of a ketone through its enol in a polar solvent. Equilibrium and rate of debromination, which are greatly dependent on structure, do not show any general parallelism with one another. These results emphasise that there can be no sharp distinction between "positive" halogen and other halogen. In no case does the mode of reaction characteristic of "positive" halogen disappear but it may become very slow and the equilibrium may become unfavourable to its occurrence.

H. W.

Mechanism of ketone formation from *trans*-indene glycol and halohydrins. C. M. Suter and H. B. Milne (*J. Amer. Chem. Soc.*, 1940, **62**, 3473—3477).—Measurement of the rate of formation of indan-2-one (I) from *cis*- and *trans*-indene glycol by acid indicates that the *trans*- is first isomerised to the *cis*-glycol which more slowly yields (I). Production of indan-1-one (II) from *trans*-indene bromohydrin in acid is more complex, Br′ being liberated faster than (II) is formed; simultaneous formation of glycol [and hence (I)] renders a quant. interpretation difficult.

R. S. C.

Sterols. CXIII. Sapogenins. XLII. Conversion of sapogenins into pregnenolones. R. E. Marker (*J. Amer. Chem. Soc.*, 1940, **62**, 3350—3352).—Conversion of sapogenins into ψ-derivatives by Ac_2O at 200° is nearly quant. Subsequent oxidation by CrO_3–AcOH and hydrolysis (KOH–EtOH) to Δ^{16}-pregnen-3-ol-20-ones gives good (38—56%) yields if defined conditions are adhered to (cf. following abstract); protection of the ethylenic linking is unnecessary. *epi*-Sarsasapogenin acetate thus gives Δ^{16}-*pregnen*-3(α)-*ol*-20-*one* (I) (52%), m.p. 194—196° (*acetate*, m.p. 96—99°). Tigogenin, *epi*tigogenin, sarsasapogenin, and diosgenin acetates gives Δ^{16}-*allo*pregnen-3(β)-ol-20-one (II) (49%), m.p. 202—204°, Δ^{16}-*allo*pregnen-3(α)-ol-20-one (56%) (III), m.p. 219—222°, Δ^{16}-pregnen-3(β)-ol-20-one (IV) (48%), m.p. (anhyd.) 188—190°, and $\Delta^{5:16}$-pregnadien-3(β)-ol-20-one (38%), m.p. 212—214°, respectively. Similarly dihydro-ψ-*epi*sarsapogenin, -ψ-sarsasapogenin, -ψ-tigogenin, and -ψ-*epi*tigogenin by acetylation and oxidation yield (I) (61%), (IV) (47%), (II) (60%), and (III) (56%), respectively. Na–EtOH and (I) give pregnane-3(α) : 20(α)-diol, m.p. 242—243° (diacetate, m.p. 175—176°). H_2–Pd–$BaSO_4$ reduces (I) in EtOH–Et_2O to pregnan-3(α)-ol-20-one, m.p. 145—147° (acetate, m.p. 112—114°), whilst H_2–PtO_2 at 45 lb. in AcOH gives pregnane-3(α) : 20(β)-diol, m.p. 231°. Oxidation (CrO_3–AcOH) of (I) affords Δ^{16}-pregnene-3 : 20-dione, m.p. 200—202°.

R. S. C.

Sterols. CXII. Sapogenins. XLI. Preparation of trillin. Its conversion into progesterone. R. E. Marker and J. Krueger (*J. Amer. Chem. Soc.*, 1940, **62**, 3349—3350).—Diosgenin, bromoacetylglucose, and $Hg(OAc)_2$ in boiling C_6H_6 give trillin tetra-acetate (I), m.p. 197°, identical with that (m.p. 199—200°) from the natural product (A., 1940, II, 378) and hydrolysed by 2% KOH–MeOH to trillin (~50% yield). *Sarsasapogenin* α-d-*glucoside tetra-acetate*, m.p. 227°, and the free *glucoside*, m.p. 245°, are similarly prepared. Ac_2O and (I) at 200° give a non-cryst. ψ-derivative, which with CrO_3–AcOH at 25° gives a product, converted by hydrolysis (conc. HCl–EtOH) and treatment with Girard's reagent into $\Delta^{5:16}$-pregnadien-3-ol-20-one, m.p. 210—212°; protection of the ethylenic linking is unnecessary. Hydrogenation (Pd–$BaSO_4$; Et_2O; 15 lb.) then gives Δ^5-pregnen-3-ol-20-one, m.p. 188—190°, which with Pt–black in CO_2 at 250—300° gives progesterone, m.p. 120—121°.

R. S. C.

Steroids. IV. Degradation products of cholic acid and synthesis of 7 : 12-dihydroxyprogesterone. M. Ehrenstein and T. O. Stevens (*J. Org. Chem.*, 1940, **5**, 660—673).—Oxidation of diphenyl-3(α) : 7 : 12-triacetoxyternorcholylcarbinol with CrO_3 in AcOH gives an acidic portion hydrolysed by KOH–aq. MeOH to *ætiocholic* [3(α) : 7 : 12-*trihydroxyætiocholanic*] *acid* (I), m.p. 254—258°, $[\alpha]_D^{27\cdot5}$ +65·2° in abs. EtOH, and a neutral portion from which Girard's reagent *T* removes 3(α) : 7 : 12-triacetoxypregnan-20-one (II), m.p. 149—151° (lit. 134—135°). Oxidation of (I) by CrO_3–AcOH affords *dehydroætiocholic* [3 : 7 : 12-*triketoætiocholanic*] *acid*, m.p. 245—246°. (II) is hydrolysed to 3(α) : 7 : 12-trihydroxypregnan-20-one, which is oxidised (CrO_3 in AcOH) to *pregnane*-3 : 7 : 12 : 20-*tetraone*, m.p. 238—242°, $[\alpha]_D^{26}$ +76·3° in $COMe_2$. Cautious alkaline hydrolysis of (II) yields 12-*acetoxypregnane*-3(α) : 7-*diol*-20-*one*, m.p. 230—233°, $[\alpha]_D^{27}$ +81·6° in $COMe_2$, oxidised to 12-*acetoxypregnane*-3 : 7 : 20-*trione*, m.p. 160·5—163·5°, $[\alpha]_D^{26}$ +125·9° in $COMe_2$, and converted by successive treatments with $Al(OPr^{\beta})_3$ in PhMe and *cyclo*hexanone and Ac_2O–C_5H_5N at 100° into 7 : 12-*diacetoxypregnane*-3 : 20-*dione* (III), m.p. 256—262°, $[\alpha]_D^{24}$ +113·7° in $CHCl_3$. Br and a little 40% HBr in AcOH transform (III) into somewhat impure 4-*Br*-derivative, m.p. 210—218° (decomp.), debrominated in collidine at ~190° to somewhat impure 7 : 12-*diacetoxy*-Δ^4-*pregnene*-3 : 20-*dione* (7 : 12-*diacetoxyprogesterone*), m.p. 249·5—252°.

H. W.

2-Guanidinoanthraquinone.—See B., 1941, II, 36.

Reaction of naphthazarin with hexadiene and piperylene. B. Arbusov and K. Nikanorov (*J. Gen. Chem. Russ.*, 1940, **10**, 649—652).—Naphthazarin with $(CHMe{:}CH)_2$ (2 hr. at 160—170°) or $CH_2{:}CH\cdot CH{:}CHMe$ (20 hr. at 125—130°) in $PhNO_2$ yields 5 : 8-*dihydroxy*-1 : 4-*dimethyl*-, m.p. 226—227°, or 5 : 8-*dihydroxy*-1-*methyl*-*anthraquinone*, m.p. 236—237°, respectively. With *allo*cimene in EtOH the product is 1 : 4-*dihydroxy*-8-α-*methylpropenyl*-5 : 5-*dimethyl*-5 : 8 : 5a : 8a-*tetrahydroanthraquinone*, m.p. 157°.

R. T.

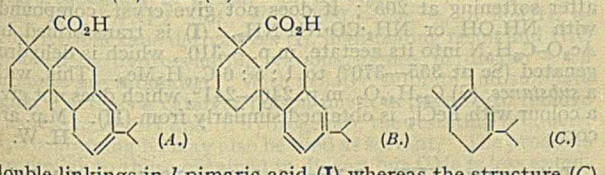
III.—TERPENES.

New degradation of cineolic acid. H. Rupe and R. Zweidler (*Helv. Chim. Acta*, 1940, **23**, 1025—1045).—The action of Mg aryl or alkyl halides on cineolic anhydride (I) consists exclusively of addition to CO attached to $C_{(6)}$. Addition of one or two radicals is a question of constitution. In the first case a CO-acid is produced which is immediately reduced to the OH-acid by the Grignard compound. In the second case a OH-acid is produced. Addition of (I) to MgPhBr (2 mols.) in Et_2O affords 6-*diphenylcarbinyleucalyptanic acid* (II), $OH\cdot CPh_2\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\O—CMe_2\end{matrix}>CH\cdot CO_2H$, m.p. 162—163°, also formed with cineolic acid when 1 mol. of MgPhBr is used. (The name "eucalyptan" is proposed for the parent 2 : 2 : 6-trimethyltetrahydropyran.) (II) is transformed by KOH–Me_2SO_4 into the *Me* ester (III), m.p. 90—91°, and by boiling Ac_2O into the *lactone*, m.p. 133—134°, which is converted by HBr in MeOH into a very unstable *compound*, $C_{23}H_{27}O_3Br$, transformed by C_5H_5N into *Me benzhydryl*-Δ^5-*eucalyptenate*, preferably obtained from (III) and P_2O_5 in boiling C_6H_6. The corresponding *acid*, m.p. 145°, is oxidised by $KMnO_4$ to $CPh_2Me\cdot CO_2H$, m.p. 172° (p-*toluidide*, m.p. 110—111°), and a little terebinic acid (II) which alone is produced by the action of O_3. (III) is oxidised by CrO_3 to $COPh_2$ and (IV) (*Ag* salt; p-*toluidide*, m.p. 186—187°). *p*-$C_6H_4Me\cdot MgBr$ and (I) yield

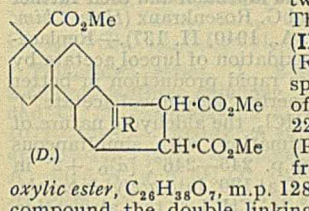
6-di-p-tolylcarbinyleucalyptanic acid, m.p. 151—152°, whilst *6-di-p-benzyl-*, m.p. 137—138°, and *6-di-1′-naphthyl-*, m.p. 210—212°, *-carbinyleucalyptanic acid* are similarly derived. (I) and MgMeBr or MgMeI afford *6-dimethylcarbinyleucalyptanic acid*, m.p. 110—111° (*Me* ester, b.p. 139—141°/12 mm.). The corresponding *lactone*, b.p. 146—148°/12 mm., m.p. 77—78°, is reduced by Na in boiling EtOH to *3-hydroxymethyl-6-dimethylcarbinyleucalyptan*, a viscous liquid which could not be distilled without loss of H_2O. (II) and MgEtBr give *6-diethylcarbinyleucalyptanic acid*, m.p. 137·5—138°, b.p. 188°/11 mm. (slight decomp.) (*Mg*, *Ca*, and *Cd* salts). The *lactone* (V), m.p. 89—90°, b.p. 163—165°/14 mm., is hydrolysed with difficulty by NaOH and is not reduced by H_2–Pd–C in $COMe_2$ or H_2–Ni–EtOAc at 90°/170 atm. Boiling HI (*d* 1·57) gives very unstable compounds containing I. The *Me* ester (VI), b.p. 162—165°/15 mm., is very stable towards boiling Ac_2O or HCO_2H. It is converted by $SOCl_2$ or PCl_5 into a very unstable *Cl*-ester, better obtained from (V) and MeOH–HCl. It is almost unaffected by attempted hydrogenation (Pd–$BaSO_4$; Zn–Cu; Zn–Pd in EtOH) and a Cl-free product is obtained only with difficulty by C_5H_5N. The corresponding unstable *Br*-ester is transformed by boiling C_5H_5N into *Me methyldiethyl-Δ⁵-eucalyptenate*, b.p. 139—141°/10 mm. [better obtained from (VI) and P_2O_5], which could not be hydrogenated (Pd–$BaSO_4$ or Ni). Incautious treatment of (V) with HBr may cause fission of the pyran ring followed by replacement of the OH produced by Br, giving a compound transformed by C_5H_5N into a doubly unsaturated *compound*, $C_{15}H_{26}O_2$, b.p. 123—127°/10 mm. The non-cryst. *diethylmethyl-Δ⁵-eucalyptenic acid* (VII) loses some CO_2 when distilled under diminished pressure and passes at atm. pressure into (?) *6-methyldiethyl-Δ⁵-eucalyptene*, b.p. 104—107°/14 mm. Ozonisation of (VII) in CCl_4 or, preferably, oxidation with $KMnO_4$ yields (IV). (VII) is with difficulty reduced (Na salt–Ni–H_2 at 142°/200 atm.) to *6-methyldiethyleucalyptanic acid*, a liquid (*Me* ester, b.p. 147—150°/11 mm.), accompanied by a neutral *liquid*, $C_{13}H_{28}O$, b.p. 119—121°/11 mm. $MgPr^{\alpha}Br$ and (I) yield *6-di-*, m.p. 111—112°, and *6-mono-*, m.p. 179°, *-propylcarbinyleucalyptanic acid*, the latter arising from the reduction of a primary CO-acid by a second mol. of $MgPr^{\alpha}Br$. (I) and $MgPr^{\beta}Br$ afford a resin and *6-isopropylcarbinyleucalyptanic acid*, m.p. 114—115° (*Ag* salt; *lactone*, m.p. 119—120°); it is hydrogenated (Ni–H_2 at 125°/185 atm.) to *βδ-dimethyl-η-isopropyloctane-γδθ-triol*, m.p. 59—60°, which consumes 1·09 mol. of $Pb(OAc)_4$ and is oxidised by CrO_3 to *6-isobutyryleucalyptan-3-carboxylic acid*, m.p. 86—87° (transformed by MgEtBr into *6-α-hydroxy-α-isopropyl-n-propyleucalyptan-3-carboxylic acid*, m.p. 150—152°), and (IV). Mg *cyclo*hexyl bromide and (II) give *6-cyclohexylcarbinyleucalyptanic acid*, m.p. 180—181° (*Ag* salt; *Me* and *p-bromophenacyl*, m.p. 109—111°, esters). *p-Nitrobenzylthiuronium chloride*, m.p. 217—218°, yields *derivatives*, $C_{20}H_{31}O_6N_3S$, m.p. 151—152°, and $C_{22}H_{35}O_6N_3S$, m.p. 130—131°, with dimethyl- and diethylcarbinyleucalyptanic acid. H. W.

Degradation of *iso*borneol by the xanthate method. A. I. Schavrigin (*J. Gen. Chem. Russ.*, 1940, **10**, 807—811).—*iso*Bornyl or bornyl xanthate decomposes at 210—220°, giving bornylene in 40—50% yield. R. T.

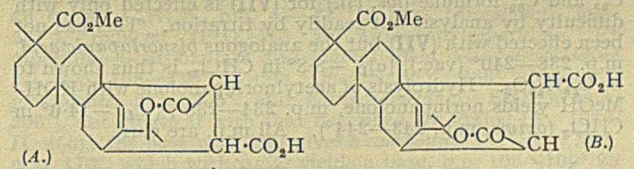
Diterpenes. XLIII. Position of the double linkings of *l*-pimaric acid. L. Ruzicka and S. Kaufmann (*Helv. Chim. Acta*, 1940, **23**, 1346—1356; cf. A., 1940, II, 184).—Two possibilities (*A*) and (*B*) remain for the distribution of the



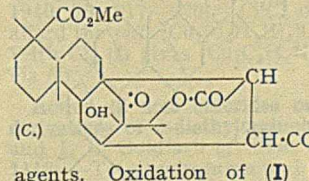
double linkings in *l*-pimaric acid (I) whereas the structure (*C*) is no longer tenable. Preference is accorded to (*A*) particularly with respect to the transformation of (I) into abietic acid since (*B*) postulates the wandering of the two double linkings over two C atoms. Ozonisation of the Me_3 ester of the adduct (II) of (I) and maleic anhydride in AcOH at room temp. and decomp. of the ozonide with H_2O gives small amounts of amorphous acids and a mixture of neutral products from which a singly unsaturated *ketotricarboxylic ester* (III), $C_{26}H_{36}O_7$, m.p. 168—169 (*oxime*, m.p. 174—176°), and a doubly unsaturated tricarboxylic *ester* (IV), $C_{27}H_{38}O_6$, m.p. 124—126°, which gives a marked yellow colour with $C(NO_2)_4$ have been isolated. Hydrogenation (PtO_2 in AcOH) of (IV) causes absorption of 2 H with re-formation of (II). Since loss of CH_2 occurs during the production of (III) it is therefore probable that ozonisation follows an unusual course. The most probable hypothesis is the entry of OH into Pr^{β} followed by elimination of H_2O during ozonisation yielding $\cdot CMe{:}CH_2$ which can react with O_3 with production of Ac. The ultraviolet absorption spectrum of (III) proves it to be an αβ-unsaturated ketone and the double linking of (II) is therefore in conjugation to the CO of the degradation product. The location of CO in a side-chain is proved by treatment of (III) with NaOBr in alkaline solution, whereby 2 CO_2Me are hydrolysed with production of $CHBr_3$ and a *Me* H_3 *tetracarboxylate* (V), $C_{23}H_{30}O_8{\cdot}0{\cdot}5H_2O$, m.p. 280—283°, converted by CH_2N_2 into a Me_4 ester, $C_{26}H_{36}O_8$, m.p. 152—153°. The absorption spectrum of (V) shows the bands characteristic of αβ-unsaturated acids and that of (IV) exhibits those required for two conjugated double linkings. The structures of (I), (IV), and (III) are represented by (*D*) (R = Pr^{β}, $CMe{:}CH_2$, and Ac respectively). Partial hydrolysis of (III) gives a Me_2 *H* ester, m.p. 226—228°, and hydrogenation (PtO_2 in AcOH) affords a mixture from which the *hydroxytricarboxylic ester*, $C_{26}H_{38}O_7$, m.p. 128—129°, can be isolated; in this compound the double linking can be detected by $C(NO_2)_4$ since it is no longer vicinal to CO. Reduction (Clemmensen) of (III) and dehydrogenation (Se) of the non-cryst. product gives a hydrocarbon, m.p. 86—87°, which must be *1-methyl-7-ethylphenanthrene* [additive *compound* with $C_6H_3(NO_2)_3$, m.p. 131—133°] provided that isomerisations have not occured during the transformations. Treatment of (III) with a large excess of MgEtI and dehydrogenation (Se) of the resulting product yields similarly *1-methyl-7-sec.-butylphenanthrene*, m.p. 60—62° [additive *compound*, m.p. 121—123°, with $C_6H_3(NO_2)_3$], oxidised (CrO_3 in AcOH) to the *quinone*, $C_{19}H_{18}O_2$, m.p. 138—140°. All m.p. are corr. H. W.



Diterpenes. XLIV. Action of ozone and permanganate on the additive product of maleic anhydride and *l*-pimaric acid. L. Ruzicka and W. A. Lalande, jun. [with S. Kaufmann] (*Helv. Chim. Acta*, 1940, **23**, 1357—1366; cf. A., 1933, 279; 1938, II, 287; Wienhaus *et al.*, A., 1936, 1385).—Ozonisation in AcOH of the additive product of maleic anhydride and Me *l*-pimarate gives the compound (I), $C_{25}H_{34}O_8$, m.p. 252—253° (decomp.) after softening, and two isomeric *Me H* esters, $C_{25}H_{34}O_6$, m.p. 289—290° (II) and 226—227° (III). (III) and CH_2N_2 give a cryst. Me_2 ester, $C_{26}H_{36}O_6$ (IV), m.p. 182—183°, whereas the corresponding derivative of (II) is amorphous. In (II) and (III) 2 O are present in CO_2H and 2 in CO_2Me and since the compounds are unsaturated towards

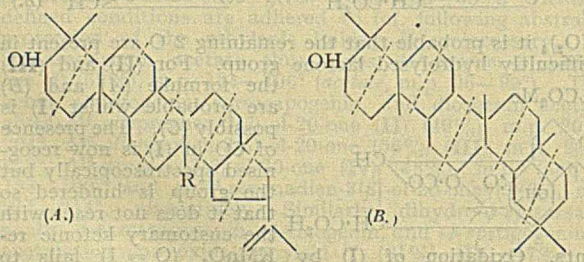


$C(NO_2)_4$ it is probable that the remaining 2 O are present in a difficultly hydrolysed lactone group. For (II) and (III) the formulæ (*A*) and (*B*) are probable whilst (I) is possibly (*C*). The presence of CO in (I) is now recognised spectroscopically but the group is hindered so that it does not react with the customary ketonic reagents. Oxidation of (I) by $KMnO_4$ (O = 1) fails to give the compound, $C_{24}H_{34}O_7$, m.p. 191—192°, recorded by Arbusov (A., 1933, 392), its place being taken by two *lactonedicarboxylic acids*, $C_{24}H_{32}O_6$ (V), m.p. 211—212°, and $C_{24}H_{34}O_6$ (VI), m.p. 250—252° after softening. (V) gives a yellow colour with $C(NO_2)_4$ and titrates as a dibasic acid, the lactone group being hydrolysed with difficulty; its Me_2 ester, m.p. 182—184°, is identical with (IV). The lactone group of (VI) is hydrolysed by N-KOH. With CH_2N_2 (VI



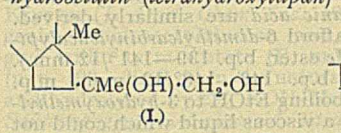
yields a Me_2 ester (**VII**), m.p. 218—220°. Neither (**VI**) nor (**VII**) gives a yellow colour with $C(NO_2)_4$. The constitution of (**VI**) remains obscure. The action of $KMnO_4$ (O = 2) on (**I**) gives (**V**) in 75% yield whereas with $KMnO_4$ (O = 3) a *substance*, $C_{24}H_{32}O_8$ (**VIII**), m.p. 307—308° (decomp.), results in 12—18% yield. (**VIII**) does not give a yellow colour with $C(NO_2)_4$, is titrated as a monobasic acid, and with CH_2N_2, gives a Me_1 ester, $C_{25}H_{34}O_8$, m.p. 276—278°. Acid and ester are readily hydrolysed, whereby 3 CO_2H are identified. In addition to CO_2H (**VIII**) therefore contains an anhydride group. Two further O atoms are probably present as OH since warm Ac_2O and C_5H_5N give a *diacetate*, $C_{28}H_{34}O_{10}$, m.p. 273—275°, although in very poor yield. 2 OH are also detected by Zerevitinov's method. The function of the final O is not explained. Reaction products could not be obtained with NH_2OH or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ but the presence of strongly masked CO is not excluded. All m.p. are corr. H. W.

Triterpenes. LIV. Lupenal and lupenalol and their further transformations. L. Ruzicka and G. Rosenkranz (*Helv. Chim. Acta*, 1940, **23**, 1311—1324; cf. A., 1940, II, 137).—Replacement of C_6H_6 by AcOH in the oxidation of lupeol acetate by SeO_2 (*loc. cit.*) leads to the more rapid production in better yield of *lupenalol acetate* (**I**) (formerly "ketolupeol acetate"), m.p. 224—226°, $[\alpha]_D$ +4·2° in $CHCl_3$, the aldehydic nature of which is established by its oximation, with simultaneous hydrolysis, to *lupenaloloxime*, m.p. 245—246°, $[\alpha]_D$ +2° in $CHCl_3$, which is converted by Ac_2O at 120° into *acetyl-lupenolonitrile*, m.p. 254°, $[\alpha]_D$ +18·6° in $CHCl_3$; the absorption spectrum of this compound is very closely similar to that of 17-cyano-3-acetoxy-$\Delta^{5:16}$-androstadiene which contains an $\alpha\beta$-unsaturated nitrile. Oxidation of α-lupene (**II**) (Heilbron *et al.*, A., 1938, II, 195) with SeO_2 in AcOH affords *lupenal* (**III**), m.p. 203°, $[\alpha]_D$ +4·3° in $CHCl_3$ [*hydrazone*, m.p. 214—216° (decomp.)], the absorption spectrum of which closely resembles that of lupenalol (**IV**). The formation of an $\alpha\beta$-unsaturated aldehyde from a compound with semicyclic CH_2 requires a migration of the double linking into the ring; this is rendered the more improbable in the present case by the re-formation of lupeol and (**II**) by the Wolff–Kishner treatment of (**IV**) and (**III**). Further the oxidative degradation of (**I**) confirms the absence of semicyclic CH_2 and renders probable the presence of $\cdot CMe{:}CH_2$; (**I**) and CrO_3 in AcOH give a saturated acetoxymonocarboxylic acid (**V**), $C_{30}H_{48}O_4$, m.p. 271—272°, $[\alpha]_D$ −17·6° in dioxan [Me ester (**VI**), m.p. 236—237°, $[\alpha]_D$ −17·1° in dioxan], which is not hydrogenated (PtO_2) and does not give a yellow colour with $C(NO_2)_4$. Alkaline hydrolysis of (**VI**) gives *Me bisnorlupanolate*, m.p. 221—223°, $[\alpha]_D$ −13·6° in dioxan, whilst similar treatment of (**V**) affords bisnorlupanolic acid (**VII**), $C_{28}H_{46}O_3$, m.p. 261—262°, $[\alpha]_D$ −14·1° in dioxan. Confirmation of the presence of $\cdot CMe{:}CH_2$ in lupeol is given by the formation of $COMe_2$ by oxidation with CrO_3, the $\cdot CMe{:}CH_2$ passing partly into $:CMe_2$ in presence of the acid reagent. Decision between the C_{28} and C_{30} formulæ (*loc. cit.*) for (**VII**) is effected only with difficulty by analysis but readily by titration. This has not been effected with (**VII**) but the analogous *bisnorlupanic acid*, m.p. 238—240° (vac.), $[\alpha]_D$ −8·8° in $CHCl_3$, is thus shown to be $C_{28}H_{46}O_2$. Hydrolysis of acetylnorlupanolone with KOH–MeOH yields norlupanolone, m.p. 234—236°, $[\alpha]_D$ −14·6° in $CHCl_3$ (*oxime*, m.p. 243—244°). All m.p. are corr.

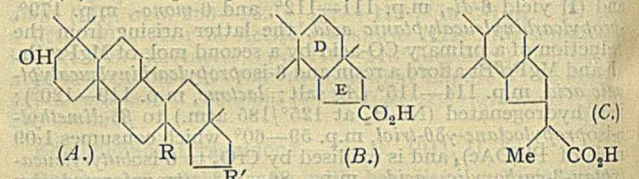


The structures of lupeol (R = Me) and betulin (R = $\cdot CH_2{\cdot}OH$) are provisionally represented by (*A*), which passes by ring enlargement of the *cyclo*pentano-group into the structure (*B*) of the oleanolic group. H. W.

Triterpenes. LV. Products of the oxidation of betulin and betulin diacetate. L. Ruzicka and M. Brenner (*Helv. Chim. Acta*, 1940, **23**, 1325—1337).—The double linking of betulin can be hydroxylated (Crieger) and the so-formed *dihydroxydihydrobetulin* (*tetrahydroxylupan*) (**I**), m.p. 303—305° (vac.) after softening at 300°, $[\alpha]_D$ −10·5° in abs. EtOH, is degraded by HIO_4 to CH_2O and *dihydroxynorlupanone* (**II**), m.p. 229—231°, $[\alpha]_D$ −20·8° in $CHCl_3$ [*diacetate* (**III**), m.p. ~190°, $[\alpha]_D$ −11·0° in $CHCl_3$]. Oxidation of betulin diacetate (**IV**) with CrO_3 affords, as neutral product, (**III**), which does not give cryst. derivatives with NH_2OH or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ but in which the presence of $:CO$ is established by the absorption spectrum and by reduction (H_2–PtO_2–AcOH at room temp.) to *diacetoxynorlupanol* (**V**), m.p. 252—254°, $[\alpha]_D$ −11·1° in $CHCl_3$, oxidised to the ketone. The acid products of the oxidation are separated as their Me esters, whereby *Me* (+)-*diacetoxylupanate*, m.p. 234—236°, $[\alpha]_D$ +18·9° in $CHCl_3$, and *Me* (−)-*diacetoxylupanate*, m.p. 213—214°, $[\alpha]_D$ −48° in $CHCl_3$, are obtained. Further, the acids can be separated from one another by stepwise extraction with alkali or by fractional dissolution of them adsorbed on Al_2O_3. *Me* (+)-*dihydroxylupanate* has m.p. 248—249°, $[\alpha]_D$ +4·9° in $CHCl_3$. With H_2O_2 and (**IV**) there result the two isomeric acids and a mixture of neutral compounds from which only *formyldiacetoxynorlupanol*, m.p. 235—237°, $[\alpha]_D$ −8·4° in $CHCl_3$, has been isolated. Its constitution is established by its synthesis by the action of HCO_2H and $COCl_2$ in C_5H_5N on (**V**) and by its hydrolysis to norlupantriol, m.p. ~315°, $[\alpha]_D$ −19·5° in dioxan. H. W.



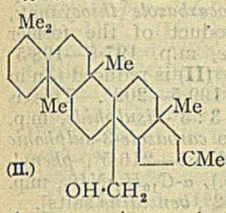
Triterpenes. LVI. Oxidation of betulin monoacetate and methyl acetylbetulinate with chromium trioxide. L. Ruzicka and A. H. Lamberton (*Helv. Chim. Acta*, 1940, **23**, 1338—1345; cf. A., 1939, II, 29).—On the basis of the formula (*A*) for betulin (R = $CH_2{\cdot}OH$, R′ = $CMe{:}CH_2$) the structures (*B*) and (*C*) are assigned provisionally to the dicarboxylic acid *A*



(**I**) and acetyldicarboxylic acid *E* (**II**) obtained (*loc. cit.*) by the oxidation of betulin monoacetate (**III**) with CrO_3. The oxidation of (**III**) and acetylbetulic acid with CrO_3 is described. Treatment of Me acetylbetulate with CrO_3 in AcOH at 80—90° gives the Me_1 ester of (**II**), m.p. 259—260°, which does not give a colour with $C(NO_2)_4$ and is converted by CH_4N_2 into the Me_2 ester of (**II**), m.p. 243—245°, $[\alpha]_D$ +19° in $CHCl_3$; hydrolysis (KOH–MeOH) of the products insol. in alkali gives the Me_1 ester of (**I**), m.p. 274—276°, which does not give a colour with $C(NO_2)_4$ and is converted by CH_2N_2 into the Me_2 ester of (**I**), m.p. 178—180°, $[\alpha]_D$ −60°±6° in $CHCl_3$. The neutral oxidation product is identified as *Me norlupanolonate* (cf. *A*, R = CO_2Me; R′ = Ac), m.p. 250—252°, $[\alpha]_D$ −33° in $CHCl_3$, which is unchanged by boiling N-KOH–MeOH and does not give a yellow colour with $C(NO_2)_4$. It is converted by boiling Ac_2O into a substance, m.p. ~235° after softening at 205°; it does not give cryst. compounds with NH_2OH or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$. (**I**) is transformed by Ac_2O–C_5H_5N into its acetate, m.p. ~310°, which is dehydrogenated (Se at 355—370°) to 1 : 5 : 6-$C_{10}H_5Me_3$. This, with a *substance*, (?) $C_{29}H_{46}O_2$, m.p. 240—241°, which does not give a colour with $FeCl_3$, is obtained similarly from (**II**). M.p. are corr. H. W.

Triterpenes. LVII. 2-Deoxybetulin and 2-deoxy*allo*betulin. L. Ruzicka and S. D. Heinemann (*Helv. Chim. Acta*, 1940, **23**, 1512—1518; cf. preceding abstract).—Betulin 2-monoacetate (**I**) is transformed by BzCl in C_5H_5N at 100° into *betulin 2-acetate x-benzoate*, m.p. 205·5—206°, which could not be smoothly hydrolysed to the Ac-free benzoate. (**I**) and PhNCO in boiling C_6H_6 give *betulin 2-acetate x-phenylcarbamate*, m.p. 226·5—227°, hydrolysed by 2% K_2CO_3 in boiling 75% MeOH to *betulin 2-phenylcarbamate*, m.p. 239·5—240·5°. This is oxidised by CrO_3 in AcOH to *betulone 2-phenylcarbamate*, m.p. 226·5—227° [*oxime*, m.p. 257·5—258°; *azine*,

$C_{60}H_{96}O_2N_2$, m.p. 356—357° (decomp.)], which is transformed by N_2H_4,H_2O, followed by C_5H_{11}·ONa in C_5H_{11}·OH at 200°, into 2-*deoxybetulin* (**II**), m.p. 140—141°, $[\alpha]_D$ +16°±2° in $CHCl_3$ (*acetate*, m.p. 164—164·5°; *formate*, m.p. 133—135°). This is cyclised by 100% HCO_2H in $CHCl_3$ at 100° to 2-*deoxy*allobetulin, m.p. 234—235°, $[\alpha]_D$ +54° ± 1° in $CHCl_3$, also obtained by the successive action of N_2H_4,H_2O and Na in C_5H_{11}·OH at 200—210° on *allo*betulone (**III**); in EtOH (**III**) is transformed into the *azine*, $C_{60}H_{96}O_2N_2$, m.p. 364—365°. All m.p. are corr.



(II.)

H. W.

Triterpenediols. IV. Constitution of onocerin. J. Zimmermann (*Helv. Chim. Acta*, 1940, **23**, 1110—1113).—The previous hypothesis (A., 1938, II, 372) that the conversion of α- into β-onocerin (**I**) consists of a transformation of a tetra- into a penta-cyclic structure cannot be maintained since titration of (**I**) with BzO_2H discloses the presence of two double linkings. Ozonisation of α-onocerin diacetate and treatment of the ozonide with steam gives CH_2O and a substance not volatile in steam which is hydrolysed (KOH–EtOH) to a *compound*, $C_{28}H_{45}O_4$, m.p. 217° (*diacetate*, m.p. 165°, and its *dioxime*, m.p. 265°). Similar treatment of β-onocerin diacetate gives $COMe_2$ and a non-cryst. resin which affords a minute amount of yellow crystals when hydrolysed (KOH–EtOH).

H. W.

Triterpene resinols and related acids. XII. Oxidation of β-amyradienyl-I acetate with selenium dioxide, a new route to Jacobs' keto-diol, $C_{30}H_{44-46}O_3$. C. W. Picard and F. S. Spring (*J.C.S.*, 1941, 35—39).—The prep. of β-amyradienol-I from β-amyrenonol (reduction with Na–EtOH or C_5H_{11}·OH) is accompanied by the formation of β-amyradienol-II, identical with the compound obtained by oxidation (SeO_2) of β-amyradienyl esters. The two ethylenic linkings as a conjugated system are located in -I in a single ring but in -II the system is not contained in a single ring. Oxidation (SeO_2) of β-amyradienyl-I acetate gives the keto-acetate, $C_{32}H_{48(46)}O_4$, of Jacobs and Fleck (A., 1930, 1292). Oxidation (Br–AcOH) of β-amyrenonyl benzoate affords *β-amyradienonyl benzoate*, m.p. 251—252°, hydrolysed (KOH) to *β-amyradienonol* (**I**), m.p. 239—240°; the *acetate*, m.p. 255°, is oxidised ($KMnO_4$) to an *acetate*, $C_{32}H_{46}O_4$, m.p. 234—235° (slight decomp.), not identical with Jacobs' keto-acetate. A provisional structure is assigned to (**I**).

F. R. S.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Mytiloxanthin, m.p. 140—144° (block; corr.).—See A., 1941, III, 123.

Nature of Haslewood's hepatols. H. B. MacPhillamy (*J. Amer. Chem. Soc.*, 1940, **62**, 3518—3519).—Hog liver yields β-7-hydroxycholesterol and Haslewood's hepatol (**I**), m.p. 277—279° (A., 1939, III, 707). However, (**I**) is digitogenin (*diacetate*, m.p. 231—233°), derived from digitonin by Haslewood's method of isolation. The second hepatol (*loc. cit.*) is probably impure (**I**).

R. S. C.

Hydrogenation of lignin. E. E. Harris (*Paper Trade J.*, 1940, **111**, *TAPPI Sect.*, 297—298).—The % of MeOH, *n*-propyl*cyclo*hexane derivatives (**I**), high-boiling resin, and H_2O obtained by hydrogenating various lignins in dioxan + Cu chromite are tabulated. With isolated sulphite and sulphate lignin S acts as a catalyst poison but it is possible to remove S as H_2S or MeSH and to hydrogenate the resulting products. H_2O containing Ni may also be used as solvent. The products are similar to those obtained in dioxan but OMe is less extensively removed. At higher temp. OH and OMe are eliminated with production of *n*-propyl*cyclo*hexane. Wood chips are completely converted into oils and products sol. in H_2O when hydrogenated at about 250°/5000 lb. MeOH, PrOH, and reduced carbohydrates are found in the portion sol. in H_2O; the identified oils consist of (**I**). At lower temp. and pressure hydrogenation can be controlled so that only a small proportion of gas is absorbed; a pulp remains.

H. W.

Sclerotiorin, $C_{20}H_{20}O_5Cl$ (?), metabolic product of *Penicillium sclerotiorum*, von Beyma.—See A., 1941, III, 138.

V.—HETEROCYCLIC.

Derivatives of furfuryl and tetrahydrofurfuryl alcohols. R. D. Kleene and S. Fried (*J. Amer. Chem. Soc.*, 1940, **62**, 3516).—*Furfuryl*, m.p. 75—77°, and *tetrahydrofurfuryl* p-*nitrobenzoate*, m.p. 46—48°, and *tetrahydrofurfuryl* 3 : 5-*dinitrobenzoate*, m.p. 83—84°, are prepared.

R. S. C.

Complex rotatory dispersion of optically active tetrahydrofuryl-2-carbinol.—See A., 1941, I, 74.

Coumarones and chromans.—See B., 1941, II, 37.

Structural interpretations of flavone spectra.—See A., 1941, I, 72.

Additive compounds of zinc, cadmium, cobalt, and nickel halides with 1 : 4-dioxan. R. Juhasz and L. F. Yntema (*J. Amer. Chem. Soc.*, 1940, **62**, 3522).—Anhyd. dioxan (**I**) gives additive *compounds*, (*a*) *X*,(**I**) in which X = $ZnCl_2$, $CdCl_2$, $CdBr_2$, CdI_2, $CoCl_2$, $NiCl_2$, and $NiBr_2$, (*b*) *X*,2(**I**), in which X = $ZnCl_2$, $ZnBr_2$, ZnI_2, $CoBr_2$, CoI_2, and NiI_2, and (*c*) $CdCl_2$,0·5(**I**), CoI_2,3(**I**), CoI_2,(**I**),+2 and $4H_2O$.

R. S. C.

Thianthren series. I. 2-Sulphothianthren sulphone and 2-chlorothianthren sulphone. V. V. Kozlov, E. P. Fruktova, and O. M. Schemjakina (*J. Gen. Chem. Russ.*, 1940, **10**, 1077—1088).—Thianthren sulphone and 62% oleum (5·5 hr. at 140—145°) yield 2-*sulphothianthren sulphone* (**I**) [*Na*, +H_2O, *K*, +0·5, 1, and 3H_2O; Cu^{II}, *Ba*, *Zn*, *Al*, Fe^{II}, Fe^{III}, Pb^{II}, *Ag* salts; *chloride*, m.p. 194° (decomp.); *amide*, m.p. 178°], which with PCl_5–$POCl_3$ (5 hr. at 180°) affords 2-*chlorothianthren sulphone*, m.p. 120°. Fusion of (**I**) with NaOH (20 min. at 300°) yields PhOH, resorcinol, and *p*-OH·C_6H_4·SO_3H.

R. T.

Attempts to prepare 7-substituted *dicyclo*[1 : 2 : 2]-azaheptanes. G. R. Clemo and E. Hoggarth (*J.C.S.*, 1941, 41—47).—Et pyridine-4-carboxylate (*picrate*, m.p. 142°) and MgMeI give dimethyl-4-pyridylcarbinol (**I**) (*picrate*, m.p. 95°, *picrolonate*, decomp. 236°, and *platinichloride*, m.p. 194°), which could not be satisfactorily reduced with Na–EtOH, yielding a small amount of 4-*iso*propylpyridine (*picrate*, m.p. 135°, *picrolonate*, m.p. 208°, and *platinichloride*, m.p. 202°), not identical with 4-α-*methylvinylpyridine*, b.p. 82°/15 mm. [*picrate* (+EtOH), and *picrolonate*, m.p. 231°], prepared by dehydration (P_2O_5) of (**I**). Reduction of 4-acetylpyridine with $Pr^{\beta}OH$ and $Al(OPr^{\beta})_3$ affords *methyl*-4-*pyridylcarbinol*, m.p. 54° (*picrate*, m.p. 125°, *picrolonate*, m.p. 232°, and *platinichloride*, m.p. 206°), which could not be hydrogenated. *Et* 1-*acetylpiperidine*-4-*carboxylate*, b.p. 135—136°/1 mm., with MgMeI gives *dimethyl*-1-*acetyl*-4-*piperidylcarbinol*, b.p. 162—165°/1 mm., which could not be deacetylated. *Et* 1-*benzoylpiperidine*-4-*carboxylate*, m.p. 77°, and MgMeI yield in small amount a mixture of $COMe_2$ and *dimethyl*-4-*piperidylcarbinol* (**II**), m.p. 136° [*picrate*, two forms, m.p. 156° and 187°; *picrolonate*, m.p. 265° (decomp.)] HBr and (**II**) give 4-α-*bromoisopropylpiperidine*, m.p. 192°, which with Ag_2O or K_2CO_3 affords (**II**) and an *amine*, $C_8H_{15}N$, b.p. 58—62°/12 mm. (*picrolonate*, m.p. 221°), reduced (PtO_2–H_2) to 4-*iso*propylpiperidine. Et piperidine-4-carboxylate and MgMeI yield 4-*acetylpiperidine* (?), b.p. 108—110°/25 mm. [*picrate*, m.p. 266° (decomp.), *picrolonate*, m.p. 206°, and *platinichloride* (+EtOH), m.p. 206°], not identical with that described by Prelog (A., 1938, II, 456); the base with MeI gives a *compound*, $C_7H_{13}ON,MeI$, m.p. 170°, which with Ag_2O yields a base, b.p. 108—109°/25 mm. (*picrolonate*, m.p. 215°).

F. R. S.

Cuprammine salts. D. A. Maruchian (*J. Gen. Chem. Russ.*, 1940, **10**, 917—920).—CuCl or CuBr and excess of C_5H_5N afford the *salts* $[Cu_2(C_5H_5N)_4]Cl_2$ (**I**) or $[Cu_2(C_5H_5N)_4]Br_2$ (**II**). With Cl_2 (**I**) gives $[Cu(C_5H_5N)_4]Cl_2$, also obtained from (**II**), via (**I**).

R. T.

Action of acid chlorides on tetrahydrofuran, and certain derivatives of δ-diethylaminobutan-α-ol. L. M. Smorgonski and J. L. Goldfarb (*J. Gen. Chem. Russ.*, 1940, **10**, 1113—1119).—Tetrahydrofuran and *p*-NO_2·C_6H_4·COCl or *p*-NO_2·C_6H_4·COBr (4 hr. at the b.p.) yield *δ-chlorobutyl*, b.p. 205—206°/7 mm., or *δ-bromobutyl* p-*nitrobenzoate*, b.p. 191—194°/3 mm., m.p. 45—46°. *δ-Bromobutyl acetate*, b.p. 95—96°/14 mm., obtained analogously, reacts with $NHEt_2$ yielding *δ-diethylaminobutyl acetate*, b.p. 112°/22·5 mm., hydrolysed to OH·$[CH_2]_4$·NEt_2 [*picrolonate*, m.p. 65—66°; p-*nitrobenzoate* (**I**) (*hydrochloride*, m.p. 158—159°; *picrate*, m.p. 151—152°)]. (**I**) is reduced ($SnCl_2$) to *δ-diethylaminobutyl* p-*aminobenzoate*,

an oil (*hydrochloride*, m.p. 171°). At room temp. (**I**) is rapidly converted into 1 : 1-diethylpyrrolidinium *p*-nitrobenzoate. R. T.

α-Nitropyridines. M. G. Bistritzkaja and A. V. Kirsanov (*J. Gen. Chem. Russ.*, 1940, **10**, 1101—1107).—When 5-chloro- or 5-bromo-2-aminopyridine is added to H_2O_2–H_2SO_4 at 0—5°, and the mixture is diluted after 48 hr. at room temp. and made neutral with aq. NH_3, 5-*chloro*-, m.p. 120·5—121°, or 5-*bromo*-2-*nitropyridine*, m.p. 149·5—150°, separates. These compounds yield the corresponding 2-aminopyridines when reduced with $Na_2S_2O_4$ or $SnCl_2$, whilst with As_2O_3 in aq. NaOH they give 5 : 5′-*dichloro*-, decomp. 204°, or 5 : 5′-*dibromo*-2 : 2′-*azoxypyridine*, decomp. 200°; with As_2O_3 and Na_3AsO_3 the products are 5 : 5′-*dichloro*-, decomp. 248°, and 5 : 5′-*dibromo*-2 : 2′-*azobenzene*, decomp. 235°. 3-Nitro-2-aminopyridine and aq. CH_2O at room temp. afford NN′-(3 : 3′-*dinitro*-2 : 2′-*dipyridyl*)*diaminomethane*. 5-Nitro-2-aminopyridine and aq. NaOCl yield a substance, $C_5H_5O_2N_3Cl_2$, probably a perchloride or a chloroamine, decomp. 60—80°. R. T.

Preparation of phenyl 2-pyridyl and 8-quinolyl sulphides and sulphones. H. C. Winter and F. E. Reinhart (*J. Amer. Chem. Soc.*, 1940, **62**, 3508—3511).—8-Chloro-5-nitroquinoline with Na_2S_2 in boiling EtOH gives *di*-5-*nitro*-8-*quinolyl disulphide*, m.p. 245°, and with PhSH or *p*-NO_2·C_6H_4·SH (**I**) and NaOAc in boiling EtOH gives *Ph*, m.p. 100°, and *p*-NO_2·C_6H_4 5-*nitro*-8-*quinolyl sulphide*, m.p. 223°, respectively. 2-Chloro-5-nitropyridine with PhSH at 135—150° gives Ph*, m.p. 121°, and with (**I**) and NaOAc in boiling EtOH gives p-NO_2·C_6H_4 5-*nitro*-2-*pyridyl sulphide*, m.p. 126—129°. Reduction of the appropriate NO_2-compound by $SnCl_2$–HCl yields Ph 5-amino-2-pyridyl*, m.p. 125—127° (lit. 120°), and 5-*amino*-8-*quinolyl**, m.p. 128° (*Ac* derivative, m.p. 97—98°), *sulphide*. H_2O_2 in AcOH oxidises the appropriate sulphide to *Ph* 5-*nitroquinolyl sulphoxide*, m.p. 145—146°, *Ph* 5-*nitro*-*, m.p. 151—153° (m-NO_2-derivative, m.p. 169—170°), and 5-*amino*-2-*pyridyl sulphone**, m.p. 169—170°, p-NO_2·C_6H_4 5-*nitro*-2-*pyridyl sulphone*, m.p. 217°, *Ph* 5-*nitro*-*, m.p. 180—181°, and 5-*amino*-8-*quinolyl sulphone**, m.p. 224° (*Ac* derivative, m.p. 268—269°). p-NO_2·C_6H_4 5-*nitro*-8-*quinolyl sulphone*, m.p. 237°, is prepared using CrO_3 (not H_2O_2) in AcOH first at room temp., later at b.p. 8-*Quinolinesulphonylsulphanilic acid**, +H_2O (Na salt), is also prepared. Compounds marked*, K 5-nitro-2-pyridinesulphonate, 5-amino-2-pyridinesulphonic acid, quinoline-8-sulphonic acid and its amide, 8-aminoquinoline-5-sulphonic acid, di-5-nitro-2-pyridyl and -8-quinolyl sulphide [prep. from 8-chloro-5-nitroquinoline by $CS(NH_2)_2$ and NaOEt] have no antistreptococcal activity. R. S. C.

6-Ethoxy-2 : 4-dimethylquinoline.—See B., 1941, II, 37.

Condensation of halogeno-pyridines, -quinolines, and -*iso*quinolines with sulphanilamide. M. A. Phillips (*J.C.S.*, 1941, 9—15).—When halogeno-pyridines, -quinolines, and -*iso*quinolines are condensed with *p*-NH_2·C_6H_4·SO_2·NH_2 (**I**) in presence of K_2CO_3–Cu, condensation generally occurs at the SO_2·NH_2 end of the mol., probably owing to the intermediate formation of the K salt of (**I**). In the absence of K_2CO_3, condensation occurs exclusively at the NH_2 end of (**I**). 2-Chloro-5-nitropyridine with (**I**) and K_2CO_3–Cu gives a mixture of 5-*nitro*-2-(p-*aminobenzenesulphonamido*)*pyridine*, m.p. 218—220° (*Ac* derivative, m.p. 279°), and p-(5′-*nitro*-2′-*pyridylamino*)*benzenesulphonamide*, m.p. 209—210° (*Na* salt; 5′-NH_2-derivative, m.p. 221°), the former predominating. The following are described: *Na* salt of 2-(*p*-aminobenzenesulphonamido)pyridine; 2-(p-*aminobenzenesulphonamido*)-*quinoline*, m.p. 194° (*Ac* derivative, m.p. 216°); p-(1′-*isoquinolylamino*)*benzenesulphonamide*, m.p. 275°; 1-(p-*aminobenzenesulphonamido*)*iso*quinoline, m.p. 263° (*Ac* derivative, m.p. 225°); 5-*amino*-2-(p-*aminobenzenesulphonamido*)*pyridine*, sinters 140—150°; and p-(2′-*pyridylamino*)*benzenesulphon*-2′-*pyridylamide*, m.p. 204°. F. R. S.

Heterocyclic amidines.—See B., 1941, II, 37, 37, 38.

Carbazole and its derivatives. I. Carbazolemonosulphonic acid. K. G. Mizutsch. **II. Bromination of carbazole and carbazole-3-sulphonic acid.** K. G. Mizutsch and A. J. Savtschenko (*J. Gen. Chem. Russ.*, 1940, **10**, 844—851, 852—854).—I. Carbazole (**I**) and KCNS in 96% AcOH are maintained for 1 hr. at 6—10°, and Br in AcOH is added gradually at 20° for 2 hr., yielding 3-thiocyanocarbazole (**II**), m.p. 111·7—112·7° (N-*Ac* derivative, m.p. 121—122°), also prepared by the Sandmeyer reaction from 3-*diazocarbazole thiocyanate*, m.p. 122—123° (decomp.). A by-product of the former reaction is 3 : 6(?)-*dithiocyanocarbazole*, m.p. 197·5—198·5° (N-*Ac* derivative, m.p. 196·5—197·5°). (**II**) is reduced (Zn in HCl–AcOH) to 3-*thiolcarbazole*, m.p. 199·5—202°. This is oxidised by I in AcOH to *dicarbazyl* 3 : 3′-*disulphide*, m.p. 240—241·5°, and by H_2O_2 in AcOH to *carbazole*-3-*sulphonic acid* (**III**) [*Na*, p-*chloroaniline*, m.p. 215·5—216·5°, *phenylhydrazine*, m.p. 223·2—223·8° (decomp.), α-$C_{10}H_7$·NH_2, m.p. 231—232°, β-$C_{10}H_7$·NH_2, m.p. 231—232°, *benzidine* salts].

II. Oxidation of (**I**) is not observed during bromination with $KBrO_3$–KBr; the products are mono-, di-, and 1 : 3 : 6-tri-bromocarbazole. (**III**) is brominated similarly to 1 : 3 : 8-*tribromocarbazole*-3-*sulphonic acid*, which with 3% HCl at 200° gives 1 : 3 : 8-*tribromocarbazole*, m.p. 178—180°. R. T.

Formation of pyrazolines from unsymmetrically substituted dibenzylideneacetones. L. C. Raiford and R. H. Manley (*J. Org. Chem.*, 1940, **5**, 590—597).—Condensation of αβ-diunsaturated unsymmetrical ketones containing the *p*-C_6H_4Cl·CH: and vanillylidene or substituted vanillylidene radicals with NHPh·NH_2 does not yield the phenylhydrazones but the isomeric pyrazolines. Oxidation ($KMnO_4$) of these gives invariably *p*-C_6H_4Cl·CO_2H and the required pyrazole-3-carboxylic acid, showing that the direction of rearrangement is away from the *p*-C_6H_4Cl·CH: radical. Vanillylideneacetone or its substitution product is mixed with *p*-C_6H_4Cl·CHO in EtOH and the liquid is kept for several hr. at 0° after being made strongly alkaline with NaOH; the Na salt which separates is treated with AcOH. Thus are obtained: *vanillylidene*-4′-*chlorobenzylideneacetone*, m.p. 137—138°, and its 5′-*Br*-, m.p. 191—192°, 6′-*Br*-, m.p. 179—180°, and 5′-NO_2-, m.p. 186—187°, derivatives. These are condensed with NHPh·NH_2 in glacial AcOH at room temp. for several days, thus giving the following *-pyrazolines*: 3-*phenyl*-1 : 5-*di*-p-*chlorophenyl*-, m.p. 135—136°; 5-*phenyl*-1 : 3-*di*-p-*chlorophenyl*-, m.p. 135—135·5°; 3-p-*chlorostyryl*-1-*phenyl*-5-4′-*hydroxy*-3′-*methoxyphenyl*-, m.p. 174°; 3-p-*chlorostyryl*-1-*phenyl*-5-5′-*bromo*-4′-*hydroxy*-3′-*methoxyphenyl*-, m.p. 170—171°; 3-p-*chlorostyryl*-1-*phenyl*-5-6′-*bromo*-4′-*hydroxy*-3′-*methoxyphenyl*-, m.p. 161—162°, and 3-p-*chlorostyryl*-1-*phenyl*-5-5′-*nitro*-4′-*hydroxy*-3′-*methoxyphenyl*-, m.p. 208—209°. Oxidation ($KMnO_4$ in C_5H_5N at room temp.) of the appropriate pyrazoline yields the following 1 : 5-*diphenylpyrazole*-3-*carboxylic acids* (substituents in C_6H_5 at $C_{(5)}$): 4′-*hydroxy*-3′-*methoxy*-, m.p. 165° after softening; 5′-*bromo*-4′-*hydroxy*-3′-*methoxy*-, m.p. 161—163°; 6′-*bromo*-4′-*hydroxy*-3′-*methoxy*-, m.p. 175°; 5′-*nitro*-4′-*hydroxy*-3′-*methoxy*-, m.p. ~90°. H. W.

Associating effect of the hydrogen atom. VII. N-H-N bond. Derivatives of pyrazole and indazole. H. T. Hayes and L. Hunter (*J.C.S.*, 1941, 1—5).—Contrasts in b.p., solubility in donor solvents, and degree of association are shown between derivatives of pyrazole and indazole possessing a free imino-H and those in which this atom has been replaced by an alkyl, aryl, or acyl group. The high vals. of these properties of the former class of compound are attributed to H-bond formation involving the imino-H. Cryoscopic measurement of mol. wt. of 16 derivatives is made over a range of concn. in C_6H_6 or $C_{10}H_8$ solution. A possible mechanism of pyrazole tautomerism is proposed. F. R. S.

2-Amino-1′ : 9′-pyrimidinoanthrone.—See B., 1941, II, 36.

Syntheses of carbaza-condensed systems from 2- and 6-aminonicotines. III. Reaction of bromopyruvic ester with 2- and 6-aminonicotine. IV. Condensation of 2-aminonicotine with acetoacetic ester. M. S. Kondakova and J. L. Goldfarb (*J. Gen. Chem. Russ.*, 1940, **10**, 1055—1064, 1065—1068).—III. 2-Aminonicotine (**I**) in Et_2O and CH_2Br·CO·CO_2Et (12 hr. at room temp.) yield an additive product which when treated with boiling EtOH and then with K_2CO_3 gives 7-(1′-*methyl*-2′-*pyrrolidyl*)-2-*carbethoxy*-1-*azaindolizine*, b.p. 233—234°/6 mm., m.p. 96—97° (*hydrobromide*, m.p. 213—214°; *picrate*, m.p. 177—178°). This is hydrolysed (50% HCl; 20 hr. at the b.p.) to 7-(1′-*methyl*-2′-*pyrrolidyl*)-2-*carboxy*-1-*azaindolizine* [*mono*-, m.p. 198—201°, *di-hydrochloride*, m.p. 232—237°; *picrate*, m.p. 113—116°; *amide*, m.p. 225° (*dihydrochloride*, m.p. 244—254°)], readily losing CO_2 at 225—235°, to yield 7-(1′-*methyl*-2′-*pyrrolidyl*)-1-*azaindolizine*, b.p. 159°/5 mm., m.p. 44—47° [*dihydrochloride*, m.p. 257° (decomp.); *platinochloride*; *picrate*, m.p. 240°]. Nitration of this compound

gives *3-nitro-7-(1′-methyl-2′-pyrrolidyl)-2-azaindolizine*, m.p. 96—97°, also obtained by hydrolysis of *Et 3-nitro-7-(1′-methyl-2′-pyrrolidyl)-1-azaindolizine-1-carboxylate* (**II**), m.p. 111—112°. (**II**) yields (**I**) when oxidised (CrO_3 in H_2SO_4) or when heated with KOH in EtOH. 6-Aminonicotine and $CH_2Br{\cdot}CO{\cdot}CO_2Et$ react as above, yielding *Et 5-(1′-methyl-2′-pyrrolidyl)-1-azaindolizine-2-carboxylate*, b.p. 235—237°/4 mm., m.p. 154° [*picrate*, m.p. 225° (decomp.)], which with 50% HCl (24 hr. at the b.p.) gives *5-(1′-methyl-2′-pyrrolidyl)-1-azaindolizine*, b.p. 160°/4 mm. (*dipicrate*, m.p. 204—205°; *platinichloride*).

IV. (**I**) and $CH_3Ac{\cdot}CO_2Et$ (3·5 hr. at 170—185°) yield *2(4)-keto-9-(1′-methyl-2′-pyrrolidyl)-4(2)-methyl-1-azaquinolizine*, m.p. 112° [*dipicrate*, m.p. 209°; *dihydrochloride*, m.p. 244—247° (decomp.); *platinichloride*], regenerating (**I**) when hydrolysed with 20% HCl or KOH–EtOH, and giving the *3-NO_2*-derivative, m.p. 120—121°, with HNO_3–H_2SO_4. MeI adds on to the pyrrolidine-N, giving a *methiodide*, m.p. 238—240° (decomp.). R. T.

4-Glyoxalinyl-4′-hydantoylmethane and its hydrolysis. M. N. Schtschukina (*J. Gen. Chem. Russ.*, 1940, **10**, 1108—1112).—A solution of histidine (**I**) and $CO(NH_2)_2$ in H_2O is boiled for 5 hr., made acid with HCl, and evaporated to dryness. This gives *4(5)-glyoxalinyl-4′-hydantoinylmethane*, m.p. 255° (*picrate*, m.p. 209°), which regenerates (**I**) when subjected to acid or alkaline hydrolysis. R. T.

Phthalocyanines.—See B., 1941, II, 40.

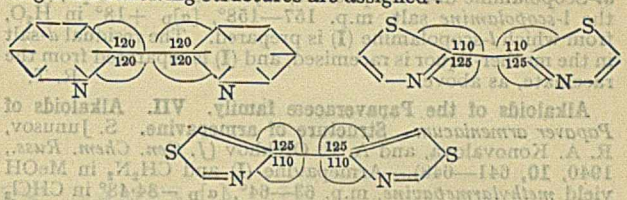
Preparation of aromatic oxazolidines. M. Meltsner, E. Waldman, and C. B. Kremer (*J. Amer. Chem. Soc.*, 1940, **62**, 3494—3495).—Boiling $OH{\cdot}[CH_2]_2{\cdot}NH_2$ (1) and ArCHO (1 mol.) in BuOH or BuOH–Bu_2O gives *2-phenyl-*, b.p. 157°/24 mm., *2-m-*, b.p. 159°/14 mm., and *2-p-tolyl-*, b.p. 153°/15 mm., *2-o-*, b.p. 195°/27 mm., and *2-p-anisyl-*, b.p. 180°/12 mm., *2-p-hydroxyphenyl-*, m.p. 169°, *2-m-*, m.p. 73°, and *2-o-nitrophenyl-*, m.p. 58°, *-oxazolidine*. *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ and *o*-$C_6H_4Cl{\cdot}CHO$ give additive *compounds*, b.p. 180°/13 mm., and 178°/22 mm., respectively. R. S. C.

2 : 6-Dimethylmorpholinoethyl alcohol.—See B., 1941, II, 38.

Polymethine dyes of the 3-hydroxythionaphthen series. II. Condensation of anils of 3-hydroxythionaphthen-2-aldehyde and its vinylene homologues with quaternary salts of 1-methylbenzthiazole. I. I. Levkoev, N. N. Sveschnikov, and V. V. Durmaschkina (*J. Gen. Chem. Russ.*, 1940, **10**, 773—778; cf. A., 1940, II, 381).—Polymethine dyes were prepared by the reaction *o*-C_6H_4<S>$C(OH)$>$C{\cdot}[CH:CH]_n{\cdot}CH:NPh$ + *o*-C_6H_4<S>NRI>$CMe \rightarrow HI + NH_2Ph$ + *o*-C_6H_4<S>CO>$C:CH{\cdot}[CH:CH]_n{\cdot}CH:C$<S>$NR$>$C_6H_4$-*o* [$n = 0$, R = *Me*, m.p. 249—250° (decomp.), R = *Et*, m.p. 212—214° (decomp.), R = *Pr*$^\alpha$, m.p. 208—209° (decomp.), R = *Bu*$^\alpha$, m.p. 177—178°; R = *Et*, $n = 1$, m.p. 219—220° (decomp.), $n = 2$, m.p. 177—178°]. The position of the band of max. absorption is not affected by varying R, but is shifted towards longer wave-lengths by increase in *n*. 1-Methylthiolbenzthiazole and *p*-$C_6H_4Me{\cdot}SO_3Et$ are heated (6 hr. at 130—140°), and the product is heated with 2-hydroxy-1 : 2-dihydrothionaphthen in EtOH, in presence of NaOAc (30 min. at the b.p.), yielding the *substance* *o*-C_6H_4<S>CO>$C:C$<S>NEt>C_6H_4-*o*, m.p. 214—216°. R. T.

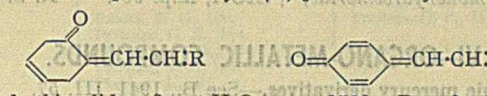
Benzoylmethyldibenzthiazyl 1-sulphide.—See B., 1941, II, 38.

Structure-chemical investigations. II. Structure of thiazole compounds and the Fe$^{\cdot\cdot}$-specific group. H. Erlenmeyer and H. Ueberwasser (*Helv. Chim. Acta*, 1940, **23**, 1268—1275).—Addition of solid $FeSO_4$ to a solution of 4 : 4′-dithiazolyl (**I**) in HBr in a closed vessel followed by NaOH gives the *compound*, $[Fe(C_6H_4N_2S_2)_2]Br_2,2H_2O$, pale red crystals which become yellow at 120°. Under these conditions 2 : 2-dithiazolyl (**II**) gives a *substance*, $[Fe(C_6H_4N_2S_2)_2]Br_2,2H_2O$, intensely coral-red crystals which are immediately decolorised by neutral H_2O. In these salts Fe has the co-ordination no. 4. The difference in the behaviour of dithiazolyls and dipyridyl (**III**) is attributed to the difference in the aromatic structure of C_5H_5N and thiazole. As a first approximation and taking account of the valency angle the following structures are assigned :



In (**I**) and (**II**) the valency angle of –N<C—C>N– differs appreciably from that in (**III**). Quinthiazole (**IV**) and $FeSO_4$ immediately give a lemon-yellow colour (capable of detecting 1 mg. Fe per l.) and the *bromide*, $[Fe(C_{10}H_6N_2S)_2]Br_2,2H_2O$, can be obtained in which Fe$^{\cdot\cdot}$ has the co-ordination no. 4. The group –N<C—C>N– in (**IV**) has not the Fe$^{\cdot\cdot}$-sp. structure which occurs in (**III**) and *o*-phenanthroline. H. W.

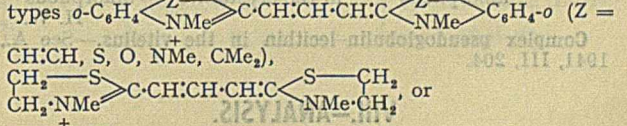
(A) Hydroxystyryl derivatives of quaternary heterocyclic salts. (B) Influence of the solvent on the colour of organic dye solutions. (C) Absorption spectra of cyanine dyes in the ultra-violet. A. I. Kiprianov and V. E. Petrunkin (*J. Gen. Chem. Russ.*, 1940, **10**, 600—612, 613—619, 620—628).—(A) *o*- or *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ was condensed with the ethiodides of quinaldine, 1-methylbenzthiazole, and 4-phenyl-2-methyl- or 2 : 4-dimethyl-thiazole, in presence of C_5H_5N, to yield the following hydroxystyryl compounds : 2-p-, m.p. 257—258° (decomp.), or 2-o-*hydroxystyryl-4-methyl-3-ethyl-*, m.p. 215°, and 2-p-*hydroxystyryl-4-phenyl-3-ethyl-thiazole iodide*, m.p. 222—223° (decomp.), 1-o-, m.p. 241° (decomp.), or 1-p-*hydroxystyryl-2-ethylbenzthiazole iodide* (**I**), m.p. 246° (decomp.), and 2-o-, m.p. 198—200°, or 2-p-*hydroxystyryl-1-ethylquinoline iodide*, m.p. 232—233°. These iodides are converted by aq. KOH into the quinonoid dyes (*A*) [R = 4-*methyl-3-ethyl-2* : 3-



dihydrothiazolidene-2-, $+H_2O$, m.p. 173°; R = 2-*ethyl-1* : 2-*dihydrobenzthiazolidene-2-*, m.p. 140—145° (decomp.); R = 1-*ethyl-1* : 2-*dihydroquinolidene-2-*, m.p. 160—163° (decomp.)], and (*B*) [R = 4-*methyl-3-ethyl-2* : 3-*dihydrothiazolidene-2-*, $+H_2O$, m.p. 178° (decomp.); R = 4-*phenyl-3-ethyl-2* : 3-*dihydrothiazolidene-2-*, m.p. 150—155° (decomp.)]. Bands of max. absorption are recorded for solutions of the quinonoid dyes in H_2O, EtOH, $CHCl_3$, and C_5H_5N; the colour of the solutions varies greatly according to the nature of the solvent used.

(B) Where resonance of apolar structure with bipolar ionic structure is possible, the colour of the solution depends on the μ of the solvent, which determines the composition of the equilibrium mixture.

(C) The absorption spectra of carbocyanine dyes of the types *o*-C_6H_4<N(Me)>Z>$C{\cdot}CH:CH{\cdot}CH:C$<N(Me)>Z>C_6H_4-*o* (Z = CH:CH, S, O, NMe, CMe_2),



all exhibit bands in the ultra-violet (285—385 mμ). The absorption spectra of the methiodides of *o*-C_6H_4<N>Z>CH or thiazole resemble those of the derived carbocyanine dyes. Max. absorption in the ultra-violet shifts towards longer wave-lengths with increase in length of the polymethine chain of the dyes *o*-C_6H_4<N(Me)>S>$C{\cdot}[CH:CH]_n{\cdot}CH:C$<N(Me)>$S$>$C_6H_4$-*o* ($n = 0$, 1, 2, 3). R. T.

Cyanine dyes.—See B., 1941, II, 40, 67.

[Stability of nicotinamide, nicotinuric acid, and trigonelline.]—See A., 1941, III, 118.

Resolution of racemic scopolamine into optical isomerides. M. N. Schtschukina, S. S. Okun, D. N. Jurigin, and N. A. Preobrashenski (*J. Gen. Chem. Russ.*, 1940, **10**, 803—806).—*dl*-Scopolamine di-*d*-camphorate, crystallised from H_2O, gives the l-*scopolamine* salt, m.p. 157—158°, $[\alpha]_D$ +18° in H_2O, from which *l*-scopolamine (**I**) is prepared. The residual *d*-salt in the mother-liquor is racemised, and (**I**) is separated from the racemate, as above. R. T.

Alkaloids of the Papaveraceæ family. VII. Alkaloids of *Papaver armeniacum*. Structure of armepavine. S. Junusov, R. A. Konovalova, and A. P. Orékhov (*J. Gen. Chem. Russ.*, 1940, **10**, 641—648).—Armepavine (**I**) and CH_2N_2 in MeOH yield *methylarmepavine*, m.p. 63—64°, $[\alpha]_D$ −84·48° in $CHCl_3$ [*methiodide* (**II**), m.p. 135—136°], oxidised by HNO_3 to anisic acid. (**II**) and KOH in MeOH (1 hr. at the b.p.) yield *de*-ON-*dimethylarmepavine*, m.p. 86° [*hydrochloride*, m.p. 229—230°; *methiodide* (**III**), m.p. 233—234°]. (**III**) when heated with KOH in MeOH gives NMe_3 and α-p-*anisyl*-β-(3 : 4-*dimethoxy*-6-*vinylphenyl*)*ethylene*, m.p. 79°, oxidised by $KMnO_4$ in $COMe_2$ to anisic acid and *m*-hemipinic acid. (**I**) and Et_2SO_4 yield *ethylarmepavine*, an oil, from which *p*-OEt·C_6H_4·CO_2H is obtained by oxidation with $KMnO_4$. (**I**) is oxidised similarly to *p*-OH·C_6H_4·CO_2H and 1-keto-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline. (**I**) is therefore 6 : 7-dimethoxy-1-*p*-hydroxybenzyl-2-methyl-1 : 2 : 3 : 4-tetrahydro-*iso*quinoline. R. T.

Cinchona alkaloids in pneumonia. VIII. Sulphur derivatives of *apo*cupreicine ethers and aminoquinolines. (Miss) A. G. Renfrew and C. L. Butler (*J. Amer. Chem. Soc.*, 1940, **62**, 3304—3305).—The prep. and toxicity of p-*acetamido*-, m.p. 105°, and -*amino-benzenesulphonylhydroxyethyl*a*pocupreicine*, m.p. 99°, N-p-*acetamido*- and -*amino-benzenesulphonylquinicine*, 6-, m.p. 240°, and 8-*amino*-5-p-*sulphonamidophenylazoquinoline*, m.p. 245°, *ethyl*a*pocupreicine monohydrochloride*, cryst., $[\alpha]_D$ −26·7° in H_2O, hydroxyethyla*pocupreicine* dihydrochloride, cryst., and *quinicine monohydrochloride* are described. They have no useful antipneumococcic activity. Hydroxyethyla*pocupreicine*, a gum, $[\alpha]_D$ −29° in N-H_2SO_4, gives a *monohydrochloride*, +EtOH, m.p. 90°. R. S. C.

VI—ORGANO-METALLIC COMPOUNDS.

Organic mercury derivatives.—See B., 1941, III, 57.

VII.—PROTEINS.

Constitution of silk fibroin. K. H. Meyer, M. Fuld, and O. Klemm (*Helv. Chim. Acta*, 1940, **23**, 1441—1444).—Silk fibroin appears to contain only 10·8% of tyrosine instead of 13·2% recorded by Bergmann and Niemann (A., 1938, III, 210). *X*-Ray interferences of silk show that the crystallites have very appreciable length and comprise at least six identical periods in the direction of the fibre axis. The position within and without the chain can be represented by the scheme (G = glycyl, A = alanyl, T = tyrosyl, Ar = arginyl, S = seryl) G ArGT GAGAGSGAGAGA GTArG.
amorphous in the crystallite amorphous
H. W.

Complex pseudoglobulin–lecithin in the vitellus.—See A., 1941, III, 204.

VIII.—ANALYSIS.

Quantitative capillary luminescence analysis.—See A., 1941, I, 90.

Systematic qualitative organic micro-analysis. Determinations of specific gravity. H. K. Alber (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 764—767).—The construction and use of micro-pipettes (capacities 100—6 cu.mm.) for determination of *d* are described. The accuracies obtained are sufficiently great for the identification of unknown liquids or solids. J. D. R.

Iodometric determination of small quantities of nitrogen without distillation.—See A., 1941, III, 64.

Apparatus for Van Slyke determination of amino-nitrogen in solid substances. O. Klemm and K. H. Meyer (*Helv. Chim. Acta*, 1940, **23**, 1444—1445).—The apparatus has been modified to allow the use of solid substances such as silk or wool. H. W.

Determination of micro-quantities of organic phosphorus. B. L. Horecker, T. S. Ma, and E. Haas (*J. Biol. Chem.*, 1940, **136**, 775—776).—1 μg. of P in protein is determined to ±3% by a modification of the method of Fiske *et al.* (A., 1926, 443), using the photo-electric spectrophotometer of Hogness *et al.* (A., 1937, I, 331). A. Li.

Micro-tests for elements in organic compounds. II. Phosphorus, arsenic, and antimony. C. L. Wilson (*Analyst*, 1940, **65**, 405—406; cf. A., 1938, II, 301).—Org. mixtures containing P, As, and Sb are oxidised in a fusion mixture (1 Na_2O_2 : 2 KNO_3). P is identified as the double Mg NH_4 salt. As and Sb are distinguished by reduction with a Sn–Pt "couple" followed by a modified Gutzeit test. The elements are detected correctly in mixtures containing 5—20 μg. of P compound, 10—20 μg. of As compound, and 20—30 μg. of Sb compound. E. C. B. S.

Determination of boron in volatile organic compounds using the Parr oxygen bomb. W. M. Burke (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 50—51).—The sample mixed with Na_2CO_3 is oxidised in the Parr bomb and the H_3BO_3 determined by titration in presence of mannitol. The method provides a means of decomp. org. B compounds without the use of large amounts of reagent and gives accuracy ≮ previous methods. J. D. R.

Elimination of formaldehyde in the analysis of formaldehyde–formic acid mixtures. A. Hickling and F. Rodwell (*J.C.S.*, 1941, 51—52).—Most of the CH_2O is pptd. by excess of H_2S in strongly acid solution, H_2S removed by $CuSO_4$, and the excess of this pptd. by boiling with NaOH. The remaining CH_2O is determined by I titration and the CH_2O + HCO_2H with $KMnO_4$. A. Li.

Analytical procedures employing Karl Fischer reagent. V. Determination of water in presence of carbonyl compounds. W. M. D. Bryant, J. Mitchell, jun., and O. M. Smith (*J. Amer. Chem. Soc.*, 1940, **62**, 3504—3505; cf. A., 1939, I, 577).—Aldehyde and ketone interference in the Karl Fischer titration for H_2O is inhibited by the presence of an excess of 2% HCN solution in C_5H_5N, the resulting cyanohydrins being inert towards the reagent. Analytical data for a series of 8 aldehydes and 5 ketones are given. W. R. A.

Microscopic identification of certain sugars and polyhydric alcohols. J. A. Quesne and W. M. Dehn (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 556—560).—Photomicrographs are reproduced of crystals of gentiobiose, *d*-lyxose, trehalose, dulcitol, mannitol, sorbitol, and binary mixtures of various sugars pptd. from saturated aq. solution by $COMe_2$, EtOH, MeCN, and dioxan. J. D. R.

Determination of pentoses. R. E. Reeves and J. Munro (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 551—553).—The pentose is boiled with HCl and xylene and the furfuraldehyde (**I**) in the xylene layer is determined colorimetrically with NH_2Ph,AcOH by comparison with standard solutions of (**I**) in xylene. 100% conversion of *d*-xylose into (**I**) is achieved. J. D. R.

Determination of methionine in certain mixtures. Precision method. J. J. Kolb and G. Toennies (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 723—724).—The purity of methionine can be determined with an accuracy of ±0·1% by oxidation with H_2O_2 in $HClO_4$ followed by determination of the unused H_2O_2 by KI–$Na_2S_2O_3$. The method is applicable to mixtures, as other NH_2-acids (except tryptophan, cysteine, and cystine) do not interfere. Procedure is detailed and data on the stability of H_2O_2 in 1—4N-$HClO_4$ are presented. J. D. R.

Photocolorimetric determination of furfuraldehyde. R. A. Stillings and B. L. Browning (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 499—502).—To a solution of neutral furfuraldehyde (**I**) in 20% NaCl is added NH_2Ph,AcOH and the transmittance of the red solution measured photometrically and compared with a known calibration curve. Beer's law is valid for concns. of (**I**) of 0·5—4·5 p.p.m. Methyl- and hydroxymethyl-furfuraldehyde introduce an error <1%, and CH_2O at 100 p.p.m. does not interfere. Procedure is detailed. J. D. R.

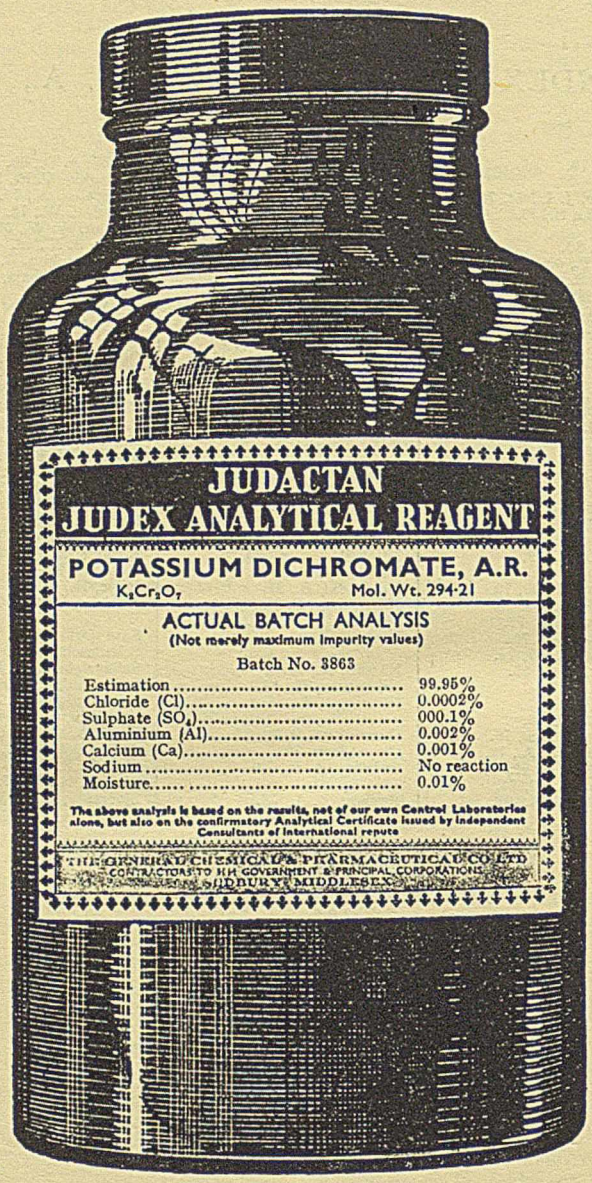
INDEX OF AUTHORS' NAMES, A., II.

MARCH, 1941.

JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL BATCH ANALYSIS



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