BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MARCH, 1939.

Occurrence of free radicals during organic reactions. G. WITTIG (Angew. Chem., 1939, **52**, 89—95).—A consideration of the following reactions in the gas phase: thermal and photochemical decomp. of MeCHO and homologous aldehydes, of $COMe_2$ and homologous ketones, of $(NMe{:})_2$ and CH_2N_2, of CH_4 and homologues; photohalogenation; action of Na on alkyl and aryl iodides. Review of the following reactions in solution: occurrence of CPh_3; benzidine transformation; isomerisation of tetraphenylsuccinodinitriles; decomp. of thermolabile azo-compounds and peroxides; photolysis of aliphatic ketones; additive reactions of olefines; photohalogenation of $CHPh{:}CH{\cdot}CO_2H$; formation of $(CH_2{\cdot}OH)_2$ from C_2H_4; autoxidation of tetraphenylxylylene and of CPh_3; polymerisation of unsaturated compounds such as $CH_2{:}CHCl$, C_2H_4, $CHPh{:}CH_2$, $CPh_2{:}CH_2$, and butadiene. H. W.

Attempts to prepare the methylene radical by the thermal decomposition of hydrocarbons. F. O. RICE (J. Amer. Chem. Soc., 1939, **61**, 213).—By using a long hot wire and long Te mirrors, Te_2Me_2 is obtained from CH_4 and other hydrocarbons. CH_2 is unstable, readily giving Me. R. S. C.

New catalytic methods of synthesis of hydrocarbons. V. N. IPATIEV (Bull. Soc. Chim. Yougoslav., 1938, **9**, 73—88).—A lecture. R. T.

Thermal stability of butane and *iso*butane. G. R. SCHULTZE and H. WELLER (Oel u. Kohle, 1938, **14**, 998—1011).—The C_4H_{10} used in previous work on its thermal decomp. (B., 1937, 20) was a mixture of *n*- and *iso*-C_4H_{10}. Pure *n*- or *iso*-C_4H_{10}, either alone or mixed with N_2, was passed through an electrically-heated SiO_2 tube (contact times 0·3—1·3 sec.). By extrapolation to zero contact time the primary decomp. reactions at 700° were found to be (*a*) $n\text{-}C_4H_{10} \rightarrow C_4H_8 + H_2$ (15%), $n\text{-}C_4H_{10} \rightarrow C_3H_6 + CH_4$ (54%), $n\text{-}C_4H_{10} \rightarrow 2C_2H_4 + H_2$ (16%), and $n\text{-}C_4H_{10} \rightarrow C_2H_4 + C_2H_6$ (13%); and (*b*) $i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_8 + H_2$ (52%), and $i\text{-}C_4H_{10} \rightarrow C_3H_6 + CH_4$ (48%). The variation of these with temp. (672—738°) and the effect thereon of the addition of N_2 are also recorded. It is concluded that chain reactions are involved. A. B. M.

Organic peroxide formed during the decomposition, by oxidation, of saturated hydrocarbons. K. IVANOV (Acta Physicochim. U.R.S.S., 1938, **9**, 421—452).—Oxidation data have been obtained for *cyclo*hexane at 316° and 328°, C_7H_{16} at 255°, and *iso*-C_7H_{16} at 295°. Non-volatile peroxides, $C_7H_{14}O_7$ and $C_4H_8O_4$, were obtained from the first compound and $C_3H_6O_4$ from the second and third. The properties and possible structures of these peroxides and the oxidation mechanism are discussed. C. R. H.

Oxidation of unsaturated hydrocarbons by hydrogen peroxide in presence of pervanadic acid. I. General course of the reaction and primary oxidation products. W. TREIBS (Ber., 1938, **72**, [*B*], 7—10).—The oxidations are conveniently effected in $COMe_2$ with pervanadic acid as catalyst and indicator. The reaction of very resistant hydrocarbons is accelerated by sunlight but it is uncertain whether this is a true photocatalysis. The presence of trimeric acetone peroxide has never been detected but it is possible that a monomeric peroxide is an unstable intermediate of the reaction. Usually there is an induction period which is more pronounced with increasing purity of the hydrocarbon. The primary products of the catalysed H_2O_2 oxidation of olefines are α-oxides and α-unsaturated alcohols. The yield of the former increases with increasing concn. of the solution and with diminishing temp. The best results are obtained with normal hydrocarbons with terminal double linking. The oxides of some *cyclo*olefines (pinene; Δ^4-carene) are very unstable; these terpenes contain a 4- or 3-membered ring in conjugation to a double linking. These oxides immediately add H_2O with fission of the rings and production of unsaturated glycols. Caryophyllene gives a very stable α-oxide in 80% yield. αβ-Unsaturated alcohols arise in very small amount by the oxidation of aliphatic olefines but are the main product from *cyclo*olefines without side-chains (*cyclo*hexene, tetrahydronaphthalene). If side-chains are present the course of the reaction depends on their position. Under drastic conditions the unsaturated alcohols are transformed into oxide-alcohols. Oxidation of alcohols to ketones is not effected by H_2O_2 or only with very great difficulty. αβ-Unsaturated ketones and certain aldehydes are transformed by H_2O_2 into their peroxides. H. W.

Stability of co-ordinated ethylene hydrocarbons. A. GELMAN (Compt. rend. Acad. Sci. U.R.S.S., 1938, **20**, 307—310; cf. A., 1938, I, 43).—$CHPh{:}CH_2$ displaces C_2H_4 in Pt complexes. All ethylenic hydrocarbons are displaced by CO. Cossa's salt may be used as a reagent for C_2H_4 in gaseous mixtures. O. D. S.

Bromination of trimethylethylene. W. E. VAUGHAN and F. F. RUST (J. Amer. Chem. Soc., 1939, **61**, 215—216).—The course of the reaction between $CMe_2{:}CH_2$ and Cl_2 depends greatly on the temp. and surface. Whereas at 109° in presence of $CaCl_2$ only 19% of HCl is liberated, at 70° 93% of

substitution occurs; much of the HCl formed adds to produce Bu$^{\gamma}$Cl. Reaction of CMe_2:CHMe is also complex, which invalidates the thermal data of Conn *et al.* (A., 1939, I, 28). R. S. C.

Bromination of trimethylethylene. J. B. Conn, G. B. Kistiakowsky, and E. A. Smith (J. Amer. Chem. Soc., 1939, **61**, 216—217).—Side reactions (cf. preceding abstract) occur only slightly under the authors' conditions (A., 1939, I, 28) and do not invalidate the results. R. S. C.

Sodium saccharin as a reagent for the identification of alkyl halides. L. L. Merritt, jun., S. Levey, and H. B. Cutter (J. Amer. Chem. Soc., 1939, **61**, 15—16).—Alkyl halides are characterised by condensing with Na saccharin in hot, aq. OH·$[CH_2]_2$·OBu. MeCl, EtCl, $(CH_2Cl)_2$, branched-chain and *tert.* chlorides do not react. N-iso*Propyl*-, m.p. 134°, -n-, m.p. 38—39·5°, -iso-, m.p. 75°, and sec.-*butyl*-, m.p. 81°, -n-*amyl*-, m.p. 58°, and -*allyl*-, m.p. 99°, -*saccharin*, are prepared. R. S. C.

Reactivity of carbon tetrachloride. H. J. Hofmann (Angew. Chem., 1939, **52**, 96—99).—Exposure of mixtures of CCl_4 and NH_2Ph to diffused daylight speedily causes the production of Cl′. In the dark the mixture appears to be stable but it is very sensitive to ultra-violet light. Irradiation of mixtures of CCl_4 and H_2O for 24 hr. does not appear to cause the formation of HCl, whilst in absence of NH_2Ph the change $2CCl_4 \rightarrow C_2Cl_6 + Cl_2$ does not occur. The products of the interaction of NH_2Ph and CCl_4 are $CO(NHPh)_2$, p-*aminobenzoic acid*-NN′-*diphenylamidine*, m.p. 196°, and its *hydrochloride*, m.p. 280°, a *compound* $C_{19}H_{18}N_3Cl$, grey-green leaflets, m.p. 248°, a *substance*, (?) $C_{33}H_{25}ON_5$, red needles, m.p. 248°, azobenzene, and NH_2Ph,HCl. Air is without influence on the change, which is not caused by the free NH_2 of NH_2Ph since $NPhMe_2$ is also active. CCl_4 can react with complex hydrocarbons if reactive positions are present in the mol. Conversely, reactivity with CCl_4 can be used in the detection of active positions in the mol. Reaction occurs also with products from mineral oils, the vigour of the change with oils of similar origin increasing from gas oil to cylinder oil. Exhaustive treatment with H_2SO_4 removes from the oils the components with groups reactive towards CCl_4 so that white oil does not react with CCl_4. Reaction with CCl_4 can lead to errors in quant. analysis. H. W.

Polymerisation of chloroprene as revealed by the Raman effect.—See A., 1939, I, 150.

Action of mineral acids on primary nitroparaffins. S. B. Lippincott and H. B. Hass (Ind. Eng. Chem., 1939, **31**, 118—120).—85% H_2SO_4 (1 mol.) is introduced into boiling $EtNO_2$ (or $PrNO_2$) (1 mol.) and the mixture boiled gently for 8 hr. [temp. rises to 117° (140°)] to give AcOH (or $EtCO_2H$), NH_2OH, and some NH_3. $PrNO_2$ (1 mol.) and 100% H_2SO_4 (1 mol.) mixed at room temp. and heated carefully to 60°, kept at 50—60° for 16 hr., then at 95—100° for 5 hr., give OH·CHEt:N·OH, m.p. 92·5—93·5°. Equimols. of $BuNO_2$ (or $Bu^{\beta}NO_2$) and 85% H_2SO_4 at 140°, then refluxed for 2 hr. (8 hr.) [temp. rises to 158° (154°)], give $PrCO_2H$ (or $Pr^{\beta}CO_2H$) (90% yields), with NH_2OH and NH_3. Steam-distillation affords unchanged nitroparaffin and fatty acid [determined by titration with alkali (neutral-red indicator)] and a residue containing NH_2OH. A. T. P.

Action of caustic alkali and of alkaline salts on alcohols. E. E. Reid, H. Worthington, and A. W. Larchar (J. Amer. Chem. Soc., 1939, **61**, 99—101).—MeOH, EtOH, Pr$^{\alpha}$OH, Bu$^{\gamma}$OH, Bu$^{\alpha}$OH, and CMeEtBu$^{\alpha}$·OH are treated with aq. NaOH and KOH in various proportions at 320—380°. The reaction, $CH_2R{\cdot}OH + NaOH \rightarrow RCO_2Na + 2H_2$, is almost quant. under some conditions (*e.g.*, excess of alkali and at least some H_2O). Under other conditions, the reaction, $2CH_2R{\cdot}CH_2{\cdot}OH \rightarrow CH_2R{\cdot}CH_2{\cdot}CHR{\cdot}CH_2{\cdot}OH$, occurs largely; it is effected with moderate yields by use of org. K or Na salts. R. S. C.

***n*-Amyl deuteralcohol and ethyl deuterothiol.**—See A., 1939, I, 143.

Action of sulphur in catalytic hydrogenations at high pressure.—See A., 1939, I, 151.

Preparation of glycols from ethylene hydrocarbons. H. Moureu, M. Dodé, and (Mme.) Dodé (Mém. Poudres, 1938, **28**, 252—264).—Methods used for preparing glycols may be used for preparing the homologues of C_2H_4. Hydrolysis of the monochlorohydrin with $NaHCO_3$ gives good yields but the solutions are very dil., and contain considerable amounts of NaCl, difficult to remove. An alternative method consists in converting the monochlorohydrins into the corresponding oxides, which are then transformed into glycols. This intermediate stage permits the separation of the components of mixtures of C_2H_4, C_3H_6, and C_4H_8. W. J. W.

Unsaponifiable matter from liver oils. I. Chimyl alcohol. Z. Nakamiya (Bull. Inst. Phys. Chem. Res. Japan, 1938, **17**, 837—852).—Sukeso-liver oil yields 6% of unsaponifiable matter, separated by fractionation of the acetates into chimyl alcohol (*diacetate*, m.p. 22°; *dibenzoate*; *di*-3 : 5-*dinitrobenzoate*, m.p. 58—59°; *diphenylurethane*, m.p. 100—100·5°; *anthraquinone*-2-*carboxylate*, m.p. 71—73°), batyl alcohol (*anthraquinone*-2-*carboxylate*, m.p. 79—80°), and a small quantity of *skesyl alcohol*, $C_{17}H_{34}O(OH)_2$, m.p. 64—65° (*diphenylurethane*, m.p. 79°). Since chimyl iodide with AgOAc gives cetyl alcohol, chimyl alcohol is glycerol monocetyl ether. A. Li.

Induced peroxide formation during the bromination of olefines. W. Bockemüller and L. Pfeuffer (Annalen, 1939, **537**, 178—196).—When exposed to O_2 and Br vapour, *cyclo*hexene, CH_2:CHPh, CH_2:CPh_2, CH_2:CH·CH_2Cl (I), or CH_2:CH·CH_2Br (II) absorbs both Br and O_2 in ratios which depend on the olefine, temp., and solvent (if any). The products are peroxides. That from (II) is isolated as an oil (impure) and is probably $(CH_2Br{\cdot}CHMe)_2O_2$, since reduction ($TiCl_3$, SO_2, or HI) gives $CH_2Br{\cdot}CHMe{\cdot}OH$ and thermal decomp. gives mainly $CO(CH_2Br)_2$ with less $COMe{\cdot}CH_2Br$, H_2O, HBr, and $C_3H_5Br_3$. Alkaline H_2O_2 and $Pr^{\beta}{}_2SO_4$ give only $Pr^{\beta}O_2H$, but $Pr^{\beta}O_2H$ and alkaline Me_2SO_4 give *Me Pr$^{\beta}$ peroxide*, b.p. 53—54°, which at 300° or

in paraffin at 200° gives CH_2O, $COMe_2$, and H_2O. Thermal decomp. of the crude peroxide from (I) gives $COMe{\cdot}CH_2Cl$ and HBr with less $COMe{\cdot}CH_2Br$ and HCl. $HgPr^{\beta}_2$ and O_3 give $COMe_2$ and HgO. R. S. C.

Reaction of thiol compounds with aliphatic olefines. V. N. IPATIEV and R. S. FRIEDMAN (J. Amer. Chem. Soc., 1939, **61**, 71—74).—AlkSH or AcSH adds to olefines contrary to Markovnikov's rule, but H_2S adds in accordance with it. An excess of H_2S gives mainly mercaptans, an excess of olefine gives mainly thioethers. Yields increase with branching of the chain. The following are reported. Bu^{β} (?) Bu^{γ}, b.p. 152—156°, Et Bu^{β} (*compound*, X,$2HgCl_2$, m.p. 107—108°), Et *iso-* (*compound*, X,$2HgCl_2$, m.p. 86—87°), and sec.-iso-*amyl*, b.p. 150—152·5°/751 mm. (*compound*, X_2,$PdCl_2$, m.p. 92·5—94°), and Bu^{α} Bu^{β} (*compounds*, X,$2HgCl_2$, m.p. 105—106°, and X_2,$PdCl_2$, m.p. 73·5°), *sulphide*. *tert.*-$C_5H_{11}{\cdot}SH$, b.p. 98—100° (lit., 78°, 97°) [$Hg^{\cdot\cdot}$ salt, m.p. 59—60° (lit., 157°)]. Bu^{β}, new b.p. 151—152°/744 mm., iso-, b.p. 175—177°/748 mm., and sec.-iso-*amyl thioacetate*, b.p. 75—76°/30 mm. R. S. C.

Halogen derivatives of triethylsulphonylmethane. E. SAMÉN (Arkiv Kemi, Min., Geol., 1938, **12**, B, No. 51, 7 pp.).—Interaction of Br and $CH(SO_2Et)_3$ (I), m.p. 218—220° (corr.) (lit. 212°), yields *bromotriethylsulphonylmethane* (II), m.p. 134—135° (corr.), which is a strong acid, oxidises HI to I, and decomposes N_2H_4 quantitatively to N_2. Similarly *chlorotriethylsulphonylmethane*, m.p. 143—144°, is formed from (I) and Cl_2 in H_2O. (II) is decomposed by HBr to (I) and Br; it is shown colorimetrically that the equilibrium (I) + $Br_2 \rightleftharpoons$ (II) + HBr is established in HBr solution. J. D. R.

Esters of sulphurous, chlorosulphinic, and chlorosulphonic acids. I. W. GERRARD (J.C.S., 1939, 99—103).—Interaction of BuOH, $SOCl_2$, and C_5H_5N (1 : 1 : 1 mol.) at 0° yields $Bu^{\alpha}{}_2SO_3$ in 80% yield, increased to 87% by carrying out the reaction in Et_2O. Similarly, *n*-amyl alcohol and Et lactate yield respectively *n*-amyl and α-carbethoxyethyl sulphite. When the above reactions are carried out at higher temp. and in presence of excess of C_5H_5N (2—3 mols.), the alkyl chloride and sulphite are produced. The alkyl chloride is formed by catalytic decomp. of the primarily formed chlorosulphinate by C_5H_5N,HCl. Bu^{α} chlorosulphinate (I) and Et α-chlorosulphinoxypropionate (II) when heated with C_5H_5N,HCl yield BuCl and $CHMeCl{\cdot}CO_2Et$, respectively. Interaction of HCO_2H and (II) yields *Et α-formoxypropionate*, b.p. 69—70°/18 mm., α^{18}_D −6·38°, but no CO. Similarly (I), Bu^{β}, Et, and *iso*-amyl chlorosulphinates with HCO_2H give the appropriate formate, HCl, and SO_2, but no CO, which affords a method of detection of $SOCl_2$ (which with HCO_2H yields CO) in presence of a chlorosulphinate. $SOCl_2$ in Et_2O with PhOH at −5° yields Ph chlorosulphinate, b.p. 100·5—101°/18 mm. J. D. R.

Reaction of esters with sodium in liquid ammonia. M. S. KHARASCH, E. STERNFELD, and F. R. MAYO (J. Amer. Chem. Soc., 1939, **61**, 215).—Addition of EtOBz to 2 Na in liquid NH_3 and evaporation gives a powder (I), which inflames spontaneously in air, with H_2O gives PhCHO and $CH_2Ph{\cdot}COPh$, with EtBr gives COPhEt, with BuBr gives COPhBu, and with CH_2PhCl gives $CH_2Ph{\cdot}COPh$. $(CPh{\cdot}ONa)_2$ and NaOEt in liquid NH_3 give (I). $Pr^{\beta}CO_2Et$ and $Bu^{\gamma}CO_2Et$ react similarly. The following reactions are postulated. $RCO_2Et + Na \rightarrow OEt{\cdot}CR{\cdot}ONa$ (II) $\rightleftharpoons$ $(OEt{\cdot}CR{\cdot}ONa)_2$ (III) $\rightleftharpoons$ $(COR)_2$ (IV) $\xrightarrow{2Na}$ $OEt{\cdot}CRNa{\cdot}ONa$ (V) [*e.g.*, (I)] $\rightleftharpoons$ (III); (IV) + 2Na → (V); (II) + 2Na → (V). R. S. C.

Constitution of nephromopsic acid. II. M. ASANO and T. AZUMI (Ber., 1939, **72**, [*B*], 35—39).—Treatment of nephromopsic acid (I) with 2 equivs. of KOH and of the solution with $AgNO_3$ gives a *Ag* salt, transformed by MeI into Me nephromopsate (II), identical with that from (I) and CH_2N_2. Hydrolysis of (II) with KOH–EtOH affords dihydro-*l*-protolichesteric acid, m.p. 103—105°, $[\alpha]^{\text{D}}_{\text{D}}$ −33·3° in $CHCl_3$, the change involving the racemisation of $C_{(2)}$. (I) is unchanged by KOH–EtOH at 100°. *Et pelargonoylacetate*, b.p. 115°/2 mm., 149—151°/16 mm., from NH_3 and Et pelargonoylacetoacetate or from Et pelargonate, EtOAc, and Na, is converted by $CHMeBr{\cdot}CO_2Et$ and Na in EtOH at 120° into *Et* α-*pelargonoyl*-α-*methylsuccinate*, b.p. 158—162°/3 mm., reduced (Na–Hg) to α-*methyl*-γ-*octylparaconic acid* (II), m.p. 112—114°, and a mixture of esters hydrolysed to (II) and γ-*keto*-α-*methyl-lauric acid*, m.p. 62—63° (*semicarbazone*, m.p. 125—126·5°). The Et ester of (II) is transformed by NaOEt–EtOH at 90—100° and subsequent hydrolysis into α-*methyl*-α′-*nonylidenesuccinic acid*, m.p. 132—134°, which with Br–H_2O gives small amounts of an unidentified *compound*, m.p. 115—120°. Et myristoylacetate, $CHMeBr{\cdot}CO_2Et$, and NaOEt give *Et* α-*myristoyl*-α-*methylsuccinate*, reduced and hydrolysed to myristic acid, lichesterylic acid, m.p. 80—83°, and α-*methyl*-γ-*tridecylparaconic acid*, m.p. 134—136°. 3-*Pelargonoyl*-6-*octylpyronone*, m.p. 70—71°, and 3-*myristoyl*-6-*tridecylpyronone*, m.p. 85·5—87° [transformed by HI (*d* 1·7) at 160—170° into *tridecylpyrone*, m.p. 65—66°], are incidentally described. H. W.

***X*-Ray and thermal examination of the glycerides. IV. Symmetrical mixed triglycerides $CH(O{\cdot}COR')(CH_2O{\cdot}COR)_2$.** T. MALKIN and M. L. MEARA (J.C.S., 1939, 103—108).—The symmetrical mixed triglycerides $CH(O{\cdot}COR')(CH_2{\cdot}O{\cdot}COR)_2$ are divided into two groups: (*a*) in which R′ is shorter than R, viz., β-decodilaurin (I), β-laurodistearin (II), β-myristodipalmitin (III), β-palmitodistearin (IV), and (*b*) in which R′ is longer than R, viz., β-*laurodidecoin* (V) (from αα′-didecoin and lauroyl chloride), β-myristodilaurin (VI), β-palmitodimyristin (VII), and β-stearodipalmitin (VIII). All the glycerides exist in four solid modifications, vitreous, α, β, and β′, the m.p. of which are, in the order given; (I), 8°, 23°, 33°, 38·5°, (II) 24°, 35°, 45°, 50°, (III) 37°, 46°, 55°, 60°, (IV) 50°, 56°, 64°, 68°, (V) 6°, 25°, 34°, 37·5°, (VI) 24°, 37°, 44°, 48°, (VII) 38°, 49°, 55°, 58·5°, (VIII) 49°, 59°, 65°, 68°. The transition from forms of lower to those of higher m.p. is more rapid than with the simple triglycerides. *X*-Ray data of the various forms (except vitreous) are given, and support the "tuning fork" structure advanced for the simple

triglycerides (A., 1934, 720). The *X*-ray spectra of the stable forms of group (*a*) are different from those of group (*b*). J. D. R.

Thermal polymerisation of ethyl elæostearate and ethyl 9κ- and 9λ-linoleate. J. S. Brod, W. G. France, and W. L. Evans (Ind. Eng. Chem., 1939, **31**, 114—118).—Et elæostearate (I) (from tung oil) and mixed Et linoleates (II) (from dehydrated castor oil) are heated at 300°. (I) turns deep yellow in 10 min., whereas (II) becomes yellow only after 12 hr.; a control of Et oleate shows no apparent change. Vals. of mol. wt., η, and diene, acid, and I vals. are observed at intervals. Unpolymerised material is separated from polymerised by high-vac. distillation. With (I), both isomerisation (probably to a cyclic form) and polymerisation (only to the dimeride) occur rapidly; equilibrium is reached at 27% of mono- [isomeric form of (I)] and 73% of di-meride. On further heating, some change in the monomeride continues until no conjugated double linkings are present. Gelation occurs in the triglycerides of the higher unsaturated fatty acids before the max. possible no. of dibasic acids have been formed by intermol. attachment at the double linkings. Since no particles are detected on ultra-microscopic examination of the polymerides in EtOH, no high polymerides or colloidal aggregates are formed. In the case of (II), the 9λ-derivative (III) probably isomerises to the 9κ-derivative, followed by mainly dimerisation of the latter. An apparent equilibrium is reached after about 5 hr. at 300°, corresponding with 2 mols. of mono- [mainly (III)] to 3 mols. of di-meride. Both dimerides, from (I) or (II), probably contain a 6-membered ring. A. T. P.

Ethyl trimesate as by-product of the electrolysis of ethyl hydrogen succinate. F. Fichter and A. Maritz (Helv. Chim. Acta, 1939, **22**, 265—267).—Et_3 trimesate, m.p. 134—134·5°, is identified among the by-products of higher b.p. obtained by the electrolysis of $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$; it appears to be formed by the anodic oxidation of intermediately formed $OH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$. H. W.

Physico-chemical properties of ascorbic and dehydroascorbic acid. J. C. Ghosh and P. C. Rakshit (Biochem. Z., 1938, **299**, 394—405).—Vals. for $[\alpha]_D^{25}$ of ascorbic acid (I), dehydroascorbic acid (II), and their Na salts are given. The dissociation of (I) and the reducing properties and reversible reduction by H_2S of (II) are described and the circular dichroism of (I) is measured. Pure (II) is obtained from (I) in presence of a small amount of colloidal Pt by adding somewhat > the calc. amount of H_2O_2. W. McC.

Esters of methanetetracarboxylic acid. H. J. Backer and J. Lolkema (Rec. trav. chim., 1939, **58**, 23—33).—Esters, $C(CO_2R)_4$ and $C(CO_2Pr^\beta)_3{\cdot}CO_2R'$, are prepared from $ClCO_2R'$ and $CNa(CO_2R)_3$ [from $CH(CO_2R)_3$ and NaOR or Na in xylene]. The following are described: Pr^α_4, b.p. 195·5—196°/10 mm.; Pr^β_4 (I), m.p. 76°, b.p. 176°/12—13 mm.; Bu^α_4, b.p. 184—185°/1·5 mm.; Bu^β_4, b.p. 177—178°/3 mm.; sec.-Bu_4, m.p. 42—43°, b.p. 173—174°/2·5 mm.; (n-$C_5H_{11})_4$, b.p. 215—215·5°/2·5 mm.; (iso-$C_5H_{11})_4$, b.p. 214—217°/4—5 mm.; $(CHEt_2)_4$, b.p. 184°/2·5 mm.; (n-$C_{10}H_{21})_4$, b.p. 240—241°/0·001 mm.; (cyclo-$C_6H_{11})_4$ (II), m.p. 110°, b.p. 180—200°/0·0005; $Me_2\ Pr^\beta_2$ [from $CH(CO_2Pr^\beta)_2{\cdot}CO_2Me$], m.p. —5°, b.p. 141°/2·5 mm.; $Me\ Pr^\beta_3$, b.p. 140—141°/2·5 mm.; $Pr^\beta_3\ CHMeEt$, m.p. 35—36°, b.p. 167—168°/5 mm.; cyclo-$C_6H_{11}\ Pr^\beta_3$, b.p. 172—173°/2·5 mm.; $Ph\ Pr^\beta_3$ (III), m.p. 73·5—74°; p-$C_6H_4Me\ Pr^\beta_3$, m.p. 62—63°. With $C(CO_2Et)_4$, $CO(NH_2)_2$ and NaOEt give barbituric acid, whilst NH_2Ph gives $CH_2(CO{\cdot}NHPh)_2$ and $CO(NHPh)_2$. Crystallographic data for (I), (II), and (III) are recorded. E. W. W.

Stepwise degradation of lycopene. P. Karrer and W. Jaffé (Helv. Chim. Acta, 1939, **22**, 69—71).—Oxidation of lycopene in C_6H_6 by aq. $KMnO_4$–Na_2CO_3 and chromatographic purification [$Ca(OH)_2$] of the product yields bixindialdehyde, m.p. 218° (dioxime, m.p. >250°), apo-1-*bixindialdehyde*, m.p. 168° (*dioxime*, sinters >210°), apo-2-*lycopenal*, m.p. 147° after softening at 144°, and apo-3-*lycopenal*, m.p. 138°. H. W.

Synthesis of long-chain ketones. J. W. H. Oldham and A. R. Ubbelohde (J.C.S., 1939, 201—202).—Various methods of synthesis of long-chain ketones are reviewed, with respect to yield, convenience, and ease of purification of the product. In the pyrogenetic synthesis by passing the vapours of the two acids over ThO_2, a large excess (10 : 1) of the short-chain acid is used. In the acetoacetic ester synthesis, the acyl derivative is first prepared and then treated with an alkyl halide, which should be <4 C. Interaction of long-chain nitriles with a short-chain Grignard reagent is recommended in certain cases, particularly for the synthesis of diketones. J. D. R.

Crystalline *D*-altrosan. N. K. Richtmyer and C. S. Hudson (J. Amer. Chem. Soc., 1939, **61**, 214—215).—D-*Altrosan*, m.p. 80—90°, $[\alpha]_D^{20}$ —215° in H_2O, is obtained from *D*-altrose and hot HCl (cf. A., 1935, 1355) and with N-HCl gives the known altrose equilibrium mixture. R. S. C.

Preparation of rhamnose from naringin. G. N. Pulley and H. W. von Loesecke (J. Amer. Chem. Soc., 1939, **61**, 175—176).—Prep. of rhamnose from naringin (obtained from grapefruit cannery waste) is detailed. R. S. C.

Synthetic sugar anhydrides. IX. Further anhydride from 2 : 3 : 6-trimethylglucose. K. Hess and K. E. Heumann (Ber., 1939, **72**, [*B*], 137—148).—2 : 3 : 6-Trimethylglucofuranose 1-acetate 5-*p*-toluenesulphonate is converted by NaOEt into a *trimethylhexose anhydride* (I), b.p. 34—35°/0·0008 mm., m.p. 8·7°, $[\alpha]_D^{20}$ —1·8° in H_2O, —1·6° in MeOH, —0·8° in $CHCl_3$, +2·84° (in substance), which is stable towards boiling Fehling's solution, is hydrolysed by 20% HCl to a reducing sugar, is not immediately affected by Na_2CO_3–$KMnO_4$, does not decolorise Br in $CHCl_3$, is unaffected by Na, and remains unchanged at 100—105° in a sealed tube. Its non-identity with idose anhydride and considerations of space models cause (I) to be regarded as a glucose derivative. (I) is very resistant towards acid hydrolysis and the reducing product (II) obtained from it with boiling 20% HCl is not identical with trimethyl-*l*-idose or trimethyl-*d*-glucose. Treatment

of (I) with Ac_2O–H_2SO_4 followed by hydrolysis of the acetate gives a hexose with different sp. rotation ($[\alpha]_D^{20}$ +9·4°) but similar composition so that Walden inversion appears to occur during hydrolysis either at $C_{(4)}$ or $C_{(5)}$ or simultaneously at $C_{(4)}$ and $C_{(5)}$ according to the nature of the reagent. Demethylation of (II) by HBr leads to elimination of only 2 Me groups whilst the use of more drastic conditions leads to humification. H. W.

Sterically homogeneous forms of 2 : 3 : 6-trimethylmethyl-*d*-glucofuranoside and its derivatives. K. Hess and K. E. Heumann (Ber., 1939, 72, [*B*], 149—158).—During glucosidification of 2 : 3 : 6-trimethylglucose by 1% HCl–MeOH at 20°, $[\alpha]_D^{20}$ of the product passes through a min. after 20 hr. The mixture thus obtained is separated by fractional distillation of its compound with $CaCl_2$ (under defined conditions) into greatly enriched samples of the α- (I) and β- (II) -forms of 2 : 3 : 6-*trimethylmethyl*-d-*glucofuranoside*. (II) is transformed by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N into 2 : 3 : 6-*trimethyl*-β-*methyl*-d-*glucofuranoside* 5-p-*toluenesulphonate* (III), m.p. 51—52°, $[\alpha]_D^{20}$ −62·1° in MeOH, −60·4° in C_6H_6, −57·7° in $CHCl_3$, reduced (Na–Hg) to homogeneous, non-cryst. (III), b.p. 70—72°/0·005 mm., $[\alpha]_D^{20}$ −97·5° in MeOH, −91·6° in $CHCl_3$, −88·0° in H_2O, re-converted into (II). $TiCl_4$ in $CHCl_3$ isomerises (III) to 2 : 3 : 6-*trimethyl*-α-*methyl*-d-*glucofuranoside* 5-p-*toluenesulphonate* (IV), a syrup, $[\alpha]_D^{20}$ +97·7° in MeOH, +92·6° in $CHCl_3$, +95·9° in C_6H_6, reduced to 2 : 3 : 6-*trimethyl*-2-*methyl*-d-*glucofuranoside*, $[\alpha]_D^{20}$ +95·7° in MeOH, +91·6° in $CHCl_3$, +88·7° in H_2O. (VI) is methylated (Ag_2O–MeI) to 2 : 3 : 5 : 6-*tetramethyl*-β-*methyl*-d-*glucofuranose*, b.p. 48—50°/0·003 mm., $[\alpha]_D^{20}$ −74·1° in $CHCl_3$, −72·7° in MeOH, −67·3° in H_2O, hydrolysed by 2% HCl to 2 : 3 : 5 : 6-tetramethyl-*d*-glucofuranose, $[\alpha]_D^{24}$ −24·8° in $CHCl_3$. BzCl in $CHCl_3$–C_5H_5N transforms (II) at 40° into 2 : 3 : 6-*trimethyl*-β-*methyl*-d-*glucofuranoside* 5-*benzoate*, m.p. 55—56°, $[\alpha]_D^{20}$ −92·6° in $CHCl_3$, −104·2° in MeOH, −138·0° in C_6H_6, converted by HCl–Et_2O into homogeneous, cryst. 1-chloro-2 : 3 : 6-trimethyl-β-*d*-glucofuranose 5-benzoate and isomerised by $TiCl_4$ into 2 : 3 : 6-*trimethyl*-α-*methyl*-d-*glucofuranoside* 5-*benzoate*, a colourless syrup, $[\alpha]_D^{20}$ +54·4° in MeOH, +53·5° in $CHCl_3$, +46·5° in C_6H_6. Under varied conditions (III) is transformed by HCl–Ac_2O, HCl–Et_2O, or liquid HCl into a non-cryst. mixture of 1-chloro-2 : 3 : 6-trimethyl-αβ-*d*-glucofuranose *p*-toluenesulphonates, $[\alpha]_D^{20}$ +15·5° in $CHCl_3$. A mixture of 2 : 3 : 6-trimethyl-*d*-glucofuranose 1-acetate 2-*p*-toluenesulphonates is derived from (III) or (IV) and H_2SO_4–Ac_2O. H. W.

Transformation of α- and β-forms of 3 : 6-anhydromethylgalactosides. W. N. Haworth, J. Jackson, and F. Smith (Nature, 1938, **142**, 1075—1076).—Liquid 2 : 4-dimethyl-3 : 6-anhydro-α-methyl-*d*-galactopyranoside (prep. given) changes to the corresponding cryst. β-form on brief contact with air containing a trace of HCl. Ebullioscopic methods, and *X*-ray examination of the β-form, indicate that both forms are monomeric. The same change can be effected by addition of a drop of a solution of HCl in EtOH or Et_2O. Hydrolysis to the free sugar, followed by mutarotation, and regeneration of the two forms of the methylglucoside, does not apply to this case. L. S. T.

Action of mercury salts on acetohalogenosugars. XII. Advantageous synthesis of primverose derivatives and of primverose. G. Zemplén and R. Bognár (Ber., 1939, 72, [*B*], 47—49; cf. A., 1938, II, 219).—α-Acetobromoxylose, α-1-chloroglucose 2 : 3 : 4-triacetate, and $Hg(OAc)_2$ in C_6H_6 at 40—50° give *acetochloroprimverose* (I), m.p. 190—192° after incipient decomp. at 186°, $[\alpha]_D^{20}$ +70·8° in $CHCl_3$, in 50·7% yield. AgOAc in Ac_2O at 100° converts (I) into a mixture (mainly β) of primverose hepta-acetates, hydrolysed to primverose and converted by $TiBr_4$ in $CHCl_3$ free from EtOH into cryst. α-acetobromoprimverose, $[\alpha]_D^{20}$ +122·6° in $CHCl_3$. H. W.

Emulsin. XXXVI. Enzymic fission of lactose, lactulose, and neolactose. B. Helferich and W. W. Pigman (Ber., 1939, 72, [*B*], 212—215).—In accordance with the β-*d*-galactosidatic action of emulsin of sweet almonds, lactose, lactulose (I), and neolactose (II) are qualitatively hydrolysed by the enzyme. With all three substrates the activity increases markedly when the enzyme purified by Ag pptn. is substituted for the crude enzyme. Since this mode of purification causes almost complete removal of α-*d*-galactosidase this increase in the rate of hydrolysis of (I) and (II) is proof of the retention of the β-configuration of galactose in (I) and (II). H. W.

Synthesis of a new glucogallic acid. F. Mauthner (J. pr. Chem., 1939, [ii], **152**, 20—23).—Addition of Ag_2O to 3 : 4 : 5 : 1-$(OMe)_2C_6H_2(OH){\cdot}CO_2Me$ and acetobromoglucose in anhyd. quinoline followed by hydrolysis of the product gives 3 : 4-*dimethoxy*-5-*glucosoxybenzoic acid*, m.p. 197—198°. H. W.

Action of amylases on substances of low mol. wt. K. Myrbäck and B. Örtenblad (Svensk Kem. Tidskr., 1938, **50**, 284—297).—Experiments with native starches and the degradation products obtained therefrom by heating in glycerol, by treatment with cold conc. HCl, or by enzymes show that β-amylase gives about 60% of maltose (I) from starch and dextrins of mol. wt. comparable with that of the parent. Apparently various starch mols. are saccharified in very varying degree, some probably completely to (I), others little or not at all. The cause must lie in anomalies in structure. The enzyme removes a mol. of (I) from the non-reducing end of the chain and the process continues until the first anomaly is reached, when fission ceases. It is impossible to assume that the substitution by PO_4 etc. plays an exclusive part or that fission ceases at a definite chain length since the β-dextrins are highly non-uniform. Malt α-amylase (II) hydrolyses starch primarily to dextrins which are not coloured by I. In the case of potato starch these have a mean mol. wt. of about 7000 (= about 45 glucose residues). Little (I) is formed during this dextrinisation but the viscosity diminishes greatly so that it is doubtful if the enzyme is actually "disaggregating." The products of the action show

a well-defined reduction, showing that glucose unions are disrupted. Starch therefore appears to contain linkings other than the normal (I) unions to some extent and these are broken by (II). The action of the enzyme does not proceed from the ends of the chains. It appears that (II) hydrolyses well-defined linkings. These are not necessarily β-glucosidic but may be α-glucosidic 1 : 6 or 1 : 3 unions or 1 : 4 linkings between glucose residues which are abnormal in some manner. Natural mixtures of α- and β-enzymes and certain amylases (taka-diastase, animal amylases) which are considered to be uniform α-compounds hydrolyse starch with production of much (I) (yield often >90%). The limit dextrins have a low mol. wt., the chain length being frequently only 4—6 glucose units. The experiments are difficult to evaluate since little is known of the enzymic uniformity of the preps. The great variations in the yield of (I) show that natural amylases in addition to the normal amylases contain substances which influence the degree of saccharification. It is considered that these substances attack linkings which are immune to the normal material and hence can hydrolyse certain limit dextrins. Hydrolysis of native starches by amylase appears to establish the existence in starch of linkings other than the customary maltose unions. The no. of these linkings is probably relatively small and the anomalies may be accumulated in the limit dextrins. The results are fully confirmed by observations with the degraded products of starch.

H. W.

Cellulose compounds. E. Berl and W. Koerber (J. Amer. Chem. Soc., 1939, **61**, 154—157).—The microscopic appearance of cellulose nitrates (12·02—13·9% N) in Et_2O, EtOH, Et_2O–EtOH (3 : 2), MeOH, AcOH, $(CH_2{\cdot}OH)_2$, Ac_2O, HCO_2H, EtOAc, and MeOAc is recorded. Some of the nitrates are more sol. in Et_2O–EtOH, MeOH, and MeOAc at −50° than at 0°, indicating formation of mol. compounds which dissociate at 0°.

R. S. C.

Oxycellulose. I. II. New reaction of hydrocellulose. F. Müller (Helv. Chim. Acta, 1939, **22**, 208—216, 217—224).—I. Oxidised cellulose adds $Na_2S_2O_4$ and thereby gains a marked increase in the reducing power proper to this compound. All methods of detecting oxycellulose (I) which depend on its reducing action are influenced by this pretreatment, the effect being most marked with Haller's gold-purple reaction. All these methods are trustworthy only in the absence of reducing impurities of non-cellulosic nature. Hydrocellulose (II) does not add $Na_2S_2O_4$. Witz's reaction with $NHPh{\cdot}NH_2$ for (I) has been extended in such a manner that it becomes more sp. than any other method since it depends on the presence of CO in the oxidised product. For this purpose diazo-components (from *p*- or *o*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$; naphthionic or Cleve acid; *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$) are coupled with arylhydrazones formed by the action of arylhydrazines or (I); azo-dyes are formed at the points of oxidative attack. Certain aromatic hydrazines (hydrazinonaphthalene- and hydrazinonaphthol-sulphonic acids and the corresponding derivatives of Ph_2) react with (I) but not with (II).

II. Reaction occurs between (II) and certain derivatives of $NHPh{\cdot}NH_2$, particularly the *p*-sulphonic acids. For its detection "true-blue salt B" and "variamine-blue salt F.G." are the sole suitable diazo-components. All the reactions of (I) establish the existence of small amounts of true oxidation products with CO groups. Primarily CO is not present in (II); this conception is in harmony with Hess' formulation of the reaction complex as cellulose-*A*.

H. W.

Preparation and properties of ethyldideuteramine and dimethyldeuteramine. E. R. Roberts, H. J. Emeléus, and H. V. A. Briscoe (J.C.S., 1939, 41—52).—Three successive treatments of NH_2Et,HCl with D_2O, each followed by evaporation of the aq. D_2O, and final liberation of the base with CaO yield *ethyldideuteramine* (I), b.p. 17·4—17·5°, m.p. −78·5°. Similar treatment of $NHMe_2$,HCl yields *dimethyldeuteramine* (II), b.p. 6·9—6·94°, m.p. −93°. The v.p. curves and ultra-violet absorption spectra of (I) and (II) are recorded, and a method of determination of their v.d. is described in which the amine and deuteramine are brought to the same density and the pressure difference is measured on a new type of differential gauge. Treatment of NH_2Et,HCl with a large excess of D_2O, or of NMe_3,HCl with D_2O, or circulation of NH_2Me–D_2O or ND_2Me–D_2O mixtures over a reduced Ni catalyst at 20—195° gives no evidence of replacement of H by D in the alkyl groups.

J. D. R.

Photolysis of organic nitrogen compounds. I. Dimethyl- and diethyl-nitrosoamines. II. Aliphatic amines. C. H. Bamford (J.C.S., 1939, 12—17, 17—26).—I. Irradiation of $NMe_2{\cdot}NO$ and $NEt_2{\cdot}NO$ by light of all λλ lying in the absorption band causes decomp. to the *sec.* amine, NO, N_2, H_2, and olefines, the quantum yield of NO in all cases being small. The vapours exhibit no fluorescence. The primary dissociation is $NR_2{\cdot}NO \rightarrow NR_2{\cdot} + NO$, the energy for this change being estimated at 12 kg.-cal. The NR_2 radical then undergoes a disproportionation reaction to NHR_2 and a bivalent radical which subsequently polymerises. Prolonged irradiation produces H_2 by photolysis of NHR_2. Other possible secondary reactions producing N_2 and olefines are suggested and the nature of the primary dissociation is discussed in relation to the absorption spectra of the nitrosoamines and the photolysis of other NO-compounds.

II. Irradiation of $NHMe_2$, NH_2Bu^{α}, $C_5H_{11}{\cdot}NH_2$, and NMe_3 in the vapour phase by the full light of the Hg arc causes decomp. From primary and *sec.* amines, the primary dissociation process produces H atoms and alkylamino- or dialkylamino-radicals, respectively. Dialkylamino-radicals then undergo exclusively disproportionation to *sec.* amine and a bivalent radical which polymerises. Alkylamino-radicals are partly disproportioned to primary amine and an unsaturated radical which polymerises, and partly converted into a Schiff's base and NH_3. *tert.*-Amines first split off alkyl, the remaining dialkylamino-radicals reacting as above. Irradiation of $NHMe_2$ and $NHEt_2$ in presence of NO gives no nitrosoamine, but irradiation of NMe_3 and NO gives HCN, probably from reaction between Me and NO.

J. D. R.

Preparation and configurative relationships of methylglucosaminides. A. NEUBERGER and R. P. RIVERS (J.C.S., 1939, 122—126).—*N*-Carbobenzyloxyglucosamine (I) in MeOH with HCl at 40° yields *N-carbobenzyloxy-α-methylglucosaminide*, m.p. 154—155°, $[\alpha]_D$ +80° in C_5H_5N, reduced (Pd–H_2 in EtOH–HCl) to *α-methylglucosaminide hydrochloride* (II), m.p. 119°, $[\alpha]_D$ +127° in H_2O, which by treatment with keten after neutralisation with Ag_2O yields *N*-acetylmethylglucosaminide. When the above glycoside synthesis with (I) is carried out at room temp., *N-carbobenzyloxy-β-methylglucosaminide*, m.p. 166—168°, $[\alpha]_D$ −38° in C_5H_5N, is formed, reduced to (II), which after neutralisation (Ag_2O) yields with keten, *N-acetyl-α-methylglucosaminide*, m.p. 195—196°, $[\alpha]_D$ −43° in H_2O. Tetra-acetylglucosamine hydrochloride in aq. $NaHCO_3$ with $ClCO_2CH_2Ph$ at 0° yields *N-carbobenzyloxytetra-acetylglucosamine*, m.p. 150—151°, $[\alpha]_D$ +21·5° in C_5H_5N, also formed by acetylation of (I). Comparison of the rates of hydrolysis of the two glucosaminides shows that the α-form has the *cis* configuration at $C_{(1)}$. It is shown that Hudson's two rules of optical superposition are closely obeyed, and it is deduced that glucosamine has the same structure as glucose. J. D. R.

"Methyl*epi*glucosamine" and 2-amino-α-methylaltroside. G. J. ROBERTSON, W. H. MYERS, and W. E. TETLOW (Nature, 1938, **142**, 1076—1077).—Cryst. derivatives of idose can be obtained from galactose derivatives by using an anhydro-compound of the $(CH_2)_2O$ type in which the ring is broken by means of alkali. With NH_3, 2 : 3-anhydro-4 : 6-benzylidene-α-methylmannoside gives a quant. yield of 3-*amino*-4 : 6-*benzylidene-α-methylaltroside*, m.p. 188°, $[\alpha]_D$ +88·9° in $CHCl_3$, which with 1% HCl yields (76%) 3-*amino-α-methylaltroside hydrochloride*, m.p. 209° (decomp.), $[\alpha]_D$ −149° in H_2O, identical with the "methyl*epi*glucosamine hydrochloride" of Fischer *et al.* Similarly, 2 : 3-anhydro-4 : 6-benzylidene-α-methylalloside gives a quant. yield of 2-*amino*-4 : 6-*benzylidene-α-methylaltroside*, m.p. 168°, $[\alpha]_D$ +104·7° in $CHCl_3$, which in turn yields (70%) 2-*amino-α-methylaltroside*, m.p. 193°, $[\alpha]_D$ +107° in $CHCl_3$. L. S. T.

New form of stereoisomerism and a new form of glycine. Theoretical interpretation. R. ENGELAND (Compt. rend., 1938, **207**, 1211—1213).—From the hydrolytic product of elastin a Cu salt of glycine, which is different in colour and cryst. form from the known salt, and loses its H_2O of hydration at 100°, is isolated. An aq. solution of the new salt when seeded with the known salt is transformed into the latter; the reverse change does not occur. The isomerism is explained by postulating the existence of the H of CH_2 in "*ortho*-" and "*para*-" positions, the two possible "*ortho*-"forms being unstable and the "*para*-"forms stable and identical thermodynamically. A similar hypothesis serves to explain the existence of several optical isomerides in certain cases, of two different optically inactive betaines of γ-amino-β-hydroxybutyric acid, of > two forms of substances of the cinnamic acid type, and of polymorphism in the fatty acids. J. L. D.

Polymeric anhydrides of glycine and asparagine. K. FREUDENBERG, G. PIAZOLO, and C. KNOEVENAGEL (Annalen, 1939, **537**, 197—204).—20N-H_2SO_4 converts polymeric glycine anhydride into a substance, which from its NH_2 content is a hepta- or octa-peptide; in agreement with this (cf. Kuhn *et al.*, A., 1932, 935), *k* for hydrolysis of the product is 0·0035—0·0036. *Azidosuccinic acid*, m.p. 95°, is converted by hot $SOCl_2$ into the *anhydride* (I), b.p. 95—96°/0·3 mm. NH_2Ph and (I) give *azidosuccinmonoanilide*, m.p. 91°, reduced by H_2–Pd-black in Et_2O to *asparagineanilide*, m.p. ~120° (decomp.). H_2–Pd reduces (I) in dioxan to polymeric asparagine anhydride. R. S. C.

Preparation of α-amino-acids through α-oximino-esters. H. MCILWAIN and G. M. RICHARDSON (Biochem. J., 1939, **33**, 44—46).—Et_2 α-acetylglutarate, prepared by a modification of the method of Clemo and Welch (A., 1928, 1252), is converted into the oximinoglutarate (I) by that of Wislicenus and Grützner (A., 1909, i, 477). (I) in AcOH is reduced (PtO_2–H_2 and Na_2SO_4 for 3 days) to the NH_2-ester, hydrolysed with boiling 5N-HCl to glutamic acid hydrochloride. The free acid is obtained by adding NH_2Ph and EtOH to the aq. solution of the hydrochloride and heating. The overall yield is 39%. δ-Chloro-α-acetyl-γ-valerolactone in cooled H_2SO_4 and NO·SO_4H in H_2SO_4 give 67% of *δ-chloro-α-oximino-γ-valerolactone*, m.p. 118°, reduced to the corresponding NH_2-compound [*acetate* (II), m.p. 177°; *hydrochloride*] by PtO_2–H_2. (II) and saturated aq. NH_3 at 30° give hydroxyproline in yield inferior to that obtained by Leuchs (A., 1905, i, 545). Et α-oximinoacetoacetate reduced and hydrolysed (Harington and Randal, A., 1932, 257) gives only NH_2·CHEt·CO_2H (III) in 80% yield: with Pd–C, HCl in EtOH, and H_2 it gives 62% of Et α-amino-β-ketobutyrate (IV), m.p. 125°. Further reduction of (IV) gives (III) or Et_2 2 : 5-dimethylpyrazine-3 : 6-dicarboxylate. W. McC.

Chemistry of the reaction of creatinine with 3 : 5-dinitrobenzoic acid. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 223—229; cf. A., 1936, 1397).—Treatment of creatinine (I) with 3 : 5-$(NO_2)_2C_6H_3$·CO_2H (II) and NaOH in EtOH gives dark purple, cryst. ppts. containing (I) and (II) in the mol. ratio 1 : 2 and varying amounts of NaOH or Na depending largely on the amounts of NaOH added. They exist also in more stable, brown forms. Under defined conditions a *compound*, $[\{(NO_2)_2C_6H_3{\cdot}CO_2H\}_2C_4H_7ON_3]$,3NaOH,3$H_2O$, is obtained, transformed by $AgNO_3$ into the *substance*, $[\{(NO_2)_2C_6H_3{\cdot}CO_2H\}_2,C_4H_7ON_3]$3Ag and decomposed by MeOH into $(NO_2)_2C_6H_3{\cdot}CO_2Na$, (I), and the *compound*, $[\{(NO_2)_2C_6H_3{\cdot}CO_2H\}_2C_4H_7ON_3]$,4NaOH,4$H_2O$, whence ($AgNO_3$) the *substance*, $[\{(NO_2)_2C_6H_3{\cdot}CO_2H\}_2,C_4H_7ON_3]$,4AgOH. H. W.

Sulphoxide of methionine. G. TOENNIES (Science, 1938, **88**, 545—546).—*dl*-Methionine perchlorate in $Pr^{\beta}OH$ with an excess of H_2O_2 consumes 1 O per mol. Neutralisation with C_5H_{11}·NH_2 ppts. pure *methionine sulphoxide* (I) (yield >90%). The amorphous ppt. is converted into microcryst. aggregates, decomp. 220—230°, by pptn. by $COMe_2$ from H_2O or aq. MeOH. L. S. T.

Preparation of methyleneaminoacetonitrile. L. H. AMUNDSEN and R. VELITZKIN (J. Amer. Chem. Soc., 1939, **61**, 212).—The yield is improved to 45—55%. R. S. C.

Nucleic acids. XII. Thymic acid. H. BREDERECK and G. MÜLLER (Ber., 1939, **72**, [*B*], 115—121; cf. Feulgen, A., 1918, i, 413).—Thymic acid (I), obtained by the hydrolysis of thymonucleic acid with $NaHSO_4$, is shown by the HCl–MeOH test to be free from guanine and adenine. Contrary to Feulgen, (I) is very stable in H_2O and becomes scarcely coloured when the aq. solution is evaporated at room temp. in a vac. At increased temp. it darkens rapidly. In neutral and, particularly, in alkaline solution there is a gradual formation of acid which is probably caused by fission into nucleotides (II) or deoxyribosephosphoric acid (III). (I) is completely hydrolysed by an enzyme prep. from sweet almonds, 100% PO_4 fission corresponding with an increase in acidity of about 3 equivs. Since a substrate solution + buffer alone does not show any change, this increase in acidity is due essentially to fission of (I) into (II) and (III) from which H_3PO_4 is eliminated in a secondary change by nucleotidase without involving an increase in the acidity towards phenolphthalein. Direct titration and determination of the increase in acidity during fermentative hydrolysis show that (I) is pentabasic and hence that Feulgen's formulation cannot be correct. (I) is considered to be phosphoric acid (IV)–deoxyribose (V)–(IV)–(V) (thymin)–(IV)–(V) (cytosine)–(IV)–(V). H. W.

Nucleic acids. XIII. Constitution of polynucleotides; basicity of thymonucleic acid. H. BREDERECK and M. KÖTHNIG (Ber., 1939, **72**, [*B*], 121—126).—It is shown by direct titration and by determination of the increase in acidity during enzymic fission that thymonucleic acid is pentabasic. The constitution $(OH)_2PO{\cdot}[O{\cdot}R{\cdot}O{\cdot}PO(OH)]_3{\cdot}O{\cdot}R$, where R = sugar base, therefore appears assured. H. W.

Decomposition of unsymmetrical organomercuric compounds. Method of establishing the relative electronegativities of organic radicals. M. S. KHARASCH and S. SWARTZ (J. Org. Chem., 1938, **3**, 405—408).—When *Hg benzyl allyl* (I) is treated with HCl one half of the Hg is recovered as $CH_2Ph{\cdot}HgCl$ but the state of the remainder is undisclosed except that it is in part inorg. *Hg Ph allyl* and HCl give HgPhCl in about 50% yield; the remainder is HgCl formed with $CHMe{:}CH_2$ by the action of HCl on Hg allyl chloride. The possible explanation that Ph and allyl have the same electronegativity is rejected in favour of the hypothesis, $HgPh{\cdot}CH_2{\cdot}CH{:}CH_2 + H^+ + Cl^- \rightarrow$ $HgPh{\cdot}CH_2{\cdot}\overset{+}{C}H + Cl \rightarrow CHMe{:}CH_2 + HgPhCl$. The explanation is applied also in the case of (I). In petroleum, $HgPh{\cdot}CH_2{\cdot}CH{:}CH_2$ is transformed by HCl, in C_6H_6 by I or HCl, into the HgPh halide in ~50% yield. Only in the first case is there any evidence of the production of Hg allyl iodide. Cleavage with HCl of unsymmetrical organomercuric compounds of the type R·Hg·allyl is not a valid method for comparing the electronegativities of the radicals in question. *Hg Bu$^\gamma$ chloride* sublimes at 131° when placed in a preheated bath. H. W.

Interpretation of secondary reactions observed in the condensation of aliphatic ketones and esters with organomagnesium compounds. Theoretical. M. TUOT (Compt. rend., 1938, **207**, 1227—1230; cf. A., 1938, II, 257, 260).—In the interaction of ketones with Mg org. compounds, the formation of ketone, ketol, and *sec.* alcohol with the liberation of saturated and unsaturated hydrocarbons always occurs but the extent of the enolisation or reduction reaction depends on the mol. wt. of the ketone. The smaller is the mol. wt. the greater is the enolisation reaction. These reactions are explained on an electronic basis. J. L. D.

Complex metallic salts. VIII, IX.—See A., 1939, I, 61.

Effect of beryllium, magnesium, zinc, and cadmium bromides on the bromination of benzene. R. PAJEAU (Compt. rend., 1938, **207**, 1420—1422; cf. A., 1936, 976).—$BeBr_2$, $CdBr_2$, and $ZnBr_2$ catalyse the bromination of dry C_6H_6 at 100° to form PhBr and *p*-$C_6H_4Br_2$, $BeBr_2$ being the most active. $MgBr_2$ has a very low activity. J. L. D.

Aromatic nitro-derivatives. XVI. 3 : 4-Dinitrotoluene : reactivity and nuclear configuration. A. MANGINI and M. COLONNA (Gazzetta, 1938, **68**, 708—718).—The configuration previously proposed (A., 1939, II, 13) is supported. 1 : 3 : 4-$C_6H_3Me(NO_2)_2$ (I) with EtOH–$N_2H_4{\cdot}H_2O$ gives 4-*nitro*-m-*tolylhydrazine* (II), m.p. 131—132° (*Ac*, m.p. 167·5—168·5°, *CO$_2$Et*-, m.p. 108—109°, *CHPh*:, m.p. 160—161°, and *CMe$_2$*:, m.p. 84—84·5°, derivatives) (oxidised by $CuSO_4$–AcOH to *p*-$C_6H_4Me{\cdot}NO_2$), and 1-*hydroxy*-5-*methyl*-1 : 2 : 3-*benztriazole*, m.p. 184° (decomp.) (*Bz*, m.p. 129—130°, and *Ac* derivative, m.p. 145·5—146·5°) (cf. Brady *et al.*, A., 1928, 308). With $NHMe{\cdot}NH_2$, (I) gives α-(4-*nitro*-m-*tolyl*)-α-*methylhydrazine*, m.p. 82—83° (*Ac*, m.p. 169—170°, and *CHPh*: derivative, m.p. 112—113°) (oxidised by $CuSO_4$–AcOH to 4 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}NHMe$). With $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl in EtOH + NaOAc, (I) slowly gives 4-*nitro*-m-*tolylsemicarbazide*, m.p. 211—212°, also obtained from (II) and KCNO–HCl. E. W. W.

Reactions of paraffins with aromatic hydrocarbons. II. Aromatic hydrocarbons and ββδ-trimethylpentane. A. V. GROSSE, J. M. MAVITY, and V. N. IPATIEV (J. Org. Chem., 1938, **3**, 448—455; cf. A., 1939, II, 13).—Destructive alkylation occurs with PhMe or Ph_2 and $CMe_3{\cdot}CH_2Pr^\beta$ (I) in presence of $AlCl_3$ and HCl giving $CHMe_3$ and *m*- + *p*-$C_6H_4MeBu^\gamma$ or p-tert.-*butyldiphenyl*, m.p. 53·1° (prep. from *p*-$C_6H_4Bu^\gamma Br$ and LiPh), respectively. With PhEt and *p*-xylene the alkylation is complicated by migration of Et and Me giving polyethyl- and polymethyl-benzenes. Fluorene and (I) give $CHMe_3$ and *difluorenyl*, m.p. 230·2—230·7°. With $C_{10}H_8$ and pyrene alkylation could not be established and substantially all the paraffin could be recovered unchanged. H. W.

Polymethylbenzenes. XXII. Action of aluminium chloride on aromatic hydrocarbons.

I. 1 : 3-Dimethyl-4-butylbenzenes [4-butyl-*m*-xylenes]. (Miss) D. Nightingale and L. I. Smith (J. Amer. Chem. Soc., 1939, **61**, 101—104; cf. A., 1938, II, 178).—1 : 3 : 4-$C_6H_3Me_2$·COPr^a, b.p. 118°/8 mm., prepared by a Friedel–Crafts reaction in CS_2 in 53% yield, with Zn–Hg–HCl gives 4-n-*butyl*-m-*xylene*, b.p. 96°/8 mm. [$(NO_2)_3$-derivative, m.p. 91°], which with $AlCl_3$ at 100° gives 5-sec.-*butyl*-m-*xylene*, b.p. 98°/15 mm. [$(NO_2)_3$-derivative, m.p. 97°], also obtained from *m*-xylene, Bu^{a}Cl, and $AlCl_3$ (method: Shoesmith *et al.*, A., 1931, 79). 4-tert.-*Butyl*-m-*xylene*, m.p. —31°, b.p. 86°/12 mm. [$(NO_2)_3$-derivative, m.p. 112°] (prep. from *m*-xylene, H_2SO_4, and Bu$^\gamma$OH or Bu$^\beta$OH at 0° in 41 and 21% yield, respectively), and 4-sec.-*butyl*-m-*xylene*, b.p. 84°/8 mm. [$(NO_2)_3$-derivative, m.p. 107°] (from *m*-xylene, CHMeEt·OH, and H_2SO_4), with $AlCl_3$ at 100° both give 5-*tert.*-butyl-*m*-xylene, m.p. —21·5° [$(NO_2)_3$-derivative, new m.p. 113°] (prep. from *m*-xylene, Bu$^\gamma$Cl, and $AlCl_3$). 4-iso*Butyl*-m-*xylene*, b.p. 96°/15 mm., is obtained from 1 : 3 : 4-$C_6H_3Me_2$·COPr$^\beta$, b.p. 121°/14 mm. (prep. by a Friedel–Crafts reaction in CS_2 in 72% yield), and with $AlCl_3$ at 100° gives a mixture of hydrocarbons. In the reactions with $AlCl_3$, *m*-xylene and (probably) higher alkylated benzenes are also formed.

R. S. C.

Effect of substitution on the dissociation of hexa-arylethanes. VI. Hexa-*m*-diphenylylethane. C. S. Marvel, E. Ginsberg, and M. B. Mueller (J. Amer. Chem. Soc., 1939, **61**, 77—78; cf. A., 1938, II, 48).—The Grignard reagent from 3-*bromodiphenyl* (prep. from *m*-C_6H_4Br·NH_2 and C_6H_6), b.p. 169—173°/17 mm., and Et_2CO_3 give (*m*-$C_6H_4Ph)_3C$·OH and thence (HCl–$CaCl_2$–Et_2O) *tri*-m-*diphenylylmethyl chloride*, m.p. 200—201°, which with Ag in C_6H_6 gives $C_2(C_6H_4Ph$-$m)_6$, which is shown by its χ to be 59—60% dissociated in C_6H_6 (~2·5% solution) at 25°, and gives the *peroxide*, m.p. 179·5—180°.

R. S. C.

Diarylmethane derivatives. IV. Properties of di-α-naphthylmethyl radical and ion. P. J. Wuis and D. Mulder (Rec. trav. chim., 1938, **57**, 1385—1396; cf. A., 1938, II, 89; Schmidlin and Massini, A., 1909, i, 561).—$CHCl(C_{10}H_7$-$1)_2$ (I) and mol. Ag in C_6H_6 (or *cyclo*hexane) in vac. afford primarily di-α-naphthylmethyl, which quickly and completely affords $[CH(C_{10}H_7$-$1)_2]_2$ (II); no colour is developed (cf. *loc. cit.*). In presence of O_2 [1 atom per mol. of (I)] or NO (<1 mol. absorbed), $[CH(C_{10}H_7$-$1)_2]_2O$ (33—39%), $(1$-$C_{10}H_7)_2CH$·OH (III) (26—27%), and a syrup (32—33%) are formed. (II) is obtained in CO_2, which is not absorbed. (II) is stable to NO in C_6H_6. Conductivities in liquid SO_2 at —10° of (I), (III), the *Me* (IV), m.p. 138°, and Et ether, m.p. 135—136°, and the *acetate* (V), m.p. 143—144°, of (III) are recorded. (IV) is obtained from (I) and boiling MeOH and from (V) and MeOH containing 1% HCl (essential). (V) [from (I) and AgOAc in Et_2O or AcOH alone in absence of H_2O] is hydrolysed (MeOH–KOH) to (III).

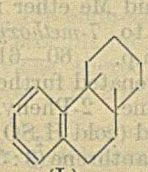
A. T. P.

Rôle of peroxides in oxidation of hydrocarbons. —See A., 1939, I, 149.

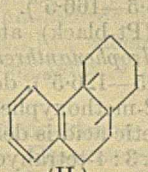
Hydrogenation of anthracene and some of the resultant products. H. I. Waterman, J. J. Leendertse, and A. C. Cranedonk (Rec. trav. chim., 1939, **58**, 83—92).—High-pressure hydrogenation (Ni–kieselguhr) of pure anthracene at 180—220° gives first octahydroanthracene, which (using fresh catalyst) further takes up 6 H to give mixed solid (m.p. 88—89°) and liquid products, of composition $C_{14}H_{24}$. The liquid portion after prolonged heating gives more solid, apparently by isomerisation. Both r_i (which is the same for all products) and [*P*] indicate the presence of 2·8—2·9 rings per mol.

E. W. W.

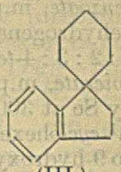
Stereochemistry of *as*-octahydrophenanthrene. J. W. Cook, C. L. Hewett, and (Mrs.) A. M. Robinson (J.C.S., 1939, 168—177).—The liquid and cryst., m.p. 95°, hexahydrophenanthrones (A., 1936, 334) are reduced (Clemmensen) to cis- (I), b.p. 88—90°/0·1—0·15 mm., and trans- (II), m.p. 23—24°, -*as*-*octahydrophenanthrene*, respectively (physical consts. given). The product from the cyclisation of



(I.)

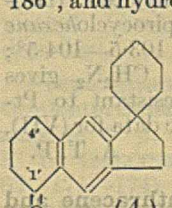


(II.)



(III.)

β-phenylethyl-Δ^1-*cyclo*hexene (cf. A., 1933, 1042) (washed with 80% H_2SO_4) or from dehydration (P_2O_5) of 1-β-phenylethyl*cyclo*hexanol (van de Kamp *et al.*, A., 1936, 1102), when oxidised (CrO_3–AcOH at room temp.) and oximated, affords in either case the oximes, m.p. 176—177° and 124° (in largest amount), of *trans*- and *cis*-keto-octahydrophenanthrenes, respectively, and that, m.p. 187°, of the spirocyclic ketone derived from hydrindene-1-*spirocyclo*hexane (III), thus proving the presence of (I), (II), and (III) (cf. also Perlman *et al.*, A., 1938, II, 57); fractionation does not give homogeneous material (cf. A., 1936, 1102). Although normally (III) is formed in small amount, in one case condensation of mixed hydrocarbons with $(CH_2$·$CO)_2O$ gave [from (III)] β-(5- or 6-)cyclo*hexane*-1-spiro*hydrindoylpropionic acid* (IV), m.p. 162—163°, together with, but more resistant to Clemmensen reduction than, β-6-*as*-octahydrophenanthroylpropionic acid (*Me* ester *semicarbazone*, m.p. 175·5—176·5°). In one case, Clemmensen reduction gave a small amount of either a mol. *compound*, $C_{18}H_{22}O_3$,$C_{18}H_{24}O_2$, m.p. 140—141°, of CO-acid and a butyric acid, or an oxide, $C_{35}H_{44}O_5$, formed by dehydration of a pinacol reduction product of (IV). (IV) can be separated without previous reduction, by successive formation of Na salt, free acid, Me ester (CH_2N_2) and its *semicarbazone*, m.p. 186°, and hydrolysis (EtOH–aq. H_2SO_4, then –NaOH) to (IV). The semicarbazone, m.p. 207°, of (IV) and EtOH–NaOEt give γ-(5 or 6-)cyclo*hexane*-1-spiro-*hydrindylbutyric acid*, m.p. 105—107°, cyclised by H_2SO_4 at 100° to 1′-(or 4′-)*keto*-1′ : 2′ : 3′ : 4′-*tetrahydro*-5 : 6-*benzhydrindene*-1-spirocyclo-*hexane* (V) (cf. *A*), m.p. 109—110°. Oxidation (dil. HNO_3 at 170—180°) of (V) gives pyromellitic acid. (V) and MgMeI give



(*A*.)

a product, dehydrogenated (Pt-black) at 295—300° to 1′-(or 4′)-*methyl*-5 : 6-*benzhydrindene*-1-spirocyclo*hexane*, m.p. 109—110°. The liquid hexahydrophenanthrone (*loc. cit.*) and KNO_3–H_2SO_4 give cis-7-*nitro*-9-*keto*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*, m.p. 151·5—152°, reduced (H_2, Pd-black, $COMe_2$) to the 7-NH_2-derivative, m.p. 118·5—119° (*Ac* derivative, m.p. 178—179°), converted (diazo-reaction) into the 7-*OH*-compound (VI), m.p. 141—142° (semicarbazone, m.p. 233—234°), oxidised ($KMnO_4$) to adipic, glutaric, and oxalic acids, and (in one case, in cold KOH) to (?) *trans*-hexahydrophthalic acid, which may be formed from the *cis*-ester. No *cis*-hexahydrohomophthalic acid (p-*phenylphenacyl* ester, m.p. 146—147°) was isolated; the *p*-bromophenacyl ester of the *trans*-acid has m.p. 178—179°. (VI) is reduced (Clemmensen) to cis-7-*hydroxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (VII), m.p. 94—95° (*benzoate*, m.p. 100—101°; 3 : 5-*dinitrobenzoate*, m.p. 165·5—166·5°). Its liquid Me ether is dehydrogenated (Pt-black) at 300° to 7-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 60—61° (*picrate*, m.p. 125·5—126·5°), dehydrogenated further by Se at 300° to 2-methoxyphenanthrene. 2-Phenyl-Δ^1-*cyclo*hexenylacetic acid is dehydrated (cold H_2SO_4) to 9-hydroxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (3 : 5-*dinitrobenzoate*, m.p. 220°). 2-Phenyl*cyclo*hexanolacetic acid and Ac_2O give 2-*phenyl*cyclo*hexylideneacetic acid*, m.p. 168—169°, but hydrogenation does not yield the saturated *trans*-acid in useful amount. Hydrogenation (PtO_2, AcOH) of (VI) gives (VII), 2 : 10-*dihydroxy*-, m.p. 239—240°, and 2-*hydroxy*-*perhydrophenanthrene* (VIII), m.p. 108—109° (3 : 5-*dinitrobenzoate*, m.p. 167—168°) [also by hydrogenation of (VII)], and perhydrophenanthrenes, b.p. 133—135°/13—14 mm. (probably a mixture of stereoisomerides). The latter and Se at 300—315° readily give phenanthrene (cf. Pinkney *et al.*, A., 1936, 1101). (VIII) and CrO_3–AcOH at room temp. give a ketone [*semicarbazone* (IX), m.p. 179—180°] and a *dicarboxylic acid*, $C_{14}H_{22}O_4$, m.p. 170°. In an oxidation of the crude carbinol, a resultant *semicarbazone* had m.p. 209—210° [isomeric with (IX)]. *cyclo*Hexanone and Mg β-*m*-anisylethyl chloride give β-*m*-anisylethyl-*cyclo*hexanol, b.p. 160—165°/0·5 mm. (3 : 5-*dinitrobenzoate*, m.p. 93·5—94·5°), dehydrated by $KHSO_4$ at 160° to the -Δ^1-cyclo*hexene* (X), b.p. 185°/22 mm., hydrogenated in EtOH (Pd-black) to the corresponding -cyclo*hexane*, b.p. 120—125°/0·5 mm. The latter is demethylated (HBr–AcOH) to a compound, b.p. 145—147°/0·8 mm., hydrogenated (PtO_2, AcOH) to β-3′-*hydroxy*cyclo*hexylethyl*cyclo*hexane* (XI), m.p. 57—58° (3 : 5-*dinitrobenzoate*, m.p. 105·5—106·5°). (X) and $AlCl_3$–CS_2 at 0° give a product [Se at 300° gives some 2-methoxyphenanthrene], demethylated (HBr–AcOH) to 5-*hydroxyhydrindene*-1-spirocyclo*hexane* (XII), m.p. 96—97° (*benzoate*, m.p. 103·5—104·5°; 3 : 5-*dinitrobenzoate*, m.p. 146—147°; CH_2N_2 gives the *Me ether*, b.p. 120°/0·15 mm., resistant to Pt-black at 300°). *X*-Ray crystallographic data for (VII), (VIII), (XI), and (XII) are recorded. A. T. P.

Photo-oxides of 9 : 10-dixenylanthracene and 9 : 10-diphenyl-2-methylanthracene. D. Duveen and A. Willemart (J.C.S., 1939, 116—118).—*p*-LiC_6H_4Ph (from *p*-C_6H_4PhBr and Li in Et_2O and N_2) with anthraquinone gives 9 : 10-*dihydroxy*-9 : 10-*di*-p-*xenyl*-9 : 10-*dihydroanthracene*, m.p. 210—212°, converted by KI–AcOH into 9 : 10-*di*-p-*xenylanthracene* (I), m.p. ~415° (all m.p. on Cu block). Insolation of (I) in CS_2 gives a *photo-oxide*, $C_{38}H_{26}O_2$, which liberates O_2 (95%) at 190—200° in a vac.; the residue is (I). 2-Methylanthraquinone and MgPhBr give 9 : 10-dihydroxy-9 : 10-diphenyl-2-methyl-9 : 10-dihydroanthracene, new m.p. 246°, reduced by KI–AcOH to 9 : 10-diphenyl-2-methylanthracene (II), m.p. 242—243°, which affords (as above) a photo-oxide, $C_{27}H_{20}O_2$, which liberates O_2 (94%) at 170—175° in a vac. The absorption spectra of (I) and (II) are determined. (I) gives colourless solutions in org. solvents and no indication of a diradical form is noted (cf. Dufraisse *et al.*, A., 1939, II, 55). A. T. P.

8-Methyl-1 : 2-benzanthracene. L. F. Fieser and W. S. Johnson (J. Amer. Chem. Soc., 1939, **61**, 168—171).—9 : 10-Dihydrophenanthrene is best prepared by H_2–Cu chromite without a solvent at 160°. β-9 : 10-Dihydro-2-phenanthroylpropionic acid (modified prep.), m.p. 157—158°, gives γ-9 : 10-dihydro-2-phenanthrylbutyric acid, m.p. 92—92·5°, and thence by $ZnCl_2$–Ac_2O–AcOH, H_2SO_4, or (best) PCl_5–C_6H_6–$AlCl_3$ 8-keto-3 : 4 : 5 : 6 : 7 : 8-hexahydro-1 : 2-benzanthracene (I), interconvertible forms, m.p. 97—98° and 92° (cf. Burger *et al.*, A., 1937, II, 423). With MgMeCl, (I) gives, after dehydration at 130—160°/1 mm., 8-*methyl*-3 : 4 : 5 : 6-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 70—70·5° (*picrate*, m.p. 140—141°), and thence by S at 230—240° or Se at 300° 8-methyl-1 : 2-benzanthracene (II), forms, m.p. 113·5—114° and 118—118·5° [picrate, m.p. 159·5—160°; $C_6H_3(NO_2)_3$ additive compound, m.p. 169·5—170°; quinone, m.p. 196·5—197° (*quinol diacetate*, m.p. 202·5—203·7°)]. Cook's (II) (A., 1938, II, 227) was thus impure. When treated first with NaOEt and then with S, the semicarbazone of (I) gives 1 : 2-benzanthracene. M.p. are corr. R. S. C.

Syntheses of *meso*-substituted 1 : 2-benzanthracene derivatives. L. F. Fieser and A. M. Seligman (J. Amer. Chem. Soc., 1939, **61**, 136—142).—Several preps. of 1′ : 9-dimethyl-1 : 2-benzanthracenes are prevented by steric hindrance. 8 : 1-$C_{10}H_6Br{\cdot}NH_2$ [prep. in 42% yield from 1 : 8-$C_{10}H_6(NH_2)_2$ through the azimide] gives (diazo-reaction) 68% of 1-*bromo*-8-*iodonaphthalene*, m.p. 99—100°, the Mg derivative from which with Me_2SO_4 in Et_2O–C_6H_6 gives 74% of 1 : 8-$C_{10}H_6MeBr$ (I), m.p. 77—78°. 1 : 8-$C_{10}H_6Br_2$ (obtained from the Br-amine), new m.p. 109—110°, reacts very slowly with Mg. 1 : 8-$C_{10}H_6Cl{\cdot}NO_2$ gives 1 : 8-$C_{10}H_6Cl{\cdot}NH_2$ and thence 1 : 8-$C_{10}H_6ClBr$, new m.p. 96·5—97° (*picrate*, m.p. 130·5—131·5°), which affords 8-*chloro*-1-*methylnaphthalene*, m.p. 68—69°, b.p. 125°/4 mm. (*picrate*, m.p. 138·5—139·5°). 1 : 4-$C_{10}H_6Me{\cdot}SO_3K$ (prep. described) and Br–NaBr give 1 : 4-$C_{10}H_6MeBr$ (II), new m.p. 7° (picrate, m.p. 128—129°). 1 : 7-$C_{10}H_6Me{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$-*o* could not be converted into the benzanthranyl acetate. *o*-$C_6H_4(CO)_2O$ and the Mg derivative from (I) give 66% of o-8-*methyl*-1-*naphthoylbenzoic acid*, m.p. 231·5—232·5°; this or its *Me* ester, m.p. 153—154° does not add MgMeCl

smoothly at the CO. *o*-C_6H_4Cl·COMe (III) (prep. from *o*-C_6H_4Cl·CHO and MgMeCl with subsequent oxidation by $Na_2Cr_2O_7$–HCl) with the Mg derivative of (II) gives a carbinol, converted by $KHSO_4$ at 200° into 4-α-o-*chlorophenylvinyl*-1-*methylnaphthalene*, b.p. ~200°/4 mm., hydrogenated (PtO_2) in AcOH to 1-α-o-*chlorophenylethyl*-4-*methylnaphthalene*, m.p. 66·5—67·5°, which with CuCN in aq. C_5H_5N at 220° gives 1-α-o-*carbamylphenylethyl*-4-*methylnaphthalene*, m.p. 171—172°. Hydrolysis thereof by *iso*-C_5H_{11}·O·NO–AcOH at 40° gives the *o-carboxylic acid*, m.p. 190·5—191·5°, which with $ZnCl_2$–Ac_2O–AcOH gives an acetate, reduced by Zn–aq. NaOH–PhMe to 3 : 9-*dimethyl*-1 : 2-*benzanthracene*, m.p. 93—93·5° [*picrate*, m.p. 137—138°; $C_6H_3(NO_2)_3$ additive *compound*, m.p. 145°; oxidised to 3-methyl-1 : 2-benzanthraquinone, new m.p. 178·5—179·5°]. However, a similar synthesis with (III) and (I) gives only 20% of vinyl compound; the reduced product could not be converted into a nitrile. The Mg derivative of (I) with *o*-C_6H_4Cl·CHO in C_6H_6 gives 44% of *o-chlorophenyl*-8-*methyl*-1-*naphthylcarbinol*, b.p. 210°/4 mm., oxidised to *o-*C_6H_4Cl 8 : 1-$C_{10}H_6Me$ *ketone*, b.p. 205°/4 mm., which is also obtained from the same Mg derivative and *o*-C_6H_4Cl·CN by way of the ketimine and gives impure materials with MgMeCl, followed by $KHSO_4$ and H_2. M.p. are corr.

R. S. C.

Synthesis of compounds related to 1 : 2-benzanthracene and cholanthrene. W. E. Bachmann (J. Org. Chem., 1938, **3**, 434—447).—5-Keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene (I) (modified prep. from γ-3-phenanthrylbutyric acid described) is reduced [$Al(OPr^\beta)_3$ in $Pr^\beta OH$] to 5-*hydroxy*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene* (II), m.p. 125·5—126·5° (*acetate*, m.p. 136—136·5°; *Me ether*, colourless plates, m.p. 76—77°, or colourless needles, m.p. 86·5—87·5°), dehydrated and dehydrogenated by Pd–C at 310° to 1 : 2-benzanthracene and converted by dry HCl in C_6H_6 containing $CaCl_2$ into 5-*chloro*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene* (III), m.p. 116°, which passes in boiling C_5H_5N into 7 : 8-*dihydro*-1 : 2-*benzanthracene*, m.p. 112—113·5° (*picrate*, m.p. 138—139°), also obtained when (III) is heated at its m.p. or (II) is kept at 200°/15 min. (III) is condensed with $CHNa(CO_2Et)_2$ and the product is hydrolysed to 5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthryl-5-malonic acid, m.p. 175—177° (decomp.), decarboxylated to the -5-*acetic acid*, m.p. 153—154° (*Me* ester, m.p. 82—83°), which is transformed by $SOCl_2$ in Et_2O containing a little C_5H_5N into the corresponding chloride, cyclised ($SnCl_4$ in CS_2) to 1-*keto*-2a : 3 : 4 : 5-*tetrahydrocholanthrene* (IV), m.p. 193—194° (*semipicrate*, $2C_{20}H_{16}O,C_6H_3O_7N_3$, m.p. 178—178·5°), which is dehydrogenated (S at 220°) to 1-ketocholanthrene. Reduction (Clemmensen) of (IV) gives 2a : 3 : 4 : 5-*tetrahydrocholanthrene*, prisms or plates, m.p. 107°, or plates, m.p. 101—101·5°, either of which gives the *picrate*, m.p. 168—168·5°; it is dehydrogenated to cholanthrene (V). Addition of (I) to Zn and $CH_2Br·CO_2Me$ in Et_2O–C_6H_6 containing a little I and treatment of the product with dil. HCl followed by HCO_2H gives *Me* 7 : 8-*dihydro*-1 : 2-*benzanthryl*-5-*acetate* (VI), m.p. 101·5—102°; the *acid*, m.p. 193—194° when brought into a bath at 185°, is dehydrogenated by S at 210° to 5-methyl-1 : 2-benzanthracene and 1 : 2-*benzanthryl*-5-*acetic acid* (VII), m.p. 233—232° (yield 10%). Alternatively (VI) is dehydrogenated by S at 200—205° to *Me* 1 : 2-*benzanthryl*-5-*acetate*, m.p. 116° (yield 90%), which is hydrolysed to (VII). Oxidation of (VII) by $Na_2Cr_2O_7$ and boiling AcOH affords 1 : 2-benzanthraquinonyl-5-acetic acid (*Me ester*, m.p. 168—169°). Successive treatments of (VII) with PCl_5–C_6H_6 and $AlCl_3$–CS_2 yield 1-*ketocholanthrene*, m.p. 230°. Modified directions are given for the conversion of *o*-C_6H_4Cl·CHO into *o*-C_6H_4Cl·CH_2·CH_2·CO_2H and thence into 4-chlorohydrindone, 4-chloro- and 4-cyano-hydrindene. The last with 1-$C_{10}H_7$·MgBr affords 4-1′-naphthoylhydrindene, b.p. 215—220°/0·2 mm., which passes at 410° into (V). *meso*-*Dihydrocholanthrene*, m.p. 161·5—162·5°, is obtained by treating (V) with Li or Na in Et_2O–C_6H_6 followed by MeOH. Maleic anhydride and (V) in boiling C_6H_6 slowly yield *cholanthrene*-6 : 12b-endo-αβ-*succinic anhydride*, m.p. 232° (decomp.) if brought into bath at 210°, which dissociates in hot xylene, thereby affording pure (V), m.p. 174·5—175° (corr.), in 80% yield.

H. W.

Carcinogenic hydrocarbons. III. 20-*iso*-Propylcholanthrene. Fluorescence and crystal forms of methyl-, ethyl-, and *iso*propyl-cholanthrene. W. F. Bruce and F. Todd (J. Amer. Chem. Soc., 1939, **61**, 157—161; cf. A., 1938, II, 271).—$Pr^\beta Cl$, PhBr, and $AlCl_3$ at 0° give *p*-bromocumene (I) (67%), b.p. 87—89°/9 mm., 215—216°/744 mm., and 20% of 4-*bromo*-1 : 3-*diisopropylbenzene*, b.p. 115—118°/9 mm., oxidised to 4 : 1 : 3-$C_6H_3Br(CO_2H)_2$. With $(CH_2O)_3$ and $ZnCl_2$, (I) gives 76% of mixed *bromoisopropylbenzyl chlorides*, b.p. 136—139°/9 mm. (and 8% of a *bromoisopropylbenzylidene dichloride*, m.p. 86—87·5°), and thence Et_2 *bromoisopropylbenzylmalonate*, b.p. 163—168°/1 mm., the corresponding *acids*, m.p. 124—126° [*Na H* salt, m.p. 236—237° (decomp.)], β-*bromoisopropylpropionic acids*, m.p. 56—58°, b.p. 216—218°/22 mm., *bromoisopropylhydrindones*, m.p. 90—94°, b.p. 168—170°/9 mm., and 4-*bromo*-7-*isopropylhydrindene* (II), b.p. 120—123°/3 mm. With CuCN in C_5H_5N at 180° (II) gives 4-*cyano*-7-*isopropylhydrindene*, b.p. 113—115°/0·8 mm., converted by 1-$C_{10}H_7$·MgBr in Et_2O into the *ketimine hydrochloride*, m.p. 262° (decomp.), of 4-α-*naphthoyl*-7-*isopropylhydrindene* (III), b.p. 210—212°/0·8 mm.; (III) is pyrolised at 410—415° to 20-*isopropylcholanthrene* (IV), m.p. 188—189° (corr.). The Mg derivative of (II) and α-$C_{10}H_7$·COCl in Et_2O at −5° give a poor yield of (III) with some 4-*isopropylhydrindene*, b.p. 88—90°/1 mm., and (α-$C_{10}H_7$·CO)$_2$O (cf. A., 1938, II, 443). The crystallo-optical properties and fluorescence of (IV), 20-methyl- (dimorphic) and 20-ethyl-cholanthrene are described.

R. S. C.

Preparation of $\Delta^{3:5}$- and $\Delta^{4:6}$-cholestadienes. Cholesterilene and "7-dehydrocholestene isomeride." J. C. Eck, R. L. van Peursem, and E. W. Hollingsworth (J. Amer. Chem. Soc., 1939, **61**, 171—174).—$\Delta^{3:5}$-Cholestadiene (I) (prep. from ψ-cholestene dibromide and quinoline), m.p. 79·5—80°, $[\alpha]_D^{25}$ −103·24° in CCl_4, is identical with cholesterilene, $[\alpha]_D^{25}$ −100·33° to −123·23° according to

the method of prep. (dehydration of cholesterol, *allo*-cholesterol, or their epimerides, removal of HHal from cholesteryl halides, or pyrolytic decomp. of cholesteryl esters). $\Delta^{4:6}$-Cholestadiene (II) (prep. from α- or β-cholestene dibromide and quinoline), m.p. 84—85°, $[\alpha]_D^{24}$ +45·77° in CCl_4, is not identical with the hydrocarbon (III), m.p. 91°, $[\alpha]_D^{24}$ +4·27° in CCl_4, of Dimroth *et al.* (A., 1936, 977). All the hydrocarbons absorb 2 Br and 2 O (from BzO_2H). H_2–PdO_2 reduces (II) or (III) to a mixture of cholestane and coprostane; Na–CMe_2Et·OH has no effect. $(CH{\cdot}CO)_2O$ does not add to (II). HCl–EtOH does not isomerise (I) or (II). Possible positions for the ethylenic linkings are discussed. R. S. C.

Derivatives of 3 : 4-benzpyrene. A. Windaus and K. Raichle (Annalen, 1939, **537**, 157—170).—The acetyl-3 : 4-benzpyrene (I) (modified prep.) of Windaus and Rennhak (A., 1937, II, 491) is shown to be the 10- or, less probably, the 9-Ac derivative. 3 : 4-Benzpyrene, Ac_2O, and $ZnCl_2$ in C_6H_6 at room temp. give (I) and a *diacetyl*-3 : 4-*benzpyrene*, m.p. 244°. With Zn–Hg–HCl–AcOH (I) gives 10-*ethyl*-3 : 4-*benzpyrene*, m.p. 112° (*picrate*, m.p. 163°), and a (?) *pinacolin*, $C_{44}H_{28}O$, m.p. >350°. With MgMeI in C_6H_6–Et_2O (I) gives an oil, converted by vac. distillation with Zn dust into 10-iso*propenyl*-3 : 4-*benzpyrene*, m.p. 114—115° (*picrate*, m.p. 164—165°). 3 : 4-Benzpyrene-10-carboxylic acid (II), m.p. ~318—319° {Me ester, m.p. 181° [*loc. cit.*, 151°; 5 : 8-*quinone*, m.p. 302° (decomp.)]}, is prepared from (I) by NaOCl in aq. C_5H_5N and converted by way of the *hydrazide*, m.p. 264—265° (*CMe*$_2$: derivative, m.p. 310°), and azide into 10-*acetamido*- (III), m.p. 309° [5 : 8-*quinone*, m.p. 290° (decomp.)], and 10-*di*-*acetamido*-3 : 4-*benzpyrene*, m.p. 190°. The *oxime*, m.p. 254°, of (I) with HCl–AcOH–Ac_2O at 100° gives (III) and thence (HCl–EtOH at 140°) 10-*amino*-3 : 4-*benzpyrene*, m.p. 211° [*picrate*, m.p. 161° (decomp.)]. With CrO_3 in aq. AcOH at 80° (I) gives 10-*acetyl*-3 : 4-*benzpyrene*-5 : 8-*quinone*, m.p. ~260° (decomp.), absence of an isomeric (5 : 10-)quinone indicating blocking of $C_{(10)}$ by Ac. (II) is similarly oxidised to a quinone-acid, which at 240°/high vac. gives CO_2 and 3 : 4-benzpyrene-5 : 8-quinone, loss of the Ac proving the presence of the Ac at $C_{(9)}$ or $C_{(10)}$. With CrO_3 in boiling AcOH (I) gives benzanthr-7-one-3 : 4-dicarboxylic anhydride. 3 : 4-Benzpyrene and SO_2Cl_2 in CCl_4 at 75° give the 5-*Cl*-derivative, m.p. 210°, which with CuCN at 250—340° yields 5-*cyano*-3 : 4-*benzpyrene*, m.p. 236—237°, also obtained by boiling Ac_2O from 3 : 4-*benzpyrene*-5-*aldoxime*, m.p. 241—243° (decomp.). R. S. C.

Antispasmodics. I. F. F. Blicke and E. Monroe. **II.** F. F. Blicke and F. B. Zienty (J. Amer. Chem. Soc., 1939, **61**, 91—93, 93—95).—With the exceptions noted, the following are prepared from an amine and a bromide in EtOH with or without Na_2CO_3. Temp. in parentheses are m.p. of the *hydrochlorides*. Salts marked * are potent antispasmodics, those marked † are inactive, the remainder being weak antispasmodics.

1. β-cyclo*Hexylethyl-methyl-*, b.p. 89—90°/14 mm. (169—170°), *-ethyl-*, b.p. 100—105°/21 mm. (231—232°), *-butyl-*, b.p. 120—123°/17 mm. (262—263°), *-allyl-*, b.p. 114—116°/18 mm. (235—236°), and *-dimethyl-*, b.p. 93—94°/28 mm. (238—239°), *-amine*. cyclo*Hexyl-*, b.p. 174—177°/35 mm. (197—198° *), and *benzyl*-β-cyclo*hexylethylamine*, b.p. 187—189°/20 mm. (227—228°). β-Phenylethyl-ethyl-, b.p. 107—110°/20 mm. (181—182° †), and *-allyl-amine*, b.p. 123—126°/19 mm. (176—177° †). NN′-*Di*-(β-*phenylethyl*)*ethylenediamine*, b.p. 235—240°/19 mm. (*dihydrochloride*, m.p. 306—307°). β-1-*Naphthylethyl-methylamine*, b.p. 175—177°/20 mm. (164—165°). γ-cyclo*Hexylpropylmethylamine*, b.p. 105—108°/20 mm. (167—168°). δ-cyclo*Hexylbutyl-methyl-*, b.p. 110—112°/20 mm. (143—144°), *-ethyl-*, b.p. 131—134°/19 mm. (202—203°), *-butyl-*, b.p. 150—156°/20 mm. (232—233° *), and *-dimethyl-amine*, b.p. 131—132°/38 mm. (196—197°). β-cyclo*Pentylethyl-methyl-* (159—160°), *-dimethyl-*, b.p. 79—81°/32 mm. (219—220°), and *-diethyl-amine*, b.p. 108—110°/37 mm. (121—122°). γ-Phenoxypropylmethylamine, b.p. 137—140°/19 mm. (156—157°). *Di*-β-cyclo*hexylethyl-methyl-* (prep. without a solvent), b.p. 188—190°/23 mm. (*hydrochloride*,* m.p. 257—258°; *nitrate*, m.p. 158—159°; *aurichloride*, m.p. 166—167°), and *-ethyl-amine*, b.p. 195—197°/21 mm. (132—133° *). *Di*-γ-cyclo*hexylpropyl-*, b.p. 200—204°/20 mm. (214—215°), *di*-δ-cyclo*hexylbutyl-*, b.p. 225—227°/36 mm. (189—190°), di-β-phenylethyl-, b.p. 192—193°/13 mm. (158—159° *), *di*-β-cyclo*pentylethyl-* (240—241°), and *di*-γ-*phenoxypropyl-*, b.p. 245—250°/21 mm. (125—126° *), *-methylamine*. *Di*-δ-cyclo*hexylbutylethylamine*, b.p. 230—236°/19 mm. (134—135°). N-β-cyclo*Hexylethylpiperidine*, b.p. 139—140°/18 mm. (255—256° †). COPhMe, $(CH_2O)_3$, and NH_2Me,HCl give $NMe(CH_2{\cdot}CH_2Bz)_2$ [hydrochloride, m.p. 191—192° (lit. 162°)].

II. cyclo*Hexylmethyl-methyl-*, b.p. 65—66°/13 mm. (193—194°, stimulant), and *-ethyl-amine*, b.p. 72—73°/12 mm. (249—250°, stimulant). β-cyclo*Hexylethyl*-β′-*hydroxyethyl-*, b.p. 138—142°/7 mm. (163—164° †), -n-, b.p. 106—107°/13 mm. (266—267°, stimulant), and -iso-*propyl-*, b.p. 102—104°/16 mm. (199—200°), *-amyl-*, b.p. 109—115°/7 mm. (265—266°), *-heptyl-*, b.p. 135—140°/7 mm. (242—243° *), -α′-cyclo*hexylethyl-*, b.p. 165—166°/10 mm. (222—223° *), *-di*-(β-*hydroxyethyl*)-, b.p. 177—179°/7 mm. (*hydrochloride* †, an oil; Bz_2 derivative *hydrochloride*, m.p. 137—138°), and *-dibutyl-*, b.p. 124—127°/5 mm. (*aurichloride*, m.p. 127—128°), *-amine*. *Phenyl*-β-cyclo*hexyl-*, b.p. 170—173°/9 mm. (122—123°), and *di*-β-cyclo*hexylethyl-*, b.p. 168—173°/8 mm. (245—246° *), *-amine*. *Di*cyclo*hexylmethyl-methyl-*, b.p. 124—125°/4 mm. (240—241°), and *-ethyl-amine*, b.p. 149—153°/12 mm. (137—138°, stimulant). *Di*-(β-cyclo*hexylethyl*)-β′-*hydroxyethyl-*, b.p. 190—193°/5 mm. (112—113° †), -n-, b.p. 160—165°/7 mm. (an oil *), and -iso-*propyl-*, b.p. 171—174°/7 mm. (an oil *), *-butyl-*, b.p. 176—178°/7 mm. (an oil), *-amyl-*, b.p. 178—181°/7 mm. (an oil), *-heptyl-*, b.p. 197—202°/6 mm. (an oil †), *-allyl-*, b.p. 170—172°/5 mm. (137—138°, stimulant), and -cyclo*hexyl-*, b.p. 190—193°/5 mm. (166—167°, stimulant), *-amine*. *Phenyl-*, b.p. 213—218°/5 mm. (149—150°), and *benzyl-di*-(β-cyclo*hexylethyl*)*amine*, b.p. 207—210°/5 mm. (142—143°, stimulant). *Tri*-(β-cyclo*hexylethyl*)*amine*, b.p. 200—208°/6 mm. (233—234°). *Di*cyclo*hexyl*-β-cyclo*hexyl-*

ethyl-, b.p. 180—182°/5 mm. (172—173° *), and *-amylamine*, b.p. 178—181°/20 mm. (113—114°). *cyclo*-Hexyl Me ketone and HCO_2NH_4, when heated gradually to 180°, give α-*cyclo*hexylethylamine, b.p. 66—67°/14 mm. (237—238°), and *di*-(α-cyclo*hexylethyl*)*amine*, b.p. 140—142°/4 mm. (304—305°). Di-*cyclo*hexyl-, b.p. 131—133°/13 mm. (193—194°), and *di*-(α-cyclo*hexylethyl*)-*methylamine*, b.p. 167—169°/12 mm. (179—180°), are obtained from the *sec.* bases by CH_2O. R. S. C.

Syntheses of spasmolytically active substances. W. Buth, F. Külz, and K. W. Rosenmund (Ber., 1939, **72**, [*B*], 19—28).—A series of di-β-phenylethylamines (I) has been investigated in the hope that the physiological properties of papaverine (II) would not be greatly modified by the opening of the hetero-ring. This is found to be the case. The presence of OMe attached to the ring of (I) is unnecessary but the spasmolytic action, which with many of these compounds exceeds that of (II), is greatly modified by the presence of an α-substituent in the side-chain, the effect increasing in the sequence, Me, Et, Pr, Bu, Ph, CH_2Ph. Physiologically, the solubilities of the compounds now described are not satisfactory. The following *sec.* amines are obtained by suitably heating the requisite primary amine containing Pd–$BaSO_4$ in H_2 until nearly the theoretical amount of NH_3 has been evolved. *Hydrochlorides* of the following are described: di-β-phenylethylamine, m.p. 268—269°; di-β-anisylethylamine, m.p. 265—266°; di-β-3 : 4-dimethoxyphenylethylamine, m.p. 199°; di-β-3 : 4-methylenedioxyphenylethylamine, m.p. 262° (free *base*, m.p. 76°). *Hydrochlorides* of the following bases, obtained by reduction of the requisite amine and CO-compound preferably in MeOH, have been prepared: benzyl-β-phenylethylamine, m.p. 265—266°; β-phenylethyl-β′-*p*-anisylethylamine, m.p. 242—243°; β-phenylethyl-β′-3 : 4-dimethoxyphenylethylamine, m.p. 189°; β-phenylethyl-β′-3 : 4-methylenedioxyphenylethylamine, m.p. 242°; β-phenylethyl-β′-phenyl*iso*propylamine, m.p. 160°; β-methoxy-β-phenylethyl-β′-phenyl*iso*propylamine (*r*- and *meso*-forms), m.p. 205° or 150—155°; β-phenylethyl-β′-anisyl*iso*propylamine, m.p. 173° (free base, b.p. 228—229°/17 mm.); β-phenylethyl-β′-3 : 4-dimethoxyphenyl*iso*propylamine, m.p. 182°; β-phenylethyl-β′-3 : 4-methylenedioxyphenyl*iso*propylamine, m.p. 200°; β-phenylethyl-β′-methoxy-β′-phenylethylamine, m.p. 146—147° (free base, b.p. 213—215°/15 mm.); di-3 : 4-dimethoxyphenyl*iso*propylamine, m.p. 206—207° (free base, b.p. 254—256°/0·1 mm.). In the prep. of the *hydrochlorides* of the following bases the requisite Schiff's base is hydrogenated under pressure: β-phenylethyl-α′-ethyl-β′-phenylethylamine, m.p. 127° (free base, b.p. 187—189°/12 mm.); β-phenylethyl-α′-propyl-β′-phenylethylamine, m.p. 154°; di-β-phenyl-*iso*propylamine, *meso*-form, m.p. 254°, and *r*-form, m.p. 197° (the *r*-base, b.p. 185—186°/13 mm., is resolved by *d*- and *l*-camphorsulphonic acid into the +-form, $[\alpha]_D^{20}$ +8° in EtOH, and −-variety, $[\alpha]_D^{20}$ −9° in EtOH). Reduction of the requisite Schiff's bases by Na and EtOH leads to the *hydrochlorides* of the following amines; β-phenylethyl-α′-*iso*butyl-β′-phenylethylamine, m.p. 261°; β-phenylethyl-α′β′-diphenylethylamine, m.p. 267—268°; β-methoxy-β-phenylethyl-α′β′-diphenylethylamine, m.p. 256°; β-phenyl-α-benzylethylphenyl*iso*propylamine, m.p. 194°. From the halide and primary amine is obtained *di*-β-*methoxy*-β-*phenylethylamine hydrochloride*, two forms, m.p. 201° and 234°. H. W.

Preparation of aromatic thiocarbimides.—See B., 1939, 127.

Nitrogenous products formed by chlorination of *iso*thiocarbamides. T. B. Johnson and J. M. Sprague (J. Amer. Chem. Soc., 1939, **61**, 176—179).—Cyanamide dihydrochloride, $NH_2{\cdot}CCl{:}NH,HCl$, m.p. 182—183°, is obtained with $Bu^{\alpha}SO_2Cl$ or $CH_2Ph{\cdot}SO_2Cl$ (I) by chlorinating $SBu^{\alpha}{\cdot}C(NH_2){:}NH,HCl$ or $CH_2Ph{\cdot}S{\cdot}C(NH_2){:}NH,HCl$, respectively, and with MeOH at room temp. gives $OMe{\cdot}C(NH_2){:}NH,HCl$. $CH_2Ph{\cdot}S{\cdot}C(NHMe){:}NH,HCl$, an oil (corresponding *picrate*, m.p. 182—183°), with Cl_2 in H_2O at <20° gives (I) and NHMe·CN. $CH_2Ph{\cdot}S{\cdot}C(NHPh){:}NH,HCl$ gives similarly (I) and 2 : 4-*dichlorophenylcyanamide*, m.p. 162—163°, also obtained from NHPh·CN and Cl_2 in aq. AcOH or 2 : 4 : 1-$C_6H_3Cl_2{\cdot}NH_2$, BrCN, and $KHCO_3$ in abs. EtOH. $CH_2Ph{\cdot}S{\cdot}C(NHPh){:}NPh,HCl$ and Cl_2 in aq. AcOH at <15° give (I) and $CO(NH{\cdot}C_6H_3Cl_2\text{-}2:4)_2$ [also obtained from $SEt{\cdot}C(NHPh){:}NPh,HCl$]. R. S. C.

Chemotherapy of bacterial infections. I. Synthesis of derivatives of sulphanilamide. K. Ganapati (J. Indian Chem. Soc., 1938, **15**, 525—531; cf. Kolloff, A., 1938, II, 228).—Synthesis is effected of compounds of general formula, *p*-$CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR$, with a view of testing their Au salts in cases of tuberculosis. $CH_2{:}CH{\cdot}CH_2{\cdot}NCS$ (I) (1 mol.) and *m*- or *p*-$C_6H_4(NH_2)_2$ (1 mol.) do not afford a monoallylthiocarbamide, but give *m*-, m.p. 95—102° (cf. Lellmann, A., 1884, 49), or p-*di*(*allylthiocarbamido*)*benzene*, m.p. 200°, respectively. $NH_2{\cdot}C_6H_4{\cdot}NHAc$ and (I) in EtOH at 100° (bath) afford N-m-, m.p. 182°, or -p-*acetamidophenyl*-N′-*allylthiocarbamide*, m.p. 175°, hydrolysed by aq. HCl (1 : 1) to the (unstable) *m*- and *p*-NH_2-derivative, m.p. 118—120° (*dihydrochloride*, m.p. 230°), respectively. (I) and *m*- (with NaOH) or *p*-aminocinnamic acid in EtOH at 100° (bath) give m-, m.p. 177° (decomp.), or p-*allylthiocarbamidocinnamic acid*, m.p. 171°, respectively. (I) and *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ or *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$-*p* (Gray *et al.*, A., 1937, II, 302) yield similarly p-*allylthiocarbamidobenzene-sulphonamide*, m.p. 182°, and *-sulphonanilide*-4′-*sulphonamide*, m.p. 180—181° (decomp.), respectively. p-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ (II) and $NHMe_2$ in C_6H_6 at room temp. afford the *Ac* derivative, m.p. 143°, of *p*-aminobenzenesulphondimethylamide, m.p. 172°; the latter and (I) in EtOH afford p-*allylthiocarbamidobenzenesulphondimethylamide*, m.p. 181°. (II) (1 mol.) and p-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$ (2 mols.) in Et_2O give p-*acetamidobenzenesulphon*-p′-*dimethylaminoanilide*, m.p. 196°, hydrolysed to the *p*-NH_2-derivative, m.p. 231° (cf. Fourneau *et al.*, A., 1938, III, 324), which when heated with (I) affords the corresponding *allylthiocarbamido*-derivative, m.p. 161°. (II) and *p*-$NHAc{\cdot}C_6H_4{\cdot}NH_2$ in H_2O afford the Ac derivative,

m.p. ~320° (hydrolysed by 6N-HCl), of *p-aminobenzenesulphon-p'-aminoanilide*, m.p. 155°, converted by boiling with (I) (2 mols.) into a (?) *monoallylthiocarbamido*-derivative, m.p. 175°. (II) and *m*- or *p*-aminocinnamic acid in H_2O or alkali give m-, m.p. 231° (decomp.), or p-, m.p. 252° (decomp.), *-p'-acetamidobenzenesulphonamidocinnamic acid*, respectively, hydrolysed by 40% aq. NaOH at 100° (bath) for 10 min. to m-, m.p. 213°, and p-, m.p. 239° (decomp.), *-p'-aminobenzenesulphonoamidocinnamic acid*. (II) and $CO_2Et{\cdot}CH_2{\cdot}NH_2{\cdot}HCl$ in 2N-NaOH–EtOH give *Et* p-*acetamidobenzenesulphonamidoacetate*, m.p. 129°, hydrolysed (boiling 5N-HCl) to the *hydrochloride*, m.p. 172° (decomp.), of *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$. A. T. P.

Preparation of 2 : 2'-diamino- and -diacetamido-diphenylamines, and their behaviour on oxidation. (Miss) M. L. Tomlinson (J.C.S., 1939, 158—163).—2 : 2'-Dinitrodiphenylamine and Zn dust in AcOH give 2 : 2'-*diaminodiphenylamine* (I), m.p. 101°; cold Ac_2O in dil. AcOH then gives the Ac_2 derivative, m.p. 199°, stable to mild oxidising agents, converted by boiling Ac_2O into 1-(2'-*acetamidophenyl*)-2-*methylbenziminazole*, m.p. 220°. 1 : 4 : 3-$C_6H_3MeI{\cdot}NO_2$, 4 : 1 : 3-$NH_2{\cdot}C_6H_3Me{\cdot}NO_2$, K_2CO_3, and Cu at 160° for 2 hr. give 2 : 2'-dinitro-4 : 4'-dimethyldiphenylamine, m.p. 195° which affords the 2 : 2' (NH_2)$_2$-derivative (II), m.p. 104° [Ac_2 derivative, m.p. 215° (stable to $FeCl_3$), whence 1-(2'-*acetamido*-4'-*methylphenyl*)-2 : 5-*dimethylbenziminazole*, m.p. 217°]. *m*-Nitro-*p*-anisidine (III) and 1 : 4 : 3-$C_6H_3MeI{\cdot}NO_2$ similarly afford 2 : 2'-*dinitro*-4-*methoxy*-4'-*methyldiphenylamine*, m.p. 188° [2 : 2'-diamine (IV) (Ac_2 derivative, m.p. 181—182°)]. 1-[2'-*Acetamido*-4'-*methoxy*- (or *-methyl*-)*phenyl*]-5-*methyl*- (or *-methoxy*-)2-*methylbenziminazole* has m.p. 202°. *o*-$C_6H_4Cl{\cdot}NO_2$ and (III) give 2 : 2'-*dinitro*-4-*methoxydiphenylamine*, m.p. 139—141° [*diamine* (V), m.p. 115° (Ac_2 derivative, m.p. 172°)]. 2 : 2'-*Diamino*-4 : 4'-*dimethoxydiphenylamine* (VI), m.p. 100° [Ac_2 derivative (VII), m.p. 233°, whence 5-*methoxy*-1-(2'-*acetamido*-4'-*methoxyphenyl*)-2-*methylbenziminazole*, m.p. 236°, hydrolysed (HCl) to the 2'-NH_2-derivative, m.p. 148°], is described. Oxidation (excess of aq. $FeCl_3$–HCl) of (I), (II), (IV), (V), and (VI) give phenazine and its 2 : 7-Me_2, 2-*methoxy*-7-*methyl*, m.p. 135°, 2-*OMe*-, m.p. 123°, and 2 : 7-$(OMe)_2$-derivative, m.p. 163° (highly unstable intermediate), respectively, in almost quant. yields. (VII) and HCl–$FeCl_3$ or –$NaNO_2$ afford 3-*acetamido*-N-(2'-*acetamido*-4'-*methoxyphenyl*)-p-*benzoquinone*-4-*imine* (VIII), m.p. 210° (decomp.), converted by Zn–AcOH into 2 : 2'-*diacetamido*-4-*hydroxy*-4'-*methoxydiphenylamine* (IX), m.p. 186° and 186—193° (dimorphous), reoxidised (atm. O_2) to (VIII) and methylated to (VII). (IX) refluxed with Ac_2O gives 5-*methoxy*- (or *-acetoxy*-)1-[2'-*acetamido*-4'-*acetoxy*- (or *-methoxy*-)*phenyl*]-2-*methylbenziminazole*, m.p. 244°, hydrolysed (HCl or KOH) to 5-*methoxy*- (or *-hydroxy*-)1-[2'-*amino*-4'-*hydroxy*- (or *-methoxy*-)*phenyl*]-2-*methylbenziminazole*, m.p. 278° (decomp.), also from (IX) and conc. HCl (reflux). (VIII) and warm, then boiling, conc. HCl give (?)-*chloro*-5-*methoxy*- (or *-hydroxy*-)1-[2'-*amino*-4'-*hydroxy*- (or *-methoxy*-)*phenyl*]-2-*methylbenziminazole*, m.p. 270°. (VII), (VIII), or (IX), and cold HNO_3 (*d* 1·43) give a NO_2-compound, $C_{17}H_{16}O_6N_4$, m.p. 215° (decomp.). The Ac_2 derivative of (IV) and $FeCl_3$–AcOH give 3-*acetamido*-N-(2'-*acetamido*-4'-*methylphenyl*)-p-*benzoquinone*-4-*imine* (X), m.p. 200° (decomp.) [NO_2-compound, m.p. 203° (decomp.)], reduced to 2 : 2'-*diacetamido*-4-*hydroxy*-4'-*methyldiphenylamine*, m.p. 222°, which with Ac_2O gives 1-[2'-*acetamido*-4'-*acetoxy*- (or *-methyl*-)*phenyl*]-5-*methyl*- (or *-acetoxy*-)2-*methylbenziminazole*, m.p. 243°; 1-[2'-*amino*-4'-*hydroxy*- (or *-methyl*-)*phenyl*]-5-*methyl*- (or *-hydroxy*-)2-*methylbenziminazole* has m.p. 248°. (X) and conc. HCl give (?)-*chloro*-1-[2'-*amino*-4'-*hydroxy*- (or *-methyl*-)*phenyl*]-5-*methyl*- (or *-hydroxy*-)2-*methylbenziminazole*, m.p. 280°. A. T. P.

Replacement of the diazo- by the acetoxy-group. II. Preparation of *m*-bromophenyl and *m*-iodophenyl acetates. L. E. Smith and H. L. Haller (J. Amer. Chem. Soc., 1939, **61**, 143—144; cf. A., 1934, 183).—*m*-Bromo-, m.p. 145°, and *m*-iodo-benzenediazonium borofluoride, m.p. 134°, in hot AcOH give m-*bromo*-, b.p. 95—96°/2 mm., and m-*iodo-phenyl acetate*, b.p. 132—133°/7 mm., respectively, hydrolysed to the phenols by aq. KOH. R. S. C.

Condensation of *tert.* aliphatic alcohols with aromatic compounds in the presence of aluminium chloride. IV. *tert.* Dimethylamylcarbinols with phenol. R. C. Huston and R. L. Guile (J. Amer. Chem. Soc., 1939, **61**, 69—71; cf. A., 1939, II, 54).—The isomeric $C_5H_{11}{\cdot}CMe_2{\cdot}OH$, PhOH, and $AlCl_3$ in light petroleum at 25—30° give, as sole products (2·1—69·5%), p-*tert.*-alkylphenols, the structure of which is proved by synthesis of the *tert.*-alkylbenzenes from $C_5H_{11}{\cdot}CMe_2{\cdot}OH$, C_6H_6, and $AlCl_3$, followed by nitration, reduction, diazotisation, and hydrolysis. Oxidation of the NO_2-derivatives gives *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ in all cases. The following appear new. β-p-*Hydroxyphenyl*-β-*methyl*-n-*heptane*, b.p. 114—117°/2 mm. (*benzoate*, m.p. 27—33°; α-*naphthylurethane*, m.p. 120—121°), -βγ-, b.p. 111—114°/2 mm. (*benzoate*, m.p. 54·2—55·2°; α-*naphthylurethane*, m.p. 105—105·5°), -βδ-, b.p. 113—116°/2 mm. (*benzoate*, m.p. 37—38°; α-*naphthylurethane*, m.p. 119·5—120·5°), and -βε-*dimethyl*-n-*hexane*, b.p. 105—107°/2 mm. (*benzoate*, m.p. 46—47°; α-*naphthylurethane*, m.p. 132·5—133·5°), -β-*methyl*-γ-*ethyl*-, b.p. 109—111°/2 mm. (*benzoate*, m.p. 69—70°; α-*naphthylurethane*, m.p. 109·5—110·5°), -ββδ-, b.p. 289°/741 mm., m.p. 83° (cf. A., 1934, 999) (*benzoate*, m.p. 73—74°; α-*naphthylurethane*, m.p. 102—103°), -βγδ-, m.p. 74° (*benzoate*, m.p. 47—48°; α-*naphthylurethane*, m.p. 114·5—115·5°), and -βγγ-*trimethyl*-n-*pentane*, m.p. 160°. β-p-*Nitrophenyl*-β-*methyl*-n-*heptane*, b.p. 148—150°/2 mm., -βγ-, b.p. 133—135°/2 mm., -βδ-, b.p. 135—137°/2 mm., and -βε-*dimethyl*-n-*hexane*, b.p. 129—131°/2 mm., -β-*methyl*-γ-*ethyl*-, b.p. 127—130°/4 mm., and -ββδ-*trimethyl*-n-*pentane*, b.p. 108—110°/4 mm., and the corresponding NH_2-compounds, b.p. 108—111°/2 mm., 115—119°/4 mm., 99—101°/2 mm., 99—102°/2 mm., 103—106°/2 mm., and 112—115°/5 mm., respectively. $CHMePr^{\beta}{\cdot}MgBr$ and AcCl in Et_2O give γδ-dimethylpentan-β-one, b.p. 135—140°/744 mm., which with MgMeI affords βγδ-*trimethyl*-n-

pentan-β-*ol*, b.p. 155—157°/752 mm. *d*, *n*, and γ are reported for the phenols. R. S. C.

Synthesis and germicidal properties of 4-fluoro-2-alkylphenols. C. M. Suter, E. J. Lawson, and P. G. Smith (J. Amer. Chem. Soc., 1939, **61**, 161—165).—*p*-C_6H_4F·OEt (I) (prep. described), b.p. 71°/18 mm., and $AlCl_3$ in C_6H_6 at 100° give 74% of *p*-C_6H_4F·OH, b.p. 87°/23 mm. (with a phenol, m.p. 153—156°), the *acetate*, b.p. 85—87°/16 mm., *propionate*, b.p. 102—103°/19 mm., n-*butyrate*, b.p. 124—125°/36 mm., n-*valerate*, b.p. 120—124°/16 mm., and n-*hexoate*, b.p. 134—140°/16 mm., of which with $AlCl_3$ at 150° give 5-*fluoro*-2-*hydroxy*-*aceto*-, b.p. 94—99°/12 mm., m.p. 56—56·5°, -*propio*-, b.p. 117—121°/22 mm., m.p. 30·5°, -n-*butyro*-, b.p. 116—118°/14 mm., m.p. 38—39°, -n-*valero*-, b.p. 131—135°/14 mm., m.p. 7—9°, and -n-*hexo*-, b.p. 146—147°/12 mm., m.p. 49—50°, -*phenone* and thence (Clemmensen) poor yields of 4-*fluoro*-2-*ethyl*-, b.p. 64—65°/3 mm., -n-*propyl*-, b.p. 67·5—68°/2·5 mm., -n-*butyl*-, b.p. 90·5—91°/4 mm., -n-*amyl*- (II), b.p. 104·5—105·5°/4 mm., and -n-*hexyl*-*phenol*, b.p. 106—107°/2·5 mm., respectively, which give the corresponding 4-*fluoro*-2-*alkylphenoxyacetic acids*, m.p. 96—97°, 73·5—74°, 73—73·5°, 63—64°, and —. The alkylphenols are better obtained as follows. Br in AcOH or, better, CCl_4 and (I) give 2-*bromo*-4-*fluorophenetole*, b.p. 108—111°/24 mm. (with some 2 : 4 : 1-$C_6H_3Br_2$·OEt), the Mg derivative from which with RCHO in Et_2O gives α-5-*fluoro*-2-*ethoxyphenyl*-*ethyl* (III), b.p. 111°/6 mm., -n-*butyl*, b.p. 158°/19 mm., -n-*amyl*, b.p. 165°/15 mm., and -n-*hexyl*, b.p. 170—172°/7 mm., *alcohol*. Dehydration of the requisite alcohol by (usually) 85% H_3PO_4 at 200° gives 4-*fluoro*-2-n-*propenyl*- (prep. by $KHSO_4$), b.p. 91—94°/6 mm., -n-*butenyl*-, b.p. 120—124°/13 mm., -n-*pentenyl*-, b.p. 108—112°/4 mm., and -n-*hexenyl*-, b.p. 134—138°/9 mm., -*phenetole*, which are readily hydrogenated (PtO_2) in EtOH at 2 atm. to 4-*fluoro*-2-n-*propyl*-, b.p. 101—102°/16 mm., -n-*butyl*-, b.p. 112—113°/14 mm., -n-*amyl*-, b.p. 122—126°/11 mm., and -n-*hexyl*-, b.p. 107—108°/3 mm., -*phenetole*, respectively. These are de-ethylated by AcOH–58% HI. 4-*Fluoro*-2-*ethylphenetole*, b.p. 68—68·5°/2·5 mm., is obtained with βγ-*di*-(5-*fluoro*-2-*ethoxyphenyl*)*butane*, m.p. 147·5—148°, from (III) by HCl–PhMe followed by reaction with Mg and hydrolysis. p-*Fluorophenoxyacetic acid* melts at 102—103°. F increases the bactericidal properties of the phenols but not to the same extent as Cl or Br; (II) is the most potent. R. S. C.

Basic lead salts of trinitro-*m*-cresol.—See B., 1939, 127.

Synthesis of 4- and 5-phenylresorcinols. "Positive" bromine of the dibromodiphenyls. C. M. Suter and P. G. Smith (J. Amer. Chem. Soc., 1939, **61**, 166—168).—1 : 3 : 5-$C_6H_3PhBr_2$, m.p. 41—41·5° (lit. 15°), a little Cu, and KOBz in BzOH at 250° give (after hydrolysis) 82% of *m*-C_6H_4Ph·OH and some PhOH. 1 : 2 : 4-$C_6H_3PhBr_2$ (prep. in 22% yield from 2 : 4 : 1-$C_6H_3Br_2$·N_2Cl, C_6H_6, and NaOH), b.p. 125° (? 215°)/2 mm., similarly gives PhOH and 9·7% of *p*-C_6H_4Ph·OH. Thus, the "positive" nature of a halogen depends partly on the reagents.

5-Phenyldihydroresorcinol, Et_2SO_4, and NaOH give 57% of Et_1 ether, converted by S at 260—265° (less well by Se at 285°) and subsequent hydrolysis by HI into 5-*phenylresorcinol* (I), m.p. 157—158°. 4-*cyclo*-Hexylresorcinol (prep. described) with S gives tars, but the dibenzoate with S at 300°, followed by NaOH in aq. EtOH, gives 4-*phenylresorcinol* (II), m.p. 145°. (I) and (II) are rather weak antiseptics. R. S. C.

Condensation products of phenols and ketones. III. Hydroxyquinol, pyrogallol, and *m*- and *p*-cresols with acetone. W. Baker and D. M. Besly (J.C.S., 1939, 195—199).—Hydroxyquinol triacetate and $COMe_2$ in AcOH–HCl afford 6 : 7 : 6′ : 7′-tetrahydroxy-4 : 4 : 4′ : 4′-tetramethylbis-2 : 2′-*spiro*chroman (I), m.p. 270° (decomp.) (darkens ~260°) (cf. Fisher *et al.*, A., 1936, 838; Sükösd, Chem. Abs., 1933, **27**, 1873). (I) is oxidised ($KMnO_4$) to phoronic anhydride (II), and methylated (Me_2SO_4–NaOH–MeOH) to the *Me*$_4$ *ether*, m.p. 214—216° (non-phenolic). The "hexa-acetate" of (I) (*loc. cit.*) is shown to be a *tetra-acetate* (+ 1 AcOH; lost over KOH at 160° or by distillation to dryness with PhMe). (I) and Br–AcOH at 40° give a (?) dibromodiquinone, which on reduction (Zn–AcOH) and acetylation (Ac_2O) affords 8 : 8′- (or 5 : 5′-)*dibromo*-6 : 7 : 6′ : 7′-*tetra*-*acetoxy*-4 : 4 : 4′ : 4′-*tetramethylbis*-2 : 2′-spiro*chroman*, m.p. 227—230°. $COMe_2$ and 1 : 2 : 3-$C_6H_3(OH)_3$ in presence of $POCl_3$ (cf. Wittenberg, A., 1882, 1289) or AcOH–HCl (cf. Fabinyi *et al.*, A., 1905, i, 888) give 5 : 6 : 7 : 5′ : 6′ : 7′-hexahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene (III), m.p. 260—265° (darkens at 240°) [*hexa-acetate*, m.p. 247° (rapid heating); *Me*$_6$ *ether*, m.p. 135—137° (Me_2SO_4–KOH, in coal gas)]. The products from *m*- or *p*-cresol and $COMe_2$ are 4 : 4 : 7 : 4′ : 4′ : 7′- (IV), m.p. 128° (after resolidifying, m.p. 136°; dimorphous), and 4 : 4 : 6 : 4′ : 4′ : 6′-hexamethylbis-2 : 2′-*spiro*chroman [m.p. 136° (after solidification, m.p. 144°); dimorphous], respectively, as suggested by Niederl (A., 1932, 842). Each is oxidised to (II). The dimeric form (V) (+ Et_2O), m.p. 76—77°, of 2-hydroxy-4-methyl*iso*propenylbenzene (cf. Fries *et al.*, A., 1908, i, 160) is converted by boiling HI (*d* 1·7) into (IV) and *m*-cresol, which suggests that (V) is an intermediate in the prep. of (IV), *e.g.*, from *m*-cresol and $COMe_2$, with HCl or H_2SO_4. A similar mechanism is suggested in the case of the *p*-cresol analogue. A. T. P.

Mode of reaction of organo-metallic compounds. III. Methods of scission of phenolic ethers. A. Lüttringhaus and G. von Sääf (Angew. Chem., 1938, **51**, 915—920).—The following methods are discussed with illustrations: (1) thermal fission into phenols and ethylenes occurring with particular ease when the ether linking is loosened by a βγ-double linking; (2) reductive fission by H_2 under high pressure and in presence of various catalysts or, in the case of polyhydroxybenzene ethers, by Na and EtOH; (3) dehydrogenative fission particularly when the production of a quinonoid system is possible [*e.g.*, action of $FeCl_3$ on $O(C_6H_4$·OH-*p*$)_2$]; (4) hydrolysis by acids including the use of AcOH–HBr and of NH_2Ph,HCl; (5) fission by metallic salt complexes, *i.e.*, by acid chlorides and anhydrides in presence of

metallic salts such as $ZnCl_2$, $AlCl_3$, $FeCl_3$, $SnCl_4$, $SbCl_5$, and BF_3 (acid bromides and, particularly, iodides are effective without these catalysts); (6) fission by alkalis or, in certain cases, by NH_3 or amines; (7) fission by alkali metal (Na, K, Na–K; or Na in liquid NH_3); (8) fission by organo-metallic compounds (Grignard's compounds; LiPh).

H. W.

Free radicals and radical stability. I. Influence of the phenoxyl group on radical stability and merisation. II. Dimethoxytriphenylmethyls. S. T. Bowden (J.C.S., 1939, 26—33; 33—41).—I. Wieland's observation (A., 1911, i, 851) that definite colour changes occur when $(\cdot CPh_2\cdot OPh)_2$ (I), m.p. (vac.) 214·5—216°, is heated in a high-boiling solvent (*e.g.*, $C_{10}H_8$, EtOBz) in absence of O_2 is confirmed; the intensity increases with rise in temp. but there is no exact reversibility in the colour changes owing to the formation of decomp. products. The thermal behaviour of (I) is analogous to that of diphenylbisdiphenylene-ethane (II). Dissociation of (I) at 160° gives the radical, $\cdot CPh_2\cdot OPh$, but in much lower concn. than that of $\cdot CPh_3$ in the $(\cdot CPh_3)_2$ system at room temp.; the stabilising influence of OPh on the radical is $\ll$ that of Ph. At elevated temp. (I) is converted into $CPh_2(OPh)_2$ and $(CPh)_2$. (I) is undissociated in boiling C_6H_6, does not give coloured solutions in liquid SO_2, and is photochemically stable. The fundamental characteristic of an ethane derivative to dissociate into radicals is termed "merisation tendency," and two classes of free radical systems are considered, viz., where the tendency is high, *e.g.*, $(\cdot CPh_3)_2$ (III), and low, *e.g.*, $(\cdot CPh_2\cdot OPh)_2$. At 18°, a solution of (III) in PhBr absorbs 1 mol. of O_2 in 3 min., whereas (I) requires 3 hr. (absorption apparatus described; cf. Gomberg *et al.*, A., 1917, i, 551). The solution of (I) becomes gradually deep yellow, ~4 mols. of O_2 are absorbed, and the primary oxidation product is not isolable; (III) forms a colourless peroxide and a yellow oil, each of composition $(CPh_3\cdot O)_2$. The rate of dissociation of (II) is 20 times that of (I). A further indication of the varied rates of oxidation of (I) and (II) is afforded by the Prussian-blue test (Conant and Evans, A., 1929, 934). (I) in C_6H_6 does not absorb I at room temp. during 24 hr., but in xylene and CO_2 at 110° absorbs an amount corresponding with 0·28 mol.; $CPh_2(OPh)_2$ does not absorb I. (I) with Na in Et_2O (inert atm.) at room temp. becomes yellow, then deep red (few days), due to formation of Na derivative, but the isomeric $(CPh_3\cdot O)_2$ does not react appreciably under these conditions.

II (cf. Gomberg *et al.*, A., 1925, i, 1266; 1926, 738). 2 : 4′-Dimethoxytriphenylcarbinol, m.p. 115° (basicity val. 9·9; $CPh_3\cdot OH$ = 1), and AcCl or AcBr in light petroleum afford the *chloride* (IV), m.p. 116°, or *bromide*, m.p. 118°, respectively. (IV) and excess of Hg in C_6H_6–Et_2O, then air treatment, afford a *peroxide*, m.p. 139°. Pure (IV) in C_6H_6 and excess of mol. Ag (in CO_2), shaken for 4—6 hr. in the dark, afford a solution of the radical (O_2 absorption determined); evaporation at 40—45°/70 mm. (CO_2) gives a pale yellow solid (V), m.p. 80° (vac.) (isomerises with traces of acid) (apparatus for isolation described in detail). It is much more stable than the 2 : 4-$(OMe)_2$-analogue (see below). In non-polar solvents the neutral radical is orange, but the ion in liquid SO_2 is bright red. 2 : 2′-*Dimethoxytriphenylmethyl chloride*, m.p. 95°, and *peroxide*, m.p. 110°, are described. The corresponding free radical (VI), m.p. 88° (vac.), forms yellowish-red solutions with non-polar solvents, but the colour in liquid SO_2 is deep brownish-black. Neither (V) nor (VI) gives additive compounds with Et_2O. The mechanism of formation of such derivatives, *e.g.*, from CPh_3, is discussed; the free radical is probably not responsible. Radical stability is not $\propto$ the no. and orientation of substituted OMe (cf. Burton and Ingold, A., 1929, 1052). Radical stabilities of (V) and (VI) are 28 and 41%, respectively, in C_6H_6, and 32 and 55% in $PhNO_2$ (cryoscopic mol. wt. determinations; apparatus described). The thermal stabilities of the corresponding CR_3I are much < that of CPh_3I (apparatus for I absorption described).

A. T. P.

Derivatives of the ethers of hydroxyquinol. H. W. Dorn, W. H. Warren, and J. L. Bullock (J. Amer. Chem. Soc., 1939, **61**, 144—147).—2 : 6 : 1 : 4-$OMe\cdot C_6H_2Br(OH)_2$ (prep. from vanillin detailed) and Me_2SO_4 give 6-*bromo*-1 : 2 : 4-*trimethoxybenzene*, m.p. 37—38°, converted by Br–C_6H_6 into the 3 : 6-*Br*$_2$-*ether* (I), m.p. 97°, which is oxidised by HNO_3 (*d* 1·41) to 3 : 6-*dibromo*-2-*methoxy*-p-*benzoquinone*, m.p. 172°, converted by SO_2–aq. EtOH into 3 : 6-*dibromo*-2-*methoxyquinol*, m.p. 155° (decomp.). With Br–AcOH at 100° 5-bromo- gives 3 : 5 : 6-*tribromo*-1 : 2 : 4-*trimethoxybenzene*, m.p. 85—86°, stable to KOH–EtOH. Prep. of *x* : 1 : 2 : 4-$NO_2\cdot C_6H_2(OAc)_3$ (II) (Thiele *et al.*, A., 1901, i, 701) gives also some 2 : 1 : 4-$OH\cdot C_6H_3(OAc)_2$, m.p. 104°. Me_2SO_4–NaOH converts (II) into 5 : 1 : 4 : 2-$NO_2\cdot C_6H_2(OMe)_3$ (III), whence it follows that *x* = 5 and that the dibromo-nitro-derivative (*loc. cit.*) is 5 : 3 : 6 : 1 : 2 : 4-$NO_2\cdot C_6Br_2(OH)_3$ (IV). The *Me*$_3$ *ether*, m.p. 127°, of (IV) with Sn–HCl gives 3 : 6-*dibromo*-2 : 4 : 5-*trimethoxyaniline*, m.p. 115°, and thence (I). 1 : 2 : 4-$C_6H_3(OMe)_3$ and warm H_2SO_4 (*d* 1·8) give 2 : 4 : 5-*trimethoxybenzenesulphonic acid* (*chloride*, m.p. 130°; *amide*, m.p. 76°; *anilide*, m.p. 170°), converted by 10N-HNO_3 into (III). Vanillin and 20% oleum give the 5-sulphonic acid, m.p. 124°, converted by H_2O_2–NaOH into 2 : 5-*dihydroxy*-3-*methoxybenzenesulphonic acid*, decomp. 290°, and thence into 2 : 3 : 5-*trimethoxybenzenesulphonyl chloride*, m.p. 98°.

R. S. C.

Derivatives of phloroglucinol trimethyl ether. G. R. Ramage, J. L. Simonsen, and W. J. I. Stowe (J.C.S., 1939, 89—91; cf. A., 1938, II, 441).—2 : 4 : 6 : 1-$(OMe)_3C_6H_2\cdot CHO$ (I) and Zn in AcOH or Ac_2O give 1 : 2 : 4 : 6-$C_6H_2Me(OMe)_3$. (I) is stable to $Al(OEt)_3$ at room temp. but $Al(OPr^\beta)_3$ in $Pr^\beta OH$ gives an unstable gum containing (?) 2 : 4 : 6 : 2′ : 4′ : 6′-hexamethoxybenzoin (2 : 4-*dinitrophenylhydrazone*, m.p. 275—276°). 2 : 4 : 6-Trimethoxybenzaldoxime and H_2 + Pd–C in AcOH give 2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethoxydibenzylamine* (II), m.p. 118—119°, but reduction (method: Schales, A., 1935, 1491) affords 2 : 4 : 6-*trimethoxybenzylamine*, (III), m.p. 59—60° [*hydrochloride* (+$7H_2O$), m.p. 92°; *Ac* derivative, m.p. 153—154°], and a little (II). The nitrite of (III) is decomposed by heat to give mainly

2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethoxydiphenylmethane*, m.p. 116—117°, also obtained from 1 : 3 : 5-$C_6H_3(OMe)_3$ and 40% CH_2O in EtOH–piperidine acetate at 100° (bath). 3 : 5 : 1-$(OMe)_2C_6H_3$·OH similarly gives an intractable resin. 2 : 4 : 6 : 1-$(OMe)_3C_6H_2$·CH_2·OH could not be obtained by the method of Freudenberg and Harder (A., 1927, 251). A. T. P.

Nitronaphthyl and aminonaphthyl alkyl sulphides. H. H. Hodgson and E. Leigh (J.C.S., 1939, 126—128).—The solid mixture of dinitrodinaphthyl mono- and di-sulphides, from $C_{10}H_6Cl·NO_2$–Na_2S_2–EtOH, is refluxed with Na_2S (cryst.) and aq. NaOH–EtOH (5 min.), the insol. monosulphide filtered off, and the filtrate (A) used as follows. (A) from 1 : 4- or 2 : 1-$C_{10}H_6Cl·NO_2$, in aq. NaOH, *i.e.*, 4 : 1- or 1 : 2-NO_2·$C_{10}H_6$·SNa, respectively, and Me_2SO_4 at 60—65° or 40—45° give 4-*nitro*-1- (I), m.p. 84·5—85°, and 1-*nitro*-2- (II), m.p. 120°, *-naphthyl Me sulphide*, respectively. 2 : 1-NO_2·$C_{10}H_6$·SH could be methylated only by heating a paste of the slightly moist Na salt, $NaHCO_3$, and Me_2SO_4 at 100° (bath) (followed by PbO); 2-*nitro*-1-*naphthyl Me sulphide*, has m.p. 104—105°. The corresponding Et sulphide could not be prepared, but 4-*nitro*-1-, m.p. 63°, and 1-*nitro*-2-, m.p. 87°, *-naphthyl Et sulphides* are readily obtained. (I) or (II) and $SnCl_2$–HCl–AcOH at 100° (bath) give the *stannichlorides*, decomposed by 5% aq. NaOH at 60° to the respective 4-amino-1-, m.p. 55° [*hydrochloride*, m.p. ~220° (decomp.)], and 1-*amino*-2-*naphthyl Me sulphide*, b.p. 253°/753 mm. [*hydrochloride*, m.p. ~210° (decomp.); *stannichloride*, decomp. ~195°]. Azo-dyes from the former base are deeper (bluer) in shade than those from the latter (cf. A., 1926, 515). Colours of the sulphides with H_2SO_4, $ClSO_3H$, and oleum are recorded. A. T. P.

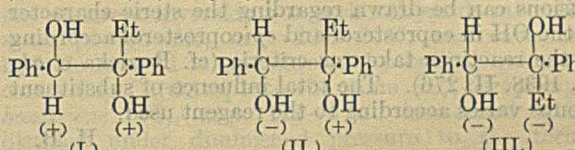
Synthesis of arylsulphonium salts. G. Dougherty and P. D. Hammond (J. Amer. Chem. Soc., 1939, **61**, 80—81).—Ph_2S and Br–AcOH give $(p\text{-}C_6H_4Br)_2S$ and thence by Cl_2–C_6H_6 the dichloride, which with C_6H_6 and $AlCl_3$ at 80° gives *phenyldi-p-bromophenylsulphonium chloride* and thence the bromide, iodide, and *platinichloride*. The derived hydroxide is alkaline and attacks (slightly) Al and Zn. Thianthrene gives similarly *phenyl-* and *p-phenetylthianthronium platinichloride*. R. S. C.

Influence of saligenin and its 5-methyl derivative on conductivity of boric acid.—See A., 1939, I, 147.

Action of mixed nitric and sulphuric acids on 5-bromo-3 : 6-dinitro-1 : 2 : 4-trimethylbenzene. I. J. Rinkes (Rec. trav. chim., 1938, **57**, 1405—1409).—The "nitrate," m.p. 150°, obtained by Huender (A., 1915, i, 129) from 1 : 2 : 4 : 5 : 3 : 6-$C_6Me_3Br(NO_2)_2$ is formed by conversion of one of the Me into $CH_2·O·NO_2$ (cf. Smith *et al.*, A., 1937, II, 338). This benzyl nitrate (I) in EtOH saturated with NH_3 affords the corresponding 5-*bromo*-3 : 6-*dinitrodimethyl-benzaldehyde*, m.p. 190—191° (*oxime*, m.p. 191—192°), and thence ($AgNO_3$, aq. EtOH–NaOH at 10°) the *-benzoic acid*, m.p. 232° (*Me* ester, m.p. 171°). (I) in $EtCO_2H$, with boiling H_2SO_4–H_2O (1 : 1) for 5 min., gives the corresponding *-benzyl alcohol*, m.p. 202° (cf. Huender, *loc. cit.*), converted by Ac_2O–H_2SO_4 into the *acetate*, m.p. 102—103°, and by HNO_3 (*d* 1·5) at 0° into (I). A. T. P.

[Synthesis of condensed polynuclear hydrocarbons by the cyclodehydration of aromatic alcohols. VII. Cyclodehydration involving the Wagner rearrangement.] M. T. Bogert (J. Org. Chem., 1938, **3**, 508).—α-Phenyl-δδ-dimethylpentan-γ-ol and its phenylurethane have been described previously by Hill and Bruce (A., 1930, 343). H. W.

Stereochemical structure. IX. Stereochemical relationship of the α- and β-forms of substituted hydrobenzoins. (*b*) Ethylhydrobenzoin (β-form). R. Roger (J.C.S., 1939, 108—111; cf. A., 1937, II, 415).—(−)-Ethylhydrobenzoin (β-form) (I), m.p. 96—97°, $[\alpha]^{17}_{5461}$ −31·5° in $COMe_2$, and MgEtI, then PhCHO–C_6H_6, afford (+)-ethylbenzoin, m.p. 71—72°, $[\alpha]^{18}_{5461}$ +254° in EtOH. Controls with (+)- (β-form, m.p. 96—97°) or partly racemised (−)-ethylhydrobenzoin (α-form, m.p. 88—90°), and MgEtI, show that no change in form occurs under the conditions (vals. of [α] unchanged). The deduction can be made that the β-form of (+)-ethylhydrobenzoin would undergo oxidation to (−)-ethylbenzoin. Configurations (II) and (III) are assigned to the α- and β-forms of (+)-ethylhydrobenzoin, respectively, which



are diastereoisomeric (cf. McKenzie *et al.*, J.C.S., 1910, **97**, 473), as also are the α- and β-forms of the (−)-glycol. The method of synthesis of such α- and β-forms is discussed, and also whether formation of optically active ethylbenzoins can be regarded as example of "asymmetric synthesis" (cf. McKenzie, "Ergebnisse der Enzymforschung," V, p. 4, Leipzig, 1936). A. T. P.

Rate of pinacolin isomerisation of two *cis*–*trans*-isomeric pinacols. R. Criegee and K. H. Plate (Ber., 1939, 72, [*B*], 178—181).—The rate of isomerisation of *cis-* (I) and *trans-* (II) -7 : 8-diphenylacenaphthene-7 : 8-diol by $CCl_3·CO_2H$ or $p\text{-}C_6H_4Me·SO_3H$ in AcOH has been measured by treating aliquot portions of the solution after definite intervals with NaOAc in AcOH followed by excess of $Pb(OAc)_4$; after completion of the oxidation of unchanged diol the unused $Pb(OAc)_4$ is determined iodometrically. The isomerisation is apparently unimol., variation in the const. being attributed to experimental error. The half period of the transformation of (I) in presence of 0·1N-$p\text{-}C_6H_4Me·SO_3H$ at 20° is 7 min., whereas that of (V) is 23 min. The rate is approx. ∝ the concn. of the catalyst, $CCl_3·CO_2H$ being much less efficient than $p\text{-}C_6H_4Me·SO_3H$. Under sufficiently energetic conditions, the solvent AcOH can cause isomerisation, which is noticeable after some days at room temp. The temp. coeff. is 3·6 in the case of (I). H. W.

Replaceability of aromatically united bromine by lithium by means of lithium phenyl. G. Wittig and U. Pockels (Ber., 1939, 72, [*B*], 89—92; cf. A., 1938, II, 441).—4 : 6 : 1 : 3-$C_6H_2Br_2(OMe)_2$ is slowly converted by LiPh in Et_2O at room temp. into the Li_2 compound; hydrolysis of the reaction mixture gives PhBr, 1 : 3-$C_6H_4(OMe)_2$, and a little 4 : 1 : 3-$C_6H_3Br(OMe)_2$ (I). The successive action of LiPh and CO_2 on (I) leads to 2 : 4-$(OMe)_2C_6H_3{\cdot}CO_2H$, 2 : 2′ : 4 : 4′-tetramethoxybenzophenone, new m.p. 137·2—139·5°, and tri-2 : 4-dimethoxyphenylcarbinol. Addition of $COPh_2$ to the product from LiPh and (I) gives 2 : 4-dimethoxytriphenylcarbinol, m.p. 137·8—138·6°, whence the 5-Br-derivative, m.p. 192·8—193·8°. *m*-$C_6H_4(OMe)_2$ is converted by successive treatments with LiPh and CO_2 in Et_2O into 2 : 6-$(OMe)_2C_6H_3{\cdot}CO_2H$ and 2 : 2′ : 6 : 6′-tetramethoxybenzophenone, m.p. 205·4—206·2°. 5 : 5′-Dibromo-2 : 2′ : 4 : 4′-tetramethoxybenzophenone, m.p. 224·2—225·2°, and tri-(5-bromo-2 : 4-dimethoxyphenyl)-carbinol, m.p. 255·5—256·5°, were prepared.

H. W.

Cisoid and transoid character of epimeric alcohols of the steroid series. K. Miescher and W. H. Fischer (Chem. and Ind., 1939, 113—114; cf. A., 1938, II, 174).—Objections to the nomenclature of Schoenheimer and Evans (A., 1936, 1105) are overcome if $C_{(3)}{\cdot}OH$ is referred to $C_{(9)}$. Opposite conclusions can be drawn regarding the steric character of the OH in coprosterol and *epi*coprosterol according to the reactions taken as criteria (cf. Ruzicka *et al.*, A., 1938, II, 276). The total influence of substituent groups varies according to the reagent used.

H. B.

Brassicasterol. I. Empirical formula and hydrogenation. E. Fernholz and H. E. Stavely (J. Amer. Chem. Soc., 1939, **61**, 142—143).—Brassicasterol [acetate, m.p. 152°, $[\alpha]_D$ −65° in $CHCl_3$, obtained by debromination of its tetrabromide, m.p. 205° (decomp.)] is shown to be $C_{29}H_{48}O$ by analysis of its 3 : 5-*dinitrobenzoate*, m.p. 219°, $[\alpha]_D^{25}$ −28° in $CHCl_3$, and hydrogenation (Pd-black) in EtOH to *brassicastanol*. (+*x*EtOH), m.p. 142°, $[\alpha]_D^{25}$ +23·6° in $CHCl_3$ (*acetate*, m.p. 143°, $[\alpha]_D^{25}$ +14·5° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 202°, $[\alpha]_D^{25}$ +13·9° in C_6H_6), which differs from stigmastanol.

R. S. C.

Ultra-violet irradiation of $\Delta^{5:7}$-androstadiene-3 : 17-diol. K. Dimroth and J. Paland (Ber., 1939, 72, [*B*], 187—190).—Parallel exposure of $\Delta^{5:7}$-androstadiene-3 : 17-diol (I) and ergosterol (II) to the Hg light causes exactly similar changes in the absorption spectra so that it is certain that analogous irradiation products result from (I) and (II) or other provitamins. Irradiated (I) is devoid of antirachitic action.

H. W.

Isomerism of *allo*pregnanetetraol. A. Serini and W. Logemann (Naturwiss., 1938, **26**, 840; cf. A., 1938, II, 322).—17-Vinyl*iso*androstane-3 : 17-diol is converted by Dimroth's method (A., 1938, II, 326) into Δ^{17}-*allopregnene*-3 : 21-*diol*, m.p. 203—205° (*diacetate*, m.p. 156°), which with OsO_4 affords the *allo*pregnane-3 : 17 : 20 : 21-tetraol (= substance *K*, m.p. 198—200°) of Steiger and Reichstein (*ibid.*, 278).

J. L. D.

Hydroxyalkylammonium mandelates.—See B., 1939, 216.

Perkin reaction. IV. Condensation of carboxylic acids and aldehydes. S. Ishikawa and H. Takeuchi (Sci. Rep. Tokyo Bunrika Daigaku, 1938, **A**, **3**, 231—237; cf. A., 1935, 1497).—$CH_2Ph{\cdot}CO_2H$ (1·3 mols.), PhCHO (1 mol.), and NEt_3 (0·3 mol.) at 180° give 27% of $CHPh{:}CPh{\cdot}CO_2H$. AcOH and $CH_2Cl{\cdot}CO_2H$ do not condense with PhCHO and NEt_3 at 180°, but AcOH, *o*-$C_6H_4Cl{\cdot}CHO$, and NEt_3 give 1% of *trans-o*-$C_6H_4Cl{\cdot}CH{:}CH{\cdot}CO_2H$. $CH_2Ph{\cdot}CO_2H$ and *o*-$C_6H_4Cl{\cdot}CHO$ in CO_2 at 200° without a catalyst give 14% of *α-phenyl-β-o-chlorophenylacrylic acid*, m.p. 175·2° (corr.; block). The reaction mechanism is discussed.

R. S. C.

Derivatives of β-naphthaldehyde. J. D. Fulton and R. Robinson (J.C.S., 1939, 200—201).—β-$C_{10}H_7{\cdot}CHO$ (I), m.p. 58° [prep. from β-$C_{10}H_7{\cdot}CN$ (method: Stephen, A., 1925, i, 1131)], and KCN–H_2O–EtOH give *β-naphthoin* (II), m.p. 125—126° (*oxime*, m.p. 172°; *Me* ether, m.p. 82°), converted by Fehling's solution into β-naphthil, m.p. 158—159° (whence 2 : 3-*di-β-naphthylquinoxaline*, m.p. 192—193°). (II) is reduced by 4% Na–Hg in EtOH to *hydro-*, m.p. 253°, or by Zn–HCl–EtOH to *deoxy-β-naphthoin*, m.p. 155—156°. (I) and $CH_2(CO_2H)_2$–AcOH at 100° (bath) give *β-naphthylidenemalonic acid* (III), m.p. 207° (decomp.); thermal decomp. then affords β-naphthylacrylic acid, new m.p. 208—209°, also obtained from (I) and $CH_2(CO_2H)_2$–C_5H_5N at 100° (bath) for 1½ hr., then boiling (10 min.). (III) and Na–Hg in EtOH give (β-naphthylmethyl)malonic acid, decomp. 150—153°. (I) and $CN{\cdot}CH_2{\cdot}CO_2Et$, gently heated in presence of a little morpholine, give *Et α-cyano-β-naphthylideneacrylate*, m.p. 125—126° (shrinks at 117°). β-Naphthylidenephenyl*iso*oxazolone heated with 2% aq. Na_2CO_3 affords α-benzamido-β-2-naphthylacrylic acid, new m.p. 240° (previous softening) (cf. Kikkoji, A., 1911, ii, 909) [Me ester, m.p. 142° (previous softening)]; with hot 10% aq. NaOH, 2-$C_{10}H_7Me$ or β-naphthylpyruvic acid, new m.p. 190° (decomp.) [whence *2-hydroxy-3-(β-naphthylmethyl)quinoxaline*, m.p. 222—223°], results. The latter acid is oxidised (H_2O_2, aq. NaOH) to β-$C_{10}H_7{\cdot}CH_2{\cdot}CO_2H$, new m.p. 141—142°.

A. T. P.

α-(*p*-Aminobenzenesulphonamido)-acids and their derivatives. F. P. Mazza and C. Migliardi (Atti R. Accad. Lincei, 1938, [vi], **28**, 152—157).—The following are prepared, using *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$: *p-acetamidobenzenesulphonylglycine*, m.p. 235°, *-alanine*, m.p. 208°, and *-tyrosine*, m.p. 221—222°, hydrolysed respectively to *p-aminobenzenesulphonyl-glycine* (I), m.p. 150°, *-alanine* (II), m.p. 107—108°, and *-tyrosine* (III), m.p. 230° (decomp.). With diazotised *p*-$NH_2{\cdot}C_6H_4{\cdot}AsO_3H_2$, (III) gives 3-p-*arsinobenzeneazo*-N-p-*aminobenzenesulphonyltyrosine*, m.p. ‹300°. Diazotised (I), (II), and (III) with *m*-$C_6H_4(NH_2)_2$ give *p-(2′ : 4′-diaminobenzeneazo)-benzenesulphonyl-glycine*, m.p. 118—119° (decomp.), *-alanine*, m.p. 114° (decomp.), and *-tyrosine*, m.p. 158—160° (decomp.). Similarly *p-(7′-amino-3′-sulpho-1′-naphthol-2′-azo)benzenesulphonyl-glycine*, *-alanine*, and *-tyrosine* (all m.p. ‹300°) are obtained.

E. W. W.

Diaroyl peroxides.—See B., 1939, 128.

Kinetics of decomposition of trinitrobenzoates in ethyl alcohol.—See A., 1939, I, 150.

"Oxidising" actions of alkalis. V. Cresols. G. Lock and F. Stitz (Ber., 1939, 72, [*B*], 77—82; cf. A., 1930, 597, 775).—In an open Ni crucible, *o*-cresol (I) is converted by KOH–NaOH at about 300—310° fairly rapidly into *o*-OH·C_6H_4·CO_2H (II), the yield of which may attain about 80%. Under similar conditions but in a Ag tube under N_2 (I) is almost completely unchanged whereas in air, H_2 and (II) are produced in the mol. ratio, 3 : 1. The experiments are not invariably reproducible. At a higher temp. the yield of H_2 increases whereas that of (II) declines in favour of CO_2. The change is apparently: OK·C_6H_4Me + 3KOH = $3H_2$ + OK·C_6H_4·$C(OK)_3$. At 300° KOBz is more extensively decomposed than NaOBz whilst at 400° decomp. is complete. NaOBz remains colourless whilst C_6H_6 is produced whereas KOBz is completely carbonised with production of Ph_2. PhMe is scarcely changed by soda-lime at 400° or 550°. MeOH appears to behave like the cresols giving H_2 and Na_2CO_3.

H. W.

Theory of allyl isomerisation. II. O. Mumm, H. Hurnhardt, and J. Diederichsen (Ber., 1939, 72, [*B*], 100—111; cf. A., 1938, II, 21).—Evidence is adduced in favour of the view that the wandering of the allyl residue from O to the *para*-C is accompanied in certain cases by a reversal of the unsaturated residue. 2 : 3 : 1-OH·C_6H_3Me·CO_2Me is converted by the successive action of NaOMe and α-chloro-Δ^{β}-pentene into *Me* 2-Δ^{β}-*pentenyloxy*-m-*toluate* (I), b.p. ~125°/1·1 mm., and by that of NaOMe and γ-chloro-Δ^{β}-pentene into *Me* 2-α-*ethylallyloxy*-m-*toluate* (II), b.p. 125—128°/0·8—1·2 mm. (I) is hydrolysed by KOH–MeOH to 2-Δ^{β}-*pentenyloxy*-m-*toluic acid*, m.p. 63—64°, whereas (II) gives 2-*hydroxy*-5-*ethylallyl*-m-*toluic acid* (III), m.p. 116°. Hydrogenation (colloidal Pd in MeOH) of (I) or (II) affords 2 : 3 : 1-OH·C_6H_3Me·CO_2Me. In boiling $NPhEt_2$, *Me* 2-*hydroxy*-5-*ethylallyl*-m-*toluate* (IV), b.p. 170—175°/17 mm. [hydrolysed to (III)], is obtained from (I) or (II). Hydrogenation (colloidal Pd in MeOH) of (III) gives 2-*hydroxy*-5-*amyl*-m-*toluic acid*, m.p. 84°. Ozonisation of (IV) in EtOAc at −20° to −12° and hydrogenation (Pd–$CaCO_3$ in EtOAc) of the ozonide affords a little CH_2O and an aldehyde, oxidised by $KMnO_4$ to 1-*Me* 3-*H* 6-*hydroxy*-5-*methylisophthalate*, m.p. 241°. Decarboxylation of (III) in boiling $NPhMe_2$ leads to 2-methyl-4-pentenylphenol, converted by 33% NaOH and 50% $CH_2Cl·CO_2H$ into 2-*methyl*-4-*ethylallylphenoxyacetic acid*, m.p. 112°, oxidised by $KMnO_4$ in aq. $COMe_2$ at 0° to 4-carboxy-2-methylphenoxyacetic acid, m.p. 285—288°. Attempts to identify the side-chain as a homoallyl or homopropenyl residue are described.

H. W.

Anomalies encountered in the synthesis of tetraphenylfulgenic anhydride. C. F. Koelsch and H. J. Richter (J. Org. Chem., 1938, 3, 473—479).—The condensation of $COPh_2$ with Et_2 diphenylitaconate in presence of NaOEt gives, after hydrolysis and treatment with AcCl, tetraphenylfulgenic anhydride (I), m.p. 267—269°, αα′ζζ′-*tetraphenyl*-$\Delta^{\alpha\gamma}$-*hexadiene*-βγ-*dicarboxylic acid* (II), m.p. 194—195·5°, αα′ζζ′-*tetraphenyl*-$\Delta^{\alpha\gamma\gamma'}$-*hexatriene*-βγ-*dicarboxylic acid* (III), m.p. 231—233° (decomp.), and the *anhydride* (IV), m.p. 222—224°, of the geometrically isomeric acid; the anhydrides of (II) and (III) are hydrolysed during isolation. Their structures point to the intermediate formation of MeCHO from NaOEt. *Me*$_2$ *diphenylitaconate* (V), m.p. 94—95° (corresponding *Me H ester*, m.p. 135—138°), condenses with $COPh_2$ and NaOMe to a product which is hydrolysed and then converted by AcCl into (I) and α-*acetoxy*-αδδ-*tetraphenyl*-Δ^{γ}-*butene*-βγ-*dicarboxylic acid*, m.p. 134—137° (*anhydride*, m.p. 163—164°), which is partly transformed at 220° into (I) and is decarboxylated in boiling quinoline containing $Cu(OAc)_2$ to tetraphenylbutadiene. (I) is converted by NaOH followed by acid into *tetraphenylfulgenic acid*, m.p. 252—255° (red at 240°). (II) is transformed by warm AcCl into its *anhydride*, m.p. 164—167°, and by boiling quinoline containing $Cu(OAc)_2$ into αα′ζζ′-*tetraphenyl*-$\Delta^{\alpha\gamma}$-*hexadiene*, m.p. 196—197°. β-Phenylcinnamaldehyde (2 : 4-*dinitrophenylhydrazone*, m.p. 205—206°), (V), and NaOMe give, after hydrolysis and treatment with AcCl, a mixture of (IV) [corresponding *acid*, m.p. 220—222° (decomp.) after becoming orange-red at 175° and softening at 184°] and (III) (corresponding *anhydride*, m.p. 212—213°). Hydrolysis of the anhydrides and dehydration of the acids proceeds without apparent inversion but each anhydride gives the same *phenylimide*, m.p. 234—235°, and each anhydride or acid is transformed by boiling quinoline containing $Cu(OAc)_2$ into the same αα′ζζ′-*tetraphenylhexatriene* (VI), m.p. 172—174°, isomerised when distilled under diminished pressure to the form, m.p. 203—206°. (VI) is reduced by Na and BuOH to αα′ζζ′-*tetraphenyl*-Δ^{γ}-*hexene*, m.p. 79—80°, and by H_2 (Pd–$BaSO_4$) to αα′ζζ′-tetraphenylhexane, m.p. 124—125·5°.

H. W.

Pechmann dyes. Scission of s-dinaphthyl compounds. P. Chovin (Compt. rend., 1938, 207, 1418—1420; cf. A., 1938, II, 333).—The dye (β-$C_{10}H_7$)$_2$($C_8H_2O_4$) (I), m.p. 361°, with 10% EtOH–KOH at 60° affords ($C_{10}H_7$)$_2$($C_8H_4O_6K_2$) (II), converted by cold AcOH–EtOH into ($C_{10}H_7$)$_2$($C_8H_4O_5$), m.p. 277° (block), which when heated alone or with Ac_2O gives (I). (II) in aq. EtOH changes from red to yellow to give (on acidification) ($C_{10}H_7$)$_2$($C_8H_6O_6$), m.p. 305°, which when heated alone or with Ac_2O gives a yellow *isomeride*, m.p. 372°, of (I) with a green fluorescence in C_6H_6.

J. L. D.

***cyclo*Hexane series. IV. Isomeric 1-carboxy-4-, -3-, and -2-methyl*cyclo*hexane-1-succinic acids.** R. D. Desai, R. F. Hunter, and G. S. Saharia (J.C.S., 1939, 84—86; cf. A., 1937, II, 290; Chatterjee, A., 1937, II, 377).—1-Hydroxy-1-cyano-4-methyl*cyclo*hexane and CN·CH_2·CO_2Et in EtOH–NaOEt give Et 1-cyano-4-methyl*cyclo*hexane-1-cyanoacetate (not isolated), which with $CH_2Br·CO_2Et$, first at room temp. and then at 100° (bath), gives *Et* 1-*cyano*-4-*methyl*cyclo*hexane*-1-α-*cyanosuccinate*, m.p. 97° (previous sintering), hydrolysed (conc. H_2SO_4 at room temp., then add H_2O and heat) to the isomeric 1-*carboxy*-4-*methyl*cyclo*hexane*-1-*succinic acids*, (*A*), m.p. 207° [*anilide-anilic acid*, m.p. 175—

176°; *anil-anilide*, m.p. 187°; p-*methylanil*-p-*toluidide*, (II), m.p. 186°], and (*B*), m.p. 178° [also affords (II), probably due to isomerisation at 220°], together with a residue, which is hydrolysed further by conc. HCl to some (*A*) and a gum. The latter is esterified and alkaline hydrolysis gives (*A*) and the two 1-carboxy-4-methyl*cyclo*hexane-1-acetic acids, m.p. 173° and 137° (cf. A., 1936, 846); an acid (? eutectic mixture), m.p. 188° (previous sintering), from which (*A*) was obtained with difficulty, was also encountered. Et 1-cyano-3-methyl*cyclo*hexane-1-cyanoacetate and $CH_2Br{\cdot}CO_2Et$ similarly afford *Et* 1-*cyano*-3-*methyl*-cyclo*hexane*-1-α-*cyanosuccinate*, b.p. 208—210°/10 mm., hydrolysed to the isomeric 1-*carboxy*-3-*methyl*-cyclo*hexane*-1-*succinic acids*, m.p. 210° and 171—172° (each yields the same p-*methylanil*-p-*toluidide*, m.p. 158—159°). The two isomeric 1-carboxy-3-methyl*cyclo*hexane-1-acetic acids, m.p. 163° and 108°, are also isolated. Similarly prepared are *Et* 1-*cyano*-2-*methyl*cyclo*hexane*-1-α-*cyanosuccinate*, b.p. 206—208°/8 mm., and the two isomeric 1-*carboxy*-2-*methyl*cyclo*hexane*-1-*succinic acids*, m.p. 195° and 175° [each gives the same p-*methylanil*-p-*toluidide*, m.p. 172°, and *di*-p-*toluidide*, m.p. 95° (previous sintering)]. No indication was obtained of isomerism connected with multiplanar forms of the *cyclo*hexane ring. A. T. P.

Arylaminophthalic acid derivatives. G. J. Marriott and R. Robinson (J.C.S., 1939, 134—139).—3-Chlorophthalanil (I), 3-*chloro*-N-p-*tolyl*- (II), m.p. 160·5°, -p-*anisyl*- (III), m.p. 198°, -β-*naphthyl*- (IV), m.p. 211°, -p-*nitrophenyl*- (V), m.p. 290° [from p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ and 3-chlorophthalic acid or by nitration of (I)] -*phthalimides*, 3 : 6- (VI), new m.p. 194°, and 3 : 4-dichlorophthalanil (VII), new m.p. 179—180°, and 3 : 6-*dichloro*-N-p-*tolylphthalimide* (VIII), m.p. 231°, are prepared. (I), NH_2Ph, K_2CO_3, and Cu-bronze (general method: Frey, A., 1912, i, 477) at 160—170° for 3 hr. give 3-*anilinophthalanil*, m.p. 144·5—145°, also obtained from (VII) and boiling NH_2Ph (Ullmann). (I) or (II) and p-$C_6H_4Me{\cdot}NH_2$ (145—150°) similarly (Frey) give 3-p-*toluidino*-N-p-*tolylphthalimide* (IX), m.p. 152°, and (I) or (III) with p-$NH_2{\cdot}C_6H_4{\cdot}OMe$ at 160—170° or 145—150° gives 3-p-*anisidino*-N-p-*anisylphthalimide* (X), m.p. 171—172° (note interchange of amine residue on N). (I) and o-$C_6H_4(NH_2)_2$ or o-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ do not yield cryst. derivatives. (IV) and β-$C_{10}H_7{\cdot}NH_2$ at 145—150° afford 3-β-*naphthylamino*-N-β-*naphthylphthalimide*, m.p. 220°, which with NH_2Ph–K_2CO_3 at 170° gives 3-β-*naphthylamino*-N-*phenylphthalimide*, m.p. 167°, thus showing reverse displacement of β-$C_{10}H_7{\cdot}N$: by :NPh. (VII) and p-$C_6H_4Me{\cdot}NH_2$ at 155—160° give 4-*chloro*-3-p-*toluidino*-N-p-*tolylphthalimide*, m.p. 208—209°, in low yield. (VI) and NH_2Ph at 150—160° (3 hr.), then 135° (20 hr.), give 3 : 6-*dianilinophthalanil*, m.p. 197°; p-$C_6H_4Me{\cdot}NH_2$ at 167—175° gives 3 : 6-*di*-p-*toluidino*-N-p-*tolylphthalimide* (XI), m.p. 164°, and (IX). (VIII) and p-$C_6H_4Me{\cdot}NH_2$ at 130—145° for 5 hr. or 220—230° for 2 hr. give 6-*chloro*-3-p-*toluidino*-N-p-*tolylphthalimide* (XII), m.p. 166—167°, and (XI); none of the latter is obtained without Cu-bronze at 140—150°. Replacement of Cu-bronze–K_2CO_3 by Cu + K acetates at 95—105° (19 hr.) gives [from (VI)] an inseparable mixture, m.p. 181—182° (remelts at 194°), of (VI) and (XII). (VI) and p-$C_6H_4Me{\cdot}NH_2$ + $CuCO_3$ at 130—140° for 4 hr. gives (IX) and 4 : 4′-azotoluene, new m.p. 144—145°. (VI) and p-anisidine at 150—160° give 3 : 6-*di*-p-*anisidino*-N-p-*anisylphthalimide*, m.p. 167—168°. (VI) and o-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ at 170—180° afford 3 : 6-*di*-, m.p. 302° (decomp.), and at 150—160° give 6-*chloro*-3-, m.p. 277—278°, -(2′-*carboxyanilino*)*phthalanil*. 3-Anilinophthalanil and N_2H_4,H_2O–C_5H_5N give 3-*anilinophthalhydrazide*, m.p. 335° (decomp.). Similarly prepared are: 3-p-*toluidino*-, m.p. ~320° (decomp.), 3-p-*anisidino*-, m.p. 320° (decomp.), 3-β-*naphthylamino*-, m.p. 325° (decomp. >320°), 3 : 6-*dianilino*-, m.p. 276—277°, and 3 : 6-*di*-p-*toluidino*-, m.p. ~285° (orange at 120°, blackens at 260°), -*phthalhydrazide*. Phthal-*N*-phenylhydrazides are not obtained from (X) and $NH_2{\cdot}NHR$ in C_5H_5N. (XI) and P_2S_5 + a trace of NH_2Ph in boiling C_6H_6 give 3 : 6-*di*-p-*toluidino*-N-p-*tolyldithiophthalimide*, m.p. 127—128° (softens at 124—125°). (IX) and 70% H_2SO_4 at 160—170° afford 3-*methylacridone*-6-*carboxylic acid*, m.p. 302° (decomp.). (X) and its β-$C_{10}H_7$ analogue do not react with $POCl_3$. The auxochromic effect of introducing NHAr in phthalimide is discussed. A. T. P.

Complex formation between polynitro-compounds and aromatic hydrocarbons and bases. VII. A further resolution of 4 : 6 : 4′- trinitrodiphenic acid. D. L. Hammick, E. H. Reynolds, and G. Sixsmith (J.C.S., 1939, 98—99; cf. A., 1936, 722).—4 : 6 : 4′-Trinitrodiphenic acid is resolved with quinine as described by Christie and Kenner (A., 1926, 408); repeated evaporation of solutions in $CHCl_3$ gives the cryst. *d*- and *l*-acids. Optically active complexes, $2C_{14}H_7O_{10}N_3,C_6H_6$, are obtained from acids of varying [α] in C_6H_6–Et_2O (2 : 1), from which mixture the Et_2O is carefully distilled until crystallisation begins. The *d*-acid *complex* has m.p. 176°, and after resolidification, 279—281°, $[\alpha]_{5461}$ +23·14° in Et_2O. Repeated crystallisation from C_6H_6–Et_2O (as above) gives acids with $[\alpha]_{5461}$ +47·8° and −37·0° in Et_2O (calc. on C_6H_6-free basis). A. T. P.

5-Halogeno- and 5-hydroxy-trimellitic acids.—See B., 1939, 128.

Oxidation of vitamin-*A* by the Oppenauer reagent. II. E. Haworth, I. M. Heilbron, W. E. Jones, A. L. Morrison, and J. B. Polya (J.C.S., 1939, 128—132).—Vitamin-*A*, $Al(OBu^{\gamma})_3$, and $COEt_2$ (or, less well, $COPr^{\beta}_2$) (H acceptor) in boiling C_6H_6 and N_2 give the aldehyde (I) (well-defined absorption max. at 4010 A.) (*oxime*, m.p. 176—177°; impure semicarbazone, max. at 4030 A.), which appears to contain an additional double linking situated in the ring (spectrographic evidence discussed); (I) is purified by Girard reagent *P*. (I) is formed probably through the initial formation of the true vitamin-*A* aldehyde (the above oxime may be derived from this), which in presence of unreactive $COEt_2$ is further oxidised in the ring with loss of 2 H. (I) and $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ afford an alcohol, characterised by an absorption max. at 3590 A. (I) and $COMe_2$ with $Al(OBu^{\gamma})_3$–C_6H_6 or NaOEt at −5° give a ketone (p-*tolylsemicarbazone*, m.p. 206—207°), not identical

with the ketone, $C_{23}H_{32}O$ (A., 1938, II, 126). The proposed formula $CH<\begin{matrix}CH_2\cdot CMe_2\\CH{-}CMe\end{matrix}>C\cdot[CH{:}CH\cdot CMe{:}CH]_2\cdot CHO$ of (I) is supported by ozonolysis, which fails to give geronic acid, but no certain conclusion is reached.

A. T. P.

Action of mixed organomagnesium derivatives on hydroxybenzamides: the phenolic ketones produced. P. L. Couturier (Ann. Chim., 1938, [xi], **10**, 559—629).—Mainly a detailed account of work already reported (A., 1936, 1107; 1938, II, 98, 361). The following appears new. In hot C_6H_6 and Bu_2O, respectively, hydroxybenzdiethylamides and an excess of MgEtBr give the following yields of hydroxypropiophenones: *o*- 82—84, —; (45% in Et_2O), *m*- 10, 70, and *p*-OH 5, 60; 2 : 4- 10—12, —; and 3 : 4-$(OH)_2$ 0, 0, and 3 : 4 : 5-$(OH)_3$ 0, 0%. With acetoxybenzdiethylamides MgEtBr effects deacetylation (to give $CMeEt_2\cdot OH$), but no ketone is formed. Methoxybenz-amides and -diethylamides and MgEtBr give good yields of the ketones (isolated partly as imines if the Mg complex is decomposed with NH_4Cl), but with MgPhBr give $NEt_2\cdot CPh_2Ar$. With Na–EtOH p-*hydroxy*-, m.p. 111°, *p*- and o-, m.p. 84°, -*methoxypropiophenoxime* give respectively α-*p*-hydroxyphenyl- [*hydrochloride*, decomp. 220—225° (begins at 180°)], α-*p*- and -o-*anisyl*-n-*propylamine*, b.p. 118°/14 mm. (*Bz* derivative, m.p. 144°). *o*-$OMe\cdot C_6H_4\cdot CO\cdot NEt_2$, m.p. 35°, *p*-$OMe\cdot C_6H_4\cdot CO\cdot NH_2$, m.p. 161°, 3 : 4 : 5-$(OMe)_3C_6H_2\cdot CO\cdot NR_2$ (R = H, m.p. 176°, and Et, m.p. 54°, b.p. 210°/4 mm.), 3 : 4-$(OMe)_2C_6H_3\cdot CO\cdot NEt_2$, b.p. 210°/18 mm., p-*anisdiethylamide*, m.p. 45°, b.p. 148°/4 mm., γ-*diethylamino*-γ-p-*anisyl*-n-*pentane picrate*, decomp. ~70—80° (block), *diphenyl*-p-*anisylmethyldiethylamine picrate*, decomp. 180—200° (block), and o-*acetoxypropiophenone*, m.p. 26°, b.p. 147°/14 mm., are described. A *compound*, m.p. 180°, obtained from gallic acid, $COCl_2$, and C_5H_5N, contains Cl and C_5H_5N, and with $NHEt_2$ gives C_5H_5N and $NHEt_2$ gallates.

R. S. C.

γ-Substitution in the resorcinol nucleus. II. Gattermann reaction with resacetophenone. H. A. Shah and R. C. Shah (J.C.S., 1939, 132—134; cf. A., 1938, II, 368; 1939, II, 22).—Resacetophenone and $Zn(CN)_2$ + KCl, $AlCl_3$, and HCl in Et_2O or EtOAc at 0° give 2 : 4-*dihydroxy*-3-*aldehydoacetophenone* (I), m.p. 112—114° [2 : 4-*dinitrophenylhydrazone*, m.p. 283—285° (decomp.); *semicarbazone*, m.p. 230—231° (decomp.); *dioxime*, m.p. 218—219° (decomp.)], converted by $CH_2(CO_2Et)_2$ + piperidine at room temp. into *Et* 5-*hydroxy*-6-*acetylcoumarin*-3-*carboxylate*, m.p. 155—156°. (I) treated successively with aq. $CN\cdot CH_2\cdot CO_2H$–NaOH at room temp. and boiling 4% aq. HCl affords 5-*hydroxy*-6-*acetylcoumarin*-3-*carboxylic acid*, m.p. 202—204° (decomp.). (I) and $CH_2Ac\cdot CO_2Et$ + piperidine give 5-*hydroxy*-3 : 6-*diacetylcoumarin*, m.p. 170—171°. (I) is reduced (Clemmensen) to 2-methyl-4-ethylresorcinol, which with $CH_2Ac\cdot CO_2Et$ gives 7-*hydroxy*-4 : 8-*dimethyl*-6-*ethylcoumarin*, m.p. 187—188°.

A. T. P.

Alkyl ethers of hydroxymethyleneacetophenone. J. Walker (J.C.S., 1939, 120—122).—Crude CHBz:CH·ONa and MeI–EtOH or Me_2SO_4–H_2O afford *methoxymethyleneacetophenone* (I), b.p. 145—147°/12 mm. $CHBz{:}CH\cdot OEt$ (prep. using EtI) (cf. v. Auwers *et al.*, A., 1925, i, 585) and $CHNa(CO_2Et)_2$–EtOH at 0° give an unstable product, which when distilled in a vac. loses EtOH to yield *Et* 6-*phenyl*-α-*pyrone*-3-*carboxylate*, m.p. 105—106°, probably identical with the compound, m.p. 107—108°, obtained by Claisen (A., 1904, i, 14). It is probably a precursor of the natural 6-phenylcoumalin, but the latter has not been obtained from it. (I) and $CHNaAc\cdot CO_2Et$ in C_6H_6 at room temp.—100° (bath) give *Et* 3-*hydroxydiphenyl*-4-*carboxylate*, m.p. 44—45° [free *acid*, m.p. 207—208°, decarboxylated at 270° (bath) by quinoline–Cu chromite to 3-hydroxydiphenyl]. A. T. P.

Catalytic dehydrogenation using ordinary or Raney nickel. L. Palfray and S. Sabetay (Compt. rend., 1939, **208**, 109—112).—β-$C_{10}H_7\cdot CHMe\cdot OH$ heated in vac. with Ni (much used as a reduction catalyst) affords a considerable proportion of β-$C_{10}H_7\cdot COMe$. $CHPhMe\cdot OH$ with 5% of Raney Ni at 170—200°/2 hr. affords PhEt and COPhMe. Menthol with previously used Ni (Sabatier–Senderens) or Raney Ni at 230° affords 42% and 33% of menthone, respectively. Similarly, *cyclo*hexane-1 : 4-diol at 250° affords 25% of *cyclo*hexane-1 : 4-dione. Cu (bronze) is much less efficient than Ni.

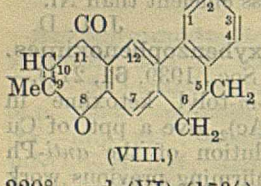
J. L. D.

Stereoisomeric o-hydroxybenzophenoximes. A. H. Blatt (J. Amer. Chem. Soc., 1939, **61**, 214).—<0·0001M-*syn*-Ph 4-hydroxy-*m*-tolyl ketoxime in Et_2O and saturated aq. $Cu(OAc)_2$ give a ppt. of Cu derivative, but a 0·05M. solution of the *anti*-Ph oxime gives no ppt., thus confirming previous work (A., 1938, II, 101).

R. S. C.

Phenanthrene series. XXIII. Synthesis of acyl compounds derived from 2-hydroxy-9 : 10-dihydrophenanthrene. E. Mosettig and A. H. Stuart (J. Amer. Chem. Soc., 1939, **61**, 1—7; cf. A., 1939, II, 55).—In the Friedel–Crafts reaction and Fries rearrangement 2-hydroxy-9 : 10-dihydrophenanthrene (I) behaves mainly, but not entirely, as a Ph_2 derivative. 9 : 10-Dihydrophenanthrene and H_2SO_4 (2 mols.) at 40° give 50—60% of the 2-sulphonic acid (II) (*chloride*, m.p. 137°; also obtained less well by $ClSO_3H$ in CCl_4), and a small amount of a (? di)sulphonic acid (chloride, m.p. 240—242°). The Na salt of (II) with KOH at 300° gives 50% of 2-hydroxyphenanthrene. (I) is best (69%) prepared by treating 2-amino-9 : 10-dihydrophenanthrene successively with $NaNO_2$–H_2SO_4–H_2O–C_5H_5N, $CO(NH_2)_2$, and boiling H_2O. With acyl halides (2·1 mols.) and $AlCl_3$ (2·1 mols.) in $PhNO_2$ at 0—5° (I) gives 7- and 3 : 7-derivatives in the following yields: 2-*hydroxy*-7-*acetyl*- (III) (60—65%), m.p. 190° [*Me ether* (IV), m.p. 134°], -3 : 7-*diacetyl*- (V) (15—20%), m.p. 155° (*Me ether*, m.p. 167—168°), -7-*propionyl*- (40%), m.p. 197—198° (*Me ether*, m.p. 125°), -3 : 7-*dipropionyl*- (35—40%), m.p. 129—130° (*Me ether*, m.p. 157°), -7-*butyryl*- (30%), m.p. 176° (*Me ether*, m.p. 61·5°), and -3 : 7-*dibutyryl*- (50%), m.p. 93—94° (*Me ether*, m.p. 102°), -9 : 10-*dihydrophenanthrene*. With 1 mol. of AcCl and $AlCl_3$ in $PhNO_2$ (I) gives only 24% of 2-*hydroxy*-3-*acetyl*-

9 : 10-*dihydrophenanthrene* (VI), m.p. 101° (*Me ether*, m.p. 102°). (V) is obtained in good yield from (VI), but only in poor yield from (III); (VI) may be an intermediate in the reaction with 2 mols. of AcCl. The *Ac* derivative (VII), m.p. 64—65°, of (I) with 2 mols. of AcCl gives (III) and (V). The *Me ether*, m.p. 55°, of (I) with 1 mol. of AcCl gives an inseparable mixture of the 3- and 7-Ac derivatives; demethylation (AcOH–HBr) gives small amounts of (III) and (VI). With $AlCl_3$, first in CS_2 and then at 140° (no solvent), (VII) gives variable yields (about equal amounts) of (III) and (VI). Structures of the acyl derivatives are proved as follows. The Me ethers with NaOCl give 2-*methoxy*-9 : 10-*dihydrophenanthrene*-7-, m.p. 210° (*Me* ester, m.p. 85·5°), and -3-*carboxylic*, m.p. 163—164° (*Me* ester, m.p. 80—81°), and -3 : 7-*dicarboxylic acid*, m.p. 308—309° (Me_2 ester, m.p. 119°), thus proving their relations to one another. The *oxime*, m.p. 161°, of (IV) with HCl–AcOH–Ac_2O gives 7-*acetamido*-2-*methoxy*-9 : 10-*dihydrophenanthrene*, m.p. 176·5°, and thence (HCl–AcOH) the *amine*, m.p. 146°, and (by a diazo-reaction) 2 : 7-*dimethoxy*-9 : 10-*dihydrophenanthrene*, m.p. 112°, and (by Pd–C at 300°) 2 : 7-dimethoxyphenanthrene. With Na and EtOAc (VI) gives 2-*hydroxy*-3-*acetoacetyl*-9 : 10-*dihydrophenanthrene*, m.p. 131—132°, which with HCl–AcOH yields 9-*methyl*-5 : 6-*dihydronaphtho*-[1 : 2-g]*chromone* (VIII), m.p. 198°, hydrolysed by hot 2N-NaOH to 2-*hydroxy*-9 : 10-*dihydrophenanthrene*-3-*carboxylic acid* (60%), m.p. 219—220°, and (VI) (15%). Dehydrogenation (Pd–C) of the H_2-acids affords 2-*methoxyphenanthrene*-3-, m.p. 213—214° (*Me* ester, m.p. 94—95°), and -7-carboxylic (*Me* ester, m.p. 135°), and -3 : 7-*dicarboxylic acid*, m.p. 320—321° (decomp.) (Me_2 ester, m.p. 161—162°). Most of the OH-ketones described above and earlier (A., 1937, II, 145; 1938, II, 494) have no œstrogenic activity, but the *Ac* derivative, m.p. 99°, of (III) is slightly active.



(VIII.)

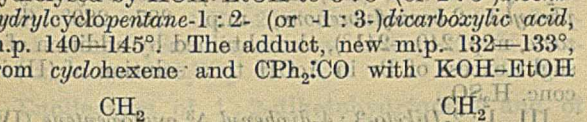
R. S. C.

Reactions of aliphatic diazo-compounds with carbonyl derivatives. D. W. Adamson and J. Kenner (J.C.S., 1939, 181—189).—Interaction of PhCHO in Et_2O with diazo-ethane (I), -*n*-propane, and -*n*-butane yields respectively propio-, butyro-, and valero-phenone. (I) and aq. $COMe_2$ at −10° to 0° yield $COMePr^{\beta}$ and OH·CMe_2·CHMe·OH (as oxide), whilst CH_2BzCl and CH_2N_2 in MeOH–Et_2O give *α-phenyl-α-chloromethylethylene oxide*, b.p. 135—137°/17 mm. Slow addition of NO·NMe·CO_2Et (II) to *cyclo*hexanone (III) in EtOH + K_2CO_3 gives suberone and after hydrolysis (0·5% H_2SO_4), 1-hydroxymethyl-*cyclo*hexanol and impure *cyclo*octanone, whilst with (I) 2-methyl*cyclo*heptanone (IV) [2 : 4-*dinitrophenylhydrazone*, m.p. 121—122°; semicarbazone, forms, m.p. 134·5—136° and 177—178·5° (cf. lit.); oxime phenylurethane, new m.p. 125—127°] is formed. n-*Octylurethane*, b.p. 152—155°/19 mm., on nitrosation yields a NO-compound which cannot be distilled, and which with (III) yields 2-n-*heptyl*cyclo*heptanone*, b.p. 153—157°/21 mm. (*oxime*, b.p. 145—148°/0·8 mm.; 2 : 4-*dinitrophenylhydrazone*, m.p. 65°). Et ε-aminohexoate is converted by $ClCO_2Et$ into ε-*carbethoxy*-n-*amylurethane*, b.p. 185°/20 mm., the NO-derivative of which with (III) yields 2-δ-*carbethoxybutyl*cyclo*heptanone*, b.p. 144—148°/0·7 mm. (*oxime*, b.p. 169—174°/0·7 mm.), hydrolysed by aq. NaOH to the acid (*semicarbazone*, m.p. 157—158°). 4-Methyl*cyclo*hexanone with (II) and K_2CO_3 in EtOH–Et_2O or with Et_2O–CH_2N_2 yields 4-*methyl*-cyclo*heptanone*, b.p. 84·5°/25 mm., 194·5°/762 mm. (*semicarbazone*, m.p. 158—160°), and 4-methyl-1-hydroxymethyl*cyclo*hexanol; with NO·NEt·CO_2Et (V), or (I) in Et_2O, a *ketone*, $C_9H_{16}O$, b.p. 204°/757 mm. (*semicarbazone*, m.p. 162·5—164·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 135—137°; *oxime* b.p. 132°/23 mm.), results. 3-Methyl*cyclo*hexanone with (II) yields 3-methyl-1-hydroxymethyl*cyclo*hexanol and a mixture of 3- and 4-methyl*cyclo*heptanones, whilst 2-methyl*cyclo*hexanone gives 3-*methyl*cyclo*heptanone*, b.p. 188·5—190·5° (*semicarbazone*, m.p. 179—181°), (IV), methyl*cyclo*octanone, and 2-methyl-1-hydroxymethyl*cyclo*hexanol. 4-Ethyl*cyclo*hexanone with MeOH–Et_2O–CH_2N_2 yields 4-*ethyl*cyclo*heptanone*, b.p. 214—215° (*semicarbazone*, m.p. 130°), whilst with (I) 2-*methyl*-4-*ethyl*cyclo*heptanone*, b.p. 102—106°/26 mm., 220—224°/754 mm. (*semicarbazone*, m.p. 153·5—154·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 100—102°), is formed. 3 : 5-Dimethyl*cyclo*hexanone with (II) or CH_2N_2 yields 3 : 5-*dimethyl*cyclo*heptanone*, b.p. 88·5—90·5°/23 mm., 205—206°/753 mm. (*semicarbazone*, m.p. 166·5°), and 3 : 5-*dimethyl*-1-*hydroxymethyl*cyclo*hexanol*, m.p. 68—70°, whilst with (V), 2 : 3 : 5-*trimethyl*cyclo*heptanone*, b.p. 215°/763 mm. (*semicarbazone*, m.p. 204—208°; 2 : 4-*dinitrophenylhydrazone*, m.p. 91—93°), is formed. 4-Methoxy-*cyclo*hexanone [2 : 4-*dinitrophenylhydrazone*, m.p. 141·5—142·5°; semicarbazone, m.p. 183—185° (lit. 178°)] with (II) gives 4-*methoxy*cyclo*heptanone*, b.p. 111·5—114°/24 mm. (*semicarbazone*, m.p. 175·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 115—117°), and (probably) 4-methoxy-1-hydroxymethyl*cyclo*hexanol. *cyclo*Pentanone with (V) or (I) yields a little 2-methyl-*cyclo*hexanone, and *cyclo*heptanone with (II) gives *cyclo*octanone (VI) and 1-hydroxymethyl*cyclo*heptanol; (VI) does not react with (I) or CH_2N_2.

J. D. R.

Reaction between diphenylketen and dienes. L. I. Smith, C. L. Agre, R. M. Leekley, and W. W. Prichard (J. Amer. Chem. Soc., 1939, **61**, 7—11).—The structure of the adduct (I) of *cyclo*pentadiene and CPh_2:CO is proved (cf. Lewis *et al.*, A., 1938, II, 20; Farmer *et al.*, A., 1939, II, 72). (I), obtained in 92% yield in light petroleum, does not react with NHPh·NH_2 or $KMnO_4$ in $COMe_2$ and only slightly with Br–$CHCl_3$. With O_3, followed by CrO_3, it gives an impure product, m.p. 77—85°, (decomp.), which solidifies at ~111° and remelts at ~200°. With hot NaOH– or KOH–EtOH it yields 2-benzhydryl-Δ^3-*cyclo*pentene-1-carboxylic acid (II), m.p. 145—147° (cf. Farmer; Staudinger *et al.*, A., 1924, i, 295), oxidised by $KMnO_4$–Na_2CO_3 to 3 : 4-*dihydroxy*-2-*benzhydryl*cyclo*pentane*-1-*carboxylic acid* (poor yield), m.p. 201·5° (decomp.) (cf. Lewis, *loc. cit.*), and by O_3–CrO_3 to δδ-diphenyl-*n*-butane-αβγ-tricarboxylic acid, m.p. 208—209·5° (decomp.). Hydrogenation of

(I) gives 6 : 6-*diphenyl*dicyclo[0 : 2 : 3]*heptan*-7-*one*, m.p. 91·5—92·5° (also obtained from *cyclo*pentene and CPh_2:CO at 60°), hydrolysed by hot KOH–EtOH to 2-benzhydrylc*yclo*pentane-1-carboxylic acid, m.p. 95—96° (Staudinger, *loc. cit.*, 85°) [anilide, m.p. 142—143° (*loc. cit.*, 139°)], also obtained by hydrogenating (Pt) (II) in Et_2O at 2·3 atm. With CPh_2:CO at 110° (I) gives the *substance* (III*a* or *b*), m.p. 249—250°, hydrolysed by KOH–EtOH to 3 : 5- (or 2 : 5-)*dibenzhydrylcyclopentane*-1 : 2- (or -1 : 3-)*dicarboxylic acid*, m.p. 140—145°. The adduct, new m.p. 132—133°, from *cyclo*hexene and CPh_2:CO with KOH–EtOH

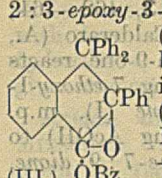


(III*a*) (III*b*)

gives 2-benzhydrylhexahydrobenzoic acid, m.p. 153—155°. Interaction of CPh_2:CO with *cyclo*hexadiene (1 : 2 addition; cf. Farmer *et al.*, A., 1938, II, 64), CH:CPh, and $(CMe{:}CH_2)_2$, but not with $(CHPh{:}CH)_2$, and failure of keten to react with *cyclo*pentadiene, are reported. R. S. C.

Constitution of eremophilone, hydroxy- and hydroxydihydro-eremophilone. III. A. R. Penfold and J. L. Simonsen (J.C.S., 1939, 87—89; cf. A., 1938, II, 289).—The constitutions of eremophilone (1-keto-5 : 10-dimethyl-3-*iso*propenyl-$\Delta^{8:9}$-octahydronaphthalene), hydroxy- (1-hydroxy-8-keto-5 : 10-dimethyl-3-*iso*propylidene-Δ^1-octahydronaphthalene), and hydroxydihydro-eremophilone (1-hydroxy-8-keto-4 : 10-dimethyl-6-*iso*propenyldecahydronaphthalene) are discussed; they appear to be exceptions to the "isoprene" rule and it cannot be assumed that this rule will apply in the polyterpene series. A possible explanation of the formation of (I) in nature is given. The keto-acid, $C_{10}H_{16}O_3$, obtained by ozonolysis of the benzoate of (II), is reduced (Clemmensen) to 1 : 2-dimethyl*cyclo*hexylacetic acid, the *Me* ester, b.p. 110—112°/19 mm., of which with Se at 360° (24 hr.) affords *o*-xylene, b.p. 135—145°, oxidised by aq. $KMnO_4$ at 100° (bath) to *o*-$C_6H_4(CO_2H)_2$. Interaction of (II) and alkaline H_2O_2 to afford two stereoisomeric $(OH)_2$-acids is not clear (cf. A., 1933, 71). (II) or (III) and Na–EtOH give 1 : 8-dihydroxy-4 : 10-dimethyl-6-*iso*propyldecahydronaphthalene, oxidised (abnormally) by $Pb(OAc)_4$ in AcOH to (probably) δδε-*trimethyl*-β-iso*propylheptane*-αη-*dicarboxylic acid*, m.p. 193—195° (*loc. cit.*). A. T. P.

Action of benzene and aluminium chloride on 2 : 3-diphenylindone. C. F. Koelsch (J. Org. Chem., 1938, 3, 456—461).—2 : 3-Diphenylindone is converted by $AlCl_3$ (2 mols.) in boiling C_6H_6 into 2 : 3 : 3-*triphenylhydrindone* (I), m.p. 191—193°, also obtained similarly from 2-phenyl-3-*p*-tolylindone. (I) is unaffected by MgPhBr, by Na and BuOH, or by CrO_3–AcOH at 50°. (I) and BzCl in C_5H_5N–$CHCl_3$ give 3-*benzoyloxy*-1 : 1 : 2-*triphenylindene* (II), m.p. 152—154° (corresponding p-*chlorobenzoate*, m.p. 203—204°, and *acetate*, m.p. 147—148°). CH_2PhCl, (I), and Na in EtOH afford 3-*benzyloxy*-1 : 1 : 2-*triphenylidene*, m.p. 149—151°; the *Me ether*, obtained by use of NaOH and Me_2SO_4, has m.p. 117—119°. (II) is oxidised by CrO_3 in AcOH at 60° to 2 : 3-*epoxy*-3-*benzoyloxy*-1 : 1 : 2-*triphenylhydrindene*



(III.)

(III), m.p. 193—195°, reduced by HI in boiling AcOH to BzOH and (I). (III) is hydrolysed (NaOMe–95% MeOH) (with rearrangement) to 3-*hydroxy*-1 : 1 : 3-*triphenylhydrind*-2-*one*, m.p. 157—159°, reduced by 47% HI in boiling AcOH to 1 : 3 : 3-*triphenylhydrind*-2-*one*, m.p. 106—109°, and cleaved by NaOH–EtOH to *o*-*benzhydrylbenzilic acid* (IV), m.p. 188—189° (decomp.) (*Me* ester, m.p. 121—123°). This is dehydrated by boiling AcOH containing a little conc. H_2SO_4 to 9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*-9-*carboxylic acid* (V), m.p. 236—238° (*Me* ester, m.p. 195—197°). Oxidation (CrO_3 in AcOH at 80°) of (V) affords 9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, m.p. 183—185°, reduced by NaI in AcOH to 9 : 10-diphenylanthracene. (IV) is oxidised to *o*-benzhydrylbenzophenone, m.p. 84—86°, whence (MgPhBr) *o*-benzhydryltriphenylcarbinol, m.p. 213—215°, dehydrated to 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene, m.p. 223—225°. H. W.

Action of aluminium chloride on certain phenylated fulgenic anhydrides. C. F. Koelsch and H. J. Richter (J. Org. Chem., 1938, 3, 465—472).—Tetraphenylfulgenic anhydride (I) is converted by $AlCl_3$ in C_6H_6 into 1 : 2 : 3 : 4-dibenzoylenenaphthalene (II), m.p. (block) 308—310°, and 2-*phenyl*-3 : 4-*benzofluorenone*-1-*carboxylic acid* (III), m.p. (block) 264—266°. (II) is a secondary product formed by dehydration of (III). In boiling quinoline containing a little $Cu(OAc)_2$ (III) passes into 2-phenyl-3 : 4-benzofluorenone, m.p. 191°. (III) is obtained synthetically from 1 : 4-diphenylnaphthalene-2 : 3-dicarboxylic anhydride, new m.p. 288—289°, C_6H_6 and $AlCl_3$. Triphenylfulgenic anhydride (IV), $AlCl_3$, and C_6H_6 give 3 : 4-benzofluorenone-1-carboxylic acid, m.p. (block) 283—286° (Me ester, m.p. 148—150°), decarboxylated to 3 : 4-benzofluorenone, m.p. 161—162° (oxime, m.p. 213—215°). (I) is converted by $AlCl_3$ in $PhNO_2$ at 60° into 3-*phenyl*-2-α-*carboxy*-ββ-*diphenylvinylindone* (V), m.p. 237—241°, decarboxylated to 3-*phenyl*-2-ββ-*diphenylvinylindone*, m.p. 147—148°, and transformed by $AlCl_3$ in boiling C_6H_6 into (III) in almost quant. yield. (V) is converted by $SOCl_2$ into its *chloride*, m.p. 183—186°, which affords (II) when boiled with $AlCl_3$ in C_6H_6 and gives an unidentified compound, m.p. 161—163°, when treated with $AlCl_3$ in $PhNO_2$. (IV) and $AlCl_3$ in $PhNO_2$ yield 3-*phenyl*-2-α-*carboxystyrylindone*, m.p. 196—199°, decarboxylated to 3-*phenyl*-2-*styrylindone*, m.p. 144—146°. ααζζ-Tetraphenylhexatriene-βγ-dicarboxylic anhydride, m.p. 222—224°, $AlCl_3$, and $PhNO_2$ give δδ-*diphenyl*-α-3-*phenyl*-2-*indonyl*-$\Delta^{\alpha\gamma}$-*pentadienoic acid*, m.p. 242—246°, softens at 235°, also obtained from the isomeric anhydride, m.p. 212—214°; it is decarboxylated to δδ-*diphenyl*-α-3-*phenyl*-2-*indonylbutadiene*, m.p. 165—167°. A mechanism for the conversion of (I) into (III) is given. (I) could not be converted into 3 : 3′-diphenyl-2 : 2′-di-indonyl. H. W.

peri*Naphthindene series. III. Action of magnesium phenyl bromide on 7-ethoxy*peri-

naphthinden-9-one. C. F. Koelsch and R. H. Rosenwald (J. Org. Chem., 1938, **3**, 462—464; cf. A., 1938, II, 19).—Contrary to Calderaro (A., 1914, i, 41), 7-ethoxy*peri*naphthinden-9-one reacts with MgPhBr by 1 : 4 addition giving 7-*ethoxy*-1-*phenyl*-1 : 9a-*dihydro*per*inaphthinden*-9-*one* (I), m.p. 156—157°, hydrolysed (HBr in boiling AcOH) to 1-*phenyl*-1 : 9a-*dihydro*per*inaphthindane*-7 : 9-*dione*, m.p. 250° when brought into a bath preheated to 240°. The position of Ph is shown by converting (I) by *p*-benzoquinone in C_6H_6 into 7-*ethoxy*-1-*phenyl*per*inaphthinden*-9-*one*, m.p. 153—154°, hydrolysed to 1-*phenyl*per*inaphthindane*-7 : 9-*dione*, m.p. 240—250° (decomp.), oxidised ($KMnO_4$) to 2-phenylnaphthalic anhydride, m.p. 239—240°. H. W.

Reactions and enolisation of cyclic diketones. IV. 1 : 2-Diketo-3 : 4 : 5-triphenyl*cyclo*pentene. C. F. Koelsch and T. A. Geissman. **III. 1 : 2-Diketo-3 : 4-diphenyl*cyclo*pentene.** T. A. Geissman and C. F. Koelsch (J. Org. Chem., 1938, **3**, 480—488, 489—502).—IV. The ketonic nature of 1 : 2-*diketo*-3 : 4 : 5-*triphenyl*-Δ^4-*cyclo*pentenone (I) is in agreement with the postulated hindrance of enolisation by the presence of a double linking in a five-membered ring. 3-Hydroxy-3 : 4 : 5-triphenyl-Δ^4-*cyclo*pentenone, m.p. 164—165° (cf. Dilthey and Hurtig, A., 1935, 204) [phenylhydrazone, m.p. 173—174° (decomp.); *p*-nitrophenylhydrazone, m.p. 214—215° (decomp.); :CHPh derivative, m.p. 217·5—218°], is converted by 45% HI in boiling AcOH into 3 : 4 : 5-*triphenyl*-Δ^3-*cyclo*pentenone, m.p. 142—143°, the 2-*oximino*-derivative, m.p. 228—229° (decomp.) (*benzoate*, m.p. 154—155°), of which is converted by CH_2O and conc. HCl in boiling AcOH into (I), m.p. 162—163·5°, with a by-product, m.p. 235° (decomp.). (I) is not sol. in dil. aq. alkali but gives in NaOMe–MeOH a dark blue-green colour which fades to yellow after several hr. at room temp. It shows no tendency to form an acetal. With *o*-$C_6H_4(NH_2)_2$ it affords a *phenazine*, $C_{29}H_{20}N_2$, m.p. 226—227° (decomp.). The possibility of its enolisation is established by its conversion by BzCl in C_5H_5N into 2-*keto*-3 : 4 : 5-*triphenyl*-$\Delta^{3:5}$-*cyclopentadienyl benzoate*, m.p. 242—243° (decomp.). The diketonic structure of (I) is established by its conversion by MgPhBr into 1 : 2 : 3 : 4 : 5-pentaphenyl-Δ^3-*cyclo*pentadiene-1 : 2-diol, the identity of which is proved by its conversion (HI) into pentaphenyl*cyclo*pentadiene, new m.p. 252—254°. (I) is cleaved by H_2O_2–NaOH to $\alpha\beta\gamma$-*triphenylglutaconic anhydride* (II), m.p. 166—167°. Br in AcOH at 65° converts (I) into 5-*bromo*-3 : 4 : 5-*triphenyl*-Δ^3-*cyclopentene*-1 : 2-*dione* (III), m.p. 145—146°, transformed by boiling dil. AcOH into (II) and converted by boiling MeOH into 5-*methoxy*-3 : 4 : 5-*triphenyl*-Δ^3-*cyclopentene*-1 : 2-*dione*, m.p. 148—150° (corresponding *phenazine*, m.p. 200—201°), which is cleaved (H_2O_2–NaOH) to α-*methoxy*-$\alpha\beta\gamma$-*triphenylglutaconic anhydride*, m.p. 161—162° (decomp.). MgPhBr and (III) afford 2-*hydroxy*-2 : 3 : 4 : 5-*tetraphenyl*-Δ^3-*cyclopentenone*, m.p. 208·5—210°, converted by warming with AcOH containing a little H_2SO_4 or by distillation under reduced pressure into tetraphenyl*cyclo*pentadienone, m.p. 217—218°, by boiling AcOH–HI into tetraphenyl*cyclo*pentenone, m.p. 162—163°, and by AcOH–HCl–Zn into tetraphenyl*cyclo*pentenol, m.p. 174—176°. With AgOAc in AcOH (III) rapidly yields AgBr and the *compound*, $CPh(OAc)\cdot CO$ / $CPh{=\!=\!=}CPh$ > CO or CPh < $C(OAc)\cdot O$ / $CPh{=}CPh$ > CO, m.p. 174—177°, converted by conc. H_2SO_4 into 3-*hydroxy*-4-*phenyl*-1 : 2-*benzofluorenone*, m.p. 237—238°, also obtained from (II) and conc. H_2SO_4. Conc. H_2SO_4 converts (III) into (?)-*bromo*-3-*hydroxy*-4-*phenyl*-1 : 2-*benzofluorenone*, m.p. 287—289° (*benzoate*, m.p. 240—241°), also obtained by addition of a slight excess of Br in AcOH to a solution of (II) in conc. H_2SO_4.

III. 1 : 2-*Diketo*-3 : 4-*diphenyl*-Δ^3-*cyclopentene* (IV) has little or no tendency to enolise and has one particularly active CO. The observation that it is less readily enolised than is (I) conforms with the postulated hindrance of enolisation in such diketones by a second H attached to C bearing H involved in enolisation. 3 : 4-Diphenyl-Δ^3-*cyclo*pentenone (improved prep.) is converted by Bu nitrite and conc. HCl in EtOH at 50—55° into 2-*oximino*-3 : 4-*diphenyl*-Δ^3-*cyclopentenone*, m.p. 223—224° (decomp.) [*benzoate*, m.p. 142—143° (decomp.)], transformed by CH_2O–HCl–AcOH into (IV), m.p. 178—182° or 186—188° (slow decomp.) [possibly dimorphous forms], which gives a *phenazine* $C_{23}H_{16}N_2$, m.p. 236—237°, and the 1-*oxime*, m.p. 237—239° (decomp.) after darkening at 215°. (IV) is cleaved by NaOH–H_2O_2 to $\alpha\beta$-*diphenylglutaconic anhydride* (V), m.p. 126—127° or [+ (?) C_6H_6], m.p. 111—112°. When boiled with 10% NaOH, dil. HCl, or AcOH containing P and I (IV) gives an $\alpha\beta$-*diphenylglutaconic acid*, m.p. 165—166° (decomp.), re-converted into (V) by distillation under 20 mm.; an isomeric *acid*, m.p. 204—205°, is obtained when (V) is boiled with Zn dust and 10% NaOH for 1 hr. Distillation of the dry Na salt derived from (V) with soda-lime affords α-methylstilbene, m.p. 80—81·5°. 3-Hydroxy-1 : 2-benzofluorenone, m.p. (block) 307—308° (benzoate, m.p. 235—236°), is obtained from (V) and conc. H_2SO_4. MgPhBr converts (IV) in C_6H_6 into 1 : 2 : 3 : 4-*tetraphenyl*-Δ^3-*cyclopentene*-1 : 2-*diol* (VI), m.p. 200—201°, converted by boiling MeOH containing a little H_2SO_4 into 1-*methoxy*-1 : 2 : 3 : 5-*tetraphenyl*cyclo*pentadiene*, m.p. 150—151°, and by boiling AcOH containing a little conc. H_2SO_4 into 2 : 3 : 4 : 5-tetraphenyl*cyclo*pentadienone, m.p. 216—218°. Oxidation of (VI) with $Pb(OAc)_4$ leads to $\alpha\beta\gamma\varepsilon$-tetraphenyl-$\Delta^\beta$-pentene-$\alpha\varepsilon$-dione, m.p. 110—112° ($Fe^{III}$ derivative, m.p. 187—188°). With the requisite proportion of Br in boiling AcOH (IV) gives 5-*bromo*-3 : 4-*diphenyl*-Δ^3-*cyclopentene*-1 : 2-*dione*, m.p. 181—182·5° (decomp.), which does not afford cryst. products with MeOH, NaOMe–MeOH, NaOAc in AcOH, or MgPhBr. With a larger proportion of Br (IV) yields 5 : 5-*dibromo*-3 : 4-*diphenyl*-Δ^3-*cyclopentene*-1 : 2-*dione*, m.p. 162—165°, decomp. ~185°, which does not yield a cryst. product with MeOH and gives NH_2Ph,HBr and a non-cryst. red oil with NH_2Ph. With NH_2Ph or *p*-$C_6H_4Me\cdot NH_2$ in boiling C_6H_6 (IV) gives substances, m.p. 81—83° and 87·5—89°, respectively. With NH_2Ph in cold Et_2O (IV) affords the unstable 1-*anilino*-1-*hydroxy*-2-*keto*-3 : 4-*diphenyl*-Δ^3-*cyclopentene*, m.p. 108—

110° (decomp.), which regenerates (IV) when treated with dil. HCl; the analogous 1-*p-toluidino*-compound has m.p. 120—122° (decomp.). (IV) is converted by boiling MeOH containing a little conc. HCl into 1 : 1-*dimethoxy*-3 : 4-*diphenyl*-Δ^3-cyclo*penten*-2-*one*, m.p. 120—121°, from which (IV) is re-formed by boiling AcOH containing a drop of HCl; it is converted by MgPhBr into 1 : 1-*dimethoxy*-2 : 3 : 4-*triphenyl*-Δ^3-cyclo*penten*-2-*ol*, m.p. 124—125°, transformed into a *dimeride*, m.p. 257—258° (darkening), of 2 : 3 : 4-triphenyl*cyclo*pentadienone by boiling AcOH containing 2% of H_2SO_4. H. W.

Enolisation of 1 : 2-diketohydrindene and of 1 : 2-diketo-3-phenylhydrindene. C. F. Koelsch and H. Hochman (J. Org. Chem., 1938, **3**, 503—505).—The ultra-violet absorption of 1 : 2-diketo-3-phenylhydrindene indicates that it exists in the enolic form whilst that of 1 : 2-diketohydrindene (I) shows that this compound is ketonic. The chemical behaviours of these substances are consistent with these structures. (I) can be boiled with Br in AcOH without change but in the presence of NaOAc or HBr it yields 3 : 3-*dibromo*-1 : 2-*diketohydrindene*, m.p. 141—142°. H. W.

2-Oximino- or 2-nitroso-indane-1 : 3-dione? G. Wanag and A. Lode (Ber., 1939, **72**, [*B*], 49—51).—The product (I) of the action of HNO_2 on indane-1 : 3-dione is oxidised by HNO_3 (*d* 1·4) in AcOH to 2-*nitroindane*-1 : 3-*dione* (II) (+$2H_2O$), m.p. 115°, also obtained by action of N oxides on indanedione (III) in AcOH or as *Na* salt from (III) and $NaNO_2$ in AcOH. (II) is reduced by boiling HCO_2H to (I), m.p. 210—212° when rapidly heated (cf. Teeters *et al.*, A., 1933, 953). (I) and Br in boiling $CHCl_3$ afford 2 : 2-dibromoindane-1 : 3-dione, m.p. 178°, bromonitrosoindanedione being probably formed intermediately. (I) gives a red solution in alkali hydroxide, probably owing to enolisation. (I) must therefore be regarded as 2-*nitrosoindane*-1 : 3-*dione* rather than as 2-oximinoindane-1 : 3-dione. In contrast with (II), characteristic ppts. are not formed from (I) and certain inorg. cations and org. bases. The ninhydrin reaction is observed when (I) and aq. α-NH_2-acids are subjected to protracted heating. H. W.

Photochemistry of Δ^4-cholestenone. E. Bergmann and Y. Hirshberg (Nature, 1938, **142**, 1037—1038).—Irradiation (Hg arc) of a 5% solution of Δ^4-cholestenone in C_6H_{14} or C_6H_6 immediately produces an insol. cryst. *substance* (I), $C_{42}H_{62}O_2$, m.p. >360°, by loss of 6 C and subsequent dimerisation. (I) is also accompanied by a resinous product. When O_2 is not rigidly excluded, cholestane-3 : 4-dione, new m.p. 157° (quinoxaline, new m.p. 228°), is also formed through photo-oxidation. Cholesteryl acetate is mainly resinified on irradiation; vac. distillation then gives (in some cases) $\Delta^{3:5}$-cholestadiene. L. S. T.

Cholestenone pinacone and its thermal decomposition. F. Galinovski and H. Bretschneider (Monatsh., 1938, **72**, 190—196).—Windaus' cholestenone pinacone, m.p. 229—230°, $[\alpha]_D^{23}$ +93·1° in $CHCl_3$ (cf. A., 1906, i, 174), is the bimol. 3 : 3′ compound, since it has 2 active H, is unchanged by Ac_2O–C_5H_5N–$CHCl_3$, is oxidised by $Pb(OAc)_4$ to cholestenone (I), is hydrogenated (Pd-black) in EtOH with loss of $2H_2O$ to an unsaturated [$C(NO_2)_4$] *hydrocarbon*, $C_{54}H_{90}$, and, when heated at 0·01 mm., gives cholestanone and (I). R. S. C.

Action of enol esters of testosterone. K. Miescher, W. H. Fischer, and E. Tschopp (Biochem. Z., 1938, **300**, 14—27; cf. A., 1938, III, 807, 908).—Partly a more detailed account of work previously reviewed (A., 1937, III, 492). The following enol esters of testosterone are described: 3-*acetate* 17-*propionate*, m.p. 140—141°, 3-*acetate* 17-n-*butyrate* (I), m.p. 96·5—98°, 3-*acetate* 17-iso*butyrate*, m.p. 134—136°, 17-*acetate* 3-*propionate*, m.p. 139·5—141°, 3-*propionate* 17-iso*butyrate*, m.p. 133·5—135°, 17-*acetate* 3-n-*butyrate*, m.p. 97—99°, 17-*propionate* 3-n-*butyrate*, m.p. 79—80°, 3-*benzoate* 17-*acetate*, m.p. 192—193°. J. N. A.

Preparation of a pregnane compound from dehydroandrosterone. H. E. Stavely (J. Amer. Chem. Soc., 1939, **61**, 79—80).—17-Acetylenyl-Δ^5-androstene-3 : 17-diol (prep. in 80—85% yield from dehydroandrosterone by C_2H_2 and CMe_2Et·OK in CMe_2Et·OH–Et_2O–C_6H_6 at room temp.), m.p. 240—242°, $[\alpha]_D^{25}$ −119° in $CHCl_3$, with $HgSO_4$ in H_2O at 110—120° gives 10% of Δ^5-pregnene-3 : 17-diol-20-one (I), m.p. 276—278°, $[\alpha]_D^{23}$ −106° in dioxan (oxime, m.p. 245—246°) (cf. Ruzicka *et al.*, A., 1939, II, 76), and a (?) Hg compound, which with NaOH–H_2S gives a further 20% of (I). Attempts to add MeOH gave only mixtures. R. S. C.

3 : 7 : 12-Trihydroxypregnan-20-one.—See B., 1939, 216.

Isolation of a keto-lactone from the urine of pregnant mares. J. D. Jacobs and E. Laqueur (Rec. trav. chim., 1939, **58**, 77—82).—The ketone in the non-phenolic extract of this urine (cf. Heard, A., 1938, II, 146) is a saturated keto-lactone (I), $C_{19}H_{26}O_3$, m.p. 258° [semicarbazone, m.p. ~310° (decomp.)], unaffected by Ac_2O, Na-Hg, CrO_3–AcOH, or Br; it gives no pure oxime, and has no œstrogenic or comb-growth-promoting effect. When boiled with 2N-EtOH–KOH, (I) gives a *OH-acid*, $C_{19}H_{28}O_4$, m.p. 240—243°. The data of Marker *et al.* (A., 1938, II, 369) on (I) are criticised. E. W. W.

Synthesis of sexual hormone glycuronides. E. Schapiro (Nature, 1938, **142**, 1036).—Me α-triacetylbromoglycuronate with dehydroandrosterone and α-œstradiol benzoate in C_6H_6 + Ag_2CO_3 gives the corresponding acetylated glycuronides (formulæ given), m.p. 194—196°, $[\alpha]_D^{25}$ −8·4° in $CHCl_3$, and m.p. 189—191°, $[\alpha]_D$ ±0°, respectively, hydrolysed (loss of acyl and Me) by MeOH–$Ba(OH)_2$ to dehydroandrosteroneglycuronide, m.p. 262—264° (decomp.), and œstradiol-17-glycuronide, m.p. 191—194° (decomp.; previous shrinking), respectively (first isolated as Ba salts), which are less active than the uncoupled hormones. L. S. T.

Conversion of dehydroandrosterone into progesterone; simple artificial preparation of the hormone of pregnancy from cholesterol. A. Butenandt and J. Schmidt-Thomé (Ber., 1939, **72**,

[*B*], 182—187).—In extension and amplification of work already reviewed (A., 1938, II, 236), $\Delta^{5:16}$-pregnadien-3-ol-20-one (I), new m.p. 216° (*acetate*, m.p. 176°, $[\alpha]_D^{20}$ —33·4° in EtOH), is oxidised by $Al(OPr^{\beta})_3$ in presence of PhMe and *cyclo*hexanone to 16-*dehydroprogesterone*, m.p. 186—188°, which is devoid of œstrogenic properties. (I) is readily partly hydrogenated (Raney Ni) to Δ^5-pregnen-3-ol-20-one which is converted by known methods into progesterone. 17-Cyano-3-acetoxy-$\Delta^{5:16}$-androstadiene (II) (*loc. cit.*) is hydrolysed to 17-*cyano*-$\Delta^{5:16}$-*androstadien*-3-*ol*, m.p. 176°, also obtained by the restricted action of MgMeBr on (II). H. W.

1 : 4-Dihydroxy-2-acetylanthraquinone. H. Willstaedt and M. Michaelis (Svensk Kem. Tidskr., 1938, **50**, 274—278).—Quinacetophenone, *o*-$C_6H_4(CO)_2O$, H_3BO_3, and conc. H_2SO_4 at 150—160° and then at 190—200° give 1 : 4-*dihydroxy*-2-*acetylanthraquinone* (I), m.p. 199—200°, in very small yield. (I) does not depress the m.p. of quinizarin (II). (I) is transformed by *p*-$C_6H_4Me{\cdot}SO_3Me$ and Na_2CO_3 in *p*-$C_6H_4Cl_2$ at 170° into 1 : 4-*dimethoxy*-2-*acetylanthraquinone*, m.p. 171°, which does not depress the m.p. of 1 : 4-dimethoxyanthraquinone. (II) cannot be chromatographically separated from its 2-Ac derivative by $CaCO_3$ or from its Me ether by Al_2O_3. The Me_2 ethers of (II) and alizarin are readily separable by Al_2O_3. Condensation of acetoveratrone, *o*-$C_6H_4(CO)_2O$, H_3BO_3, and conc. H_2SO_4 gives alizarin Me_2 ether. H. W.

Halogenoanthraquinone-β-carboxylic acids.—See B., 1939, 128.

Diaminodiphenoxyanthraquinonedisulphonic acids.—See B., 1939, 128.

Walden inversion. III. Reaction of sulphonic esters with alcohols. W. Hückel and W. Tappe (Annalen, 1939, **537**, 113—131; cf. A., 1938, II, 315).—Menthyl *p*-toluenesulphonate (I) in boiling *cyclo*hexane decomposes completely into *dl*-menthene (II) and high-boiling products; this is due to traces of *p*-$C_6H_4Me{\cdot}SO_3H$ formed, as $CaCO_3$ stabilises the ester and the small amount of decomp. occurring in its presence yields *d*-(II). When distilled in steam, (I) gives much (II) and some *l*-menthol (III); in presence of $CaCO_3$ much less (II) and neomenthol (IV) are formed. In boiling EtOH (I) gives much (II), α_D +34°, and some of the Et ethers of *l*-(III) and *d*-(IV); in presence of $CaCO_3$ less (II), α_D +78°, much of the Et ether of *d*-(IV), and less of the Et ether of *l*-(III), (III), and (IV) are formed. NaOEt does not affect (I) in PhMe or Et_2O; in EtOH it gives (II) and a little *l*-(III) and its Et ether. (I) decomposes less fast in MeOH or $Pr^{\beta}OH$ than in EtOH, and the products are similar but differ in relative amounts. Menthyl benzenesulphonate behaves similarly. The *p*-toluenesulphonate of *trans*-decahydro-β-naphthol (V), m.p. 75°, with $CaCO_3$ in EtOH gives about 40% of octahydronaphthalene (VI), 60% of Et ether [80% thereof from *trans*-decahydro-β-naphthol (VII), m.p. 53°], and a little free (VII). The *p*-toluenesulphonate of (VII) similarly gives 65% of (VI), about 35% of Et ether [90% thereof from (V)], and a little (V). Reaction mechanisms and the homogeneity of (II) are discussed. R. S. C.

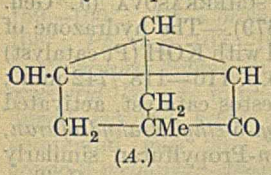
Organic sulphur compounds. IV. Action of hydrocyanic acid, ammonia, and hydrogen sulphide on carvone. K. Aber (Sci. Rep. Tokyo Bunrika Daigaku, 1938, **A**, **3**, 217—230; cf. A., 1936, 212).—Carvone treated with KCN (2 mols.) in aq. EtOH, then made slightly acid, kept, and finally treated with NH_3 and H_2S gives 2-*amino*-2 : 6-*dicyano*-Δ^8-*p*-*menthene* (I), m.p. 129·5° [*hydrochloride*, m.p. >225°]; converted by H_2O into 6-cyanodihydrocarvone (II), m.p. 93·5—94·5°], and *dihydrothiocarvone*-6-*carboxthioamide* (III), m.p. 198—199°. If 1 mol. of KCN or, better, NaCN is used, 2-*imino*-Δ^8-*p*-*menthene*-6-*carboxthioamide* (IV), m.p. 151—152° (*platinichloride*), and, sometimes, a *substance* (C 59·3, H 8·4, N 14·8, S 14·7%), m.p. 149—150°, are obtained. The *hydrochloride*, m.p. 165—166°, of (IV) in hot H_2O gives *dihydrocarvone*-6-*carboxthioamide*, m.p. 133°, hydrolysed by hot 10% HCl to β-dihydrocarvone-6-carboxylic acid (Lapworth, J.C.S., 1906, **89**, 963). By KCN–NH_3–H_2S treatment (II) gives (III) and by NH_3–H_2S in EtOH yields (IV) and its *H sulphide* (V), m.p. 171—172° (converted by hot, dil. HCl into a *substance*, $C_{11}H_{18}O_3S$, m.p. 138°). With NH_3–H_2S in EtOH 6-cyanodihydrocarvone cyanohydrin, m.p. variable, 104—108° and 134—135° (*loc. cit.*, p. 1819), or (I) gives (III) and (IV), but (IV) gives only (V). With H_2S in EtOH (II) gives a *substance*, $C_{11}H_{17}NS_2$, m.p. 80—81° [possibly an isomeride of (III); also obtained from (I)], and a *substance*, $C_{11}H_{17}ONS,1{\cdot}5H_2S$, m.p. 219—220°. R. S. C.

Complexes of magnesium bromide with terpene ketones and alcohols. G. V. Tschelinceva (J. Gen. Chem. Russ., 1938, **8**, 588—591).—$MgBr_2,3Et_2O$ in Et_2O and camphor yield the complexes $MgBr_2,2C_{10}H_{16}O$ (I) and $MgBr_2,3C_{10}H_{16}O$. (I) and borneol in Et_2O give $MgBr_2,2C_{10}H_{16}O,2C_{10}H_{17}{\cdot}OH$; this with EtOH or *iso*-$C_5H_{11}{\cdot}OH$ gives oily products, with $Pr^{\alpha}OH$ give $MgBr_2,2C_{10}H_{16}O,Pr^{\alpha}OH$, and with PhOH gives $MgBr_2,2C_{10}H_{16}O,PhOH$. R. T.

Camphor series. V. Some derivatives of oximinothiocamphor. D. C. Sen (J. Indian Chem. Soc., 1938, **15**, 537—542; cf. A., 1936, II, 856).—The formation of oximinothiocamphor (I) (*Bz* derivative, m.p. 115—116°) from *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$ and Na thiocamphor involves a migration of NO from S to C. (I) can act as the thiol, $C_8H_{14}{<}\begin{matrix}C{\cdot}NO\\C{\cdot}SH\end{matrix}$ or the thioketone, $\cdot CS{\cdot}C(N{\cdot}OH)\cdot$. *dl*-(I) and NH_2OH,HCl in NaOH or NaOAc or C_5H_5N afford α- (II), m.p. 201°, and β-camphorquinonedioxime (III), m.p. 248°, and *bornylene*-dl-1 : 2 : 5-*thiodiazole* (IV), m.p. 218°, $C_8H_{14}{<}\begin{matrix}C{\cdot}N\\C{\cdot}N\end{matrix}{>}S$. *l*-(I) similarly gives (II), (III), and *α-bornylene*-1 : 2 : 5-*thiodiazole*, m.p. 221°, $[\alpha]_D^{34}$ +75·27° in EtOH. (IV) is also obtained from (III) and H_2S–EtOH–NaOAc, and is reduced by Zn–AcOH at 100° (bath) to bornylenediamine (*dihydrochloride*, m.p. 287—288°). (I) and MgMeI afford (?) the anhydride of oximinomethylthioborneol,

$C_8H_{14}<\begin{matrix}C=N\\CMe\cdot S\end{matrix}$, b.p. 105—106°/6 mm. (I) and MeI–NaOEt at 80° give *S*-methylnitrosothiocamphor, $C_8H_{14}<\begin{matrix}C\cdot NO\\C\cdot SMe\end{matrix}$, b.p. 95—96°/6 mm., hydrolysed by dil. HCl (1 : 1) to MeSH and oximinocamphor, m.p. 152°. (I), CH_2O, and a little H_2SO_4, then fuming HCl, at 100° (bath), afford camphorquinone, m.p. 198°, and a little monothiocamphorquinone, m.p. 196° [NH_2OH gives H_2S and (III)] (cf. Lapworth, J.C.S., 1907, **91**, 1134). During the prep. of (I) (*loc. cit.*), an *isomeride*, b.p. 105—106°/5 mm., is isolated in small yield. Solid *l*-(I) is pink, but dissolves in org. solvents with a blue colour. The blue EtOH solution, rapidly cooled, gives prismatic crystals, but slow cooling gives octahedra. *dl*-(I) is blue in solid and solution. Absorption spectra are recorded. A. T. P.

Degradation of dimethylcamphor in the animal organism. Biological oxidation of methyl groups in terpenes. F. Reinartz and K. Meessen (Ber., 1939, **72**, [*B*], 1—7).—If dimethylcamphor is administered to a dog, the Me attached to $C_{(3)}$ are by far the most readily hydroxylated since 3-*methylcamphorcarboxylic acid*, m.p. 98—100·5° (decomp.) [*Me* ester, m.p. 87° (corr.)], is isolable in considerable amount. When melted it gives CO_2 and 3-methylcamphor. The main component of the degradation products is 4-hydroxydimethylcamphor [*p-nitrobenzoate*, m.p. 178·4—180·4° (corr.)]. Small amounts of camphoric acid and anhydride are also obtained, probably due to the oxidation of both Me groups at $C_{(3)}$. The oxidation of campherol to the *substance* A, m.p. 137—138·5° (*monosemicarbazone*), is described. H. W.



(*A*.)

Fenchene series. IX. Stereoisomeric *dl*-β-fenchocamphorols. G. Komppa and S. Beckmann (Annalen, 1939, **537**, 140—143; cf. A., 1938, II, 371).—β-Fenchocamphorol, m.p. 44—45° (A., 1936, 729), is resolved into β-*fenchocamphorol* (mainly), m.p. 64—65°, b.p. 198—199° (*H phthalate*, m.p. 126—127°; *phenylurethane*, m.p. 96—97°), and iso-β-*fenchocamphorol*, m.p. 60—61° (*H phthalate*, m.p. 130—131°). R. S. C.

***epi-iso*Fenchone.** G. A. Nyman (Annalen, 1939, **537**, 131—139).—The Na derivative (prep. by $NaNH_2$ in C_6H_6 or Et_2O) of *dl-iso*fenchone (I) with CO_2 in C_6H_6 gives a 70% yield of dl-iso*fenchone*-3-*carboxylic acid* (II), m.p. 114°, the reaction being sterically homogeneous owing to the proximity in space of $C_{(3)}$ and one of the *gem*-Me. When kept alone, (II) gives (I), and with NH_2OH or $NH_2\cdot CO\cdot NH\cdot NH_2$ in EtOH (II) gives CO_2 and the CO-derivatives of (I). Electrolytic reduction of (II) in aq. K_2CO_3 gives homogeneous dl-iso*fencho*-3-*carboxylic acid* (III), m.p. 137—139°, converted by AcCl and distillation of the resulting acetate at 16 mm. into δ-*fenchene*-3-*carboxylic anhydride*, m.p. 133—135°, and thence into the corresponding *acid* (IV), m.p. 139—140°, the structure of which is proved by oxidation by $KMnO_4$ to *dl-iso*fenchocamphoric acid (V) and (III). With $SOCl_2$ (IV) gives the *chloride*, b.p. 112°/17 mm. (converted on storage into HCl and a *substance*, m.p. 133—135°), which gives the azide and thence by hot, conc. HCl dl-epi-iso*fenchone*, b.p. 195—198° [gives no semicarbazone; *oxime*, m.p. 64—65° (*Bz* derivative, m.p. 86—87·5°)], oxidised to (V). R. S. C.

1-Methylsantene oxide and methylsantene glycol. G. Komppa and G. A. Nyman (Ber., 1939, **72**, [*B*], 16—18; cf. A., 1935, 865).—1-Methylsantene is smoothly transformed by BzO_2H in $CHCl_3$ at 0° into 1-*methylsantene oxide* (I), b.p. 57·5—58°/7·5 mm., hydrated by 10% H_2SO_4 at 0° to *methylsantene glycol* [2 : 3-*dihydroxy*-1-*methyl*-2 : 3-*dihydrosantene*] (II), m.p. 197—198°. Oxidation of (II) with NaOBr yields 1-methyl*cyclo*propane-1 : 3-dicarboxylic acid in very small amount. When (I) is distilled with SiO_2 gel at atm. pressure or when (I) or (II) is distilled in vac. an unidentified *compound*, b.p. 215—216°, results. This gives a strong aldehyde reaction with magenta–H_2SO_3 but only slowly reduces Ag_2O. It gives an intense colour with $C(NO_2)_4$ and strongly reduces $KMnO_4$. It yields a *semicarbazone*, $C_{11}H_{19}ON_3$, m.p. 179—180°. It appears to be monocyclic but is not fenchone. H. W.

Structure of the triterpenes. C. W. Picard, K. S. Sharples, and F. S. Spring (Chem. and Ind., 1939, 58—59; cf. A., 1938, II, 416, 448).—On the assumption that the hydrocarbon obtained by dehydrogenating basseol is identical with that from hederagenin, *i.e.*, 1 : 2 : 6-trimethylphenanthrene (cf. Ruzicka and Smith, A., 1939, II, 80), structures are suggested for basseol and for β-amyrenol. Any possibility, during cyclisation of basseol, of migration of an inert ethenoid linking is discounted by the fact that dihydrobasseol (bassenyl) acetate is oxidised to "β-amyrenyl acetate oxide" (β-amyranonyl acetate), m.p. 293°, obtained also by oxidising β-amyrenyl acetate (formulæ given). A modified formulation is recorded for oleanolic acid, which allows representation of keto-oleanolic acid as a γ-keto-acid, and of *iso*keto-oleanolic acid as a δ-keto-βγ-unsaturated acid; the relative ease of saponification of the derived esters is thus more easily understood. A. T. P.

Active principles of *Cannabis indica* resin. I. T. S. Work, F. Bergel, and A. R. Todd (Biochem. J., 1939, **33**, 123—127).—The resin obtained from Indian hashish has b.p. 185—190°/0·6 mm. *p*-$NO_2\cdot C_6H_4\cdot COCl$ in C_5H_5N yields cannabinol *p*-nitrobenzoate (I), m.p. 160° (*p-aminobenzoate*, m.p. 149—150°), and a non-cryst. ester (II). Hydrolysis of (I) yields cannabinol as an oil which is very toxic in rabbits but gives a negative Gayer test (abolition of corneal reflex). The hydrolysis product of (II), after adsorption on Al_2O_3, yields a product which gives a positive Gayer test in a dose of 0·25 mg. per kg. of body-wt. P. G. M.

Beech lignin. O. Müller and K. Storch (Ber., 1939, **72**, [*B*], 73—76).—Red beech is extracted with 4% NaOH at room temp., whereby a portion of the lignin (I) is dissolved. Treatment of the alkaline solution with Me_2SO_4 gives an ochre-yellow product identical in properties and analytical composition

with methyl-lignin. Acidification of the alkaline solution, after removal of hemicelluloses by MeOH–H_2SO_4, ppts. (I) closely allied to cuproxam lignin; it condenses with *p*-C_6H_4Cl·OH. Evidence is thus afforded that (I) is an actual substance formed under natural conditions. H. W.

Constituents of resins. XI. Resin alcohols of lactucarium. K. H. Bauer and K. Brunner (Arch. Pharm., 1938, 276, 605—617).—Extraction of lactucarium with 96% EtOH gives α- (I), m.p. 239—240°, and β-*lactucerin* (II), m.p. 231—233°. The mixture obtained by alkaline hydrolysis of the light petroleum extract is separated into α- (III), m.p. 223—224°, $[\alpha]_D^{20}$ +89·33° in $CHCl_3$ [acetate = (I); *benzoate*, m.p. 255—257°], and β-*lactucerol* (IV), $C_{30}H_{50}O$, m.p. 178—180°, $[\alpha]_D^{20}$ +50·77° in $CHCl_3$ [acetate = (II); *benzoate*, m.p. 222—224°; p-*bromobenzoate*, m.p. 208—210°] (cf. A., 1929, 1187), which are saturated towards Br and $KMnO_4$, but give a colour with $C(NO_2)_4$. CrO_3-oxidation yields α-, m.p. 178—180° (*oxime*, m.p. 253—255°; 2 : 4-*dinitrophenylhydrazone*, m.p. 263—265°), and β-*lactucerone*, m.p. 186—188° (*oxime*, m.p. 235—236°; 2 : 4-*dinitrophenylhydrazone*, m.p. 243—244°), but a crude (III) yielded also γ-*lactucerone*, m.p. 153—155° [*oxime*, m.p. 239—240°; 2 : 4-*dinitrophenylhydrazone*, m.p. 255—257° (decomp.)]. More profound CrO_3-oxidation of (III) gives also an *acid*, $C_{21}H_{34}O_3$, m.p. 204—205°, but (IV) yields similarly an *acid*, $C_{20}H_{32}(CO_2H)_2$, loses gas at ~115°, m.p. 158—160°. With H_2O_2–AcOH at 100° (III) gives α-*lactucerol oxide*, m.p. 152—154° (*acetate*, m.p. 208—210°), but (IV) gives an unsaturated *diacetate*, $C_{34}H_{54}O_4$, m.p. 245—246°. H_2–$PdSO_4$ converts (IV) with difficulty into *dihydro*-β-*lactucerol*, m.p. 191—193° (*acetate*, m.p. 250—251°). With PCl_5 in light petroleum (III) or (IV) gives lactucadiene (previously termed lactucene), $C_{30}H_{48}$, m.p. 153—154°; the compound previously termed lactucane is renamed lactucene. (II) is related to (IV) as CH_2R·CHR'·OH is to OH·CHR·CH_2R'. R. S. C.

Constituents of natural phenolic resins. XIV. Synthesis of *dl*-, *d*-, and *l*-matairesinol dimethyl ether. R. D. Haworth and D. Woodcock (J.C.S., 1939, 154—156).—Veratraldehyde, $(CH_2{\cdot}CO_2Na)_2$, and NaOEt give meso-αβ-*di*-(3 : 4-*dimethoxybenzyl*)*succinic acid*, m.p. 223—224°, which with Ac_2O affords dl-(trans)-αβ-*di*-(3 : 4-*dimethoxybenzyl*)*succinic anhydride*, m.p. 110—112°, reduced (Al–Hg) to dl-(trans)-αβ-*di*-(3 : 4-*dimethoxybenzyl*)-*butyrolactone* (I), m.p. 113—115° [Br_2-, m.p. 112—113°, and $(NO_2)_2$-derivatives, m.p. 191—192°], and hydrolysed to dl-αβ-*di*-(3 : 4-*dimethoxybenzyl*)*succinic acid* (+$4H_2O$), m.p. 95—105°. Resolution of this acid, through the strychnine salts [*strychnine* salt of *l*-acid (+$3H_2O$), decomp. about 240°, $[\alpha]_D^{15}$ −27·3° in $CHCl_3$], gives d- (+$3H_2O$), $[\alpha]_D^{15}$ +25·8° in $CHCl_3$, and l-αβ-*di*(3 : 4-*dimethoxybenzyl*)*succinic acids* (+$3H_2O$), m.p. 95—105°, $[\alpha]_D^{15}$ −25·3° in $CHCl_3$. From these acids, the corresponding active anhydrides and lactones can be obtained: d(−)-, m.p. 131°, $[\alpha]_D^{15}$ −37·6° in $COMe_2$, and l(+)-αβ-*di*-(3 : 4-*dimethoxybenzyl*)*succinic anhydrides*, m.p. 131°, $[\alpha]_D^{15}$ +38·4° in $COMe_2$; l-(trans)-αβ-*di*-(3 : 4-*dimethoxybenzyl*)*butyrolactone*, m.p. 127°, $[\alpha]_D^{15}$ −32·3° in $CHCl_3$ [Br_2-derivative, m.p. 123°, $[\alpha]_D^{15}$ −39·8° in $CHCl_3$; $(NO_2)_2$-derivative, m.p. 172—173°, $[\alpha]_D^{15}$ −124° in $CHCl_3$], and d-(trans)-αβ-*di*-(3 : 4-*dimethoxybenzyl*)*butyrolactone*, m.p. 126°, $[\alpha]_D^{15}$ +32·2° in $CHCl_3$ [Br_2-derivative, m.p. 123°, $[\alpha]_D^{15}$ +40·2° in $CHCl_3$; $(NO_2)_2$-derivative, m.p. 173—174°, $[\alpha]_D^{15}$ −126° in $CHCl_3$]. (I) and its *d*- and *l*-forms are identical with natural *dl*-, *d*-, and *l*-matairesinol Me_2 ether, respectively. F. R. S.

Acids of the juice of *Euphorbia biglandulosa*, Desf. I. N. P. Kirjalov (J. Gen. Chem. Russ., 1938, 8, 740—745).—The dried juice contains 15% of Ca salt of *biglandulic acid*, $C_7H_8O_2(CO_2H)_2$, +H_2O, m.p. 170—171° (*anhydride*, m.p. 210—212°; Me_2 ester, m.p. 63—64°; Et_2 ester, m.p. 57—58°), converted by heating with red P and HI into *dihydrobiglandulolactone*, m.p. 129—131°, and by hydrogenation (Pd catalyst) into *dihydrobiglandulic* acid, m.p. 165° (Me_2 ester, m.p. 56°). R. T.

Catalytic hydrogenation of the furan ring by the continuous method. N. I. Schuikin and V. I. Bunina (J. Gen. Chem. Russ., 1938, 8, 669—673).—27 : 73 Ni–Al alloy treated with 10% NaOH yields a very active and stable catalyst for hydrogenating furan or sylvan to the H_4-derivatives, at 100—140°. R. T.

Synthesis of γ-oxides by catalytic hydrogenation of the furan ring. N. I. Schuikin, E. V. Schemastina, and E. D. Tscherkasova (J. Gen. Chem. Russ., 1938, 8, 674—679).—The hydrazone of 2-acetyl-5-methylfuran heated with KOH (Pt catalyst) yields 2-*methyl*-5-*ethylfuran*, b.p. 116—118°/742 mm.; this is hydrogenated (Pd–asbestos catalyst, activated with KOH) at 150° to 2-*methyl*-5-*ethyltetrahydrofuran*, b.p. 118—119°/756 mm. 2-*n*-Propylfuran similarly yields 2-*n*-propyltetrahydrofuran. R. T.

Tetrahydrofurfuryl mesityl oxide oxalate.—See B., 1939, 222.

Constitution of karanjin from the roots of *Pongamia glabra*, Vent. B. L. Manjunath, A. Seetharamiah, and S. Siddappa (Ber., 1939, 72, [*B*], 93—96).—Karanjin (I), m.p. 158·5°, becomes intensely yellow when exposed to sunlight or ultraviolet light. It is demethylated (HI, *d* 1·7, and boiling Ac_2O) to the corresponding *OH*-compound, m.p. 199—200° (*acetate*, m.p. 177°). Degradation of (I) with boiling KOH–EtOH affords 3-*hydroxybenzfuran*-4-*carboxylic acid* (II), m.p. 218° (decomp.), BzOH, and 3-*hydroxy*-4-*methoxyacetylbenzfuran* (III), m.p. 96° (3-*methoxy*-4-*methoxyacetylbenzfuran*, m.p. 87°). With H_2O_2 (II) in alkaline solution gives furan-2 : 3-dicarboxylic acid. (II) is decarboxylated by Cu-bronze in quinoline at 180—200° to 4-hydroxycoumarone and transformed by O_3 in $CHCl_3$ into 2 : 4-dihydroxy-3-formylbenzoic acid. (I) is obtained synthetically from (III), Bz_2O, and NaOBz at 180—185°. H. W.

Chalkones: new synthesis of chrysin, apigenin, and luteolin. W. A. Hutchins and T. S. Wheeler (J.C.S., 1939, 91—94).—*o*-Hydroxychalkone dibromides in general give flavones when they are heated above the m.p. or are treated with KCN–EtOH. Bromination of 2-hydroxy-4 : 6-dimethoxyphenyl styryl ketone affords 5-*bromo*-2-*hydroxy*-4 : 6-

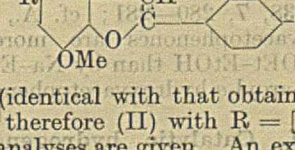
dimethoxyphenyl αβ-*dibromo*-β-*phenylethyl ketone*, m.p. 186°, which, when heated above the m.p. under reduced pressure, gives 6-*bromo*-5 : 7-*dimethoxyflavone*, m.p. 242°, converted by HI into chrysin. Apigenin is similarly derived from 5-*bromo*-2-*hydroxy*-4 : 6-*dimethoxyphenyl* αβ-*dibromo*-β-p-*anisylethyl ketone*, m.p. 165°, and 6-*bromo*-5 : 7 : 4′-*trimethoxyflavone*, m.p. 250°. The latter compound with NaOH yields 4-*bromo*-3 : 5-*dimethoxy*-1-*anisylidenecoumaran*-2-*one*, m.p. 243°, and with C_5H_5N affords 5-*bromo*-2-*hydroxy*-4 : 6-*dimethoxyphenyl* p-*methoxystyryl ketone*, m.p. 184—185°. 5-*Bromo*-2-*hydroxy*-4 : 6-*dimethoxyphenyl* αβ-*dibromo*-β-3 : 4-*dimethoxyphenylethyl ketone*, m.p. 165°, converted into 6-*bromo*-5 : 7 : 3′ : 4′-*tetramethoxyflavone*, m.p. 258°, gives luteolin. F. R. S.

Chalkones : reactivity of aryl *o*-alkoxystyryl ketone dibromides and the synthesis of flavones therefrom. N. A. Bhagwat and T. S. Wheeler (J.C.S., 1939, 94—96).—Aryl β-2-dialkoxystyryl ketones yield flavones when treated with HBr–AcOH; in both the *o*- and the *p*-alkoxystyryl dibromides, the side-chain halogen adjacent to the nucleus containing the alkoxy-group is replaced by alkoxyl when treated with alcohols. The following are described : *Ph* 5-*bromo*-2-*methoxystyryl ketone* (+2H_2O), m.p. 110°; *Ph* αβ-*dibromo*-β-5-*bromo*-o-*anisyl ketone*, m.p. 158°; *Ph* αβ-*dibromo*-β-m-*anisylethyl ketone*, m.p. 122°; p-*tolyl* αβ-*dibromo*-β-5-*bromo*-o-*anisylethyl ketone*, m.p. 159—160°; *Ph* α-*bromo*-o-*methoxystyryl ketone*, m.p. 106°; *Ph*, m.p. 103—104°, and p-*tolyl* α-5-*dibromo*-o-*methoxystyryl ketone*, m.p. 127°; *Ph* α-*bromo*-m-*methoxystyryl ketone*, m.p. 100—101°; *Ph* 5-*bromo*-β : 2-*dimethoxystyryl ketone*, m.p. 122°, and the p-*tolyl* compound, m.p. 96°; *Ph*, m.p. 127°, and p-*tolyl* 5-*bromo*-2-*methoxy*-β-*ethoxystyryl ketone*, m.p. 113°; *Ph* 6-*bromo*-β : 3-*dimethoxy*-, m.p. 93°, and -3-*methoxy*-β-*ethoxy*-*styryl ketone*, m.p. 96°; *benzoyl*-5-*bromo*-o-*anisoylmethane*, m.p. 96°, and the *bromobenzoyl* compound, m.p. 166°; 5-*bromo*-o-*anisoyl*-p-*toluoylmethane*, m.p. 122°, and the *Br*-compound, m.p. 178°; and 6-*bromo*-4′-*methylflavone*, m.p. 197°. F. R. S.

Chalkones : reactivity of naphthyl *p*-alkoxystyryl ketones and their dihalides. G. V. Deshmukh and T. S. Wheeler (J.C.S., 1939, 96—98).—The following chalkones are described : 1-*hydroxy*-2-*naphthyl* 6-*bromo*-3 : 4-*methylenedioxystyryl ketone*, m.p. 210°, and its 1-*Ac*, m.p. 173—174°, and 1-*OMe*-derivatives, m.p. 144—145°. Chalkones condense with OAc·CH_2·CO_2Et to form *Et* 4-*phenyl*-6-(6′-*bromo*-3′ : 4′-*methylenedioxyphenyl*)-Δ^3-cyclo*hexen*-2-*one*-1-*carboxylate*, m.p. 133—134°, and *Et* 4-(1′-*hydroxy*-2′-*naphthyl*)-6-(6″-*bromo*-3″ : 4″-*methylenedioxyphenyl*)-Δ^3-cyclo*hexen*-2-*one*-1-*carboxylate*, m.p. 219—220°. Halogenation of the chalkones leads to 4-*bromo*-1-*hydroxy*-2-*naphthyl* 6-*bromo*-3 : 4-*methylenedioxystyryl*, m.p. 249°, and αβ-*dibromo*-β-(6-*bromo*-3 : 4-*methylenedioxyphenyl*)*ethyl ketone*, m.p. 215—216° (1-*OMe*-derivative, m.p. 187—188°); 1-*acetoxy*-2-*naphthyl* αβ-*dibromo*-β-(6-*bromo*-3 : 4-*methylenedioxyphenyl*)*ethyl ketone*, m.p. 184°; and *Ph* αβ-*dichloro*-β-(6-*bromo*-3 : 4-*methylenedioxyphenyl*)*ethyl ketone*, m.p. 149—150°. With NH_3–EtOH these dihalides give *Ph* 6-*bromo*-β-*amino*-3 : 4-*methylenedioxystyryl ketone*, m.p. 153°, and β-*benzoyl*-α-(6-*bromo*-3 : 4-*methylenedioxyphenyl*)*propionitrile*, m.p. 120°. Interaction with alcohols affords 4-*bromo*-1-*methoxy*-2-*naphthyl* α-*bromo*-β-*ethoxy*-β-(6-*bromo*-3 : 4-*methylenedioxyphenyl*)*ethyl ketone*, m.p. 126—127°, and the corresponding β-*OMe*-compound, m.p. 150—151°. C_5H_5N with the chalkones gives 4-*bromo*-1-*methoxy*-2-*naphthyl* α : 6-*dibromo*-3 : 4-*methylenedioxystyryl ketone*, m.p. 127—128°, and *Ph* α : 6-*dibromo*-, m.p. 123—124°, and α-*chloro*-6-*bromo*-3 : 4-*methylenedioxystyryl ketone*, m.p. 125°, whilst NHPh·NH_2 yields 1 : 3-*diphenyl*-5-(6′-*bromo*-3′ : 4′-*methylenedioxyphenyl*)*pyrazole*, m.p. 163—164°. Chalkone dihalides not containing OH *o*- to the CO-group give β-alkoxystyryl derivatives on treatment with excess of NaOEt–EtOH, whilst those containing OH *o*- to CO yield flavones unless a β-alkoxy-compound is intermediately formed : *Ph* 6-*bromo*-β-*ethoxy*-, m.p. 134—135°, and -β-*methoxy*-3 : 4-*methylenedioxystyryl ketone*, m.p. 79—80°; 6-*bromo*-3 : 4-*methylenedioxydibenzoylmethane*, m.p. 125—126°; 6 : 6′-*dibromo*-, m.p. above 275°, and 6′-*bromo*-3′ : 4′-*methylenedioxy*-7 : 8-*benzoflavone*, m.p. 245—246°; and 6′-*bromo*-3′ : 4′-*methylenedioxy*-1-*benzylidene*-5 : 6-*benzocoumaran*-2-*one*, m.p. 264°. F. R. S.

Colorimetric determination of α-tocopherol (vitamin-*E*). A. Emmerie and C. Engel (Rec. trav. chim., 1938, 57, 1351—1355; cf. Karrer *et al.*, A., 1938, II, 466).—α-Tocopherol and $FeCl_3$ in EtOH (with or without C_6H_6) give a Fe^{II} salt which is determined colorimetrically with 2 : 2′-dipyridyl (better than *o*-phenanthroline); the results are comparable with those obtained by the potentiometric titration with $AuCl_3$. Carotene is completely oxidised and decolorised by $FeCl_3$ in presence of dipyridyl. A. T. P.

Egonol. Synthesis of two egonol degradation products—dihydroconiferyl alcohol and styraxinolic aldehyde. S. Kawai and N. Sugiyama (Proc. Imp. Acad. Tokyo, 1938, 14, 348—352; cf. A., 1938, II, 501; 1939, II, 29, 80).—The substance (I) obtained by vac. distillation of styraxinolic acid (*bis*-p-*nitrobenzoate*) differs from both 2-*methoxy*-4-*methyl*-6- and 2-*methoxy*-6-*methyl*-4-β-*hydroxyethylphenol*, which have been synthesised. (I) is oxidised ($KMnO_4$) to veratric acid, and is identical with 2-*methoxy*-4-ω-*hydroxy*-n-*propylphenol* (dihydroconiferyl alcohol) (*bis*-*benzoate*, -p-*nitrobenzoate*, and -*phenylcarbamate*), which has been synthesised (cf. Nomura *et al.*, A., 1928, 1005), and converted (Reimer–Tiemann) into styraxinolic



(II.)

aldehyde (identical with that obtained from egonol). Egonol is therefore (II) with R = $[CH_2]_3$·OH. No details or analyses are given. An explanation of the colours given by egonol and by 2-phenylcoumarone with conc. H_2SO_4 is suggested. A. Li.

Natural coumarins. XL. Coumarins from the drug, Semen angelicæ. E. Späth and F. Vierhapper (Monatsh., 1938, 72, 179—189).—Isolation of imperatorin (I) (0·5%), bergapten (0·1%), umbelliprenin (0·04%), a phenol (0·03%), m.p. 224—

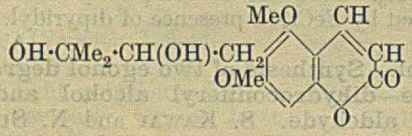
226°, xanthotoxin (0·02%), and xanthotoxol (0·02%) from the seeds of *Angelica archangelica*, L., is described (cf. A., 1937, II, 163, and following abstract). Removal of (I) is best effected by converting it by distillation into the phenolic *allo*imperatorin.

R. S. C.

Natural coumarins. XLIII. Synthesis of *iso*imperatorin and of oxypeucedanin. E. Späth and E. Dobrovolny (Ber., 1939, 72, [*B*], 52—53).—Bergaptol (I) is converted by prenyl [γ-methyl-Δ^{β}-butenyl] bromide and NaOMe–MeOH at 20° into *iso*imperatorin (II), thus effecting the complete synthesis of the latter compound since that of (I) has been effected by Späth *et al.* (A., 1937, II, 206). Since (II) has been transformed by BzO_2H into oxypeucedanin (III) (Späth and Kahovec), the synthesis of (III) is also accomplished.

H. W.

Natural coumarins. XLIV. Structural formula of toddalolactone. E. Späth, B. B. Dey, and E. Tyray (Ber., 1939, 72, [*B*], 53—56).—1 : 2 : 4 : 6-$C_6H_2Me(OH)_3$, conveniently obtained from 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$, is condensed with malic acid and conc. H_2SO_4 at 115° to a mixture of coumarins, converted by repeated treatment with CH_2N_2 into 5 : 7-dimethoxy-8- (I), m.p. 188—190°, and 5 : 7-dimethoxy-6-methylcoumarin (II), m.p. 132—133°. (II) is converted by NaOH and Et_2SO_4 followed by hydrolysis into 2 : 4-dimethoxy-6-ethoxy-3-methylcinnamic acid, oxidised ($KMnO_4$–NaOH) and then esterified (CH_2N_2) to *Me*$_2$ 2 : 4-*dimethoxy*-6-*ethoxybenzene*-1 : 3-*dicarboxylate*, m.p. 89—90°, identical with



(*A*.)

the substance obtained by the degradation of toddalolactone (A., 1938, II, 451), which is therefore *A*; analogous treatment of (I) leads to *Me*$_2$ 4 : 6-*dimethoxy*-2-*ethoxybenzene*-1 : 3-*dicarboxylate*, m.p. 125—126°.

H. W.

[Pechmann reaction with ethyl α-acetylglutarate.] N. M. Shah and R. C. Shah (Ber., 1939, 72, [*B*], 215; cf. A., 1938, II, 502).—7 : 8-Dihydroxy-4-methylcoumarin-3-propionic acid has m.p. 185°.

H. W.

Preparation of flavones from *o*-aroyloxyacetophenones. V. V. Ullal and T. S. Wheeler (Current Sci., 1938, 7, 280—281; cf. A., 1938, II, 452).—*o*-Aroyloxyacetophenones are more readily converted by NaOEt–EtOH than by Na–Et_2O or by Na–PhMe into ω-aroyl-*o*-hydroxyacetophenones.

J. L. D.

***iso*Flavans. I. Catalytic hydrogenation of *iso*flavones.** F. Wessely and F. Prillinger (Monats., 1938, 72, 197—199).—Hydrogenation (Pd–C) of formononetin (A., 1933, 614) in AcOH gives 7-*hydroxy*-4′-*methoxyisoflavan*, m.p. 160° (sinters at 155·5°) (*Me ether*, m.p. 116·5—117·5°). *iso*Anthocyanidin could not be obtained from *p*-OMe·C_6H_4·CH_2·CHO and 2 : 4 : 1-OH·C_6H_3(OMe)·CHO.

R. S. C.

Dihydrothiophen. J. M. Slobodin (J. Gen. Chem. Russ., 1938, 8, 714—718).—$(CH_2Br·CH{:})_2$ and Na_2S in 90—95% EtOH yield a rubber-like product, $(C_4H_6S_2)_n$, a highly unstable liquid product (I), probably $[S(CH·CH{:})_2]_2$, and divinyl; in 50% EtOH at the b.p. the sole products are (I) and *dihydrothiophen*, b.p. 103—105° (*compound* with $HgCl_2$, m.p. 92—94°; *methiodide*, m.p. 122—123°).

R. T.

Thioindigo dyes with ability to couple, obtained from β-naphtholthioglycollic acids. E. Jusa and R. Steckler (Monats., 1938, 72, 143—167).—Attempts to cyclise β-naphtholthioglycollic acids are described, the following being the most successful. Distillation of 2 : 7-OH·$C_{10}H_6$·S·CH_2·CO_2H, first at 180—220°/12 mm. and then at 10^{-3} mm., gives 4 : 7′-*dihydroxynaphtha*-2′ : 1′-2 : 3-*thiophen* (I), m.p. 92°. 2 : 6-OH·$C_{10}H_6$·S·CH_2·CO_2H and P_2O_5 in hot C_6H_6 give 4 : 6′-*dihydroxynaphtha*-2′ : 1′-2 : 3-*thiophen*, m.p. 130—133°, as 2-naphthol-6-thioglycollate; 4 : 6′-*dihydroxynaphtha*-1′ : 2′-, m.p. 102—105°, 4 : 6′-*dihydroxynaphtha*-2′ : 1′-, m.p. 130—133° (decomp.), 4 : 7′-*dihydroxynaphtha*-1′ : 2′-, m.p. 137—139° (decomp.), -2 : 3-*thiophen*, and (I) are similarly obtained. The products are oxidised by air to *dyes*, which have little val. owing to the care necessary for prep. ($Na_2S_2O_4$) of vats and to the dull tone and lack of substantivity or fastness to light of the products obtained therefrom by coupling.

R. S. C.

Stereoisomeric forms of 2-piperidino- and 2-dimethylamino-methyl*cyclo*pentanol. C. Mannich and P. Schaller (Arch. Pharm., 1938, 276, 575—582).—Piperidine hydrochloride, 40% aq. CH_2O, and *cyclo*pentanone at 100° give 2-*piperidinomethyl*cyclo*pentanone*, b.p. 123—125°/16 mm. [*semicarbazone*, m.p. 195°; *oxime*, m.p. 132—133°; *phenylhydrazone*, m.p. 88—89° (*hydrochloride*, m.p. 161—162°)], the *hydrochloride*, m.p. 145° (decomp.), of which at ~160° gives 2-methylene*cyclo*pentanone, an oil [*semicarbazone*, m.p. 219—220° (decomp.)], and with Na–Hg gives α- (I), b.p. 130—132°/11 mm. (*hydrochloride*, m.p. 210—211°; *benzoate*, m.p. 182—183°], and β-, b.p. 133—135°/14 mm. (*hydrochloride*, m.p. 204°; *benzoate*, m.p. 135—137°), *forms* of 2-*piperidinomethyl*cyclo*pentanol*, separated by way of the *p*-*nitrobenzoates*, m.p. 226—227° (decomp.) and 187—188°, respectively. $SOCl_2$–$CHCl_3$ converts (I) into 1-*chloro*-2-*piperidinomethyl*cyclo*pentane hydrochloride*, m.p. 186—187°. Similarly are prepared 2-*dimethylaminomethyl*-cyclo*pentanone*, b.p. 88—90°/15 mm. [*hydrochloride*, m.p. 131—132°; *semicarbazone*, m.p. 184—185° (decomp.); *oxime*, m.p. 158—159°], and -cyclo*pentanol*, α-, b.p. 95—97°/12 mm. [*hydrochloride*, m.p. 144—145°; *benzoate*, m.p. 199—200°; *p*-*nitrobenzoate*, m.p. 220° (decomp.)], and β-*form*, b.p. 96—98°/14 mm. (*hydrochloride*, m.p. 134—136°; *benzoate*, m.p. 177°; *p*-*nitrobenzoate*, m.p. 178—179°), and 1-*chloro*-2-*dimethylamino*cyclo*pentane*, b.p. 80—82°/14 mm. [*hydrochloride*, m.p. 176—177°; *methiodide*, m.p. 164—165° (decomp.); *methochloride*, m.p. 144—146°].

R. S. C.

Enimine betaines. I. F. Kröhnke (Ber., 1939, 72, [*B*], 83—89).—Addition of Br to $CH_2Bz·CN$ in

$CHCl_3$ followed successively by C_5H_5N and BzOH gives the *enol* form of *ω-cyanophenacylpyridinium benzoate* (I), OH·CPh:C(CN)·NC_5H_5·OBz, m.p. 149—150°, converted by N-NaOH into the free *enol-betaine*, m.p. 142—143° (*picrate*, m.p. 173° after softening). CH_2Br·CN and C_5H_5N in C_6H_6 at room temp. gradually yield cyanomethylpyridinium bromide (II), m.p. 161° (corresponding *perchlorate*, m.p. 125°), converted by BzCl and N-NaOH in $CHCl_3$ into (I). *ω-Cyanomethylpyridinium picrate* has m.p. 142—143°. (II) and *p*-NO·C_6H_4·NMe_2 in EtOH containing $NHEt_2$ yield the green *nitrone*, CN·CH:NO·C_6H_4·NMe_2, m.p. >140° (decomp.) dependent on the rate of heating. Cyanomethyl*iso*quinolinium bromide has m.p. 196—197°. CHPhBr·CN affords *cyanobenzylpyridinium bromide*, m.p. 160° (corresponding *perchlorate*, m.p. 121°), whence the corresponding betaine. *Cyanobenzyliso-quinolinium bromide*, m.p. 176° (decomp.), gives a violet ppt. with N-K_2CO_3. Similarly a green ppt. is obtained from *cyanobenzylquinolinium perchlorate*, m.p. 159°. CN·CH_2·CO_2Et affords *cyanocarbethoxy-methylpyridinium betaine*, m.p. 112—113° (*picrate*, 123—124°); Et_3 tricyanotrimethylenetricarboxylate, m.p. 119—120°, is obtained as by-product.

H. W.

3-Diazo-2-phenylindole. IV. S. CAPUANO (Gazzetta, 1938, **68**, 733—737).—The reaction between 3-amino-2-phenylindole and $NaNO_2$–AcOH (A., 1938, II, 68), when interrupted before completion, gives a *substance*, $C_{14}H_{12}O_3N_4$, decomp. 172°, which in AcOH forms diazophenylindole. E. W. W.

Quinoline derivatives as sources of medicinal products. VII. Anti-malarial compounds with branched side-chains in position 8, also 6-chloro- and 6-hydroxy-derivatives, and the influence of dimethylamino- and amino-groups in the side-chain. O. J. MAGIDSON and M. D. BOBISCHEV (J. Gen. Chem. Russ., 1938, **8**, 899—915).—NEt_2·$[CH_2]_2$·COMe and Na–Hg in dil. AcOH yield NEt_2·$[CH_2]_2$·CHMe·OH, b.p. 109—110°/52 mm., which with SO_2Cl_2 in C_6H_6 gives NEt_2·$[CH_2]_2$·CHMeCl (I), and with HBr gives *β-bromo-δ-diethylamino-butane*, b.p. 89—95°/9 mm. This condensed with 8-amino-6-methoxyquinoline (II) in EtOH (12 hr. at 105°, then 8 hr. at 110°) gives 8-(*γ-diethylamino-α-methylpropyl*)*amino-6-methoxyquinoline* (III), b.p. 203—206°/4 mm. [*dimeconate*, m.p. 145° (decomp.)]; the yield of (III) obtained with (I) is somewhat smaller. $NHEt_2$ and propylene oxide in EtOH at the b.p. yield OH·CHMe·CH_2·NEt_2, which with SO_2Cl_2 in Et_2O affords *β-chloro-α-diethylaminopropane*, b.p. 73—75°/50 mm. This with (II) in EtOH (36 hr. at 120°) yields 8-(*β-diethylamino-α-methylethyl*)*amino-6-methoxyquinoline* (IV), b.p. 185—190°/3 mm. The product of condensation of CHAcNa·CO_2Et and Cl·$[CH_2]_3$·NEt_2 (V) in xylene (15 hr. at 130°) is hydrolysed with 35% H_2SO_4 to *α-diethylaminohexan-ε-one*, b.p. 95—101°/10 mm., reduced (H_2, Pt) to *α-diethylaminohexan-ε-ol*, b.p. 110—112°/10 mm., which with HBr gives *β-bromo-ζ-diethylaminohexane*. This with (II) (40 hr. at 110°, then 20 hr. at 120°) gives 8-(*ε-diethylamino-α-methylamyl*)*amino-6-methoxyquinoline* (VI), b.p. 205—208°/1·5 mm. 6-Chloro-8-aminoquinoline with (V) (40 hr. at 110°) affords *6-chloro-8-(γ-diethylaminopropyl)aminoquinoline* (VII), b.p. 186—188°/5 mm.; the analogous product with (I) (40 hr. at 120°) is *6-chloro-8-(γ-diethylamino-α-methylpropyl)aminoquinoline* (VIII), b.p. 192—194°/6 mm. (II) and Cl·$[CH_2]_3$·NMe_2 (40 hr. at 125°) yield *8-(γ-dimethylaminopropyl)amino-6-methoxyquinoline* (IX), b.p. 190—191°/4 mm. 8-(γ-Diethylaminopropyl)amino-6-methoxyquinoline (X) with HBr at 170—175° (3 hr.) gives *8-(γ-diethylaminopropyl)-amino-6-hydroxyquinoline* (XI), b.p. 240—250°/5 mm. (*dihydrobromide*, $+1H_2O$, m.p. 135—137°). The chemotherapeutic indices (100 × min. curative/max. tolerated dose) of a series of substituted aminoalkylaminoquinolines are: (IV) 2, (III) 25, 8-(γ-diethylamino-α-methylbutyl)amino-6-methoxyquinoline 40, (VI) 25, (VII) 2·5, (VIII) 6·6, 8-(γ-aminopropyl)-amino-6-methoxyquinoline 13·3, (IX) 16·5, (X) 26·6, and (XI) 18·5. R. T.

Quinoline derivatives with a basic side-chain. C. MANNICH and O. SCHILLING (Arch. Pharm., 1938, **276**, 582—592).—3 : 4-CH_2O_2:C_6H_3·CH:CH·COMe (I) and 65% HNO_3 at −5° give 60—65% of the 6-NO_2-derivative, forms, m.p. 153° and 168° (cf. lit.). A 60% yield of *6-nitroveratrylideneacetone*, m.p. 179—180°, is similarly obtained. Piperidine hydrochloride, $(CH_2O)_3$, and (I) in hot, abs. EtOH give *γ-keto-ε-piperidino-α-6-nitro-3 : 4-methylenedioxyphenyl-Δ^α-butene hydrochloride, forms*, m.p. 178° and 148—149° (free base unstable), obtained much less well by nitration of CH_2O_2:C_6H_3·CH:CH·CO·$[CH_2]_4$·$C_5H_{11}N$ and converted by $SnCl_2$–HCl into 6 : 7-*methylenedioxy-2-β-1′-piperidinoethylquinoline*, m.p. 135°. *γ-Keto-ε-di-methyl-*, m.p. 205—206°, and *-ethyl-amino-α-3 : 4-methylenedioxyphenyl-Δ^α-butene hydrochloride*, m.p. 139° (free *base*, m.p. 97°), *γ-keto-ε-piperidino-*, m.p. 186°, *-ε-dimethylamino-*, m.p. 185°, and *-ε-diethylamino-α-3 : 4-dimethoxyphenyl-Δ^α-butene hydrochloride*, m.p. 179° (free *base*, m.p. 79°), 6 : 7-*methylenedioxy-2-β-di-methyl-* (II), m.p. 107° (*dihydrochloride*), and *-ethyl-aminoethylquinoline*, m.p. 80°, 6 : 7-*dimethoxy-2-β-1′-piperidino-*, an oil [*dihydrochloride*, m.p. 197—199° (decomp.)], *-β-dimethylamino-* (III), an oil (*hydrochloride*, m.p. 176°), and *-β-diethylaminoethylquinoline*, an oil (*dihydrochloride*, m.p. 182°), are obtained similarly. MeI attaches to the NMe_2 of (II) giving the *methiodide*, m.p. 203°, converted by NaOH into NMe_3 and 6 : 7-*methylenedioxy-2-vinylquinoline*, m.p. 138—139°, which with H_2–Pd in AcOH gives 6 : 7-*methylenedioxy-2-ethylquinoline*, m.p. 119°, and with $KMnO_4$ gives 6 : 7-*methylenedioxyquinoline-2-carboxylic acid*, m.p. 240°. (III) gives similarly a *methiodide*, m.p. ~215° (decomp.), and thence 6 : 7-*dimethoxy-2-vinyl-*, an oil [*hydrochloride*, m.p. ~225° (decomp.)], and *-2-ethyl-quinoline* (*hydrochloride*, m.p. 211°), and 6 : 7-*dimethoxyquinoline-2-carboxylic acid*, m.p. 216°. R. S. C.

Synthesis of *iso*quinoline acids. F. T. TYSON (J. Amer. Chem. Soc., 1939, **61**, 183—185).—NH_2·CH_2·$CH(OEt)_2$ and C_6H_4Br·CHO at 100° give ~90% yields of *o-* (I), b.p. 167—170°/6 mm., *m-* (II), b.p. 152—154°/4 mm., and *p-bromobenzylideneaminoacetal* (III), b.p. 160—165°/4 mm. With H_2SO_4–P_2O_5 at 160° (I) and (III) give 8- (6%) and

6-*bromo*isoquinoline (29%), oils, which with CuCN at 250° give 8- (53%), m.p. 133°, and 6-*cyano*isoquinoline (25%), m.p. 152°, hydrolysed by HCl at 150° to iso*quinoline*-8-, m.p. 292—294° (decomp.), and -6-*carboxylic acid*, m.p. 355—360° (decomp.), respectively. 4- and 5-Bromo*iso*quinoline (Claus *et al.*, A., 1893, i, 366) give similarly 4-, m.p. 104°, and 5-*cyano*isoquinoline, m.p. 139°, and iso*quinoline*-4-, m.p. 264—266°, and -5-carboxylic acid (IV) (Jeiteles, A., 1895, i, 393), m.p. 280—282°. (II) gives mixed bromo- and cyano-*iso*quinolines, hydrolysed to (I) and iso*quinoline*-7-*carboxylic acid*, m.p. 295—297°, which are separated by crystallising the Na salts from aq. dioxan. R. S. C.

Direct introduction of the amino-group into aromatic and heterocyclic nuclei. V. Action of metallic amides on phenyl- and benzo-quinolines. F. W. Bergstrom (J. Org. Chem., 1938, **3**, 424—433).—2-Phenylquinoline (I) is converted by the prolonged action of KNH_2 in liquid NH_3 followed by hydrolysis into a *diphenyltetrahydrodiquinolyl*, m.p. >280°. Less protracted action with alkali amides in liquid NH_3 gives additive compounds of unknown structure but of the type, $C_9H_6NPh,NaNH_2$; (I) is regenerated from them by the action of NH_4 salts. On keeping, secondary additive compounds are formed which do not react with NH_4 salts to give (I) but react with KNH_2 ($NaNH_2$) and KNO_3 ($NaNO_3$) or Hg to give 4-amino-2-phenylquinoline, m.p. 164·0—164·9°, thus: (I) + $2KNH_2$ + KNO_3 = KOH + KNO_2 + NH_3 + $C_9H_5NPh{\cdot}NHK$ (II) or (I) + $3KNH_2$ + xHg = K_2Hg_x + $2NH_3$ + (II). The yields of (II) are excellent. There is no evidence for or against the assumption that these reactions are stepwise. By using the same methods, 2(?)-*amino*-6-*phenyl*-, m.p. 243—243·5°, -8-*phenyl*-, m.p. 156—159°, -7 : 8-*benzo*-, m.p. 104—105° [*hydrochloride*, m.p. >288°; *picrate*, m.p. 259—262° (decomp.)], and -5 : 6-*benzo*-, m.p. 235°, -*quinoline* are obtained. In these cases the prep. may also be accomplished with $Ba(NH_2)_2$, when H_2 is evolved. 2-*p*-Tolylquinoline has not been converted into an NH_2-derivative. KNH_2 also converts 6- and 8-phenylquinoline into tars. The two benzoquinolines react with KNH_2 to form NH_2-derivatives in fair yield (25—35%) with small amounts of H_2. H. W.

Structure and absorption [spectra] of diamino-derivatives of acridine dyes. P. Ramart, M. Grumez, and M. Martynoff (Compt. rend., 1938, **207**, 1106—1109).—Hydrochlorides of acridine-yellow and -orange, benzoflavine, and tetramethylflaveosine in H_2O or EtOH have similar absorption spectra (*p*-quinonoid form). The spectra of 0·00005N. solutions of the bases resemble those of the hydrochlorides, but in 0·0005N. solutions the spectra are different, due to the *o*-quinonoid form, which is the only one present in 0·1N-NaOH or anhyd. dioxan. J. L. D.

Hydroxy- and methoxy-derivatives of acridine. S. M. Scherlin, G. I. Braz, A. J. Jakubovitsch, E. I. Vorobieva, and F. E. Rabinovitsch (J. Gen. Chem. Russ., 1938, **8**, 884—898).—1-Methoxyacridone (I), $NaHCO_3$, and Na–Hg in EtOH (CO_2 atm.) yield 1-methoxy-5 : 10-dihydroacridine, oxidised by $K_2Cr_2O_7$ to 1-methoxyacridine (II); reduction of (I) with Na in boiling $C_5H_{11}{\cdot}OH$, and oxidation of the product, gives a mixture of (II) and 1-hydroxyacridine. 4 : 2 : 1-$OMe{\cdot}C_6H_3Cl{\cdot}CO_2K$ and NH_2Ph in *iso*-$C_5H_{11}{\cdot}OH$ with Cu-bronze at 130—140° for 90 min. yield 5-methoxydiphenylamine-2-carboxylic acid, which with PCl_5 and $AlCl_3$ in C_6H_6 at 30—40° gives 2-methoxyacridone. This is reduced as above to 2-*methoxy*-5 : 10-*dihydroacridine*, m.p. 131—132°, oxidised (HNO_2) to 2-*methoxyacridine*, m.p. 248—250° (decomp.). 4-Methoxydiphenylamine-2′-carboxylic acid is condensed (PCl_5 and $AlCl_3$ in C_6H_6, at room temp.) to 3-methoxyacridone (III), m.p. 291—292° [Borsche *et al.* (A., 1933, 1170) give m.p. 263—265°]; condensation in boiling C_6H_6 yields 3-*hydroxyacridone* (IV), +H_2O, m.p. 337—340° (decomp.); (III) and (IV) are reduced as above to the corresponding 5 : 10-H_2-derivatives, m.p. 140—141° and 181—185°, respectively, and these are oxidised to 3-methoxy-[*hydrochloride*, m.p. 237—239° (decomp.)], or 3-*hydroxy-acridine*, sinters at 278°, m.p. 282—284°. 3-Methoxydiphenylamine-2′-carboxylic acid in C_6H_6 and PCl_5 in presence of $AlCl_3$, at room temp., yield a mixture of 2- and 4-*methoxyacridone*, m.p. 155—156°. 2 : 5-Dimethoxyaniline in *iso*-$C_5H_{11}{\cdot}OH$ and *o*-$C_6H_4Cl{\cdot}CO_2K$ in presence of Cu and CuCl (3 hr. at 135—140°) yield 2 : 5-*dimethoxydiphenylamine*-2′-*carboxylic acid*, m.p. 164·2—164·8°, which with PCl_5 and $AlCl_3$ in C_6H_6 (2 hr. at the b.p.) gives 5-*chloro*-1 : 4-*dimethoxyacridone* (V), +EtOH, m.p. 200—201°, whilst with $POCl_3$ at 130—140° the product is 5-*chloro*-1 : 4-*dimethoxyacridine*, +$2H_2O$, m.p. 145·5—146°. This when boiled with HCl yields 1 : 4-*dimethoxyacridone*, m.p. 222—223°, also obtained from (V) and PCl_3 at 70°, and from which 1 : 4-*dimethoxyacridine*, m.p. 130—130·5°, is obtained as before. 2-Chloro-3-methoxybenzoic acid, *o*-anisidine, K_2CO_3, and Cu-bronze in boiling *iso*-$C_5H_{11}{\cdot}OH$ (3 hr.) yield 2 : 2′-*dimethoxydiphenylamine*-6-*carboxylic acid*, m.p. 176—177°, which with $POCl_3$ (2·5 hr. at 160°) gives 1 : 9-*dimethoxyacridone*, m.p. 274—275°, converted as above via the 5 : 10-H_2-derivative, m.p. 91—92·5°, into 1 : 9-*dimethoxyacridine*, m.p. 195—196°. R. T.

***meso*-Derivatives of acridine. IX. Chlorides of diphenylaminecarboxylic acids, and their conversion into acridones.** N. S. Drozdov (J. Gen. Chem. Russ., 1938, **8**, 937—942).—The following acid chlorides are obtained from diphenylaminecarboxylic acids and PCl_5 in light petroleum (at room temp. or at the b.p.): *chloride* of 4′-*methoxy*-, m.p. 73°, 5-*chloro*-4′-*methoxy*-, m.p. 110—111°, and 2′ : 4′-dinitro-diphenylamine- (I), and *diphenylamine*-2-*carboxylic acid*, m.p. 50°. (I) fused with PhOH at 100° yields *Ph* 2′ : 4′-*dinitrodiphenylamine*-2-*carboxylate*, m.p. 183—184°; the remaining chlorides give acridone under these conditions, or when heated at above their m.p. R. T.

Synthesis of the next higher and lower homologues of *l*-carnosine: γ-aminobutyryl- and glycyl-*l*-histidine. M. Hunt, and V. du Vigneaud (J. Biol. Chem., 1939, **127**, 43—48).—Carbobenzyloxyglycyl chloride (cf. A., 1932, 935) with histidine Me ester (I) in dry $CHCl_3$ at 0° affords a

product hydrolysed (NaOH at room temp.) to *carbobenzyloxyglycyl-l-histidine* (II), m.p. 175°, $[\alpha]_D^{25}$ +22° in H_2O, reduced (H_2–Pd) in aq. HCl to glycyl-*l*-histidine (*hydrochloride* + $1H_2O$, m.p. 175°) (cf. A., 1931, 1191). Reduction (H_2–Raney Ni) of aq. $CH_2Br{\cdot}CH_2{\cdot}CO_2Na$ containing NaCN at 40—50° followed by interaction with $CH_2Ph{\cdot}COCl$ at 0° gives *carbobenzyloxy-γ-aminobutyric acid* (III), m.p. 66°. (III) with PCl_5 in Et_2O at 0° affords the chloride, which with (I) in $CHCl_3$, followed by hydrolysis (cold 4N-NaOH) and reduction [as for (II)], affords γ-aminobutyryl-*l*-histidine (*sulphate*, m.p. 235°, $[\alpha]_D^{25}$ +5° in H_2O). Neither peptide in 20 times the dose of *l*-carnosine has any effect on the blood pressure of cats anæsthetised with amytal. The β-NH_2-group in the acyl moiety of carnosine is mainly responsible for its depressor action. J. L. D.

Synthesis of barbituric acid derivatives with an acid side-chain. B. REICHERT and W. WILKE (Arch. Pharm., 1938, **276**, 596—605).—$CRNa(CO_2Et)_2$ and $Br{\cdot}[CH_2]_3{\cdot}CO_2Et$ in abs. EtOH give *Et*$_3$ Δ^δ-*heptene*-αδδ-, b.p. 188—192°/12 mm., *η-methyloctane*-αδδ-, b.p. 189—191°/11 mm., and *ε-phenylpentane*-αδδ-*tricarboxylate*, b.p. 232—234°/15 mm. By condensation with $CO(NH_2)_2$ and NaOEt in EtOH at 150° are obtained γ-2 : 4 : 6-*triketo*-5-*ethyl*- (I), m.p. 222°, -5-n-*propyl*-, m.p. 208°, -5-iso*amyl*-, m.p. 191—192°, -5-*allyl*-, m.p. 182°, and -5-*benzyl*-, m.p. 214°, -*hexahydro*-5-*pyrimidyl*-n-*butyric acid*. Attempts to convert the *Et* ester, m.p. 112°, of (I) into the amide failed. Similar syntheses lead to *Et*$_2$ *diethylcarbamylmethylethylmalonate*, b.p. 194—196°/14 mm., ββ-*dicarbethoxy*-n-*valer*-, b.p. 198—200°/18 mm., -Δ^δ-*hexeno*-, b.p. 192°/14 mm., and -δ-*phenylbutyr-diethylamide*, b.p. 235—236°/8 mm., 2 : 4 : 6-*triketo*-5-*ethyl*-, m.p. 221°, -5-n-*propyl*-, m.p. 206—207°, -5-*allyl*-, m.p. 190°, and -5-*benzyl-hexahydro*-5-*pyrimidylacetdiethylamide*, m.p. 247—248°, 4 : 6-*diketo*-2-*thio*-5-n-*propylhexahydro*-5-*pyrimidylacetdiethylamide* (prep. at 170°), m.p. 196°, and 2 : 4 : 6-*triketo*-5-*ethylhexahydro*-5-*pyrimidylbutyrdiethylamide*, m.p. 172°. $Br{\cdot}[CH_2]_3{\cdot}Cl$, $CHR(CO_2Et)_2$, and NaOEt in hot EtOH give $CH_2[CH_2{\cdot}CR(CO_2Et)_2]_2$, which yield *αγ-di*-(2 : 4 : 6-*triketo*-5-*ethyl*-, m.p. 317—318°, -5-n-*propyl*-, m.p. 253—254°, and -5-*allyl-hexahydro*-5-*pyrimidyl*)-*propane*, m.p. 218°, *αγ-di*-(2 : 4 : 6-*triketo*-1-*methyl*-5-*ethyl*-, m.p. 261°, and -5-*benzyl*-1-*methyl-hexahydro*-5-*pyrimidyl*)*propane*, m.p. 272—273°. *Et*$_4$ *αη-diphenylheptane*-ββζζ-*tetracarboxylate*, m.p. 77°, b.p. 300—305°/12 mm., is described. R. S. C.

Substituted vinylbarbituric acids. I. *iso*-Propenyl derivatives. A. C. COPE and E. M. HANCOCK (J. Amer. Chem. Soc., 1939, **61**, 96—98).—Et_2 alkyl*iso*propenylmalonates with $CO(NH_2)_2$ or $CS(NH_2)_2$ and NaOEt in abs. EtOH at 105° give 5-*methyl*-, m.p. 181—181·5°, -*ethyl*-, m.p. 184—184·2°, -*propyl*-, *forms*, m.p. 149—150° and (unstable) 158·5—159·5°, respectively, -*allyl*-, m.p. 144·4—145°, -n-, m.p. 156—157°, and -iso-*butyl*-, m.p. 161·5—162·5°, -n-, m.p. 123—124°, and -iso-*amyl*-, m.p. 128—129°, -*benzyl*-, m.p. 231·5—232·5°, 1-*methyl*-5-*ethyl*-, m.p. 125·5—126°, 1 : 5-*diethyl*-, m.p. 67—68°, and 5-*ethyl*-1-*allyl*-, m.p. 65—66°, -5-iso*propenylbarbituric acid* and 5-*methyl*-, m.p. 154—155°, -*ethyl*-, m.p. 191—192°, -*propyl*-, m.p. 184—185°, -*allyl*-, m.p. 176·5—177°, -n-, m.p. 160—161°, and -iso-*butyl*-, m.p. 164—165°, -n-, m.p. 139—140°, and -iso-*amyl*-, m.p. 165·5—166·5°, and -*benzyl*-, m.p. 157—158°, -5-iso*propenylthiobarbituric acid*. Pharmacological data are recorded. Alcoholysis during the preps. leads to smaller amounts of β-*methyl*-α-*ethyl*-, m.p. 151—151·5°, -α-n-, m.p. 115—116°, and -α-iso-*butyl*-, m.p. 128—128·2°, -α-n-, m.p. 111—112°, and -α-iso-*amyl*-, m.p. 108—109°, and -α-*benzyl*-, m.p. 122—122·5°, -*crotonamide*, the structure of which is shown by production of $COMe_2$, and not of CH_2O, by O_3. *Et*$_2$ *benzyl*iso-*propenylmalonate* boils at 141—142°/1 mm. R. S. C.

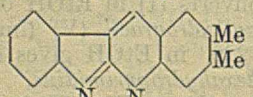
Pyrimidines. CLX. Catalytic hydrogenation of 5- and 6-benzyluracils. J. C. AMBELANG and T. B. JOHNSON (J. Amer. Chem. Soc., 1939, **61**, 74—77).—The CH_2Ph of 5- (I), but not of 6- (II), -benzyluracil is hydrogenated catalytically in EtOH. H_2–Raney Ni at 175° reduces (II) to *benzylhydrouracil* (III), m.p. 223—224° (hydrolysed by 15% aq. NaOH to $CHPh{:}CH{\cdot}CH_2{\cdot}CO_2H$), but at 225° gives 2-*keto*-6-*benzylhexahydropyrimidine* (IV), m.p. 184—185°, obtained similarly from (III), oxidised to BzOH, and hydrolysed to αγ-diamino-δ-phenylbutane (*dihydrochloride*, m.p. 145—146°; *Bz*$_2$ derivative, m.p. 174—175°). H_2–Cu–Cr_2O_3 at 200° converts (II) into (IV). H_2–Raney Ni at 175° converts (I) in EtOH or, less well, dioxan into 5-*benzylhydrouracil* (V) (impure), m.p. 232°, but at 200—220° in EtOH gives slowly 2-*keto*-5-cyclo*hexylmethylhexahydropyrimidine*, m.p. 221—223°. H_2–Cu–Cr_2O_3 reduces (I) or (V) in EtOH (very slowly in dioxan) to 2-*keto*-5-*benzylhexahydropyrimidine*, m.p. 214—215°. R. S. C.

Pyrimidines and quinazolines.—See B., 1939, 177.

Simple cyanines. B. BEILENSON and (MISS) F. M. HAMER (J.C.S., 1939, 143—151).—The known methods for preparing monomethincyanines are reviewed. 2-Thiolquinoline with Me_2SO_4 gives 2-*methyl*- (I), m.p. 55°, and with Et_2SO_4 affords 2-*ethyl-thiolquinoline*, b.p. 177—178°/26 mm. [*ethiodide*, m.p. 165° (decomp.); *etho*-p-*toluenesulphonate*, m.p. 116°]. (I) yields a *methiodide*, m.p. 193°, and *metho*-p-*toluenesulphonate*, m.p. 160°, and with EtI gives 2-*ethylthiolquinoline methiodide*, m.p. 185° (decomp.). This and 2-aminoquinoline ethiodide afford (K_2CO_3) 1-*methyl*-1′-*ethyl*-2 : 2′-*azacyanine iodide* [(1-*methyl*-2-*quinoline*)(1-*ethyl*-2-*quinoline*)*azamethincyanine iodide*], m.p. about 235° (decomp.); 1 : 1′-*dimethyl*-2 : 2′-*azacyanine iodide*, m.p. 273—275° (decomp.), is similarly prepared. 1-Methylthiolbenzthiazole forms a *methiodide*, m.p. 146° (decomp.), *ethiodide* (II), m.p. 135—137° (decomp.), and *metho*-p-*toluenesulphonate*, m.p. 167—168°. 1-Ethylthiolbenzthiazole yields an *ethiodide*, m.p. 95—96°. From the appropriate reagent and (II), the following dyes have been prepared: 2 : 2′-*diethyl*-5 : 6-*benz*-, m.p. 299° (decomp.), 2 : 2′-*diethylselena*-, m.p. 284° (decomp.), 2 : 2′-*diethyl*-3 : 4-*benzoxa*-, m.p. 288° (decomp.), and 2 : 2′-*diethyl*-5 : 6-*benzoxa-thiacyanine iodide*, m.p. 278° (decomp.). Methylation of the appropriate reagent leads to 1-*methylthiolbenzoxazole* (III), b.p. 139—140°/21 mm., 2-*methylthiol*-β- (IV), m.p. 73° (from 2-thiol-β-naphth-

oxazole, m.p. 264°), and 1-*methylthiol*-α-*naphthoxazole* (V), m.p. 64°. Lepidine, (III), and Et *p*-toluenesulphonate give 2 : 1′-*diethyloxa*-4′-*cyanine iodide*, m.p. 233° (decomp.), and (V) with β-naphthaquinaldine similarly forms 2 : 1′-*diethyl*-5 : 6 : 5′ : 6′-*dibenzoxa*-2′-*cyanine iodide*, m.p. 288° (decomp.). MeI with (IV), (V), and (III) yields respectively 2-*thio*-1-*methyl*- (VI), m.p. 185—187°, and 1-*thio*-2-*methyl*-1 : 2-*dihydro*-α-*naphthoxazole*, m.p. 226°, and 1-*thio*-2-*methyl*-1 : 2-*dihydrobenzoxazole*, m.p. 133°; EtI and (V) give 1-*thio*-2-*ethyl*-1 : 2-*dihydro*-α-*naphthoxazole*, m.p. 215°. 1-Methylbenzthiazole, (VI), and Me *p*-toluenesulphonate afford 2 : 2′-*dimethyl*-3 : 4-*benzoxathiacyanine p-toluenesulphonate*, m.p. 262°. 2-Thio-1-methyl-1 : 2-dihydroquinoline and Me *p*-toluenesulphonate give a *salt*, m.p. 160—161°, which with 1-methylbenzthiazole methiodide forms 2 : 1′-dimethylthia-2′-cyanine iodide. F. R. S.

Azines. W. Bednarczyk and L. Marchlewski (Biochem. Z., 1938, **300**, 46—55).—Alloxan, o-$C_6H_4(NH_2)_2$,2HCl and excess of NaOAc in H_2O at 100° give 2-*hydroxy*-3-*carbamylcarbamylquinoxaline* (I), m.p. 238—239°. 2-*Hydroxy*-3-o-*aminophenylquinoxaline* (II), m.p. 258—260°, is obtained by condensing acetylisatin with o-$C_6H_4(NH_2)_2$ and hydrolysing the product. *N*-Ribitylaminoxylidine and isatin give N-*ribityldimethylindophenazine* (III). The absorption



(III.)

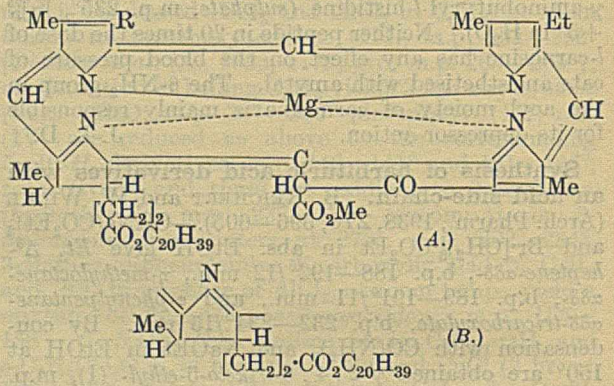
$CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}OH$

spectra of (I) in aq. and alkaline solution have been determined. In the former case the mol. extinction curve has 2 max. and 2 min., whilst in the latter case there are only 1 max. and 1 min. The absorption spectra of alcoholic solutions of indophenazine, (II), (III), and coumarophenazine together with their mol. extinction curves have been determined. J. N. A.

Union of nucleotides in ribonucleic acid. R. S. Tipson and P. A. Levene (J. Biol. Chem., 1939, **127**, 105—110).—The "guanine-uridylic acid" of Bredereck and Richter (A., 1936, 868) is a mixture of ribonucleosides, nucleotides, and free purines. J. L. D.

Constitution of polynucleotides. Deamination of yeast- and thymo-nucleic acid.—See A., 1939, III, 326.

Chlorophylls. LXXXIV. Chlorophyll. H. Fischer and H. Wenderoth (Annalen, 1939, **537**, 170—177; cf. A., 1938, II, 297).—Oxidation of chlorophyll derivatives is so conducted that acidic and basic products are isolated or proved to be absent. Porphyrins, but not chlorins or phorbides, give hæmatic acid (I). Vinyl, HCO-, and CO_2H-derivatives give no basic products, but deuterohæmin gives citraconimide (II), and pyrroporphyrin and phyllochlorin give a 1 : 2 mixture of (II) and methylethylmaleimide (III). Pyrrolines (crypto- and opso-pyrroline) give no (III), but crypto- and opso-pyrrole do so. Lævorotatory fractions are isolated from the acids obtained from phæopurpurin-7 [gives also (III)], phyllochlorin, mesophæophorbide-*a* [gives also (III)], and phæophorbide-*b*, but not from pyrroporphyrin [gives also (I), (II), and (III)]. It follows that chlorophyll-*a* is (*A*) (R = CH:CH_2) or, less probably, a structure containing the unit (*B*) with the necessary rearrangement of the other linkings. Chlorophyll-*b* is (*A*) (R = CHO). Oxidation of bacteriochlorin-e_6 gives a dextrorotatory basic and a lævorotatory acidic fraction; thus bacteriochlorophyll is probably a 3 : 4 : 7 : 8-H_4-derivative, and bacteriochlorin and bacteriophorbide are derived from (*B*). The following oxidation products are also recorded, those not named being absent:



(*A*.)

(*B*.)

phæophorbide-*a*, pyrophæophorbide-*a*, chlorin-e_6, and mesorhodochlorin give (II); phæoporphyrin-a_5 gives (I) and (II); deuterohæmin gives (I) and (II); protoporphyrin gives (I); rhodin-g_7 does not give (I), (II), or (III). R. S. C.

New case of chemoluminescence. II. Benzoporphins. V. J. H. Helberger and D. B. Hevér (Ber., 1939, **72**, [*B*], 11—15; cf. A., 1938, II, 510).—Only a very slight luminescence, mainly at the zone of contact of solution and air, is observed when Mg phthalocyanine (I) is introduced into boiling, pure tetrahydronaphthalene (II), which thus behaves very differently from the technical product. The hypothesis that the active agent is a peroxide (III) of (II) is confirmed by the observation that this compound provokes luminescence slightly in boiling C_6H_6, more markedly in boiling PhMe. Technical PhMe contains small amounts of a non-volatile, active material whilst pure PhMe can be "activated" by prolonged passage of air at 50—60°. Experiments in PhMe show that 1 mol. of (I) requires 13—16 mols. of (III) for complete reaction; the formation of H_2O and NH_3 is speedily obvious. The first phase of the change appears to result in the removal of Mg and the cyclic residue is then decomposed with formation of NH_3 and o-$C_6H_4(CO)_2NH$. The necessary H_2O results from the decomp. of (III) into H_2O and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. Similar complexes of Zn and Pb behave analogously but more feebly. Cu and Fe complexes and metal-free pigments give luminescence with (III) only in solvents of high b.p. [PhCl; cymene (IV); tetrahydronaphthalene]. The luminescence of (I) is more marked in xylene than in PhMe and is particularly obvious in (IV). Zn tetrabenzoporphin and (I) give an unidentified *substance*, $C_{10}H_{16}O_2$, m.p. 157—158°. Peroxidised oil of turpentine and technical decahydronaphthalene are very "active," whereas PhCl and PhBr are

ineffective. Little or no luminescence is observed when BuOH, amyl alcohol or acetate, dioxan, C_5H_5N, quinoline, piperidine, or Ac_2O is used.

H. W.

Phenylpropiolthio-*p*-chloroanilide. D. E. Worrall and E. Lavin (J. Amer. Chem. Soc., 1939, **61**, 104—105).—*Phenylpropiolthio*-p-*chloroanilide* (I), m.p. 138—139° (decomp.), obtained from CPh:CNa and *p*-C_6H_4Cl·NCS in Et_2O at room temp., gives with NaOH in hot Et_2O a *dimeride*, m.p. 245—246° (decomp.), which with Br–$CHCl_3$ affords a poor yield of the *dibromide*, m.p. 229—230° (decomp.), of (I). With NH_2OH, (I) gives 3-p-*chloroanilino*-5-*phenyl*iso*oxazole*, m.p. 166—167° [and a small amount of 5-*chloro*-1-*phenacylbenzthiazole*, m.p. 192—193° (decomp.)], and thence 4-*bromo*-3-4′-*chloro*-2′-*bromo*-, m.p. 133—134°, 4-*chloro*-3-2′ : 4′-*dichloro*-, m.p. 95—96°, and 4-*nitro*-3-4′-*chloro*-2′-*nitro*-*anilino*-5-*phenyl*iso*oxazole*, m.p. 165—166°. With N_2H_4 (I) yields 3-p-*chloroanilino*-5-*phenylpyrazole*, m.p. 174—175°, and thence 4-*bromo*-3-4′-*chloro*-2′-*bromoanilino*-5-*phenylpyrazole*, m.p. 198—199°. *Phenylpropiolthio*-m-*chloroanilide*, m.p. 115—116° (decomp.), also yields [as for (I)] a *polymeride*, m.p. 227—228° (decomp.).

R. S. C.

Reactions of phenylpropiol[thio]-*p*-iodoanilide and related thioamides. D. E. Worrall, M. Lerner, and J. Washnock, jun. (J. Amer. Chem. Soc., 1939, **61**, 105—106).—CPh:CNa and RNCS in Et_2O give *phenylpropiol*-p-*iodoanilide*, m.p. 140—141° (*dimeride*, m.p. >173°), -m-*bromoanilide*, m.p. 120—121° (*dimeride*, m.p. indefinite), -p-*phenetidide*, m.p. 111—112° (*dimeride*, m.p. 199—200°), -4′-*xenylamide*, m.p. 128—129° (*dimeride*, m.p. 230—232°), and -α-*naphthalide*, m.p. 184—185°, which with NH_2OH or N_2H_4 yield 3-p-*iodoanilino*-, m.p. 148—149°, and 3-4′-*xenylamino*-5-*phenyl*iso*oxazole*, m.p. 176—177°, 3-p-*iodoanilino*-, m.p. 175—176°, 3-m-*bromoanilino*-, m.p. 205—206°, and 3-4′-*xenylamino*-5-*phenylpyrazole*, m.p. 219—220°, converted by substitution into 4-*bromo*-, m.p. 172—173°, 4-*chloro*-, m.p. 151—152°, and 4-*nitro*-3-p-*iodoanilino*-5-*phenyl*iso*oxazole*, m.p. 243—244°, 4-*bromo*-3-2′-*bromo*-4′-*iodoanilino*-, m.p. 201—202°, 4-*chloro*-3-p-*iodoanilino*-, m.p. 206—207°, and 4-*bromo*-3-m-*bromoanilino*-5-*phenylpyrazole*, m.p. 178—179°. 4-*Bromo*-3-3′-*bromo*-, m.p. 130—131°, and 4-*chloro*-3-3′ : 5′-*dichloro*-p-*toluidino*-5-*phenyl*iso*oxazole*, m.p. 229—230°, 3-p-*toluidino*-, m.p. 157—158°, 4-*bromo*-3-3′-*bromo*-p-*toluidino*-, m.p. 181—182°, and 4-*nitro*-3-3′ : 5′-*dinitro*-p-*toluidino*-5-*phenylpyrazole*, m.p. 245—247°, are also prepared.

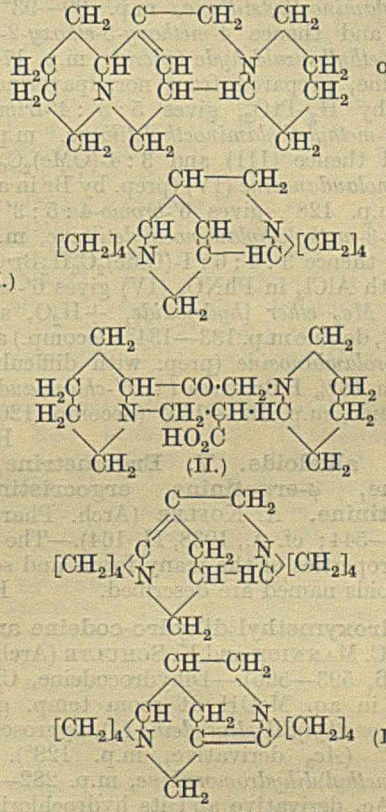
R. S. C.

Cyanine dyes.—See B., 1939, 217, 218.

The green fluorescent pigment of *Pseudomonas fluorescens*. A. Turfreijer, J. P. Wibaut, and T. Y. Kingma Boltjes (Rec. trav. chim., 1938, **57**, 1397—1404; cf. Turfitt, A., 1937, III, 145; Giral, A., 1937, III, 145).—The pigment (I) isolated by the Giral method (cf. György *et al.*, A., 1934, 461) (absorption on C; treating with $COMe_2$–H_2O; pptg. with phosphotungstic acid and decomp. with HCl) is isolated as an amorphous double *salt*, (?) $C_{32}H_{41}O_8N_7$,2HAuCl$_4$. A second pigment in the culture (medium used: NH_4 lactate, K_2HPO_4, and $MgSO_4$ in H_2O, of p_H 7·2) is not absorbed on the C. (I) and H_2O_2–KOH afford *salts*, (?) $C_{27}H_{35}O_2N_7$,2HAuCl$_4$, decomp. ~170°, and (?) $C_{11}H_{16(18)}ON_8$,3AuCl or $C_{18}H_{25}O_2N_{13}$,5AuCl. (I) and soda-lime at 400°, in N_2, give a *compound*, (?) $C_{32}H_{41}O_8N_7$, in which the green fluorescence persists. The configuration responsible, possibly of one O and a heterocyclic ring with 2 N, is stable.

A. T. P.

Lupin alkaloids. XVI. Oxidative degradation of Wolffenstein's dehydrosparteine. K. Winterfeld and M. Schirm (Arch. Pharm., 1938, **276**, 544—552; cf. A., 1938, II, 72).—Wolffenstein's dehydrosparteine (I) (modified prep.; cf. A., 1927, 887), m.p. 172—173°, $[\alpha]_D$ −236° in $CHCl_3$, −192° in EtOH [*aurichloride*, $+H_2O$, m.p. 181° (decomp.); *platinichloride*, $+3{\cdot}5H_2O$, m.p. 250° (decomp.); *picrate*, m.p. 181—182° (decomp.)], with CrO_3–H_2SO_4 gives a *keto-acid* (II), $C_{15}H_{24}O_3N_2$ [*dihydrochloride*,



m.p. 248° (decomp.); *platinichloride*, $+2H_2O$, m.p. 256°; *diaurichloride*, m.p. 211° (decomp.); *Me* ester *dihydrochloride* and *diaurichloride*, m.p. 202° (decomp.)]. HNO_3 gives $(CH_2{\cdot}CO_2H)_2$. These and recorded data indicate the structures shown. Spartyrine is (IIIa) or (IIIb).

R. S. C.

Synthetic experiments in the benzyl*iso*quinoline series. III. Laudanosoline 3′ : 7-dimethyl ether from laudanosine. C. Schöpf and K. Thierfelder (Annalen, 1939, **537**, 143—156; cf. A., 1932, 1040).—With 4·5 mols. of $AlCl_3$ in $PhNO_2$, first at 18—50° and then at 80—85°, laudanosine (I) is only partly changed and gives 8% of laudanine (*hydro-*

bromide, $+3H_2O$, sinters at 72°, m.p. 76—77°, loss of H_2O at 117—119°) (*i.e.*, demethylation at $C_{(3)}$), which with Et_2SO_4 gives the Et ether ethosulphate and thence by NaOH crude 4 : 5 : 4′-*trimethoxy*-3′-*ethoxy*-2-β-*methylethylaminoethylstilbene*, m.p. 107—109° (sinters at 100°), oxidised by O_3 to 3 : 4-OEt·C_6H_3(OMe)·CHO and 4 : 5-*dimethoxy*-2-β-*methylethylaminoethylbenzaldehyde* (II) [*picrate*, m.p. 185° (sinters at 182°)]. However, with 6 mols. of $AlCl_3$ (I) gives *laudanosoline* 3′ : 7-Me_2 *ether*, an oil [*hydrobromide*, $+H_2O$, m.p. 175—176° (sinters at 167°)], similarly degraded to 5 : 3′-*dimethoxy*-4 : 4′-*diethoxy*-2-β-*methylethylaminoethylstilbene*, m.p. 114—116° (*picrate*, m.p. 193—194°), and thence to 4 : 3 : 1-OEt·C_6H_3(OMe)·CHO and 5-*methoxy*-4-*ethoxy*-2-β-*methylethylaminoethylbenzaldehyde* (III) (*picrate*, m.p. 144—145°). Codamine, prepared from protopapaverine methohydroxide by H_2–PtO_2 in EtOH at 50—55°, gives crude 4 : 3′ : 4′-*trimethoxy*-5-*ethoxy*-2-β-*methylethylaminoethylstilbene*, m.p. 90—93° (sinters at 82°), and thence 4-*methoxy*-5-*ethoxy*-2-β-*methylethylaminoethylbenzaldehyde* (*picrate*, m.p. 174—175°). ψ-Laudanine, prepared from norpapaverine methochloride by H_2–PtO_2, gives 5 : 3′ : 4′-*trimethoxy*-4-*ethoxy*-2-β-*methylethylaminoethylstilbene*, m.p. 110—111°, and thence (III) and 3 : 4-$(OMe)_2C_6H_3$·CHO. dl-6′-*Bromolaudanosine* (IV) (prep. by Br in aq. AcOH at 3°), m.p. 128°, gives 6′-*bromo*-4 : 5 : 3′ : 4′-*tetramethoxy*-2-β-*methylethylaminoethylstilbene*, m.p. 128—129°, and thence 3 : 4 : 6 : 1-$(OMe)_2C_6H_2Br$·CHO and (II). With $AlCl_3$ in $PhNO_2$ (IV) gives 6′-*bromolaudanosoline* Me_2 *ether* [*hydriodide*, $+H_2O$, sinters at 115—117°, double m.p. 133—134° (decomp.) and 215°]. (?6′-)*Chlorolaudanosine* (prep. with difficulty), m.p. 131°, with 48% HBr gives (?) 6′-*chlorolaudanosoline hydrobromide*, m.p. 100—105° (decomp. 120°).

R. S. C.

Ergot alkaloids. V. Ergometrine, ergometrinine, ψ-ergotinine, ergocristine, and ergocristinine. A. Kofler (Arch. Pharm., 1938, **276**, 525—544; cf. A., 1938, II, 164).—The crystallo-optical properties of the many forms and solvates of the alkaloids named are described. R. S. C.

Di(hydroxymethyl)dihydro-codeine and -morphine. C. Mannich and K. Schulte (Arch. Pharm., 1938, **276**, 593—596).—Dihydrocodeine, CH_2O, and $Ca(OH)_2$ in aq. MeOH at room temp. give 7 : 7-*di*(*hydroxymethyl*)*dihydrocodeine* (I), hygroscopic, m.p. 110—113° (Ac_3 derivative, m.p. 128°). 7 : 7-*Di*(*hydroxymethyl*)*dihydromorphine*, m.p. 282—283° (decomp.) (Ac_4 derivative and its hydrochloride, amorphous), is similarly prepared and with CH_2N_2 in MeOH–Et_2O gives (I). R. S. C.

Decomposition of alkaloids in aqueous solution. IX. Photochemical change of codeine and codeinone. R. Dietzel and L. Stadelman (Arch. Pharm., 1938, **276**, 621—633; cf. B., 1934, 780).—Photochemical decomp. of codeine (I) involves oxidation, is independent of the solvent, but varies with the temp., not occurring at −3°. Acetylcodeine is stable. Codeinone (II) undergoes similar decomp., which, however, is independent of O_2. Decomp. of (I) thus proceeds by way of (II), but attempts to isolate (II) from the products failed. R. S. C.

Belladonnine. W. Küssner (Arch. Pharm., 1938, **276**, 617—620).—At 110° *apo*atropine gives *belladonnine*, $C_{34}H_{42}O_4N_2$, m.p. 129° (corr.) (*sulphate*; *dihydrochloride*, m.p. ~195—196°), resistant to fission by acid, but converted by NaOH–aq. EtOH at 100° into β-isatropic acid and tropine. R. S. C.

New synthesis of aromatic arsenic compounds. W. A. Waters (Nature, 1938, **142**, 1077).—Aromatic As compounds are formed by warming a diazonium chloride with powdered As and $CaCO_3$ under $COMe_2$. PhN_2Cl yields a H_2O-sol. product from which $AsPh_3S$ is pptd. by H_2S. Bi is attacked under similar conditions, but aromatic bismuthines are either not formed or are unstable under the conditions prevailing. Au yields $AuCl_3$, but Tl is unattacked. L. S. T.

Amides of β-*p*-arsonophenylpropionic acid. E. Walton (J.C.S., 1939, 156—158).—β-p-*Arsonophenylpropionic acid* (*Na* salt), prepared from the NH_2-acid, gives the *Me* ester (*Na* salt), which reacts with the appropriate amine to form β-*phenylpropionamide*- [*Na* salt ($+H_2O$)], β-*phenylpropionomethyl*- (*Na* salt), -*dimethyl*- [*Na* salt ($+H_2O$)], -*ethyl*- [$NHEt_2$ salt; *Na* salt ($+2H_2O$)], and -n-*propyl-amide*- [*Na* salt ($+H_2O$)], -*piperidide*- (*Na* salt), and -*anilide*-p-*arsinic acid* (*Na* salt). These amides show some trypanocidal activity, but they are all more toxic than the analogues of the corresponding AcOH series. F. R. S.

***p*-Acetonyl- and *p*-phenacyl-oxyphenylarsinic acid.**—See B., 1939, 216.

Arsonium compounds. II. F. F. Blicke, H. H. Willard, and J. T. Taras (J. Amer. Chem. Soc., 1939, **61**, 88—90; cf. A., 1938, II, 166).—From AsR_3 and RHal at 100° are prepared: *triphenyl-allyl*-, m.p. 180—181° (*iodide*, m.p. 163—164°), -p-*nitrobenzyl*-, m.p. 160—162°, -p-*bromophenacyl*-, m.p. 170—171°, *Et*$_2$ *triphenylmalonate*-, m.p. 169—171°, -*arsonium bromide*; *triphenylbenzylarsonium iodide*, m.p. 155—157°, and *chloride*, m.p. 180—181°; *tribenzylallylarsonium bromide*, m.p. 180—182°; *diphenyl*-α-*naphthylbenzylarsonium iodide*, m.p. 171—172°; and *trisdiphenylallylarsonium bromide*, m.p. 244—246°. None of these salts reacts quantitatively with I, ClO_4', ReO_4', or $CdCl_4''$. With $AgNO_3$ or conc. HNO_3 the halides give $AsPh_4$·NO_3, *triphenyl-iodomethyl*-, m.p. 189—190°, -*benzyl*-, m.p. 178—180°, -methyl-, m.p. 131—133°, -β-*hydroxyethyl*-, m.p. 138—140°, and -*allyl-arsonium nitrate*, m.p. 146—148°. Prep. of $AsPh_4Cl$ is improved. R. S. C.

Binary systems containing arsenic trichloride or 5-chloro-5 : 10-dihydrophenarsazine.—See A., 1939, I, 145.

Lipophilic chemotherapeuticals. I. E. Bergmann and R. Haskelberg (J.C.S., 1939, 1—5).—In seeking a type of chemotherapeutical intended to have affinity to the lipins and not to the proteins, experiments in the introduction of "fatty" radicals into substances known to contain chemotherapeutically active groups, and synthesis of "fatty" substances containing chemically active groups not yet known to have any chemotherapeutical effect, are recorded. Quinine and cholesteryl formate (I) give a *hydro-*

chloride, m.p. 246—247° (decomp.), $[\alpha]_D^{19}$ +8·4° in $CHCl_3$, yielding a *base*, m.p. 150°, $[\alpha]_D^{19}$ −2·0° in $CHCl_3$. Similar condensation of the appropriate reagents affords *stearoylquinine hydrochloride*, m.p. 227—228° (decomp.); 1-*benzeneazo*-2-*stearamidonaphthalene*, m.p. 88°; *substance*, m.p. 196°, from benzeneazo-β-naphthylamine and (I); 4-*benzeneazo*-1-*stearamidonaphthalene*, m.p. 140·5°; *compound*, m.p. 193°, from (I) and benzeneazo-α-naphthylamine; N-*palmitoyl*- and -*stearoyl-arsanilic acid*; *compound*, decomp. 294°, from 4-arsonobenzeneazo-β-naphthylamine and palmitoyl chloride, and *compound*, m.p. 290° (decomp.), from the amine and (I); 4-*cetylaminoazobenzene*-4′-*arsinic acid*, m.p. 283° (decomp.); 1-4′-*arsonobenzeneazo*-2-*octylaminonaphthalene*, m.p. 206° (decomp.); 4-*octylaminoazobenzene*-4′-*arsinic acid*, m.p. 155° (decomp.); 6-*methoxy*-8-*cholesterylcarbamidoquinoline*, m.p. 129°; 8-*palmitamido*-6-*methoxyquinoline*, m.p. 74—75°; *compound*, m.p. 232°, from (I) and 5-*acrylaldehyde*-p-*ethylaminoanil*, m.p. 210°; 5-(m-*nitrostyryl*)*acridine methiodide*, m.p. 232° (decomp.); N-*nitroso*-N-*cholesterylaniline*, m.p. 147·5°, from HNO_2 and cholesterylaniline; N-*nitrosocetylaniline*, m.p. 53°, from *cetylaniline hydrochloride*, m.p. 102°; and N-*methyl*-N-*cetylaniline hydrochloride*, m.p. 104°. F. R. S.

Glyoxalines. VIII. Arsonophenylglyoxalines. R. Weidenhagen and H. Reinäcker (Ber., 1939, 72, [*B*], 57—67).—ω-Bromoacetophenone-*p*-arsinic acid (Elson and Gibson, A., 1931, 1316) is converted by boiling H_2O into ω-*hydroxyacetophenone*-p-*arsinic acid*, m.p. >340° (also $+1H_2O$; *phenylhydrazone*, m.p. >400°), transformed by CH_2O, $Cu(OAc)_2$, and NH_3 in boiling H_2O into 4(5)-p-*arsonophenylglyoxaline* ($+1H_2O$), m.p. 310° (decomp.) (*Cu* compound; *nitrate*). Under similar conditions MeCHO affords 4(5)-p-*arsonophenyl*-2-*methylglyoxaline* (I), decomp. >300° without melting, the *Cu* derivative of which is either converted by 10% HCl into the *base hydrochloride* ($+1H_2O$) which with NaOAc yields (I) or is treated successively with KI and NaH_2PO_2 and then oxidised (H_2O_2) to (I). By use of the requisite aldehyde the following 4(5)-p-*arsonophenyl-glyoxalines* are obtained; -2-*ethyl*-, m.p. 315° (decomp.) [*Cu* salt; *hydrochloride*, m.p. 275° (decomp.)]; -2-n-*propyl*-, m.p. 250° (decomp.) (also $+2·5H_2O$) (*Cu* salt; *hydrobromide*); -2-n-*butyl*-, decomp. 270° (*Cu* salt; *nitrate*); -2-n-*hexyl*-, needles, m.p. 195—197° (decomp.) after softening at 190°, or prisms, decomp. 256—260° (*Cu* salt; *hydrochloride*, decomp. 290°); 2-*phenyl*-, decomp. 330° (*Cu* salt; *hydrochloride*, decomp. 303°); 2-p-*anisyl*-, decomp. 310° (*Cu* salt; *hydrochloride*, decomp. 270°); -2-p-*nitrophenyl*-, m.p. 320—323° (decomp.) (*Cu* salt), which does not appear to yield a hydrochloride; -2-*furyl*-, decomp. 297° (*Cu* salt; *hydrochloride*); 2-p-*carboxyphenyl*-, m.p. 320° (decomp.) (*Cu* salt and unstable *hydrochloride*); α-p-*hydroxy*-m-*carboxyphenyl*-, gradual decomp. >300° [*Cu* salt; *hydrochloride*, m.p. 307° (decomp.)]. H. W.

Penta(acetoxymercuri)methylacetanilide. M. Ragno (Gazzetta, 1938, 68, 738—740).—$Hg(OAc)_2$ (5 mols.) and NPhMeAc (1 mol.) at 150—180° give 2 : 3 : 4 : 5 : 6-*penta*(*acetoxymercuri*)*methylacetanilide*, decomp. 190—230°, which forms colloidal solutions in H_2O. E. W. W.

Mercury derivatives of antipyrine. M. Ragno (Gazzetta, 1938, 68, 741—747).—The compound $C_{11}H_{13}O_2N_2ClHg$, from $HgCl·NH_2$ and antipyrine (I) (A., 1921, i, 378), with 2 I gives iodoantipyrine. The product from (I) and $Hg(OAc)_2$ (II) with HCl, KBr, and NaOH gives respectively the *compounds*, $C_{11}H_{11}ON_2ClHg$, m.p. 95°, $C_{11}H_{11}ON_2BrHg$, m.p. 130°, and $C_{11}H_{12}O_2N_2Hg$, m.p. 163°. In these compounds, Hg is apparently attached to a ·C:. At 150°, (I) and (II) form *dimercuriantipyrine diacetate*, $C_{11}H_{10}ON_2(HgOAc)_2$, m.p. 133°. E. W. W.

Metallation as a side reaction in the preparation of organolithium compounds. H. Gilman, W. Langham, and A. L. Jacoby (J. Amer. Chem. Soc., 1939, 61, 106—109).—*p*-$C_6H_4Br·OMe$ (I) and Li in Et_2O give $LiC_6H_4·OMe$-*p* (II) (evidenced by production of *p*-$OMe·C_6H_4·CO_2H$ by CO_2), but the reaction, (I) + (II) → PhOMe and $LiC_6H_3Br·OMe$-1 : 5 : 2 [evidenced by production of 2 : 5 : 1-$OMe·C_6H_3Br·CO_2H$ (III) by CO_2], also occurs, particularly if the solution is heated under reflux. LiBu^a gives the same products. Li or LiBu^a and *p*-$C_6H_4Br·OPh$ give similarly 2 : 5 : 1-$OPh·C_6H_3Br·CO_2H$, obtained also from PhOK and 5 : 2 : 1-$NO_2·C_6H_3Cl·CO_2H$ by way of 2 : 5 : 1-$OPh·C_6H_3(NO_2)·CO_2H$ and 2 : 5 : 1-$OPh·C_6H_3(NH_2)·CO_2H$. However, *o*-$C_6H_4Br·OMe$ and LiC_6H_4Me-*p* give only *o*-$OMe·C_6H_4·CO_2H$ [and $CO(C_6H_4Me$-*o*$)_2$] and *p*-$C_6H_4Me·CO_2H$ (IV) [and $CO(C_6H_4Me$-*p*$)_2$], respectively. Interaction of LiBu^a (1 mol.) with PhOMe (1 mol.) and *p*-$C_6H_4Br·OMe$ (1 mol.) gives 30% of (III) and some (IV). R. S. C.

Relative reactivities of organometallic compounds. XX. Metallation. H. Gilman and R. L. Bebb (J. Amer. Chem. Soc., 1939, 61, 109—112; cf. A., 1938, II, 515).—3-Methoxydibenzfuran and LiBu^a give 60% of a 4 : 1 mixture of 3-methoxydibenzfuran-4- and -2-carboxylic acid. PhOMe gives the following yelds of $OMe·C_6H_4·CO_2H$: by LiBu^a in Et_2O 19, by NaBu^a in light petroleum 42, by NaPh in C_6H_6 44—64%. Ph_2O and CH:CNa in liquid NH_3 give only a little *o*-$C_6H_4Ph·OH$, and CPh_3Na has no effect; LiBu^a in light petroleum gives 7 and in Et_2O 60% of *o*-$OPh·C_6H_4·CO_2H$. Ph_2S gives similarly 24—56% of *o*-$SPh·C_6H_4·CO_2H$. Ph_2Se and LiBu^a give mainly SePhBu^a and LiPh, but a little PhSeH is also obtained. Only slight metallation of Ph_2 occurs. CH_2Ar_2 and LiBu^a give the following yields of $CHAr_2·CO_2H$: CH_2Ph_2 20, $CHPh·C_6H_4Me$-*p* 50, $CH_2Ph·C_{10}H_7$-*α* 80%. $(CH_2Ph)_2$ with NaBu^a or KBu^a gives $(CHPh·CO_2H)_2$, best in C_6H_6, but LiBu^a gives only 1% of *m*- and *p*-$Ph·[CH_2]_2·C_6H_4·CO_2H$. $C_{10}H_8$ gives 2·5 : 1 mixtures of α- and β-$C_{10}H_7·CO_2H$. Acenaphthene gives a mixture. 9 : 10-Dihydroanthracene and LiBu^a give 80% of 9 : 10-dihydroanthracene-9 : 10-dicarboxylic and 8% of the 9-carboxylic acid. Dibenzthiophen gives 23—90% of acid, the more reactive organometallic compounds causing also some dimetallation and the solvent also having considerable effect. Furan gives 7·5—40% yields of 2-furoic acid. By interaction of the Na salts with one another and with $COPh_2$, the following order of

decreasing acidity is established: CPh:CH, C_5H_{11}·C:CH, C_2H_2. $C_{16}H_{34}$ and *cyclo*hexene are unaffected by $LiBu^a$. NaC_5H_{11}-*n* and $NPhMe_2$ in light petroleum give *o*-NMe_2·C_6H_4·CO_2H. $NaBu^a$ and $HgPh_2$ in light petroleum give 40% of BzOH, establishing the reaction, $LiBu^a + HgPh_2 \rightarrow NaPh + HgPhBu^a$. R. S. C.

Allylic rearrangements. VIII. Action of magnesium on cinnamyl chloride. W. G. Young, G. Ballou, and K. Nozaki (J. Amer. Chem. Soc., 1939, **61**, 12—15; cf. A., 1938, II, 214).—The Mg compound from CHPh:CH·CH_2Cl is shown to contain 73% of MgCl·CHPh·CH:CH_2 and 27% of CHPh:CH·CH_2·MgCl by hydrolysis to CH_2Ph·CH:CH_2 and CHPh:CHMe (with coupling products and a little PhPr), followed by $KMnO_4$-oxidation and determination of BzOH and AcOH. The Mg compound does not dissociate into MgCl and a resonating ion. R. S. C.

Analogous organic derivatives of sulphur, selenium, and tellurium. N. M. Cullinane, A. G. Rees, and C. A. J. Plummer (J.C.S., 1939, 151—153).—Diphenylene sulphide, prepared by diazotisation of 2-amidodiphenyl sulphide or from diphenylene selenide and S, with AcCl–$AlCl_3$ gives 3 : 6-*diacetyldiphenylene sulphide*, m.p. 210°, which with NaOH–$CaOCl_2$ affords *diphenylenesulphone*-3 : 6-*dicarboxylic acid*, m.p. above 400°. K selenophenoxide and *o*-C_6H_4·Cl·NO_2 yields 2-nitrodiphenyl selenide, reduced to the 2-NH_2-compound; the diazotised amine with H_2SO_4 gives Ph_2 diselenide and benzeneseleninic acid. Diphenylene selenide can be obtained only in small yield under special conditions from this amine but can be prepared from selenanthren and Cu. Diphenylenesulphone and Te afford diphenylene telluride in small yield. F. R. S.

Natural organic high-molecular substances. K. Freudenberg (Naturwiss., 1939, **27**, 17—22).—The formation (by continuous condensation processes), mol. size, and configuration of proteins, cellulose, rubber, lignin, tannins, etc. are discussed. A. Li.

Phosphatide acid–protein compounds: chaulmoogroylglycerophosphate–protein compounds. T. Wagner-Jauregg and H. Arnold (Biochem. Z., 1938, **299**, 274—280; cf. A., 1937, II, 365; 1938, II, 353).—The hydrochloride of clupein Me ester in H_2O with Na dichaulmoogroyl-β-glycerophosphate gives a H_2O-insol. *compound* (I) containing N 9·43, P 3·05%. ψ-Globulin (II) and albumin (III) from horse serum yield, in neutral or slightly acid solution, corresponding *compounds* with Na monochaulmoogroyl-β-glycerophosphate. The (II) compound has N 12·47, P 0·88% and contains 25—50 mols. of phosphatide acid per protein mol. and the (III) compound has P 0·93%. As regards pptn. with $(NH_4)_2SO_4$ the (II) compound behaves like euglobulin. Probably phosphatide acid–protein compounds are produced under physiological conditions. (I) appears to have no antigenic properties. (II) and (III) adsorb lactoflavinphosphoric acid but do not combine with it. W. McC.

Peptone derivatives of gelatin. II. Fractionation of the ereptic hydrolysate of gelatin-peptone and -tryptone. III. Fractionation of gelatin-peptone and -tryptone. T. Mori (J. Biochem. Japan, 1938, **28**, 333—343, 345—354; cf. A., 1939, III, 198).—II. Data for the total, NH_2-, and arginine-N (the last being indicated by hydrolysis by arginase) of fractions obtained by the ereptic digestion of the peptone and tryptone are tabulated and discussed.

III. Data for the distribution of N, colour and pptn. reactions, and arginase hydrolysis of fractions obtained by pptn. of the aq. peptone and tryptone with phosphotungstic acid are tabulated and discussed. F. O. H.

Simplification of Pregl's method of determining carbon and hydrogen. K. Bürger (Ber., 1939, **72**, [*B*], 40—45).—The chief modification consists in the attachment of the absorption tubes to the combustion tube and to one another by ground-glass joints instead of rubber stoppers. Considerable simplification of the apparatus and economy of time are thereby rendered possible. H. W.

Sub-micro-determination of nitrogen in organic material by Kjeldahl's method. C. Dumazert (Bull. Soc. Chim. biol., 1938, **20**, 1405—1418).—A modification of the Parnas and Wagner micro-Kjeldahl apparatus by which 10—260 μg. of N can be determined with an error of 1% is described. Approx. 1 mg. of substance is heated for 2 hr. with 0·3 c.c. of H_2SO_4 and 10 mg. of a mixed catalyst prepared from 1 g. of $HgSeO_3$ and 24 g. of $KHSO_4$. A control is done at the same time. The NH_3 is liberated in the usual way and absorbed in 1 or 2 c.c. of 0·01N-H_2SO_4. After addition of KI and KIO_3, the liberated I is determined by 0·01N-$Na_2S_2O_3$. J. N. A.

Determination of organic sulphur. G. H. Young (Ind. Eng. Chem. [Anal.], 1938, **10**, 686).—The method of Brunck (A., 1905, ii, 762) is of general applicability and is preferable to most other methods for the analysis of sulphones and sulphoxides. Details of apparatus and procedure are given. F. N. W.

Microanalytical determination of mercury in organic and inorganic compounds. Accurate determination in presence of chlorine, bromine, iodine, nitrogen, and sulphur. M. Boëtius (J. pr. Chem., 1938, [ii], **151**, 279—306).—For compounds free from N the combustion tube is drawn out at one end and into it are inserted successively a hollow glass cylinder–asbestos–Ag deposited on porcelain–asbestos–ignited PbO contained in a boat–substance–diffusion tube. For nitrogenous compounds the filling is hollow cylinder–Ag–asbestos–fine Cu–asbestos –granular $PbCrO_4$–asbestos–substance–diffusion tube (combustion is effected in CO_2). The Hg is absorbed on fine threads of Au. H. W.

Chlorometric determination of the ethylene linking. L. Palfray and S. Sabetay (Ann. Chim. Analyt., 1938, [iii], **20**, 288—289).—The sample (0·15—0·2 g.) is dissolved in CCl_4, 25 c.c. of a solution containing ~1 g. of Cl_2 in 100 c.c. of CCl_4 are added, and the whole is well agitated and then kept in the dark for 30 min. KI is added and the liberated I titrated with 0·1N-$Na_2S_2O_3$ (starch). Results given

by this method with oleic and stearic acids and several oils are compared with those obtained by Hanus' method. L. S. T.

Quantitative separation of alcoholic substances. G. Sandulesco and A. Girard (Compt. rend., 1938, **207**, 874—876; cf. A., 1936, 1397).—Material (*e.g.*, natural products) containing an alcohol (ROH) is treated with $(CH_2Cl{\cdot}CO)_2O$ (amount $\propto$ Ac val.) in dioxan at 100° (bath)/3—4 hr. in absence of H_2O, the resulting product is freed from excess of anhydride and acid by aq. $NaHCO_3$, and then heated with NEt_3 (or NMe_3) (10—20% excess) in dioxan at 100° (bath)/1—2 hr. (sealed tube). The $NEt_3Cl{\cdot}CH_2{\cdot}CO_2R$ thus formed is readily sol. in 10—20% AcOH, and treatment with NaOH at room temp. in presence of Et_2O gives the ROH. The method is applicable to phenolic alcohols provided the phenolic OH is first benzoylated (Schotten–Baumann). Cholesterol (1 g.) is separable from olive oil (1 litre), but is accompanied by (alcoholic) impurities. J. L. D.

New general reagent for enols; mercurous nitrate. IV. Interpretation of the reaction mechanism. E. V. Zappi and A. Manini (Anal. Asoc. Quím. Argentina, 1938, **26**, 89—105).—Pptn. of Hg by $Hg_2(NO_3)_2$ with enols and active substances is attributed to formation of complexes between the latter and $Hg(NO_3)_2$ with consequent disturbance of the equilibrium $Hg_2(NO_3)_2 \rightleftharpoons Hg + Hg(NO_3)_2$. $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ with $Hg_2(NO_3)_2$ (1 mol.) gives Hg (1 mol.) and a cryst. *complex*, also obtained from $Hg(NO_3)_2$ without separation of Hg. C_5H_5N similarly forms a *complex*, $2C_5H_5N,Hg(NO_3)_2$, m.p. 246—248°. F. R. G.

Identification and determination of carbonyl by *p*-carboxyphenylhydrazine. S. Viebel and N. Hauge (Bull. Soc. chim., 1938, [v], **5**, 1506—1509).—A modified prep. of p-$CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$, and a method of determining CO: by titration of hydrazone in EtOH against $Ba(OH)_2$, are recorded. A. T. P.

Use of Lovibond Tintometer for colorimetric determination of formaldehyde by the phloroglucinol method. R. C. Hoather and P. G. T. Hand (Analyst, 1939, **64**, 29—30).—The $C_6H_3(OH)_3$ reagent is added in varying quantity according to the CH_2O present. The Tintometer is set at 1·0 unit of brightness and observations of colour are made from 2 min. after mixing until the max. colour is passed (~4 min. longer). The p.p.m. of $CH_2O = (R - 1{\cdot}2)/0{\cdot}414t$, where R = red units and t = thickness of cell in inches. E. C. S.

Conductometric micro-titration of organic acids. M. Furter and H. Gubser (Helv. Chim. Acta, 1938, **21**, 1725—1734).—The org. acid (5—30 mg.) is dissolved in aq. EtOH (10—14 c.c.) in a special conductivity cell in which the solution can be stirred by a stream of N_2, and is titrated with 0·1N. aq. NaOH or LiOH from a micro-burette. Preferred concns. of solvents for mono-, di-, and poly-basic acids are 25—75%, 99%, and 80—95% EtOH, respectively. J. W. S.

Dyer method for identification and determination of volatile fatty acids. E. P. Clark (J. Assoc. Off. Agric. Chem., 1938, **21**, 684—688).—The consts. obtained by Dyer (A., 1917, ii, 157) relate to the conditions, not adequately specified, under which his observations were made. An accurately described apparatus is illustrated and a procedure detailed for the distillation, and the consts. so obtained for HCO_2H, AcOH, $EtCO_2H$, $Pr^{\alpha}CO_2H$, and $Pr^{\beta}CO_2H$ are tabulated. The titrations are carried to a definite end-point by comparison with a buffered solution at p_H 8·6 of equal vol. E. C. S.

Schryver–Fosse reaction applied to analysis. M. Paget and R. Berger (Compt. rend., 1938, **207**, 800—802).—$H_2C_2O_4$ (2 c.c.; 5—70 mg. per l.) when shaken with N-HCl (1 c.c.) and Zn gives $CHO{\cdot}CO_2H$, which with $NHPh{\cdot}NH_2,HCl$ at 100° followed by conc. HCl (1·8 c.c.) and 10-vol. H_2O_2 (2 drops) at room temp. gives a colour which is compared with a standard. 5 μg. can be identified. Ascorbic acid (1 c.c. of 0·1%) with conc. H_2SO_4 (2 drops)–3% of $KMnO_4$ (2 drops) at room. temp. affords $H_2C_2O_4$ which is determined as above. 10—20 μg. can be determined. 0·1% aq. lactic, malic, citric, or tartaric acid is oxidised like ascorbic acid. Tartaric acid gives $CHO{\cdot}CO_2H$ (traces), $H_2C_2O_4$, and $\beta\gamma$-diketobutane-$\alpha\delta$-dicarboxylic acid. Most commercial samples of Na urate (or uric acid heated with Na_2CO_3) give the Schryver–Fosse reaction directly, owing to the presence of allantoic acid. J. L. D.

Iodometric determination of small quantities of glucose. E. C. Noyons (Rec. trav. chim., 1939, **58**, 17—22).—The iodometric method (A., 1923, ii, 346) can be used to determine 0·2—2 mg. of glucose, after 30 min. oxidation at room temp. The accuracy is not greatly affected by the presence of various other substances found in blood. A glucose solution treated with $Cd(OH)_2$ to remove albumin (A., 1932, 75) gives inaccurate results by this method unless buffered with $2KH_2PO_4 + 3NaOH$. E. W. W.

Micro-method for the determination of reducing sugars. I. A. Obergard, B. O. Ljubin and A. J. Tschuliatikova (Arch. sci. biol. U.S.S.R., 1935, **38**, 343—352; Ger., 352—353).—The sugar is oxidised titrimetrically with a modified Fehling's solution (cf. A., 1932, 529) using methylene-blue as an internal indicator (cf. A., 1923, ii, 193; 1924, ii, 707). A conversion table is given. Ch. Abs. (*c*)

Micro-determination of sugar alcohols. W. R. Todd, J. Vreeland, J. Myers, and E. S. West (J. Biol. Chem., 1939, **127**, 269—273).—0·1—0·7 mg. of the sugar is heated at 100° for 30 min. with $K_3Fe(CN)_6$ and Na_2SO_4–NaOH. After cooling $ZnAc_2$–KI–AcOH is added and the liberated I is titrated. The titration val.–concn. curve is not linear and must be determined for each sugar. Sorbitol and mannitol are recovered to the extent of 95—110% from aq. solutions and 85—105% from blood and urine previously treated with $HgSO_4$ and $BaCO_3$. A correction for the reducing action of glucose and its effect on the reducing power of sugar alcohol is described. J. L. D.

Use of drop analysis for investigation of medicaments. V. Detection of small quantities of primary aromatic amines. O. Frehden and

K. Fürst (Mikrochim. Acta, 1938, **3**, 197—200; cf. A., 1938, II, 465).—The "mustard oil test" for aromatic amines is applied as a colour reaction by detecting by means of alkaline plumbite solution the H_2S liberated in the first stage of the test. Aliphatic amines do not react. The substance under investigation is mixed with 20 drops of EtOH–CS_2 (~0·02 g. in 50 c.c. of 96% EtOH), carefully evaporated in a special apparatus, and the vapour tested with paper moistened with alkaline plumbite solution. The limiting sensitivities given for the different amines tested in this way vary from 1·0 to 4·0 μg. L. S. T.

Determination of cholesterol. F. E. Kelsey (J. Biol. Chem., 1939, **127**, 15—22).—The method described depends on the pptn. of cholesterol from EtOH–Et_2O extracts of tissues as the digitonide, purification of this by light petroleum, decomp. by boiling C_6H_6, and isolation of the free sterols by extraction with light petroleum. The product is assayed by the Liebermann–Burchard reaction. Where phospholipins are present, these must first be removed by $COMe_2$ pptn. Both free and total cholesterol can be determined on the same sample. P. G. M.

Copper precipitation method for kojic acid determination. H. N. Barham (Ind. Eng. Chem. [Anal.], 1939, **11**, 31—33; cf. A., 1938, II, 372).—The method is accurate if the solution to be analysed is neutralised and then diluted to ~0·142 g. of kojic acid in 70 c.c. before adding dil. aq. $Cu(OAc)_2$ in >50% excess. At least 48 hr. are required for complete pptn.; the ppt. $(C_6H_5O_4)_2Cu$ is dried in vac. over $CaCl_2$ or at 100—105°. The p_H of the solution is not crit. F. N. W.

Colorimetric determination of *dl*-α-tocopherol (vitamin-*E*). A. Emmerie and C. Engel (Nature, 1938, **142**, 873).—The determination is based on the reduction of $FeCl_3$ by α-tocopherol (I) in EtOH, the $Fe^{..}$ formed being determined colorimetrically by means of 2 : 2′-dipyridyl. The amounts of (I) varied from 0·01 to 0·4 mg. The results agree with those obtained by potentiometric titration with $AuCl_3$ (A., 1938, II, 450). L. S. T.

Determination of free and combined pentoses in purine compounds. K. Gerhardt (Czasopismo Towarz. Apt. Lwow, 1936, **51**, No. 9, 8 pp.; Chem. Zentr., 1937, i, 943).—The nos. quoted after the following compounds are respectively the max. yield of furfuraldehyde and the optimal [HCl] (g. per 100 c.c.), when Hoffman's method (A., 1927, 687) is used: arabinose (80·4, 18·46), which is less readily decomposed than xylose (>80·4, 17·14); yeast (88·2, 17·89 and muscle (22·4—28·5, 16·66—18·33) adenine nucleotides. H. B.

Determination of tryptophan by a modified glyoxylic acid method employing photo-electric colorimetry. J. L. D. Shaw and W. D. McFarlane (Canad. J. Res., 1938, **16**, B, 361—368).—Winkler's adaptation (A., 1934, 1376) of the Hopkins–Cole reaction is modified for use with a photo-electric colorimeter. 0·5 c.c. of Pesez's glyoxylic acid solution (A., 1936, 745) and 0·5 c.c. of 0·04N. aq. $CuSO_4$ are mixed with 0·1—2·0 c.c. of an aq. solution containing 0·005—0·150 mg. of tryptophan (I) and the mixture is made up to 3·0 c.c. with H_2O. 5 c.c. of conc. H_2SO_4 are added gradually, with cooling, and the mixture after 10 min. at room temp. and then 5 min. at 100° is cooled and made up to 10 c.c. with 60% H_2SO_4. The colour developed is measured after 15 min. in an Evelyn colorimeter (*ibid.*, 1223) and the (I) content obtained from calibration curves. The method is applied to four samples of casein (II) by dissolution in 10—20% aq. NaOH or 5% aq. HCO_2H and it is shown that the age and origin of the (II) are factors causing variation in the (I) content. F. N. W.

Iodometric determination of potassium mercuri-iodide; volumetric determination of morphine. H. Wachsmuth (Bull. Soc. Chim. biol., 1938, **20**, 1419—1428).—K_2HgI_4 is oxidised to KIO_3 by Br–H_2O, and after addition of KI and acid, the I is determined by 0·1N- or 0·05N-$Na_2S_2O_3$. For the determination of morphine, a slightly acid solution is treated with excess of K_2HgI_4, and after removal of the ppt., the excess of K_2HgI_4 is determined in an aliquot of the filtrate. 0·01—0·03 g. of morphine can be determined even in presence of NaCl. Other methods of determination of morphine as its insol. mercuri-iodide are discussed. J. N. A.

Stability of solutions of nicotindiethyl-amide. F. Reimers (Dansk Tidsskr. Farm., 1939, **13**, 9—18).—Nicotinic acid is determined by extraction with $CHCl_3$–$Pr^{\beta}OH$ (3 : 1) at the isoelectric point [after first removing nicotindiethylamide (I)], followed by evaporation, dissolution in H_2O, and titration against 0·1N-NaOH (phenolphthalein). (I) is not hydrolysed in aq. solution (p_H 3—7·5) in 1 year at room temp. or by heating to 120°. The yellow colour of old solutions of (I) is probably due to a nitropyridylpyrazole. M. H. M. A.

Determination of strychnine and brucine in mixtures of both. N. J. A. Groen and P. van der Wielen (Pharm. Weekblad, 1939, **76**, 3—10).—The method of the British Pharmacopœia is preferred and gives satisfactory results for strychnine. The brucine is determined by Zeisel's OMe method. S. C.

Volumetric determination of organic lead compounds. F. Hein, A. Klein, and H. J. Mesée (Z. anal. Chem., 1939, **115**, 177—183).—In EtOH, $PbEt_2$ can be determined by direct titration with 0·1N-I (in EtOH), $PbEt_4 + I_2 = PbEt_3I + EtI$, until the yellow colour persists at least 15 min. If the determination is accelerated by addition of excess of I and back-titration with $Na_2S_2O_3$ or by warming secondary reactions occur. The reaction is more rapid in MeOH. A solution of $PbEt_4$ in petrol can be treated with excess of I in petrol, and back-titrated with aq. $Na_2S_2O_3$. After addition of MeOH titration may also be carried out directly with I in MeOH. $PbEt_3$ can be determined by direct titration with I in MeOH solution: $2PbEt_3 + I_2 = 2PbEt_3I$. $PbPh_4$ in C_6H_6 is treated with excess of I (in C_6H_6), reaction being accelerated by warming almost to the b.p. and irradiating with light. Reaction occurs: $PbPh_4 + 3I_2 = PbI_2 + 4PhI$. The excess of I is finally titrated with aq. $Na_2S_2O_3$. J. W. S.