BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

DECEMBER, 1939.

Separation of organic compounds containing oxygen from their mixtures with hydrocarbons. A. S. Osokin (J. Gen. Chem. Russ., 1939, **9**, 1315—1325).—Alcohols, aldehydes, ketones, esters, and acid anhydrides are pptd. from their solutions in light petroleum by dry $MgCl_2$. If a mixture of hydrocarbons with substances containing O is present, the acids, phenols, etc. are eliminated by alkali, the rest is pptd. by $MgCl_2$, and the residue containing aromatic ethers, furan, etc. is analysed by combustion. J. J. B.

Cadmium-photosensitised reactions of ethane.—See A., 1939, I, 620.

Isomerisation of butanes and their equilibrium ratios. B. L. Moldavski and T. V. Nisovkina (Compt. rend. Acad. Sci. U.R.S.S., 1939, **23**, 919—920).—The equilibrium $n\text{-}C_4H_{10} \rightleftharpoons iso\text{-}C_4H_{10}$ has been examined in the liquid phase at 70° in presence of $AlCl_3$ + $CuSO_4$,2HCl and at 110—180° by passing the vapours, mixed with HCl, over $AlCl_3$. H. W.

Kinetics of cyclisation of di*iso*butyl at platinised charcoal catalyst.—See A., 1939, I, 618.

Polymerisation of gaseous butadiene.—See A., 1939, I, 614.

Catalysed polymerisation of butadiene at a liquid–gas interface.—See A., 1939, I, 619.

Structure of the mixed polymeride of butadiene and acrylonitrile. E. N. Alexeeva (J. Gen. Chem. Russ., 1939, **9**, 1426—1430).—Butadiene and CH_2:$CH\cdot CN$ are heated at 60° for 116 hr. in presence of 1% of BzO_2H, and the reaction product is treated successively with O_3 and H_2O_2. The ozonolysis products are succinic, butanetri-, hexanetetra-, and dodecanepenta-carboxylic acids. These results are explicable on the assumption that the polymerisation product consists of chains of $\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot$ and $\cdot CH_2\cdot CH(CN)\cdot$ units. R. T.

Synthesis of piperylene from furfuraldehyde. I. A. M. Berkenheim and T. F. Dankova (J. Gen. Chem. Russ., 1939, **9**, 924—931).—Piperylene was obtained from furfuraldehyde (I) by the following reactions, the yields being shown in parentheses: (I) with CH_2O and NaOH yields furfuryl alcohol (90—91%), which is converted by HCl into $CH_2Ac\cdot CH_2\cdot CO_2H$ (62—64%), reduced to γ-valerolactone by Na–Hg (81·5%), or electrolytically (88%), from which $OH\cdot CHMe\cdot[CH_2]_3\cdot OH$ is obtained by reduction with Na–EtOH in xylene (59%), converted into $CHMeBr\cdot[CH_2]_3\cdot Br$ by saturated HBr at 0°, from which a *bromopentene*, b.p. 127—128° (59—60%), is obtained by heating with $NPhMe_2$ at 175—180°, converted by KOH–EtOH into $CHMe{:}CH\cdot CH{:}CH_2$ (60%) and an *ether*, $C_5H_9\cdot OEt$, b.p. 120—123° (17%). V. A. P.

Fluorocarbons. Reactions of fluorine with carbon. J. H. Simons and L. P. Block (J. Amer. Chem. Soc., 1939, **61**, 2962—2966).—F_2 was passed direct from the generator through a Cu tube containing finely-divided C and 1% of a Hg^I or Hg^{II} salt, and heated to a dull redness. The reaction takes place steadily and without explosion and the gas, after successive treatment with aq. NaOH, H_2O, aq. NaOH, conc. H_2SO_4, and P_2O_5, was fractionated by means of a low-temp. fractionating column. Besides CF_4 and C_2F_6 and a mixture (of fluorocarbons) boiling from 25° to 160°, six fractions of const. b.p. have been obtained and analysed. Various physical data (m.p., b.p., ρ, v.p., heats of vaporisation) are given for these fractions, which correspond with *octafluoropropane*, *decafluorobutane* (two isomerides), *decafluorocyclopentane*, *dodecafluorocyclohexane*, *tetradecafluorocycloheptane*. Since their properties are not those of hydrocarbon derivatives a new nomenclature is suggested for them. The mixture (b.p. 25—160°) consists essentially of two parts, one of b.p. 25—95° probably containing fluorocarbons of from 3—8 C atoms, the other, b.p. 95—160°, probably containing fluorocarbons with 8—12 C. W. R. A.

Halogenation of hydrocarbons. Chlorination of olefines and olefine–paraffin mixtures at moderate temperatures; induced substitution. H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan (Ind. Eng. Chem., 1939, **31**, 1239—1244).—Analyses for free Cl_2 in olefine–Cl_2 mixtures are liable to error, owing to extraneous catalysed reactions in the absorption vessel. Cl may be determined, *e.g.*, with C_2H_4, by 10% aq. KOH at room temp. or 10% aq. KI at 80°; with C_3H_6 or $n\text{-}C_4H_8$, 10% aq. KOH at 80°; with Δ^{β}- or $\Delta^{\gamma}\text{-}C_4H_8$, 10 or 5% aq. KOH at 80°, with diluent N_2. Olefines react with Cl_2 (O_2-free) only slowly, if at all, in the gas phase over clean Pyrex glass at 125—135°. Packing with Pyrex rods, or saturation of C_2H_4 with $C_2H_4Cl_2$ or H_2O, has no effect. Illumination (high-intensity Hg arc) of a non-reacting equimol. mixture of C_2H_4 and Cl_2 at 25° allows complete utilisation of Cl_2; once begun, reaction proceeds in absence of light, owing to presence of a liquid phase (cf. Stewart *et al.*, A., 1936, 37). If the temp. of reactor through which C_2H_4 + Cl_2 are flowing at 135° is lowered, no reaction occurs until 20—23°, when all the Cl_2 reacts rapidly. "Onset temp." are also recorded for the above olefines, with or without N_2 dilution; % Cl substituted

or added is given. Once started, reaction proceeds at temp. ⩾ onset val.; *e.g.*, chlorination of C_2H_4 begun at 20° continues at 65°. The compositions of the products of chlorination of the olefines are recorded. In presence of O_2, the % Cl reacting by substitution with olefines or mixtures, *e.g.*, $C_3H_6 + C_3H_8$, $C_4H_8 + C_4H_{10}$, is decreased; substitution into the paraffin is more strongly inhibited than that into the additive product (induced reactions; Stewart *et al.*, A., 1931, 610). Even when catalysts, *e.g.*, $CaCl_2$, are present, O_2 strongly inhibits some substitution reactions in the liquid phase. Reaction in liquid phase, once begun, is little, if at all, affected by catalyst. Catalytic vapour-phase chlorination of olefines or olefine–paraffin mixtures, *e.g.*, $C_4H_8 + C_4H_{10}$ at 80—100°, occurs in absence of liquid. Concurrent substitution reactions are not inhibited by O_2 (even in large amount) and are thus due to thermal and catalytic conditions, rather than to induction. A. T. P.

Action of hexachloroethane on Grignard reagents. V. V. Korschak (J. Gen. Chem. Russ., 1939, 9, 1153—1154).—The action of various Grignard reagents on C_2Cl_6 does not lead to the substitution of the Cl of C_2Cl_6 by alkyl R. The products are C_2Cl_4, $CHCl_2{\cdot}CHCl_2$, $CCl_3{\cdot}CH_2Cl$, and C_2HCl_5, the last three formed by reduction of C_2Cl_6, with products derived from the free radical formed in the reaction $C_2Cl_6 + 2MgRBr = C_2Cl_4 + 2R + 2MgClBr$, such as C_2H_6 and C_2H_4 resulting from the disproportionation of Et. G. A. R. K.

Aliphatic chloro-derivatives. XVI. Vicinal effect. D. V. Tischtschenko (J. Gen. Chem. Russ., 1939, 9, 1380—1388).—The velocity of hydrolysis in aq. NaOH–EtOH of $(CH_2{\cdot}CMe_2Cl)_2$, $CH_2(CMe_2Cl)_2$, $(CHMeCl)_2$, $(CH_2{\cdot}CHMeCl)_2$, $CH_2(CHMeCl)_2$, $(CMe_2Cl)_2$, $Cl{\cdot}[CH_2]_4{\cdot}Cl$, $Cl{\cdot}[CH_2]_3{\cdot}Cl$, and $Cl{\cdot}[CH_2]_2Cl$ rises with increasing distance between the Cl, and falls in the order $CH_2Cl < CHMeCl < CMe_2Cl$. R. T.

Peroxide effect in the addition of reagents to unsaturated compounds. XXI. "Normal" and "abnormal" additions of hydrogen bromide. M. S. Kharasch, S. C. Kleiger, and F. R. Mayo (J. Org. Chem., 1939, 4, 428—435).—Study has been made of the addition of HCl and HBr to $CH_2{:}CHMe$, $CH_2{:}CMe_2$, $CH_2{:}CH{\cdot}CH_2Br$, $CH_2{:}CH{\cdot}CH_2Cl$, $CH_2{:}CMeBr$, $CH_2{:}CMeCl$, $CH_2{:}CHCl$, $CH_2{:}CHBr$, $CCl_2{:}CHCl$, $CHBr{:}CHMe$, and $CHCl{:}CHMe$ in the presence and absence of $FeCl_3$ as catalyst. The direction of addition of HCl is the same as that of the "normal" addition of HBr. Fe^{III} halides greatly accelerate the rate but do not change the "normal" direction of addition of both halogen acids. It is suggested that the "normal" addition of HBr be defined as that corresponding with the following equiv. additive reactions: the addition of HCl with or without $FeCl_3$ and the addition of HBr in the presence of $FeCl_3$. H. W.

Mechanism of the oxygen effect on hydrogen bromide reacting with ethenoid compounds. Y. Urushibara and O. Simamura (Bull. Chem. Soc. Japan, 1939, 14, 323—336).—In the presence of traces of O_2, addition of HBr to $CH_2{:}CH{\cdot}CH_2Br$ gives $CH_2(CH_2Br)_2$ exclusively. Peroxides and H_2O are formed only in presence of excess of O_2. The reversal of the normal addition of HBr to allyl and vinyl bromides, and the isomerisation of *iso*stilbene by HBr and O_2, can be explained by a chain mechanism involving initial formation of Br radicals by Br atoms. L. J. J.

Aliphatic chloro-compounds. XV. Chlorination of *iso*butylene. I. Diakonov and D. Tischtschenko (J. Gen. Chem. Russ., 1939, 9, 1258—1264).—$CMe_2{:}CH_2$ and Cl_2 combine to give $Bu^{\gamma}Cl$, *iso*butenyl chloride (I), and a mixture of 40% of $CHCl{:}CMe{\cdot}CH_2Cl$ and 60% of $CH_2{:}C(CH_2Cl)_2$, identified by ozonisation to chloro- and dichloro-acetone respectively. A similar mixture of unsaturated Cl_2-compounds is produced by chlorination of (I) in presence of Na_2CO_3. The production of these Cl_2-compounds is due to an abnormal Lvov–Kondakov reaction and is less marked than with $CMe_2{:}CHMe$, in which steric hindrance plays a greater part in preventing the normal addition of Cl_2 to the double linking, in agreement with the theoretical considerations already put forward. G. A. R. K.

Isomeric transformations of halogen derivatives of unsaturated aliphatic hydrocarbons. II. Hydrolysis of α-chloro-γ-methylallene. T. A. Favorskaja (J. Gen. Chem. Russ., 1939, 9, 1237—1242).—$CMe_2{:}C{:}CHCl$ (I) when heated with H_2O and $CaCO_3$ yields γ-chloro-γ-methyl-Δ^{α}-butinene (II), a large amount of α-chloro-γ-methyl-$\Delta^{\alpha\gamma}$-butadiene, a small amount of dimeric chloride $C_{10}H_{14}Cl_2$ (A., 1930, 574), and allylene (III), identified by conversion into mesityl oxide by H_2SO_4. The formation of (III) is thought to proceed through the intermediate formation of the unstable 4-chloro-2-methyl-Δ^1-*cyclo*butene, which then breaks up into (III) and vinyl chloride, this being polymerised. ββ-Dimethylacraldehyde is also formed; the production of it from $OH{\cdot}CMe_2C{:}CH$ is now interpreted as an anionotropic change, similar to the formation of (I) from (II) (cf. A., 1939, II, 354). G. A. R. K.

Exchange reactions in deuteroalcohol. II. W. G. Brown, M. S. Kharasch, and W. R. Sprowls (J. Org. Chem., 1939, 4, 442—455; cf. A., 1937, II, 364).—Re-investigation shows that $NPhMe_2$ does not exchange H for D in EtOH in the absence of acid. $NHPh_2$ exchanges 1 H (presumably from NH) in the absence of acid whilst in presence of acid the exchange no. is 6. The most probable val. for the no. of exchangeable H is 7 and it is therefore likely that the exchange reaction in the presence of acid involves the *ortho* and *para* positions in each ring in addition to the H of NH. NPh_3 behaves similarly, the observed exchange no., 7·9, corresponding with the exchange of 9 H. There is, therefore, no marked diminution in the ability of the nuclear H atoms to exchange which would parallel the very great decrease of basicity in the series $NPhMe_2$, $NHPh_2$, and NPh_3; these results provide convincing evidence against the normal salt (or ion) as an intermediate in the exchange reaction. Under the experimental conditions adopted *o*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$ exhibits no exchange. With *p*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$ 2 H are completely replaced in

presence of acid whereas with *m*-$NO_2 \cdot C_6H_4 \cdot NMe_2$ the theoretical limit of 3 is not attained. The possibilities of steric hindrance and damped resonance are discussed. The alkali-catalysed exchange reaction of fluorene is representative of a different type of H lability, viz., a type in which labile H is acidic; it is found also in xanthone, indene, and 9-phenylfluorene but not in $CHPh_3$, which is less acidic. The origin of the lability of H is to be sought in the *cyclo*pentadiene nucleus, which would be converted by formation of an anion by loss of a proton into a structure in which various possibilities for resonance are present. In neutral solution 9-fluorenol exchanges 1 H whilst in presence of alkali a second H, presumably attached to $C_{(9)}$, is also replaced. In acid solution the compound decomposes rapidly to didiphenylene-ethylene. 9-Methoxyfluorene also decomposes in acid solution but no change is observed in neutral or alkaline solution. 9-Amino- and 9-dimethylamino-fluorene suffer decomp. in neutral, acid, or alkaline solution. The exchange reaction of acetomesitylene (I) takes place to a greater extent than the corresponding reaction of COPhMe, the difference being particularly noticeable in neutral solution where, under the experimental conditions adopted, the (I) change is ~50% complete whilst that of COPhMe is ~5% complete. The process of enolisation in the former, whether acid- or base-catalysed, is appreciably faster than in COPhMe. Contrary to previous observations, the exchange of 2-methylquinoline at 110° for 106 hr. corresponds with somewhat < 1 atom. The change is subject to acid catalysis. H. W.

Synthesis of an alcohol with two conjugated triple linkings. J. S. Salkind and M. A. Aizikovitsch (J. Gen. Chem. Russ., 1939, **9**, 961—964).—$(OH \cdot CMe_2 \cdot C{:}C)_2$, when heated with KOH, $Ba(OH)_2$, or CaO, yields $COMe_2$, $(CH{:}C)_2$, and *ε-methyl-*$\Delta^{\alpha\gamma}$*-hexadi-inen-ε-ol*, b.p. 59—61°/6 mm. R. T.

Catalytic action of *p*-toluenesulphonic acid on acetylene γ-glycols. I. βε-Dimethyl-Δ^{γ}-hexinene-βε-diol and γζ-dimethyl-Δ^{δ}-octinene-γζ-diol. A. Babajan (J. Gen. Chem. Russ., 1939, **9**, 1410—1411).—The glycols when heated at 140—150° with *p*-$C_6H_4Me \cdot SO_3H$ give $(CH_2{:}CMe \cdot C{:})_2$ or $(CHMe{:}CMe \cdot C{:})_2$ in >90% yield. R. T.

Synthesis of glycols of the diacetylene series. J. S. Salkind and I. M. Gverdtziteli (J. Gen. Chem. Russ., 1939, **9**, 971—974).—Acetylenic alcohols react with CuCl and NH_4Cl in H_2O, at room temp., as follows: $OH \cdot CHR \cdot C{:}CH \rightarrow (OH \cdot CHR \cdot C{:}C)_2$. The following were thus prepared: *αδ-di-(1-hydroxy*cyclo*pentyl)-*$\Delta^{\alpha\gamma}$*-butadi-inene*, m.p. 133·2—134·2° [hydrogenated (Pt-black) to *αδ-di-(1-hydroxy*cyclo*pentyl)ethane*, m.p. 91·8—92·5°], $(OH \cdot CHMe \cdot C{:}C \cdot)_2$, *Δ$^{\epsilon\eta}$-dodecadi-inene-δι: 9-diol*, b.p. 159—162°/7 mm., and *αζ-diphenyl-*$\Delta^{\beta\delta}$*-hexadi-inene-αζ-diol*, m.p. 132—133°. R. T.

Preparation of ethers. P. G. Stevens and S. A. V. Deans (Canad. J. Res., 1939, **17**, B, 290—292).—The Na derivative of $C_{10}H_8$ or Ph_2 prepared in $(CH_2 \cdot OMe)_2$ according to Scott *et al.* (A., 1937, II, 55) is cooled and the intensely coloured solution is treated gradually with the alcohol (I) which is to be converted into its Me ether. The colour disappears when one equiv. of (I) has been added. MeI or Me_2SO_4 is added slowly, keeping the solution at >20°, and the mixture is kept overnight. If the ether has a low b.p. Me_2SO_4 is used and the products can be fractionally distilled directly. If it has a high b.p. MeI is used and the mixture is treated with H_2O and the product extracted with Et_2O, dried, and distilled. In some cases the hydrocarbon can be removed by distillation with steam. Alcohols of lower mol. wt. give less satisfactory results owing to manipulative losses. The difficulties may be partly overcome by use of Me_2O as solvent, thus avoiding the separation of $CH_2{:}CH \cdot OMe$ formed by cleavage of $(CH_2 \cdot OMe)_2$. OH-compounds with other functional groups, *e.g.*, $OH \cdot CHMe \cdot CO_2Et$, can be etherified in this manner by merely reversing the process of addition. The yields are lower but about equal to those obtained by Purdie's method. Optically active alcohols yield ethers of high rotatory power. The process has been applied to $Pr^{\beta}OH$, $Bu^{\gamma}OH$, CHMeBu·OH, linalool, cholesterol, and $OH \cdot CHMe \cdot CO_2Et$. H. W.

Ether peroxides. M. S. Kharasch and M. Gladstone (J. Chem. Educ., 1939, **16**, 498).—Triacetone peroxide (I) has been isolated from an old sample of Pr^{β}_2O. (I) explodes on rubbing or heating, and with diacetone peroxide may be responsible for the explosions during the distillation of old Pr^{β}_2O (A., 1936, 1091). L. S. T.

Isomerisation of geranyl acetate. V. I. Issagulianz and G. A. Serebrennikov (J. Gen. Chem. Russ., 1939, **9**, 917—923).—Geranyl acetate (I) and 85% H_3PO_4 at −5° give *cyclo*geranyl acetate (22% yield) + terpin hydrate + an *alcohol*, b.p. 174—175°. (I) and 92% H_3PO_4 at −5° yield 36% of *cyclo*-isomeride. Cyclisation is not effected by $ZnCl_2$, $ZnBr_2$, *p*-$C_6H_4Me \cdot SO_3H$, or HCO_2H. cyclo*Geranyl butyrate*, b.p. 106°/6 mm., and *hexoate*, b.p. 126°/5 mm., are described. V. A. P.

***X*-Ray and thermal examination of glycerides. VII. Unsymmetrical mixed triglycerides, $COR \cdot O \cdot CH_2 \cdot CH(O \cdot COR) \cdot CH_2 \cdot O \cdot COR'$.** M. G. R. Carter and T. Malkin (J.C.S., 1939, 1518—1521; cf. A., 1939, II, 403).—The following unsymmetrical triglycerides have been prepared by the methods used previously (A., 1939, II, 97) and all exist in four solid modifications, vitreous, α, β′, and β, the m.p. being given in that order; *α-decodimyristin* (15°, 32°, 38°, 43·5°), α-laurodipalmitin (32°, 45°, 49·5°, 54°), α-myristodistearin (44°, 54°, 57·5°, 62°), *α-myristodidecoin* (3°, 20°, 31°, 34·5°), α-palmitodilaurin (20°, 33°, 43°, 46·5°), *α-stearodimyristin* (36°, 46°, 52°, 56°), α-decodipalmitin (23°, 37°, 41°, 45·5°), α-laurodistearin (36°, 47°, 52°, —), *α-palmitodidecoin* (2°, 24°, 32°, 35°), α-stearodilaurin (20°, 31°, 41·5°, 45°), *α-stearodidecoin* (13°, 32°, 38°, 41°), α-decodistearin (33°, 42·5°, 46°, 49°). Long spacings of the above, with the exception of the first three, correspond with twice the length of a single mol., but side spacings are of the normal type. The importance of the *X*-ray method in the identification of natural glycerides is discussed. J. D. R.

Reaction between the oxides of olefines and sulphur monochloride. M. S. Malinovski (J.

Gen. Chem. Russ., 1939, **9**, 832—839).—$(CH_2)_2O$ + S_2Cl_2 yield S, $(CH_2Cl)_2$, $CHMeCl_2$, $CH_2Cl{\cdot}CHO$, $CH_2Cl{\cdot}CH_2{\cdot}OH$, and $(Cl{\cdot}[CH_2]_2)_2SO_3$. Propylene oxide and S_2Cl_2 yield S, ββ′-dichlorodipropyl sulphite, $OH{\cdot}CHMe{\cdot}CH_2Cl$, and $CHMeCl{\cdot}CHO$. Epichlorohydrin and S_2Cl_2 when heated give S, $OH{\cdot}CH(CH_2Cl)_2$, and $CO(CH_2Cl)_2$. V. A. P.

Xanthates. I. Reactions of some xanthic acids with metallic [salts]. K. Atsuki and T. Takada (J. Cellulose Inst. Tokyo, 1939, **15**, 321—327).—Me, Et, Pr, Bu, amyl, and CH_2Ph xanthates and 48 metal xanthates have been prepared from the appropriate alkoxides and hydroxides or by double decomp. between the Na xanthate and a metallic salt. The yield decreases with increasing valency of the metal, and the most stable compound is that containing the metal in its lowest valency state. The colour is characteristic of the metal, not of the alcohol, but is not the same as that of the corresponding metallic sulphide. Xanthates of univalent metals are insol. and those of multivalent metals are sol. in Et_2O. The solubility in H_2O decreases with increasing mol. wt. of the alcohol. Cellulose xanthates are similar to other xanthates containing the same metal, but owing to their high mol. wt. they decompose readily, and the decomp. products affect the colour. W. A. R.

Reaction of sodamide with salts of organic acids. L. C. Freidlin and A. I. Lebedeva (J. Gen. Chem. Russ., 1939, **9**, 996—1006).—$NaNH_2$ and salts of carboxylic acids react as follows: $R{\cdot}CO_2M + NaNH_2 \rightarrow NH_2{\cdot}CR(ONa){\cdot}OM \rightarrow MOH + NH{:}CR{\cdot}ONa \rightarrow R{\cdot}CO{\cdot}NHNa$ $(+ NaNH_2) \rightarrow NH_2{\cdot}CR(NHNa){\cdot}ONa \rightarrow NaHCN_2 + NaOH + RH$; $R{\cdot}CO_2M + MOH \rightarrow M_2CO_3 + RH$ (R = H, Me, Et, Ph). With dibasic acids the reactions are: $Na_2C_2O_4 + 2NaNH_2 \rightarrow NaHCN_2 + Na_2CO_3 + NaOH + H_2$, and $(CH_2{\cdot}CO_2Na)_2 + 2NaNH_2 \rightarrow NaHCN_2 + NaCN + Na_2CO_3 + NaOH + CH_4 + 2H_2$. R. T.

Electrolysis of mixtures of pivalates with nitrates. F. Fichter and R. Gunst (Helv. Chim. Acta, 1939, **22**, 1300—1307).—The identified products of the electrolysis of the mixture are $Bu^{\gamma}O{\cdot}NO$, $Bu^{\gamma}OH$, $CMe_2{:}CH_2$, $NO_2{\cdot}O{\cdot}CH_2{\cdot}CMe_2{\cdot}O{\cdot}NO_2$, $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ (*dicarbanilide*, m.p. 138°), *Bu^{γ} pivalate*, $OBu^{\gamma}{\cdot}CH_2{\cdot}CMe_2{\cdot}ONO_2$, and $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}OBu^{\gamma}$. The formation of alkyl nitrate is not observed. It therefore appears that these are not formed from intermediate alkenes but that the simple members are derived from alcohol and HNO_3 and their homologues from the simpler compounds and alkenes. Glycol dinitrates with the simple or multiple mol. wt. of the hydrocarbon residue are formed from the alkene and electrolysed HNO_3. H. W.

Oxidation of stearic acid by oxygen.—See A., 1939, I, 619.

Effect of periodic acid on lactic acid and its degradation products (acetaldehyde, methyl alcohol, formaldehyde, formic acid). P. Fleury and R. Boisson (J. Pharm. Chim., 1939, [viii], **30**, 145—162; cf. A., 1937, II, 273).—Lactic acid (I) with HIO_4 in N-H_2SO_4 at 100° (sealed tube) in 16 days is oxidised completely to CO_2 and H_2O as shown by the disappearance of HIO_4 (cf. A., 1933, 486). The rate of reaction increases with the temp., the acidity, and with increasing amounts of HIO_4. After 1 atom of O is used per mol. of (I), the reaction rate increases (especially under acid conditions) until 4 O per mol. is reached, the utilisation of O_2 then becoming very low. The initial reaction (1 hr.) in which 1 O is utilised per mol. of (I) liberates CO_2 and MeCHO quantitatively if the latter is removed as it is formed. MeCHO under similar conditions requires 5 O for complete oxidation, the factors governing the rate of reaction being similar to those for (I). The rates of oxidation of MeCHO determined by a reduction method (cf. Malaprade, A., 1934, 1090) and by the rate of disappearance of HIO_4 do not agree, because CH_2O which is identified in the reaction product after 13·5 hr. is an intermediate degradation product. HCO_2H and MeOH are also identified. HCO_2H, CH_2O, and MeOH are oxidised under similar conditions to CO_2 and H_2O. J. L. D.

Catalytic hydrogenation of the oxides of unsaturated acids. G. V. Pigulevski and Z. J. Rubaschko (J. Gen. Chem. Russ., 1939, **9**, 829—831).—Catalytic hydrogenation (Pd-black in abs. EtOH at room temp.) of the oxide of Et oleate (new m.p. 21°) leads to rupture of the oxide ring with formation of Et ι-hydroxystearate. V. A. P.

Diethyl methylenemalonate. G. B. Bachman and H. A. Tanner (J. Org. Chem., 1939, **4**, 493—501).—Yields between 4% and 17% of Et_2 methylenemalonate (I) are obtained when $CH_2(CO_2Et)_2$ and CH_2O [as formalin, paraformaldehyde (II), or a solution of CH_2O in the ester] are passed over $AlPO_4$, glass wool, soda-lime, Al_2O_3, Na_3PO_4, Na_2HPO_4, or $Ca_3(PO_4)_2$ at temp. varying from 250° to 420°. (I), b.p. 210°/760 mm., is obtained in 40% yield by heating a mixture of $CH_2(CO_2Et)_2$ (II), $Ca(OAc)_2$, and KOAc in glacial AcOH at 100° until a clear solution is obtained and then distilling the product under diminished pressure. Impure (I) polymerises only with difficulty. The ease with which freshly prepared (I) polymerises is probably due to the presence in it of acrylic acid or Et acrylate, both of which polymerise with great ease and are capable of initiating the polymerisation of (I). The polymeride obtained from highly purified (I) is a colourless, transparent glass which changes rapidly to a hard but brittle porcelain-like solid. It dissolves slowly in AcOH, $COMe_2$, or EtOH and is pptd. by H_2O or light petroleum as a white, granular powder. It decomposes at 230—240° to the monomeride and products of high b.p. It co-polymerises with butadiene to *Et_2 Δ^3-cyclohexene-1 : 1-dicarboxylate*, b.p. 117°/6 mm., with β-methylbutadiene to *Et_2 3-methyl-Δ^3-cyclohexene-1 : 1-dicarboxylate*, b.p. 127°/6 mm., with βγ-dimethylbutadiene to *Et_2 3 : 4-dimethyl-Δ^3-cyclohexene-1 : 1-dicarboxylate*, b.p. 136°/6 mm. [*acid*, m.p. 186·5—188° (decomp.), decarboxylated to *3 : 4-dimethyl-Δ^3-cyclohexene-1-carboxylic acid*, m.p. 80—81°], and with anthracene to a *compound*, m.p. 126—127°. (I) does not resemble maleic anhydride (II) in the ease or completeness of its co-polymeris-

ation with other olefines. Also there is no apparent tendency to form co-polymerides in a definite ratio with other unsaturated substances. The films obtained from (I) and vinyl acetate, Me methacrylate, Me_2 itaconate, styrene, and Et vinyl ether in presence of Bz_2O_2 are described. (I) does not appear to react with (II) or Me *iso*propenyl ketone under these conditions. H. W.

Ethyl hydrogen methyldiglycollates. P. Vièles and M. Amir (Compt. rend., 1939, **209**, 457—459).—*dl*-Methyldiglycollic anhydride with EtOH gives *Et H* dl-*methyldiglycollate* (I), b.p. 168—170°/20 mm. Partial saponification of the Et ester of (I) gives (I) and probably some *Et H* dl-*methyldiglycollate* (II), b.p. 168—170°/20 mm., which is more rapidly esterified than (I). (I) with excess of boiling MeOH and a little $CuSO_4$ gives Me Et *dl*-methyldiglycollate, b.p. 126—128°/25 mm., $[\alpha]_{5461}^{25}$ −12·6° (cf. A., 1936, 823). J. L. D.

Chloralides. Condensation of butylchloral with α-hydroxycarboxylic acids. N. M. Shah (J. Indian Chem. Soc., 1939, **16**, 285—286; cf. A., 1934, 869).—Citric, malic, and tartaric acids with $CHMeCl{\cdot}CCl_2{\cdot}CHO,H_2O$ in conc. H_2SO_4 give their respective *butylchloralides*, $CHMeCl{\cdot}CCl_2{\cdot}CH<\begin{matrix}O{\cdot}CHR\\O{\cdot}CO\end{matrix}$, m.p. 187—188°, 139°, and 156°. E. W. W.

Citric acid compounds of zinc. F. S. Schpilev (J. Gen. Chem. Russ., 1939, **9**, 1286—1293).—1 mol. of $ZnSO_4$ + 1 mol. of Na_3 citrate (I) give in a neutral solution $Zn_3(C_6H_5O_7)_2$ (II), and in an alkaline solution $Na_2ZnC_6H_4O_7$. An excess of (I) gives with (II) in acid solution $Na_3ZnH(C_6H_5O_7)_2$, in almost neutral solution $Na_4Zn(C_6H_5O_7)_2$, and in alkaline solution $Zn(Na_3C_6H_4O_7)_2$. The mechanism of the reactions is discussed. J. J. B.

Optical activity of vitamin-*C*.—See A., 1939, III, 1073.

Oxalate formation in ascorbic acid solutions. A. E. Jurist and W. G. Christiansen (Amer. J. Pharm., 1939, **111**, 347—350).—Solutions of Na, Ca (kept for 3 months), and monoethanolamine ascorbate are stored at 27° or 38° for ~ 1 year, and the $H_2C_2O_4$ is determined. The process is probably one of auto-oxidation (cf. Ghosh, A., 1938, II, 217). Discrepancy between loss of ascorbic acid and formation of $H_2C_2O_4$ is attributed to presence of other oxidation products. A. T. P.

Synthesis of *l*-ascorbic acid (vitamin-*C*). V. I. Maximov, V. V. Nikonova, A. F. Lazarev, and L. A. Zvereva (J. Gen. Chem. Russ., 1939, **9**, 936—943).—The prep. of *l*-ascorbic acid from *l*-sorbose has been improved to give a yield of 52—54%. Catalytic hydrogenation of *d*-glucose (+ 2% of chalk) with Raney Ni at 120—130°/8—10 atm. yields *d*-sorbitol in quant. yield. Oxidation with *Bacterium melanogenum* gives *l*-sorbose (70% yield), from which di*iso*propylidene-*l*-sorbose is obtained in 90—92% yield by treating with $COMe_2$, anhyd. $CuSO_4$, and H_2SO_4. Oxidation with $KMnO_4$–KOH yields 65—68% of α-ketodi*iso*propylidene-*l*-gulonic acid, isolated as the hydrate, from which *l*-ascorbic acid is obtained in 76—78% yield by heating with HCl–EtOH in $CHCl_3$ at 60—62° for 45 hr. V. A. P.

Synthesis of uronic acids. M. Stacey (J.C.S., 1939, 1529—1531).—β-*d*-Glucose 1 : 2 : 3 : 4-tetra-acetate oxidised in AcOH with $KMnO_4$ in $COMe_2$ yields *d*-glucuronic acid tetra-acetate, which on hydrolysis with $Ba(OH)_2$ gives glucurone. By the same method, galactose 1 : 2 : 3 : 4-tetra-acetate yields *d*-galacturonic acid. J. D. R.

Reactivity of the mercaptido-group. V. N. Hellström (Arkiv Kemi, Min., Geol., 1939, **13**, A, No. 6, 7 pp.; cf. A., 1932, 26).—An oxidation–reduction action is observed between $SH{\cdot}CH_2{\cdot}CO_2H$ and $CH_2I{\cdot}CO_2H$, $CH_2I{\cdot}CO{\cdot}NH_2$, $CHMeI{\cdot}CO_2H$, $CO_2H{\cdot}CH_2{\cdot}CHI{\cdot}CO_2H$, and $CHBr(CO_2H)_2$ without solvent at 20° or in presence of H_2O at 20—25° and sometimes at 100° or in presence of C_6H_6 at 20—25° and occasionally at 60°. Such action is not observed between $SH{\cdot}CH_2{\cdot}CO_2H$ and $I{\cdot}[CH_2]_2{\cdot}CO_2H$, $CH_2Cl(Br){\cdot}CO_2H$, $CH_2Cl(Br){\cdot}CO{\cdot}NH_2$, or $CO_2H{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H$. The mode of reaction appears to be due to vicinal CO_2H, which exert a more marked effect on I than on Br. H. W.

Esters of aliphatic thio-acids of high mol. wt. A. W. Ralston, E. W. Segebrecht, and S. T. Bauer (J. Org. Chem., 1939, **4**, 502—505).—The following esters have been obtained as stable compounds which can be distilled under reduced pressure without decomp. by the action of the appropriate acid chloride on the requisite mercaptan: *Me*, b.p. 112—115°/1 mm., *Et*, b.p. 115—117°/1 mm., *Pr*^{a}, b.p. 126—128°/1 mm., and *Bu*^{a}, b.p. 133—135°/1 mm., *thiolaurate*; *Me*, m.p. 34—35°, *Et*, b.p. 134—136°/1 mm., *Pr*^{a}, b.p. 148—150°/1 mm., and *Bu*^{a}, b.p. 149—151°/1 mm., *thiomyristate*; *Me*, m.p. 44—45°, *Et*, b.p. 172—175°/1 mm., *Pr*^{a}, m.p. 27—28°, and *Bu*^{a}, m.p. 29—30°, *thiopalmitate*; *Me*, m.p. 50—51°, *Et*, m.p. 38—39°, *Pr*^{a}, m.p. 34—35·5° and *Bu*^{a}, m.p. 31—32°, *thiostearate*; *Pr*^{a} *thio-oleate*, b.p. 175—178°/1 mm. H. W.

Racemisation of optically active α-alkyl- and α-phenyl-sulphonylpropionic acids.—See A., 1939, I, 618.

Kinetics of oxidation of aldehydes by selenium dioxide.—See A., 1939, I, 616.

Formation of formaldehyde by electrolysis of acetate. E. Baur (Helv. Chim. Acta, 1939, **22**, 1120—1123).—CH_2O is formed as anodic, "trivial" product during the electrolysis of solutions of AcOH; $AcOH \rightarrow OH{\cdot}CH_2{\cdot}CO_2H \rightarrow CH_2O + CO_2$. It is determined when a diaphragm is used. Without the latter there is a greater production of CH_2O owing to the change: $AcOH \rightarrow AcO_2H \rightarrow CH_2O + CH_4 + O_2$. The production depends on the use of d.c. and concentric Pt gauze electrodes. Formation is not observed when commutated d.c. is used and is not favoured by addition of preformed AcO_2H in Et_2O to the catholyte. Addition of EtOAc is very advantageous. The experiments support the view that the esterified CO_2H of photodynamic dyes is responsible for the CH_2O observed when they are exposed to light. H. W.

Decomposition of acetaldehyde and deutero-acetaldehyde.—See A., 1939, I, 615.

Use of hydrogen sulphide in acetone. PÉRONNET and R. H. RÉMY (J. Pharm. Chim., 1939, [viii], **30**, 170—172).—Pure $COMe_2$ saturated with dry H_2S forms a solution (22·4 g. per l.) stable for 6—12 months. The H_2S is not readily lost by exposure to air. After ~1 year thioketones (?) are formed in solution. J. L. D.

Transition from carbohydrates to carbocyclic compounds. I. Transformation of glucose into phenol. P. SCHORIGIN and N. N. MAKAROVA-SEMLIANSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1939, **23**, 915—918).—When Na is added gradually to a solution of trimethyl-β-glucosan in liquid NH_3 and the solution kept at room temp. for several days, PhOH is formed in ~20% yield. Ring-closure between $C_{(1)}$ and $C_{(6)}$ is caused by addition of Na org. compounds which are slowly formed to the bridge O and subsequent removal of O. In support of this theory it is shown that $CHPh{:}CH_2$ (I) is obtained in ~75% yield by the action of Na on $Ph{\cdot}[CH_2]_2{\cdot}OH$ (II): (II) + Na → $Ph{\cdot}[CH_2]_2{\cdot}ONa$ (III) + H; (III) → (I) + NaOH; (II) + NaOH ⇌ (III) + H_2O. H. W.

Production of reducing sugars from glycosides by ultra-violet light.—See A., 1939, I, 620.

Oxidation of aldoses by hypoiodite.—See A., 1939, I, 615.

Kinetic study of the formation of *d*-glucose-phenylhydrazone.—See A., 1939, I, 616.

Biochemical synthesis of higher β-galactosides. I. VINTILESCU, C. N. IONESCU, and M. SOLOMON (Bul. Soc. Chim. România, 1938, **20**, 115—125).—From determination of the solubility of galactose in mixtures of $n\text{-}C_5H_{11}{\cdot}OH$ and $COMe_2$ and polarimetric investigation of the competing reactions therein induced by emulsin, it is shown that β-n-*amylgalactoside*, m.p. 115—116°, $[\alpha]_D^{20}$ −9·50° in H_2O, is best obtained in 2 : 5 $n\text{-}C_5H_{11}{\cdot}OH$–$COMe_2$. The galactoside is quantitatively hydrolysed by HCl or emulsin. R. S. C.

Structure of cellulose and other polymerides related to simple sugars. W. N. HAWORTH (Chem. and Ind., 1939, 917—925).—A lecture.

Arrangement of substituents in cellulose derivatives.—See A., 1939, I, 552.

Hydrolysis of glucosaminides by an enzyme in *Helix pomatia*. A. NEUBERGER and R. V. PITT RIVERS (Biochem. J., 1939, **33**, 1580—1590).—An enzyme has been prepared from *H. pomatia* which hydrolyses only the β-forms of *N*-acetylmethylglucosaminides: it is freed from β-glucosidase by filtration through bauxite. Acyl compounds other than *N*-CHO and *N*-Ac are not hydrolysed, nor are non-acylated glucosaminides. The following have been prepared: N-p-*toluenesulphonylglucosamine tetra-acetate*, m.p. 128—129°, $[\alpha]_D$ −3° in $CHCl_3$; 1-*bromo*-N-p-*toluenesulphonylglucosamine triacetate*, m.p. 148°, $[\alpha]_D$ +63·5° in $CHCl_3$; N-p-*toluenesulphonylphenylglucosaminide*, m.p. 213—214°, $[\alpha]_D$ −83° in C_5H_5N, and its *triacetate*, m.p. 200—201°, $[\alpha]_D$ −52·8° in C_5H_5N; N-*carbobenzyloxy*-β-*methylglucosaminide triacetate*, m.p. 147—149°, $[\alpha]_D$ +15° in $CHCl_3$; β-*methylglucosaminide formate triacetate*, m.p. 120°; N-*formyl*-β-*methylglucosaminide*, m.p. 204—205°, $[\alpha]_D$ −47·2° in H_2O, and its *triacetate*, m.p. 165; N-*propionyl*-β-*phenylglucosaminide*, m.p. 230° (decomp.), $[\alpha]_D$ +8° in C_5H_5N, and its *triacetate*, m.p. 197—197·5°; N-*butyryl*-β-*phenylglucosaminide triacetate*, m.p. 178—179°, $[\alpha]_D$ −10° in $CHCl_3$. Enzymic experiments support the theory that chitobiose, chitotriose, and chitin have a β-configuration. P. G. M.

Synthesis of α-amino-alcohols from the pyrolysis products of gas oil and the identification of some hydrocarbons contained in them. L. S. DEDUSENKO (J. Gen. Chem. Russ., 1939, **9**, 1294—1302).—The light oil, b.p. 27—50° (I), obtained by the pyrolysis of gas oil at 700° was converted by addition of HOCl and distillation with KOH (or preferably NaOH, which gives a 10% better yield) into oxides in ~30% yield; of these 50% boiled at the b.p. of amylene oxides. Previous removal of a small amount of *cyclo*pentadiene by maleic anhydride has little effect on the yield. The oxides were converted by NH_3 into α-NH_2-alcohols from which the *picrate* of $OH{\cdot}CMe_2{\cdot}CHMe{\cdot}NH_2$ (II), m.p. 134—135°, was isolated and also synthesised; this points to the presence of $CMe_2{:}CHMe$ in (I). (II) forms a *H oxalate*, m.p. 121—122°, and a normal *oxalate*, m.p. 210—210·5°, but the separation of the mixed NH_2-alcohols through their oxalates was impracticable. α-Glycols obtained as by-products in the prep. of the oxides were dehydrated to $COMePr^{\beta}$ and $COEt_2$, showing the presence of glycols derived from $CMe_2{:}CHMe$ and $CHMe{:}CHEt$ in (I). They gave with PhNCO the urethanes of an amylene glycol, m.p. 220°, and of *cis-cyclo*pentanediol, the latter derived from *cyclo*pentene in (I). The *mono-* and *di-urethane* of $OH{\cdot}CMe_2{\cdot}CHMe{\cdot}OH$, m.p. 125·5° and 134·4—135·5°, respectively, have been prepared. G. A. R. K.

Amino-derivatives of pentaerythritol. II. Tetra(aminomethyl)methane. III. Di(hydroxymethyl)di(aminomethyl)methane. F. GOVAERT and M. BEYAERT (Proc. K. Akad. Wetensch. Amsterdam, 1939, **42**, 637—640, 641—648; cf. A., 1934, 638).—II. $C(CH_2{\cdot}NH_2)_4$, $+H_2O$, m.p. 41—42°, b.p. 108°/0·7 mm., gives a s-*Ac*$_4$, m.p. 60°, b.p. 72·5—73°/2 mm., and s-*tetracarbamido*-derivative, m.p. 230° (decomp.), *dicarbonate*, m.p. 125° (evolution of CO_2), and *dimercurichloride*, *B*,2$HgCl_2$.

III. $C(CH_2Br)_2(CH_2{\cdot}OH)_2$, obtained in 50% yield with some Br_1- and Br_2-derivative from $C(CH_2{\cdot}OH)_4$ by 66% HBr at 140°, is converted by NH_3–EtOH (saturated at 0°) at 150° into mixed bases, whence Ac_2O–NaOAc yields among other products 3 : 3-*diacetamido*-1-*oxa*cyclo*butane*, $O<\begin{matrix}CH_2\\CH_2\end{matrix}>C(CH_2{\cdot}NHAc)_2$, m.p. 79°, b.p. 79—80°/0·1 mm., which with boiling 48% HBr gives β-*bromomethyl*-β-*hydroxymethylpropylene*-αγ-*diamine dihydrobromide*, m.p. 246° (decomp.). $C[(CH_2)_2O]_2$ (modified prep.) is converted by H_2O at 150—160° quantitatively into $C(CH_2{\cdot}OH)_4$, is unaffected by liquid NH_3 at 100° but decomposed at 200°, and with aq. NH_3 (saturated at 0°) at 190° gives 78% of ββ-*di*(*hydroxymethyl*)*propylene*-αγ-*diamine*,

+H_2O, cryst., b.p. ~200°/0·002 mm. [H_2 *oxalate*, m.p. 168° (decomp.); *dipicrate*, m.p. 223° (decomp.); *carbonate* at 164° gives CO_2 and the diamine hydrate]. R. S. C.

Syntheses of basic amino-acids and glycine. D. W. Adamson (J.C.S., 1939, 1564—1568).—Slow addition of HN_3 in $CHCl_3$ to *d*-glutamic acid in H_2SO_4–$CHCl_3$, followed by pptn. with phosphotungstic acid and decomp. of the phosphotungstate with $Ba(OH)_2$, gives *d*-α*γ*-diamino-*n*-butyric acid (isolated as oxalate) (*dipicrate*, m.p. 180—181°). NaN_3 may be used in place of HN_3, and after decomp. of the phosphotungstate with $Ba(OH)_2$, the NH_2-acid may be isolated, via the picrate, as the *dihydrochloride*, m.p. 195—196° (decomp.). Similarly, α-aminopimelic acid (I) in $CHCl_3$–H_2SO_4 treated with HN_3 in $CHCl_3$ or with NaN_3 yields *dl*-lysine (II) (isolated as monopicrate or dihydrochloride via the phosphotungstate) (*dipicrate*, m.p. 188—190°). Et *cyclo*hexanone-2-carboxylate and HN_3 in C_6H_6, on treatment with HCl (gas) yields impure (I), and (II). The reaction also succeeds in $CHCl_3$ using HCl (gas) or conc. aq. HCl. α-Aminoadipic acid in H_2SO_4, when treated with HN_3 in $CHCl_3$, yields *dl*-ornithine (III) [sulphate, m.p. 223° (decomp.) (lit. 213° to 234°)]. Et *cyclo*pentanone-2-carboxylate and HN_3 in $CHCl_3$, treated with HCl, also yields (III). Treatment of $CH_2(CO_2H)_2$ in H_2SO_4 with HN_3 in $CHCl_3$ yields glycine. J. D. R.

Poly-condensation of α-amino-acid esters. M. Frankel and E. Katchalski (Nature, 1939, **144**, 330—331).—Solutions of $NH_2{\cdot}CH_2{\cdot}CO_2Et$ (I) in solvents such as C_6H_6 or xylene on keeping at room temp. or at the b.p. deposit horn-like products insol. in H_2O and containing polypeptide esters of different chain lengths. (I) gradually solidifies, and after keeping for several weeks hexadecaglycine Et ester was isolated from the O_2-treated ester and eikosiglycine Et ester from that treated with H_2. Under suitable conditions $NH_2{\cdot}CHMe{\cdot}CO_2Et$ yields, *inter alia*, condensation products which give a strong biuret reaction and appear to be alanine polypeptide esters. L. S. T.

Condensation of the hexapeptide ester of glycine into the 96- and higher (3×2^n) peptide esters. E. Pacsu (Nature, 1939, **144**, 551).—At 102°±1°, the hexapeptide ester undergoes the type of condensation characteristic of the tripeptide ester yielding, in a series of successive bimol. reactions, the 12-, 24-, 48-, 96- (3×2^n) peptide esters. With $n > 4$ the average rate of the reaction, with 1 hr. as the time unit, is $k = 150 \times 10^{-4}$. The activation energy is ~38 kg.-cal. Neither " cyclol 6 " nor nonapeptide ester is formed during the reaction. The esters obtained are colourless, amorphous substances, slightly sol. in cold H_2O, insol. in EtOH, sol. in conc. HCl and in conc. aq. $CO(NH_2)_2$; the biuret reaction is strong. L. S. T.

Configuration of glutamic and aspartic acids from pathogenic bacteria.—See A., 1939, III, 1015.

Combination of cysteine with sugars. M. P. Schubert (J. Biol. Chem., 1939, **130**, 601—603; cf. A., 1936, 824).—Cysteine hydrochloride and the sugar are shaken with H_2O and the solution is kept for 48 hr. at room temp., after which C_5H_5N is added after an additional period of 50—70 hr., and then abs. EtOH is introduced. Cysteine (I) thus give *compounds*, $C_8H_{15}O_6NS$, with *d*-arabinose (*Zn* salt) and *d*-xylose, m.p. 153° and 133° respectively, *substances*, $C_9H_{17}O_7NS$, with *d*-glucose (II), *d*-mannose (*acetate*, m.p. 150—152°), and *d*-galactose (III), m.p. 167°, 171°, and 138°, and *compound*, $C_{15}H_{27}O_{12}NS$, m.p. 130°, with lactose (IV). Fructose does not form a compound with (I). The properties of these compounds are similar to those of the thiazolidines formed by condensation of (I) with simple aldehydes. Their solutions are acid to litmus. In solutions containing an excess of $NaHCO_3$ none of these compounds gives a positive SH test with Na nitroprusside (V). In a dil. solution of NH_3 and $(NH_4)_2SO_4$ only the compounds formed from (II) and (IV) give fair tests with (V); the remainder give only very faint reactions. Aq. solutions of all these compounds absorb I as rapidly as does free (I) and in amount equiv. to the (I) which they contain; such solutions which have been titrated with I slowly deposit crystals of cystine. In solutions containing $NaHCO_3$ in which a negative test with (V) is given, these compounds rapidly yield *S*-carboxymethylcysteine with $CH_2I{\cdot}CO_2Na$. In glacial AcOH (III) gives gelatinous *galactose*-2 : 4-*dinitrophenylhydrazone*, m.p. 171—173°; under these conditions the compound from (I) and (III) remains unaffected. (III) does not appear to unite with $SH{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ or $SH{\cdot}CPh_2{\cdot}CO_2H$. H. W.

Reaction of α-thiocyanopropionic acid with water.—See A., 1939, I, 617.

Reduction of certain amides and substituted amides. I. Electro-reduction of cyclopeptide and open peptide groups. N. I. Gavrilov and A. V. Koperina (J. Gen. Chem. Russ., 1939, **9**, 1394—1401).—The CO group of amides of aromatic acids readily undergoes electro-reduction. For the amides $R{\cdot}CO{\cdot}NHR'$ or $R{\cdot}CO{\cdot}NR_2'$ reduction is possible when R = H or Me and R′ = Me or Ph, but not when R contains >1 C. The CO group of peptides does not, but those of diketopiperazine do, undergo reduction at a Pb cathode. R. T.

Silico-organic compounds. I. Preparation of silicon analogues of aliphatic ortho-esters. H. W. Post and C. H. Hofrichter, jun. (J. Org. Chem., 1939, **4**, 363—364).—The esters are prepared by heating $Si(OEt)_4$ with a Grignard reagent and treating the product with an aliphatic alcohol, *e.g.*, $Si(OEt)_4 + MgEtBr \rightarrow MgBr{\cdot}OEt + SiEt(OEt)_3$ (I) and (I) + $3Pr^{\alpha}OH \rightleftharpoons 3EtOH + SiEt(OPr^{\alpha})_3$. In an individual case $SiCl_4$ is treated with a Grignard reagent followed by $Pr^{\alpha}OH$. The following are described: Et_3, b.p. 158—160°, Pr^{α}_3, b.p. 202—204°/760 mm., Bu^{α}_3, b.p. 235—238°/760 mm., *tri*-n-, b.p. 285°/760 mm. and -iso-*amyl*, b.p. 266—269°/760 mm., *orthosilicopropionate*, Et_3 *orthosilicobutyrate*, b.p. 179—180°/760 mm.; Et_3, b.p. 235—238°/760 mm., and Pr^{α}_3, b.p. 192°/7 mm., *orthosilicobenzoate*, n-*heptyl orthosilicate*, b.p. 213·5°/4 mm. H. W.

Organic reineckates. M. Coupechoux (J. Pharm. Chim., 1939, [viii], **30**, 118—129).—Limiting concns., the Cr and CNS contents, and the solubilities

in H_2O and MeOH at room temp. and in EtOH at 96° of the reineckates of 45 org. bases, prepared by adding a solution of the base in 5% HCl to excess of $[Cr(NH_3)_2(CNS)_4]NH_4,H_2O$, are recorded. New *reineckates* are those of betaine (I), β-methylcholine, bromocholine, neurine, $N(C_2H_4{\cdot}OH)_3$ (II), *p*-$NH_2{\cdot}C_6H_4{\cdot}OH$, *o*- and *p*-$C_6H_4(NH_2)_2$ (III), 1 : 2 : 5-$C_6H_4Me(NH_2)_2$, benzidine, hydroxyquinoline, $C_{10}H_7{\cdot}NH_2$, brucine, stovaine, cocaine, and ephedrine. The small amounts of CNS′ left in solution can be determined by the method described previously (A., 1936, 1219). Most of the reineckates are micro-cryst.; (I) forms lance-shaped plates; (II), small hexagonal plates; and (III), fern-like leaflets. The reineckates are anhyd., stable at room temp., slowly hydrolysed by cold and rapidly by hot H_2O. In general, the formula is $[Cr(NH_3)_2(CNS)_4]_2base^1$; the reineckates of antipyrine, pyramidone, and quinine are not well-defined. All are sol. in $COMe_2$. Factors affecting solubility are discussed. L. S. T.

New class of ammines. Complex thiostannates.—See A., 1939, I, 622.

New complex ammines belonging to the group of iron and cobalt dinitrosothiosulphates.—See A., 1939, I, 623.

Constitution of complex metallic salts. X. Further evidence for the structure of bridged dipalladium derivatives. J. Chatt and F. G. Mann (J.C.S., 1939, 1622—1634).—*n*-$C_8H_{17}{\cdot}SH$ with CH_2Br_2 and NaOEt gives *ethylene-*αβ*-bis-*(n-*octyl sulphide*), m.p. 29°, which with $(NH_4)_2PdCl_4$ (I) yields *ethylene-*αβ*-bis-*(n-*octyl sulphide)dichloropalladium* (II), darkens ~270°, m.p. ~280°. *o*-Phenylenebis(dimethylarsine) in EtOH with (I) gives *di-o-phenylenebis(dimethylarsine)palladium dichloride*, which with (I) in HCl–EtOH gives *di-*o*-phenylenebis(dimethylarsine)-palladium palladochloride* and o*-phenylenebis(dimethylarsine)dichloropalladium* (III). *o*-Phenylenebis(di-*n*-butylarsine) similarly gives *di-*o*-phenylenebis(di-*n*-butylarsine)-palladium dichloride tetrahydrate* and *-dichloropalladium* (IV), m.p. 273—275°. $AsPhCl_2$ with the Grignard reagent from $Bu^{\alpha}Br$ gives *phenyldi-*n*-butylarsine*, b.p. 158—161°/21 mm., which with (I) gives *bis(phenyldi-*n*-butylarsine)dichloropalladium*, m.p. 47°, which when boiled with (I) in EtOH or $COMe_2$ yields *dichlorobis(phenyldi-*n*-butylarsine)-*μ*-dichlorodipalladium*, m.p. 166°. PPh_3 with (I) in EtOH gives *bis(triphenylphosphine)dichloropalladium*, decomp. ~250—270°, which with (I) in EtOH and $CHCl_3$ yields *dichlorobis(triphenylphosphine)-*μ*-dichlorodipalladium* (V). Ethylene-αβ-bis(diphenylarsine) with (I) yields *ethylene-*αβ*-bis(diphenylarsine)-dichloropalladium* (VI), decomp. at high temp. The *BuPh* (VII), α-form, m.p. 172—174°, and β-form, m.p. 185—186°, derivative was prepared similarly. $AsBu^{\alpha}_2Cl$ with NaOH and $C_2H_4Br_2$ yields *ethylene-*αβ*-bis(arsinic acid)*, m.p. 201—202° (decomp.), which in dil. HCl with aq. KI gives *ethylene-*αβ*-bis(butylchloroarsine)*, b.p. 160—165°/0·05 mm., and this with the Grignard reagent from $Bu^{\alpha}Br$ under H_2 provides *ethylene-*αβ*-bis(dibutylarsine)*, b.p. 161—162°/0·04 mm., which with (I) yields *ethylene-*αβ*-bis(dibutylarsine)dichloropalladium* (VIII), m.p. 221°. All attempts to bridge (II), (III), (IV), (V), (VI), (VII), and (VIII) with (I) were unsuccessful. Dichlorobis-(tributylarsine)-μ-dichlorodipalladium (IX) in Et_2O with NH_3 (2 mols.) in EtOH gives *dichloromonoamminotributylarsinepalladium*, m.p. 73—74° (decomp.), which in cold *cyclo*hexane deposits (IX). $AsBu^{\alpha}_3$ with $K_2Pd(NO_2)_4$ yields $(Bu_3As)_2Pd(NO_2)_2$ but with $K_2Pd(SCN)_4$ gives both $(Bu_3As)_2Pd(SCN)_2$ and $(Bu_3As_2)Pd_2(SCN)_4$. It is concluded that reactions previously described (A., 1936, 1184, 1496) do not support an unsymmetrical structure for bridged dipalladium derivatives, the tautomerism deduced from the dipole moments being attributed to the *cis* and *trans* symmetrical forms. F. R. G.

Kinetics of vapour-phase reaction of *cyclo*propane with iodine.—See A., 1939, I, 615.

Isomerisation of polymethylene hydrocarbons with aluminium chloride. M. B. Turova-Pollak and Z. Makaeva (J. Gen. Chem. Russ., 1939, 9, 1279—1282).—When heated with $AlCl_3$ for 20 hr. at 110—115° ethyl*cyclo*pentane (I) is isomerised to the extent of 97% into methyl*cyclo*hexane (II), recognised by dehydrogenation with Pt–asbestos at 300—310° to PhMe. (II) with $AlCl_3$ only gives 6·3% of (I). G. A. R. K.

Synthesis of *tert.*-butyl- and *tert.*-amyl-*cyclo*pentane and of intermediate products. H. Pines and V. N. Ipatiev (J. Amer. Chem. Soc., 1939, 61, 2728—2730).—H_2–Ni at 125°/100 atm. converts *p*-$C_6H_4Bu^{\gamma}{\cdot}OH$ and p-*tert.*-amylphenol into 4-*tert.*-butyl-, m.p. 82°, and 4-tert.-*amyl*-cyclo*hexanol*, m.p. 24—25°, b.p. 154—155°/40 mm. (α-*naphthylurethane*, m.p. 113°), oxidised by 50% HNO_3 in presence of a little NH_4 vanadate to β-tert.-*butyl*-, m.p. 117°, and β-tert.-*amyl-adipic acid*, m.p. 77—78°, which with $Ba(OH)_2$ at 280° give 3-tert.-*butyl*-, b.p. 200—201°/759 mm. [*semicarbazone*, m.p. 194—194·5° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 139°], and 3-tert.-*amyl*-cyclo*pentanone*, b.p. 120°/27 mm. (*semicarbazone*, m.p. 189°; 2 : 4-*dinitrophenylhydrazone*, m.p. 174·5°), respectively. H_2–Ni at 80°/100—60 atm. then gives 3-tert.-*butyl*-, b.p. 196—198°/744 mm. (α-*naphthylurethane*, m.p. 95°), and 3-tert.-*amyl*-cyclo*pentanol*, b.p. 217°/738 mm. (α-*naphthylurethane*, m.p. 82°), dehydrated by activated Al_2O_3 at 345° to 3- or 4-tert.-*butyl*-, b.p. 139·6°/760 mm., and -tert.-*amyl*-Δ^1-cyclo*pentene*, b.p. 163—165°/743 mm., hydrogenated (Ni; 60°/100 atm.) to tert.-*butyl*-, m.p. −96°±0·2°, b.p. 145·2°/760 mm., and tert.-*amyl*-cyclo*pentane*, b.p. 173·9°/760 mm., respectively. Physical consts. of the products are given. R. S. C.

Hydrogenation catalysis of phenyl*cyclo*pentane and its homologues. J. I. Denisenko (J. Gen. Chem. Russ., 1939, 9, 1068—1076).—Phenyl*cyclo*pentane is hydrogenated (Pt–C catalyst at 300°) to a mixture of α-, β-, and γ-phenylpentane, showing that rupture of the *cyclo*pentane ring takes place in all three possible positions. The same applies to *cyclo*pentylphenyl-methane, -ethane, -propane, -butane, and -pentane, which yield mixtures of isomeric hexyl-, heptyl-, octyl-, nonyl-, and decyl-benzene, respectively. R. T.

Contact isomerisation of ε-*cyclo*hexyl-Δ^{α}-pentene and ε-*cyclo*hexyl-Δ^{α}-pentinene. P. J. Levina, G. B. Golub, and K. M. Smirnov (J. Gen.

Chem. Russ., 1939, **9**, 825—828).—A mixture of amylbenzene and amyl*cyclo*hexane in the proportions of 1 : 2 and 2 : 1, respectively, is formed from ε-*cyclo*hexyl-Δ^{α}-pentene and from ε-*cyclo*hexyl-Δ^{α}-pentinene, by passage over Pt–C at 200—205°. V. A. P.

Directive influence of the electric moment on substitution in the benzene ring.—See A., 1939, I, 551.

Electronic interpretation of the halogenation of toluene. A. P. KRESCHKOV (J. Gen. Chem. Russ., 1939, **9**, 1251—1257).—Theoretical. The author introduces the term "electronisation" to denote the electron density surrounding a given atom, which is affected both by structure and external conditions, and explains the behaviour of PhMe in terms of this. Side-chain halogenation is due to tautomerism which includes as one of the limiting phases one with a semicyclic double linking (Schorigin); this form is favoured by external activation. G. A. R. K.

Ozonisation of *o*-xylene and the structure of the benzene ring. J. P. WIBAUT and P. W. HAAYMAN (Nature, 1939, **144**, 290).—Ozonisation of *o*-xylene (I) in $CHCl_3$ at −25° and conversion of the decomp. products of the ozonides into oximes [20% yield on (I)] gave dimethylgloxime (0·88 mol.), methylglyoxime (2 mols.), and glyoxime (3·2 mols.). This supports the qual. results of Levine *et al.* (A., 1932, 259), and affords chemical evidence for the occurrence of two resonating Kékulé structures in (I). L. S. T.

Mechanism of aromatisation. Thermal isomerisation of the xylenes. A. F. DOBRIANSKI and F. J. SAPRIKIN (J. Gen. Chem. Russ., 1939, **9**, 1313—1314).—Pyrolysis of *o*- (I), *m*- (II), and *p*- (III) -xylene in a porcelain tube heated in an electric oven at 700—770° gives in each case PhMe, condensation products, gases, and unchanged xylene. The recovery of (II) was the highest and it appears to be the most stable, (I) the least stable and the most easily demethylated. Some isomerisation of (I) into (II) and (III) and of (III) into (II), but not into (I), is also observed; (II) is not isomerised. It is probable that demethylation and isomerisation proceed concurrently and that (II) is not an intermediate in the formation of PhMe. G. A. R. K.

Relative reactivity of chloro- and bromo-nitrobenzenes. N. N. VOROSHCOV, jun., and V. A. KOBELEV (J. Gen. Chem. Russ., 1939, **9**, 1047—1048). —Na_2SO_3 does not react with *o*-, *m*-, or *p*-$C_6H_4Cl{\cdot}NO_2$ or -$C_6H_4Br{\cdot}NO_2$ under the conditions of Sprung's experiments (A., 1930, 759). The alleged reactivity of halogens in the *m*-position is thus not confirmed. R. T.

Properties of nitro-groups. Trinitrobenzene derivatives. D. RĂDULESCU, L. NOVAC, I. PETREANU, and S. POPA (Bul. Soc. Chim. România, 1938, **20**, 49—88).—An electronic interpretation of the structure of additive compounds of $C_6H_3(NO_2)_3$ etc. is given; formation of such complexes loosens substituents such as CO_2H, CHO, and NO_2, and even H (reaction with BzCl in absence of $AlCl_3$). 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ with NO-compounds gives products (*A*), in which R = *p*-$C_6H_4{\cdot}NMe_2$ (cf. Secăreanu, A., 1931, 752), *Ph*, m.p. 146—149° (explosive), p-, m.p. 151—153° (explosive), m-, m.p. 155—157° (explosive), and o-C_6H_4Me, m.p. 147—149° (explosive), and p-$C_6H_4{\cdot}NPh_2$ (I), m.p. 221—223° (decomp.), which lose NO_2 when heated alone or in neutral solvents [in $COMe_2$ or $CHCl_3$ for (I)] and give only small amounts of the amine and $(NO_2)_3C_6H_2{\cdot}CHO$ (II) when hydrolysed. 2 : 4 : 6-*Trinitrobenzylidene*-p-, m.p. 201—202° (decomp.), -m-, m.p. 193—194° (decomp.), and -o-*toluidine*, m.p. 197—198° (decomp.), and *di*-2 : 4 : 6-*trinitrobenzylidine*-p *phenylenediamine*, m.p. 208° (explosive), are prepared from (II) and the appropriate amine, are readily hydrolysed to the components, and do not lose NO_2 when heated. In accordance with electronic considerations, *o*-, *m*-, and *p*-$NO{\cdot}C_6H_4{\cdot}CO_2H$, *p*-$C_6H_4(NO)_2$, $NO{\cdot}C_6H_4{\cdot}Hal$, and $C_6HMe_2(NO_2)_3$ do not give compounds of type (*A*), but failure by $C_6H_2Et(NO_2)_3$ is inexplicable. 5 : 1 : 2-$NO{\cdot}C_6H_3(NH_2){\cdot}CO_2Me$ and $C_6H_2Me(NO_2)_3$ give a compound which is neither a Schiff's base nor of type (*A*). 2 : 4 : 6 : 1 : 3-$(NO_2)_3C_6H(CO_2H)_2$ (III), m.p. 204—206°, is best obtained by adding solid $KMnO_4$ to 1 : 3 : 2 : 4 : 6-$C_6HMe_2(NO_2)_3$ in oleum (*d* 1·87); it loses 2 CO_2 when heated in H_2O. *Trinitrotrimesic acid* (IV), m.p. ~208° (decomp.) (*Ag* salt), is similarly obtained in presence of 0·5—0·7% of fuming HNO_3 as catalyst from 2 : 4 : 6 : 1 : 3 : 5-$C_6Me_3(NO_2)_3$. (III) and (IV) are very sol. in H_2O, EtOH, etc., insol. in hydrocarbons, give sol. salts, are fully ionised (all CO_2H) in 0·0001M. aq. solution, and, as also is $(NO_2)_3C_6H_2{\cdot}CO_2H$, are determined by their nitron *salts* (1 mol. of nitron per CO_2H). *s*-$C_6H_3(NO_2)_3$ (V) and saturated aq. $Ba(OH)_2$ at 40° in absence of air give a red *salt*, $[C_6H_3(NO_2{\cdot}OH)_3]_2Ba_3$, + $12H_2O$, which with HCl regenerates (V) and over H_2SO_4 at room temp. in vac. gives the reddish-brown "*salt*," $C_6O_6N_3Ba_{1\cdot5}$, +$3H_2O$; further drying at 140° over P_2O_5 in vac. then gives the "*salt*," $C_6(NO_2)_3Ba_{1\cdot5}$, unusually stable to acid and converted thereby into a brown insol., micro-cryst. substance, $[C_6H_3(NO_2)_3]_x$. The Ba in the last-mentioned "salt" is considered to be attached to the nuclear C. $Sr(OH)_2$ gives an unstable, hydrated salt, converted by drying at 110° into an explosive, reddish-brown "*salt*," $[C_6(NO_2)_3]_2Sr_3$. TlOH gives only a reddish-violet, hydrated Tl_1 salt, converted over H_2SO_4 at room temp. into a *substance*, $C_6H_3(NO_2)_3$,TlOH. Guanidine gives a red *salt*, $[C_6H_3(NO_2)_3]_2,(CH_5N_3)_3$, $+H_2O$. 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}CO_2H$ and $Ba(OH)_2$ give first the normal, colourless $Ba_{0\cdot5}$ salt and then a red "*salt*," $(NO_2)_3C_6Ba{\cdot}CO_2Ba_{0\cdot5},Ba_{0\cdot5}OH$, + $3H_2O$, dehydrated at 114° to the anhyd. "*salt*"; "*salts*," $C_7H_3O_8N_3Sr_2$, + 2·5H_2O and anhyd., are similarly obtained. (III) gives a *salt*, $[C_6H(NO_2)_3{\cdot}CO_2]_2Ba_5(OH)_6$,+$H_2O$, dehydrated in vac. and reconverted by HCl into (III). (IV) and $BaCO_3$ give a colourless $Ba_{1\cdot5}$ salt, +$12H_2O$ and anhyd., converted by $Ba(OH)_2$ into a "*salt*," $[C_6(NO_2)_3(CO_2)_3](BaOH)_3$,+$6H_2O$ and anhyd., reconverted into (IV) by HCl. $[C_6H_2(NO_2)_3]_2$ and $Ba(OH)_2$ give, with loss of NO_2, an impure *product*,

$C_{12}H_4(NO_2)_6[Ba(OH)_2]_3$, which at 114° loses $\sim 4H_2O$. 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ gives a mixture, $C_6H_2Me(NO_2)_3[Ba(OH)]_n$, in which n is partly 2 and partly 3. $C_6HMe_2(NO_2)_3$ gives a coloured solution, but no solid salt, and $C_6Me_3(NO_2)_3$ does not give even a colour. 2 : 4 : 6-$(NO_2)_3C_6H_2{\cdot}OH$ gives a *product*, $C_6H_2(NO_2)_3{\cdot}OH,(BaOH)_2,+0{\cdot}5H_2O$, which at 107—110°/vac. loses H_2O. 2 : 4 : 6 : 1 : 3-$(NO_2)_3C_6H(OH)_2$ gives a *substance*, $[(NO_2)_3C_6HO_2]Ba_3(OH),+2H_2O$. Trinitro-orcinol gives only the Ba_1 salt, $+2H_2O$. n are recorded for some polynitro-compounds. R. S. C.

Synthesis of sulphonyl chlorides by chlorination of sulphur compounds. T. B. Johnson (Proc. Nat. Acad. Sci., 1939, **25**, 448—452).—The production of RSO_2Cl by the action of Cl_2–H_2O on $SR{\cdot}C\langle^{N:CX}_{N{\cdot}CH}\rangle CH$ (I), $SR{\cdot}C(NR'){\cdot}NR'_2$ (*e.g.*, R′ = H or Me), and RSCN (cf. Johnson *et al.*, lit. 1935—1939) is considered to involve preliminary formation of the sulphoxide (*A*) and then RSOCl; (*A*) may undergo oxidation (to the sulphone) or hydrolysis (to RSO_2H or RSOCl). $SR{\cdot}C\langle^{NH{\cdot}CO}_{N—CH}\rangle CH$ can be differentiated from (I) since these give $CO\langle^{NH———CO}_{NH{\cdot}CH(OH)}\rangle CCl_2$ and RSO_3H.

Preparation of styrenes by the action of organomagnesium compounds on *p-cyclo*hexylacetophenone. I. Zugravescu and (Mme.) S. Zugravescu (Bul. Soc. Chim. România, 1938, **20**, 225—230).—*p-cyclo*Hexylacetophenone and the appropriate Mg alkyl bromide give β-p-cyclo*hexyl*-Δ^{β}-n-*butene*, b.p. 169°/4 mm., -n-*pentene*, b.p. 157—158°/12 mm., and -n-*hexene*, b.p. 191—192°/15 mm. MgPhBr gives α-p-cyclo*hexylphenylstyrene*, b.p. 223—224°/13 mm. The structure of the products is proved by $KMnO_4$-oxidation. R. S. C.

Ease of polymerisation of substituted styrenes in relation to their structure. II. P. P. Schorigin and N. V. Schorigina (J. Gen. Chem. Russ., 1939, **9**, 845—854).—Polymerisation at 100° and at 170° in absence of catalysts has been studied in the cases of styrene, *o*- and *p*-bromo-, *o*- and *p*-methoxy-, and *o*- and *p*-amino-styrene, Δ^{α}-octene, *cyclo*hexylethylene, anethole, safrole, *iso*safrole, eugenol, *iso*eugenol, CHPh:CHMe, CPhMe:CH_2, CPh_2:CH_2, and CHPh:CHBr. It is concluded that in substituted ethylenes, polymerisation takes place only when the double linking is conjugated with an aromatic nucleus. Polymerisation of the styrenes is retarded by substitution at α and β and by increase of mol. wt. Rise in temp. leads to increase in velocity of polymerisation, but to decrease in chain length of the polymeride. The following are described: β-p-*diphenylylethyl alcohol*, m.p. 93—94°, from $(CH_2)_2O$ and p-$C_6H_4Ph{\cdot}MgI$; α-p-, b.p. 145°/20 mm., and α-o-*bromophenylethyl alcohol*, b.p. 128°/15 mm., from *p*- and *o*-$C_6H_4Br{\cdot}CHO$ and MeMgI. Dehydration of the ethanols with $KHSO_4$ at 130—140° gives p- and o-*bromostyrene*, b.p. 102—104°/20 mm. and 102—104°/22 mm., respectively. V. A. P.

Effect of substitution on the dissociation of hexa-arylethanes. VIII. Disproportionation of tri-*p*-tolylmethyl. C. S. Marvel, W. H. Rieger, and M. B. Mueller. **IX. Disproportionation of hexa-*p*-alkylphenylethanes. Effect of *o*-, *m*-, and *p*-alkyl groups on the dissociation of hexaarylethanes.** C. S. Marvel, M. B. Mueller, C. M. Himel, and J. F. Kaplan (J. Amer. Chem. Soc., 1939, **61**, 2769—2771, 2771—2775; cf. A., 1939, II, 498).—VIII. It is shown by χ (extrapolated to zero time) that, when pure (p-$C_6H_4Me)_3CCl$ (I) is shaken with Ag in C_6H_6, 20% of (p-$C_6H_4Me)_3C$ (II) is present in 0·05M. solution. After a few hr. at 25—30°, the orange colour has completely disappeared and χ shows absence of (II). This is due to disproportionation of (II) to (p-$C_6H_4Me)_3CH$ (which is recovered by distillation at $\sim 85°/10^{-4}$ mm.) and (p-$C_6H_4Me)_2C{:}C_6H_4{:}CH_2$, which polymerises to a colourless glass. A similar glass is obtained from (I) by C_5H_5N in absence of O_2.

IX. It is shown by χ that (p-$C_6H_4R)_3C$ (R = Et, Pr^{α}, Pr^{β}, CHMeEt, or Bu^{β}), when kept at 30°, disproportionate into (p-$C_6H_4R)_3CH$ and (p-$C_6H_4R)_2C{:}C_6H_4{:}CHR'$ (*A*). However, decolorisation does not occur, since (*A*) are coloured and do not polymerise. The relative rates of disproportionation decrease in the order of R given above. Initial degrees of dissociation (extrapolated to zero time) are R = Et 17, Pr^{α} 21, Pr^{β} 26, CHMeEt 33, and Bu^{β} 27% (all ±2%). This interpretation of the results is supported by the fact that (m-$C_6H_4Me)_3C$, which exists <40% as free radical and cannot yield a quinonoid disproportionation product, is quite stable in C_6H_6. o-$C_6H_4Me{\cdot}CPh_2Cl$ gives an ethane, dissociated to 25 (±1)% to a stable radical; the stability and high degree of dissociation are probably due to steric reasons. (p-$C_6H_4Bu^{\gamma}{\cdot}CPh_2$) dissociates to 8—9 (±1)% to a radical, which is stable as it cannot give a quinonoid product, but (p-$C_6H_4Me{\cdot}CPh_2)_2$ and (p-$C_6H_4Pr^{\beta}{\cdot}CPh_2)_2$ dissociate to 5 and 8—10 (±1)%, respectively, to radicals which disproportionate, but more slowly than does (p-$C_6H_4R)_3C$. The following data are incidentally recorded. *Diphenyl*-p-iso*propyl*-, m.p. 90—91°, and -p-tert.-*butylphenylmethyl chloride*, m.p. 133—134°; *diphenyl*-o-*tolyl*-, m.p. 148—149°, -p-iso*propylphenyl*-, m.p. 139—140°, and -p-tert.-*butylphenyl-methyl peroxide*, m.p. 156—157°. R. S. C.

Cracking of decalin under pressure.—See A., 1939, I, 615.

Conversion of 1- into 2-bromonaphthalene. H. E. Fisher and R. H. Clark (Canad. J. Res., 1939, **17**, B, 251—252).—Conversion of 1- into 2-$C_{10}H_7Br$ (I) by $AlCl_3$–CS_2 (method: Roux, A., 1886, 806) gives a max. yield of 9·1%. Addition of Ni, Mo, W, Sb, Se, or Cr increases the yield of (I) to 25·5, 25·0, 23·5, 22·5, 16, or 14·4%, respectively. Replacement of CS_2 by $COMe_2$, C_6H_6, EtOH, aq. EtOH, dioxan, aq. or anhyd. C_5H_5N, or $MeNO_2$, or of $AlCl_3$ by $FeCl_3$, gave no conversion. A. T. P.

Dehydrogenation. IV. [Tetrahydronaphthalene*spirocyclo*pentanes.] S. C. Sen-Gupta (J. Indian Chem. Soc., 1939, **16**, 349—356).—The anhydride (I) of 1-carboxy*cyclo*pentane-1-acetic acid in

PhMe with $AlCl_3$ gives 1-p-*tolacyl*cyclo*pentane*-1-*carboxylic acid* (II), m.p. 149—150° (*semicarbazone*, m.p. 164—165°), the *Me* ester, b.p. 170—175°/5 mm., of which is obtained from Me *cyclo*pentane-1-acetate-1-carboxyl chloride (III), PhMe, and $AlCl_3$ [during which reaction a rearrangement of (III) is assumed]. Zn–Hg in conc. HCl reduces (II) to 1-β-p-*tolylethyl*-cyclo*pentane*-1-*carboxylic acid*, m.p. 68—69°, b.p. 186—190°/5 mm. (*anilide*, m.p. 124°; *Et* ester, b.p. 160—162°/5 mm.), converted by 85% H_2SO_4 into the 1-*keto*-derivative, b.p. 160—163°/5 mm. (*semicarbazone*, m.p. 141—142°), of 7-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 2-spirocyclo*pentane* (IV), b.p. 135—136°/6 mm., to which it is reduced by Zn–Hg in conc. HCl. Se dehydrogenation of (IV) at 340—350° gives 3-methylphenanthrene and 2-methylanthracene (?). With PhEt and $AlCl_3$ in CS_2, (I) and (III) give respectively 1-p-*ethylphenacyl*cyclo-*pentane*-1-*carboxylic acid* (V), m.p. 128—129° (*semicarbazone*, m.p. 130°), and its *Me* ester, b.p. 195—198°/10 mm. (V) is reduced to 1-β-p-*ethylphenylethyl*cyclo*pentane*-1-*carboxylic acid*, m.p. 51—53°, b.p. 200—202°/9 mm. (*anilide*, m.p. 117°; *Et* ester, b.p. 144—146°/5 mm.). This gives the 1-*keto*-derivative, b.p. 175°/9 mm., of 7-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 2-spirocyclo*pentane*, b.p. 154—156°/9 mm., dehydrogenated to 3-ethylphenanthrene and 2-ethylanthracene (?). The mechanism proposed by Linstead (Ann. Rep. Chem. Soc., 1936, **33**, 304) for dehydrogenations of this type (cf. A., 1934, 1003) is rejected in favour of 1 : 2-fission of the *cyclo*pentane ring during dehydrogenation. E. W. W.

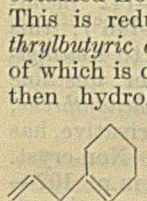
Halogen derivatives of acenaphthene. M. M. Daschevski and A. P. Karischin (Prom. Org. Chim., 1939, **6**, 507—511).—Acenaphthene and SO_2Cl_2 in presence of I at room temp. give 3 : 4-dichloro-acenaphthene (I), in 50—60% yield. (I) and H_2SO_4 (1 hr. at 100°) give 3 : 4-*dichloroacenaphthene*-1-*sulphonic acid*, m.p. 192° (decomp.) [*chloride*, m.p. 179°; *amide*, m.p. 270—272° (decomp.)], oxidised ($K_2Cr_2O_7$) to 4 : 5-*dichloro*-2-*sulphonaphthalic acid*, m.p. 229—230° (*anhydride*, m.p. 160°; *chloride*, m.p. 219—220°; *amide*, decomp. 380—382°). 3 : 4-*Dichloro-acenaphthene*-1 : 6-*disulphonic acid*, m.p. 265—266° (decomp.) (*chloride*, m.p. 198—200°; *diamide*, m.p. >400°), prepared analogously to (I), is oxidised ($K_2Cr_2O_7$) to 4 : 5-*dichloro*-2 : 7-*disulphonaphthalic acid*, m.p. 176—177° (decomp.). 3 : 4-*Dibromo-acenaphthene*-1-*sulphonic acid*, m.p. 240° (decomp.) (*chloride*, m.p. 190—191°; *amide*, m.p. 260—262°), and -1 : 6-*disulphonic acid*, m.p. 252° (decomp.) [*chloride*, m.p. 197—198° (decomp.); *amide*, m.p. 274—275°], and 4 : 5-*dibromo*-2-*sulpho*-, m.p. 235—236°, and -2 : 7-*disulpho-naphthalic acid*, m.p. 159—160°, were prepared analogously. R. T.

Dehydration of cholesterol. J. C. Eck and R. L. van Peursem (Iowa State Coll. J. Sci., 1939, **13**, 115—128).—Cholesterol (I) when warmed (65°) briefly (3 min.) with 1 : 1 (vol.) H_2O–H_2SO_4 affords *a*- (II), m.p. 344° (block), 240—265° (decomp.) (tube) (lit. 240°; 260° after sintering at 210—220°), $[\alpha]_D^{23}$ +96·85° in CCl_4, and *c*- (III), m.p. 200° (block), 144—172° (decomp.) (tube) (lit. 127°), $[\alpha]_D^{23}$ +34·5° in CCl_4, but no *b*-cholesterylene. (I) with Br–$CHCl_3$ and (II) with Br–AcOH–Et_2O yield bromides, m.p. 245° (block) and 235° (block), respectively, with evolution of HBr. (II) is also formed from (I), cholesterylene (IV), cholesteryl acetate, and cholesterol Bu ether, but not from cholestene, cholesteryl chloride, and dicholesteryl ether (V), with AcOH–H_2SO_4 at 85—90°. (II) may be related to *i*-cholesterol, from which it is obtained [but not from (I)] by Ac_2O–H_2SO_4 at 85—90°. Other conditions for the prep. of (II) are given. A detailed review of the literature is given and it is suggested that $\Delta^{2:4}$-cholestadiene, (II), (III), (IV), and (V) should be regarded as different dehydration products of (I). J. L. D.

Synthesis of derivatives of chrysene. W. E. Bachmann and W. S. Struve (J. Org. Chem., 1939, **4**, 456—463; cf. A., 1936, 1380).—Clemmensen reduction of β-2-phenanthroylbutyric acid leads to γ-2-*phenanthryl*-β-*methylbutyric acid*, m.p. 127·5—129°, cyclised by $SOCl_2$ in Et_2O containing a little C_5H_5N followed by $SnCl_4$ in dry C_6H_6 at 0° to 6-*keto*-4-*methyl*-3 : 4 : 5 : 6-*tetrahydrochrysene*, m.p. 141—142°, which is reduced to 4-*methyl*-3 : 4 : 5 : 6-*tetrahydrochrysene*, thin leaflets or thin prisms, m.p. 141·5—142° (*hemipicrate*, $2C_{19}H_{18},C_6H_3O_7N_3$, m.p. 145·5—146°); this is dehydrogenated by Pd–C at 300—320° to 4-*methylchrysene*, m.p. 229—230° (corr.) (rather unstable *picrate*, m.p. 143—146°). 2-n-*Propylphenanthrene*, obtained by reduction of the propionyl derivative, has m.p. 35—36° (*picrate*, m.p. 92—93°). Non-cryst. 3-n-*propylphenanthrene* and its *picrate*, m.p. 107—108°, are described. β-2-9 : 10-Dihydrophenanthroyl-propionic acid, Zn–Hg, AcOH, conc. HCl, and PhMe yield γ-2-9 : 10-dihydrophenanthrylbutyric acid, m.p. 91—92°, which is esterified with MeOH, dehydrogenated by Pd–C at 240—260°, and then hydrolysed to γ-2-phenanthrylbutyric acid, m.p. 133—134°. This is cyclised to 6-keto-3 : 4 : 5 : 6-tetrahydrochrysene (I), m.p. 125—126°, which is transformed by MgMeI in Et_2O–C_6H_6 into 6-*hydroxy*-6-*methyl*-3 : 4 : 5 : 6-*tetrahydrochrysene*, m.p. 124—125°, converted by Pd–C at 300—320° into 6-*methylchrysene*, m.p. 151—151·2° (corr.) (*picrate*, m.p. 134—135°). $Al(OPr^{\beta})_3$ reduces (I) to 6-*hydroxy*-3 : 4 : 5 : 6-*tetrahydrochrysene* (II), m.p. 160—162°, which yields a *Me ether*, m.p. 79—80·5°, and an *acetate*, m.p. 119—120·5°. Dry HCl transforms (II) suspended in dry C_6H_6 containing $CaCl_2$ at room temp. into 6-*chloro*-3 : 4 : 5 : 6-*tetrahydrochrysene*, m.p. 115—117° (decomp.) and, after re-solidification, m.p. 174—178°, which is transformed by boiling C_5H_5N into 3 : 4-*dihydrochrysene* (III), m.p. 182·5—184·5° (*picrate*, m.p. 155—156°). (I) is reduced (Clemmensen) to 3 : 4 : 5 : 6-*tetrahydrochrysene*, m.p. 180·5—181·5° (*picrate*, m.p. 134—135·5°), which, like (III), is dehydrogenated by Pd–C in N_2 at 300—320° to chrysene. H. W.

Reactions of tetrahydrophenanthrene. Synthesis of triphenylene and methyltriphenylene. W. E. Bachmann and W. S. Struve (J. Org. Chem., 1939, **4**, 472—479).—$C_{10}H_8$, $(\cdot CH_2\cdot CO)_2O$, and $AlCl_3$ in $PhNO_2$ give a mixture of β-1- and -2-naphthoylpropionic acid which is reduced (Clemmensen) and then cyclised by $SOCl_2$ in abs. Et_2O containing a little C_5H_5N followed by $SnCl_4$ in C_6H_6 at 0° to 1- and 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene, which are

converted (Clemmensen) into 1 : 2 : 3 : 4-tetrahydrophenanthrene (I), m.p. 32·5—33·5°. AcCl, (I), and $AlCl_3$ afford 9-*acetyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II), m.p. 56·5—58°, dehydrogenated by S at 210—220° to 9-acetylphenanthrene. Addition of 1-$C_{10}H_7Et$ to a solution of $(\cdot CH_2\cdot CO)_2O$ and $AlCl_3$ in $PhNO_2$ at 0° gives β-4-*ethyl*-1-*naphthoylpropionic acid*, m.p. 129·5—131°, reduced by Zn–Hg, AcOH, and conc. HCl in presence of PhMe to γ-4-*ethyl*-1-*naphthylbutyric acid*, m.p. 115—116·5°. This is cyclised to 1-*keto*-9-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 52—53°, which is reduced (Clemmensen) to 9-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 23—25° (*picrate*, m.p. 125·5—126·5°), also obtained similarly from (II); it is dehydrogenated (Pd–C at 300—320°) to 9-ethylphenanthrene, m.p. 63·5—64·5° (picrate, m.p. 120·5—122·5°). (II) is converted by Br in well-cooled Et_2O into 9-*bromoacetyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 90·5—91·5°; this is condensed with $CHNa(CO_2Et)_2$ in C_6H_6 and the product is hydrolysed and then decarboxylated to β-9-1 : 2 : 3 : 4-*tetrahydrophenanthroylpropionic acid*, m.p. 167·5—169°, also obtained from (I), $(\cdot CH_2\cdot CO)_2O$, and $AlCl_3$ in $PhNO_2$. This is reduced to γ-9-1 : 2 : 3 : 4-*tetrahydrophenanthrylbutyric acid* (III), m.p. 133—134°, the Me ester of which is dehydrogenated (Pd–C at 250—270°) and then hydrolysed to γ-9-phenanthrylbutyric acid, m.p. 171—172°. (III) is cyclised to 1-*keto*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrotriphenylene* (IV), m.p. 121—122°, whence 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrotriphenylene*, m.p. 120·5—122° (*picrate*, m.p. 193—195°), which is dehydrogenated (Pd–C at 300—320°) to triphenylene, m.p. 196·5—197·5°. MgMeI and (IV) in Et_2O–C_6H_6 yield 1-*hydroxy*-1-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrotriphenylene*, m.p. 104—105°, dehydrated and dehydrogenated (Pd–C at 300—320°) to 1-*methyltriphenylene*, m.p. 93—94° (*picrate*, m.p. 172·5—174°). H. W.


(IV.)

Methyl homologues of triphenylene. L. F. Fieser and L. M. Joshel (J. Amer. Chem. Soc., 1939, **61**, 2958—2961).—γ-Keto-γ-9-phenanthryl-*n*-butyric acid [prep. from Mg 9-phenanthryl bromide (I) and $(\cdot CH_2\cdot CO)_2O$ improved to give a 45% yield], m.p. 179·5—180·5° (Me ester, new m.p. 88·6—89·4°, does not condense with MgMeCl or MgMeI), and Zn–Hg–PhMe–HCl give γ-9-phenanthryl-*n*-butyric acid (79%), m.p. 172·8—174°, cyclised by anhyd. HF at 0° to 87% of 1-keto-1 : 2 : 3 : 4-tetrahydrotriphenylene, m.p. 97—99°. With MgMeCl this gives a carbinol, which by dehydration by I at 200—220° and subsequent heating with S at 230° and then at 230—250° gives 1-*methyltriphenylene* (42·5%), m.p. 93·4—94·2° (*picrate*, m.p. 177·2—178·2°). With methylsuccinic anhydride, (I) yields similarly γ-*keto*-γ-9-*phenanthryl*-α-*methyl*-n-*butyric acid* (33%), m.p. 155—156° (structure proved by conversion by Br–$CHCl_3$, followed by NaOH–EtOH–H_2O, into 9-acetophenanthrene), γ-9-*phenanthryl*-α-*methyl*-n-*butyric acid*, m.p. 136·6—137·4°, and 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrotriphenylene* (II), m.p. 85—86·5°. Zn–Hg–PhMe–HCl and (II) give 2-*methyl*-1 : 2 : 3 : 4-*tetrahydrotriphenylene*, m.p. 116·2—116·8°, converted by Pd–C–N_2 at 215—230° and then at 310° into 2-*methyltriphenylene*, m.p. 102·6—103·6° (*picrate*, m.p. 192·4—193°), which is also obtained directly from (II) by Pd–C–N_2 at 300—310°. With MgMeCl in C_6H_6–Et_2O, (II) gives a crude carbinol, converted by Pd–C at 290—315° into 1 : 2-*dimethyltriphenylene*, m.p. 86·8—87·4° (*picrate*, m.p. 154—155°). OMe·CH_2·CN and (I) in boiling C_6H_6 give 9-*phenanthryl methoxymethyl ketone*, m.p. 67·2—68°, b.p. 220—225°/3 mm., converted by MgMeCl in C_6H_6 at room temp. into α-9-*phenanthryl*-β-*methoxy*isopropyl *alcohol*, m.p. <0°, b.p. 192—195°/1 mm. $KHSO_4$ at 180° then yields α-9-*phenanthrylpropaldehyde*, m.p. 65·5—67·6°, which with $CH_2(CO_2H)_2$ and a little piperidine in C_5H_5N at 100° gives γ-9-*phenanthryl*-Δ^{α}-*pentenoic acid*, m.p. 178·8—179·4° (softens at 173°), hydrogenated (PtO_2; AcOH) to γ-9-*phenanthryl*-n-*valeric acid*, m.p. 83—85°. This is cyclised by HF at room temp. to 1-*keto*-4-*methyl*-1 : 2 : 3 : 4-*tetrahydrotriphenylene* (82%), m.p. 99—100·5°, which affords (Grignard reaction; I; S) 1 : 4-*dimethyltriphenylene* (35%), m.p. 108·4—109·2° (*picrate*, m.p. 148·4—149·4°). M.p. are corr. R. S. C.

Syntheses of picene. N. L. Drake and W. C. McVey (J. Org. Chem., 1939, **4**, 464—471).—$C_{10}H_8$ and $(\cdot CH_2\cdot CO)_2O$ are condensed to a mixture of β-1- and -2-naphthoylpropionic acids, the separation of which is described. γ-1-Naphthylbutyric acid in C_6H_6 is converted by successive treatments with PCl_5 and $AlCl_3$ into 1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (I), b.p. 145—150°/1 mm., m.p. 95—96° [2 : 4-*dinitrophenylhydrazone*, m.p. 283—285° (decomp.)]. *o*- and *p*-C_6H_4Me·MgBr and $(CH_2)_2O$ yield β-o-, b.p. 99—105°/1 mm. (3 : 5-*dinitrobenzoate*, m.p. 126—128°), and β-p-*tolylethyl alcohol*, b.p. 100—106°/1 mm., 235°/atm. pressure (3 : 5-*dinitrobenzoate*, m.p. 147—149°), respectively, converted by $SOCl_2$ and $NPhMe_2$ into the respective *chlorides*, b.p. 80—84°/1 mm., 223°/atm. pressure, and b.p. 81—85°/1 mm., 222°/atm. pressure. $CH_2Ph\cdot CH_2\cdot MgBr$ and (I) in Et_2O–C_6H_6 (1 : 1) afford 1-*phenylethyl*-3 : 4-*dihydrophenanthrene* (II), b.p. 185—187°/0·5—1 mm., m.p. 62—63° [additive *compound*, m.p. 91—92°, with *s*-$C_6H_3(NO_2)_3$]. Similarly prepared are 1-β-o- (III), b.p. 190—195°/0·5—1 mm. [additive *compound*, m.p. 101·5—102·5°, with *s*-$C_6H_3(NO_2)_3$], and 1-β-p- (IV), b.p. 200—205°/0·5—1 mm., m.p. 79·5—81° (*picrate*, m.p. 101—102°), -*tolylethyl*-3 : 4-*dihydrophenanthrene*. (II) is dehydrogenated by Pd–C at 270—320° to 1-*phenylethylphenanthrene*, m.p. 86·5—89·5° [additive *compound* (1 : 2), m.p. 149—151° with *s*-$C_6H_3(NO_2)_3$], which yields only tarry material from which picene (V) cannot be extracted when cyclisation is attempted with $AlCl_3$ in CS_2 at the b.p. or at a lower temp. Cyclisation of (II) by $AlCl_3$ in CS_2 at 0—5° gives a pasty product which does not give a compound with 2 : 4 : 6-$C_6H_2(NO_2)_3$·OH or *s*-$C_6H_3(NO_2)_2$; it is dehydrogenated by Pd–C at 390—400° to 1% of (V), m.p. 367—368·5°, which is also obtained by a similar procedure from (III). (IV) could not be converted into (V). H. W.

Synthesis of rubicene from fluorenone, using metallic calcium. V. I. Chmelevski and G. I. Fedorov (J. Gen. Chem. Russ., 1939, **9**, 1423—

1425).—Fluorenone and Ca when heated give rubicene in 13% yield. 9 : 10-Diphenylanthracene is obtained analogously from $COPh_2$ (20% yield). R. T.

Hydroxy-derivatives of diphenylethylamine. A. Lespagnol, J. Turlur, and L. Lespagnol (Bull. Sci. Pharmacol., 1939, **41**, 305—311).—$CH_2Ph{\cdot}CO_2H$, *o*-$C_6H_4(OH)_2$, and $ZnCl_2$ at 150° yield 3 : 4-dihydroxydeoxybenzoin, the *oxime*, m.p. 83°, of which is reduced (Na–Hg, EtOH–AcOH) to β-phenyl-α-3 : 4-dihydroxyphenylethylamine, m.p. 135° (*hydrochloride*, m.p. 186°). The *oxime*, m.p. 121—122°, of 4′-hydroxydeoxybenzoin (I) similarly yields α-*phenyl*-β-p-*hydroxyphenylethylamine*, m.p. 159°. 4-Nitrobenzil is reduced (Sn, aq. EtOH–HCl) to 4′-aminodeoxybenzoin [*hydrochloride*, m.p. 265° (decomp.)], converted (diazomethod) into (I). R. T.

Kinetics of reaction of *o*-chloronitrobenzene with aqueous ammonia.—See A., 1939, I, 616.

Alkanolamines. VII. Condensation products of monoethanolamine and the isomeric dichloronitrobenzenes. C. B. Kremer and A. Bendich (J. Amer. Chem. Soc., 1939, **61**, 2658—2661; cf. A., 1939, II, 366).—Nitration of 2 : 4 : 1-$C_6H_3Cl_2{\cdot}NH_2$ gives at best very poor yields. *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ and HCl–$KClO_3$ at 70° give varying amounts of 4 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}NH_2$ and 4 : 2 : 6 : 1-$NO_2{\cdot}C_6H_2Cl_2{\cdot}NH_2$, the latter product being converted by a diazo-reaction into 3 : 5 : 1-$C_6H_3Cl_2{\cdot}NO_2$, m.p. 65°. Sn–HCl then gives 3 : 5 : 1-$C_6H_3Cl_2{\cdot}NH_2$, m.p. 51°, the Ac derivative, m.p. 186°, of which with HNO_3 (*d* 1·51) yields 4 : 3 : 5 : 1- (I), m.p. 222°, and 2 : 3 : 5 : 1-$NO_2{\cdot}C_6H_2Cl_2{\cdot}NHAc$ (II), m.p. 138°. Hydrolysis (conc. H_2SO_4 at 110°) and a subsequent diazo-reaction convert (I) into 2 : 6 : 1-$C_6H_3Cl_2{\cdot}NO_2$, m.p. 70·5°, b.p. 100—101°/4—5 mm., and (II) into 2 : 4 : 1-$C_6H_3Cl_2{\cdot}NO_2$, m.p. 34°, b.p. 105—107°/3—4 mm. *m*-$NO_2{\cdot}C_6H_4{\cdot}NHAc$ and HNO_3 (*d* 1·5) at 20° give (mainly) 2 : 3 : 1-$(NO_2)_2C_6H_3{\cdot}NHAc$, m.p. 186—187°, and thence (with H_2SO_4 at 110°) 2 : 3 : 1-$(NO_2)_2C_6H_3{\cdot}NH_2$, m.p. 127°, and (diazo-reaction) 1 : 2 : 3-$C_6H_3Cl_2{\cdot}NO_2$, m.p. 61°. Condensation of the appropriate $C_6H_3Cl_2{\cdot}NO_2$ in boiling BuOH with 2—3 mols. of $NH_2{\cdot}[CH_2]_2{\cdot}OH$ or slightly >1 mol. in presence of MgO (1 mol.) gives 6-, b.p. 155—157°/2 mm., 5-, m.p. 116° [also from 1 : 3 : 4-$C_6H_3Cl(NO_2)_2$], 4-, m.p. 107·5°, and 3-*chloro*-2-*nitro*-, m.p. 78·5°, and 6-*chloro*-4-*nitro*-N-β-*hydroxyethylaniline*, m.p. 120°, reduced by alkaline $Na_2S_2O_4$ to 6-, b.p. 135—137°/2 mm., 5-, m.p. 104·5°, 4-, m.p. 122·5°, and 3-*chloro*-2-*amino*-, m.p. 74°, and 6-*chloro*-4-*amino*-N-β-*hydroxyethylaniline*, decomp. 185°/1 mm. 2 : 6 : 1-$C_6H_3Cl_2{\cdot}NO_2$ is the least reactive isomeride. 2 : 5 : 1- is more reactive than 3 : 4 : 1-$C_6H_3Cl_2{\cdot}NO_2$. M.p. are corr. R. S. C.

Separated auxo-enoid systems. VII. Influence of a second auxo-group on the coloration of nitrobenzylarylamines. V. A. Izmailski and V. I. Stavrovskaja (J. Gen. Chem. Russ., 1939, **9**, 1007—1014).—*m*- or *p*-Substitution in the Ph of 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}CH_2{\cdot}NHPh$ has a bathochromic effect, the auxochromes being ·NH·C_6H_4R (R = *m*- or *p*-Me or -NHAc). The following compounds are described: 2 : 4-*dinitrobenzyl*-m-, m.p. 86°, and -*p*-toluidine, m.p. 101° (lit. 93°), -m-, m.p. 136°, and -p-*acetamidoaniline*, m.p. 131°. R. T.

[Condensation of] aromatic amines and 2-bromo-5 : ω-dinitrostyrene. D. E. Worrall and J. Finkel (J. Amer. Chem. Soc., 1939, **61**, 2969—2970).—*o*-$C_6H_4Br{\cdot}CHO$, $MeNO_2$, and NEt_3 at 25—30° give *o-bromo-ω-nitrostyrene* (I), m.p. 84°, which with fuming HNO_3 gives 2-*bromo*-5 : ω-*dinitrostyrene* (II), m.p. 144—145°, oxidised by $KMnO_4$ to 5 : 2 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}CO_2H$. The corresponding chlorodinitro-compound was previously (A., 1939, II, 57) wrongly named. With Br, followed by warm KOAc–EtOH, (II) gives 2 : ω-*dibromo*-5 : ω-*dinitrostyrene* (III), m.p. 146—147° (corresponding ω-chloro-2-bromo-compound, m.p. 140—141°). By adding the appropriate amine in hot EtOH, (II) gives α-*nitro*-β-o-, m.p. 108—109°, -m-, m.p. 103—104°, and -p-*toluidino*-, m.p. 132—133°, -o-, m.p. 139—140°, -m-, m.p. 159—160° (?), and -p-*anisidino*-, m.p. 105—106°, -p-*phenetidino*-, m.p. 134—135°, -p-*dimethylaminoanilino*-, m.p. 140—141°, and -*phenylhydrazino*-β-2-*bromo*-5-*nitrophenylethane*, m.p. 147—148°, and NN′-*di*-(β-*nitro*-α-2-*bromo*-5-*nitrophenylethyl*)-*amine*, m.p. 146—147°, -p-*phenylenediamine*, and -*benzidine*, m.p. indefinite. Similarly, (I) gives NN′-*di*-(β-*nitro*-α-o-*bromophenylethyl*)-p-*phenylenediamine*, m.p. 146—147°, and (III) gives a similar product, m.p. indefinite.
p-$C_6H_4Me{\cdot}NH_2$ adds to (III), yielding a product, m.p. 103—104°. R. S. C.

Structure of naphthalene, hydrindene, and tetrahydronaphthalene derivatives. R. B. Sandin and T. H. Evans (J. Amer. Chem. Soc., 1939, **61**, 2916—2919).—Fixation of ethylenic linkings in aromatic compounds may be judged by the relative lability of Br (replacement by H on treatment with $SnCl_2$–HCl) in bromo-hydroxy- and -amino-derivatives, lability being caused by separation of the Br from OH or NH_2 by an ethylenic linking or a conjugated system. Results with 1 : 2-, 4 : 1-, and 3 : 2-$C_{10}H_6Br{\cdot}NH_2$ and 1 : 3 : 2-$C_{10}H_5Br_2{\cdot}NH_2$ indicate stability of the Erlenmeyer system, which is also borne out by the results of Franzen *et al.* (A., 1920, i, 730; 1922, i, 450). Results with 4 : 6-dibromo-5-amino- (I) and 4-*bromo*-5-*amino-hydrindene* [prep. from (I) by $SnCl_2$–HCl], m.p. 54—55°, favour the Mills–Nixon formula. Br is removed fairly readily from 5-bromo-6-amino-1 : 2 : 3 : 4-tetrahydronaphthalene. Fairly ready removal of Br from *o*-$C_6H_4Br{\cdot}NH_2$ favours existence of both Kékulé or resonating forms. R. S. C.

Steric nature of the *ortho* effect in the hydrogen exchange reactions of aromatic tertiary amines.—See A., 1939, I, 617.

Cleavage of quaternary ammonium salts by sodium sulphide. II. H. R. Snyder and J. C. Speck (J. Amer. Chem. Soc., 1939, **61**, 2895—2897; cf. A., 1939, II, 207).—$CH_2Ph{\cdot}NR_3Cl$ are decomposed by Na_2S most readily if the N carries or is part of an aromatic ring, but even more stable salts decompose at higher temp. With hot, aq. Na_2S, $CH_2Ph{\cdot}NMe_3Br$, $NPhMe_3I$, and $NBu^a{}_4I$ are unaffected; cyclo*hexylbenzyldiethylammonium chloride*, m.p. 179° (decomp.), is only slightly affected, $(CH_2Ph)_2NEt_2I$ gives only 3% of $(CH_2Ph)_2S$ (I) in 3 hr., and benzylpyridinium

chloride gives 65% of C_5H_5N and 69% of (I). $CH_2Ph{\cdot}NMe_3Br$ with $Na_2S,9H_2O$ in $(OH{\cdot}[CH_2]_2)_2O$ at 135—150° gives 54% of NMe_3 and 47% of (I). NBu^a_4I at 175° similarly gives 70% of NBu^a_3. *Phenyltrimethylallylammonium bromide*, hygroscopic, and aq. Na_2S give 41% of $NPhMe_2$ and 44% of $(CH_2{:}CH{\cdot}CH_2)_2S$. $CH_2Ph{\cdot}NPhMe_2Cl$ and boiling, aq. $Na_2S_2O_4$ give 58% of $NPhMe_2$ and 60% of $CH_2Ph{\cdot}S{\cdot}SO_3NPhMe_2{\cdot}CH_2Ph$, possibly owing to prior hydrolysis of the $Na_2S_2O_4$ to $Na_2S_2O_3$ and $NaHSO_3$.

R. S. C.

Preparation of sulphanilamide. O. Baine (J. Chem. Educ., 1939, **16**, 278).—The reactions involved in the synthesis of the amide from NH_2Ph are discussed. The prep. is suitable as a laboratory experiment.

L. S. T.

Purification of *p*-acetamidobenzenesulphonyl chloride. L. H. Pence and H. C. Winter (J. Amer. Chem. Soc., 1939, **61**, 2977—2978).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ (70) (stable if pure), from NHPhAc (67·5) and $ClSO_3H$ (290 g.), is obtained pure by suitable crystallisation from $Et_2O + C_6H_6$.

R. S. C.

Sulphanilamide derivatives. IV. N^1N^4-Diacyl- and N^1-acyl-sulphanilamides. M. L. Crossley, E. H. Northey, and M. E. Hultquist (J. Amer. Chem. Soc., 1939, **61**, 2950—2955; cf. A., 1938, II, 439).—N^1-Acylsulphanilamides are prepared, usually best by condensing *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (I) with RCOCl in C_5H_5N at 100—110° (less well in boiling PhMe etc.) and hydrolysing the diacyl derivative by boiling with a slight excess of aq. NaOH. Alternatively, (I) is heated with $(RCO)_2O$ at 70—80° or the Na derivative of (I) is heated with RCOCl in dioxan or C_5H_5N. The following are described. N^1N^4-Diacetylsulphanilamide, new m.p. 253·5—255°; N^4-*acetyl*-N^1-*propionyl*-, m.p. 242·5—244·3°, -n-, m.p. 238·2—240°, and -iso-*butyryl*-, m.p. 247—248°, -iso-*valeryl*-, m.p. 215—217·5°, -β-*ethylbutyryl*-, m.p. 270—272°, -*hexoyl*-, m.p. 191—193°, -*heptoyl*-, m.p. 205—207·5°, -β-*ethylhexoyl*-, m.p. 214—215·6° (*Na* and *Mg* salts), -*octoyl*-, m.p. 195—197·6°, -*decoyl*-, m.p. 143·2—144·8°, -*undecoyl*-, m.p. 153·2—155°, -*dodecoyl*-, m.p. 130—136°, -*tetradecoyl*-, m.p. 144·2—145°, -Δ⁴-*octadecenoyl*-, m.p. 131—135°, -*chaulmoogryl*-, -*benzoyl*-, m.p. 280—285°, -*hexahydrobenzoyl*-, m.p. 210—222°, -p-*nitrobenzoyl*-, m.p. 270—272°, -p-*aminobenzoyl*-, m.p. 260—263°, -β-*phenylpropionyl*-, m.p. 202·8—205·4° (sinters at 160°), -*cinnamoyl*-, m.p. 228—229·5°, -*diphenylacetyl*-, m.p. 248·5—251°, -2′-*furoyl*-, m.p. 240·5—241·5°, -2′-*phenylcinchoninyl*-, m.p. 166—170°, and -*nicotinyl*-, m.p. 295—300°, -*sulphanilamide*; N^1N^4-*didodecoylsulphanilamide*, m.p. 144—145°; N^4-p-*acetamidobenzenesulphonyl*-, m.p. 150—152° (sinters at 120°), and N^4-*sulphanilyl*-, m.p. 102—104°, -N^1-*dodecoylsulphanilamide*; N^1-acetyl-, m.p. 182—184° (Na, $+H_2O$, NH_4, and NH_2Et_2 salts), -*propionyl*-, m.p. 134—135°, -n-, m.p. 125·4—126·6°, and -iso-*butyryl*-, m.p. 198·5—200°, -β-*ethylbutyryl*-, m.p. 189—193·5°, -*hexoyl*-, m.p. 129·2—129·9°, -*heptoyl*-, m.p. 121·8—123·6°, -β-*ethylhexoyl*-, m.p. 165·5—168°, -*octoyl*-, m.p. 101—103°, -*decoyl*-, m.p. 119—121°, -*undecoyl*-, dimorphic, m.p. 112·5—114·5° and 115°, -*dodecoyl*- (II), m.p. 127—128·5° (*Ag*, Hg^{II}, and *Ca* salts), -*tetradecoyl*-, m.p. 113·5—117·7°, -*octadecoyl*- (crude), m.p. 98—102°, -Δ⁴-*octadecenoyl*-, amorphous, -*hexahydrobenzoyl*-, m.p. 198·5—200°, -*chaulmoogryl*-, m.p. 97·9—99°, -*benzoyl*-, m.p. 181·2—182·3°, -p-*nitrobenzoyl*-, m.p. 235—240°, -p-*aminobenzoyl*-, m.p. 197·8—199°, -β-*phenylpropionyl*-, m.p. 160·3—161·5°, -*cinnamoyl*-, *forms*, (*a*), m.p. 174—175°, and (*b*), m.p. 145° (immediate; resolidifies) (sinters at 130°), -p-*carboxybenzoyl*-, m.p. >225° (decomp.), -*mandelyl*-, m.p. 192·5—194·5° (decomp.), -*diphenylacetyl*-, m.p. 210·5—212°, -2′-*furoyl*-, m.p. 191·5—192°, -2′-*phenylcinchoninyl*-, m.p. 305—310°, -*nicotinyl*-, m.p. 256—257·5°, and -3′-*hydroxy*-2′-*naphthoyl*-, m.p. 245—250°, -*sulphanilamide*. Acylation of the appropriate nitrobenzenesulphonamide and subsequent reduction by Fe–AcOH yields N^1-*acetyl*-, m.p. 153·5—155°, and -*tetradecoyl*-*metanilamide*, m.p. 113·5—114·2°, and N^1-*dodecylsulphanilmethylamide*, m.p. 59·3—60·5°. The long-chain amides are sol. in fats and their absorption after oral administration is accelerated by feeding fats. (II) is at least as effective as *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ against various β-hæmolytic streptococci in mice and very effective in preventing spread of mycobacterium tuberculosis in guinea-pigs.

R. S. C.

Para- and dia-magnetic tetramminonickel salts of phenylethylenediamines.—See A., 1939, I, 624.

Colour and dyeing properties of alkyl, alkoxy-, and aryloxy-derivatives of aminoazobenzene. J. C. Earl and A. O. Robson (J. Proc. Austral. Chem. Inst., 1939, **6**, 268—278).—By coupling diazotised NH_2R with NH_2R', the following are prepared: 4-*dimethylamino*-2′-*methyl*-, m.p. 67—68° (all m.p. corr.), and -2 : 2′-*dimethyl*-, m.p. 79—80°, 3 : 2′-*dinitro*-4-*amino*-, m.p. 199—200°, and 4-*amino*-2 : 3′-*dimethoxy*-, m.p. 165—166° (from *m*-$OMe{\cdot}C_6H_4{\cdot}NH_2$ diazotised by $NaNO_2$–AcOH in presence of $K_2C_2O_4$ and saponin), -2-*phenoxy*-, m.p. 129—130°, and -2-*methoxy*-*azobenzene*, m.p. 160—161°. The extinction coeffs. (λ of heads of bands recorded) and dyeing properties of these and 6 other aminoazo-compounds show that a 2-substituent in the 4-NH_2-ring has the most pronounced effect and causes colour-deepening in the order OMe > Me > OPh; NO_2 or Cl in this position has a lightening effect. Diazotised NH_2Ph and (?) *m*-$NH_2{\cdot}C_6H_4{\cdot}O{\cdot}C_{10}H_7$ give a *compound*, m.p. 90—91°, which is not 4-amino-2-naphthoxyazobenzene.

E. W. W.

Alleged isomerism of α- and β-*p*-azophenol. W. M. Lauer, H. P. Klug, and S. A. Harrison (J. Amer. Chem. Soc., 1939, **61**, 2775—2779).—The α- and β-forms of *p*-azophenol (I) are shown by *X*-ray powder photographs, ebullioscopy, and polarographic analysis to be identical and not *cis*–*trans*-isomerides (cf. Willstätter *et al.*, A., 1907, i, 566). Only one set of derivatives could be prepared, viz., $(NO_2)_2$- (prep. by conc. HNO_3–AcOH at 0°), m.p. 235—236°, $(NO_2)_4$- (prep. by fuming HNO_3–AcOH at <0°), m.p. 261—262° (decomp.), Br_4-, m.p. 273—274° (*diacetate*, m.p. 263—264°; *dibenzoate*, m.p. 297—298°), and dibromodinitro-derivative, m.p. 281—282°. (I) exists in hydrated and green and red anhyd. forms.

R. S. C.

Diazo-chemistry. H. H. Hodgson (Rec. trav. chim., 1939, **58**, 928—930).—Controversial with Schoutissen (A., 1939, II, 209). A. T. P.

Preparation of diazo-compounds through the agency of organo-metallic derivatives. L. G. Markova and A. N. Nesmejanov (J. Gen. Chem. Russ., 1939, **9**, 771—779).—The action of $NO–N_2O_3$ on aromatic organo-metallic compounds leads to the formation of diazonium nitrates: $2N_2O_3 \rightarrow N_2O_4 + 2NO$; $MPh_2 + 2N_2O_4 \rightarrow 2PhNO + M(NO_3)_2$; $PhNO + 2NO \rightarrow PhN_2{\cdot}NO_3$. The following were studied (yield of diazonium nitrate in parentheses): $HgPh_2$ (85%); HgPh·OAc (quant.); $SnPh_4$ (40%); $SnPh_3Cl$ (48%); $SnPh_2Cl_2$ (49%); $SnPhCl_3$ (80%); $PbPh_4$ (quant.); $PbPh_3Cl$ (50%); $BiPh_3$ (54%); $TiPh_2Cl$ (8%); MgPhBr (15%). The yields were considerably reduced by using only N_2O_3. The diazonium salt was not obtained using LiPh, $AsPh_3$, $SbPh_3$, $PbPh_2Cl_2$, $SiPh_4$, and $ZnPh_2$. V. A. P.

Structure of diazoamino-salts. F. P. Dwyer (J. Proc. Austral. Chem. Inst., 1939, **6**, 348—361).—The theory advanced by Mangini *et al.* (A., 1934, 68; 1935, 969) to account for highly coloured forms of metal salts of diazoamino-compounds is untenable, since such forms are actually derived from diazoamino-azo-compounds either present in the starting materials or formed (*e.g.*, under the influence of acid) during the prep. of the salts. Details are given for the prep. of the K and Hg^{II} salts of diazoaminobenzene (I), the Ag salt of 3-nitro- and the Ag (II) and Hg^{II} salts of 4-nitro-diazoaminobenzene. These salts exist in one (yellow) form; (II) dissolves in C_5H_5N to a red solution (see following abstract). The *Hg*^{II} salt of diazoaminoazobenzene and the *Ag* salts of 3- and 4-nitrobenzenediazoaminoazobenzene are all red (varying shades). 2 : 2′-Dinitrodiazoaminobenzene (in $COMe_2$) with C_5H_5N–MeOH–$AgNO_3$ + NaOAc gives a red (aci) *Ag* salt (+ C_5H_5N), which loses C_5H_5N at 100°/2 hr. and yields the yellow (triazen) *Ag* salt. 3 : 3′-Dinitrodiazoaminobenzene similarly affords only a yellow Ag salt, sol. in hot C_5H_5N to an orange-yellow solution. The above and previous results (A., 1938, II, 483; 1939, II, 152) show that pure (I) and its (nuclear) Me derivatives give no colour with EtOH–alkali and yield only yellow salts. Diazoamino-compounds with *o*- or *p*-NO_2 give intense colours with alkali and are strongly adsorbed on $Mg(OH)_2$ with formation of brilliantly coloured lakes; *m*-NO_2-compounds similarly give an orange colour and are only feebly adsorbed. In all cases, methylation of the labile H causes loss of salt-forming properties. Structures for the different types of salts are elaborated (cf. *loc. cit.*). H. B.

Isomerism of diazoamino-salts. F. P. Dwyer (J. Proc. Austral. Chem. Inst., 1939, **6**, 362—368).—3 : 4′-Dinitrodiazoaminobenzene (I), m.p. 225—226° [obtained in small yield from carefully neutralised *m*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ in $COMe_2$–EtOH–NaOAc (large excess)], is dissolved in EtOH–NaOH and added to C_5H_5N–MeOH–$AgNO_3$ + NaOAc at 20°; the pptd. salt (II) dissolves in hot C_5H_5N to a deep red solution from which EtOH ppts. the pure, yellow (triazen) *Ag* salt (III). Suitable crystallisation from C_5H_5N at <−5° to −2° affords the scarlet (aci) *Ag* salt (+C_5H_5N) (IV), which when freed from C_5H_5N (at 100° or in boiling $COMe_2$) affords a yellow

(IV.) *m*-$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}N$·····Ag<·····$C_5H_5N$
p-$C_6H_4{:}N$—>O

salt [= (III)] which is a mixture of the two possible isomerides since this with MeI–$COMe_2$ gives a mixture (*A*), m.p. 153—157° (shrinks at 145—146°), of *m*-$NO_2{\cdot}C_6H_4{\cdot}NMe{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2$-*p* and *m*-$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NMe{\cdot}C_6H_4{\cdot}NO_2$-*p*. (*A*) is also similarly obtained from (I), (II), or (III). Suitable treatment with, and crystallisation from, cold C_5H_5N also affords a scarlet *salt* (+C_5H_5N) from the yellow Ag salt (V) of 4-nitrodiazoaminobenzene (preceding abstract). Removal of C_5H_5N [as for (IV)] and subsequent methylation show that (V) is a mixture of isomerides since a mixture (*B*), m.p. 94—95°, of *p*-$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NPhMe$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}NMe{\cdot}N{:}NPh$ is obtained. Proof of the mixture (*B*) is afforded by hydrolysis with conc. HCl–CuCl at room temp. whereby PhCl, *p*-$C_6H_4Cl{\cdot}NO_2$, *p*-$NO_2{\cdot}C_6H_4{\cdot}NHMe$, and NHPhMe are obtained. H. B.

Mechanism of halogenation of phenols. E. A. Schilov (J. Gen. Chem. Russ., 1939, **9**, 780—781).—Polemical (cf. A., 1938, II, 405). V. A. P.

Reaction between diphenylketen and phenylacetylene. L. I. Smith and H. H. Hoehn (J. Amer. Chem. Soc., 1939, **61**, 2619—2624).—Contrary to Staudinger (Annalen, 1907, **356**, 94), $CPh{:}CH$ adds $CPh_2{:}CO$ at room temp., giving 3 : 4-*diphenyl*-α-*naphthol* (I), dimorphic, m.p. 143—144° and 154° [positive Folin reaction; 1 active H; *acetate*, m.p. 162—162·5°; *Me ether*, m.p. 203—203·5° (2-NO_2-derivative, m.p. 202°)], but in light petroleum reaction is much slower. (I) is sol. in KOH–MeOH and unstable in air. $Pb(OAc)_4$ in AcOH oxidises (I) to 3 : 4-*diphenyl*-1 : 2-*naphthaquinone* (II), m.p. 249—250° (*phenazine* derivative, m.p. 274—275°), obtained also in poor yield as sole product by HNO_3–H_2SO_4–$CHCl_3$, but $K_2Cr_2O_7$–AcOH gives BzOH, *o*-$C_6H_4Bz{\cdot}CO_2H$, and a substance, m.p. 280—286°. Zn in AcOH–H_2O (10 : 1) or $Na_2S_2O_4$ reduces (II) to the quinol, which readily regenerates (II) in air, but Zn dust and NaOAc in Ac_2O give 1 : 2-*diacetoxy*-3 : 4-*diphenylnaphthalene*, m.p. 166—167°. With *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ and NaOAc in AcOH, (I) gives the red 2-azo-compound, reduced by alkaline $Na_2S_2O_4$ to an unstable amine, which is oxidised by $FeCl_3$ to (II). Br–Et_2O converts (I) into the 2-*Br*-derivative, m.p. 157—158° (*acetate*, m.p. 199—200°; *Me ether*, m.p. 209—210°), which with CrO_3–AcOH at 100° yields (II). Franssen's interpretation (A., 1925, i, 1146) of the reaction of 1 : 4-naphthaquinone and MgPhBr is incorrect; 5 mols. of MgPhBr in Et_2O give 1-*hydroxy*-4-*keto*-1 : 2-*diphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 207° (*oxime*, m.p. 196—197°), oxidised by $K_2Cr_2O_7$ in AcOH to (II), BzOH, and *o*-$C_6H_4Bz{\cdot}CO_2H$, dehydrated by a little H_2SO_4 in boiling AcOH to (I) or in boiling Ac_2O to the Ac derivative thereof. R. S. C.

α-**Nitro**-β-**naphthol.**—See A., 1939, I, 625.

Bromination of 2-hydroxyanthracene. J. S. Joffe, L. S. Efros, and C. N. Schtscheglova (J.

Gen. Chem. Russ., 1939, **9**, 1128—1132).—2-Acetoxyanthracene and Br in AcOH at room temp. yield 9-*bromo*-2-*acetoxyanthracene*, m.p. 110—112°, oxidised by $K_2Cr_2O_7$ in AcOH to 2-acetoxyanthraquinone, and hydrolysed (dil. NaOH) to 9-*bromo*-2-*hydroxyanthracene*, m.p. 112—114° (1-p-*nitrobenzeneazo*-derivative, m.p. 254°). Bromination of 2-hydroxyanthracene gives 2-hydroxy-1 : 1′ : 9 : 2′-dianthrylene oxide and 1 : 10-*dibromo*-2-*hydroxyanthracene*, m.p. 198—199°, which with p-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ gives 10-*bromo*-2-*hydroxy*-1-p-*nitrobenzeneazoanthracene*, m.p. 284°. Acetylation of the bromination product gives 1 : 10-, m.p. 198—199°, and 1 : 9-*dibromo*-2-*acetoxyanthracene*, m.p. 157—159°, both yielding 1-*bromo*-2-*acetoxyanthraquinone*, m.p. 174°, when oxidised ($K_2Cr_2O_7$ in AcOH). R. T.

αγ-Di-*p*-hydroxyphenylpropane, m.p. 104—105°. Diacenaphthylidene diketone, m.p. 285—286°.—See A., 1939, III, 982.

Diaryls and their derivatives. XXI. Oxidation of α-naphthol. J. S. Joffe and B. K. Kritschevtzov. **XXII. Diphenanthryl dioxide.** J. S. Joffe (J. Gen. Chem. Russ., 1939, **9**, 1136—1142, 1143—1144).—XXI. α-$C_{10}H_7{\cdot}OH$ and aq. $FeCl_3$ at 70—80° yield a mixture of 4 : 4′-*dihydroxy*-1 : 1′- (I), m.p. 300° (*Ac*$_2$, m.p. 217°, and 3-*mono*- and 3 : 3′-*di*-p-*nitrobenzeneazo*-derivatives), and 1 : 1′-*dihydroxy*-2 : 2′-*dinaphthyl* (II), m.p. 220° (*Ac*$_2$, m.p. 169°, and 4-*mono*- and 4 : 4′-*di*-p-*nitrobenzeneazo*-derivatives). (I) yields 3 : 10-dihydroxyperylene when heated with $AlCl_3$. (II) and $ZnCl_2$ similarly give 2 : 2′-dinaphthyl 1 : 1′-oxide.

XXII. 2 : 2′-Dihydroxy-1 : 1′-diphenanthryl and CuO in C_6H_6 (6 hr. at the b.p.) yield 1 : 1′-*diphenanthryl* 2 : 10′ : 10 : 2′-*dioxide*, m.p. 280°. R. T.

Use of tri-iodophenyl ethers for the identification of alkyl halides. R. D. Drew and J. M. Sturtevant (J. Amer. Chem. Soc., 1939, **61**, 2666).—Alkyl bromides are characterised by boiling with 2 : 4 : 6 : 1-$C_6H_2I_3{\cdot}OH$ and NaOEt–EtOH (cf. Brenans, A., 1901, i, 643), which give 2 : 4 : 6-$C_6H_2I_3$ *Pr*$^{\beta}$, m.p. 43°, Me, m.p. 98·5°, Et, m.p. 83·5°, Pr$^{\alpha}$, m.p. 82°, *Bu*$^{\alpha}$, m.p. 66°, *Bu*$^{\beta}$, m.p. 48°, n-*amyl*, m.p. 47°, n-*hexyl*, m.p. 44·5°, CH_2Ph, m.p. 122·5°, $[CH_2]_2{\cdot}Ph$, m.p. 88°, $[CH_2]_3{\cdot}Ph$, m.p. 63·5°, p-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}$, m.p. 207·5°, $[CH_2]_2{\cdot}OH$, m.p. 137·5°, $CH_2{\cdot}CO_2Et$, m.p. 124° (lit. 128·5°), and *CHMe·CO*$_2$*Et ether*, m.p. 80·5°. M.p. are corr. R. S. C.

Molecular compounds of α-naphthyl methyl ether with dinitro-compounds. S. I. Burmistrov (Trans. Ivanovo Chem. Tech. Inst., 1939, 14—17).—This ether forms equimol. *compounds* with m-$C_6H_4(NO_2)_2$ (m.p. 57·5°), 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ (m.p. 71°), 2 : 4-dinitrophenol (m.p. 96°), 2 : 4-dinitroanisole (m.p. 66°), 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ (m.p. 66·5°), and 3 : 5 : 4 : 1-$(NO_2)_2C_6H_2Cl{\cdot}CO_2H$ (m.p. 124°). R. C.

Condensation of diarylcarbinols with naphthyl ethers. S. I. Burmistrov (Trans. Ivanovo Chem. Tech. Inst., 1939, 17—20).—By condensation with $ZnCl_2$ in AcOH there have been obtained *diphenyl*-4-*methoxy*-1-*naphthylmethane*, m.p. 151°, *phenyl*-p-*xenyl*-4-*methoxy*-1-*naphthylmethane*, m.p. 155° (decomp.), *diphenyl*-4-*ethoxy*-1-*naphthylmethane*, m.p. 159·5°, *phenyl*-p-*tolyl*-4-*methoxy*-1-*naphthylmethane*, m.p. 132·5°, *phenyl*-4-*methoxy*-1-*naphthylmethane*, m.p. 161—162°, *di*-p-*xenyl*-4-*ethoxy*-1-*naphthylmethane*, m.p. 114—116°, and *phenyl*-p-*xenyl*-4-*ethoxy*-1-*naphthylmethane*, m.p. 163—165°. R. C.

Iodo-derivatives of diphenyl ether. II. Orientation. R. Q. Brewster and H. S. Choguill (J. Amer. Chem. Soc., 1939, **61**, 2702—2704; cf. A., 1934, 293).—Halogenation of *o*- (I) and *p*-$OPh{\cdot}C_6H_4{\cdot}OMe$ (II) occurs in position 4′ (if free), but nitration is guided by the OMe and is homonuclear. (II), obtained in 70% yield from KOPh and *p*-$C_6H_4Br{\cdot}OMe$ or in 20% yield from *p*-$OH{\cdot}C_6H_4{\cdot}OMe$ and PhBr, is converted by ICl in AcOH at 100° into 4-*iodo*-4′-*methoxydiphenyl ether* (III), m.p. 115°, which is also obtained from the 4-NH_2-derivative by the Sandmeyer reaction. $AlCl_3$, first at 130° and then at 140—150°, converts (II) into *p*-$OPh{\cdot}C_6H_4{\cdot}OH$, m.p. 84°, the *benzoate*, m.p. 97°, of which with ICl–AcOH at 100° gives 4-*iodo*-4′-*benzoyloxy*-, m.p. 122°, and thence (boiling NaOH–aq. EtOH) 4-*iodo*-4′-*hydroxy*-*diphenyl ether*, m.p. 116°. 4 : 3 : 1-$OMe{\cdot}C_6H_3(NO_2){\cdot}OPh$ (IV), prepared by HNO_3–AcOH in 70% yield, is quantitatively hydrogenated (PtO_2) to 3-*amino*-4-*methoxydiphenyl ether*, m.p. 70° (*Ac* derivative, m.p. 148°), which affords (diazo-reactions) 3-*iodo*- (V), m.p. 76°, and 3-*bromo*-4-*methoxydiphenyl ether* (VI), m.p. 55°, b.p. 182—187°/10 mm. ICl and Br convert (VI) and (III), respectively, in AcOH into 3-*bromo*-4′-*iodo*-4-*methoxydiphenyl ether*, m.p. 88°. ICl–AcOH converts (III) or (V) into 3 : 4′-*di*-*iodo*-4-*methoxydiphenyl ether* (VII), m.p. 101°. ICl–AcOH converts (IV) into 4′-*iodo*-3-*nitro*-4-*methoxydiphenyl ether*, m.p. 92°, obtained also from (III) by HNO_3 (*d* 1·42) in AcOH and reduced by Fe powder in AcOH to 4′-*iodo*-3-*amino*-4-*methoxydiphenyl ether*, m.p. 85° [gives (VII) by a diazo-reaction]. 2-*Nitro*-4′-*methoxydiphenyl ether* (VIII), m.p. 77°, is obtained in 70% yield from *o*-$C_6H_4Cl{\cdot}NO_2$ and *p*-$OH{\cdot}C_6H_4{\cdot}OMe$, and with ICl–AcOH gives 4-*iodo*-2-*nitro*-4′-*methoxydiphenyl ether*, m.p. 70°, and thence (Fe powder; AcOH) 4-*iodo*-2-*amino*-4′-*methoxydiphenyl ether*, m.p. 102°. Nitration of (VIII) gives (? 3 : 2′-)*dinitro*-4-*methoxydiphenyl ether*, m.p. 132°. 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and *p*-$OH{\cdot}C_6H_4{\cdot}OMe$ give 2 : 4-*dinitro*-4′-*methoxydiphenyl ether*, m.p. 110°. *o*-$OMe{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}NH_2$-*p* gives (Sandmeyer) 4-*iodo*-2′-*methoxy*-, b.p. 228°/28 mm., and thence (HNO_3–AcOH) 4′-*iodo*-5-*nitro*-2-*methoxydiphenyl ether* (IX), m.p. 115°. Nitration of (I) or condensation of KOPh with 2 : 1 : 5-$OMe{\cdot}C_6H_3Br{\cdot}NO_2$ gives 5-*nitro*-2-*methoxydiphenyl ether*, m.p. 72°, previously (Lea *et al.*, A., 1926, 397) considered to be the 6-NO_2-compound and converted by ICl–AcOH into (IX). 5-*Iodo*-4′-*nitro*-2-*methoxydiphenyl ether*, m.p. 109°, is obtained from *o*-$OMe{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}NO_2$-*p* by ICl or from 2 : 5 : 1-$OMe{\cdot}C_6H_3I{\cdot}OK$ and *p*-$C_6H_4F{\cdot}NO_2$. R. S. C.

Labile union of oxygen to carbon. Spontaneous dissociation of dimethoxydiphenylanthracene photo-oxide. C. Dufraisse, L. Velluz, and (Mme.) L. Velluz (Compt. rend., 1939, **209**, 516—518).—Dissociation of 1 : 4-dimethoxy-9 : 10-diphenyl-

anthracene photo-oxide (I) (cf. A., 1939, II, 365) is a unimol. reaction which proceeds regularly up to 33% decomp. and then progressively more slowly, probably due to dissolution of solid (I) in the decomp. product. Decomp. occurs at the same rate even at 140 atm. pressure of O_2 so that the reaction is probably irreversible. (I) separated from a photographic plate by black paper produces an image which indicates that activated O_2 (O_3 or H_2O_2 from moisture present) is probably liberated in the reaction. (I) is luminous in the dark, the luminosity increasing with rise in temp. (cf. A., 1933, 1284). J. L. D.

Manufacture of 4 : 4′-diaminodiphenyl sulphone and its monoacyl derivatives.—See B., 1939, 1102.

Chemistry and chemotherapy of 4 : 4′-diaminodiphenyl sulphone, 4-amino-4′-hydroxydiphenyl sulphone, and related compounds. G. W. Raiziss, L. W. Clemence, M. Severac, and J. C. Moetsch (J. Amer. Chem. Soc., 1939, **61**, 2763—2765).—*p*-$NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}NH_2$-*p* (prep. from *p*-$C_6H_4Cl{\cdot}NO_2$ and an excess of aq. Na_2S), new m.p. 145°, is reduced by Sn–HCl to (*p*-$NH_2{\cdot}C_6H_4)_2S$, m.p. 108°, the Ac_2 derivative, new m.p. 223—224°, of which with $K_2Cr_2O_7$–H_2SO_4–AcOH gives (*p*-$NHAc{\cdot}C_6H_4)_2SO_2$, new m.p. 285°, hydrolysed (HCl) to (*p*-$NH_2{\cdot}C_6H_4)_2SO_2$ (I), new m.p. 175°. *p*-$NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}NHAc$-*p*, new m.p. 198°, gives 4-*nitro*-4′-*acetamidodiphenyl sulphone*, m.p. 229—230°, reduced by $SnCl_2$–EtOH to 4-*amino*-4′-*acetamidodiphenyl sulphone*, m.p. 242—243°, which by a diazo-reaction affords 4-*amino*-4′-*hydroxydiphenyl sulphone*, m.p. 193—194° (N-*Ac*, m.p. 274—275°, and NO-Ac_2 derivative, m.p. 171—172°). (I) is superior, and some of the other products are equal, to sulphanilamide in therapeutic effect. R. S. C.

Reactions of αβ-unsaturated cyclic aldehydes and ketones. V. *dl*-Cryptone and *cis*- and *trans*-*dl*-cryptol. D. T. C. Gillespie and A. K. Macbeth (J.C.S., 1939, 1531—1534; cf. A., 1939, II, 165).—*dl*-Cryptone (prep. from a crude *l*-cryptone by boiling Et_2O + conc. HCl), b.p. 78°/2·8 mm. (*semicarbazone*, m.p. 188°; p-*nitro*-, m.p. 160—161°, and 2 : 4-*dinitro-phenylhydrazone*, m.p. 130—131°), and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ (prep. described) give readily trans-, b.p. 90°/4 mm. [isolated as p-*nitrobenzoate*, m.p. 76·5°; α-*naphthyl*-, m.p. 136°, and *phenylurethane*, m.p. 108°; *H phthalate*, m.p. 97—97·5°; 3 : 5-*dinitrobenzoate*, m.p. 108° (α-$C_{10}H_7{\cdot}NH_2$ *compound*, m.p. 140°)], and with difficulty cis-dl-*cryptol*, b.p. 86°/6 mm. [isolated as 3 : 5-*dinitrobenzoate*, m.p. 96·5° (α-$C_{10}H_7{\cdot}NH_2$ *compound*, m.p. 102—104°); α-*naphthylurethane*, m.p. 105·5°; p-*nitrobenzoate*, m.p. 34·5—35·5°]. Structures of the products are proved by hydrogenation (Pd–C) to the known H_2-derivatives. R. S. C.

Isomerisation of β-substituted styrene oxides. Effect of degree of unsaturation of the substituent. M. Tiffeneau and P. K. Kuriaki (Compt. rend., 1939, **209**, 465—468; cf. A., 1935, 750; 1937, II, 415; 1939, II, 419).—*cyclo*Hexene with $CH_2Ph{\cdot}COCl$ in presence of $SnCl_4$ gives cyclo*hexenyl benzyl ketone*, m.p. 54°, b.p. 192—194°/25 mm. (*semicarbazone*, m.p. 167°; *oxime*, m.p. 118°), converted by $Al(OPr^{\beta})_3$ into α-cyclo*hexenyl*-β-*phenylethyl alcohol*, b.p. 149—151°/7 mm. (p-*nitrobenzoate*, m.p. 79°), dehydrated (H_2SO_4 on pumice) to α-cyclo*hexenyl*-β-*phenylethylene*, b.p. 137°/5 mm., which with $NH_2{\cdot}CO{\cdot}NHCl$ in aq. AcOH gives a chlorohydrin, converted by KOH into α-cyclo*hexenyl*-β-*phenylethylene oxide* (I), b.p. 147—150°/7 mm. (I) with hot $MgBr_2$ etherate gives cyclo*hexenylphenylacetaldehyde*, b.p. 150—152°/10 mm. (*semicarbazone*, m.p. 203°; *oxime*, m.p. 156°), oxidised (Ag_2O) to the corresponding *acid*, m.p. 162°, which is reduced (H_2–Raney Ni) to cyclo*hexylphenylacetic acid* (II), m.p. 150°. *cyclo*Hexylphenylcarbinol with $SOCl_2$ gives the *chloride*, m.p. 27°, b.p. 153—154°/15 mm., the Mg derivative of which with CO_2 gives (II). β-cyclo*Hexyl*-α-*phenylethyl alcohol*, b.p. 156—157°/17 mm. (from PhCHO and Mg *cyclo*hexylmethyl iodide), with H_2SO_4 gives α-cyclo*hexyl*-β-*phenylethylene*, b.p. 148—150°/17 mm. (*dibromide*, m.p. 153°), oxidised (perphthalic acid) to α-cyclo*hexyl*-β-*phenylethylene oxide* (III), b.p. 158—160°/15 mm. When (III) is heated with $MgBr_2$ etherate it gives cyclo*hexyl benzyl ketone* (IV) (50—60%), m.p. 26°, b.p. 163—165°/15 mm. (*semicarbazone*, m.p. 142°). $CH_2Ph{\cdot}CHO$ with Mg *cyclo*hexyl chloride gives α-cyclo*hexyl*-β-*phenylethyl alcohol*, m.p. 57°, b.p. 167—168° (p-*nitrobenzoate*, m.p. 18°), oxidised (CrO_3) to (IV). J. L. D.

Hydrogenation of acetylenic compounds. XXXI. Catalytic hydrogenation of acetylenic γ-glycols with a *cyclo*pentyl radical. J. S. Salkind and I. M. Gverdtziteli (J. Gen. Chem. Russ., 1939, **9**, 855—862).—*cyclo*Pentanone and (:C·MgBr)$_2$ yield αβ-*di*-(1-*hydroxy*cyclo*pentyl*)*acetylene*, m.p. 109·8—110·8° (*diacetate*, m.p. 44·5—45·5°), hydrogenated (Pd on starch) to isomeric *ethylenic glycols*, m.p. 82—83° and 129·6—130·6°, converted by dil. H_2SO_4 into the γ-*oxide*, m.p. 81—82°, and completely hydrogenated (Pt-black) to αβ-*di*-(1-*hydroxy*cyclo*pentyl*)-*ethane*, m.p. 131·2—132·4°. γ-*Hydroxy*-α-(1-*hydroxy*-cyclo*pentyl*)-γ-*methyl*-Δ^{α}-*butinene*, m.p. 56—58°, b.p. 125—126°/6 mm., synthesised from MgEtBr, $CH{:}C{\cdot}CMe_2{\cdot}OH$, and *cyclo*pentanone, is hydrogenated (Pd) to the H_2-derivative, m.p. 89—90°. It is concluded that the rates of hydrogenation of *ditert.*-acetylenic glycols are influenced by steric hindrance and by the mol. wts. and vols. of the substituents. V. A. P.

Behaviour of *cis*- and *trans*-isomerides in the dehydration of 1-methyl*cyclo*pentane-1 : 2-diols and dehalogenation of the corresponding halogenohydrins. M. Tiffeneau and G. Vaissière (Compt. rend., 1939, **209**, 449—453; cf. A., 1935, 340; 1938, II, 97).—2-Chloro*cyclo*pentanone (I) with MgMeBr affords *cis*-2-chloro-1-methyl*cyclo*pentanol (II), the ·O·MgBr derivative (prep. by MgEtBr) of which when heated gives (after hydrolysis) 2-methyl-*cyclo*pentanone (III) (semicarbazone, m.p. 184°) by a semipinacolic change. 1-Methyl-Δ^1-*cyclo*pentene with $NH_2{\cdot}CO{\cdot}NHCl$ in aq. AcOH gives *trans*-(II), similarly converted into (III). (I) with boiling H_2O (+ $BaCO_3$) affords a ketol converted by MgMeBr into *cis*-1-methyl*cyclo*pentane-1 : 2-diol (IV), b.p. 105°/15 mm., m.p. 23°, dehydrated by hot 10% H_2SO_4 to (III). *trans*-(IV) with hot dil. H_2SO_4 gives only resins but the

vapour passed over Al_2O_3 at 300°/20 mm. gives unsaturated hydrocarbons and their polymerides and a small amount of (III). J. L. D.

Triarylcarbinols. VII. Diphenyl-4′-dimethylaminodiphenylylcarbinol and its relation to the theory of colour of dyes. A. A. Morton and W. H. Wood. **VIII. Occurrence of colour with trixenylcarbonium salts.** A. A. Morton and L. F. McKenney (J. Amer. Chem. Soc., 1939, **61**, 2902—2905, 2905—2908; cf. A., 1938, II, 137).—VII. *Diphenyl-4′-dimethylamino-*p*-diphenylylcarbinol*, m.p. 177—178° [prep. from *p*-$C_6H_4Br{\cdot}C_6H_4{\cdot}NMe_2$-*p* (I), $COPh_2$, and Na in boiling C_6H_6], gives no colour with dil. acids; the NMe_2 is more basic than the $\geq C{\cdot}OH$, and halochromism is not observed until after neutralisation of the NMe_2. This does not accord with the carbenium theory of $CHAr_3$ dyes. The following orders of basicity are established: $(p\text{-}C_6H_4Ph)_3C{\cdot}OH > NH_2Ac$, $NH_2Bz > CPh_3{\cdot}OH$; *m*- ≫ *o*-, *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. The yield of (I) from *p*-$C_6H_4Br{\cdot}C_6H_4{\cdot}NH_2$-*p*, MeOH, and conc. HCl at 140—150° is much greater in a short than in a long tube.

VIII. *Trixenylcarbonium perchlorate* (I), m.p. 219·5—220°, and sulphate (impure), $(C_6H_4Ph)_3CX,HX$, are prepared by adding HX to $(C_6H_4Ph)_3C{\cdot}OH$ (II) in Ac_2O. The *nitrate* is prepared by HNO_3 (*d* 1·6). Salts of weaker acids could not be obtained, but HCl produces a colour with (II) in AcOH if a trace of H_2O, $MeNO_2$, MeCN, $HCO{\cdot}NH_2$, $CO(NH_2)_2$, MeOH, NH_2Bz, etc. is present. HNO_3 gives a colour in AcOH in presence of a little $MeNO_2$. Electrolysis of (I) in org. solvents causes disappearance of colour at the cathode; with a very dil. solution of (I) in $PhNO_2$ there is appearance of colour at the anode. With (I) in $MeNO_2$ the bulk of the (II) is recovered from the cathode compartment. $CPh_3{\cdot}ClO_4$ behaves similarly. Colour is thus dependent on presence of ClO_4'. With crystal-violet, however, colour follows the ammonium ion. R. S. C.

Saponins and sapogenins. XIII. Precipitability of steroid sapogenins by digitonin. C. R. Noller (J. Amer. Chem. Soc., 1939, **61**, 2717—2719; cf. A., 1939, II, 517).—The solubility products of digitonides of steroid sapogenins, all > those of cholesterol and β-cholestanol digitonides, have configurational val. only when epimeric pairs are compared. Behaviour under arbitrary conditions is misleading. R. S. C.

Steroids and sex hormones. LVIII. Transformation of 17-acetylenylandrostene-3 : 17-diol into pregnadien-3-ol. L. Ruzicka, M. W. Goldberg, and E. Hardegger (Helv. Chim. Acta, 1939, **22**, 1294—1300).—Gradual addition of a solution of Δ^5-17-acetylenylandrostene-3 : 17-diol in abs. EtOH to a suspension of Na in boiling xylene and treatment of the product with Ac_2O–C_5H_5N gives *pregnadien-3-ol acetate*, m.p. 143—144°, $[\alpha]_D$ −70·3±0·3° in $CHCl_3$, hydrolysed (KOH–MeOH) to *pregnadien-3-ol* (I), m.p. 132—133°, $[\alpha]_D$ −74±1° in $CHCl_3$. This is oxidised [$Al(OBu^{\gamma})_3$–C_6H_6–$COMe_2$] to *pregnadien-3-one*, m.p. 142—143°, $[\alpha]_D$ +117·5±1° in $CHCl_3$. (I) is hydrogenated (PtO_2 in EtOH–AcOH) to allo*pregnan-3-ol*, m.p. 137—138°, $[\alpha]_D$ +16±1° in $CHCl_3$ (*acetate*, m.p. 115—116°), which is oxidised (CrO_3 in AcOH) to allo*pregnan-3-one*, m.p. 116—117° [*semicarbazone*, m.p. ~230° (decomp.)]. The corresponding *hydrazone*, m.p. ~226° (decomp.), is transformed by N_2H_4,H_2O and NaOEt in EtOH at 200° into allo*pregnane*, m.p. 84—85°, $[\alpha]_D$ +18·0±0·7° in $CHCl_3$. M.p. are corr. H. W.

Stigmasterol 22 : 23-dibromide. E. Fernholz and H. E. Stavely (J. Amer. Chem. Soc., 1939, **61**, 2956—2957).—Stigmasteryl acetate tetrabromide and NaI in C_6H_6–EtOH at room temp. (not when heated) give the *acetate* 22 : 23-*dibromide* (60%), m.p. 212—213°, $[\alpha]_D^{25}$ +30° in $CHCl_3$, hydrolysed by hot 5% KOH–MeOH to *stigmasterol* 22 : 23-*dibromide*, m.p. 209—210°, which with $Al(OBu^{\gamma})_3$ in C_6H_6–$COMe_2$ gives *stigmastadienone* 22 : 23-*dibromide*, m.p. 182—184°, $[\alpha]_D^{22}$ +53° in $CHCl_3$, and thence (Zn dust–AcOH; 100°) *stigmastadienone*, m.p. 124—125°, $[\alpha]_D^{25}$ +63° in $CHCl_3$, also obtained from stigmasterol by $Al(OPr^{\beta})_3$ in *cyclo*hexanone–PhMe. R. S. C.

Introduction of nitrogen into sterols. III. Preparation of deoxycholamine. M. Vanghelovici (Bul. Soc. Chim. România, 1938, **20**, 231—235; cf. A., 1938, II, 405).—Deoxycholhydrazide (modified prep. from the acid by way of the Et ester) gives the azide, decomp. ~67°, and thence the *urethane*, m.p. 110°, which, when distilled with CaO at 4 mm., gives *deoxycholamine*, m.p. 118° [*hydrochloride*, m.p. 247° (decomp.); *platinichloride*, decomp. 194°]. R. S. C.

Action of sulphur monochloride on phenylacetonitrile. V. V. Korschak and A. F. Lisseenko (J. Gen. Chem. Russ., 1939, **9**, 1329—1331).—$CH_2Ph{\cdot}CN$ and S_2Cl_2 in the cold yield $CHClPh{\cdot}CN$ (I), $CCl_2Ph{\cdot}CN$ (II) and $(CPh{\cdot}CN)_2$ (III); on heating (I) is no longer formed and the principal product is *s-dichlorodiphenylsuccinodinitrile*, m.p. 189—190°, hydrolysed by KOH–EtOH to αβ-diphenylmaleic anhydride and converted into (III) by heating. G. A. R. K.

Stereochemical studies. XX. Optically active phenylethylthiolacetic acids and phenylethyl mercaptans. B. Holmberg (Arkiv Kemi, Min., Geol., 1939, **13**, A, No. 8, 9 pp.).—*r*-α-Phenylethylthiolacetic acid (I) is resolved by α-phenylethylamine in H_2O. The non-cryst. (−)-*acid* (II), $[\alpha]_D$ −333·2° in abs. EtOH, −234° in H_2O, −208° in 0·1N-HCl [(−)-*phenylethylamine*, m.p. 124—125°, $[\alpha]_D$ −180·8° in abs. EtOH, and β-$C_{10}H_7{\cdot}NH_2$, m.p. 76—77°, $[\alpha]_D$ −193·5° in abs. EtOH, salts], and the (+)-*acid* (III) [(+)-*phenylethylamine*, m.p. 124—125°, $[\alpha]_D$ +180·7° in abs. EtOH, and β-$C_{10}H_7{\cdot}NH_2$, m.p. 76—77°, $[\alpha]_D$ +191·7° in abs. EtOH, salts] are described. (I) gives cryst. *salts*, m.p. 53—55°, 56—57·5°, 65—66°, and 105—106°, respectively, with NH_2Ph, *m*- and *p*-$C_6H_4Me{\cdot}NH_2$, and β-$C_{10}H_7{\cdot}NH_2$, whereas that with *o*-$C_6H_4Me{\cdot}NH_2$ is non-cryst. With benzenoid bases (II) and (III) yield non-cryst. salts. Slight racemisation is observed when (II) or (III) is heated in neutral and possibly in alkaline aq. solution but not in 0·1N-HCl. (II) is oxidised by KSO_4 to the sulphinacetic acid, m.p. 126—127° (decomp.), $[\alpha]_D$ −120·2° in abs. EtOH, which is converted by H_2SO_4 into (−)-α-*phenylethyl mercaptan* (IV), b.p.

82—83°/10 mm., $[\alpha]_D^{20}$ −105·6°, $[\alpha]_D$ −89·0° in abs. EtOH. Oxidation of (III) with H_2O_2 gives an acid, m.p. 126—127° (decomp.), $[\alpha]_D$ +142·0° in abs. EtOH, which gives (+)-α-*phenylethyl mercaptan* (V), b.p. 81—83°/10 mm., $[\alpha]_D^{20}$ +105·8°. Oxidation (EtOH–I) of (V) and (IV) gives (+)- (VI) and (−)-*di-α-phenylethyl*) *disulphide*, $[\alpha]_D$ +271·9° and −272·1° in abs. EtOH, respectively. Prolonged treatment of (V) with H_2O_2 yields (VI) and α-phenylethanesulphonic acid (*Na*, $[\alpha]_D$ +4·7° in H_2O, and β-$C_{10}H_7{\cdot}NH_2$ salt, m.p. 196—197° after darkening, $[\alpha]_D$ +9·5° in abs. EtOH). H. W.

3 : 5-Di-iodo-*l*-tyrosine, its properties and preparation. A. J. Savitzki (J. Gen. Chem. Russ., 1939, **9**, 1342—1344).—*l*-Tyrosine in aq. NH_3 affords with I in KI at 6—8° >80% of crude di-iodotyrosine, which is purified by repptn. from HCl; the yield of pure product, m.p. 200—203°, is ~72%. It has $2H_2O$ of crystallisation, which it loses on prolonged drying over H_2SO_4. The *dl*-compound retains $1H_2O$ under the same conditions and is therefore a true racemate, not a mixture of the two forms. G. A. R. K.

α-Benzoyl-, m.p. 200—202°, $[\alpha]_D$ +3·3° in H_2O (2·8%), and α-hippuryl-*l*-lysine amide hydrochlorides, m.p. 255—258°, $[\alpha]_D^{28}$ −11·7° in H_2O (5%); ε-carbobenzyloxy-α-hippuryl-lysine, m.p. 148—149°.—See A., 1939, III, 1009.

Hydrolysis of benzoic and related esters in varying media.—See A., 1939, I, 615.

Interaction of sulphuryl chloride with arylamides of aromatic acids. II. Orienting influences of groups in substitution reactions in aromatic compounds. N. W. Hirwe, G. V. Jadhav, and D. R. Sukhtankar (J. Indian Chem. Soc., 1939, **16**, 281—284; cf. A., 1939, II, 263).—Salicyl-anilide and *-o-*, *-m-*, and *-p*-toluidide and SO_2Cl_2 in boiling C_6H_6 give respectively 5-*chlorosalicyl-anilide*, m.p. 203—204°, and -4′-*chloroanilide*, m.p. 215—216°, and 3 : 5-*dichlorosalicyl*-2′ : 4′-*dichloroanilide*, m.p. 174—175°; 5-*chloro-*, m.p. 171—172°, and 3 : 5-*dichloro-salicyl*-5′-*chloro*-o′-*toluidide*, m.p. 197—198°; 5-*chlorosalicyl*-m′-*toluidide*, m.p. 144—145°, and -6′-*chloro*-m′-*toluidide*, m.p. 221—222°, and 3 : 5-*dichlorosalicyl*-4′ : 6′-*dichloro*-m′-*toluidide*, m.p. 214—215°; and 5-*chlorosalicyl*-p′-*toluidide*, m.p. 216—217°, and 3 : 5-*dichlorosalicyl*-3′-*chloro*-p′-*toluidide*. *o*-Methoxybenz-anilide and *-o′*-anisidide give o-*methoxybenz*-p′-*chloroanilide*, m.p. 75—76°, and -5′-*chloro*-o′-*anisidide*, m.p. 135—136°. *o*-Tolu-anilide and *-o′-*, *-m′-*, and *-p′*-toluidide give respectively o-*tolu*-p′-*chloroanilide*, m.p. 133—134°, and -2′ : 4′-*dichloroanilide*, m.p. 128°, -5′-*chloro*-o′-*toluidide*, m.p. 182°, -4′ : 6′-*dichloro*-m′-*toluidide*, m.p. 120—121°, and -3′-*chloro*-p′-*toluidide*, m.p. 119—120°. *o*-Chlorobenz-anilide and *-m′*-chloroanilide give o-*chlorobenz*-p′-*chloro-*, m.p. 119—120°, and -3′ : 4′-*dichloro-anilide*, m.p. 143°. The structures of the products are proved by hydrolysis to known amines and acids, and in three cases by synthesis. E. W. W.

Stereochemistry of diphenyls. XLVIII. Comparison of the racemisation rates of three isomeric 2 : 2′ : 6-nitrocarboxymethyldiphenyls. R. Adams and J. B. Hale. **XLIX. Comparison of the racemisation rates of the 2 : 2′ : 6-nitrocarboxymethoxydiphenyls.** R. Adams and G. C. Finger (J. Amer. Chem. Soc., 1939, **61**, 2825—2828, 2828—2830; cf. A., 1939, II, 505).—XLVIII. 3 : 2 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}CO_2Me$, *o*-$C_6H_4MeI$, and Cu powder at 225—230° give an ester, hydrolysed to 6-*nitro*-2′-*methyldiphenyl*-2-*carboxylic acid* (15%), m.p. 162—163°, resolved to the l-, m.p. 153—155°, $[\alpha]_D^{25}$ −65° in EtOH [*quinine* salt (+$x H_2O$), m.p. 135—140° and (anhyd.) m.p. 168—171°, $[\alpha]_D^{25}$ −133·5° in $CHCl_3$], and d-*acid* (I), m.p. 153—156°, $[\alpha]_D^{25}$ +61·5° in EtOH [*quinine* salt, m.p. (+$x H_2O$) 118—123° and (anhyd.) 128—131°, $[\alpha]_D^{25}$ (+$x H_2O$) −105° in $CHCl_3$]. 3 : 2 : 1-$C_6H_3MeI{\cdot}CO_2Me$, *o*-$C_6H_4I{\cdot}NO_2$, and Cu powder at 230° (later 250°) give 2′-*nitro*-2-*methyldiphenyl*-6-*carboxylic acid* (50%), m.p. 157°, resolved by brucine in MeOH into the d-, m.p. 179—181°, $[\alpha]_D^{25}$ +73·5° in $CHCl_3$ (*brucine* salt, m.p. 165—167°, $[\alpha]_D^{25}$ +48° in $CHCl_3$), and l-*acid* (II), m.p. 175—179°, $[\alpha]_D^{25}$ −72·6° in $CHCl_3$ (*brucine* salt, m.p. 153—160°, $[\alpha]_D^{25}$ −51° in $CHCl_3$). *d-* and *l*-6-Nitrodiphenic acid (III) are prepared having $[\alpha]_D^{25}$ +39·0° and −37·5° in EtOH. 3 : 2 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}CO_2Me$, *o*-$C_6H_4I{\cdot}NO_2$, and Cu-bronze at 220—225° give 2 : 2′-*dinitrodiphenyl*-6-*carboxylic acid* (30%), m.p. 164°, resolved by quinine in 75% EtOH into the d-, m.p. 135—137°, [α] +201·5° in EtOH (*quinine* salt, m.p. 195—197°, $[\alpha]_D^{25}$ +52·5° in $CHCl_3$), and l-*acid* (IV), m.p. 127—130°, $[\alpha]_D^{25}$ −199·5° in EtOH (*quinine* salt, m.p. 121—125°, $[\alpha]_D^{25}$ −238° in $CHCl_3$). [α] are given for the acids also in other solvents. Relative stability against racemisation is 2-nitro-6-methyldiphenyl-2′-carboxylic acid > (II) > (I), which does not accord with theory. (III) is more stable than (IV) in Bu^{a}OH, but less stable in AcOH or aq. NaOH.

XLIX. 1 : 2 : 3-OMe·$C_6H_3I{\cdot}CO_2Me$, *o*-$C_6H_4I{\cdot}NO_2$, and Cu-bronze at 200° give 2′-*nitro*-2-*methoxydiphenyl*-6-*carboxylic acid*, m.p. 234—236°, which affords the l-*acid* (V), m.p. 229—232°, $[\alpha]_D^{27}$ −213·3° in EtOH (*brucine* salt, m.p. 222—225°, $[\alpha]_D^{27}$ −47·1° in $CHCl_3$). 1 : 2 : 3-OMe·$C_6H_3Cl{\cdot}NO_2$ (prep. described), *o*-$C_6H_4I{\cdot}CO_2Me$, and Cu-bronze at 255—280° give 6-*nitro*-2-*methoxydiphenyl*-2′-*carboxylic acid*, m.p. 196—198° (and 6 : 6′-*dinitro*-2 : 2′-*dimethoxydiphenyl*, m.p. 226—228°), resolved by brucine in abs. EtOH into the l-*acid* (VI), m.p. 195—199°, $[\alpha]_D^{27}$ −127·9° in abs. EtOH (*brucine* salt, m.p. variable, [α] ~0). Half-life periods of (V) and (VI) in abs. EtOH are 271 and 219—288 min., respectively, but that of 2-nitro-2′-methoxydiphenyl-6-carboxylic acid, $[\alpha]_D^{27}$ +59·4° in abs. EtOH, is only 10·2 min. R. S. C.

Naphthenic acids (from Grosny petroleum). I. I. I. Lapkin (J. Gen. Chem. Russ., 1939, **9**, 1332—1341).—Fractionation and analysis of the Me esters of naphthenic acids suggest that they contain from 10 to 18 C; C_{10} and C_{11} are monocyclic, C_{12} and C_{13} mono- and di-cyclic, and above C_{14} dicyclic only; no tri- or poly-cyclic acids were detected. No appreciable amounts of aliphatic acids can be present in the original mixture, judging from the max. crit. solution temp. in NH_2Ph, of the hydrocarbons prepared by reducing the esters to the alcohols, conversion into the iodides, and reduction with Zn dust.

The parachors of the esters below C_{13} point to the presence of 5- and 6-membered rings. The rate of esterification of the acids is in agreement with the primary character of the CO_2H group. G. A. R. K.

Cyclisation of benzylbenzylidenesuccinic acid. E. Bergmann and A. Weizmann (Compt. rend., 1939, **209**, 539—540; cf. A., 1938, II, 415; Dufraisse and Houpillart, A., 1938, II, 194).—Interaction of Me benzylsuccinate and PhCHO gives a product (I) which when distilled in a vac. is converted into 1-*hydroxy*-2-*benzyl*-3-*naphthoic acid*, b.p. 184—188°/0·02 mm., m.p. 65—68°. (I) with AcOH gives α-benzyl-α′-benzylidenesuccinic acid, converted by conc. H_2SO_4 at 70°/1 hr. into 1 : 5-*diketo*-2 : 3 : 6 : 7-*dibenzo*-1 : 4 : 5 : 10-*tetrahydronaphthalene*, m.p. 265°, which with a large excess of LiPh gives 6-*hydroxy*-12-*phenylnaphthacene*, m.p. 255°. J. L. D.

Alkyl hydrogen phthalates from normal aliphatic alcohols. J. F. Goggans, jun., and J. E. Copenhaver (J. Amer. Chem. Soc., 1939, **61**, 2909—2910).—Heating ROH with o-$C_6H_4(CO)_2O$ under reflux (R = Me to Bu) or, in other cases, at 105—110° gives Me, m.p. 82·4—82·7°, Et, *Pr*, m.p. 54·1—54·4°, *Bu*, m.p. 73·1—73·5°, *amyl*, m.p. 75·4—75·6°, *hexyl*, m.p. 24·6—25·4°, C_7H_{15}, m.p. 16·5—17·5°, C_8H_{17}, m.p. 21·5—22·5°, C_9H_{19}, m.p. 42·4—42·6°, $C_{10}H_{21}$, m.p. 37·8—38·0°, $C_{11}H_{23}$, m.p. 43·8—44·1°, $C_{12}H_{25}$, m.p. 50·2—50·4°, $C_{13}H_{27}$, m.p. 52·4—52·7°, $C_{14}H_{29}$, m.p. 59·8—60·0°, $C_{15}H_{31}$, m.p. 60·3—60·5°, $C_{16}H_{33}$, new m.p. 66·7—66·9°, $C_{17}H_{35}$, m.p. 66·6—66·8°, $C_{18}H_{37}$, m.p. 72·4—72·6°, $C_{19}H_{39}$, m.p. 70·8—71·0°, and $C_{20}H_{41}$, m.p. 77·1—77·3°, *H phthalate*. All alkyl are *n*. M.p. are corr. R. S. C.

Reaction of the Grignard reagent with homophthalic anhydride. C. C. Price, F. M. Lewis, and M. Meister (J. Amer. Chem. Soc., 1939, **61**, 2760—2762).—Under all conditions, homophthalic anhydride (I) and MgMeI give dimethylhomophthalide. (I) is readily prepared from o-$C_6H_4Me{\cdot}CO_2H$ by way of o-$C_6H_4Me{\cdot}COCl$, o-$CH_2Br{\cdot}C_6H_4{\cdot}COBr$, o-$CH_2Br{\cdot}C_6H_4{\cdot}CO_2Et$, o-$CN{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2Et$, and o-$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ (by 50% H_2SO_4 at 100°) in 70—75% over-all yield. Phthalide and KCN at 180—190° give 80—85% of o-$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$. R. S. C.

Friedel and Crafts reactions affected by steric hindrance. B. Hoï (Compt. rend., 1939, **209**, 562—564; cf., A., 1939, II, 429).—When phthalonic or homophthalic anhydride is submitted to the Friedel–Crafts reaction or to esterification, the incoming group is always separated from the ring by 2 C because of steric effects. J. L. D.

Steroids and sex hormones. LV. Preparation of $\Delta^{5:17}$-3-hydroxypregnadiene-21-carboxylic acid and its hydrogenation products. P. A. Plattner and W. Schreck (Helv. Chim. Acta, 1939, **22**, 1178—1184).—Δ^5-3 : 17-Dihydroxyandrostene-17-acetic acid yields a *Me* ester, m.p. 159°, $[\alpha]_D$ −89±2° in $CHCl_3$ (3-*acetate*, m.p. 117°, $[\alpha]_D$ −68±2° in $CHCl_3$), the *diacetate*, two forms, m.p. 113° and 121°, $[\alpha]_D$ −70±2° in $CHCl_3$, of which is converted by distillation under 15 mm. into *Me* $\Delta^{5:17}$-3-*acetoxypregnadiene*-21-*carboxylate* (I), m.p. 159°, $[\alpha]_D$ −69±2° in $CHCl_3$, hydrolysed by KOH–MeOH to $\Delta^{5:17}$-3-*hydroxypregnadiene*-21-*carboxylic acid*, m.p. 249—250°, $[\alpha]_D$ −82±1° in dioxan [*Me* ester (II), m.p. 188—189°, $[\alpha]_D$ −73±1° in dioxan]. (II) in $COMe_2$ is oxidised by $Al(OBu^{\gamma})_3$ in C_6H_6 to *Me* $\Delta^{4:17}$-3-*ketopregnadiene*-21-*carboxylate*, m.p. 151—152°, $[\alpha]_D$ +80±1° in dioxan. Hydrogenation (PtO_2 in EtOH) of (I) affords *Me* Δ^5-3-*acetoxypregnene*-21-*carboxylate*, m.p. 128—129°, $[\alpha]_D$ 57±1° in $CHCl_3$, which is hydrolysed (KOH–MeOH) to Δ^5-3-*hydroxypregnene*-21-*carboxylic acid*, m.p. 241—242°, $[\alpha]_D$ −56·4±1° in dioxan, converted by CH_2N_2 into the *Me* ester (III), m.p. 132—133°, $[\alpha]_D$ −63·5±1° in dioxan. Oxidation [$Al(OBu^{\gamma})_3$ in C_6H_6–$COMe_2$] of (III) affords *Me* Δ^4-3-*ketopregnene*-21-*carboxylate*, m.p. 146—147°, $[\alpha]_D$ +84±1° in dioxan. (I) is hydrogenated (Pt in AcOH) to *Me* 3-*acetoxy*allo*pregnane*-21-*carboxylate*, m.p. 150—151°, $[\alpha]_D$ 0±1° in dioxan. All m.p. are corr. H. W.

Introduction of nitrogen into the sterol molecule. IV. Condensation of bile acid hydrazides with carbonyl compounds. M. Vanghelovici (Bul. Soc. Chim. România, 1938, **20**, 237—241).—Cholhydrazide and RCHO in dil. HCl give the *CHPh:*, m.p. 148°, p-*OMe*·C_6H_4·*CH:*, m.p. 140°, *salicylidene*, m.p. 160°, *CHPh:CH·CH:*, m.p. 150°, *furfurylidene*-, m.p. 145°, CH_2:, m.p. 210°, and $CO_2Et{\cdot}CH_2{\cdot}CMe$:, m.p. 210° (could not be cyclised), derivatives. Deoxycholhydrazide gives the CH_2:, m.p. 214° (decomp.), furfurylidene, m.p. 136°, *p*-OMe·C_6H_4·CH:, m.p. 167°, and CHPh: derivative, m.p. 75°. Cholanhydrazide gives CH_2:, m.p. 130°, and *CHPh:* derivatives, m.p. 146°. Other alkylidene derivatives could not be obtained. R. S. C.

Sterols. LXXII. Oxidation products of sarsasapogenin. C_{19}-Dibasic acid. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 2722—2724).—(?) 3-*Hydroxyætiobilianic acid* (I), m.p. 220—222° [Me_2 ester, m.p. 121—122° (*acetate*, m.p. 103—104°); *acetate anhydride*, m.p. 203—204°, hydrolysed to (I) by KOH–EtOH], is obtained by CrO_3 from sarsasapogenin acetate at 85° (cf. A., 1939, II, 322), sarsasapogenoic acid acetate (12% yield) at 90—95°, or tetrahydrosarsasapogenin acetate at 90—95°. CrO_3–AcOH at room temp., followed by hot Zn–Hg–HCl, converts (I) into (?) ætiobilianic acid, m.p. 230—232° (anhydride, m.p. 205·5—207°). R. S. C.

Degradation of αθ-diphenyloctatetraene to ζ-phenylheptatrienal. P. Karrer and H. Obst (Helv. Chim. Acta, 1939, **22**, 1191—1192).—αθ-Diphenyloctatetraene in $CHCl_3$ is oxidised by acid $KMnO_4$ to trans-trans-trans-ζ-*phenylheptatrienal*, m.p. 112·5—113° [*oxime*, m.p. 186—187° (decomp.)]. H. W.

Polyene series. I. E. Barraclough, J. W. Batty, I. M. Heilbron, and W. E. Jones. **II.** I. M. Heilbron, W. E. Jones, and A. Spinks. **III.** J. W. Batty, I. M. Heilbron, and W. E. Jones. **IV.** I. M. Heilbron, A. W. Johnson, and W. E. Jones (J.C.S., 1939, 1549—1554, 1554—1556, 1556—1560, 1560—1563).—I. Data in brackets refer to max. of absorption spectra. Citral, CHMe:CH·CHO, piperidine, and AcOH (excess) give (cf. A., 1937, II,

342) citrylidenecrotonaldehyde-*a* (I) [3140 A.; ε 12,490] (semicarbazone, m.p. 160° [3255 A.; ε 27,100]) and less -*b* (II) [3160 A.; ε 12,800] (semicarbazone, m.p. 206° [3255 A.; ε 24,400]), yields of both products being increased by addition of SiO_2 gel; use of piperidine acetate and SiO_2 gel gives somewhat larger amounts; use of $NaNH_2$ in Et_2O leads to (I) [no (II)] and a cyclic aldehyde (III), $C_{14}H_{20}O$ (*semicarbazone*, m.p. 186° [2860 A.; ε 50,000], absorbs 4 H_2). Citral, MeCHO, and $NaNH_2$ in Et_2O give citrylideneacetaldehyde (semicarbazone, m.p. 166—168° [3045 A.; ε 49,000]), and a little (III). $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ reduces (I) and (II) to *ηλ-dimethyl-*$\Delta^{\beta\delta\xi\nu}$*-dodecatrien-α-ol*, b.p. 200—210°/30 mm. [2680 A.; ε 12,000] (absorbs 4 H_2), and an alcohol [2650 A.; ε 10,000], respectively. Citral, CMe_2:CH·CHO, and $NaNH_2$ in Et_2O give *ψ*-ionylideneacetaldehyde-*a* (IV) [3150 A.; ε 14,700] (*semicarbazone*, m.p. 178—179° [3250 A.; ε 33,000], absorbs 5 H_2) and -*b* (V) [3150 A.; ε 11,000] (*semicarbazone*, m.p. 112° [3240 A.; ε 24,000]), reduced to alcohols [2650 and 2660 A.; ε 11,000 and 10,000, respectively]. O_3 yields 0·77 mol. of $COMe_2$ from (I) and 0·70 mol. from (IV), but no MeCHO from either. CHPh:CH·CHO, MeCHO, and $NaNH_2$–Et_2O give CHPh:CH·CH:CH·CHO (semicarbazone, m.p. 218—218·5° [3390 A.; ε 52,460]). $COMe_2$, (I), and NaOEt–EtOH at 0° give *κξ*-dimethyl-$\Delta^{\nu\varepsilon\eta\iota\nu}$-pentadecapentaen-β-one, b.p. 140—145°/1 mm. [3580 A.; ε 14,500] (*semicarbazone*, m.p. 171° [3500 A.; ε 15,750]); (IV) gives similarly *ζκξ*-trimethyl-$\Delta^{\nu\varepsilon\eta\iota\nu}$-pentadecapentaen-β-one, b.p. 164°/0·5 mm. [3580 A.; ε 15,400] (*semicarbazone*, m.p. 161° [3500 A.; ε 15,000]).

II. The semicarbazone [2995 A.; ε 45,400] of *ψ*-ionone [2910 A.; ε 21,800] and H_3PO_4 (*d* 1·75) at room temp. give (after subsequent hydrolysis) nearly pure β-ionone [2935 A.; ε 9,200] (semicarbazone [2765 A.; ε 23,300]), but *ψ*-ionone itself gives mainly α-ionone [2285 A.; ε 14,300]. The semicarbazone [3045 A.; ε 47,200] of citrylideneacetaldehyde [2900 A.; ε 15,960] gives similarly β-*cyclo*citrylideneacetaldehyde [β-2 : 6 : 6-Δ^1-*cyclo*hexenylacraldehyde] [2930 A.; ε 8,000] (*semicarbazone*, m.p. 186—187° [2950 A.; ε 27,000]), yielding with O_3 geronic acid and with $COMe_2$–NaOEt–EtOH *ζ*-2 : 6 : 6-Δ^1-*cyclo*hexenyl-$\Delta^{\nu\varepsilon}$-hexadien-β-one, b.p. 140—145°/0·17 mm. [3190 A.; ε 8280] (*semicarbazone*, m.p. 186° [3160 A.; ε 38,000]).

III. The semicarbazone of (I) and H_3PO_4 give (?) 5 : 5 : 9-*trimethyl*-5 : 6 : 7 : 8 : 9 : 10-*hexahydro*-1-*naphthaldehyde*, m.p. 60—61° [3210 A.; ε 13,260] (*semicarbazone*, +MeOH, m.p. 114° [3230 A.; ε 28,000]; 2 : 4-*dinitrophenylhydrazone*, m.p. 186°), reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ to the corresponding *alcohol* [2680 A.; ε 10,000] (absorbs 3 H_2) and yielding with O_3 a keto-dicarboxylic acid, $C_{12}H_{18}O_5$ (*semicarbazone*, m.p. 163°), and no geronic acid. The semicarbazones of (II), (IV), and (V) yield similarly dicyclic *aldehydes*, m.p. 56·5—60·5° [2350 A.; ε 14,000] (*semicarbazone*, m.p. 221—222° [2680 A.; ε 33,300]; 2 : 4-*dinitrophenylhydrazone*, m.p. 253—254°; gives the derived *alcohol*, an oil, showing no selective ultra-violet absorption), an oil [3160 A.; ε 10,900] (*semicarbazone*, m.p. 189° [3250 A.; ε 24,000]; derived alcohol, an oil [2720 A.; ε 9,000]; with O_3 gives no geronic acid), and an oil [2400 A.; ε 8000] (*semicarbazone*, m.p. 214—215° [2670 A.; ε 27,500]).

IV. Vitamin-*A*, $Al(OPr^{\beta})_3$, and $COMe_2$ in boiling C_6H_6 give the same ketone, now termed axerophthylideneacetone (VI), as is obtained by $Al(OBu^{\gamma})_3$–$COMe_2$ (A., 1938, II, 126). $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ reduces this to the corresponding alcohol [3545 A.; $\varepsilon^{1\%}_{1\,cm.}$ 1250] [which, as also does (VI), gives geronic acid with O_3], but once a hydrocarbon [3700, 3900, and 4110 A.] was obtained. CHPh:CH·CH_2·OH with $Al(OBu^{\gamma})_3$–$COPr^{\beta}_2$ in C_6H_6 gives 5% of CHPh:CH·CHO, but with $Al(OBu^{\gamma})_3$–$COEt_2$ in C_6H_6 gives δ-*phenyl-α-methyl-*$\Delta^{\alpha\gamma}$*-butadienyl Et ketone*, m.p. 63° [3220 A.; ε 33,400] (2 : 4-*dinitrophenylhydrazone*, m.p. 232°). With $Al(OBu^{\gamma})_3$–$COEt_2$ in C_6H_6, CH_2Ph·OH and 2-furfuryl alcohol give α-benzylidene-, b.p. 160°/20 mm. [2730 A.; ε 25,000] (semicarbazone, m.p. 187°), and α-2-furfurylidene-ethyl Et ketone, b.p. 135—140°/21 mm. (*semicarbazone*, m.p. 181° [3160 A.; ε 74,000]; 2 : 4-*dinitrophenylhydrazone*, m.p. 188°), respectively. R. S. C.

Vapour-phase production of *o*-tolualdehyde and phthalic anhydride from *o*-xylene.—See B., 1939, 1098.

Acylation of aldoximes. II. Inversion of configuration in the preparation of carbanilino-aldoximes from phenylcarbimide and *syn*-aldoximes. A. E. Rainsford and C. R. Hauser (J. Org. Chem., 1939, **4**, 480—492).—Brady's conclusion that PhNCO is capable of converting certain *syn*-aldoximes (I) into carbanilino-derivatives of the *anti*-compounds is confirmed and an explanation based on the intermediate formation of an "inner" salt is described. Inversion does not occur when (I) are treated with PhNCO in the presence of certain *tert.* amines, thus supporting the hypothesis that there is no inversion of configuration during the prep. of acyl derivatives when the reaction is carried out in solution in the presence of a sufficiently strong base. Investigation has been made of the action of C_5H_5N and NH_2Bu^{α} on carbanilino-derivatives of *syn*-3 : 4-methylenedioxy-, *syn*- and *anti*-*m*-nitro-, *syn*- and *anti*-*p*-dimethylamino-benzaldoxime and on the α-naphthylcarbanilino-compounds of *syn*- and *anti*-3 : 4-methylenedioxy-, *syn*-*p*-methoxy-, *syn*-*p*-dimethylamino-, and *anti*-*m*-nitro-benzaldoxime.

Brady's conclusion that there is no inversion of configuration when (I) are treated with 1-$C_{10}H_7$·NCO has been confirmed. α-Naphthylcarbanilino-*syn*-aldoximes may be recovered unchanged from C_5H_5N but are decomposed by NH_2Bu^{α} to *syn*-aldoximes; the corresponding *anti*-isomerides give nitriles with C_5H_5N or NH_2Bu^{α}. *Carbanilino*-syn-3 : 4-*methylenedioxybenzaldoxime*, m.p. 127°, is new. H. W.

Structure of barbatolic acid. E. E. Suominen (Suomen Kem., 1939, **12**, **B**, 26—28).—Prolonged extraction of *Alectoria implexa* with boiling Et_2O gives barbatolic acid (3%) (I), decomp. 205—206° (dioxime, decomp. 207—208°), which with CH_2N_2 in Et_2O–dioxan at —5° gives *Me barbatolate* (II), decomp. 193° (sinters at 190°), converted by AcOH at 140—145° (sealed tube)/15 hr. into 2 : 6 : 4 : 1-

$(OH)_2C_6H_2Me{\cdot}CHO$ (atranol) (III) and 2 : 6-*dihydroxy*-3-*carboxy*-4-*hydroxymethylbenzaldehyde* (*barbatol-carboxylic acid*) (IV), decomp. 243—244°, which indicates that the CO_2H of (I) is in the barbatol nucleus. (II) with HI (*d* 1·7)–AcOH–Zn dust at 70—100° (or H_2–Pd–C) gives a *compound* (V), $C_{19}H_{20}O_8$, decomp. 189—190° (sinters at 186°), as well as β-orcinol and Me β-orcinolcarboxylate, which indicates that (III) and (IV) are probably linked through the $CH_2{\cdot}OH$ of (IV). (V) with CH_2N_2 in Et_2O gives a product, hydrolysed (boiling 0·2N-EtOH–KOH) to rhizoninic acid, its Me ether, and the *lactone*, m.p. 173·5°, of 2 : 6-dimethoxy-4-hydroxymethyl-*m*-toluic acid (*Ag* salt). (I) is thus 3 : 5-dihydroxy-4-aldehydo-2-carboxybenzyl 3 : 5-dihydroxy-4-aldehydo-*o*-toluate. J. L. D.

***cyclo*Hexane series. II. Synthesis of ketones.** G. Vasiliu and S. Radvan (Bul. Soc. Chim. România, 1938, **20**, 243—250; cf. A., 1938, II, 408).—*cyclo*Hexylphenylacetonitrile (I) and 4 mols. of certain Grignard reagents give moderate yields of the ketones by way of the imine hydrohalides, but α-*cyclohexyl*-α-*phenylpropionitrile* (prep. from CHPhMe·CN by *cyclo*hexyl bromide and $NaNH_2$ in Et_2O), b.p. 166°/11 mm., and $C_6H_{11}{\cdot}CPhR{\cdot}CN$ (R = Et, Pr, or *cyclo*hexyl) do not react in Et_2O, C_6H_6, or PhMe. Thus are obtained α-*cyclohexylbenzyl Et* (by MgEtBr in Et_2O), b.p. 163—164°/14 mm. [*semicarbazone*, m.p. 189°; *imine hydrobromide*, m.p. ~220° (decomp.)], *Pr*$^{\alpha}$ (by $MgPr^{\alpha}Br$ in Et_2O), b.p. 174°/13 mm. (*oxime*, m.p. 104°; *imine hydrobromide*, m.p. 193—194°), *Pr*$^{\beta}$ (by $MgPr^{\beta}Br$ in PhMe), m.p. 66—67° [*imine hydrobromide*, m.p. ~270° (decomp.)], and *CH$_2$Ph ketone* (by $CH_2Ph{\cdot}MgCl$ in PhMe), m.p. 74°, b.p. 219—220°/10 mm. Other CO-derivatives could not be obtained. MgMeI, $MgBu^{\alpha}Br$, and Mg *cyclo*hexyl bromide do not react with (I). MgPhBr and (I) in Et_2O give *cyclo*hexyldeoxybenzoin, m.p. 121°. R. S. C.

Relative rates of reaction between ketones and liquid ammonia.—See A., 1939, I, 615.

Effect of nuclear and side-chain substitution on the oxonium-ion catalysed iodination of acetophenone derivatives. Kinetics of the iodination of acetophenone in sulphuric and perchloric acid solutions. Mechanism of the acid-catalysed enolisation of acetophenone derivatives.—See A., 1939, I, 617.

Isomerisation of *cyclo*hexylphenylacetaldehyde. E. D. Venus-Danilova and A. I. Bolschuchin (J. Gen. Chem. Russ., 1939, **9**, 975—984).—α-*cyclo*Hexyl-β-phenylethyl alcohol (I) in AcOH and CrO_3 in H_2SO_4 at room temp. yield *cyclo*hexyl benzyl ketone (II). β-*cyclo*Hexyl-α-phenylethyl alcohol (III) is oxidised similarly to *Ph hexahydrobenzyl ketone* (IV), b.p. 161—162°/10 mm. (*semicarbazone*, m.p. 192—193°; *oxime*, m.p. 99°). (II) when heated with KOH yields $CH_2Ph{\cdot}CO_2H$ and (I), whilst (IV) gives only (III) under these conditions. *cyclo*Hexylphenylacetaldehyde yields (I), together with a small amount of a *dimeride*, m.p. 150—151°, when treated with $HgSO_4$ in H_2SO_4 (6 hr. at 128—135°), or with H_2SO_4 at −5°. R. T.

Chalkones. I. Chalkones derived from resacetophenone and its dimethyl ether. J. B. Lal (J. Indian Chem. Soc., 1939, **16**, 296—300).—2 : 4 : 1-$(OMe)_2C_6H_3{\cdot}COMe$ (I), *iso*vanillin, MeOH, and 30% KOH–MeOH at 50—60° (24 hr.) give 2 : 4-*dimethoxyphenyl* 3′-*hydroxy*-4′-*methoxystyryl ketone*, m.p. 115°. With 6 : 2 : 1-, 3 : 2 : 1- (II), and 5 : 2 : 1-$OMe{\cdot}C_6H_3(OH){\cdot}CHO$, MeOH, and 50% aq. KOH, (I) gives 2 : 4-*dimethoxyphenyl* 2′-*hydroxy*-6′-*methoxy*-, m.p. 116·5°, 2′-*hydroxy*-3′-*methoxy*-, m.p. 117°, and 2′-*hydroxy*-5′-*methoxy-styryl ketone*, m.p. 129°, respectively. 2 : 4 : 1-$(OH)_2C_6H_3{\cdot}COMe$ and (II) similarly give 2 : 4-*dihydroxyphenyl* 2′-*hydroxy*-3′-*methoxystyryl ketone*, m.p. 211°. Varying yields of the above substances under varying conditions are reported. E. W. W.

Functional aptitude of the methyl group. IV. Derivatives of acetophenone and chalkone. L. Chardonnens and J. Venetz (Helv. Chim. Acta, 1939, **22**, 1278—1286; cf. A., 1939, II, 419).—Interaction of 3 : 4 : 1-$NO_2{\cdot}C_6H_3Me{\cdot}COMe$ (I) and *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ (II) in boiling EtOH containing Na_2CO_3 gives a very complex mixture of products which appear to be formed by changes involving both Me groups; under these conditions COPhMe does not react. *m*-$NO_2{\cdot}C_6H_4{\cdot}COMe$ and (II) yield a very small amount of 3-*nitrophenylglyoxal*-ω : p′-*dimethylaminoanil*, m.p. 170° after softening; under like conditions *p*-$NO_2{\cdot}C_6H_4{\cdot}COMe$ gives a rather better yield of the 4-*NO$_2$-isomeride*, m.p. 158—160°, whilst *o*-$NO_2{\cdot}C_6H_4{\cdot}COMe$ gives only 4 : 4′-bisdimethylaminoazoxybenzene, m.p. 242°, which arises from (II). PhCHO and (I) in aq. EtOH containing NaOH at room temp. or at 140° in presence of a little piperidine give 2-*nitro*-p-*tolyl styryl ketone*, m.p. 151—152°, which condenses with (II) in $COMe_2$–EtOH containing Na_2CO_3 to 2-*nitro*-4-*cinnamoylbenzald*-4′-*dimethylaminoanil*, decomp. ~210° (yield 38%), and with PhCHO containing piperidine at 190—200° to 2-*nitro*-4-*cinnamoylstyrylbenzene*, m.p. 164—165°. 2 : 6-*Dinitro*-p-*toluoyl chloride*, m.p. 59—60°, from the acid and $SOCl_2$, is converted by condensation with $CHAcNa{\cdot}CO_2Et$ and hydrolysis of the product with H_2SO_4 into 3 : 5-*dinitro*-4-*methylacetophenone*, b.p. 198—200°/15 mm., m.p. 66—67° [*phenylhydrazone*, m.p. 255° (decomp.)]. This condenses with PhCHO in presence of piperidine at 140° to 2 : 6-*dinitro*-4-*cinnamoyltoluene*, m.p. 206—207° (yield 58%), transformed by PhCHO at 170° into 2 : 6-*dinitro*-4-*cinnamoylstyrylbenzene*, m.p. 191°. The yield is scarcely better than that obtained with the $(NO_2)_1$-derivative, possibly owing to the thermal instability of the chalkones. H. W.

Benzoylformic acid from styrene. C. D. Hurd, R. W. McNamee, and F. O. Green (J. Amer. Chem. Soc., 1939, **61**, 2979—2980).—$BzCO_2H$ is readily obtained from styrene (≯50% pure) by $KMnO_4$–NaOH at 70°. R. S. C.

Mixed magnesium alkoxides and their molecular compounds. IV. Action of ketones on ethereal magnesium butoxyiodide. V. M. Tolstopiatov and A. T. Riskaltschuk (J. Gen. Chem. Russ., 1939, **9**, 1148—1150).—MgI·OBu$^{\alpha}$ (I) in Et_2O and *p*-$C_6H_4Me{\cdot}COPh$ yield *MgI$_2$*,3p-*C$_6$H$_4$Me·COPh*.

In these conditions fluorenone and $CO(CH{:}CHPh)_2$ give 1 : 1 compounds with (I). R. T.

4 : 4′-Dihydroxy-3 : 3′-dimethylbenzophenone. M. H. Hubacher (J. Amer. Chem. Soc., 1939, **61**, 2664—2665).—Contrary to Doebner *et al.* (A., 1890, 898), *o*-cresol-benzein or -phthalein with KOH at 260—265° gives 4 : 4′-*dihydroxy*-3 : 3′-*dimethylbenzophenone*, m.p. 247—247·8° [*diacetate*, m.p. 106·8—107·2°; *Me*$_1$, m.p. 203·7—204·2°, and *Me*$_2$ *ether*, m.p. 113·7—114·2° (*oxime*, m.p. 160·9—161·2°)], slowly converted by KOH at 280° into *o*-cresol and 4 : 3 : 1-$OH{\cdot}C_6H_3Me{\cdot}CO_2H$. M.p. are corr. R. S. C.

Preparation of nitrophenyl α-naphthyl ketones. J. S. Joffe and S. S. Bravina (J. Gen. Chem. Russ., 1939, **9**, 1133—1135).—*m*- or *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ and $C_{10}H_8$ yield (Friedel–Crafts) *m*-, m.p. 124° (lit. 117°) (*phenylhydrazone*, m.p. 194°), and *p*-nitrophenyl α-$C_{10}H_7$ ketone, m.p. 89° (lit. 95°). R. T.

Substituted ring compounds. I. Synthesis of 2 : 2 : 4-trimethyl*cyclo*pentanone. M. Qudrat-i-Khuda and S. K. Ghosh (J. Indian Chem. Soc., 1939, **16**, 287—295).—$COMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2Et$ (I) (*semicarbazone*, m.p. 165°) with $CH_2Br{\cdot}CO_2Et$ and Mg in C_6H_6 gives (dil. H_2SO_4) *Et* αα*γ-trimethylbutyrolactone-γ-acetate*, b.p. 148—150°/7 mm. (with a product, b.p. 170—175°/6 mm.), which with PCl_5 followed by EtOH yields *Et*$_2$ *γ-chloro-*αα*γ-trimethyladipate*, b.p. 113—115°/5 mm., reduced (Zn–AcOH) to the *Et*$_2$ ester (II), b.p. 145—146°/16 mm., of αα*γ-trimethyladipic acid* (III), m.p. 80°. Alternatively, (I) and $CN{\cdot}CH_2{\cdot}CO_2Et$ (piperidine; Na_2SO_4) give *Et*$_2$ α*-cyano-*βδ*-dimethyl-*Δ^{α}*-pentene-*αδ*-dicarboxylate*, b.p. 162°/4 mm., reduced (Al–Hg in Et_2O–H_2O) to *Et*$_2$ α*-cyano-*βδ*-dimethylpentane-*αδ*-dicarboxylate*, b.p. 155—156°/8 mm., which is hydrolysed (conc. HCl) to (III). With NaOEt–EtOH, (II) gives *Et* 2 : 2 : 4-*trimethyl*cyclo*pentanone*-5-*carboxylate*, b.p. 88—90°/5 mm., converted by boiling dil. HCl into 2 : 2 : 4-*trimethyl*cyclo*pentanone* (IV), b.p. 65—66°/45 mm. (*semicarbazone*, m.p. 173°; 5-*CHPh*: derivative, m.p. 125—126°). The compound obtained by Wallach (A., 1916, i, 487) from the dibromodihydro*iso*phorone (V), m.p. 90°, and regarded by him as 2 : 4 : 4-trimethyl*cyclo*pentanone, is identical with (IV); intermediate products in its prep. from (V) (now regarded as 2 : 2-*dibromo*-3 : 3 : 5-*trimethyl*cyclo*hexanone*) are 3 : 3 : 5-*trimethyl*cyclo*hexane*-1 : 2-*dione*, m.p. 168—169° (Wallach, m.p. 89—90°), and 2 : 2 : 4-*trimethyl*-cyclo*pentan*-1-*ol*-1-*carboxylic acid*, m.p. 90° (cf. *loc. cit.*). E. W. W.

Tetrahydrocitrylidene- and citronellylideneacetic acids. Syntheses of *sec.-iso*octyl*cyclo*pentane derivatives. H. N. Rydon (J.C.S., 1939, 1544—1549).—Tetrahydrocitral, $CH_2(CO_2H)_2$, and (*a*) $N([CH_2]_2{\cdot}OH)_3$ or (*b*) C_5H_5N give mixtures containing (*a*) 66% and (*b*) 25% of Δ^{β}-isomeride, separated by preferential esterification of that isomeride, yielding δθ-*dimethyl*-Δ^{β}- (I), b.p. 162°/13 mm. (*Et*, b.p. 134—135°/15 mm., and p-*bromophenacyl* ester, m.p. 39°), and -Δ^{α}-*decenoic acid*, b.p. 158—160°/7 mm. (p-*bromophenacyl* ester, m.p. 47°), equilibrated [47% of (I)] by NaOH–EtOH–H_2O. The structure of (I) is proved by oxidation to αε-dimethylheptoic acid. In conc. H_2SO_4 at room temp. (I) gives *γ*-sec.-iso*octyl-γ-butyrolactone*, b.p. 158—162°/13 mm. When kept in HBr–AcOH at room temp. and then esterified, (I) gives (?) *Et γ-bromo-*δθ*-dimethyldecoate*, b.p. 145—150°/1·5 mm., obtained also from the lactone by HBr–EtOH and condensing poorly with $CN{\cdot}CHNa{\cdot}CO_2Et$. Partial esterification of citronellylideneacetic acid gives δθ-*dimethyl*-$\Delta^{\alpha\eta}$-*decadienoic acid*, b.p. 173—175°/13 mm., and 28% of *Et* δθ-*dimethyl*-$\Delta^{\beta\eta}$-*decadienoate*, b.p. 139—141°/13 mm., hydrolysed to the $\Delta^{\beta\eta}$-*acid* (II), b.p. 163—165°/1 mm. Equilibration by alkali gives 75% of (II). The K derivative of Et *cyclo*pentanone-2-carboxylate and $Pr^{\beta}{\cdot}[CH_2]_3{\cdot}CHMeI$ (III) in boiling xylene give *Et* 2-sec.-iso*octyl*cyclo*pentanone*-2-*carboxylate*, b.p. 165—175°/14 mm., converted by boiling aq. $Ba(OH)_2$ into 2-sec.-iso*octyl*cyclo*pentanone* (IV), b.p. 134—136°/16 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°), and α-sec.-iso*octyladipic acid*, m.p. 54° [with $Ba(OH)_2$ at 350—360° gives 52% of (IV)]. MgMeI in Et_2O converts (IV) into a carbinol, dehydrated by boiling aq. $H_2C_2O_4$ to yield 1-*methyl*-2-sec.-iso*octyl*-(?Δ^1)-cyclo*pentene*, b.p. 112—115°/18 mm. Grignard condensation of (III) and *cyclo*pentanone failed. *cyclo*Pentyl bromide, $CH_2Ac{\cdot}CO_2Et$, and NaOEt–EtOH give Et *cyclo*pentylacetoacetate, b.p. 125—130°/18 mm. (yields 4-cyclo*pentyl*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, m.p. 133—134°), which with NaOEt–EtOH–MeI gives *Et* cyclo*pentylmethylacetoacetate*, b.p. 128—131°/13 mm., hydrolysed by 10% aq. KOH to α-cyclo*pentylethyl Me ketone*, b.p. 76—79°/17 mm. (*semicarbazone*, m.p. 98°). R. S. C.

Catalytic oxidation of *cyclo*heptylamine. V. S. Smirnov (J. Gen. Chem. Russ., 1939, **9**, 1283—1285).—*cyclo*Heptylamine on oxidation with O_2 in presence of Cu-bronze affords suberone in yields up to 64%. G. A. R. K.

Products of the cyclising dehydration of 1-β-phenylethyl*cyclo*hexanol and synthesis of *spirocyclo*hexane-1 : 1-indan-3-one. M. Levitz, D. Perlman, and M. T. Bogert (Science, 1939, **90**, 114—115).—Formulæ showing the stages in the synthesis of *spirocyclo*hexane-1 : 1-indan-3-one, m.p. 58—59° [oxime (I), m.p. 137—137·8°; NO_2-derivative, m.p. 192°, also obtained by nitration (KNO_3–H_2SO_4) of (I) and subsequent hydrolysis], are given. The product from 1-β-phenylethyl*cyclo*hexanol and 85% H_2SO_4, when oxidised and oximated, affords (I) and oximes, m.p. 187—188° and 123—124° (derived NO_2-ketone, m.p. 149—150°); the oxime, m.p. 177°, of Cook *et al.* (A., 1939, II, 103) could not be isolated. The oxime, m.p. 187·5° (Cook), may be that of *trans*-keto-octahydrophenanthrene. M.p. are corr. L. S. T.

Sulphonation. IV. Sulphonation of benzanthrone. J. S. Joffe and N. N. Melteva. **V. Sulphonation of phenyl α-naphthyl ketone.** J. S. Joffe and G. Z. Naumova (J. Gen. Chem. Russ., 1939, **9**, 1104—1108, 1121—1123).—IV. Benzanthrone and 22% oleum (24 hr. at room temp.) yield a mixture of *benzanthrone*-2- and -3-*sulphonic acid* (*quinine* salts, m.p. 80—82° and 240—242°, respectively). A mixture of disulphonic acids is obtained by sulphonation with 100% H_2SO_4 at 170°.

V. α-$C_{10}H_7$·COPh and 95% H_2SO_4 at 160—170° afford BzOH and $C_{10}H_6(SO_3H)_2$. With 10% oleum at room temp. the product is 1 : 5-$C_{10}H_6$Bz·SO_3H. R. T.

Spirans. XXIII. Derivatives of phenylindanedione. D. Rădulescu and F. Bărbulescu (Bul. Soc. Chim. România, 1938, **20**, 29—37; cf. A., 1938, II, 31).—When bis-1 : 3-diketo-2-hydrindenyl (I) (1 mol.) and KOH–EtOH (2 mols.) are evaporated to dryness and the resulting K_2 salt is boiled with Br·[CH_2]$_3$·Br (II) (1 mol.) in PhOMe, 2 : 2′-*trimethylenebis*-1 : 3-*diketo*-2-*hydrindenyl*, m.p. 253°, is obtained. Replacement of (II) by *o*-$C_6H_4(CH_2Br)_2$ leads to 2 : 3-*diphthaloyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 268° (becomes yellow in light), which in KOH–EtOH gives a transient blue colour and then a colourless substance, m.p. 285°. Although these products are colourless, substituted 2 : 2′-diaminobis-1 : 3-diketo-2-hydrindenyls and 2-amino-1 : 3-diketohydrindenes are yellow and very feebly basic, which confirms the structure ascribed to the product obtained from (CH_2·NH_2)$_2$ (A., 1924, i, 215). The 2 : 2′-Br_2-derivative of (I) with $NHEt_2$ in boiling abs. EtOH gives *bis*-2-*diethylamino*-1 : 3-*diketo*-2-*hydrindenyl*, m.p. 219°, yellow. 2-Bromo-1 : 3-diketo-2-phenylhydrindene and an excess of the appropriate amine in a little boiling EtOH or C_6H_6 give 2-*anilino*- (III), m.p. 212°, 2-p-*toluidino*- (IV), m.p. 195°, and 2-1′-*piperidino*-1 : 3-*diketo*-2-*phenylhydrindene*, m.p. 142°, and 1 : 4-*di*-1′ : 3′-*diketo*-2′-*phenyl*-2′-*hydrindenylpiperazine*, m.p. 275°, with varying amounts (even in absence of air) of *bis*-1 : 3-*diketo*-2-*phenyl*-2-*hydrindenyl*, m.p. 210°, which is obtained with a *product*, m.p. 277°, also by photochemical oxidation of 1 : 3-diketo-2-phenylhydrindene in EtOH. Hot KOH–EtOH hydrolyses (III) and (IV) to o-*carboxyphenyl* α-*anilino*-, m.p. 175° (decomp.) (*Na* and *Ba* salts), and α-*toluidino*-*benzyl ketone* (*K* salt), respectively, ring-closure of which could not be effected. R. S. C.

Sterols. LXXIV. Acetic acid derivatives of œstrone and α-œstradiol. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 2974).—$\Delta^{1:3:5}$-*Œstratrien*-17-*on*-3-*oxyacetic*, m.p. 209—211° [*oxime*, m.p. 230—232° (decomp.); *Me* ester, m.p. 130—132°], α-$\Delta^{1:3:5}$-*œstratrien*-17-*on*-3-*oxypropionic*, m.p. 195—198° (*Me* ester, m.p. 137—139°), and $\Delta^{1:3:5}$-*œstratrien*-17(α)-*ol*-3-*oxyacetic acid*, m.p. 182—184° (*Me* ester, m.p. 94—96°), are prepared by condensing the appropriate alcohol and CHRCl·CO_2Et by boiling NaOEt–EtOH (excess) and subsequently hydrolysing by KOH–EtOH. R. S. C.

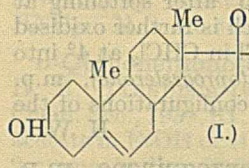
Δ^5-3-Hydroxy-7-ketoætiocholenic acid and related compounds. T. Reichstein and H. G. Fuchs (Helv. Chim. Acta, 1939, **22**, 1160—1170).—Me Δ^5-3(β)-acetoxyætiocholenate is oxidised by CrO_3 in AcOH at 55° to *Me* Δ^5-7-*keto*-3(β)-*acetoxyætiocholenate* (I), m.p. 182—186° (corr.), $[\alpha]_D^{24}$ −74·8±2°, $[\alpha]_{5461}^{24}$ −89·7±3° in $COMe_2$, and some *Me* $\Delta^{3:5}$-7-*ketoætiocholadienoate*, m.p. 197—199° (corr.), also obtained from boiling MeOH–HCl and (I). Hydrogenation (PtO_2 in AcOH) of (I) gives a mixture of Me 7(α + β)-hydroxy-3(β)-acetoxyætio*allo*cholanate, which is oxidised (CrO_3 in AcOH) at 30° to *Me* 7-*keto*-3(β)-*acetoxyætio*allo*cholanate*, m.p. 176—179° (corr.), and is converted by Ac_2O in C_5H_5N at 70—80° into Me 3(β) : 7(α)- (II), m.p. 147—149° (corr.), $[\alpha]_D^{24}$ +64·1±6°, $[\alpha]_{5461}^{24}$ +77·7±6° in $COMe_2$, and 3(β) : 7(β)- (III), m.p. 159—162° (corr.), $[\alpha]_D^{24}$ −3·1±1°, $[\alpha]_{5461}^{24}$ −2·30±1·5° in $COMe_2$, -*diacetoxyætio*allo*cholanate*. (II) is hydrolysed by KOH–aq. MeOH to 3(β) : 7(α)-dihydroxyætio*allo*cholanic acid, m.p. 252—257° (corr.; decomp.) [Me ester (IV), m.p. 194—197° (corr.)], transformed by Ac_2O and C_5H_5N at 100° into the 3(β) : 7(α)-Ac_2 acid, m.p. 237—241° (corr.), whereas (III) yields 3(β) : 7(β)-dihydroxyætio*allo*cholanic acid, m.p. ~230° [Me ester (V), m.p. 224—229° (corr.)]. (IV) or (V) is oxidised by CrO_3 in AcOH at room temp. to *Me* 3 : 7-*diketoætio*allo*cholanate*, m.p. 194—197° (corr.). This is reduced by Zn–Hg and conc. HCl to ætio*allo*cholanic acid, m.p. 228—230° (corr.) [Me ester, m.p. 143—144° (corr.)]. H. W.

Constituents of the adrenal cortex and related substances. XXVIII. *allo*Pregnane-3 : 21-diol-20-one diacetate and *allo*pregnan-21-ol-3 : 20-dione acetate. T. Reichstein and J. von Euw (Helv. Chim. Acta., 1939, **22**, 1209—1212).—3-Acetoxyætio*allo*cholanic acid is converted by the successive actions of $SOCl_2$ at 5° and CH_2N_2 in abs. Et_2O at −10° into 21-diazo*allo*pregnan-3-ol-20-one acetate, m.p. 134—134·5° (decomp.), which with KOH–H_2O–MeOH at room temp. gives 21-diazo*allo*-pregnan-3-ol-20-one, m.p. 170—172° (decomp.), converted by AcOH at 95—100° into 21-*acetoxy*allo-*pregnan*-3-*ol*-20-*one* (I), m.p. 202—204°, which with Ac_2O–C_5H_5N at room temp. yields the 3 : 21-*diacetate*, m.p. 151—152·5° after becoming opaque at 90—100°. CrO_3 in AcOH oxidises (I) to allo*pregnan*-21-*ol*-3 : 20-*dione acetate*, m.p. 197—199°. M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. XXIX. Action of lead tetra-acetate on *allo*pregnanolone acetate, pregnenolone acetate, and progesterone. T. Reichstein and C. Montigel (Helv. Chim. Acta, 1939, **22**, 1212—1221; cf. Ehrhart *et al.*, A., 1939, II, 327).—*allo*-Pregnan-3-ol-20-one acetate is oxidised by $Pb(OAc)_4$ in glacial AcOH preferably containing Ac_2O at 68—70° mainly to allo*pregnane*-3 : 21-*diol*-20-*one diacetate*, m.p. 152—153·5°, with ~2% of (?) allo*pregnane*-3(β) : 17(β) : 21-*triol*-20-*one triacetate* (I), m.p. 190—192° (corr.). Hydrolysis of (I) by $KHCO_3$ in aq. MeOH at room temp. followed by oxidation of the product with HIO_4 and subsequent energetic hydrolysis leads to 3(β) : 17(β)-dihydroxyætio*allo*cholanic acid, m.p. 272—274° (corr., decomp.) [Me ester, m.p. 238—242° (decomp.)]. Similarly pregnenolone acetate gives mainly pregnene-3 : 21-diol-20-one diacetate, m.p. 164—165° (corr.), and a (?) *pregnenetriolone triacetate*, m.p. 182—185° (corr.). Contrary to B.P. 502,474 (B., 1939, 995) and Ehrhart (*loc. cit.*) it has not been found possible to isolate deoxycorticosterone acetate as the main product of the oxidation of progesterone; refined methods of isolation result in a yield of ~3% but the method has no practical significance. H. W.

Steroids and sex hormones. LVII. Addition of aniline to Δ^5-17-acetylenylandrostene-3 : 17-diol. M. W. Goldberg and R. Aeschbacher (Helv. Chim. Acta, 1939, **22**, 1188—1190).—Δ^5-17-

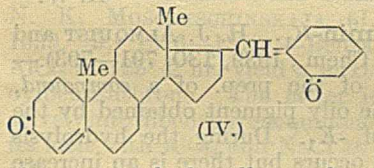
Acetylenylandrostene-3 : 17-diol, $HgCl_2$, and NH_2Ph at 60—70° give Δ^5-3 : 17-*dihydroxypregnenone*-20-*anil* (I), m.p. 190—192°, $[\alpha]_D$ −197·5±2° in $CHCl_3$, oxidised by $Al(OBu^\gamma)_3$ in boiling C_6H_6–$COMe_2$ to Δ^4-3-*keto*-17-*hydroxypregnenone*-20-*anil*, m.p. 221—223°, $[\alpha]_D$ −19±1° in $CHCl_3$. Δ^5-3 : 17-*Diacetoxypregnenone*-20-*anil* has m.p. 207—209°, $[\alpha]_D$ −155±2° in $CHCl_3$. All m.p. are corr. (vac.).



(I.)

H. W.

Steroids. XXIII. Homologues of the testicular hormone. I. K. Miescher and A. Wettstein (Helv. Chim. Acta, 1939, **22**, 1262—1268; cf. A., 1939, II, 431).—Addition of EtOH to Me Δ^5-3-hydroxyætiocholenate (I) and finely divided Na in xylene at 160—170° gives Δ^5-17-*hydroxymethylandrosten*-3-*ol* (II), m.p. 209—211° (*diacetate*, m.p. 136—137°), and a little Δ^5-3-hydroxyætiocholenic acid. Successive bromination, oxidation (CrO_3, AcOH), and debromination of (II) leads to Δ^4-3-*ketoætiocholenic acid* (III), m.p. 258—262° [*Me* ester, m.p. 134—135°, also obtained by treatment of (I) with $Al(OPr^\beta)_3$ in boiling PhMe–*cyclo*hexanone]. (II) is dehydrogenated by $Al(OPr^\beta)_3$ and the ketone fraction is isolated by Girard's reagent; it is separated by $(\cdot CH_2\cdot CO)_2O$ into the doubly unsaturated *ketone* (IV), m.p. 190—193°, which with 1 : 4-$C_{10}H_6(OH)_2$ gives a marked yellow colour with intense green fluorescence, and Δ^4-17-*hydroxymethylandrosten*-3-*one* (V), m.p. 158—159° [*acetate*, m.p. 114—115° (*semicarbazone*, m.p. 214—215°)], which does not give a colour with 1 : 4-$C_{10}H_6(OH)_2$. Oxidation (CrO_3 in AcOH) of (V) yields (III). M.p. are corr.



(IV.)

H. W.

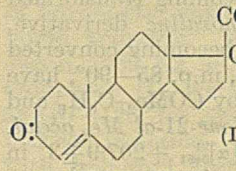
Steroids and sex hormones. LVI. Transformation of Δ^5-17-acetylenylandrostene-3 : 17-diol into progesterone. M. W. Goldberg and R. Aeschbacher (Helv. Chim. Acta, 1939, **22**, 1185—1188).—Successive treatments of Δ^5-17-acetylenylandrostene-3 : 17-diol with $Hg(NHAc)_2$ in boiling abs. EtOH and H_2S give $\Delta^{5:16}$-3-hydroxypregnadien-20-one, m.p. 211—213° [acetate, m.p. 175—177°, $[\alpha]_D$ −30·1±1·5° in 95% EtOH; oxime, m.p. 219—220° (decomp.)], hydrogenated to Δ^5-3-hydroxypregnen-20-one, which is oxidised (Oppenauer) to progesterone, m.p. 127°, $[\alpha]_D$ +185·3±2·5° in 95% EtOH.

H. W.

Sterols. LXXI. Urane derivatives. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 2719—2722).—Urane-3 : 11-dione (I), Br, and a little HBr in AcOH give a (? 4-)*Br*-derivative, m.p. 202—203° (decomp.), converted by boiling C_5H_5N into a *pyridinium* salt, m.p. >300°, which, when heated at 5—10 mm., gives a *urenedione*, m.p. 168—170°. H_2–PtO_2 at 25°/3 atm. reduces (I) in abs. EtOH to *uran*-3(β)-*ol*-11-*one* (II), m.p. 205—208° [*acetate*, m.p. 170·5—172°; CrO_3 gives (I)], as sole product. $Al(OPr^\beta)_3$–$Pr^\beta OH$ also gives mainly (II), the *epi*-isomeride not being isolated. Urane-3 : 11-diol is oxidised by CrO_3 to (II), but by *cyclo*hexanone–$Al(OPr^\beta)_3$ in PhMe to *uran*-11-*ol*-3-*one*, m.p. 169·5—171° [*acetate*, m.p. 195—197°; *semicarbazone*, m.p. 251—253° (decomp.)]. Zn–HCl–EtOH reduces (I) to *uran*-11-*one*, m.p. 135—136·5° (no semicarbazone), hydrogenated (PtO_2; AcOH; 25°/3 atm.) to *uran*-11-*ol*, m.p. ~110° (*acetate*, m.p. 140—142°). Zn–HCl–EtOH reduces uranetrione to *urane*-11 : 20-*dione*, m.p. 199—201°.

R. S. C.

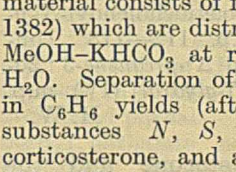
Constituents of the adrenal cortex and related substances. XXVI. Proof of the adherence of substance *S* to the 17(β)-series. T. Reichstein, C. Meystre, and J. von Euw (Helv. Chim. Acta, 1939, **22**, 1107—1113; cf. A., 1939, II, 77).—The annexed formula of substance *S* (I) is confirmed. (I) is converted by successive treatments with HIO_4 and CH_2N_2–Et_2O into *Me* 17(β)-*hydroxy*-3-*keto*-Δ^4-*ætiocholenate* (II), m.p. 216—218° (corr.). Saturation of the double linking of Me 3(β) : 17(α)-dihydroxy-Δ^5-ætiocholenate (III) with Br followed by cautious oxidation with CrO_3 and debromination with Zn affords *Me* 17(α)-*hydroxy*-3-*keto*-Δ^4-*ætiocholenate*, m.p. 182—185° (corr.), which is very difficult to purify and is better obtained by oxidation of (III) with boiling $COMe_2$–C_6H_6 and $Al(OBu^\gamma)_3$ followed by purification with Girard's reagent *T*. Although not obtained pure it is certainly not identical with (I). (II) is also obtained (Oppenauer) from Me 3(β) : 17(β)-dihydroxy-Δ^5-ætiocholenate.



(I.)

H. W.

Constituents of the adrenal cortex and related substances. XXX. Substance *T*. T. Reichstein and J. von Euw (Helv. Chim. Acta, 1939, **22**, 1222—1227; cf. A., 1938, II, 499).—The initial material consists of fractions *C*17, *A*2 and 3 (A., 1936, 1382) which are distributed (after hydrolysis with aq. MeOH–$KHCO_3$ at room temp.) between C_6H_6 and H_2O. Separation of the amorphous mixture present in C_6H_6 yields (after acetylation) the acetates of substances *N*, *S*, *Fa*, *M*, dehydrocorticosterone, corticosterone, and a *diacetate* (I), $C_{25}H_{34-36}O_6$, m.p. 212—213° (corr.). (I) does not reduce alkaline Ag solution at room temp. and hence does not contain a ketol group. The absorption spectrum proves it to be an αβ-unsaturated ketone. Hydrolysis of (I) with K_2CO_3 in aq. MeOH gives substance *T* (II), which is oxidised by CrO_3 in AcOH to Δ^4-3 : 11-diketoætiocholenic acid [Me ester, m.p. 178—180° (corr.)]. Under similar conditions (I) is stable towards CrO_3.

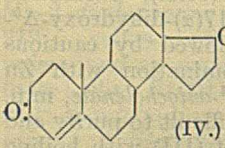


(II.)

H. W.

Constituents of the adrenal cortex and related substances. XXVII. Δ^4-3-Ketoandrostenyl-17-glyoxal and related substances. H. Reich and T. Reichstein (Helv. Chim. Acta, 1939, **22**, 1124—1138).—Δ^5-21-Chloro-3-hydroxypregnen-20-one (I) (improved prep.) is converted by C_5H_5N at 100° into

the *pyridinium chloride*, m.p. 289—293° (corr.; decomp.) [corresponding bromide, m.p. ~300° (corr.; decomp.)], either of which is converted by *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ in presence of alkali into Δ^5-3-*hydroxyætiocholenoyl*-N-*p*-*dimethylaminophenylnitrone* (+ $1H_2O$), m.p. 133—134°. This is transformed by dil. HCl into Δ^5-3-*hydroxypregnen*-20-*one*-21-*al*, two forms, (+ H_2O) m.p. 135—136° (corr.) and 170° (corr.), which are difficult to purify and are possibly different hydrates or polymerides. Both forms reduce Ag-diammine solution and gave the same *Me*$_2$ *acetal* (II), m.p. 112—113° (corr.), $[\alpha]_D^{22}$ +39·1±1°, $[\alpha]_{5461}^{22}$ +52·2±1° in MeOH, when treated with MeOH–HCl at room temp. or, more rapidly, when heated. A *dioxime*, m.p. 285—290° after becoming transformed into needles at ~225°, a *quinoxaline* derivative, $C_{27}H_{34}ON_2$, m.p. 229—231° after becoming converted into needles at 200°, and a *dianil*, m.p. 85—90°, have been prepared. (II) is oxidised by $COMe_2$–C_6H_6 and $Al(OBu^{\gamma})_3$ to Δ^4-*pregnene*-3 : 20-*dione*-21-*al Me*$_2$ *acetal*, m.p. 84—86°, $[\alpha]_D^{21}$ +170·3±2°, $[\alpha]_{5461}^{21}$ +207·9±3° in $COMe_2$, which has the absorption spectrum characteristic of αβ-unsaturated ketones. Cautious hydrolysis with acids gives with difficulty impure (IV) (below). (I) is readily oxidised by $COMe_2$ and $Al(OBu^{\gamma})_3$ to 21-*chloroprogesterone*



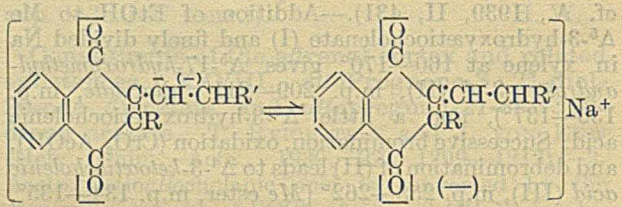
(IV.)

(III), m.p. 203—205° (corr.), $[\alpha]_D^{24}$ +209·5±6°, $[\alpha]_{5461}^{22}$ +255·2±7° in $CHCl_3$, with, possibly, Δ^4-3-ketoætiocholenic acid [*Me* ester, m.p. 170—174° (corr.)]. (III) is converted by NaOAc–AcOH into deoxycorticosterone acetate, m.p. 159—160° (corr.), from which it is regenerated by PCl_5 and $CaCO_3$ in $CHCl_3$. 21-*Bromoprogesterone* has m.p. 190—191° (decomp.). (III) yields the corresponding *pyridinium chloride*, m.p. 274—275° (corr.; decomp.), and bromide, m.p. 265—268° (corr.; decomp.), the former of which with *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ gives Δ^4-3-ketoætiocholenoyl-*N*-*p*-dimethylaminophenylnitrone, m.p. 112—118°, converted by dil. HCl in Et_2O into Δ^4-*pregnene*-3 : 20-*dion*-21-*al* [Δ^4-3-*ketoandrostenyl*-17-*glyoxal*] (IV), m.p. 104—106°. H. W.

Steroids. I. 6-Ketoprogesterone and the stereochemical configuration of several 3 : 5 : 6-triols. M. Ehrenstein (J. Org. Chem., 1939, 4, 506—518).—Androstan-5-ol-3 : 6 : 17-trione, m.p. 249·5—251° (decomp.), is obtained by direct oxidation of dehydro*iso*androsterone (I) with CrO_3 in glacial AcOH, by transforming dehydro*iso*androsterone acetate by H_2O_2 in AcOH into androstane-3(β) : 5 : 6-(*trans*)-triol-17-one, m.p. 295—298°/(decomp.), which is oxidised further by CrO_3, and by converting (I) by OsO_4 in Et_2O into *androstane*-3(β) : 5 : 6-(cis)-*triol*-17-*one*, m.p. 243—245·5°, $[\alpha]_D^{20}$ +79·5° in MeOH, which is oxidised by CrO_3 in AcOH. *Pregnan*-5-*ol*-3 : 6 : 20-*trione* (II), m.p. 267—268° (slight decomp.), is obtained by direct oxidation of Δ^5-pregnen-3-ol-20-one (III) with CrO_3 in AcOH. Alternatively (III) is transformed into its acetate, which is oxidised (30% H_2O_2 in AcOH) and then hydrolysed to *pregnane*-3(β) : 5 : 6-(trans)-*triol*-20-*one*, m.p. 256—258°, which is further oxidised by CrO_3. In a third method (III) is oxidised by OsO_4 in abs. EtOH or dioxan to *pregnane*-3(β) : 5 : 6-(cis)-*triol*-20-*one*, m.p. 231—232·5° after softening at 229°, $[\alpha]_D^{26}$ +59·8° in MeOH, which is further oxidised to (II). (II) is converted by HCl in $CHCl_3$ at 4° into Δ^4-*pregnene*-3 : 6 : 20-*trione* (6-*ketoprogesterone*), m.p. 185—188°. The stereochemical configurations of the substances are discussed. H. W.

5-Anilino-4-hydroxy-1 : 2-benzoquinone, m.p. 210° (decomp.), and prep. of 1 : 2 : 4-$C_6H_3(OH)_3$.—See A., 1939, III, 1008.

The blue alkali salts of α-phylloquinone (vitamin-K_1) and similar compounds. P. Karrer (Helv. Chim. Acta, 1939, 22, 1146—1149).—Reasons are advanced for assigning the mesomeric formulæ:



R′ = :CMe·$[CH_2]_3$·(CHMe·$[CH_2]_3)_2$·Pr^{β}

to the blue salts of α-phylloquinone; related salts are discussed. H. W.

Derivative of vitamin-K_1. H. J. Almquist and A. A. Klose (J. Biol. Chem., 1939, **130**, 791—793).—Description is given of the prep. of a *compound*, (?) $C_{31}H_{50}O_4$, from the oily pigment obtained by the alkaline hydrolysis of -K_1. During the hydrolysis no appreciable fission occurs but there is an increase in mol. wt. accompanied by the addition of 2 O and several H. At least one added O is phenolic. The absence of fission strongly indicates that the side structure is united to the 1 : 4-naphthaquinone nucleus by a C–C linking and for this group phytyl appears the only logical choice. The purest synthetic specimens of 2-methyl-3-phytyl-1 : 4-naphthaquinone have nearly the same activity as -K_1, with which they are probably identical. H. W.

Synthesis of iodinated benzoylbenzoic acids and anthraquinones. R. W. Higgins and C. M. Suter (J. Amer. Chem. Soc., 1939, **61**, 2662—2664).—4 : 5 : 1 : 2-$C_6H_2I_2(CO)_2O$ (I) (1 mol.) and $AlCl_3$ (2·2 mols.) in boiling C_6H_6 give 80% of 4 : 5-*di-iodo*-2-*benzoylbenzoic acid*, m.p. 244—245°, converted by 100% H_2SO_4 at 140° (more dil. acid causes loss of I) into 2 : 3-*di-iodoanthraquinone* (80% yield), m.p. 291—292° (cf. Eckert *et al.*, A., 1929, 701). Similarly are obtained (?) 3 : 4-, m.p. 223—224°, and 3 : 6-*di-iodo*-2-*benzoylbenzoic acid*, m.p. 218—220°, and thence 1 : 2-, m.p. 236—237°, and 1 : 4-*di-iodoanthraquinone*, m.p. 218—219°. 3 : 4 : 6 : 1 : 2-$C_6HI_3(CO)_2O$ yields approx. equal amounts of 3 : 4 : 6- and 3 : 5 : 6-*tri-iodo*-2-*benzoylbenzoic acid* (acids, m.p. 257—258° and 225—227°, were isolated), each cyclised at 105° in 25% yield to 1 : 2 : 4-*tri-iodoanthraquinone*, m.p. 202—204°. *o*-$C_6H_4(CO)_2O$ could not be caused to react with *m*-$C_6H_4I_2$. 3 : 4 : 5 : 6 : 1 : 2-$C_6I_4(CO)_2O$ or (I) reacts ($AlCl_3$) with PhOMe, *o*- or *m*-$C_6H_4Me{\cdot}OMe$, but not with *o*-$C_6H_4(OMe)_2$ or 4 : 1 : 2-$C_6H_3Cl(OMe)_2$. I

in iodoanthraquinones is determined by Na–EtOH, followed by digestion of the crude AgI with dil. HNO_3. M.p. are corr. R. S. C.

o-Quinonemono-oxime inner complexes. H. M. Haendler [with G. McP. Smith] (J. Amer. Chem. Soc., 1939, **61**, 2624—2626).—Adding the metal acetate in EtOH or H_2O to phenanthra-9 : 10-quinone-9-oxime in hot EtOH and adjusing the p_H by aq. NH_3 or AcOH to effect coagulation gives coloured *complexes*, $\left(C_{14}H_8\langle^{O\rightarrow}_{N\cdot O}\rangle\right)_2M$, in which M = Cd (unstable compound + xC_5H_5N), Cu, Pb, Mn, UO_2, anhyd. and + 2EtOH. Chrysenequinonemono-oxime gives similar *complexes*, in which M = Cu, Pb, Mn, Ni (prep. by $NiCl_2$), UO_2, anhyd. and + 2EtOH. Cr, Hg, Pd, Rh, and Zn also give complexes. Retenequinone- and 2- and 4-nitrophenanthraquinone-oximes also give complexes. R. S. C.

Sulphonation. VI. Sulphonation of 1 : 2-benzanthraquinone. J. S. Joffe and E. N. Kaschnitzkaja (J. Gen. Chem. Russ., 1939, **9**, 1124—1127).—1 : 2-Benzanthraquinone and 95% H_2SO_4 at 140—150° yield a mixture of 1 : 2-benzanthraquinone-2′-, -3′-, and -4′-sulphonic acids. R. T.

Preparation of dibenzpyrenequinone. I. Reaction of benzanthrone with benzoyl chloride. N. K. Moschtschinskaja (J. Gen. Chem. Russ., 1939, **9**, 1376—1379).—Benzanthrone, BzCl, and $AlCl_3$ at 125°/2 hr. yield a mixture of 2- and 3-benzoylbenzanthrone. The latter is converted quantitatively into dibenzpyrenequinone by passing O_2 through its melt with $AlCl_3$ and NaCl at 155—160°. R. T.

Effect of high-tension electrical discharge on catalytic reaction. IV, V. I. Seto and M. Ozaki (J. Soc. Chem. Ind. Japan, 1939, **42**, 271—274B).—IV. *dl-* + *l*-Menthone (94%) + menthol (6%, free and combined), in paraffin oil, are reduced by H_2–Ni at 135—155° under ordinary pressures (apparatus : A., 1937, I, 470). The system is subjected to a high electric tension which promotes catalytic action of Ni and thus increases speed of reaction. Optimum conditions, viz., 145° for 3 hr., give 78·5% of menthol (I) (*dl-* + *dl*-neo + *-iso-* + -neo*iso*-menthol).

V. Thymol (II) at 140—160° for 2—3 hr. similarly gives 66—68% of (I). Initial formation of menthone (*dl-* + *-iso*-menthone) suggests that (II) gives menthenol, converted into menthone and thence into (I). A. T. P.

***d*-Menthyl phenylurethane, m.p. 112—113° (corr.), $[\alpha]_D^{20}$ +75·7° in $CHCl_3$, and 3 : 5-dinitrobenzoate, m.p. 153—154° (corr.), $[\alpha]_D^{20}$ +771° in $CHCl_3$, and glycuronide, m.p. 120—122°, $[\alpha]_D^{20}$ +6·4° in EtOH [NH_4 salt, m.p. 200—202° (decomp.), $[\alpha]_D^{20}$ +8·1° in H_2O].**—See A., 1939, III, 998.

Intramolecular rearrangements occurring during the dehydration of ditertiary dicyclic glycols of the camphene series. I. L. J. Briusova (J. Gen. Chem. Russ., 1939, **9**, 905—911).—2 : 3-*Dihydroxy*-2 : 3 : 4-*trimethylcamphane*, m.p. 132—135°, formed from 4-methylcamphoquinone and MeMgI, yields on dehydration ($KHSO_4$–Na_2SO_4; 5 hr. at 150—155°) a *ketone*, b.p. 126—127°/20 mm., characterised by a *semicarbazone*, $C_{14}H_{25}ON_3$, m.p. 193—194°. 2 : 3-Dihydroxy-2 : 3-dimethylcamphane similarly gives an unsaturated *ketone*, $C_{12}H_{20}O$, b.p. 104·8—105°/10 mm. (oxime, m.p. 108—112°), isolated through the *semicarbazone*, m.p. 180—181°. Reduction of the ketone with Na–EtOH gives the unsaturated alcohol, $C_{12}H_{22}O$, b.p. 122—123°/10 mm., and with H_2–Raney Ni, the saturated *ketone*, b.p. 110—110·5°/12 mm. Possible structures are discussed and it is concluded that dehydration of the glycols is accompanied by rupture of the dicyclic system and formation of monocyclic ketones. V. A. P.

Action of acetic acid on camphene in presence of boroacetic anhydride or acetic anhydride and boric trioxide. M. Imoto (J. Soc. Chem. Ind. Japan, 1939, **42**, 267—268B; cf. A., 1939, II, 434).—Camphene (I), AcOH, and $B(OAc)_3$ or Ac_2O–B_2O_3 at 110—120° for 23 hr. give esters, hydrolysed to *iso*borneol (reaction *A*). The reaction is reversible; with *iso*bornyl acetate (II) and Ac_2O–B_2O_3–AcOH at 110—120° for 22 hr. the amount of (II) is reduced from 97 to 67%, and some (I) is formed. Addition of H_2SO_4 to reaction *A* at 50—60° for 3—4 hr. gives increased yields. A. T. P.

Intramolecular asymmetric induction. A. McKenzie and A. D. Wood (J.C.S., 1939, 1536—1544).—(−)-*Menthyl H*, m.p. 166—167°, $[\alpha]_D^{20}$ −55·8° in EtOH, *di*-(−)-*menthyl*, m.p. 61—62°, $[\alpha]_D^{20}$ −74° in EtOH, (−)-*bornyl H* (I), m.p. 178—179°, $[\alpha]_D^{20}$ −28·9° in $CHCl_3$, and *di*-(−)-*bornyl* 4 : 4′-*dinitrodiphenate*, m.p. 201—202°, $[\alpha]_D^{20}$ −46·9° in EtOH, are lævorotatory in all solvents and show no sign of intramol. asymmetric induction during prep. Similarly (I) gives (by way of the acid *chloride*, m.p. 48—49°) (+)-*bornyl* (−)-*bornyl* 4 : 4′-*dinitrodiphenate*, m.p. 212—213°, which is inactive although unesterified H ester has a slightly altered α. Kuhn's views (A., 1932, 269) are disputed on the basis of these and other facts. The following are also described. (−)-Menthyl, $[\alpha]_D^{20}$ −81·3° in EtOH, and (−)-*bornyl* m-*nitrobenzoate*, m.p. 76—77°, $[\alpha]_D^{20}$ −36·4° in EtOH; (−)-dimenthyl phthalate, $[\alpha]_D^{20}$ −96·9° in EtOH; di-(−)-bornyl phthalate, new m.p. 104—105°, $[\alpha]_D^{20}$ −82·9° in EtOH; *di*-dl-*bornyl* 4 : 4′-*dinitrodiphenate*, m.p. 200—201°, α 0. Cinchonine, m.p. 220—221°, $[\alpha]_{5461}^{18}$ −185·6° in $CHCl_3$, quinidine, $[\alpha]_D^{20\cdot5}$ −87° in $CHCl_3$, and quinine H 4 : 4′-dinitrodiphenate, m.p. 229—231°, $[\alpha]_D^{21}$ (anhyd.) +102·4°, (+2C_6H_6) +87·2° in $CHCl_3$. [α] of the esters for other solvents are also detailed. R. S. C.

New method of resolving a racemic compound. G. M. Henderson and H. G. Rule (J.C.S., 1939, 1568—1573; cf. A., 1938, II, 286).—By repeating the process previously described on activated lactose a complete micro-resolution of *dl-p*-phenylenebisiminocamphor has been obtained. A partial resolution has been achieved in the case of β-naphtholazomandelic acid. F. R. S.

Vitexin. E. Péteri (J.C.S., 1939, 1635—1637).—Oxidation of vitexin (I) with H_2O_2, Fehling's solution, and $K_3Fe(CN)_6$ gives no new degradation products. Nitration (15% HNO_3) of (I) gives tetranitroapigenin.

Sublimation of (I) with Zn (vac.) gives a *polyphenol*, $C_{15}H_{12}O_6$, acetylated to triacetylapigenin. F. R. S.

Bitter principle from *Andrographis paniculata*, Nees. I. A. Moktader and S. S. Guha-Sircar (J. Indian Chem. Soc., 1939, **16**, 333—338).—Andrographolide, $C_{20}H_{30}O_5$ (I), new m.p. 220° (decomp.), heated with aq. EtOH–KOH and acidified gives iso*andrographolic acid*, $C_{20}H_{32}O_6$, m.p. 156° [*Ba* salt, also obtained from (I) and aq. $Ba(OH)_2$], which with warm aq. NH_3 followed by HCl gives *andrographolic acid*, m.p. 180°. With Br, (I) in conc. HCl gives a *product*, $C_{20}H_{30}O_5Br_2$ (?), m.p. 128—140°, or in AcOH a *compound*, $C_{20}H_{30}O_5Br_2$ (?), m.p. 110—112°. In aq. HBr, (I) gives a *hydrobromide*, m.p. 117—124°; with HCl in AcOH a hydrochloride, m.p. 56—57°. I–ICl_3 shows only one double linking. With Pd–H_2 in MeOH (I) gives *dihydroandrographolide*, m.p. 205° (decomp.), and with $SnCl_2$–HCl an *isomeride*, m.p. 200° (decomp.) (mixed m.p. 183—185°). When heated with Ac_2O–NaOAc for 5—10 min., (I) is unchanged, Gorter's Ac_3 derivative (A., 1914, i, 1204) not being obtained; after 1 hr., a *product*, $C_{40}H_{58}O_9$ (?), is formed. With $POCl_3$, (I) gives a *product*, m.p. 85—90° (decomp.), containing P and Cl, but lacking the CH_2O_2 group of (I); with PhNCO, (I) forms a *product*, m.p. 90—95°. E. W. W.

Ethereal extract of bark of Cajaput tree. M. Isii and Y. Osima (J. Agric. Chem. Soc. Japan, 1939, **15**, 841—842).—Extraction of the bark of *Melaleuca leucadendron*, Linn., yields 20% of material which contains a resinol, *melaleucin*, $C_{28}H_{45}O_3$, m.p. 304° (*monoacetate*, m.p. 280°). J. N. A.

Kikyo root. VIII. Constitutional formula of platycodigenin. IX. Mol. wt. of platycodigenin. M. Tsujimoto and R. Senju (J. Agric. Chem. Soc. Japan, 1939, **15**, 857—861, 862—864; cf. A., 1939, II, 470).—VIII. Platycodigenin, m.p. 242—243°, $[\alpha]_D^{31\cdot7}$ +59·45°, is an unsaturated monobasic acid and gives a positive Liebermann sterol reaction. It can be purified by crystallisation of the K salt or by adsorption on Al_2O_3 and elution with $COMe_2$.

IX. Determination of mol. wt. by titration, Barger's method, micro-Pregl titration, and analysis of K salt confirms the formula $C_{30}H_{48}O_7$. J. N. A.

Velocity of reaction of aldehydes with ammonia. I. Reaction of furfuraldehyde with ammonia. E. K. Nikitin and M. A. Abramova (J. Gen. Chem. Russ., 1939, **9**, 1347—1355).—The velocity of formation of furfuramide at 12·5° is greatest when 2 vols. of a solution containing 27—30 g. of Na_2CO_3 and 7·5—8·5 g. of NH_3 per 100 ml. are added per vol. of aq. furfuraldehyde (I). The concn. of (I) solutions is determined by comparing the time required for appearance of turbidity with that found for solutions of known concn. R. T.

Dihydro-1 : 4-pyrans. VI. Opening and closing of the ring. R. C. Fuson, R. E. Christ, and C. K. Bradsher (J. Org. Chem., 1939, **4**, 401—409).—Et α-hydroxy-δ-2 : 4 : 6-trimethylbenzoylsorbate (I) (*benzoate*, m.p. 109°) is hydrogenated (Raney Ni in EtOH) and then hydrolysed by boiling 10% aq. Na_2CO_3 to 2-*mesityl*-5 : 6-*dihydro*-1 : 4-*pyran*-6-*carboxylic acid* (II), m.p. 149—150°, which is not hydrogenated in presence of PtO_2, Ni, or Pt, is not reduced by Na–Hg, but is converted by boiling HI containing red P into adipic acid. (II) is unchanged by alkaline H_2O_2 but is oxidised by O_3 or boiling dil. HNO_3 to 2 : 4 : 6-$C_6H_2Me_3{\cdot}CO_2H$. Br in CCl_4 converts (II) into a *compound*, $C_{15}H_{17}O_3Br$, m.p. 139°. Treatment of (II) with conc. HNO_3 and conc. H_2SO_4 gives 3-*nitro*-2-3′ : 5′-*dinitromesityl*-5 : 6-*dihydro*-1 : 4-*pyran*-6-*carboxylic acid*, m.p. 255° [*Me* ester (III), m.p. 162—163°]. Boiling MeOH containing conc. H_2SO_4 transforms (V) into *Me* α-*hydroxy*-δ-2 : 4 : 6-*trimethylbenzoylvalerate*, m.p. 43—44°. The crude ester obtained from (I) gives on alkaline hydrolysis an oily acid which is shown to contain α-hydroxy-δ-2 : 4 : 6-trimethylbenzoylvaleric acid by the isolation of the 1-*naphthylurethane*, $C_{26}H_{27}O_5N$, m.p. 145—146°. Under reduced pressure the acid can be distilled almost without residue but is converted under these conditions into (II). Oxidation by $KMnO_4$ of the hydrolysed pure ester and treatment of the non-cryst. acid with conc. H_2SO_4–conc. HNO_3 affords 3 : 5 : 2 : 4 : 6-$(NO_2)_2C_6Me_3{\cdot}CO_2H$. Nitration of the ester yields (III). With MgPhBr the ester gives a *solid*, $C_{27}H_{30}O_3$, m.p. 134—135°, and a liquid which has not been identified. Liquid NH_3 converts the ester into the *amide*, m.p. 111·5—112·5°. Hydrogenation (PtO_2 in acidic EtOH) of (I) gives 10—15% of (II) and an oil from which by treatment with Na_2CO_3, followed by *p*-$C_6H_4Ph{\cdot}CH_2{\cdot}COBr$, p-*phenylphenacyl* δ-2 : 4 : 6-*trimethylbenzoylvalerate*, m.p. 79°, is isolated; fractional distillation of the oil and hydrolysis of the fraction of highest b.p. yields (?) α-*keto*-ε-*hydroxy*-ε-2 : 4 : 6-*trimethylphenylhexoic acid*, m.p. 81° (*phenylhydrazone*, m.p. 103—104°). δ-2 : 4 : 6-*Trimethylbenzoylvaleric acid* (IV), m.p. 60°, is obtained with αδ-di-2 : 4 : 6-trimethylbenzoylbutane, m.p. 106°, by the action of $AlCl_3$ on adipic anhydride and mesitylene in CS_2. Bromination of (IV) in CCl_4 at 0° affords the *compound*, $C_{15}H_{19}O_3Br$, m.p. 90—92°, whilst oxidation of it gives $(CH_2{\cdot}CO_2H)_2$ and mesitylglyoxylic acid. H. W.

Structure of fluorescein, sulphonefluorescein, and their halogenated derivatives. R. B. Sandin, A. Gillies, and S. C. Lynn (J. Amer. Chem. Soc., 1939, **61**, 2919—2922).—Bromination (Phillips, A., 1932, 400) of fluorescein and sulphonefluorescein gives first the 4 : 5-Br_2-derivatives, since hydrolysis of the products gives 2 : 1 : 3-$C_6H_3Br(OH)_2$. 4 : 5-Dibromofluorescein, m.p. 285°, gives a diacetate, m.p. 228—229° (lit. 211°). $SnCl_2$–HCl in dioxan–AcOH (10 : 1) converts tetrabromofluorescein into 2 : 7-*dibromofluorescein*, m.p. 300—301° (*diacetate*, m.p. 259° after darkening), hydrolysed to 4 : 1 : 3-$C_6H_3Br(OH)_2$ and (?) o-5′-*bromo*-2′ : 4′-*dihydroxybenzoylbenzoic acid*, m.p. 240—241° after darkening and sintering. 2 : 7-*Dichloro*-4 : 5-*dibromofluorescein* [prep. from the 2 : 7-Cl_2-compound (I) (modified prep.) by Br (2 mols.)] similarly gives (I). These replacements indicate a fixed bond structure for the fluorescein derivatives. R. S. C.

Simple hydroxychromans and hydroxycoumarans. P. Karrer, R. Escher, and H. Rentschler (Helv. Chim. Acta, 1939, **22**, 1287—1291;

cf. A., 1938, II, 450; 1939, II, 174).—γ-Methyl-Δ^{β}-butenyl bromide, from CH_2:$CH{\cdot}CMe_2{\cdot}OH$ and PBr_3 in light petroleum at −15° and subsequently at 10—15°, and trimethylquinol (I) in presence of $ZnCl_2$ give exclusively 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman, m.p. 95°. The prolonged action of $COEt{\cdot}CHNa{\cdot}CO_2Et$ on (I) in C_6H_6 at room temp. yields 4-*hydroxy*-3 : 5 : 6-*trimethyl*-1-*ethylcoumarone*, m.p. 108°, reduced (Pd–C in MeOH) to the corresponding *coumaran* (II), m.p. 120° (*allophanate*, m.p. 214°). (II) is obtained as by-product of the condensation of (I) with crotyl bromide. H. W.

Steric relationships of α-tocopherol and further investigation of the lower homologues of α-tocopherol. P. Karrer, H. Koenig, B. H. Ringler, and H. Salomon (Helv. Chim. Acta, 1939, 22, 1139—1145; cf. A., 1939, II, 335).—The 3 : 5-dinitrobenzoate, allophanate, and *p*-nitrophenylurethane of *dl*-α-tocopherol (I) from synthetic phytol (II) have been further purified so that their m.p. agree with those of the corresponding compounds prepared from natural (II). The compounds are therefore identical and hence *dl*-α-tocopherol (III) from natural (II) is a racemic compound or mixture of racemic compounds with respect to the asymmetric centres δ and θ. Conclusions with regard to the spatial relationships in the aliphatic side-chain of natural (I) are not warranted since it is not impossible that racemisation occurs during the isolation of (II) from chlorophyll or that only a definite form of (IV) is used in the enzymic synthesis of (III) in the plant. The bromocamphorsulphonate of (I) has now been separated into a series of fractions of differing m.p. so that (I) is almost certainly a mixture of diastereoisomerides; it cannot at present be decided whether the sample, m.p. 52°, is identical with the derivative of natural (I). Biologically there appears no measurable difference between natural (I) and the diastereoisomeric forms of synthetic (I). (I) (5 : 7 : 8-trimethyltocol) is biologically the most active of all the tocols. Elimination of Me from the aromatic nucleus somewhat diminishes the activity (apparently least with 5 : 7-dimethyltocol) and replacement of Me by Et is accompanied by slight weakening of the activity. Improvements in the methods of preparing *dl*-5 : 8- and -7 : 8-dimethyltocol are recorded. H. W.

Vitamin-*E*. XIV. Absorption spectra of tocopherols, chromans, coumarans, and related compounds. T. J. Webb, L. I. Smith, W. A. Bastedo, jun., H. E. Ungnade, W. W. Pritchard, H. H. Hoehn, S. Wawzonek, J. W. Opie, and F. L. Austin (J. Org. Chem., 1939, 4, 389—396).—The absorption spectra of *o*-allyl-, 3 : 5 : 6-trimethyl-2-allyl-, and 2 : 6-dihexenyl-phenol, 2 : 2-dimethyl-3 : 4-dihydrocoumaran, 1-methyl-1 : 2-dihydro- and 1 : 3 : 5 : 6-tetramethyl-1 : 2-dihydro-benzfuran, 6-methoxy-2 : 2 : 3-trimethyl-3 : 4-dihydro- and 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethyl-3 : 4-dihydro-coumaran, 4-hydroxy-1 : 3 : 5 : 6-tetramethyl-1 : 2-dihydrobenzfuran, 4-hydroxy-1 : 3 : 5 : 6-tetramethylbenzfuran, 6-hydroxy-5 : 7 : 8-trimethyl-3 : 4-dihydro- and 6-hydroxy-3-carbethoxy-7 : 8-dimethyl-coumarin, 6-hydroxy-2 : 5 : 7 : 8-tetramethyl-2-hexadecyl-3 : 4-dihydro- and 6-hydroxy-2 : 5 : 7-trimethyl-2-hexadecyl-3 : 4-dihydro-coumaran are described and discussed. H. W.

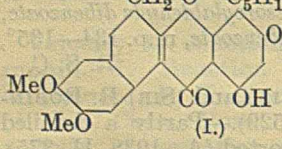
Vitamin-*E*. XV. Extension of the analytical method of Furter and Meyer. H. E. Ungnade and L. I. Smith (J. Org. Chem., 1939, 4, 397—400).—Examination of several simple chromans and coumarans by the colorimetric method of Furter and Meyer (A., 1939, III, 404) shows the method to be sp. for all tocopherols and for 6-hydroxychromans (I) generally. By this means it is possible to distinguish clearly between (I) and 4-hydroxycoumarans. H. W.

Constitution of natural tannins. VI. Colouring matters derived from 2 : 5-dihydroxyacetophenone. A. Russell and S. F. Clark (J. Amer. Chem. Soc., 1939, 16, 2651—2658; cf. A., 1937, II, 206).—Passage of dry HCl into an EtOAc solution of 2 : 5 : 1-$(OBz)_2C_6H_3{\cdot}COMe$ and 3 : 4 : 1-$(OBz)_2C_6H_3{\cdot}CHO$ at 0° for several days gives 2 : 5 : 3′ : 4′-*tetrabenzoyloxychalkone*, m.p. 182—184°, hydrolysed by KOH (special procedure essential in this and other cases) to a mixture of 2 : 5 : 3′ : 4′-*tetrahydroxychalkone* (I), m.p. 225—227°, and 6 : 3′ : 4′-*trihydroxyflavanone* (II), m.p. 218—220° (decomp.). Solid (I) and (II) are stable, but in EtOH an equilibrium mixture is formed, containing, particularly when hot, much (II). Zn dust and HCl–EtOH reduce (II) alone or in admixture with (I) to *bis*-(6 : 3′ : 4′-*trihydroxy*)*flavopinacol*, a light red amorphous material indistinguishable by colour reactions and in adsorption on hide powder from hemlock or mimosa tannins. Similar condensations using other aldehydes give 2 : 5 : 4′-*tri*-, m.p. 134—136°, 2 : 5 : 3′-*tri*-, m.p. 174—175°, 2 : 5 : 2′-*tri*-, m.p. 137—139°, 2 : 5 : 2′ : 4′-*tetra*-, m.p. 137—139°, and 2 : 5 : 2′ : 4′ : 6′-penta-, an oil, -*benzoyloxychalkone*, 2 : 5 : 4′-*tribenzoyloxy*-3′-*methoxychalkone*, m.p. 145—147°, and 2 : 5 : 2′ : 4′-*tetrabenzoyloxy*-6′-*methylchalkone*, m.p. 125—127°, and thence by hydrolysis 2 : 5 : 4′-, m.p. 222—224°, and 2 : 5 : 3′-*trihydroxychalkone*, m.p. 204—206°, 2 : 5 : 4′-*trihydroxy*-3′-*methoxychalkone*, m.p. 172—173°, 6 : 3′-, m.p. 234—236°, and 6 : 2′-*dihydroxyflavanone*, m.p. 178—180° (decomp.), 2′ : 5′-*di*-, $+0{\cdot}5H_2O$, m.p. 175° (decomp.), 7 : 2′ : 5′-*tri*-, $+5{\cdot}5H_2O$, m.p. 190° (decomp.), and 5 : 7 : 2′ : 5′-*tetra-hydroxy*-2-*phenylbenzpyrylium chloride*, $+2H_2O$, m.p. >300°, and 7 : 2′ : 5′-*trihydroxy*-2-*phenyl*-5-*methylbenzpyrylium chloride*, $+H_2O$, m.p. 285—287° (decomp.). m-*Benzoyloxybenzaldehyde*, m.p. 37—38°, *resorcylaldehyde dibenzoate*, m.p. 98°, and *orcylaldehyde dibenzoate*, m.p. 134—135°, are also described. R. S. C.

Dunnione. I. J. R. Price and (Sir) R. Robinson (J.C.S., 1939, 1522—1529).—Partly a detailed account of work already reported (A., 1938, II, 375). Dunnione (I) [*semicarbazone* (II), m.p. 232—233°; 2 : 4-*dinitrophenylhydrazone*, m.p. 266—268°] is probably 2 : 3 : 3-trimethyl-6 : 7-benzcoumaran-5 : 6-quinone, although other structures of the heterocyclic ring are possible, and its reactions are interpreted on this basis. With Zn dust and Ac_2O–C_5H_5N it gives *dihydrodunnione diacetate*, m.p. 143—144°, which with $NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$ gives only (II). With *o*-$C_6H_4(NH_2)_2$ it gives a (?) *phenazine*, $C_{21}H_{18}ON_2$, dimorphic, m.p. 140—141° and ~125°. It dissolves slowly in 5% aq. NaOH, from which the red chelated

Na salt is then removed by EtOAc or *iso*-C_5H_{11}·OH; immediate neutralisation gives a colourless solution, probably containing *o*-C_6H_4<CO·C·OH / CO·C·CMe$_2$·CHMe·OH (becomes red at once with alkali), and an excess of acid regenerates (I). After (I) has been heated in alkali, acidification gives allo*dunnione* (II), *o*-C_6H_4·C(CO—O)(CO—C·CMe$_2$·CHMe), m.p. 161—162° [2 : 4-*dinitrophenylhydrazone*, m.p. 315° (decomp.) after darkening at ~290°], a mechanism for formation of which is suggested. When kept in 5% NaOH at room temp. or heated in 20% HCl, (I) gives α-*dunnione* [2 : 3 : 3-*trimethyl*-5 : 6-*benzcoumaran*-3 : 7-*quinone*], m.p. 120—122° (2 : 4-*dinitrophenylhydrazone*, m.p. 278—280°), converted by alkali into (I) and (II) and by conc. H_2SO_4 at 100° into β-iso*dunnione* [4 : 4-*dimethyl*-7 : 8-*benzchroman*-5 : 6-*quinone*], m.p. 129—131°. With boiling 20% HCl this gives α-iso*dunnione* [4 : 4-*dimethyl*-6 : 7-*benzcoumaran*-5 : 8-*quinone*], m.p. 118—119°. With $KMnO_4$, (I) gives *o*-$C_6H_4(CO_2H)_2$; with H_2O_2–aq. NaOH it gives MeCHO, *o*-$C_6H_4(CO_2H)_2$, and (?) α-iso*propylphthalide*-α-*carboxylic acid* (III), m.p. 205—206°. With H_2O_2–aq. AcOH, (II) gives *o*-$C_6H_4(CO_2H)_2$, but with aq. H_2O_2–NaOH it gives MeCHO and (III), formation of which is postulated as involving fission of two rings and loss of MeCHO by a reversed aldol change. Alkaline H_2O_2 generates *o*-$C_6H_4(CO_2H)_2$ and $COMe_2$ from lapachol or β-lapachone (2 : 4-*dinitrophenylhydrazone*, sinters at ~250°, m.p. 283—285°; with CrO_3 gives 0·59 AcOH). α-*Lapachone*-2 : 4-*dinitrophenylhydrazone* melts at 277—278°. CrO_3 forms 1·3 AcOH from (I) or (II) (proof of a Me in a side-chain and a CMe_2) and 0·5 AcOH from (III) (proof of CMe_2). R. S. C.

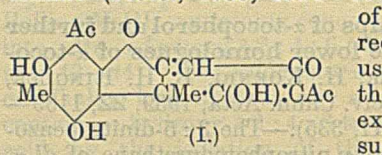
Sumatrol. II. Synthesis of dehydrotetrahydrosumatrol. T. S. Kenny, A. Robertson, and (in part) S. W. George (J.C.S., 1939, 1601—1604).—Phlor*iso*valerophenone, m.p. 145° (improved prep.; 2 : 4-*dinitrophenylhydrazone*, m.p. 196°), is reduced (Zn–Hg) to iso*amylphloroglucinol*, m.p. 126°, which condenses with Me 2-cyanomethyl-4 : 5-dimethoxy*phenoxyacetate*, followed by hydrolysis, to give *tetrahydrosumatrolic acid*, m.p. 206°, and a phenolic substance, $C_{22}H_{30}O_5$, m.p. 134° (acetate, m.p. 51°). The acid and Ac_2O–NaOAc yield *O*-diacetyl-, hydrolysed to dehydrotetrahydrosumatrol (I), identical with the natural specimen. The probable structure suggested is (I). F. R. S.



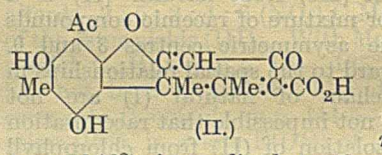
(I.)

Sterols. LXXIII. Reactions of digitogenin and gitogenin. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1939, **61**, 2724—2726).—Prep. of gitogenin (I), m.p. 266—268° [diacetate (II), m.p. 241—243°], from *Chlorogalum pomeridianum*, and of digitogenin (III) is described. (I) and (III) both form digitonides. Zn–Hg–HCl has no effect on (I) or (III). H_2–PtO_2 in AcOH at 70°/3 atm. gives *dihydro-gitogenin*, m.p. 195—197° (*tri*-p-*nitrobenzoate*, m.p. 189—191°; stable to SeO_2), and *-digitogenin*, m.p. 184—186°. SeO_2 oxidises (I) and (III). Br converts (II) into a *Br*-derivative, m.p. 219—220° (decomp.), reduced by Na in abs. EtOH to (I). CrO_3–AcOH at 95° oxidises (II) to *gitogenin lactone diacetate*, m.p. 248—251°, hydrolysed by KOH–EtOH to *gitogenin lactone*, m.p. 276—278° (*dibenzoate*, m.p. 275—278°). Similarly are obtained *bromodigitogenin triacetate*, m.p. 142° (decomp.), and *digitogenin lactone*, m.p. 279—282° (*triacetate*, m.p. 281—283°). R. S. C.

Usnic acid. VII. Analogues of usnolic acid. R. T. Foster, A. Robertson, and (in part) T. V. Healy (J.C.S., 1939, 1594—1601).—A brief review of the structures recently proposed for usnic acid (I) leads to the adoption of the expression shown, first suggested (Robertson, *et al.*, A., 1937, II, 347; cf. Asahina *et al.*, A., 1939, II, 32), and supported by the work of Schöpf and Ross (A., 1939, II, 82). A new structure for usnolic acid (II) is deduced and its formation from (I) is discussed. The comparison of the analogues of (II) gives independent evidence in support of structure (II). 3-Methoxyphenoxyacetone (2 : 4-*dinitrophenylhydrazone*, m.p. 146°) is cyclised to 6-methoxy-3-methylcoumarone, which with HCN–HCl gives the 2-*formyl* compound, m.p. 105° (2 : 4-*dinitrophenylhydrazone*, m.p. 262°). This aldehyde with hippuric acid–Ac_2O affords the *azlactone*, m.p. 194°, hydrolysed (NaOH) to 6-*methoxy*-3-*methylcoumarone*-2-*pyruvic acid*, m.p. 196° (*oxime*, m.p. 166°), which with H_2O_2 yields the *-acetic acid*, m.p. 145° (*amide*, m.p. 162°). The chloride of the acetic acid condenses with $CH_2Ac·CO_2Et$ to give 6′-*methoxy*-3′ : 3-*dimethyl*-2′ : 3′-*dihydrobenzofurano*-(2′ : 3′ : 5 : 4)-$\Delta^{2\cdot5}$-cyclo*hexadienone*-2-*carboxylic acid* (+H_2O), m.p. 147° (*Me* ester, m.p. 101°; *Et* ester, m.p. 122°).



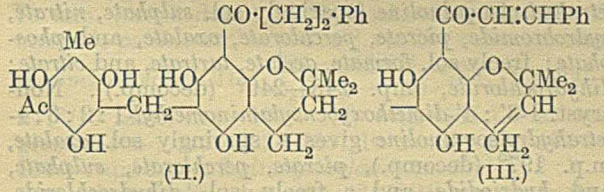
(I.)



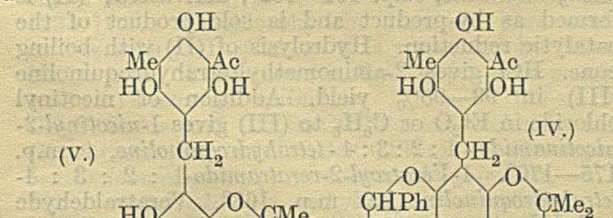
(II.)

2-Hydroxy-4-methoxy-3-methylacetophenone and $CH_2Br·CO_2Et$–K_2CO_3 give Et 3-methoxy-6-acetyl-2-methylphenoxyacetate, b.p. 180—185°/15 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 167°; *acid*, m.p. 133°), which is cyclised to *Et* 6-*methoxy*-3 : 7-*dimethylcoumarone*-2-*carboxylate*, m.p. 75°, hydrolysed to the *acid*, m.p. 225° (decomp.). This acid with NaOAc–Ac_2O forms 6-*methoxy*-3 : 7-*dimethylcoumarone*, b.p. 92—93°/0·1 mm. (*picrate*, m.p. 92°), which with HCl–HCN yields the 2-*formyl* derivative, m.p. 102° (2 : 4-*dinitrophenylhydrazone*, m.p. 284°). The aldehyde condenses with hippuric acid to the *azlactone*, m.p. 218°, hydrolysed to 6-*methoxy*-3 : 7-*dimethylcoumarone*-2-*pyruvic acid*, m.p. 228° [*oxime*, m.p. 162° (decomp.)], and some 6-*methoxy*-2 : 3 : 7-*trimethyl-coumarone*, m.p. 41° (reduced to the *-coumaran*). Oxidation (H_2O_2) of the pyruvic acid gives 6-*methoxy*-3 : 7-*dimethylcoumarone*-2-*acetic acid*, m.p. 158° (*amide*, m.p. 179°), the chloride of which condenses with $CH_2Ac·CO_2Et$ to form 6′-*methoxy*-3′ : 7′ : 3-*trimethyl*-2′ : 3′-*dihydrobenzofurano*-(2′ : 3′ : 5 : 4)-$\Delta^{2:5}$-cyclo-*hexadienone*-2-*carboxylic acid*, m.p. 150° (*Et* ester, m.p. 115°). F. R. S.

Rottlerin. IV, V. Tetrahydro*allo*rottlerin. A. McGookin, A. Robertson, and E. Tittensor (J.C.S., 1939, 1579—1587, 1587—1593).—IV. Octahydrorottlerone (I), previously assigned the structure of the H_4-compound (cf. A., 1939, II, 485), is hydrolysed by 10% NaOH or NaOH–Zn to a mixture of 5 : 7-dihydroxy-8-β-phenylpropionyl-2 : 2-dimethylchroman, Ph·[CH_2]·CO_2H, and 5 : 7-dihydroxy-2 : 2-dimethylchroman [*bisbenzeneazo*-derivative, m.p. 256° (decomp.)]. 5 : 7-Dihydroxy-8-acetyl-2 : 2-dimethylchroman and CH_2O give 5 : 7 : 5′ : 7′-*tetrahydroxy*-8 : 8′-*diacetyl*-2 : 2 : 2′ : 2′-*tetramethyl*-6 : 6′-*dichromanylmethane*, m.p. 240°, whilst the corresponding -8-β-phenylpropionyl compound similarly affords (I). *C*-Methylphloracetophenone with CH_2O gives 2 : 4 : 6 : 2′ : 4′ : 6′-*hexahydroxy*-5 : 5′-*diacetyl*-3 : 3′-*dimethyldiphenylmethane*, m.p. 291° (decomp.) [(*OMe*)$_6$-derivative, m.p. 103°], also obtained together with (I) from tetrahydrorottlerin (II) and AcOH. Reinvestigation of a no. of derivatives of rottlerin (III) has not evaluated (III) as either $C_{30}H_{28}O_8$ or $C_{31}H_{30}O_8$ but mol. wt. determinations exclude formulæ based on C_{60} or C_{62}. The (*OMe*)$_3$-*ether*, m.p. 153°, of (II) and O-*tetramethylrottlerone*, m.p. 136°, are described. The isolation of 2 : 4 : 6-trihydroxy-5-acetyl-3-methylazobenzene from (II) and diazoaminobenzene confirms the presence of *C*-methylphloracetophenone residue in (III). This residue is joined to the rest of the mol. by CH_2 and hence the structures (II) and (III) are assigned. The available evidence shows (III) not to contain a lactone group.



V. *iso*Rottlerin (IV) (cf. Brockmann *et al.*, A., 1938, II, 334) is hydrogenated, according to the conditions, to the H_2-derivative and *tetrahydro*a*llo*r*ottlerin* (V), m.p. 241°. Methylation (Me_2SO_4–K_2CO_3) of (V) gives the (*OMe*)$_5$-derivative, m.p. 136°, which is hydrogenated (Pd–C) to O-*pentamethyltetrahydro*a*llo*r*ottlerin*, m.p. 101°. Methylation of dihydro*iso*rottlerin affords O-*tetra*-, m.p. 149°, and -*penta-methyldihydro*iso-*rottlerin*, m.p. 135°. Diazoaminobenzene and (V) yield 2 : 4 : 6-trihydroxy-5-acetyl-3-methylazobenzene and 8-*benzeneazo*-5 : 7-*dihydroxy*-6-β-*phenylpropionyl*-2 : 2-*dimethylchroman*, m.p. 162°, identical



with a synthetic specimen, and not identical with either 6-*benzeneazo*-5 : 7-*dihydroxy*-8-β-*phenylpropionyl*-, m.p. 181°, or -8-*acetyl*-2 : 2′-*dimethylchroman*, m.p. 232°. These results indicate that (V) is constituted as shown. NaOH (4%) and (V) give *octahydro*a*llo*-*rottlerone* (VI), m.p. 175—175·5°, which has properties similar to those of (I). 5 : 7-Dihydroxy-6-β-phenylpropionyl-2 : 2′-dimethylchroman and CH_2O afford (VI), whilst the corresponding 6-Ac derivative gives 5 : 7 : 5′ : 7′-*tetrahydroxy*-6 : 6′-*diacetyl*-2 : 2 : 2′ : 2′-*tetramethyl*-8 : 8′-*dichromanylmethane*, m.p. 209°. The conversion of (III) into (V) by way of (IV) is explained and the structure which has been deduced for (IV) is supported by its behaviour on hydrogenation and methylation. F. R. S.

Cyclic acetals of furfuraldehyde. E. J. Salmi and I. J. Jansson (Suomen Kem., 1939, **12**, B, 28—30; cf. A., 1938, II, 427).—Equimol. amounts of furfuraldehyde (I) and $(CH_2·OH)_2$ in hot C_6H_6 containing *p*-$C_6H_4Me·SO_3H$ give the *ethylene acetal* (~70%), b.p. 91—93°/16 mm., of (I). Similarly prepared, the *αβ-propylene* (78%), *αγ-propylene*, and *αγ-butylene acetal*, have b.p. 97—99°/19—21 mm., 114·8—116·5°/16 mm., and 121·5—122·5°/18—20 mm., respectively. J. L. D.

Thio-compounds derived from *o*-aroylbenzoic acids. J. O'Brochta and A. Lowy (J. Amer. Chem. Soc., 1939, **61**, 2765—2768).—*Di-α-phenylphthalidyl sulphide* (I), $(o\text{-}C_6H_4{<}^{CPh=}_{CO-}{>}O)_2S$, m.p. 247°, is obtained from *o*-$C_6H_4Bz·CO_2H$ (II) by P_2S_5 in hot C_6H_6 or alone at 115°, or from *o*-$C_6H_4Bz·COCl$ and H_2S in hot C_6H_6. It is converted by 5% KOH–EtOH, CrO_3– or HNO_3–AcOH, or $Pb(OAc)_2$–EtOH–H_2O into (II). With H_2SO_4, (I) gives anthraquinone. 30% H_2O_2–AcOH converts (I) into (II) and α-phenylphthalide. Cu dust or Ag converts (I) in cymene into di-α-phenylphthalidyl, m.p. 265—266°. With $AlCl_3$ and C_6H_6, (I) gives thiodiphenylphthalide, $o\text{-}C_6H_4{<}^{CPh_2}_{CO-}{>}S$, m.p. 162°, converted by AcOH–H_2O_2 into αα-diphenylphthalide and by P_2S_5 into dithiodiphenylphthalide. With P_2S_5 in boiling xylene, (II) gives 2-*phenyl*-3 : 4-*benzthiophen*, m.p. 236—237°. *p*-$C_6H_4Me·CO·C_6H_4·CO_2H$-*o* and *p*-$C_6H_4Cl·CO·C_6H_4·CO_2H$-*o* give similarly *di*-α-p-*tolyl*-, m.p. 212°, and *di*-α-p-*chlorophenyl-phthalidyl sulphide*, m.p. 232°, *di*-α-p-*tolyl*-, m.p. 247—248°, and *di*-α-p-*chlorophenyl-phthalidyl*, m.p. 247°, α-*p*-tolyl, m.p. 128°, and α-p-*chlorophenyl-phthalide*, m.p. 124°, and 2-p-*tolyl*-, m.p. 217°, and 2-p-*chlorophenyl*-3 : 4-*benzthiophen*, m.p. 241—242°. R. S. C.

Photo-oxidation of pyrrole. F. Bernheim and J. E. Morgan (Nature, 1939, **144**, 290).—Pyrrole dissolved in H_2O, EtOH, or $COMe_2$ and mixed with $0·5 \times 10^{-4}$M-methylene-blue (I) rapidly absorbs O_2 in light but not in the dark. The rate of O_2 uptake is a linear function of the light intensity, and effective λλ lie between 5200 and 5800 A. Eosin, but not fluorescein, can replace (I). No decarboxylation or deamination occurs. The cryst. product, C 49·1, H 5·3, N 14·1%, m.p. 102·5°, yield 58%, gives 72% of succinic acid and 14% of NH_3-nitrogen on alkaline hydrolysis. *N*-Methyl- and -ethyl-pyrrole are also oxidised under the same conditions, but only 1 instead of 2 O per mol. is taken up. L. S. T.

Formation of 2 : 3 : 4 : 6-tetrabromopyridine during bromination of 2 : 6-dibromopyridine at about 500°. J. P. WIBAUT and A. F. BICKEL (Rec. trav. chim., 1939, **58**, 994—997).—Bromination of 2 : 6-dibromopyridine in the gaseous phase, in presence of pumice, at 510—520°, gives 2 : 4 : 6-tribromo- and 2 : 3 : 4 : 6-*tetrabromo-pyridine*, m.p. 105·3—106° (cf. 2 : 3 : 5 : 6-isomeride, A., 1932, 1260), and a small amount of Br_5-derivative, m.p. 209—210°.

A. T. P.

Pyridine series. I. Improved synthesis of 2 : 3-dimethylpyridine and conversion of the latter into an analogue of thiamin. J. FINKELSTEIN and R. C. ELDERFIELD (J. Org. Chem., 1939, **4**, 365—375).—Addition of $Br{\cdot}[CH_2]_3{\cdot}OEt$ to $CHAcNa{\cdot}CO_2Et$ in abs. EtOH gives *Et δ-methoxy-α-methylvalerate*, b.p. 96—97°/13 mm., hydrolysed to the *acid*, b.p. 137—139°/11 mm. If the substances react in dioxan the product is *Et α-methyl-α-γ-ethoxypropylacetoacetate* (I), b.p. 141—143°/16 mm., and an unidentified *substance*, b.p. 128—130°/0·5 mm. When heated with NaOH–aq. EtOH at 250° under H_2 at 1000 lb. per sq. in. (I) yields *ζ-ethoxy-γ-methyl-n-hexan-β-one* (II), b.p. 96—99°/17 mm., and a *compound*, b.p. 141—143°/17 mm. At 100° (II) is transformed by AcOH saturated with HBr at 0° into ζ-bromo-γ-methyl-*n*-hexan-β-one, b.p. 70—74°/1·5 mm., which is converted by 10% NH_3–abs. EtOH into the very hygroscopic 2 : 3-dimethyltetrahydropyridine (III), b.p. 154—157° (picrate, m.p. 154—157°). Dehydrogenation of (III) with Zn dust gives a small yield of 2 : 3-dimethylpyridine (IV), b.p. 162—164° (picrate, m.p. 187—188°). In model experiments it is shown that 2-methylpyridine (V) is converted into C_5H_5N by $AgNO_3$ in 10% AcOH at 180°, Me being lost, and that 2-methyl-5-ethylpiperidine is dehydrogenated by Pd–asbestos at 270—280° without loss of alkyl groups. In this manner (III) is satisfactorily dehydrogenated to (IV). Successive addition of PhBr, (V), and CH_2O to Li in abs. Et_2O leads to 2-β-hydroxyethylpyridine, b.p. 88—90°/2 mm. [platinichloride, m.p. 176° (decomp.)], oxidised by boiling aq. $KMnO_4$ containing K_2CO_3 to picolinic acid. Similarly (IV) yields *3-methyl-2-β-hydroxyethylpyridine* (VI), b.p. 94—95°/1 mm. (*picrate*, m.p. 137—138°). Addition of (VI) to a suspension of 4-amino-2-methyl-5-bromomethylpyrimidine hydrobromide in light petroleum at 100° gives *1-4′-amino-2′-methyl-5′-pyrimidylmethyl-2-β-hydroxyethylpyridinium bromide hydrobromide* (VII), m.p. 240—245° (decomp.); *1-4′-amino-2′-methyl-5′-pyrimidylmethyl-3-methyl-2-β-hydroxyethylpyridinium bromide hydrobromide* (VIII), m.p. 240—242° (decomp.), is obtained similarly. (VII) and (VIII) show no antipolyneuritic activity but approximate to the activity of thiamin as measured by carbon dioxide evolution in the yeast test.

H. W.

Derivatives of 2-aminomethyltetrahydroquinoline and -*iso*quinoline. A. GASSMANN and H. RUPE (Helv. Chim. Acta, 1939, **22**, 1241—1262).—Gradual addition of BzCl to a solution of KCN and 6-methoxyquinoline, b.p. 146—148°/11 mm., m.p. 28°, in H_2O at 5° affords *6-methoxy-1-benzoyl-1 : 2-dihydroquinoline-2-nitrile*, m.p. 127°, converted by NH_2OH in MeOH at −3° into the *amidoxime*, m.p. 148—149° (decomp.), and (?) *6-methoxyquinoline-2-nitrile*, m.p. 176—177°, transformed by conc. HCl–Et_2O into the corresponding *amide*, m.p. 202—203° (*hydrochloride*, m.p. 237—238° after softening at 225°), and hydrolysed by boiling conc. HCl to *6-methoxyquinoline-2-carboxylic acid*, m.p. 235—236° (decomp.) after softening at 233—234° (*Na* salt). (I) is reduced (freshly reduced Na in EtOAc) by H_2 at ~90°/120 atm. to *6-methoxy-2-benzamidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline* (II), m.p. 131—132° (*NO*-derivative, m.p. 138—139°). Boiling conc. HCl slowly hydrolyses (II) to *6-methoxy-2-aminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline*, b.p. 196—197°/12 mm. (*tartrate*, decomp. 195°; *perchlorate*, m.p. 278°; *dihydrochloride*, m.p. 224—225°), which is condensed with piperonal and then reduced (H_2 at 65°/100 atm.; Ni) to *6-methoxy-2-3′ : 4′-methylenedioxybenzylaminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 53—54° (sparingly sol. *sulphate, nitrate, phosphate, oxalate, perchlorate, picrate, mono-*, m.p. 212—213°, and *di-*, m.p. 179—180° after softening at 171°, *-hydrochloride*). Similarly (I) and veratraldehyde afford a non-cryst. Schiff's base, hydrogenated to *6-methoxy-2-3′ : 4′-dimethoxybenzylaminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline* (sparingly sol. *sulphate, nitrate, phosphate, formate, oxalate, perchlorate, picrate*; freely sol. *acetate, citrate, tartrate*; *hydrochloride*, m.p. 182—183° after softening at 179°). 1-Aminomethyltetrahydro*iso*quinoline and piperonal give a non-cryst. Schiff's base, hydrogenated to *1-3′ : 4′-methylenedioxybenzylaminomethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline* [sparingly sol. *sulphate, nitrate, hydrobromide, picrate, perchlorate, oxalate*, and *phosphate*; freely sol. *formate, acetate, tartrate*, and *citrate*; *dihydrochloride*, m.p. 248—249° (decomp.)]. Non-cryst. *1-3′ : 4′-dimethoxybenzylaminomethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline* gives a sparingly sol. *oxalate*, m.p. 197° (decomp.), *picrate, perchlorate, sulphate*, and *hydriodide* and a freely sol. *dihydrochloride*, m.p. 221° (decomp.), *hydrobromide, nitrate, phosphate, acetate, tartrate*, and *citrate*. Improved methods of obtaining 1-benzoyl-1 : 2-dihydroquinoline-2-nitrile and 2-benzamidomethyltetrahydroquinoline (II) are indicated. Reduction of 1-nitroso- by Zn dust in EtOH–50% AcOH at 0° gives *1-amino-2-benzamidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 156° [*picrate*, m.p. 165° (decomp.)], which shows all the properties characteristic of a hydrazine and gives a *benzylidene*, m.p. 158—159°, *piperonylidene*, m.p. 184—185° after softening at 182°, and an *α-phenylethylidene*, m.p. 161—162°, derivative; (II) is formed as by-product and is sole product of the catalytic reduction. Hydrolysis of (II) with boiling conc. HCl gives 2-aminomethyltetrahydroquinoline (III) in 93—95% yield. Addition of nicotinyl chloride in Et_2O or C_6H_6 to (III) gives *1-nicotinyl-2-nicotinamido-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 175—176°. *1-Veratroyl-2-veratramido-1 : 2 : 3 : 4-tetrahydroquinoline* has m.p. 168°. Veratraldehyde and (III) give a non-cryst. product (*picrate*), hydrogenated (Ni in MeOH) to *2-3′ : 4′-dimethoxybenzylaminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline*, m.p. 75° (*hydrochloride*, m.p. 191—192°; *sulphate*, m.p. 161·5°). Similarly condensation with piperonal followed by reduction leads to *2-3′ : 4′-methylenedioxybenzyl-*

aminomethyl-1 : 2 : 3 : 4-*tetrahydroquinoline* (*hydrochloride*, m.p. 213—214°; *sulphate*, m.p. 177—178°; *phosphate*, m.p. 204—205°). 1-*Methyl*-2-*nicotinamidomethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 159—160°, gives a *mono*-, m.p. 223°, and *di*-*hydrochloride*, 1-*Methyl*-2-*veratramidomethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 161—162°, and its *hydrochloride*, m.p. 161—162°, are described. With piperonal and veratraldehyde 1-methyl-2-aminomethyltetrahydroquinoline gives non-cryst. Schiff's bases, reduced respectively to 1-*methyl*-2-3′ : 4′-*methylenedioxybenzylaminomethyl*-(*hydrochloride*, m.p. 207—208°) and 1-*methyl*-2-3′ : 4′-*dimethoxybenzylaminomethyl*- [*perchlorate*, m.p. 193° (decomp.)] -1 : 2 : 3 : 4-*tetrahydroquinoline*. H. W.

2-Aminomethyltetrahydroquinoline and its derivatives. H. VON BIDDER and H. RUPE (Helv. Chim. Acta, 1939, **22**, 1268—1278).—2-Aminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline (I) (improved prep. from 2-cyano-1-benzoyl-1 : 2-dihydroquinoline; cf. A., 1939, II, 345) gives a *monohydrochloride*, m.p. 257°, *dihydrochloride*, b.p. 265° (decomp.), *monohydrobromide*, decomp. 235—236°, *Ac* derivative, m.p. 48·5—49·5°, :*CHPh* compound, m.p. 75—76°, *formate*, m.p. 117·5—118·5°, and a very hygroscopic *formyl* derivative, b.p. 178—180°/10 mm., m.p. between 20° and 40° (*perchlorate*). Addition of $CH_2Cl{\cdot}CO_2Et$ to (I) in C_6H_6 affords the non-cryst. *Et* 2-*tetrahydroquinolylmethylaminoacetate* [normal *oxalate*, m.p. 169—170° (decomp.)]. Similarly, (I) and $ClCO_2Et$ afford *Et* 2-*tetrahydroquinolylmethylaminoformate*, b.p. 120—125°/10 mm. (much decomp.) [*hydrochloride*, m.p. 135·5°; unstable *perchlorate*, m.p. 124°], readily converted into the *iminazolone*, $CH_2<^{CH_2-CH\cdot CH_2}_{C_6H_4\cdot N-CO}>NH$, b.p. 245—247°/10 mm., m.p. 197°. (I) with $(CH_2)_2O$ at 100° gives *mono*-, b.p. 232—235°/10 mm., m.p. 105·5—106·5°, and *di*-2-β-*hydroxyethylaminomethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b.p. 235—245°/10 mm., m.p. 92—93° [Bz_1, m.p. 115—116°, and Bz_3 derivative, m.p. 95—96°, and its primary *diorthophosphate*, m.p. 151—152° (decomp.), and *monohydrochloride*, m.p. 100·5—103·5° (decomp.)]. 2-Benzamidomethyltetrahydroquinoline (II) and $(CH_2)_2O$ at 110—120° afford 2-benzamidomethyl-1-β-hydroxyethyltetrahydroquinoline, m.p. 113—114·5° after softening at 110°. 1-Methyl-2-aminomethyltetrahydroquinoline (III) and $(CH_2)_2O$ at 110° yield 1-*methyldi*-2-β-*hydroxyethylaminomethyltetrahydroquinoline*, b.p. 260—265°/12·5 mm., 177—179°/0·005 mm., which does not give cryst. salts. (III) gives a normal *dicarbonate*, m.p. 123—125°. Epichlorohydrin does not give useful results with (III) whereas it is converted by (II) at 100° into 1-*benzamidomethyl*-1-βγ-*oxidopropyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 118—119°. $CH_2Cl{\cdot}COMe$ and $CH_2Br{\cdot}COPh$ react violently with (I) whereas (II) and $CH_2Br{\cdot}COPh$ give 1-*phenacyl*-2-*benzamidomethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 163°. 2-β-*Hydroxy*-β-*methylamylaminomethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* is a viscous, yellow liquid [*hydrochloride*, m.p. 171—173° (decomp.)]. H. W.

Condensation of arsenic halides with hydrohalides of pyridine and quinoline. P. P. POPOV (J. Gen. Chem. Russ., 1939, **9**, 1264—1273).—As halides form complexes when heated with the hydrohalides of C_5H_5N and quinoline in $CHCl_3$. The following are described: $2C_5H_5NHCl,AsCl_3,CHCl_3$, deliquescent needles; $C_5H_5NHBr,AsCl_3$, microcryst. powder giving colourless needles of $3C_5H_5NHBr,2AsBr_3,CHCl_3$ when crystallised from $CHCl_3$, and yellow needles of $2C_5H_5NHBr,AsBr_3,CHCl_3$, which lose $CHCl_3$ when dried at 100° and when boiled with C_6H_6 give $5C_5H_5NHBr,2AsBr_3$, a yellow powder; the reverse change can be brought about by boiling with $CHCl_3$; $C_5H_5NHI,2AsI_3$, small red crystals giving orange crystals of C_5H_5NH,AsI_3 when boiled with $CHCl_3$. $C_9H_7NHCl,AsCl_3$, needles, m.p. 122—123°; $C_9H_7NHBr,AsBr_3$, greenish-yellow crystals, m.p. 147—148°; $C_9H_7NHI,2AsI_3$, pale orange ppt. giving golden-yellow leaflets of C_9H_7NHI,AsI_3 when boiled with $CHCl_3$. All these complexes are hygroscopic, those containing I less than the others. When dissolved in H_2O they decompose, the whole of the halogen becoming ionic and the $CHCl_3$ being split off intact. The new compounds and the analogous Sb and Bi compounds can be classified into 5 groups and a scheme of formulation is suggested. G. A. R. K.

4-Amino-2-phenylquinoline derivatives. U. P. BASU and P. K. DAS-GUPTA (J. Indian Chem. Soc., 1939, **16**, 301—304).—4-Amino-2-phenylquinoline (I) heated (12—24 hr.) with $NEt_2{\cdot}[CH_2]_2{\cdot}Br$ or $NEt_2{\cdot}[CH_2]_3{\cdot}Cl$ (II), K_2CO_3, and a trace of Cu powder in xylene gives respectively 4-(β-*diethylaminoethyl*)-, b.p. 272—276°/6 mm. (*hydrochloride*; *picrate*, m.p. 238—239°), and 4-(γ-*diethylaminopropyl*)-*amino*-2-*phenylquinoline*, b.p. 265—270°/6 mm. (*picrate*, m.p. 234°). 4-Chloro-2-phenylquinoline (III) with $NEt_2{\cdot}[CH_2]_4{\cdot}NH_2$ (IV), K_2CO_3, and Cu in $C_5H_{11}{\cdot}OH$ at 110—120°, or with $NEt_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}NH_2$ at 150—160°, gives respectively 4-(δ-*diethylaminobutyl*)-(*picrate*, m.p. 203°) and 4-(δ-*diethylamino*-α-*methylbutyl*)-*aminoquinoline* (*picrate*, m.p. 162°). 4-Amino-6-methoxy-2-phenylquinoline (V), new m.p. 159° (cf. John, A., 1931, 965), with (II) at 160—170° followed by addition of K_2CO_3 and steam-distillation gives 4-(γ-*diethylaminopropyl*)- (*picrate*, m.p. 185°), while 4-chloro-6-methoxy-2-phenylquinoline with (IV) gives 4-(δ-*diethylaminobutyl*)-*amino*-6-*methoxy*-2-*phenylquinoline* (*picrate*, m.p. 192°). With *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ or *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NEt_2$ and a little Cu powder at 160—170°, (III) gives respectively 4-(p-*sulphonamido*)-, m.p. 250°, and 4-(p-*sulphondiethylamido*)-*anilinoquinoline*, m.p. 144°. With (I) in C_6H_6 at the b.p. or with (V) in $NPhMe_2$ at 150°, *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ gives 4-p′-*acetamidobenzenesulphonamido*-2-*phenyl*-, m.p. 297°, and -6-*methoxy*-2-*phenylquinoline*, m.p. 268°; these are respectively hydrolysed to the 4-p′-NH_2-compounds, m.p. 293° and 268°. E. W. W.

8-Hydroxyquinoline derivatives.—See A., 1939, I, 625.

Action of nitric acid on polycyclic indole derivatives. XIII. Indeno-(2′ : 3′ : 2 : 3)-indole. N. M. BEYTS and S. G. P. PLANT (J.C.S., 1939, 1534—1536).—1-*Acetylindeno*-(2′ : 3′ : 2 : 3)-*indole*, m.p. 131°, is nitrated (HNO_3–AcOH) to a mixture of 3-*nitro*-2-*acetoxy*-1-*acetyl*-2 : 3-*dihydroindeno*-(2′ : 3′ : 2 : 3)-

indole, m.p. 177—180° (decomp.), and 6(?)-*nitro*-1-*acetylindeno*-(2′ : 3′ : 2 : 3)-*indole*, m.p. 275° (decomp.); the latter compound is not identical with 5-*nitro*-1-*acetylindeno*-(2′ : 3′ : 2 : 3)-*indole*, m.p. 247°, prepared by acetylating the 5-*nitro*-*indeno*-compound, m.p. 255°, the product of the Fischer reaction on β-hydrindone-*p*-nitrophenylhydrazone. 1-*Benzoylindeno*-(2′ : 3′ : 2 : 3)-*indole*, m.p. 169—170°, does not give a similar additive product on nitration. The β-*naphthylhydrazone* of β-hydrindone, m.p. 176° (decomp.), with AcOH gives *indeno*-(2′ : 3′ : 2 : 1)-β-*naphthindole*, m.p. 208—209°, the 3-*Ac* derivative, m.p. 185°, of which with HNO_3–AcOH affords only ?-*nitro*-3-*acetylindeno*-(2′ : 3′ : 2 : 1)-β-*naphthindole*, m.p. 265° (decomp.), indicating that additive tendency is diminished by the presence of the extra C_6H_6 nucleus.

F. R. S.

Meso-derivatives of acridine. XII. 5-Chloroacridine and acridol. N. S. Drozdov. **XIII. Preparation and anti-malarial action of substituted 5-aminoacridines.** O. M. Tscherntzov and N. S. Drozdov (J. Gen. Chem. Russ., 1939, **9**, 1373—1375, 1435—1440).—XII. 5-Chloro- and 5-chloro-2-methyl-acridine gradually decompose in air and light, to give substances of the type $C_6H_4<^{CO-}_{NH}>C_6H_4\cdot C_6H_4<^{CCl}_{N-}>C_6H_4,HCl$, which yield acridone when distilled. To this are due the reports made by a no. of authors to the effect that acridone or acridol are obtained by distillation of 5-chloroacridine derivatives.

XIII. 3-Dimethylamino-5-phenoxyacridine in PhOH and γ-piperidino-β-hydroxypropylamine, heated at 100° for 1 hr., yield 3-*dimethylamino*-5-(γ-*piperidino*-β-*hydroxypropyl*)*aminoacridine*, m.p. 213—215°. The following are prepared analogously: 8-*chloro*-3-*dimethylamino*-5-(γ-*piperidino*-β-*hydroxypropyl*)-, an oil, 8-*chloro*-3-*dimethylamino*-5-(γ-*diethylamino*-β-*hydroxypropyl*)-, m.p. 108—109°, 3-*dimethylamino*-5-(δ-*diethylamino*-α-*methylbutyl*)-, an oil, 8-*chloro*-3-*dimethylamino*-5-(δ-*diethylamino*-α-*methylbutyl*)-*aminoacridine* (I), an oil, 5-(δ-*diethylamino*-α-*methylbutyl*)*amino*-3-*methoxy*-, an oil, 2-*chloro*-5-(γ-*piperidino*-β-*hydroxypropyl*)*amino*-7-*methoxy*- (II), m.p. 130—131·5° [*hydrochloride*, m.p. 255° (decomp.)], 3-*nitro*-9-(γ-*piperidino*-β-*hydroxypropyl*)*amino*-7-*methoxy*-, m.p. 170—171°, 4-*nitro*-5-*methylamino*-1-*methoxyacridine*, m.p. 211—213°. 2 : 5-Dichloro-7-methoxyacridine, sulphanilamide, and PhOH (3 hr. at 100°) afford 4-(2′-*chloro*-7′-*methoxy*-5′-*acridyl*)*aminobenzenesulphonamide*, not melting at 300°. (I) and (II) have a pronounced schizotropic action in avian malaria.

R. T.

Acridine derivatives as antimalarials. IV. S. J. Das-Gupta (J. Indian Chem. Soc., 1939, **16**, 364—368; cf., A., 1939, I, 282).—5 : 2 : 1-$SO_2Cl\cdot C_6H_3Cl\cdot CO_2H$ (I) and *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH_2$ (2 mols.) give 2-*chloro*-5-p′-(*amidosulphonyl*)*anilidosulphonylbenzoic acid*, m.p. 240°, which with *p*-$OMe\cdot C_6H_4\cdot NH_2$ and K_2CO_3 in $C_5H_{11}\cdot OH$ gives 4-p″-(*amidosulphonyl*)*anilidosulphonyl*-4′-*methoxydiphenylamine*-2-*carboxylic acid*, m.p. 246°, converted by $POCl_3$ at 100° into 5-*chloro*-3-p-(*amidosulphonyl*)-*anilidosulphonyl*-, m.p. 212—215°, which in PhOH with $NH_2\cdot CHMe\cdot[CH_2]_3\cdot NEt_2$ and $NH_2\cdot[CH_2]_4\cdot NEt_2$ at 100° gives 3-p-(*amidosulphonyl*)*anilidosulphonyl*-5-(δ-*diethylamino*-α-*methyl*-n-*butylamino*)-, m.p. 254—256°, and -5-(δ-*diethylamino*-n-*butylamino*)-7-*methoxyacridine*, m.p. 220—222°, respectively. Similarly (I) and *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NEt_2$ give 2-*chloro*-5-p′-(*diethylamidosulphonyl*)*anilidosulphonylbenzoic acid*, m.p. 194—195°, whence 4-p″-(*diethylamidosulphonyl*)*anilidosulphonyl*-4′-*methoxydiphenylamine*-2-*carboxylic acid*, m.p. 202—203°, 5-*chloro*-3-p-(*diethylamidosulphonyl*)*anilidosulphonyl*-, m.p. 187—189°, and 3-p-(*diethylamidosulphonyl*)*anilidosulphonyl*-5-(δ-*diethylamino*-α-*methyl*-n-*butylamino*)-, m.p. ~160°, -5-(δ-*diethylamino*-n-*butylamino*)-, m.p. ~130°, and -5-(γ-*diethylamino*-n-*propyl*)-7-*methoxyacridine*, m.p. ~200°, are obtained. *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NEt_2$ and *p*-$NHAc\cdot C_6H_4\cdot SO_2Cl$ give the *Ac* derivative, m.p. 228°, of p′-*aminobenzenesulphonanilido*-p-*sulphondiethylamide*, m.p. 176°, which with 2 : 5-dichloro-7-methoxy- or -7-methyl-acridine gives respectively 2-*chloro*-5-p′-(*diethylamidosulphonyl*)*anilido*-p-*sulphonylanilino*-7-*methoxy*-, m.p. 160—161°, and -7-*methyl*-*acridine*, m.p. 133—134°.

E. W. W.

Action of ethyl acetoacetate on 2-aminopyridine. S. N. Chitrik (J. Gen. Chem. Russ., 1939, **9**, 1109—1117).—2-Aminopyridine and $CH_2Ac\cdot CO_2Et$, heated at 150—160° (4—5 hr.), yield 6-*methyl*-1 : 2-*benz*-4-*pyrimidone* (II), m.p. 122° [+H_2O, m.p. 105—107°; +1¼H_2O, m.p. 84°; *platinichloride*, m.p. 229° (decomp.); *hydrochloride*, m.p. 315°; *picrate*, m.p. 177° (decomp.); *methiodide*, not melting at 280°; *compound* with maleic anhydride, m.p. 135—136°; 5-*NO*$_2$-derivative, m.p. 184°]. At 100° (4 hr.) the product is 2-*acetoacetamidopyridine*, m.p. 113° [*methiodide*, m.p. 133—134° (decomp.)], which with H_2SO_4 (24 hr. at room temp.) gives (I). At 130° the product is the 2-*pyridylamide* of β-2-*pyridylaminocrotonic acid*, m.p. 166°.

R. T.

Oxidation products of indole. C. Toffoli (R. Ist. San. Pubbl., 1939, **2**, 565—572).—Mg 2-methylindolyl bromide (I) and O_2 give a yellow, cryst. product (II), $C_{18}H_{16}ON_2$, m.p. 208° (cf. Oddo, A., 1921, i, 127), and *di*-(2-*methyl*-3-*indolyl*), m.p. 237—238°, also afforded by (I) with Mg Et acetoacetate. Mg indolyl bromide and O_2 give a small amount of a product, m.p. 255—260° (decomp.). Spontaneous oxidation of 2-methylindole also affords (II) and a product (2-ketoindole ?), m.p. 120°.

F. O. H.

Molecular combination of iminomethenyl compounds. C. Toffoli (R. Ist. San. Pubbl., 1939, **2**, 677—708).—The yellow compound (I), m.p. 208°, of Oddo (cf. preceding abstract) is considered to be di-(2-methyl-3-indolyl) oxide; if this is true, it should be colourless. Various reactions of (I) with alkalis, $NaHSO_3$, NH_2OH, etc. are always attended by formation of 2-methylindole. These and parallel reactions indicate that (I) is formed not by a reaction involving an active H, viz., —CH:N— + HR → —CHR·NH—, but by a mol. combination of the type —CH:N···H—R. Such a concept is applicable to, *e.g.*, theobromine and indigotin.

F. O. H.

Acids derived from various heterocyclic types. —See B., 1939, 1104.

Canavanine picrolonate; deaminocanavanine picrate, decomp. 216—217°, and flavianate, decomp. 225—226°.—See A., 1939, III, 1004, 1005.

Constitution of uric acid riboside.—See A., 1939, III, 986.

Isolation and structure of bonelline, the green pigment of *Bonellia viridis*. E. LEDERER (Compt. rend., 1939, **209**, 528—530).—Bonelline (I) (prep. described), m.p. >300°, exhibits dichroism in conc. solution in org. solvents, and forms with CH_2N_2 a OMe-derivative which gives complex Cu, Fe, and Zn salts. The absorption spectra of (I) and mesopyrrochlorin (II) in dioxan and 12% HCl and the two fluorescence spectra are nearly identical (cf. Stern and Molvig, A., 1937, I, 165). (I) is probably $C_{34}H_{36}O_4N_4 \pm H_2$, which is 6-γ-dihydroxymesopyrrochlorin (cf. Herrle, *et al.*, A., 1936, 1272), the OH groups being remnants of the *iso*cyclic ring in α-chlorophyll. J. L. D.

Melanin and its precursors. I. W. L. C. VEER (Rec. trav. chim., 1939, **58**, 949—955).—Tyrosine in H_2O is oxidised with O_2 + tyrosinase (p_H 6—6·5) to give an aq. solution (I) of "red substance" (II) (cf. Raper, A., 1927, 278). (I) and NHPh·NH_2, *p*-NO_2·C_6H_4·NH·NH_2, or *p*-C_6H_4Br·NH·NH_2, in 30% aq. AcOH, give the corresponding *monohydrazones*, m.p. ~168° (decomp.) (indefinite) (+H_2O), m.p. ~190° (decomp.) (indefinite) (+H_2O), or m.p. ~174° (decomp.) (+2H_2O), respectively. (I) and NH_2OH, NH_2·CO·NH·NH_2, or 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH·NH_2 do not react. Results support the constitution of (II) given by Raper (*loc. cit.*); it may be important as an anti-pernicious anæmia principle. A. T. P.

Synthesis of 4-methyl-5-β-hydroxyethylthiazole and its homologues. A. G. PESINA (J. Gen. Chem. Russ., 1939, **9**, 804—813).—OH·$[CH_2]_2$·CHAcCl (I) is synthesised: (i) CHAcNa·CO_2Et and $(CH_2Br)_2$ give *Et γ-bromo-α-acetylbutyrate*, b.p. 67—75°/5—6 mm., converted by SO_2Cl_2 at 0° into *Et α-chloro-γ-bromo-α-acetyl butyrate*, b.p. 119—123°/7—9 mm., yielding (I) on hydrolysis with AcOH–H_2SO_4, and (ii) CHAcNa·CO_2Et and OH·$[CH_2]_2$·Br yield *Et γ-hydroxy-α-acetylbutyrate*, b.p. 75—80°/20—22 mm., converted by SO_2Cl_2 into *Et α-chloro-γ-hydroxy-α-acetylbutyrate*, b.p. 95—103°/12—14 mm., which gives (I) on hydrolysis with AcOH–H_2SO_4. (I) and NH:CH·SH yield 4-methyl-5-β-hydroxyethylthiazole (A., 1936, 1394). The synthesis of the following is described: 2 : 4-*dimethyl*-5-β-*hydroxyethylthiazole*, b.p. 130—131°/7—8 mm. (*picrolonate*, m.p. 139—140°); 4-*methyl*-2-*ethyl*-5-β-*hydroxyethylthiazole*, b.p. 133—136°/3—5 mm. (*picrolonate*, m.p. 149—151°); 4-*methyl*-2-*propyl*-5-β-*hydroxyethylthiazole*, b.p. 140—142°/3—5 mm., and 4-*methyl*-5-β-*hydroxyethylthiazole* (*picrolonate*, m.p. 196—197°). V. A. P.

Reactions in the thiazole series. II. Reaction of 1-chlorobenzthiazole with thiocarbamide in aqueous media. G. W. WATT (J. Org. Chem., 1939, **4**, 436—441).—Protracted action of 1-chlorobenzthiazole and $CS(NH_2)_2$ in H_2O at room temp. gives 1-thiolbenzthiazole (I), m.p. 179·2—180° corr.), and 1 : 1′-*dibenzthiazolyl sulphide* (II), m.p. 98·7—99·1° (corr.). The yields of (I) and (II) are decreased with decrease in concn.; at any particular concn. the yield increases with increased time of action and the rate at which these reactions approach completion is increased by the presence of either (I) or (II). The formation of (II) is dependent on the formation and ionisation of an intermediate additive compound. H. W.

High mol. wt. fatty acid derivatives. I. Characterisation of acids. H. GILMAN and G. M. FORD (Iowa State Coll. J. Sci., 1939, **13**, 135—147).—Carbazole (0·01 mol.) with the acid chloride (0·01 mol.) (prepared from the acid and $SOCl_2$) at 100—150° until no more HCl is evolved affords the *N*-acylcarbazole. The following are prepared: N-*lauryl*-, m.p. 78—79°, -*myristyl*-, m.p. 81—82°, -*palmityl*-, m.p. 85—86°, -*oleyl*-, an oil, and -*stearyl-carbazole*, m.p. 91—92°. The following *N*-acylphenthiazines are prepared similarly: N-*lauryl*-, m.p. 70°, -*myristyl*-, m.p. 75°, -*palmityl*-, m.p. 80°, -*oleyl*-, an oil, and -*stearyl-phenthiazine*, m.p. 86°. Equiv. amounts of *p*-C_6H_4Me·SO_2·NH_2 and the acid chloride at 100—125°/2 hr. afford N-*lauryl*-, m.p. 83—84°, -*myristyl*-, m.p. 89—90°, -*palmityl*-, m.p. 93—94°, -*oleyl*-, an oil, and -*stearyl*-p-*toluenesulphonamide*, m.p. 98—99°. *p*-C_6H_4Ph·CO·CH_2Br with the appropriate acid and Na_2CO_3 affords p-*phenylphenacyl myristate*, m.p. 90°, *palmitate*, m.p. 94°, and stearate, m.p. 97° (lit., 91°). *p*-NO_2·C_6H_4·NH_2 with the acid chloride affords *laur-*, m.p. 78°, *myrist-*, m.p. 84°, *palmit-*, m.p. 93°, and *stear*-p-*nitroanilide*, m.p. 96°. The Na derivative of saccharin (0·01 mol.) with the acid chloride (0·01 mol.) in boiling $CHCl_3$/3 hr. gives N-*lauryl*-, m.p. 88—89°, -*myristyl*-, m.p. 90—91°, -*palmityl*-, m.p. 90°, -*oleyl*-, an oil, and -*stearyl-saccharin*, m.p. 95°. The following are prepared according to Cerezo and Olay's directions (A., 1936, 1251): *lauryl*, m.p. 110—111°, *myristyl*, m.p. 118°, *palmityl*, m.p. 120—121°, and oleyl 2 : 4-*dinitrophenylhydrazide*. Equimol. amounts of 2-nitro-*p*-toluidine and the acid chloride at 100—150°/3 hr. give N-*lauryl*-, m.p. 62—63°, -*myristyl*-, m.p. 73—74°, -*palmityl*-, m.p. 78—79°, and -*stearyl*-2-*nitro*-p-*toluidide*, m.p. 85°. Similarly, Hg(*p*-$C_6H_4Me)_2$ and the acid chloride in boiling xylene/8 hr. afford *Hg* p-*tolyl laurate*, m.p. 93—94°, *myristate*, m.p. 95—96°, *palmitate*, m.p. 99°, oleate, an oil, and *stearate*, m.p. 102—103°. The following are prepared similarly: *Hg Ph laurate*, m.p. 82°, *myristate*, m.p. 86°, *palmitate*, m.p. 93°, oleate, an oil, and *stearate*, m.p. 95°. Equimol. amounts of $PbPh_4$ and the acid in boiling xylene/10 hr. give *Pb* Ph_3 *laurate*, m.p. 91°, *myristate*, m.p. 102—103°, *palmitate*, m.p. 110°, and *stearate*, m.p. 112°. $SnPh_4$ and stearic acid do not react even in presence of SiO_2 gel or when heated under pressure. Equimol. amounts of $CO(NH_2)_2$ and the acid chloride in boiling dry C_5H_5N afford (cf. Stendal, A., 1933, 806; Jacobson, A., 1936, 1495): *lauryl*-, m.p. 182°, *myristyl*-, m.p. 178°, and *palmityl-carbamide*, m.p. 175°. *Lauryl*-, m.p. 138°, *myristyl*-, m.p. 135°, *palmityl*-, m.p. 135—136°, *stearyl*-, m.p. 133°, and *oleyl-thiocarbamide*, m.p. 112—113°, are prepared similarly. Et stearate with $CS(NH_2)_2$ in 25% NaOEt–C_5H_5N gives *distearylthiocarbamide*, m.p. 100°. Equimol. amounts of the acids and *p*-xenylamine (I) at

135—140°/5 hr. (sealed tube) or of the acid chloride and (I) at 150—200°/5 hr. (sealed tube) afford (cf. Kimura and Nihayashi, A., 1936, 53) *laur-*, m.p. 146°, *myrist-*, m.p. 143°, *palmit-*, m.p. 142°, and *stear-p-phenylanilide*, m.p. 143°. 4-*Lauryl-*, m.p. 101—102°, *-myristyl-*, m.p. 102—103°, *-palmityl-*, m.p. 103—104°, and *-stearyl-diphenyl*, m.p. 106—107°, are prepared by the Friedel–Crafts reaction in CS_2. Carbazole (0·005 mol.), the appropriate acid chloride (0·01 mol.), and $AlCl_3$ (0·02 mol.) in $PhNO_2$ yield 3 : 6-*dilauryl-*, m.p. 176°, *-dimyristyl-*, m.p. 169°, and *-dipalmityl-carbazole*, m.p. 162°. *p*-$NH_2 \cdot C_6H_4 \cdot CO_2H$ (0·01 mol.) and acid chloride (0·01 mol.) in boiling C_5H_5N/5 hr. give p-*laur-*, m.p. 227—228°, *-myrist-*, m.p. 224—225°, *-palmit-*, m.p. 226—227°, and *-stear-amidobenzoic acid*, m.p. 221°. N-*Palmityl-* and *-stearyl-anthranilic acid*, m.p. 100° and 113°, respectively, are prepared similarly by refluxing in $CHCl_3$. Equimol. amounts of 2-aminodiphenylene oxide and acid chloride at 125—160°/5 hr. give 2-*palmit-*, m.p. 130°, and *-stear-amidodiphenylene oxide*, m.p. 134°. Benzidine (0·005 mol.) with the acid chloride (0·01 mol.) in boiling dry C_5H_5N/5 hr. gives *dilauryl-*, m.p. 248°, *dimyristyl-*, m.p. 241—242°, *dipalmityl-*, m.p. 233°, and *distearyl-benzidine*, m.p. 232°. Equimol. amounts of 3-stearylcarbazole (II) and stearyl chloride at 150—200° give 3 : N-*distearylcarbazole* (III), m.p. 86—87°. A Friedel–Crafts reaction on the same reactants gives 3 : 6-distearylcarbazole. (III) with boiling EtOH–HCl/4 hr. gives (II) and stearic acid. J. L. D.

Alkaloids of *Mitragyna rotundifolia*. I. G. Barger, E. Dyer, and L. J. Sargent (J. Org. Chem., 1939, 4, 418—427).—Percolation of the air-dried leaves of *M. rotundifloria* with 95% EtOH leads to rhynchophylline (I) and *rotundifoline* (II). (I) is identical with the mitrinermine of Raymond-Hamet *et al.* (A., 1935, 366) and the alkaloid of *Ouronparia rhynchophylla*. (I), $C_{22}H_{28}O_4N_2$, m.p. 208—209°, $[\alpha]_D^{15}$ −14·5° in $CHCl_3$, contains 2 OMe, one of which is present as CO_2Me, but no CH_2O_2. One N is *tert.* and basic whereas the other belongs to an indole ring. NMe is absent. The function of the fourth O is unknown since (I) gives negative tests for OH, enol, or CO. The active H (Zerevitinov) may be assigned to NH. The suggestion that (I) is a OMe-derivative of yohimbine does not appear to be supported by chemical or optical evidence. (I) is hydrolysed to amorphous *rhynchophyllic acid*, slow decomp. >150° after softening at 140°, which, when distilled with CaO, gives an unidentified oil and a neutral *substance*, $C_{10}H_9ON$, m.p. 182—184° after softening at 180°, which dissolves in boiling alkali and gives a substance yielding a positive Ehrlich action when distilled with Zn dust; it is possibly a methylcarbostyril. Degradation of (I) by heating with soda-lime gives a mixture of oxygenated indoles, NH_3, and a base, C_8H_9ON or $C_8H_{11}ON$ (*picrate*, m.p. 123—125° after softening at 115°), which resembles C_5H_5N. CO_2 is evolved when (I) is boiled with 30% H_2SO_4 and a residue resembling that derived from mitragynine is obtained. (II), m.p. 233—234°, $[\alpha]_D^{15}$ +124° in $CHCl_3$, is $C_{22}H_{26}O_5N_2$. It contains 2 OMe (one present in CO_2Me), but no CH_2O_2 or NMe. It contains 1·4 active H, part of which may be ascribed to an enolic OH since a deep red colour is produced with $FeCl_3$ in non-hydroxylic solvents. The nature of the remaining two O is uncertain since (II) does not give definite products of acetylation and does not yield a semicarbazone. One of the N is basic and *tert.*; the other is a member of an indole ring. (II) is hydrolysed to the amorphous, amphoteric *rotundifolic acid*, $C_{21}H_{24}O_5N_2$, which softens at 160°, effervesces at >165°, and becomes brown at 170°. Decarboxylation of (II) by CaO leads to the *base*, $C_{20}H_{24}O_3N_2$, m.p. 200—202° after softening at 198°. When heated with soda-lime (II) gives a mixture of indoles, NH_3, and bases resembling C_5H_5N. CO_2 is eliminated when (II) is boiled with 30% H_2SO_4 and the residue is similar to that derived from (I). Dehydrogenation of (II) by Se gives a mixture from which the *base*, $C_9H_{13}N$ (*picrate*, m.p. 134—135°), is isolated; it is optically inactive, does not give a NO-derivative, but yields a non-cryst. *methiodide*. A quantity of amorphous alkaloid, the composition of which is similar to that of (I) and (II), was isolated. Its corresponding acid yields the substances $C_{10}H_9ON$ and $C_9H_{13}N$. H. W.

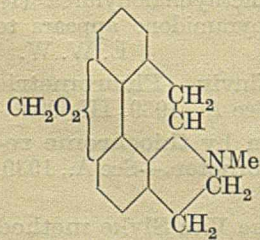
Crystalline alkaloid of the Rubiaceæ described by Schumann as *Adina rubrostipulata*. Raymond-Hamet (Bull. Sci. Pharmacol., 1939, **41**, 327—336).—Rubradinine (Denis, A., 1937, II, 266) is identical with mitraphylline (*ibid.*, 217). R. T.

Synthesis of the alkaloid pilosinine. A. M. Poljakova, V. A. Preobrashenski, and N. A. Preobrashenski (J. Gen. Chem. Russ., 1939, **9**, 1402—1409).—$(\cdot CH_2 \cdot CO_2Et)_2$ and HCO_2Et condensed in NaOMe–MeOH (2 days at 0°, then 2 days at room temp.) yield Et_2 formylsuccinate, reduced (Al–Hg) to Et_2 itaconate, converted by distillation into *Et pilosininate*, b.p. 273—276°, hydrolysed to *pilosininic acid*, $CO<^{CH_2}_{O\text{—}}>CH \cdot CO_2H$, m.p. 64—65°, the *chloride*, b.p. 107°/12 mm., of which is treated with CH_2N_2. The resulting pilosininyl diazomethyl ketone, shaken with Ag_2O in EtOH, yields *Et homopilosininate*, b.p. 161°/15 mm., hydrolysed to *homopilosininic acid*, m.p. 86·5—87·5°, the *chloride*, b.p. 126°/0·2 mm., of which is treated with CH_2N_2, and the homopilosininyl diazomethyl ketone thus obtained is converted into *homopilosininyl acetoxymethyl ketone* (I), b.p. 168°/0·5 mm., by the action of AcOH at 70°, and into the *chloromethyl ketone* (II), b.p. 163°/0·7 mm., by saturation of its Et_2O solution with HCl. (II) in EtOH and K phthalimide (8 hr. at 100°) give *homopilosininyl phthalimidomethyl ketone*, m.p. 146—147°. This, heated with 1 : 1 HCl (8 hr. at the b.p.), affords *homopilosininyl aminomethyl ketone* (*hydrochloride*, m.p. 140—143°), which with aq. KCNS (8 hr. at 100°) gives 2-*thiolpilosinidine*, m.p. 202·5—203°, and this is converted by boiling with aq. $FeCl_3$ into pilosinidine (III) (*nitrate*, m.p. 117—118°), from which pilosinine is prepared by treatment successively with MeI and KOH. (III) is also prepared by shaking (I) with aq. $Cu(OAc)_2$, aq. CH_2O, and aq. NH_3, and then passing H_2S at 100° (Weidenhagen reaction). R. T.

Constitution and synthesis of the alkaloid anonaine. G. Barger and G. Weitnauer (Helv.

Chim. Acta, 1939, **22**, 1036—1047; cf. Santos, A., 1931, 242).—Anonaine (I), m.p. 122—123°, $[\alpha]_D^{20}$ −52° in $CHCl_3$, obtained by percolating the bark of *Anona reticulata* with 95% EtOH, is $C_{17}H_{15}O_2N$. The *hydrochloride* has m.p. 277·5° (decomp.). It is a *sec.* non-phenolic base since it gives the basic N-*methylanonaine* [*hydriodide*, m.p. 246—247° (decomp.)], a neutral *NO*-derivative, m.p. 229—230°, and an *Ac* compound, m.p. 229—230°. It contains 1 active H (Zerevitinov) and CH_2O_2 but not NMe, OMe, CO_2H, or CO. MeI and (I) in H_2O afford the quaternary *iodide*, $C_{19}H_{20}O_2NI$, m.p. 217°, transformed by KOH–EtOH–H_2O into the *methine* base, m.p. 87—90°, the *methiodide*, m.p. 270·5° (decomp.), of which is converted into *methylenedioxyvinylphenanthrene* (II), m.p. 87°. This is oxidised to *methylenedioxyphenanthrenecarboxylic acid*, sublimes at 240° (partial decomp.), which is decarboxylated by Cu chromite in quinoline to methylenedioxyphenanthrene [*picrate*, m.p. 168° (decomp.)]. *o*-NO_2·C_6H_4·CH_2·COCl and homopiperonylamine in C_6H_6 afford *o-nitrophenylacet*-β-3 : 4-*methylenedioxyphenylethylamide*, m.p. 119°, cyclised by $POCl_3$ in $CHCl_3$ at room temp. to 6 : 7-*methylenedioxy*-1 : *o*′-*nitrobenzyl*-3 : 4-*dihydro*isoquinoline (III), m.p. 165°. This is reduced (Zn dust and HCl) to the corresponding, non-cryst. NH_2-compound (*dihydrochloride*, m.p. 257°). This is diazotised and reduced to dl-*anonaine*, m.p. 285° (decomp.) (Ac derivative, m.p. 217°). The synthetic product is degraded (Hoffmann) in the same manner at (I), thus giving (II). MeI and (III) at 100° afford 6 : 7-*methylenedioxy*-1-*o*′-*nitrobenzyl*-3 : 4-*dihydro*isoquinoline *methiodide*, m.p. 243° (decomp.), converted by Zn dust and HCl at 100° into 6 : 7-methylenedioxy-1-*o*′-aminobenzyl-2-methyltetrahydro*iso*quinoline [*dihydrochloride*, m.p. 259—260° (decomp.)], which when diazotised and reduced gives *dl*-2-methylanonaine [*hydriodide*, m.p. 244° (decomp.); methiodide, m.p. 210—211°]. H. W.

Alkaloids of *Roemeria refracta*, D.C. III. Alkaloids of plants of the Papaveraceæ family. R. A. Konovalova, S. Junusov, and A. P. Orekhov (J. Gen. Chem. Russ., 1939, **9**, 1356—1364).—The plant contains *l*-ephedrine, *d*-ψ-ephedrine, and *roemerine*, $C_{18}H_{17}O_2N$, m.p. 101—102·5° (*hydrochloride*, m.p. 262—263°; *picrate*, m.p. 195—196°), the *methiodide*, m.p. 215—216°, of which gives (by the Hofmann degradation) *de*-N-*methylroemerine*, m.p. 73—74°; the *methiodide*, m.p. 274—275°, of this, heated with KOH–EtOH, gives a *product*, $C_{17}H_{12}O_2$, m.p. 86—87°. This is oxidised ($KMnO_4$) to an *acid*, $C_{16}H_{10}O_4$, m.p. 264°, which, when heated with Cu–Cr_2O_3, yields CO_2 and a *methylenedioxyphenanthrene*, m.p. 84—85° (*picrate*, m.p. 167—168°; *Br*$_2$-derivative, m.p. 196—197°). Roemerine (annexed structure) yield phenanthrene when distilled with Zn dust.



R. T.

Dichloro-substituted phenylarsinic acids and their derivatives. G. I. Braz and I. V. Tuturin (J. Gen. Chem. Russ., 1939, **9**, 992—995).—2 : 5-$C_6H_3Cl_2$·NH_2 in AcOH is diazotised in presence of $AsCl_3$ and CuCl, and the solution is heated at 100°, yielding 2 : 5-*dichlorophenylarsinic acid*, not melting at 250°, whence is obtained 2 : 5-*dichlorophenyldichloroarsine*, m.p. 56—57°. 2 : 4- and 3 : 4-*Dichlorophenylarsinic acid*, both not melting at 250°, and 2 : 4-, b.p. 167—168°/12 mm., and 3 : 4-*dichlorophenyldichloroarsine*, b.p. 175—176°/12 mm., are described. R. T.

Certain side-chain substituted derivatives of *p*-tolylarsinic acid. S. M. Scherlin, G. I. Braz, A. J. Jakubovitsch, and A. I. Konovaltschik (J. Gen. Chem. Russ., 1939, **9**, 985—991).—*p*-NH_2·C_6H_4·CH_2·OH in H_2SO_4 and $AsCl_3$ is diazotised, and the product is heated with CuCl, yielding 4-*hydroxymethylphenylarsinic acid*, m.p. 165—171° (decomp.), which is converted into 4-*hydroxymethylphenyldichloroarsine* (I), an oil, and 4-*hydroxymethylphenylarsine oxide*, sinters at 260°, decomp. 264—265°. (I) in C_6H_6 and PCl_3 afford 4-*chloromethylphenyldichloroarsine*, m.p. 29—30°, converted by aq. H_2O_2 at room temp. into 4-*chloromethylphenylarsinic acid*. *p*-NH_2·C_6H_4·CH_2·CN in MeOH is similarly converted into 4-*carboxymethylphenyldichloroarsine* (II), m.p. 89—90°, and 4-*cyanomethylphenyldichloroarsine* (III), m.p. 56—57°. This treated successively with $NaHCO_3$ and H_2O_2, affords 4-*cyanomethylphenylarsinic acid* (IV), not melting at 280°. (IV) in HCl and SO_2 give (III), converted into the *oxide*, sinters at 216°, m.p. 218—220° (decomp.), by aq. $NaHCO_3$. (IV) in conc. HCl and SO_2 afford the *amide*, m.p. 143—145°, of 4-*carboxymethylphenyldichloroarsine*, m.p. 107·5—109°. R. T.

Introduction of arsenic into the aromatic nucleus by means of mercury compounds. C. D. Nenitzescu, D. A. Isăcescu, and C. Gruescu (Bul. Soc. Chim. România, 1938, **20**, 135—138).—HgPhCl (2 mols.) and $AsCl_3$ (1 mol.) at 110° give 61% of $AsPh_2Cl$ and 8% of $AsPhCl_2$, separated by light petroleum. *p*-C_6H_4Cl·HgCl (78) and $AsCl_3$ (60 g.) at 110° give *p*-C_6H_4Cl·$AsCl_2$ (29 g.), converted by boiling aq. Cl_2 into *p*-C_6H_4Cl·AsO_3H_2 (63%), which with $NaNO_3$ in H_2SO_4 gives the 3-NO_2-acid and thence by 40% KOH at 100° 65% of 3 : 4 : 1-NO_2·C_6H_3(OH)·AsO_3H_2. R. S. C.

Mercuration of benzene and chlorobenzene. C. D. Nenitzescu, D. A. Isăcescu, and C. Gruescu (Bul. Soc. Chim. România, 1938, **20**, 127—134).—92% of HgPh·OAc is obtained by heating $Hg(OAc)_2$ (1 mol.) in C_6H_6 (35 mols.) and AcOH (20 mols.) at 100° for 9 hr. Other mixtures give lower yields. *p*-C_6H_4Cl·Hg·OAc, similarly obtained in 50% yield, with aq. Br gives *p*-C_6H_4ClBr, and with NaCl in AcOH gives *p*-C_6H_4Cl·HgCl, m.p. 240°. HgPh·OAc and $Hg(OAc)_2$ are separated by the solubilities in C_6H_6 [1·6 g. of HgPh·OAc compared with 0·008 g. of $Hg(OAc)_2$ per 100 c.c.]. R. S. C.

Mercury derivatives of phenacetin. M. Ragno (Annali Chim. Appl., 1939, **29**, 414—418; cf. A., 1939, III, 396).—$Hg(OAc)_2$ and phenacetin give 2-*mercuriphenacetin acetate*, $C_{12}H_{15}O_4NHg$, m.p. 169—170° (decomp.), converted by NaI and KOH into the

corresponding *bromide*, m.p. 225°, and *hydrate*, m.p. 255—258° (decomp.), respectively, and, by aq. EtOH–$Na_2S_2O_4$, into 2-*mercuridiphenacetin*, $C_{20}H_{24}O_4N_2Hg$, decomp. 245°. F. O. H.

Reaction between mercury diphenyl and monobasic organic acids. M. M. Koton (J. Gen. Chem. Russ., 1939, **9**, 912—916).—$HgPh_2$ reacts with monobasic org. acids as follows: $HgPh_2 + R{\cdot}CO_2H \rightarrow C_6H_6 + R{\cdot}CO_2HgPh$. The following are described: Hg Ph formate, m.p. 135—138° (lit. m.p. 171°), acetate, propionate, m.p. 80—81°, (lit. m.p. 145—165°), *lactate*, m.p. 154—155°, n-*butyrate*, m.p. 91°, α-*hydroxybutyrate*, m.p. 159°, *hexoate*, m.p. 82—83°, *stearate*, m.p. 90—92°, *benzoate*, m.p. 97—98°, and *salicylate*, m.p. 200°. V. A. P.

Decomposition of iodonium salts. Reactions with mercury, tellurium, and antimony. R. B. Sandin, F. T. McClure, and F. Irwin (J. Amer. Chem. Soc., 1939, **61**, 2944—2946).—IR_2Cl (R = Ph or p-C_6H_4Me) and Hg in boiling $Pr^{\alpha}OH$ or H_2O give HgRCl. Similarly, IR_2Cl (R as before) and Te in boiling $Pr^{\alpha}OH$ or H_2O–EtOH–H_2S at room temp. give TeR_2, isolated as TeR_2Br_2. Heating IPh_2Cl and Te alone gives $TePh_2Cl_2$. IPh_2Cl, Na_2S, and Sb in Et_2O–H_2O at room temp. give $(SbPh_3)_2S$. Probably some at least of the IR_2Cl decomposes by a non-ionic mechanism, the octet of the I expanding to absorb the Cl and form a complex which then decomposes to PhI, Ph, and Cl. R. S. C.

Reaction between triphenylbenzylphosphonium bromide and sodium. L. N. Parfenteev and A. A. Schamschurin (J. Gen. Chem. Russ., 1939, **9**, 865—867).—Na reacts with $PPh_3Br{\cdot}CH_2Ph$ with elimination of HBr to give $PPh_3{:}CHPh$, identified by hydrolysis to PPh_3O and PhMe. V. A. P.

Micro-gas-analytical determination of the nitrogen content of organic compounds. H. Gysel (Helv. Chim. Acta, 1939, **22**, 1088—1095).—The front portion of the "supremax" tube contains wire-form CuO and three spirals of reduced Cu gauze. It is heated electrically by a fixed furnace at 720—730°. The back portion of the tube contains the substance mixed in a porcelain boat with CuO and $PbCrO_4$; it is followed by a Cu gauze. This portion of the tube is heated by a movable furnace operated at 800—810°. By means of a thermo-element it is possible to obtain a graph of the relation between temp. and distance between the fixed and movable furnaces and hence to regulate suitably the temp. to which the substance is exposed. The liberated N_2 is measured. Arrangement is made so that CO_2 can be passed through the tube in either direction, thus allowing fresh boats to be introduced during series analyses without infiltration of air or necessity of altering the heating by the fixed furnace. A complete analysis can be made in 35—45 min. and the error is $\gtrsim \pm 0{\cdot}2\%$. H. W.

Potentiometric studies in oxidation–reduction reactions. VI. Iodometric determination of organic acids. VII. Determination of aromatic compounds with potassium chlorate. B. Singh and S. Singh (J. Indian Chem. Soc., 1939, **16**, 343—345; 346—348).—VI. $H_2C_2O_4$, tartaric, citric, malic, and glycollic acids have been determined potentiometrically by the iodometric method, using Ba, Zn, or Mg salts as pptg. agents. The liberated I was titrated with $Na_2S_2O_3$ at 10°, using a Pt electrode coupled with a saturated HgCl electrode.

VII. PhOH, p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, $NHPh_2$, and benzoquinone have been determined potentiometrically by titration against standard $KClO_3$, at 25°, in presence of HCl. W. R. A.

Rapid determination of esters of volatile fatty acids. L. E. Grandchamp and J. Vollaire-Salva (Ann. Falsif., 1939, **32**, 244—247).—Volatile acidity is determined before and after hydrolysis (NaOH; 20°). The validity of the method is supported by chemical and organoleptic tests, and its forensic application is indicated. I. A. P.

[Determination of] carotene. V. E. Munsey (J. Assoc. Off. Agric. Chem., 1939, **22**, 664—673).—Peterson and Hughes' method (cf. *ibid.*, 79) gives consistent results when tested by collaborative analysis. Those by Fraps' and Russell's methods are lower and more variable, but the former may be used when no spectrophotometer is available, using 0·1N-$K_2Cr_2O_7$ as standard. E. C. S.

Colorimetric silicomolybdic acid method for determining small quantities of nicotine. G. L. Sutherland, R. P. Daroga, and A. G. Pollard (J.S.C.I., 1939, **58**, 284—288).—Hofmann's method (B., 1933, 365) is modified. Conditions of pptn. of nicotine silicomolybdate and the subsequent development of the blue colour by aq. glycine–$NaHSO_3$ requisite for max. colour intensity are prescribed. The method is adapted to determining nicotine (0·2 mg. upward) in steam distillates etc. using the tintometer. Details are given for determinations in soil samples. A. G. P.

Colour reaction for identification of 8-(diethylamino*iso*amyl)amino-6-methoxyquinoline (Plasmoquine, Praequine). A. E. Tschitschibabin and C. Hoffmann (Bull. Sci. Pharmacol., 1939, **41**, 231—232).—5 c.c. of 10% HIO_3 are added to 10 c.c. of solution, when a violet coloration develops in presence of $\lesssim$ 0·5 p.p.m. of Plasmoquine. The reaction is sp. R. T.

Reactions of diethylmalonylurea and of certain pyrazolone derivatives. A. Perotti (Boll. Chim. farm., 1939, **78**, 497—505).—Colour reactions of various compounds and additive products are compared. The product from diethylmalonylurea (I), antipyrine, and 2 mols. of pyramidone appears to contain no free (I). E. W. W.

Determination of riboflavin. Fluorometric and biological methods.—See A., 1939, III, 993.

Determination of aneurin by thiochrome reaction with Pulfrich refractometer.—See A., 1939, III, 1070.

Use of amyl alcohol in the Van Slyke method for determining the nitrogen distribution in proteins.—See A., 1939, III, 1113.

Application of micro-methods in analysis of zein.—See A., 1939, III, 1020.