BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1937.

Mechanism of the photochemical decomposition of methane.—See A., I, 91.

Free radicals and atoms in primary photochemical processes. Free propyl radical from di*iso*propyl ketone. H. G. Glazebrook and T. G. Pearson (J.C.S., 1936, 1777—1779).—On exposure to ultra-violet light, $COPr^{\beta}_2$ yields free *iso*(?)propyl which with Hg gives $HgPr^{\alpha}_2$. The half-life periods of Pr^{α} and Pr^{β} are 4·0 and 4·4 × 10^{-3} sec., respectively. F. N. W.

Catalytic polymerisation of ethylene at atmospheric pressure. I, II. Y. Konaka (J. Soc. Chem. Ind. Japan, 1936, **39**, 447B).—I. No polymerisation occurs in presence of Al_2O_3, SiO_2 gel, or Cu, but with Co or Ni at 350° a colourless liquid and C result; the latter is much reduced in amount by Cu. ThO_2, U_3O_8, TiO_2, Al_2O_3, and ZnO promote the activity of Co slightly.

II. The Co catalyst is best prepared from CoO which is obtained from $CoCO_3$ or $Co(NO_3)_2$. 300° is the optimum temp. of polymerisation; above 300° much H_2, CH_4, and C are formed. Co deposited on kieselguhr has a longer life than the unsupported catalyst. J. L. D.

Reactions between ethylene and halogens and their products. A. Sherman, O. T. Quimby, and R. O. Sutherland (J. Chem. Physics, 1936, **4**, 732—740; cf. A., 1934, 736).—Theoretical considerations indicate that (1) Cl_2, Br, and I will tend to give symmetrical additive products with C_2H_4; (2) HCl and HBr will combine with the corresponding vinyl compound rather than react to give C_2H_4 and halogen, whilst the I compounds will react in both ways; (3) decomp. of *s*- or *as*-$C_2H_4Br_2$ or -$C_2H_4I_2$ will give rise to C_2H_4 and Br or I, whereas $C_2H_4Cl_2$ will give HCl and CH_2:CHCl; (4) usually mechanisms involving free radicals are more probable than the corresponding uni- or bi-mol. reactions. F. L. U.

Addition of hydrogen halides to butadiene. S. N. Ganguly (J. Indian Chem. Soc., 1936, **13**, 580—585).—Addition of anhyd. HBr to butadiene gives α-bromo-Δ^{β}-butene only. With HCl β-chloro-Δ^{γ}- and α-chloro-Δ^{β}-butene are formed: the absence of any α-chloro-Δ^{γ}-butene was not established, and attempts to prepare this compound from allylcarbinol failed. H. G. M.

Addition of hydrogen bromide to allyl bromide in the presence of various substances. Y. Urushibara and M. Takebayashi (Bull. Chem. Soc. Japan, 1936, **11**, 692—694; cf. A., 1933, 805).—Interaction of HBr and CH_2:CH·CH_2Br in the presence of air, reduced Fe, or reduced Ni affords $CH_2(CH_2Br)_2$ principally, whilst in the presence of S, NO, Pt-black, $FeBr_2$, or $MnSO_4$ the production of αβ-dibromopropane is favoured. Fe, Ni, and Pt alone increase the total yield. F. N. W.

Addition of hydrogen bromide to allyl bromide in presence of various substances. II. Effects of ferro-magnetic catalysts. Y. Urushibara and M. Takebayashi (Bull. Chem. Soc. Japan, 1936, **11**, 754—756).—Reduced Fe and Ni in presence of $NHPh_2$ accelerate the abnormal addition of HBr to allyl bromide and afford chiefly $CH_2(CH_2Br)_2$. Co, Fe–sand, and surface-oxidised Ni have no influence on the normal addition. J. D. R.

Photochemical formation of carbonyl chloride from chloroform, chlorine, and oxygen.—See A., I, 91.

Rearrangements of α-propylcrotyl chloride and phenyl α-propylcrotyl ether. C. D. Hurd and J. W. Williams (J. Amer. Chem. Soc., 1936, **58**, 2636—2637).—The previously prepared (A., 1931, 838) α-propylcrotyl chloride [δ-chloro-Δ^{β}-heptene], Ph α-propylcrotyl ether (I), and *o*-α-methyl-Δ^{β}-hexenylphenol (II) are shown (by ozonolysis) to contain about 20% of their respective isomerides, viz., β-chloro-Δ^{γ}-heptene (formed by anionotropic change), Ph α-methyl-Δ^{β}-hexenyl ether, and *o*-α-propylcrotylphenol. The rearrangement of (I) into (II) involves an inversion of the propylcrotyl group, thus supporting the view that allyl undergoes inversion during rearrangement of Ph allyl ether to *o*-allylphenol. H. B.

Constitution of tetranitromethane. R. Robinson (Nature, 1936, **138**, 975—976).—Arguments in favour of $C(NO_2)_4$ and against the proposed revision (*ibid.*, 807) are advanced. L. S. T.

Preparation of tetranitromethane. C. Krauz and J. Štěpánek (Chem. Obzor, 1935, **10**, 137—140; Chem. Zentr., 1936, i, 1707).—An improved prep. (95% yield) from N_2O_5 and Ac_2O is described. Nitration of $COMe_2$ with fuming HNO_3 yields *acetylmethylnitrolic acid* (*Ag* salt). $C(NO_2)_4$ and KOEt, followed by decomp. with H_2SO_4, yield $CH(NO_2)_3$. H. N. R.

Bromination of acetylene in light.—See A., I, 91.

Differentiation of monohydric primary, secondary, and tertiary alcohols. Micro-determination of velocity of esterification. S. Murahashi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, **30**, 272—277).—2—5 mg. of alcohol and pure $CH_2Ph·CO_2H$ (1 mol.) are heated at 155—156° for 1 hr. The free acid is then titrated with 0·01*N*-NaOH.

The % esterification is for *n*-nonyl and -hexyl alcohol and tetrahydrogeraniol 57·8—62·3, for *sec.*-octyl and -butyl alcohol, 24·5—30·6, and for $Bu^{\gamma}OH$, linalool, and tetrahydrolinalool 1·1—12·1. R. S. C.

Detection and approximate determination of primary in the presence of secondary and tertiary alcohols by the formation of triphenylmethyl ethers. S. Sabetay (Compt. rend., 1936, 203, 1164—1166).—$CH_2R{\cdot}OH$ with excess of CPh_3Cl in boiling dry PhMe affords a CPh_3 ether (>80%) and HCl which can be removed by CO_2 and determined titrimetrically. $CHR_2{\cdot}OH$ and $CR_3{\cdot}OH$ in the same period react to <25% and <5%, respectively. By choosing a suitable reaction period the method is approx. quant. J. L. D.

Exchange of hydrogen between ethyl alcohol and calcium deuteroxide.—See A., I, 81.

Electrolytic oxidation of alcohols and aldehydes in alkaline solution. T. Kurenniemi and E. Tommila (Suomen Kem., 1936, **9**, B, 25—26).—$Pr^{\alpha}OH$ has been oxidised at 20° on smooth Pt anodes in 1—4*N*-NaOH with a good yield, which decreases with NaOH of concn. >4*N*. The anodic gas consisted of 80—90% of C_2H_4, 3—10% of CH_4, and C_2H_6, O_2, and CO; the anolyte contained EtCHO and a good yield of HCO_2H, $EtCO_2H$, and CO_2. EtCHO gave O_2, a little CO, C_2H_4, and HCO_2H, and mainly $EtCO_2H$. In 1—2*N*-NaOH, $Pr^{\beta}OH$ gave $COMe_2$, $Bu^{\alpha}OH$ and $Bu^{\beta}OH$ gave mainly unsaturated hydrocarbons, HCO_2H, and the corresponding fatty acids, and a little unsaturated hydrocarbons. On Fe and Ni electrodes the respective fatty acids were obtained with traces of the above side products. The aldehydes probably act either in the hydrated or in the enolic form: $CHR(OH)_2 + O = RCO_2H + H_2O$ (i) and $CHR{:}CH{\cdot}OH + O \rightarrow \begin{matrix}R{\cdot}CH\\OH{\cdot}CH\end{matrix}\!>O \rightarrow OH{\cdot}CHR{\cdot}CHO \rightarrow OH{\cdot}CHR{\cdot}CH(OH)_2 \rightarrow RCHO + HCO_2H + H_2O$ (ii). Reaction (ii) is not observed with Fe and Ni, since oxidation is milder on these electrodes than on Pt. $Pr^{\alpha}OH$ produces considerable yields of HCO_2H in contrast to EtCHO because with the former EtCHO is oxidised before it can hydrate. R. S. B.

Stereochemical relationships of isomeric butane-β*γ*-diols and related compounds; evidence of Walden inversion. C. E. Wilson and H. J. Lucas (J. Amer. Chem. Soc., 1936, 58, 2396—2402).—The mixture (I) of *cis*- and *trans*-Δ^{β}-butene obtained by dehydration (H_2SO_4) of $Bu^{\alpha}OH$ is converted (aq. HOCl) into a mixture, b.p. 50—60°/30 mm., of *γ*-chlorobutan-β-ols; this with aq. KOH at 90° gives an approx. 35 : 65 mixture of *cis*- (II), b.p. 59·9—60·4°/747 mm., and *trans*- (III), b.p. 53·6—54·1°/747 mm., -β*γ*-oxidobutanes, thus confirming the composition (A., 1930, 888) of (I). (II) and (III) are slightly impure but subsequent hydration (aq. $HClO_4$) affords the diols which are purified by crystallisation; (II) thus yields *dl*-butane-β*γ*-diol (IV), b.p. 86°/16 mm., 176·7°/742 mm., m.p. 7·6° [diacetate (V), b.p. 70°/5·5 mm., m.p. 41—41·5°; dibenzoate, m.p. 53—54°; *di*-p-*bromobenzoate*, m.p. 205—209°], whilst (III) furnishes *meso*-butane-β*γ*-diol (VI), b.p. 89°/16 mm., 181·7°/742 mm., m.p. 34·4° [diacetate (VII), b.p. 66°/5·5 mm., m.p. 2·5—3°; dibenzoate, m.p. 75·5—76·2°; *di*-p-*bromobenzoate*, m.p. 139—139·8°]. The f.-p. curve for (IV) and (VI) is given. (IV) and (VI) undergo a pinacol rearrangement (COMeEt isolable) with conc. HBr but (V) and (VII) similarly give *meso*-, b.p. 73·2—73·4°/50 mm., and *dl*-, b.p. 76·4—76·6°/50 mm., -β*γ*-dibromobutane, respectively, which are debrominated (Zn) to *trans*- (VIII) and *cis*- (IX) -Δ^{α}-butene, respectively. The above reactions afford a method for the interconversion of (VIII) and (IX). It is proved (below) that the change (III) → (VI) occurs through a Walden inversion, and it is believed that five inversions occur in, *e.g.*, the conversion of (VIII) into (IX), viz., (VIII) —O→ chlorohydrin —O→ (III) —O→ (VI) → (VII) —O→ *dl*-dibromide —O→ (IX).

(II) and (III) with aq. $NHMe_2$ at 100° give *dl-threo*-, b.p. 141—142°/743 mm., and *dl-erythro*- (X), b.p. 152·5—153·5°/743 mm., -*γ*-dimethylaminobutan-β-ol, respectively, the *methiodides* of which with Ag_2O–H_2O followed by distillation regenerate (II) and (III), respectively. The methohydroxide from (X) is resolved (partly) through the *tartrate*, $[\alpha]_{H_g}$ +19·1°; similar decomp. affords an active oxide [*i.e.*, (III)] (not isolated), which is hydrated to an inactive glycol [*i.e.*, (VI)]. The configurations of (IV) and (VI) are established by the formation of (VI) from the optically active (III), by the production of optically active (IV) when (II) is hydrated in presence of *d*-tartaric or *d*-camphorsulphonic acid (XI) [(III) similarly gives (VI)], and by the isolation of an active fraction which has not reacted when (IV) is partly esterified with (XI). H. B.

Cyclic ethers from glycols. A. Franke and A. Kroupa [with F. Schweizer, M. Winischofer, H. Klein-Lohr, M. Just, M. Hackl, I. von Reyher, and R. Bader] (Monatsh., 1936, **69**, 167—203).—The action of 55% H_2SO_4 on diols containing the OH groups in α*ζ* or more distant positions gives very little ωω′-oxide, change proceeding mainly as follows:

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}OH \rightarrow SO_3H{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}OH \rightarrow CH_2{:}CH{\cdot}[CH_2]_n{\cdot}CH_2O \rightarrow$$

$CH_3{\cdot}CH(O{\cdot}SO_3H){\cdot}[CH_2]_n{\cdot}CH_2{\cdot}OH$ and so onwards until the OH are in a position favourable for ring-closure. Oxidation of the products with CrO_3 gives small amounts of the corresponding CO-acids, but mainly fatty acids and $(\cdot CH_2{\cdot}CO_2H)_2$, whilst much unchanged product remains; $KMnO_4$ gives less satisfactory results. The constitution of the products is therefore determined by their transformation by conc. HBr into the corresponding dibromides, thence into the dinitriles and dicarboxylic acids, which are separated from one another through their mono- or di-amides. The product obtained from hexane-α*ζ*-diol and 57% H_2SO_4 at 133° contains about 10% of α*ζ*-, 25% of α*ε*-, and 65% of α*δ*-oxidohexane. Heptane-α*η*-diol gives about 33% of *α-δ-oxidoheptane*, b.p. 128—131·5°. Octane-α0-diol gives about 70% of α*δ*- and 30% of α*ε*-oxido-octane. Undecane-α*κ*-diol, undecane-α*λ*-diol, undecylenyl alcohol, and undecene-α*λ*-diol give the same *oxide*, b.p. 220—223°. Decane-α*κ*-diol and dodecane-α*μ*-diol give mainly α*δ*-oxidodecane and -dodecane, respectively. The following substances are prepared for purposes of comparison.

$CHEt(CO_2Et)_2$,Na, and $CH_2(CH_2Br)_2$ give *Et*$_2$ *ethyl-γ-bromopropylmalonate* (I), b.p. 152—156°/9 mm., whence *Et*$_2$ *ethyl-γ-cyanopropylmalonate*, b.p. 171—174°/10 mm., hydrolysed by KOH–EtOH–H_2O to n-*hexane-αδδ-tricarboxylic acid*, m.p. 150° (decomp.), decarboxylated at 180° to *α-ethyladipic acid*, b.p. 166—167°/1 mm., m.p. 53° (*diamide*, m.p. 180°; *monoamide*, m.p. 135·4°). Similarly *Et*$_2$ *propyl-γ-bromopropylmalonate* (II), b.p. 162—166°/11·5 mm., affords successively *Et*$_2$ *propyl*-n-*cyanoproylmalonate*, b.p. 179—182°/10·5 mm., n-*heptane-αδδ-tricarboxylic acid*, and *α-propyladipic acid*, b.p. 182—183°/1 mm., m.p. 56° (*diamide*, m.p. 181·2°; *monoamide*, m.p. 146·8°). *Et*$_2$ *γ-bromopropyl*-n-*butylmalonate*, b.p. 171°/10·5 mm., affords *Et*$_2$ *γ-cyanopropyl*-n-*butylmalonate*, b.p. 153—156°/1 mm., n-*octane-γδδ-tricarboxylic acid*, m.p. 171° (decomp.), and n-*butyladipic acid*, b.p. 176°/0·25 mm., m.p. 63° (*diamide*, m.p. 180·9°; *monoamide*, m.p. 142·2°). αε-Dibromohexane yields the corresponding *dinitrile*, b.p. 162—168°/11 mm., hydrolysed by alkali to α-methylpimelic acid, b.p. 166°/1 mm., m.p. 55° (*diamide*, m.p. 151°). (I) and $CHNa(CO_2Et)_2$ afford *Et*$_4$ n-*heptane-αααε-tetracarboxylate*, b.p. 220—222°/13 mm., hydrolysed to n-*heptane-αααε-tetracarboxylic acid*, which passes at 180° into *α-ethylpimelic acid*, b.p. 210—211°/9 mm., m.p. 42·3° (*diamide*, m.p. 161—162°; *monoamide*, m.p. 108—109°). Similarly, (II) and $CHNa(CO_2Et)_2$ afford successively *Et*$_4$ n-*octane-αααε-tetracarboxylate*, b.p. 195·5—197°/0·75 mm., n-*octane-αααε-tetracarboxylic acid*, and *α-propylpimelic acid*, b.p. 212°/3 mm., m.p. 61·5° (*diamide*, m.p. 150·2°). Bu$^{\alpha}$Br is transformed by Mg and trioxymethylene into *n*-amyl alcohol, whence the bromide and *Et*$_2$ n-*amylmalonate*, b.p. 124—125°/9 mm., which gives *Et*$_2$ *γ-bromopropyl*-n-*amylmalonate*, b.p. 175—178°/8 mm. This with $CHNa(CO_2Et)_2$ affords *Et*$_4$ n-*decane-αααε-tetracarboxylate*, b.p. 225—228°/8 mm.; the corresponding *acid* passes at 200° into α-n-*amylpimelic acid*, b.p. 232—234°/11 mm. (*diamide*, m.p. 164·2°; *monoamide*, m.p. 109·4°). *n*-Heptyl alcohol, obtained by reducing heptaldehyde with Al–Hg in EtOH, gives the bromide and thence successively *Et*$_2$ n-*heptylmalonate*, b.p. 146—149°/9 mm., *Et*$_2$ *γ-bromopropyl*-n-*heptylmalonate*, b.p. 161—165°/1 mm., *Et*$_4$ n-*dodecane-αααε-tetracarboxylate*, the corresponding free *acid*, and n-*heptylpimelic acid*, b.p. 190—193°/1 mm., m.p. 60° (*diamide*, m.p. 166·4°; *monoamide*, m.p. 110°). The *semicarbazone*, m.p. 170° (block), of γ-keto-*n*-hexoic acid, m.p. 41—42°, is described. Et heptoylacetate, Na, and $CH_2Br{\cdot}CO_2Et$ yield *Et*$_2$ *heptoylsuccinate*, b.p. 130—134°/0·5 mm., converted by conc. HCl in boiling AcOH into *γ-keto*-n-*decoic acid*, m.p. 70°. Et propionylacetoacetate is transformed by Na and $CH_2I{\cdot}CH_2{\cdot}CO_2Et$ into *Et*$_2$ *α-propionylglutarate*, b.p. 150—152°/9 mm., hydrolysed by boiling HCl (1 : 2) to *δ-ketoheptoic acid*, b.p. 152—153°/9 mm., m.p 50° [*Ag* salt; *semicarbazone*, m.p. 193° (block; decomp.)]. *Et*$_2$ *α-butyrylglutarate*, b.p. 161—163°/10·5 mm., gives *δ-keto-octoic acid*, b.p. 156—162°/10 mm., m.p. 35° [*Ag* salt; *semicarbazone*, m.p. 195° (block; decomp.)]. *Et*$_2$ *α-valerylglutarate*, b.p. 115—125/0·5 mm., yields *δ-ketononoic acid*, m.p. 43·5° [*Ag* salt; *semicarbazone*, m.p. 142° (block)]. Et hexoylacetate (*Cu* derivative, m.p. 107°) affords *Et*$_2$ *α-hexoylglutarate*, b.p. 140—142°/0·2 mm., whence *δ-ketodecoic acid*, b.p. 155—161°/2 mm., m.p. 56·5° (*Ag* and *Ba* salts; *semicarbazone*, m.p. 126°). *Et*$_2$ *α-heptoylglutarate*, b.p. 130—136°/0·5 mm., gives *δ-ketoundecoic acid*, m.p. 60° (*Ag* and *Ba* salts; *semicarbazone*, m.p. 132·5°).

Decan-α-ol-ε-one is converted by conc. HBr at 70° into *ε-ketodecyl bromide*, b.p. 140—146°/10 mm., transformed by NH_3–EtOH into 2-n-*amyl*-Δ^2-*tetrahydropyridine*, b.p. 94·5—95°/9 mm. (*hydrochloride*; *platinichloride*, m.p. 165·5—166°; *picrate*, m.p. 67°; *stannochloride*, m.p. 127°; non-cryst. *mercurichloride*; *picrolonate*, decomp. about 170°; *perchlorate*, m.p. 88·5°), reduced by Sn and conc. HCl to 2-n-*amylpiperidine*, b.p. 86·5—87°/10 mm. (*hydrochloride*; *platinichloride*, m.p. 117°; non-cryst. *picrate* and *mercurichloride*; *picrolonate*, m.p. 154°). *Heptan-α-ol-ζ-one*, b.p. 119—122°/9 mm., is converted by H_3PO_4 into substances of high mol. wt.; with HCl it appears to yield a trace of oxide but mainly unchanged material and complex compounds. *ζ-Ketoheptyl bromide*, b.p. 107—108°/8 mm., does not appear to react with NH_3–EtOH at room temp., whereas at 60—70° it yields mainly complex bases non-volatile with steam; a seven-membered ring does not appear to be formed. H. W.

Electrochemical preparation of nitric esters. V. Öhman (Z. Elektrochem., 1936, 42, 862—872).—The prep. of several esters by electrolysis of mixtures of unsaturated org. compounds in AcOH or $COMe_2$ with aq. HNO_3, $NaNO_3$, or $Ca(NO_3)_2$, using a polished Pt anode, is described. The influences of concn. of org. compound, H_2O content of the anolyte, c.d., and anode material have been investigated. E. S. H.

Reactions of alkyl sulphates, ethyl orthosilicate, and ethyl carbonate in Friedel–Crafts syntheses. H. L. Kane and A. Lowy (J. Amer. Chem. Soc., 1936, 58, 2605—2608).—The effects of time, temp., and proportions of reagents on the formation of PhAlk (I) from C_6H_6, $AlCl_3$, and various alkyl esters are investigated. The max. yields of (I) obtained are: from Me_2SO_4 59·8, Et_2SO_4 71·4, $Pr^{\beta}_2SO_4$ 44·2, Bu_2SO_4 43·6, Et_4SiO_4 53·3, and Et_2CO_3 56·4%. Pure compounds could not be obtained from $C_{10}H_8$, Et_2SO_4, and $AlCl_3$ in CS_2 or *o*-$C_6H_4Cl_2$. EtCl is not formed from $AlCl_3$ and Et_2SO_4 or Et_2CO_3 in light petroleum. H. B.

Esters of chlorosulphonic, sulphurous, and sulphuric acids. R. Levaillant (Ann. Chim., 1936, [xi], 6, 459—581).—A compilation of 13 papers previously published (cf. A., 1935, 729, 733, and earlier abstracts). F. N. W.

β-Octyl thiocyanate. W. G. Rose and H. L. Haller (J. Amer. Chem. Soc., 1936, 58, 2648—2649).—β-Octyl bromide, $[\alpha]_D^{20}$ −32·15° (from *d*-β-octanol, $[\alpha]_D^{20}$ +9·7, and PBr_3), and MeOH–KCNS give *β-octyl thiocyanate*, b.p. 98·5—99°/4 mm., $[\alpha]_D^{20}$ +51·7°, the *d* of which is > that of the (−)-form of Kenyon *et al.* (A., 1935, 1230). H. B.

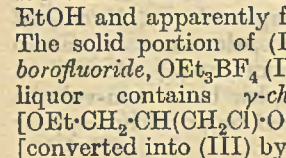
***X*-Ray and thermal examination of α-monoglycerides.**—See A., I., 17.

Synthesis of glycerides. I. C. L. Tseng and M. C. Chiang (J. Chinese Chem. Soc., 1936, 4, 463—

472).—The prep. of glycerol α-*p*-bromobenzoate (I), m.p. 74·4° (lit. 70°), and its CMe_2: derivative is modified. (I) gives the *CPh_3 ether*, m.p. 178·6° [hydrolysed by HBr–AcOH at 0° to (I)], and thence *glycerol α-CPh_3 ether* β-*benzoate* α′-p-*bromobenzoate*, m.p. 76·1—83·1°, converted by HBr–AcOH at 0° into *glycerol* β-*benzoate* α-p-*bromobenzoate*, a syrup, and thence into *glycerol* β-*benzoate* α-p-*bromobenzoate* α′-p-*nitrobenzoate*, m.p. 152·6°, and β-*benzoate* αα′-*di*-(p-*bromobenzoate*), m.p. 153·1°. M.p. are corr.

R. S. C.

Tertiary oxonium salts. I. H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil (J. pr. Chem., 1937, [ii], **147**, 257—285).—Gradual addition of epichlorohydrin (I) to $Et_2O\cdots BF_3$ in Et_2O gives a semi-solid mass (II) which on decomp. with 2*N*-Na_2CO_3 or H_2O affords *γ-chloro-α-ethoxypropanol* (III), b.p. 72—74°/13·5 mm., in 72% yield identical with the additive product from (I) and EtOH and apparently free from the isomeric β-ether. The solid portion of (II) consists of *triethyloxonium borofluoride*, OEt_3BF_4 (IV), whilst the ethereal mother-liquor contains *γ-chloro-α-ethoxy-β-propyl borate* $[OEt\cdot CH_2\cdot CH(CH_2Cl)\cdot O]_3B$, b.p. 210—216°/12 mm. [converted into (III) by Na_2CO_3], with small amounts of the *substance*, $C_5H_{11}O_2Cl,BF_3$, m.p. 108° (decomp.), also obtained from (III) and BF_3. Addition of (I) to $Me_2O\cdots BF_3$ in Me_2O yields *trimethyloxonium borofluoride* (V), *γ-chloro-α-methoxy-β-propyl borate*, b.p. 150—152°/2 mm., and the non-homogeneous *adduct* of BF_3 and *γ-chloro-2-methoxypropan-β-ol*, b.p. 64—66°/12 mm. (V) after purification by dissolution in $PhNO_2$ containing SO_2 and separation by removal of the latter has m.p. 124·5° (decomp.). (IV), m.p. 92° (decomp.) greatly dependent on purity, is very hygroscopic. When pure it can be preserved for considerable periods in sealed tubes, but slightly impure specimens soon liquefy with loss of HF. When heated, (IV) dissociates into $Et_2O\cdots BF_3$ and EtF with minor amounts of gases, including C_2H_4. The best method for the prep. of (IV) consists in the slow addition of EtF to $Et_2O\cdots BF_3$ and Et_2O in a sealed tube at room temp. $Me_2O\cdots BF_3$ and EtF unite more rapidly to *dimethylethyloxonium borofluoride* (VI), m.p. 120—121° (decomp.), which passes when heated into $MeEtO\cdots BF_3$ and MeF with minor amount of $Me_2O\cdots BF_3$ and EtF; decomp. thus occurs as with mixed quaternary ammonium halides containing Me. Addition of (IV) to Na picrate gives *triethyloxonium picrate*, m.p. 58° (decomp.), which in contact with the mother-liquor gives picric acid and Et picrate and has limited stability when solid. Attempts to prepare triethyloxonium iodide from (IV) and NaI in $COMe_2$ gave $NaBF_4$ and EtI. The following examples of the powerful ethylating action of (IV) are described. H_2O is converted into Et_2O and EtOH in 89·2 and 89% yield, respectively. (III) and (IV) at room temp. give γ-chloro-αβ-diethoxypropane, b.p. 69·8—70·4°/14 mm., in 55% yield. PhOEt is obtained in 73% or 91·1% yield from PhOH and (IV) at room temp. or from NaOPh–H_2O and (IV) at 0°. AcOH and (IV) give EtOAc in 46% yield, whilst NaOBz in H_2O and (IV) afford EtOBz (yield 70·8%). Aq. NaI and (IV) give EtI (77%). Na 3 : 5-dinitrobenzoate and (VI) give a mixture of 70% of Me and 30% of Et 3 : 5-dinitrobenzoate. $CHNa(CO_2Et)_2$ in EtOH and (IV) afford $CHEt(CO_2Et)_2$ in 35·8% yield, whereas $CHNaAc\cdot CO_2Et$ gives $CHEtAc\cdot CO_2Et$ (46·7%). (IV) (1 mol.) and NH_3 (1·1 mol.) give mainly $NHEt_2$ and NEt_3 with some NH_2Et. Gradual addition of C_5H_5N to well-cooled (IV) affords Et_2O (94·3%) and 1-*ethylpyridinium borofluoride*, m.p. 58·5—59·5°, which does not give EtF when heated and is oxidised by $K_3Fe(CN)_6$ to 1-ethylpyridone, b.p. 124—125°/13 mm. (IV) and an excess of Et_2S give *triethylsulphonium borofluoride*, m.p. 105·5°. 2 : 6-Dimethyl-4-pyrone and (IV) in CH_2Cl_2 at room temp. afford 4-*ethoxy*-2 : 6-*dimethylpyrylium borofluoride*, m.p. 90—91°, whence the corresponding *perchlorate*, m.p. 126—128°; either salt is transformed by $(NH_4)_2CO_3$ into 4-ethoxy-2 : 6-dimethylpyridine, m.p. 112°. Similarly (IV) and coumarin in CH_2Cl_2 give 2-*ethoxybenzopyrylium borofluoride*, m.p. 106° (decomp.). Camphor (VII) and (IV) yield the *compound* (VIII), m.p. 104·5—105·5° (decomp.), from which H_2O regenerates (VII).



(III.)

αβ-Unsaturated ketones such as distyryl ketone give intensely coloured salts with (IV), but differentiation between the structures $(CHR{:}CH)_2C(OEt)\cdot BF_4$ and $(CHR{:}CH)_2C{:}OEt\cdot BF_4$ is not at present possible. The *compound* $[(OMe\cdot C_6H_4\cdot CH{:}CH)_2C\cdot OEt]BF_4$ gives EtF when heated.

H. W.

Bromination of aliphatic αα-disulphones.—See A., I, 88.

Synthesis of esters by dehydration of alcohols by copper–cerium catalysts. III. M. M. Koton (J. Gen. Chem. Russ., 1936, **6**, 1291—1294).—The condensate obtained by passing EtOH over Cu–Zr catalyst (0·9% Zr) at 250° contains 50% of EtOAc and 3—6% of AcOH; the yield of EtOAc may be raised to 65% by repeating the process four times. The inactivated catalyst may be regenerated by passing air at 150—170°, followed by reduction in H_2 at 150°.

R. T.

Rates of alcoholysis of acyl chlorides.—See A., I, 87.

Reaction between esters and acid chlorides. B. Z. Amitin and E. V. Hirschberg (Proc. Charkov State Univ., 1936, **4**, 55—58).—The yield of alkyl chlorides in presence of $ZnCl_2$ (cf. Kyrides *et al.*, A., 1934, 72) in the reactions AcCl + EtOAc, AcCl + $C_5H_{11}\cdot OAc$, BzCl + furyl benzoate, and phthalyl chloride + furyl phthalate is very small or non-existent. When an alkyl chloride is formed the corresponding unsaturated hydrocarbon seems to be an intermediate product.

J. J. B.

Preparation of trichloroacetic acid. E. S. Chotinski and E. Alexandrova (Proc. Charkov State Univ., 1936, **4**, 59—61).—$CCl_3\cdot CHO$ and NO_2 at 40—60° yield up to 70% of $CCl_3\cdot CO_2H$. The NO formed can be oxidised by air to NO_2 and used again.

J. J. B.

Selective hydrogenation of mixtures of unsaturated compounds.—See A., I, 90.

Fats. XXXII. Preparation of unsaturated fatty acids by debromination of their additive

products with bromine. H. P. KAUFMANN and H. E. MESTERN (Ber., 1936, 69, [*B*], 2684—2685).—A stream of an indifferent gas is passed through a boiling solution of the pure bromide in C_5H_5N containing Zn. After 1 hr. the mixture is poured into dil. HCl and the fatty acids are extracted with Et_2O or C_5H_{12}. Examples cited are: elaidic acid from its dibromide; linoleic and linolenic acid from tetra- and hexa-bromostearic acid, respectively; tiglic acid from its dibromide. H. W.

Fats. XXIX. Thiocyanogen iodide and its addition to unsaturated fatty acids. H. P. KAUFMANN and H. G. OETRINGHAUS (Ber., 1936, 69, [*B*], 2670—2676).—Interaction of inorg. thiocyanates with I in various media generally leads to the appearance of I and CNS separately, and only in *n*-C_5H_{12} is a mixture produced which probably contains I(SCN) which could not be isolated from KCNS and IBr in absence of solvent. Indications of its production when equiv. amounts of CNS and I are boiled in C_6H_6 are given by the enhanced stability of the solution; polymerisation occurs only after several hr., and then proceeds very rapidly. Gradual addition of this solution to CHPh:CH_2, C_2H_4, C_2H_2, CH_2:CH·CH_2·CO_2H, anethole, or antipyrine causes decolorisation (I solution is not decolorised), and the products are yellowish-red oils which could not be purified and contain I and S. CHPh:CH·CO_2H and tiglic acid do not react. Addition of this solution to elaidic acid (I) in boiling C_6H_6 yields a mixture of *0-iodo-ι-thiocyanostearic acid* (II) and 0ι-dithiocyanostearic acid, the proportion of (I) being augmented by use of an excess of I in the reagent. (II) is transformed by $NaHCO_3$ in boiling EtOH into *ι-thiocyanoelaidic acid*, which could not be completely purified, and by KOH in boiling MeOH into *ι-ketostearic acid*, m.p. 74—75°. Treatment of (II) with Zn dust in boiling AcOH affords nearly homogeneous (I). The products derived from oleic acid are similar to those derived from (II), but give stearic acid when reduced. Erucic acid yields μ-iodo-ν-thiocyanobehenic acid, whence non-homogeneous *ν-thiocyanoerucic acid* and *ν-ketobehenic acid*, m.p. 82—83° (*Me* ester, m.p. 57—58°). H. W.

Fats. XXXI. Diene synthesis with fats. III. Oiticica oil. H. P. KAUFMANN and J. BALTES (Ber., 1936, 69, [*B*], 2679—2683).—α-Licanic acid (I) is converted by maleic anhydride (II) in boiling C_6H_6 in absence of light into the *adduct*, $C_{22}H_{30}O_6$, m.p. 81—82°. β-Licanic acid, m.p. 97°, best obtained by the action of a trace of I on (I) or the total fatty acids of oiticica oil in Et_2O, does not give a readily purified adduct. Kaufmann's method is inapplicable to the determination of the I val. of (I), the observed vals. being particularly high if the solution is irradiated. CNS is added to 1 of the 3 double linkings of (I) and the diene no. corresponds with the addition of 1 mol. of (II). Bromination of the fatty acids after removal of (I) does not give a sparingly sol. hexabromide, thus proving the absence of linolenic acid, but a Br_4-compound, m.p. 107—108°, is obtained. The oil contained (I) 70·0%, unsaturated non-conjugated acids 15·2%, saturated acids 9·9%, unsaponifiable matter 0·4%, and glyceryl residue 4·5%. H. W.

Wool fat. III. Lanopalmic and lanoceric acid. T. KUWATA and Y. ISHII (J. Soc. Chem. Ind. Japan, 1936, **39**, 358—359B).—Me lanopalmate (I) with red P and boiling HI affords *lanopalmitic acid*, $C_{16}H_{32}O_2$, m.p. 42—43·5°, whereas with CrO_3 in Ac_2O at 50° followed by hydrolysis, *lanopalminonic acid*, m.p. 50—51·5° (*monoxime*), is formed, which indicates that (I) is a *sec.* alcohol. Hydrolysis of wool fat affords *K lanocerate*, converted by boiling conc. HCl into the *lactide* (II), $C_{64}H_{122}O_5$, m.p. 98·5—99°, of lanoceric acid. When heated at 400° with Se, (II) affords a *substance*, $C_{25}H_{40}$ or $C_{26}H_{52}$, b.p. 170—190°/5 mm. [*picrate*, m.p. 156—170° (decomp.)]. J. L. D.

Polymerisation of methyl esters of higher unsaturated acids. XVIII. Polymerisation products [obtained by heating] the methyl esters of linseed fatty acids. XIX. Increase in iodine value of the hydrogenated intermolecular polymerised ester. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, **30**, 244—248, 249—251; cf. A., 1936, 705).—XVIII. If the Me esters of linseed fatty acids are heated at 280—290° in H_2 and then fractionated, all the fractions obtained give, when reheated, similar fractions, including one having b.p. <178°/3 mm. Fission of a C·C linking is indicated. With continued heating *n* and the I val. decrease.

XIX. The increase (on heating) in I val. of the esters of linseed and sardine oil acids decreases only very slightly after hydrogenation of the esters and is thus not due to absorption at conjugated linkings. R. S. C.

Highly unsaturated acids in sardine oil. XII. Separation of octadecatrienoic acid $C_{18}H_{30}O_2$. XIII. Oxidation of methyl clupanodonate with potassium permanganate in acetone. XIV. Oxidation of potassium clupanodonate with potassium permanganate in aqueous solution. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1936, **11**, 741—744, 745—750, 751—753; cf. A., 1935, 960).—XII. Fractionation of highly unsaturated acids by pptn. as Na salts from $COMe_2$ indicates the presence of a small proportion of octadecatrienoic acid, which was not characterised.

XIII. Oxidation of Me clupanodonate with $KMnO_4$ in $COMe_2$ affords $EtCO_2H$, $(·CH_2·CO_2H)_2$, Me H succinate, and AcOH, and confirms results obtained from O_3 on amyl clupanodonate (cf. A., 1935, 1482).

XIV. In agreement with the above, oxidation of K clupanodonate with $KMnO_4$ in KOH solution affords AcOH, $EtCO_2H$, and $(·CH_2·CO_2H)_2$. J. D. R.

α-Ethoxy-ethylenic acids. M. MEYER (Compt. rend., 1936, **203**, 1074—1077).—Further examples of the reaction previously outlined (A., 1933, 491) are given: CH_2:CH·CH_2Br → *Et α-ethoxy-α-allylmalonate*, b.p. 139°/15 mm., → *α-ethoxy-α-allylmalonic acid*, m.p. 93°, → *α-ethoxy-α-Δ^γ-pentenoic acid*, b.p. 120°/15 mm. (acid *chloride*, b.p. 56°/13 mm.; *amide*, m.p. 69·5°). $CHBu^β$:CH·CH_2Br → *Et α-ethoxy-α-ε′-methyl-Δ$^{β′}$-hexenylmalonate*, b.p. 145°/4 mm., *Et α-ethoxy-α-ε′-methyl-Δ$^{β′}$-hexenylmalonic acid* → *α-ethoxy-ζ-methyl-Δ^γ-octenoic acid*, b.p. 136°/3·5 mm. (acid *chloride*, b.p. 108°/14 mm.; *amide*, m.p. 56°). CHPh:CH·CH_2Br → *Et α-ethoxy-α-cinnamylmalonate*, b.p. 183°/4 mm., →

α-ethoxy-α-cinnamylmalonic acid, m.p. 130°, → *α-ethoxy-δ-phenyl-Δ$^{\gamma}$-pentenoic acid*, b.p. 170°/3 mm. (acid *chloride*, b.p. 126—127°/3·5 mm.; *amide*, m.p. 98°). *Undecenyl chloride* (from undecenoic acid and $SOCl_2$ in $NHMe_2$), b.p. 120°/15 mm., → *Et α-ethoxy-α-undecenylmalonate*, b.p. 150°/3 mm., → *α-ethoxy-α-undecenylmalonic acid*, m.p. 56°, → *α-ethoxy-Δ$^{\lambda}$-tridecenoic acid*, b.p. 170°/4 mm. (*chloride*, b.p. 136°/4 mm.; *amide*, m.p. 49°). F. N. W.

Highly unsaturated compounds. VI. Triene acid from pomegranate seeds. E. H. Farmer and F. A. Van Den Heuvel (J.C.S., 1936, 1809—1811).—Evidence is given confirming Toyama and Tsuchiya's claim (A., 1935, 960) to have isolated an elæostearic acid (punicic acid) differing from the α- and β-forms of the acid. F. N. W.

α-Ketol carboxylic acids. I. θ-Hydroxy-ι-keto- and ι-hydroxy-θ-keto-stearic acids. G. King (J.C.S., 1936, 1788—1792).—Controlled oxidation (aq. $KMnO_4$–KOH; 8—10 min.; 8—10°) of oleic acid affords 30—40% of a mixture of *θ-hydroxy-ι-* (I), m.p. 74° (*semicarbazone*, m.p. 152°; *dinitrophenylosazone*, m.p. 146·5°), and *ι-hydroxy-θ-ketostearic acid* (II), m.p. 75·5° (*semicarbazone*, m.p. 138·5°; *dinitrophenylosazone*, m.p. 146·5°), and 20—35% of dihydroxystearic acid (II). Elaidic acid similarly (but at 25°) affords 50—60% of (I) and (II) and 10—20% of (III). (I) or (II) on mild oxidation (AcOH–CrO_3; 24 hr.; room temp.) gives stearoxylic acid; stringent oxidation (2*N*-H_2SO_4–$KMnO_4$; 10 min.; 100°) yields mainly nonoic (IV) and azelaic acids. Oxidation (HIO_4; 48 hr.; room temp.) of (I) affords (IV) and azelaldehyde (2 : 4-*dinitrophenylhydrazone*, m.p. 120°), whilst (II) gives nonaldehyde and azelaic acid. (I) on reduction (Zn–Cu; 48 hr.; 60—70°) yields (III), but (II) similarly treated is unaffected. Interconversion of (I) and (II) is complete in 24—36 hr. at room temp. or in 5 min. at 100°. F. N. W.

Hydrates of molecular compounds of zirconyl oxalate with oxalic acid and alkali oxalates.—See A., I, 93.

Chemical and biochemical dehydrogenation of αα′-dideuterosuccinic acid. H. Erlenmeyer, W. Schoenauer, and H. Süllmann (Helv. Chim. Acta, 1936, **19**, 1376—1380).—$(CHD{\cdot}CO_2Et)_2$ and SeO_2 give $CO_2Et{\cdot}CD{:}CH{\cdot}CO_2Et$, H and D being removed with almost equal ease. $(CHD{\cdot}CO_2H)_2$ (I) and succinodehydrase give a $CO_2H{\cdot}CD{:}CH{\cdot}CO_2H$ with an increased D : H ratio; this is probably because this reaction is reversible and the D reacts more slowly. In conformity with this explanation (I) reacts more slowly than does $(CH_2{\cdot}CO_2H)_2$ in Thunberg's dehydrogenation and Warburg's O_2-consumption experiments. R. S. C.

Michael reaction with acetylenic esters. E. H. Farmer, S. C. Ghosal, and G. A. R. Kon (J.C.S., 1936, 1804—1809; cf. A., 1932, 1127).—Et phenylpropiolate (I) with $CHNa(CO_2Et)_2$ (II) affords a *Na* derivative, which with EtI (7 days; 100°) gives *Et α-carbethoxy-β-phenyl-α-ethylglutaconate*, b.p. 212—213°/10 mm., which on ozonolysis affords oxalic (III) and ethylmalonic acid. Similarly (I) with $CMeNa(CO_2Et)_2$ (IV) yields a *Na* derivative, which with EtI gives *Et α-carbethoxy-β-phenyl-α-methyl-γ-ethylglutaconate*, b.p. 211—213°/15 mm. (hydrolysed to *β-phenyl-α-methyl-γ-ethylglutaconic acid*, m.p. 75—76°; ozonised to $EtCO_2H$ and Et benzylmethylmalonate), which with $CH_2Br{\cdot}CO_2Et$ gives $CO_2Et{\cdot}CH_2{\cdot}C(CO_2Et){:}CPh{\cdot}CMe(CO_2Et)_2$ [ozonolysis products: (III), Et oxaloacetate, and Et benzoylmethylmalonate] and with NaOEt, Et α-carbethoxy-β-phenyl-α-methylglutaconate is formed. $(:C{\cdot}CO_2Et)_2$ (V) (modified prep.) with (IV) affords a *Na* derivative, which with EtI affords *Et α-carbethoxy-α-methyl-γ-ethylaconitate*, b.p. 210—211°/20 mm. (ozonised to Et α-ketobutyrate and Et oxalylmethylmalonate), and with HCl gives *Et α-carbethoxy-α-methylaconitate* (VI), b.p. 206—207°/20 mm. [ozonised to (III)], and Et oxalylmethylmalonate. (V) and (II) give a *Na* derivative (corresponding free *ester*, b.p. 204—205°/15 mm.), which with MeI (reflux in C_6H_6; 5 days) yields (VI). Et tetrolate with (IV) in presence of NaOEt [or with (II) followed by methylation] gives *Et α-carbethoxy-αβ-dimethylglutaconate*, b.p. 170°/15 mm., which on ozonolysis affords Et acetylmethylmalonate (*semicarbazone*, m.p. 137°) and a *compound*, b.p. 110—130°/17 mm. Similarly Et propiolate affords a *compound*, b.p. 175°/20 mm., a *compound*, m.p. 134—135°, b.p. 22°/20 mm., and Et α-carbethoxy-α-methylglutaconate, which on ozonolysis gives (III) and Et formylmethylmalonate (?) (*semicarbazone*, m.p. 178°). (IV) with Et oxalochloride forms a *compound*, b.p. 173—175°/22 mm., which with $NHPh{\cdot}NH_2$ (1 mol.) affords $NHPh{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}CMe(CO_2Et)_2$, m.p. 120°, and with $NHPh{\cdot}NH_2$ (2 mol.) affords $NHPh{\cdot}NH{\cdot}CO{\cdot}C(N{\cdot}NHPh){\cdot}CMe(CO_2Et)_2$, m.p. 275°. F. N. W.

Dihydroxystearic acid in castor oil. Y. Toyama and T. Ishikawa (Bull. Chem. Soc. Japan, 1936, **11**, 735—741).—*Me dihydroxystearate* (I), m.p. 111—112°, slightly dextrorotatory in MeOH (*diacetate*, $[\alpha]_D^{30}$ +0·19°), obtained by "methanolysis" of castor oil, is hydrolysed to dihydroxystearic acid (II) (*Et* ester, m.p. 104—105°, and its *diacetate*, $[\alpha]_D^{30}$ +0·31°). (II) is oxidised by $K_2Cr_2O_7$ to *n*-nonoic and azelaic acid. (I) with HBr, followed by debromination with Zn and MeOH and hydrolysis, gives elaidic and oleic acids. (II) is thus *d*-θι-dihydroxystearic acid. Attempts to resolve the racemic acid (from oxidation of oleic acid) failed. J. D. R.

Reaction mechanism of the electrolytic oxidation of tartaric acid. V. Sihvonen (Suomen Kem., 1936, **9**, B, 32; cf. this vol., 44; A., 1936, 54; 1933, 914).—The reaction mechanism is interpreted in the light of the results of other investigations. J. L. D.

Metallic complex salts of aliphatic polyhydroxy-compounds. W. Traube and F. Kuhbier [with W. Schröder] (Ber., 1936, **69**, [*B*], 2655—2663; cf. A., 1933, 1272).—Addition of aq. $BaCl_2$ to solutions of suitable quantities of tartaric acid, $CuCl_2$, and NaOH gives the very sparingly sol. *salts*, $[C_4H_2O_6Cu]Ba,H_2O$ and $[(C_4H_3O_6)_2Cu]Ba_2,3H_2O$. Gluconic acid (I), $Cu(OH)_2$, and NaOH with $BaCl_2$ yield the *compounds*, $[C_6H_8O_7Cu]Ba,3H_2O$ and $[(C_6H_9O_7)_2Cu]Ba_2,9H_2O$; similar *substances* are derived from glucoheptonic acid. Mannitol (II),

$Cu(OH)_2$, NaOH, and $BaCl_2$ yield the *compound*, $[(C_6H_9O_6)_2Cu_4]Ba,3H_2O$; removal of mannitol is almost quant. if NaOH and $BaCl_2$ are replaced by $Ba(OH)_2$. $[C_6H_{10}O_6Cr]K,2H_2O$ is obtained from the Ba salt (*loc. cit.*) and $KHSO_4$. Gradual addition of $CrCl_3$ and (I) in H_2O to 14·5% NaOH followed by $BaCl_2$ yields the *salt*, $[C_6H_7O_7Cr]Ba,7H_2O$ (also anhyd.), whence $[C_6H_8O_7Cr]K,2H_2O$; the *complexes*, $[C_6H_7O_7Al]Ba,3H_2O$, (whence $[C_6H_8O_7Al]K,2H_2O$) and $[C_6H_7O_7Be]Ba,2H_2O$ (whence $[C_6H_8O_7Br]K,2H_2O$) are obtained analogously. Similarly (II) gives the *compound*, $[C_6H_{10}O_6)_2Bi_2]Ba,3H_2O$. Quinic acid, $Be(NO_3)_3$, and NaOH followed by $BaCl_2$ yield the *salt*, $[C_{14}H_{17}O_{12}Bi]Ba_2,7H_2O$. (II), Sb_2O_3, and 7% $Ba(OH)_2$ at 100° afford the *complex*, $[(C_6H_{12}O_6)_4Sb_2]Ba,4H_2O$ or $[C_6H_{12}O_6)_2Sb]K,2H_2O$ if KOH replaces $Ba(OH)_2$. (I) similarly yields the *salt*, $[C_6H_7O_7Sb]Ba,H_2O$, whence $[C_6H_8O_7Sb]K,H_2O$. Addition of $SbCl_5$ followed by $BaCl_2$ to (II) and 10% NaOH yields the *substance*, $[(C_6H_5O_7)_2Sb_4]Ba_3,H_2O$, whence $[(C_6H_8O_8)_2Sb_3]K_3,9H_2O$. (I), $Ni(NO_3)_2$, and NaOH followed by $BaCl_2$ yield the *compound*, $[C_6H_8O_7Ni]Ba,2H_2O$, whence $[C_6H_9O_7Ni]K$. With Na_2CO_3 and $Co(NO_3)_2$ or $MnCl_2$ (I) yields the *complexes*, $[C_6H_9O_7Co]Na$ and $[C_6H_9O_7Mn]Na$, respectively. Passage of air through a solution of (I), NaOH, and $Co(NO_3)_2$ in H_2O followed by addition of $BaCl_2$ yields the *substance*, $[C_6H_7O_7Co]Ba,H_2O$, whence $[C_6H_8O_7Co]K,H_2O$. The *compound*, $[C_6H_7O_7Fe]Ca,3H_2O$, is transformed by (I) into the *substance*, $[C_{12}H_{19}O_{14}Fe]Ca,2H_2O$. H. W.

Determination of ascorbic acid.—See A., III, 79.

Acetyl derivatives of monobasic sugar acid lactones. F. W. Upson, J. M. Brackenbury, and C. Linn (J. Amer. Chem. Soc., 1936, **58**, 2549—2552; cf. A., 1932, 43).—The $[\alpha]_D^{25}$-time curves for the Ac derivatives of 10 γ- and 3 δ-lactones in $COMe_2$–H_2O (80 : 20) are very similar to those for the parent lactones in H_2O. 2 : 3 : 5 : 6-*Tetra-acetyl-γ*-d-*galactono*-, m.p. 67—68°, -d-*gulono*-, m.p. 103—104°, -d-*talono*-, and -l-*rhamnono*- and 2 : 3 : 4 : 6-*tetra-acetyl*-δ-l-*rhamnono*-, m.p. 71°, and -d-*mannono*-, m.p. 99—101°, *-lactones* are new. H. B.

Derivatives of *l*-allonic and *l*-altronic acid. I. F. L. Humoller, W. F. McManus, and W. C. Austin (J. Amer. Chem. Soc., 1936, **58**, 2479—2481).—Rapid vac. evaporation of a freshly prepared aq. EtOH solution of *l*-allonic acid (phenylhydrazide, m.p. 142—145°, $[\alpha]_D$ −23·6°), dissolution of the residual syrup in EtOH, and re-evaporation gives δ-l-*allonolactone* (I), m.p. 140—144°, $[\alpha]_D$ −54·8° → +3·66°, which can be titrated against dil. bases (phenolphthalein) in cold aq. solution. (I) mutarotates more rapidly than γ-*l*-allonolactone (II), m.p. 129—130°, $[\alpha]_D$ +7·2° → +3·6° (24 days) (A., 1934, 759). Fusion of (I) affords (II). A lactone could not be prepared from l-*altronic acid*, m.p. 110°, $[\alpha]_D$ −8·1° (phenylhydrazide, m.p. 151—152°, $[\alpha]_D$ +18·4°) [from its Ca salt (*loc. cit.*) and $H_2C_2O_4$]. Oxidation of (II) with HNO_3 (*d* 1·15) give *allomucic acid*, m.p. 187·5° (decomp.) (inactive), which appears to differ from the acid obtained by C_5H_5N-rearrangement (method: Fischer, A., 1891, 1193, 1444) of mucic acid (cf. Posternak, A., 1935, 846). All rotations are in H_2O at 20—25°. H. B.

Autoxidation of the complex metallic compounds of gluconic acid. W. Traube and F. Kuhbier [with W. Schröder] (Ber., 1936, **69**, [*B*], 2664—2666; cf. A., 1932, 362).—Autoxidation of the alkali Cu and Co complexes of gluconic acid occurs at [OH′] corresponding with that of Na_2CO_3; the amount of complex-united metal can be very greatly reduced, further for Cu than for Co. Similar experiments with the Ni and Mn complexes are recorded. H. W.

Acetyl derivatives of gluconic and xylonic acids. R. T. Major and E. W. Cook (J. Amer. Chem. Soc., 1936, **58**, 2474—2477).—Acetylation (Ac_2O–$ZnCl_2$ at 0°—room temp.) of δ-gluconolactone followed by cold H_2O gives 2 : 3 : 4 : 6-tetra-acetyl-*d*-gluconic acid hydrate (I), m.p. 114—115°, $[\alpha]_D^{20}$ −5° in EtOH (cf. Upson and Bartz, A., 1932, 43), also prepared by oxidation (Br–aq. $KHCO_3$) of glucose tetra-acetate (II). (I) is similarly further acetylated to *penta-acetyl*-d-*gluconic acid* (+H_2O), m.p. 72—73°, $[\alpha]_D^{20}$ +7·5° in $CHCl_3$, anhyd. m.p. 110—111°, $[\alpha]_D^{20}$ +11·5° in $CHCl_3$ (*Et* ester, m.p. 103—104°, $[\alpha]_D^{20}$ +20·5° in $CHCl_3$; *phenylhydrazide*, m.p. 152—154°, $[\alpha]_D^{20}$ +28° in EtOH, obtained by similar acetylation of gluconphenylhydrazide), also prepared by oxidation (as above) of *aldehydo-d*-glucose penta-acetate. The semicarbazone from (II) is the ring-form (cf. Wolfrom *et al.*, A., 1934, 1092). Acetylation (Ac_2O–C_5H_5N at 60—70°) of *d*-xylosesemicarbazone gives (mainly) the *tetra-acetate*, m.p. 232—233°, $[\alpha]_D^{20}$ +21° in MeOH (ring structure); the residual product with HNO_2 affords *aldehydo-d*-xylose tetra-acetate (III). Successive treatment of the crude semicarbazone of *l*-xylose triacetate with Ac_2O–C_5H_5N, MeOH–$H_2C_2O_4$, and HNO_2 gives aldehydo-l-*xylose tetra-acetate* (IV), m.p. 90—91°, $[\alpha]_D^{20}$ +22·5° in $CHCl_3$. Oxidation (Br–H_2O + $CaCO_3$) of (III), (IV), and the *dl*-compound, m.p. 85—86°, affords *tetra-acetyl*-d-, m.p. 86—88°, $[\alpha]_D^{20}$ +5° in EtOH, -l-, m.p. 86—88°, $[\alpha]_D^{20}$ −4·5° in EtOH, and -dl-, m.p. 134—135°, *-xylonic acid*, respectively. H. B.

Preparation and properties of penta-acetyl-α-keto-*d*-glucoheptonic acid. R. T. Major and E. W. Cook (J. Amer. Chem. Soc., 1936, **58**, 2477—2478).—*Penta-acetyl*-d-*gluconyl chloride*, m.p. 68—70°, $[\alpha]_D^{20}$ +2° in $CHCl_3$ (from the anhyd. acid and PCl_5 in Et_2O; $SOCl_2$ is unsatisfactory), with EtOH and Et_2O–NH_3 gives the Et ester and amide, respectively; with AgCN at 120—125° the *nitrile* (I), m.p. 116°, $[\alpha]_D^{20}$ +7° in $CHCl_3$, of *penta-acetyl-α-keto*-d-*glucoheptonic acid*, m.p. 160—161°, $[\alpha]_D^{20}$ ±0° in EtOH (*Et* ester, m.p. 97—98°, $[\alpha]_D^{20}$ ±0° in EtOH), results. (I) is hydrolysed by dioxan–HCl containing a little H_2O. *Tetra-acetyl*-dl-*xylonyl chloride*, m.p. 90—92°, similarly gives *Et tetra-acetyl*-dl-*xylonate*, m.p. 70—72°, *tetra-acetyl*-dl-*xylonamide*, m.p. 130—132°, and *tetra-acetyl-α-keto*-dl-*gulononitrile*, m.p. 125—126°. Acetylation (Ac_2O–$ZnCl_2$ at 0°—room temp.) of Me α-keto-*d*-gluconate affords a Ac_4 derivative, m.p. 168—169°, $[\alpha]_D^{20}$ −133° in $CHCl_3$ (cf. Ohle and Wolter, A., 1930, 744). H. B.

Carbohydrate theory of origin of petroleum. I. Conversion of acetaldehyde into hydrocarbons. N. A. Orlov and E. M. Tarasenkova (Ann. Leningrad State Univ., Chem. Ser., 1935, 1, 113—122).—Paracetaldehyde, H_2O, and CaO (300—330°; 3 hr.) yield tarry, liquid, and gaseous products. EtOH, HCO_2H, AcOH, $EtCO_2H$, and $PrCO_2H$ were identified in the aq. layer, whilst the gas contained CO_2 62, C_nH_{2n} 2·14, CO 7·48, O_2 1·87, and H_2 25%. The tar was hydrogenated [MoS_3 and $Al(OH)_3$ catalyst] at 370—380°/100 atm. (2 hr.), to yield liquid hydrocarbons, b.p. 34—150°, and a solid residue, which when oxidised gave BzOH and phthalic acid. The liquid product contained 70% of aromatic (C_6H_6, PhMe, PhEt, xylene, $C_{10}H_8$, 2-$C_{10}H_7Me$, and $C_{10}H_6Me_2$), 20% of naphthene, and 10% of paraffin hydrocarbons. R. T.

Depolymerisation of paraldehyde.—See A., I, 88.

Thermal decomposition of crotonaldehyde. F. A. DeLisle, W. R. T. Fowler, E. L. Lovell, and W. Ure (Trans. Roy. Soc. Canada, 1936, [iii], 30, III, 65—73).—The principal products of the thermal decomp. of crotonaldehyde between 430° and 482° and initial pressures from 25 mm. to 352 mm. are CO and propylene. CH_4, H_2, and O_2 are formed in small quantity. The reaction appears heterogeneous and approx. bimol. O. D. S.

Reaction of crotonaldehyde and amine salts. C. Mannich and K. Roth (Arch. Pharm., 1936, 274, 527—537).—CHMe:CH·CHO (I) and amine salts give complex mixtures of substances in dynamic equilibrium with each other. If piperidine is used under the simplest conditions (p_H 7·5, falling to 5 during the reaction), hydrogenation (PtO_2) of the reaction mixture gives 80% of 1-*n*-butylpiperidine (II), but this is of no constitutional significance, as it is formed also by hydrogenation of a mixture of PrCHO and piperidine. The crude reaction mixture of PrCHO and piperidine. The crude reaction mixture with Na–Hg and HCl gives amongst other products (II) (8%), γ-piperidino-*n*-butyl alcohol (III) (20%), and *αγ-dipiperidino*-n-*butane* (IV) (*dihydrobromide*, m.p. 272—276°). (III) arises from β-*piperidino*-n-*butaldehyde*, the *semicarbazone*, m.p. 116—117°, of which is isolated in 20% yield from the crude reaction mixture; (IV) is formed from *αγ*-dipiperidino-Δ^{α}-butene, which, however, partly decomposes into CHMe:C:CH·$C_5H_{10}N$, 10% of which is isolated from the crude reaction mixture. $NHMe_2$ leads similarly (Na–Hg) to NMe_2·CHMe·CH_2·CH_2·OH; NH_2Me leads (Na–Hg) to much γ-methylamino-*n*-butyl alcohol (V), b.p. 81—82°/13 mm. (lit. 65°/14 mm.) [(p-NO_2·C_6H_4·*CO*)$_2$ derivative, m.p. 132°)], and some NHMeBu, b.p. 89—90° (*picrate*, m.p. 115°; *platinichloride*, m.p. 190°), and *αγ-di*(*methylamino*)*butane*, b.p. 157—158° [*hydrochloride*, hygroscopic, m.p. 186—187°; H_2 *dioxalate*, m.p. 190—190·5° (decomp.)]. (V) with 35% CH_2O or PhCHO (at 60—70°) gives 3 : 4-*dimethyl*-, b.p. 40—45°/20 mm. [*hydrochloride*, m.p. 175°; *methiodide*, m.p. 223—225° (decomp.)], and 2-*phenyl*-3 : 4-*dimethyl-tetrahydro*-1 : 3-*oxazine*, b.p. 131—135°/19 mm. (*hydrochloride*, m.p. 173—174°), respectively. R. S. C.

Condensation of β-*cyclo*citral with dimethylacraldehyde. R. C. Fuson and R. E. Christ (Science, 1936, 84, 294—295).—The solution obtained by the action of $Al(OPr^{\beta})_3$ on the crude reaction product of the condensation of β-*cyclo*citral with dimethylacraldehyde gives a blue colour with $SbCl_3$ in $CHCl_3$. The ultra-violet spectrum shows a max. at 328 mμ. L. S. T.

Rapid approximate determination of acetone in aqueous solutions. E. K. Nikitin (J. Appl. Chem. Russ., 1936, 9, 1543—1546).—1 ml. of 0·001—0·05% aq. $COMe_2$ and 1 ml. of 0·2% aq. furfuraldehyde are shaken with 1 ml. of 50% KOH, when the time elapsing before appearance of turbidity is a linear function of the $COMe_2$ content. Solutions containing >0·05% of $COMe_2$ should be diluted accordingly. R. T.

Pseudo-binary fusion diagram of monomeric and dimeric dihydroxyacetone.—See A., I, 82.

Condensation of ketones with formaldehyde in alkaline media. J. Descombe (Compt. rend., 1936, 203, 1077—1079).—Condensation of the appropriate ketone in large excess with CH_2O in presence of K_2CO_3 affords γ-keto-β-methyl-β-hydroxymethylbutyl alcohol, m.p. 66° (lit. 60°), b.p. 142—144°/14 mm. (*diphenylurethane*, m.p. 116°; *oxime benzoate*, m.p. 129°; *acetobromohydrin*, b.p. 106—107°/2 mm.), γ-keto-β-methyl-β-hydroxymethyl-*n*-amyl alcohol, m.p. 55°, b.p. 148—150°/16 mm. (*diphenylurethane*, m.p. 103—104°; *acetobromohydrin*, b.p. 140—143°/16 mm.), *γ-keto-ββ-dimethylbutyl alcohol*, b.p. 85—86°/16 mm. (*oxime*, m.p. 82°; p-*nitrobenzoate*, m.p. 82—83°), and *γ-keto-ββδ-trimethyl*-n-*amyl alcohol*, b.p. 97—98°/20 mm. (*isooxazoline*, m.p. 101—102°; p-*nitrobenzoate*, m.p. 82—83°). In addition $COMePr^{\beta}$ also forms a *compound*, m.p. 58°. F. N. W.

Aliphatic and aliphatic-aromatic metalloketyls. I. B. Nazarov (Ann. Leningrad State Univ., Chem. Ser., 1935, 1, 123—168).—Aliphatic ketones of the type $COBu^{\gamma}R$ react with Na in an inert atm. to yield intensely coloured Na ketyls, ONa·$CBu^{\gamma}R$, which combine to afford Na-ethylene glycols of the type (ONa·$CBu^{\gamma}R$·)$_2$. The intermediate ketyl has only an instantaneous existence when R = Me, Et, or Pr^{α}, and lasts only a few hr. or days when R = Pr^{β}, Bu^{γ}, $CHEt_2$, or CMe_2Et; it is comparatively stable, existing in equilibrium with the glycols, when R = $CMeEt_2$ or CEt_3. Ketones of type COPhR do not in any case behave analogously to those of the first group; those in which R = Me, Et, Pr^{α}, or Pr^{β} react similarly to those of the second, and in which R = $CHEt_2$, Bu^{γ}, CMe_2Et, $CMeEt_2$, or CEt_3 to those of the third, group. Na and $COBu^{\gamma}_2$ (24 hr. at room temp., followed by 6 hr. at 100—120°) afford a product, which with aq. H_2SO_4 yields a mixture of $CHBu^{\gamma}_2$·OH and ββεε-*tetramethyl*-γδ-*di*tert.-*butylhexane*-γδ-*diol*, m.p. 85—86°, converted by conc. H_2SO_4 into *Bu*$^{\gamma}$ *tri*tert.-*butylmethyl ketone*, b.p. 119—121°/12 mm. When dry CO_2 is passed through $COBu^{\gamma}_2$ in Et_2O in presence of Na, and aq. H_2SO_4 is added to the reaction mixture, the products are $COBu^{\gamma}_2$ and *di*tert.-*butylglycollic acid*, an oil. $COMeBu^{\gamma}$ and Na afford $CHMeBu^{\gamma}$·OH, *pentamethyl*tert.-*butylacetone* (I), b.p. 200—209°, and

βγ-*di*tert.-*butyl*-Δ^{α}-*buten*-γ-*ol*, b.p. 105—107°/15 mm., converted by distillation from $H_2C_2O_4$ into (I) and βγ-*di*tert.-*butyl*-$\Delta^{\alpha\gamma}$-*butadiene*, b.p. 168—170°, which condenses with maleic anhydride in C_6H_6 to yield 4 : 5-*di*tert.-*butyl*-1 : 2 : 3 : 6-*tetrahydrophthalic anhydride*, m.p. 128—129°. (I) in EtOH and Na afford ββδ-*trimethyl*-δ-tert.-*butylpentan*-γ-*ol*, b.p. 99°/15 mm. (*benzoate*, m.p. 48—49°). $COPr^{\beta}_2$ and Na yield $CHPr^{\beta}_2$·OH and βε-*dimethyl*-γδ-*di*iso*propylhexane*-γδ-*diol*, m.p. 90—91° (*dibenzoate*, b.p. 150—153°/19 mm.). $COBu^{\gamma}R$ (R = Pr^{β}, $CHEt_2$, CEt_3, $CMeEt_2$, CMe_2Et) and Na yield unstable pinacones, decomposed by aq. AcOH to give mixtures of the original ketones and their corresponding alcohols. COPhR (R = Pr^{β}, $CHEt_2$) and Na, followed by aq. acid, yield mixtures of the original ketones and their alcohols, whilst when R = Et or Pr^{α} γδ-*diphenylhexane*-γδ-*diol*, m.p. 130—133°, or δε-*diphenyloctane*-δε-*diol*, m.p. 94—96°, are obtained in addition. When R = Bu^{γ}, CMe_2Et, $CMeEt_2$, or CEt_3, the free Na ketyls are isolated; the second two react with H_2O to yield the original ketone and its alcohol, whilst the first two give, in addition, γδ-*diphenyl*-ββεε-*tetramethylhexane*-γδ-*diol*, m.p. 127—130°, and δε-*diphenyl*-γγζζ-*tetramethyloctane*-δε-*diol*, m.p. 87—88°. $CPhBu^{\gamma}$·ONa and BzCl in Et_2O yield α-*phenyl*-α-*benzoylpropyl alcohol*, m.p. 68—70°. ββ-*Dimethyl*-δδ-*diethylhexan*-γ-*ol*, b.p. 225—228° (by reduction of the corresponding ketone), and $H_2C_2O_4$ (3 hr. at 140—200°) yield $CHMe{:}CMe_2$ (II), $CHMe{:}CEt_2$ (III) (*nitrosochloride*, m.p. 74°), and a mixture of $C_{12}H_{24}$ hydrocarbons, which were also the only products isolated from the dehydration products of $OH·CHBu^{\gamma}·CMe_2Bu^{\gamma}$. $CMe_2Et·CHBu^{\gamma}·OH$ when dehydrated by heating with 1 : 4-$C_{10}H_6Br·SO_3H$ at 180° affords $CH_2{:}CMeEt$, (II), $CHEt{:}CMe_2$ (IV), and decenes, whilst ββδ-*trimethyl*-δ-*ethylhexan*-γ-*ol*, b.p. 207—211°, gives (II), (III), (IV), and unidentified products of higher b.p. R. T.

Ketol condensation. T. Voitila (Suomen Kem., 1936, 9, B, 30—32).—$COMeEt$ and boiling $COMe_2$ during three weeks in presence of $Ba(OH)_2$ afford ketols which are oxidised by I to mesityl oxide, β-methyl-Δ^{β}-hexen-δ-one, and a compound, $C_7H_{12}O$, b.p. 147—149°/761 mm. (*dinitrophenylhydrazone*, m.p. 155—156° after sintering at 153°), derived from β-hydroxy-βγ-dimethylpentan-δ-one (cf. A., 1929, 1273) are obtained. A probable mechanism is suggested. J. L. D.

(A) Interconversion of ketose and aldose sugars in dilute aqueous solution. H. R. Garbutt and R. S. Hubbard. **(B) Changes in composition of dilute buffered carbohydrate solutions produced by boiling.** R. S. Hubbard and H. R. Garbutt (Proc. Soc. Exp. Biol. Med., 1935, 33, 270—273, 274—279).—(A) When an aq. solution of glucose, fructose, or mannose is boiled, slow conversion of the sugar into a mixture of aldose and ketose forms takes place (4—6 hr.). O_2 has no effect on the reaction.

(B) Similar results are obtained in presence of OAc′ or PO_4''' buffers, the rate of conversion increasing with rise in p_H. In presence of PO_4''' buffer the loss in reducing power when O_2 is bubbled through the solution is more rapid than when OAc′ or no buffer at all is employed. W. O. K.

Asymmetric oxidation of sugars by optically active alkaline copper solutions. N. K. Richtmyer and C. S. Hudson (J. Amer. Chem. Soc., 1936, 58, 2540—2544; cf. A., 1935, 1355).—Oxidation of *d*- and *l*-altrose by alkaline $K_3Fe(CN)_6$ (prep. essentially that of Hanes, A., 1929, 478) and by Cu reagents prepared (method: Shaffer and Somogyi, A., 1933, 699) with *dl*- or *meso*-tartaric acid occurs to the same extent (for individual reagents). Cu reagents prepared with *d*- or *l*-tartaric acid oxidise the sugars asymmetrically, *e.g.*, the *d*-sugar is oxidised to a greater extent by the *l*-reagent. The behaviour of *d*- and *l*-arabinose is strictly parallel. *d*-Glucose is, however, oxidised to approx. the same extent by all four Cu reagents. The relative reducing powers of 11 other sugars towards the *d*-, *l*-, and *dl*-reagents are compared. H. B.

Mechanism of carbohydrate oxidation. XXIII. Alkaline hydrolysis of oligosaccharides. H. Gehman, L. C. Kreider, and W. L. Evans (J. Amer. Chem. Soc., 1936, 58, 2388—2395).—Alkaline hydrolysis of oligosaccharides can occur if :C·OR (R is, *e.g.*, glucosido) is present or if the original mol. can assume such a structure under the influence of the alkali. The disaccharides previously studied (A., 1930, 326; 1932, 148) give rise to intermediates which are then assumed to form glucosidic enediols; these are then hydrolysed to glucose [which can yield lactic acid (I)] and the enediol [triose converted into (I); tetrose converted into saccharinic acid (II)]. The yields of (I) obtained from gentiobiose (III) and glucosidodihydroxyacetone (IV) (as penta-acetate) with aq. KOH support the view that β-glucosidoglyceraldehyde is produced from (III). Comparison of (IV) with cellobiosidodihydroxyacetone (V) (as octa-acetate), (III) with gentiobiosidodihydroxyacetone (as octa-acetate), and cellobiose with (V) confirms the view (*loc. cit.*) that the hexosido-group of the 4-hexosidohexoses is the source of (I). The yields of (I) from the various oligosaccharides (*A*) investigated are < those from mixtures of the possible hydrolytic products except when $CO(CH_2·OH)_2$ is initially produced; these results are ascribed to slow degradation of (*A*) and/or to concurrent rearrangements leading to (II). The yields of (I) and (II) from a mixture of cellobiose octa-acetate and $OH·CH_2·CO·CH_2·OAc$ are compared. All experiments are carried out at 50° in N_2. H. B.

Preparation of *d*-arabinose. C. Neuberg and H. Collatz (Cellulosechem., 1936, 17, 128).—*d*-Arabonolactone in dil. aq. H_2SO_4 is reduced by Na–Hg to *d*-arabinose. A. G.

Heats of activation in the mutarotation of glucose.—See A., I, 89.

Preparation of *aldehydo*-sugar acetates. E. W. Cook and R. T. Major (J. Amer. Chem. Soc., 1936, 58, 2410).—*aldehydo*-*d*-Glucose penta-acetate is obtained in nearly quant. yield by reduction (H_2, Pd–$BaSO_4$, boiling xylene) of penta-acetyl-*d*-gluconyl chloride. H. B.

Structure of osazones and isolation of a new hexosazone anhydride. E. G. V. Percival (J.C.S., 1936, 1770—1774; cf. A., 1935, 1484).—Deacetylation [aq. NaOH (1·5%) in $COMe_2$; 24 hr.; room

temp.] of either glucosazone tetra-acetate or galactosazone tetra-acetate affords a *dianhydrohexosazone*, m.p. 238°, $[\alpha]_D^{20}$ −88° in $COMe_2$ [*Ac*$_1$ derivative, m.p. 135°, $[\alpha]_D$ +108° in $CHCl_3$; *Me*$_1$ *ether*, m.p. 172°, $[\alpha]_D^{20}$ −170° in $CHCl_3$; *dibromide*, m.p. 240° (decomp.)], a structure for which is proposed, involving the presence of a 2 : 6-oxide ring, a pyrazolidine and a pyrazoline ring, and the probable mechanism of its formation is discussed. F. N. W.

Decomposition of *d*-fructose-6-phosphoric acid to *d*-arabonic acid-5-phosphoric acid and the enzymic scission of the latter. C. Neuberg and H. Collatz (Cellulosechem., 1936, **17**, 125—128).—A 90% yield of *d*-arabonic acid-5-phosphoric acid (I) is obtained when *d*-fructose-6-phosphoric acid in aq. $Ba(OH)_2$ is shaken with O_2. The H_3PO_4 is split off from (I) by phosphatases. A. G.

Micro-determination of maltose. S. M. Strepkov (Biochem. Z., 1936, **289**, 38—40).—Maltose is oxidised by alkaline I to maltobionic acid, which on acid hydrolysis gives *d*-gluconic acid + glucose (I), the latter then being determined by the $K_3Fe(CN)_6$ method. Any (I), mannose, galactose, or pentose in admixture with maltose is oxidised to the corresponding acid and during hydrolysis forms a non-reducing lactone. Any fructose present is partly oxidised by alkaline I and on hydrolysis is converted into lævulic acid, whilst sucrose is first inverted by heating with acid before oxidation. P. W. C.

Addition compounds of the carbohydrates. III. Potassium hydroxide derivatives of cellobiose, lactose, and galactose. E. G. V. Percival and G. G. Ritchie (J.C.S., 1936, 1765—1770; cf. A., 1935, 964).—Cellobiose (I) (or its octa-acetate) with KOH in dry EtOH affords the *compound* (II), $C_{12}H_{22}O_{11}$,2KOH, which with Me_2SO_4 affords unchanged (I) and after acetylation β-methylcellobioside hepta-acetate with monomethylmethylcellobioside hexa-acetate from which, on hydrolysis followed by removal of glucose and treatment with $NHPh{\cdot}NH_2$, 6-methylglucosazone is obtained. In (II), therefore, one KOH is associated with the reducing group and the other with one of the primary alcohol groups. Similarly lactose forms the *compound* (III), $C_{12}H_{22}O_{11}$,3KOH, methylation of which followed by acetylation yields a non-reducing *syrup* from which by hydrolysis and acetylation 2 : 4-dimethylgalactose triacetate and 2-methylgalactose tetra-acetate are obtained, which after complete methylation are able to give tetramethylgalactopyranoseanilide, but no glucose derivatives. A structure is suggested for (III). Galactose penta-acetate similarly affords the *compound*, $C_6H_{12}O_6$,KOH [similar to the corresponding glucose compound (A., 1934, 1092)], which after methylation and subsequent acetylation gives a mixture of methylgalactoside α- and β-tetra-acetate. F. N. W.

Rearrangement of sugar acetates by aluminium chloride. Celtrobiose and its derivatives. N. K. Richtmyer and C. S. Hudson (J. Amer. Chem. Soc., 1936, **58**, 2534—2540).—Cellobiose octa-acetate and $AlCl_3$ + PCl_5 (2 : 1) in $CHCl_3$ give 40—45% of α-acetochloroceltrobiose (I), m.p. 141—142°, $[\alpha]_D^{20}$ +64·2° in $CHCl_3$ (cf. A., 1926, 941), converted by Ac_2O–NaOAc into *celtrobiose* α-*octa-acetate* (II), two forms, m.p. 112°, resolidifying with m.p. 129—130°, and m.p. 129—130°, $[\alpha]_D^{20}$ +48° in $CHCl_3$, which with $AlCl_3$ in $CHCl_3$ affords (I). (I) and Ag_2CO_3 in $COMe_2$ + a little H_2O give *celtrobiose* α-*hepta-acetate* (III), m.p. 130—131°, $[\alpha]_D$ (in $CHCl_3$) +22·3° → +15·1° (5 days) [+2Et_2O, m.p. 60° (decomp.), resolidifying with m.p. 130—131°], β-*hepta-acetate* (+Et_2O) (IV), m.p. 80° (decomp.), $[\alpha]_D$ (in $CHCl_3$) +3·9° → +15·1° (7 days; on Et_2O-free basis) (main product), and a little of a β-*hepta-acetate* (V) (ortho structure), m.p. 216°, $[\alpha]_D$ +1° in $CHCl_3$ (no mutarotation). Acetylation (Ac_2O–C_5H_5N at −10° to room temp.) of (IV) and (V) gives (mainly) *celtrobiose* β-*octa-acetate* (VI), 2 forms, m.p. 103—105° and 113—114°, $[\alpha]_D^{20}$ −13° in $CHCl_3$ (*hydrate*, m.p. 87—93°), which forms a 1 : 2 *compound* (+3Et_2O), m.p. 70° (decomp.), $[\alpha]_D$ +25·8° in $CHCl_3$, m.p. (Et_2O-free) 70—85°, with (II). (III) is similarly acetylated to (mainly) (II). De-acetylation [MeOH–$Ba(OMe)_2$] of (II)—(VI) affords *celtrobiose* (+H_2O) (VII), m.p. 148° (decomp.) (softens at 133°), $[\alpha]_D$ +13·6° in H_2O, which is the β-form since cautious acetylation gives 85% of (VI). Hydrolysis (*N*-HCl) of (VII) affords *d*-glucose and *d*-altrose, whilst oxidation (method: A., 1929, 1043) followed by hydrolysis (*N*-H_2SO_4) yields *d*-glucose and *d*-altronic acid (VIII). (VII) is thus 4-β-d-*glucosido*-d-*altrose*. Preliminary work has shown that the Ca salt (+3·5H_2O) of (VIII) is a convenient substance for the prep. (by degradation) of *d*-ribose. H. B.

Enzymic hydrolysis of β-glucosides of tertiary alcohols.—See A., III, 30.

Colour reactions for cardiac glucosides. Digitoxin, strophanthin-*K*, ouabain, and Digitalis verum. J. A. Sanchez (J. Pharm. Chim., 1936, [viii], **24**, 549—558).—Digitoxin (I), strophanthin-*K* (II), and ouabain (III) in AcOH give with a 0·3% solution of vanillin in conc. HCl at 100°, indigo-blue, deep blue, and violet colours, respectively. Evaporation of a solution of 0·1% $NMe_2{\cdot}C_6H_4{\cdot}CHO$ (in 20 c.c. of EtOH and 14 drops of conc. H_2SO_4) with D. verum (IV) and digitonin (V) at 100° and dissolution in AcOH give deep eosin-red solutions, whereas (I), (II), and (III) do not. With a solution of one drop of Br–H_2O in 20 c.c. of H_2SO_4 (IV) and (V) give a cerise and no colour, respectively. Modifications for application to pharmacological preps. are given. R. F. P.

Size of polysaccharide molecules. W. N. Haworth (Monatsh., 1936, **69**, 314—318).—Evidence is adduced that under various conditions starch can be acetylated without appreciable rise in the reducing power. The acetates can possess all degrees of viscosity. By direct methylation without passing through the acetate, or by methylation of the above acetates, derivatives of varying degrees of viscosity can be obtained. It appears that there is no relationship between viscosity and observed chemical chain length, which remains invariable for specimens of undegraded starch derivatives. When hydrolytic degradation of starch into dextrins is attempted the val. for the chemical assay of the end group diminishes progressively. The chemical end group method of assay indicates the presence of 12 or 18 glucose units in glycogen from rabbit liver, fish liver, and fish

muscle. Similar results are given by viscosity measurements using the Staudinger formula, but osmotic pressure measurements with a Cellophane membrane indicate a much larger particle size. Chemical assay of methylated inulin indicates a chain of about 30 fructose units, confirmed by determination of the osmotic pressure. Viscosity measurements, using Staudinger's factor for cellulose, show the presence of only 9 fructose units. In any comparison of the mol. wt. of various polysaccharides it is necessary to recognise that aggregation may be caused by lengthening of the chain and also by lateral combination between chains. Thus the chemical unit of methylated xylan is composed of about 18 pentose residues, whilst physical evidence suggests that <4 of these chains are grouped together by co-ordination or other type of union between the reducing end of the chain and an intermediate OH positon of an adjoining chain. H. W.

Mol. wt. of inulin. B. B. Westfall and E. M. Landis (J. Biol. Chem., 1936, **116**, 727—734).—The mol. wt. of inulin was determined by a thermoelectric v.-p. technique (cf. Baldes, A., 1934, 986). That of the purest sample averaged 5100. E. A. H. R.

Micro-determination of inulin. S. M. Strepkov (Biochem. Z., 1936, **288**, 301—302).—The application of the phosphomolybdic acid method of Stöhr (A., 1934, 315) for fructose is described. F. O. H.

Acetylation and methylation of cellulose. Constitution of carbohydrates. P. Karrer and E. Escher (Helv. Chim. Acta, 1936, **19**, 1192—1198).—Methylation of cellulose which has not been degraded ceases at 42·2% OMe in the product, which contains no free OH (Ac_2O–C_5H_5N; Zerevitinov) and yields some 2 : 3-dimethylmethylglucoside (isolated as di-*p*-toluenesulphonate) when hydrolysed. The unreactive OH may be at 2 or 6 and may be sterically hindered or bound in anhydride linkings. There is one unreactive OH for each 4—5 C_6 units. The completely symmetrical formula for cellulose (and other polysaccharides) is thus in doubt. R. S. C.

Syntheses from ethanolamine. III. Synthesis of ethyl *N*-β-chloroethylcarbamate and β-chloroethylcarbimide. H. Wenker (J. Amer. Chem. Soc., 1936, **58**, 2608).—$OH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO_2Et$ (I) and $SOCl_2$ afford Et *N*-β-chloroethylcarbamate, b.p. 128—130°/13 mm., converted [as is (I)] by PCl_5 into *β-chloroethylcarbimide*, b.p. 135°, which with NH_2Ph and p-$OEt{\cdot}C_6H_4{\cdot}NH_2$ gives *N*-phenyl-, m.p. 124°, and N-p-*phenetyl*-, m.p. 149°, -N′-β-*chloroethylcarbamide*, respectively. H. B.

Betaine aurichloride. M. Becker (Biochem. Z., 1936, **288**, 348—350).—The betaine (*B*) aurichlorides of Fischer (A., 1902, i, 428) and Willstätter (*ibid.*, 661) were not as described ($HBAuCl_4$,$1\frac{1}{2}H_2O$ and $HBAuCl_4$,$2H_2O$, respectively), but basic compounds with $B : AuCl_3 = >1 : 1$ mol. The formation of such compounds is avoided by the use of excess of $AuCl_3$ in *N*-HCl. F. O. H.

Synthesis of serine. L. R. Schiltz and H. E. Carter (J. Biol. Chem., 1936, **116**, 793—797).—60% $CH_2{:}CH{\cdot}CO_2Me$ in MeOH with $Hg(OAc)_2$ gives $OMe{\cdot}CH_2{\cdot}CH(CO_2Me){\cdot}Hg{\cdot}OAc$, converted by aq. KBr into the corresponding mercuribromide, which with Br–$CHCl_3$ (sunlight) yields *Me α-bromo-β-methoxypropionate*, b.p. 70—80°/6 mm., hydrolysed by 0·5*N*-NaOH at room temp. to the corresponding *acid*, b.p. 91°/2 mm. This with conc. aq. NH_3 at 80—90° affords the *α-NH_2-acid*, m.p. 200—210° (decomp.) (*Bz*, m.p. 147—148°, and *formyl* derivative, m.p. 151—152°), demethylated by HBr to serine (31—39% over-all yield). J. W. B.

Multivalent amino-acids and peptides. VII. Derivatives of *dl*-α-aminotricarballylic acid. J. P. Greenstein (J. Biol. Chem., 1936, **116**, 463—467).—α-Aminotricarballylic acid (I) is converted by cold $AgNO_2$–*N*-HCl into *dl-iso*citric acid, isolated as its Ba salt and converted into its lactone, m.p. 153°. (I) with HCl–MeOH affords its *βγ-Me_2* ester, m.p. 165°, converted by 28% aq. NH_3 into the *NH_4* salt, m.p. 214°, of *4-carboxylamidopyrrolidone-5-carboxylic acid*, m.p. 178°, which is obtained by the action of H_2S on the Ag salt. J. W. B.

Synthesis of glutathione. V. du Vigneaud and G. L. Miller (J. Biol. Chem., 1936, **116**, 469—476).—*s*-Benzylcysteinylglycine (A., 1935, 1486) is converted by HCl–MeOH at $<0°$ into its *Me ester hydrochloride*, from which the free *Me* ester (I) is liberated with $NHEt_2$–$CHCl_3$. α-Me *N*-carbobenzyloxyglutamate (Harington *et al.*, A., 1935, 1110) with PCl_5 in Et_2O at 0° affords its *γ-chloride*, excess of which is condensed with (I) in $CHCl_3$, cooled in solid CO_2, to give the Me ester of α-methyl-*N*-carbobenzyloxy-γ-glutamyl-*S*-benzylcysteinylglycine (II), which is obtained (73% yield) by hydrolysis using Harington's method (*loc. cit.*). Reduction of (II) with Na–liquid NH_3 affords glutathione (27% yield), isolated and purified through its Hg and Cu salts. J. W. B.

Formation of taurine by decarboxylation of cysteic acid. A. White and J. B. Fishman (J. Biol. Chem., 1936, **116**, 457—461).—Decarboxylation of cysteic acid (from *l*-cystine) to taurine, m.p. 327—328° (decomp.) (corr.) (Friedmann, A., 1903, i, 75), occurs only within a limited temp. range and was always successful at 235—240°. J. W. B.

Formation of lactams from lactones. E. Späth and J. Lintner (Ber., 1936, **69**, [*B*], 2727—2731).—Lactones appear to be convertible into lactams by NH_3, primary aliphatic, fatty-aromatic, or aromatic amines if the reaction partners can withstand the requisite temp. Lactones derived from OH-acids with phenolic OH form a present exception. Butyrolactone (I) and NH_3 in absence of solvent at 200° afford pyrrolidone, m.p. 23—24°, in 64% yield. Similarly, 5-methylpyrrolid-2-one, m.p. 43—44°, is obtained from γ-valerolactone and $ZnCl_2$,$6NH_3$ at 220—230°. (I) and NH_2Me at 200° yield *γ-hydroxybutyrmethylamide*, b.p. 125—130° (bath)/1 mm., whereas at 280° the product appears to be 1-methylpyrrolid-2-one. Under like conditions (I) and allylamine afford *γ-hydroxybutyrallylamide*, m.p. 27—27·5°, and *1-allylpyrrolid-2-one*, b.p. 115—120° (bath)/12 mm. (*hydrochloride*), whilst (I) and $CH_2Ph{\cdot}NH_2$ give *γ-hydroxybutylbenzylamide*, m.p. 74—75°, and non-cryst. *1-benzylpyrrolid-2-one*, b.p. 130—140° (bath)/1 mm. 1-Phenyl-, m.p. 68—69°, and 1-*p*-tolyl-, m.p.

81—82°, -pyrrolid-2-one are obtained from (I) and NH_2Ph or *p*-$C_6H_4Me{\cdot}NH_2$ at 215° and 210—220°, respectively. H. W.

***NN'*-Dimethyldiamide of tartaric acid and the *NN'*-dinitrodimethyldiamide of tartaric acid dinitrate.** T. Urbański (Rocz. Chem., 1936, **16**, 334—338).—The velocity of reaction between NH_2Me and esters of tartaric acid, and the yield of *NN'*-dimethyldiamide (I) of tartaric acid, m.p. 213—214° (lit., 189°), fall in the series Me > Et > Pr$^{\alpha}$ tartrate. *Tartaric acid dinitrate* NN'-*dinitrodimethyldiamide* (II), m.p. 114° (decomp.), is obtained by adding 60 g. of Ac_2O to 10 g. of (I) in 180 g. of HNO_3, at ≯ −2°. (II) is readily detonated by shock or heat, and yields gels with cellulose nitrate. R. T.

Determination of allylthiocarbimide in air. M. S. Gerschenovitsch, R. S. Belova, and I. A. Samartzeva (J. Appl. Chem. Russ., 1936, **9**, 1547—1549).—The air is aspirated at the rate of 7 litres per hr. through three wash-bottles containing 95% EtOH at 40—45°, 25 ml. of 0·1*N*-$AgNO_3$ and 5 ml. of 10% aq. NH_3 are added, the solution is heated to 80° and filtered, and residual Ag is determined by the Volhard method. R. T.

Andrussov's theory of the catalytic preparation of hydrocyanic acid.—See A., I, 90.

Preparation of zinc and cadmium cyanides.—See A., I, 92.

Synthesis of azido-derivatives of acetylenic hydrocarbons. Synthesis of CH:C·[CH_2]$_8$·CH_2·N_3. A. P. Oskerko (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, **3**, 415—436).—The reduction of CH:C·[CH_2]$_8$·CO_2Et by Na in anhyd. MeOH, EtOH, or Bu$^{\alpha}$OH gives Δ$^{\kappa}$-*undecinen-α-ol*, m.p. >4°, b.p. 108—109°/2 mm. (*phenylurethane*, m.p. 51°; *acetate*, b.p. 114—115°/4 mm.), which adds Br_2 and is converted by $AgNO_3$ into the *salt*, $AgNO_3$,$C_{11}H_{19}OAg$, and by PBr_3 in α-*bromo*-Δ$^{\kappa}$-*undecinene* (I), b.p. 98—99°/2 mm. Interaction of (I) and NaN_3 in aq. $COMe_2$ yields α-*azido*-Δ$^{\kappa}$-*undecinene*, a liquid, which adds Br_2, evolves with conc. H_2SO_4 2 atoms of N, and is converted by $AgNO_3$ into the *compound*, $AgNO_3$,$C_{11}H_{18}N_3Ag$. J. J. B.

Chloride of allylphosphorous acid, and certain of its reactions. V. M. Pletz (J. Gen. Chem. Russ., 1936, **6**, 1198—1202).—$PCl_2{\cdot}CH_2{\cdot}CH{:}CH_2$ (I) yields $CH_2{:}CH{\cdot}CH_2Br$ and $POCl_2Br$ with Br in CCl_4, and *allylthiophosphoric dichloride*, b.p. 74°/25 mm., when heated with S in CS_2. (I) and MgEtI or Mg allyl iodide in Et_2O afford $CH_2{:}CH{\cdot}CH_2I$ and ethyl- or *allyl-phosphinic acid*, decomp. 120°. R. T.

Constitution of complex metallic salts. V.—See A., I, 15.

Introduction of silicon into fats. H. P. Kaufmann (Ber., 1936, 69, [*B*], 2685).—A comment on the communication of Klein *et al.* (A., 1936, 1368). H. W.

Complex compounds of mercury and copper halides with aliphatic amines.—See A., I, 92.

Complex compounds with two co-ordination shells from hexamminechromic and triethylenediaminechromic ions.—See A., I, 94.

Stereochemistry of co-ordinative quadrivalent nickel.—See A., I, 15.

Dipole measurements of isomeric plato-complexes.—See A., I, 14.

Isomerism of ethylene compounds of platinum. I. I. Tscherniaev and A. D. Gelman (Compt. rend. Acad. Sci. U.R.S.S., 1936, **4**, 181—184).—By treating K_2PtCl_4 first with C_2H_4 and then with NH_3 or C_5H_5N (*B*), *trans*-[$C_2H_4BPtCl_2$] is formed, contrary to the Peyronnet rule. A *cis*-compound was obtained by passing C_2H_4 through a solution of a M^1[NH_3PtCl_3] (M = metal). These results are ascribed to the great *trans*-influence of C_2H_4. R. C. M.

Dehydrogenation of *cyclo*hexane catalysed by chromic oxide.—See A., I, 90.

Phenyl*cyclo*pentylmethane and *cyclo*pentyl-*cyclo*hexylmethane in relation to catalytic hydrogenation. J. I. Denisenko (J. Gen. Chem. Russ., 1936, **6**, 1263—1266).—CH_2PhCl, *cyclo*pentanone, and Mg in Et_2O yield 1-*benzyl*cyclo*pentan*-1-*ol*, b.p. 129—130°/11 mm., converted by heating with anhyd. $H_2C_2O_4$ into 1-*benzyl*-Δ^1-cyclo*pentene*, b.p. 120—122°/10 mm., and this gives *benzyl*cyclo*pentane* (I), b.p. 234—236°/750 mm., when hydrogenated (Pt black–EtOH). (I) yields cyclo*pentyl*cyclo*hexylmethane* (II), b.p. 224—226°/750 mm., when passed with H_2 over Pt–C catalyst at 196—200°, and both (I) and (II) give chiefly *n*-hexylbenzene and H_2 when passed over the same catalyst at 300—310°. R. T.

Photo-oxidation of carotene. E. Baur [with P. E. Chrétien] (Helv. Chim. Acta, 1936, **19**, 1210—1212).—Ultra-violet irradiation of α-carotene in $CHCl_3$ causes an initial, rapid, autocatalysed absorption of O_2 with deepening of colour, followed by a slow further absorption, independent of light and causing loss of colour. The first step is reversible; its inception and extent depend on the O_2 pressure, and irradiation in vac. after completion of the first step causes evolution of O_2. R. S. C.

Reactivity of aromatic chloro-derivatives. Action of certain amines on halogens substituted in the nucleus. A. Marcinków and E. Płażek (Rocz. Chem., 1936, **16**, 395—402).—The reactivity of aq. amines with aromatic halogen derivatives ∝ the dissociation const. of the amine, and rises in the series NH_3 < NH_2Me < $NHMe_2$. In the case of higher amines (NH_2Et, $NHEt_2$, NH_2Bu^{β}, $NHBu^{\beta}_2$, and mono- and di-*iso*amylamine) the reactivity is determined by other factors, and falls with increasing mol. wt. R. T.

Pyrogenic decomposition of aliphatic-aromatic hydrocarbons. A. Dobrjanski (Ann. Leningrad State Univ., Chem. Ser., 1935, **1**, 105—112).—When heated at 600—650° PhMe and xylene remain unchanged, PhEt gives C_6H_6, PhMe, and $CHPh{:}CH_2$ (I) in approx. equal amounts, $PhPr^{\alpha}$, $PhBu^{\beta}$, and *iso*amylbenzene yield chiefly PhMe, $PhPr^{\beta}$ chiefly (I), with C_6H_6 and PhMe as admixtures, $PhBu^{\alpha}$ and *n*-amylbenzene afford chiefly (I) and PhMe, and $PhBu^{\gamma}$ gives chiefly C_6H_6. It is concluded that the products of pyrolysis are PhMe, (I), or C_6H_6, according to whether the Ph is combined with a primary, *sec.*, or *tert.* C. R. T.

Constitution of the two *tert.*-butyl-*p*-cymenes. H. Barbier (Helv. Chim. Acta, 1936, **19**, 1345—1354).—The orientations of the hydrocarbons obtained by butylation of *p*-cymene and that of certain NO_2-derivatives are established. The product (I), m.p. 132°, of musk-like odour is 2 : 6-dinitro-3-*tert.*-butyl-*p*-cymene (Me = 1). Crude *tert.*-butyl-*p*-cymene (II) and 70% HNO_3 at 0—5° give a *nitro*-3-tert.-*butyl*-*p*-*cymene*, m.p. 62°, b.p. 125°/2—3 mm., volatile in steam, reduced by $SnCl_2$ to the NH_2-compound, m.p. 76°, which yields (HNO_2–$SnCl_2$) pure 3-tert.-*butyl*-*p*-*cymene* (III), b.p. 226°/729 mm. (III) with $CrOCl_2$ gives 4-iso*propyl*-3-tert.-*butylbenzaldehyde*, b.p. 101°/2—3 mm., m.p. 43° (*semicarbazone*, m.p. 222°), oxidised by 20% HNO_3 to 4-iso*propyl*-3-tert.-*butylbenzoic acid*, m.p. 187°, which, when distilled with NaOEt at 2—3 mm., gives o-iso*propyl*tert.-*butylbenzene*, b.p. 208°/729 mm. [$(NO_2)_2$-derivative, m.p. 142°, obtained by HNO_3 (*d* 1·5)], stable to oxidation by HNO_3. PhBu$^\gamma$, Pr$^\beta$Cl, and $AlCl_3$ give m-iso*propyl*tert.-*butylbenzene*, b.p. 216°/729 mm. [$(NO_2)_2$-derivative, m.p. 149°], oxidised by hot 20% HNO_3 to *m*-$C_6H_4Bu^\gamma\cdot CO_2H$. *p*-$C_6H_4Pr^\beta Bu^\gamma$ (obtained from PhPr$^\beta$, Bu$^\gamma$OH, and conc. H_2SO_4 at −5°), b.p. 222°/729 mm., with 20% HNO_3 gives *p*-$C_6H_4Bu^\gamma\cdot CO_2H$, but is resinified by HNO_3 (*d* 1·5). Menthone does not react with MgBu$^\gamma$Cl, but pure carvone gives a fair yield of 2-*methyl*-3-tert.-*butyl*-5-iso*propenyl*cyclo*hexanone* (cf. lit.), b.p. 103°/2—3 mm. (*semicarbazone*, m.p. 62°), resinified by Na–EtOH, but smoothly hydrogenated (Ni) to 6-tert.-*butyltetrahydrocarveol* (Me = 1), b.p. 203—206°/2—3 mm., which by dehydration ($ZnCl_2$) and dehydrogenation (S) yields the 2-*tert.*-butyl-*p*-cymene, b.p. 237°, contained in small amounts in (II). The $(NO_2)_2$-derivative, m.p. 141°, obtained from (II), with phenanthraquinone gives a *quinoxaline* derivative, m.p. 191—192°, and is thus the 5 : 6-$(NO_2)_2$-compound; the other, (I), does not react. R. S. C.

Thermal polymerisation of pure styrene.—See A., I, 86.

Mechanism of addition of hydrogen and bromine to ω-nitrostyrenes and α-nitrostilbenes. B. Reichert (Arch. Pharm., 1936, **274**, 505—519).—The addition of H_2 to ω-nitrostyrenes and α-nitrostilbenes is greatly influenced by the formation of mol. compounds with the solvent (evidenced by bathochromy). C_5H_5N adds to the O of the *aci*-form, acid to the O of the NO_2-form. The following reactions occur: (*a*) $CHAr{:}C{:}N(OH){:}O\cdots C_5H_5N$ (I) → $CHAr{:}CH\cdot NH(OH){:}O\cdots C_5H_5N$ → $CH_2Ar\cdot CH{:}NH(OH)_2$ → $CH_2Ar\cdot CH{:}N\cdot OH$ (II), the C_5H_5N then acting as partial poison to the catalyst and preventing further reduction to the amine; (*b*) (I) → $-CHAr\cdot CH{:}NO\cdot OH$ → $(\cdot CHAr\cdot CH_2\cdot NO_2)_2$; (*c*)

$$CHAr{:}CH\cdot NO{:}O\cdots H_2SO_4 \rightarrow$$
$$CH_2Ar\cdot CH{:}N(OH){:}O\cdots H_2SO_4 \rightarrow$$
$$CH_2Ar\cdot CH_2\cdot NH(OH){:}O\cdots H_2SO_4 \rightarrow$$

$CH_2Ar\cdot CH_2\cdot NO$ [=(I)], further reduction to the amine occurring in presence of acid, *e.g.*, H_2SO_4; reduction to the amine does not occur in HCl–EtOH, as the HCl is destroyed during the first stages of reduction. Reactions (*a*) and (*b*) always occur simultaneously, but to extents which vary according to the conditions. Reduction of α-nitrostilbenes proceeds analogously. α-Nitrostilbene and Br at 100° give a *dibromide*, m.p. 119°, which can be crystallised from ligroin, but loses 2 Br in hot EtOH or $COMe_2$ or cold C_5H_5N, and resists attempts to remove HBr. 3 : 4 : 5-$(NO_2)_3C_6H_2\cdot CH{:}CH\cdot NO_2$ gives (H_2–Pd–C; C_5H_5N) 3 : 4 : 5-*trimethoxyphenylacetaldoxime*, m.p. 82—83°, further hydrogenated (PtO_2) in EtOH–$H_2C_2O_4$ at 50° to mescaline and *di*-(β-3 : 4 : 5-*trimethoxyphenylethyl*)*amine* (*hydrochloride*, m.p. 229°). β-Nitro-3 : 4-methylenedioxystilbene and H_2–PtO_2 in AcOH–H_2SO_4 give the corresponding saturated base. R. S. C.

Derivatives of 4-*cyclo*hexyldiphenyl. F. R. Basford (J.C.S., 1936, 1780—1781).—4′-*Bromo*-4-cyclo*hexyldiphenyl* (I), m.p. 154°, is obtained by the interaction of 4-bromodiphenyl and *cyclo*hexyl bromide in presence of $AlCl_3$ (6 hr. at 18° followed by 15 min. at 40°) or by the addition of Br to 4-*cyclo*hexyldiphenyl (II) in AcOH containing NaOAc (10 min.; 120°). Oxidation (AcOH–$Na_2Cr_2O_7$–H_2SO_4) of (I) (90 min.; 95°) affords *p*-$C_6H_4Br\cdot CO_2H$, whilst Se dehydrogenation (30 min.; 330—360°) gives *p*-$C_6H_4Ph_2$. (I) with Br (15 min.; 160° followed by 15 min.; 200°) yields *p*-$C_6H_4Br\cdot C_6H_4Ph$-*p*′ (III). 4′-*Bromo*-4-(*tribromocyclohexyl*)*diphenyl*, m.p. 148°, which on thermal decomp. at 160—220° affords (III) with loss of HBr, is obtained by the addition of Br to (II) (24 hr.; 18°) or to (I) (2 hr.; room temp. finished at 50°; Fe catalyst). F. N. W.

Synthesis of alkylated polycyclic aromatic hydrocarbons. M. Lerer (Ann. Office nat. Combust. liq., 1935, **10**, 455—464; Chem. Zentr., 1936, i, 1422).—In the presence of alkyl halides, Na reacts with otherwise unreactive hydrocarbons; the reaction is probably between hydrocarbon and Na alkyl. An improved prep. of 9 : 10-di*iso*amyl-9 : 10-dihydroanthracene from *iso*-$C_5H_{11}Cl$, Na, and anthracene is described. Bu$^\beta$Cl, Na, and 2 : 3-$C_{10}H_6Me_2$ yield 2 : 3-*dimethyl*-1-iso*butyl*-1 : 4-*dihydronaphthalene*, b.p. 150°/0·1 mm., with a little 2 : 3-*dimethyl*-1 : 4-*diiso*-*butyl*-1 : 4-*dihydronaphthalene*, b.p. 180°/0·1 mm. Fluoranthene with Na and Bu$^\beta$Cl affords 1 : 4-*diiso*-*butyl*-1 : 4-*dihydrofluoranthene*, b.p. 160°/cathode-ray vac.; a similar product from chrysene could not be distilled. H. N. R.

Induced oxidation of naphthalene with ascorbic acid as inductor. W. P. Jorissen (Natuurwetensch. Tijds., 1937, **19**, 15—16).—Solutions of 0·1 g. of $C_{10}H_8$ and 0·4 g. of ascorbic acid in 40 c.c. of $COMe_2$ and 10 c.c. of H_2O contained only oxidation products of $C_{10}H_8$ [$C_6H_4(CO_2H)_2$] after keeping for 2 weeks under aërated conditions. S. C.

[Additive compound of] sodium [and] naphthalene. I. Preparation of additive compounds of alkali metals and polycyclic aromatic hydrocarbons. N. D. Scott, J. F. Walker, and V. L. Hansley (J. Amer. Chem. Soc., 1936, **58**, 2442—2444).—$C_{10}H_8$ and Na react rapidly in Me_2O at −30° or, more conveniently, in $(\cdot CH_2\cdot OMe)_2$ (I) at −10° to 30° in N_2 to give the additive compound (II), $C_{10}H_8Na_2$ or $C_{10}H_8Na_2$,$C_{10}H_8$. (I) and (II) react slowly at room temp.: $C_{10}H_8Na_2 + 2(\cdot CH_2\cdot OMe)_2 \rightarrow C_{10}H_{10} + 2NaOMe + 2OMe\cdot CH{:}CH_2$. Reaction between $C_{10}H_8$

and Na in Me_2O is inhibited by Et_2O, and an excess of Et_2O causes decomp. of any (II) present to $C_{10}H_8$ and Na. (II) could not be isolated; the solvent appears to be necessary for its existence. (II) reacts with H_2O, alcohols, and compounds (*e.g.*, C_2H_2) which form Na derivatives (*A*), forming dihydronaphthalene and (*A*). With O_2, Hg, and CH_2PhCl, solutions of (II) behave as $C_{10}H_8$ + Na. Me_2O and (I) can be used with other alkali metals and they facilitate reaction between Na and $COPh_2$ or anthracene. Compounds similar to (II) can be prepared from $C_{10}H_7Me$, Ph_2, acenaphthene, and phenanthrene in Me_2O (not in Et_2O) or (I). H. B.

Rate of decomposition of tetralin peroxide. I. Thermal decomposition. II. Effect of quinol. III. Effect of antioxidants. T. YAMADA (J. Soc. Chem. Ind. Japan, 1936, **39**, 450—452B, 452—455B, 455—457B).—I. Decomp. of tetrahydronaphthalene (I) peroxide (II) [prep. of sample containing 0·25 mol. of peroxide per mol. of (I) described] at 120°, 130°, and 140° is a first-order reaction (cf. B., 1936, 1055) which is interpreted by a chain mechanism.

II. The rate of decomp. of (II) at 130° in presence of quinol is const. and independent of the concn. of quinol. A chain reaction is postulated.

III. α-$C_{10}H_7$·OH, phloroglucinol, gallic and protocatechuic acids, and *o*-NH_2·C_6H_4·OH resemble quinol in their effect on the decomp. of (II). J. L. D.

Sterol hydrocarbon, $C_{18}H_{16}$, and two isomerides thereof. H. HILLEMANN (Ber., 1936, **69**, [*B*], 2610—2617; cf. A., 1933, 1154).—After adequate purification the "sterol $C_{18}H_{16}$" (I) of Diels (A., 1933, 1047; 1935, 481) is devoid of fluorescence, which also is not shown by synthetic isomeric hydrocarbons; the absorption spectrum does not indicate the nature of the causative impurity. The m.p., 130—131°, assigned by the authors to the picrate (*loc. cit.*) is confirmed. Treatment of 3-acetylphenanthrene with CH_2Br·CO_2Me and Zn in boiling C_6H_6 and of the product with $POCl_3$ affords *Me* β-3-*phenanthrylcrotonate*, b.p. 201—205°/0·02 mm., m.p. 56—57°, hydrolysed to β-3-*phenanthrylcrotonic acid*, m.p. 194·5—196·5°, which is hydrogenated (Pd–$BaSO_4$) to β-3-*phenanthrylbutyric acid*, (II), m.p. 105—107°. Cyclisation of (II) by successive action of $SOCl_2$ and $AlCl_3$ in $PhNO_2$ gives 3-*methyl*-6 : 7-7′ : 8′-*naphthahydrind*-1-*one* (III), m.p. 91°, and 3-*methyl*-5 : 6-1′ : 2′-*naphthahydrind*-1-*one* (IV), m.p. 140—141°. Reduction (Clemmensen) of (III) and (IV) gives 1′-*methyl*-3 : 4-, b.p. 172—173°/0·05 mm., m.p. 28—29°, and 3′-*methyl*-2 : 3-, m.p. 75—76°, -cyclo*pentenophenanthrene*, respectively. Oxidation of (III) and (IV) by HNO_3 (*d* 1·4) affords, respectively, 1 : 2 : 3 : 4- and 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$. The identity of the NO-compounds from (I) and synthetic 3′-methylcyclopentenophenanthrene (*loc. cit.*) is confirmed. *Me* β-3-*phenanthroylpropionate* has m.p. 67—70°. H. W.

Reduction of aromatic nitro-compounds with sodium stannite. G. LOCK and E. BAYER (Ber., 1936, **69**, [*B*], 2666—2669).—The aromatic NO_2-compound, if necessary in EtOH, is briskly stirred for 2 hr. at 80° with the amount of Na_2SnO_2 solution calc. for reduction to the azo-stage. $PhNO_2$ gives 71% of azoxybenzene (I) and 21% of NH_2Ph or under more drastic conditions 52% of NH_2Ph and a very difficultly separable mixture of much (I) and little PhN_2Ph. *o*-C_6H_4Me·NO_2 yields 9% of *o*-C_6H_4Me·NH_2 (II) and 87% of *oo*′-azoxytoluene (III), the proportion of (II) at the expense of (III) being increased if the conditions are more drastic. *m*-C_6H_4Me·NO_2 is smoothly reduced to *mm*′-azoxytoluene without appreciable amounts of other reduction products. *p*-C_6H_4Me·NO_2 gives about 15% of *p*-C_6H_4Me·NH_2 and a difficultly separable mixture of azoxy- and azo-compounds; *o*-C_6H_4Cl·NO_2 behaves similarly. *m*-C_6H_3Cl·NO_2 yields *m*-C_6H_4Cl·N_2·C_6H_4Cl-*m*′ and *m*-NO_2·C_6H_4·SO_3Na gives the corresponding azo-compound. *p*-C_6H_4Cl·NO_2 affords 17% of *p*-C_6H_4Cl·NH_2 and *pp*′-dichloroazoxybenzene. Contrary to Witt, therefore, reduction of NO_2-compounds by Na_2SnO_2 is not a general method for the prep. of azo-derivatives. H. W.

Decomposition of salts of thiocarbamic acid. Mechanism of formation of diarylthiocarbamides. N. S. DROZDOV (J. Gen. Chem. Russ., 1936, **6**, 1368—1374).—$(NHPh·CS_2)_2Cu$ in H_2O at 100° yields PhCNS (I), $CS(NHPh)_2$ (II), and CuS. In presence of excess of Cu·· $CO(NHPh)_2$ is also obtained, whilst in presence of $(NH_4)_2CO_3$ the products are (II) and NH_2·CS·NHPh (III), and when both excess of Cu·· and $(NH_4)_2CO_3$ are present (I) and (III) are formed. $(NHPh·CS_2)_2Pb$ and $(NH_4)_2CO_3$ in H_2O at 100° yield (II) and (III). NH_2Ph, CS_2, and aq. NaOH yield exclusively (II) at 75°, (I) and (II) at 20—35°, and (II) and $NHPh·CS_2Na$ (IV) at 5—10°. The mechanism of the reactions is: $2NH_2Ph + 2CS_2 + 2NaOH \rightarrow 2(IV) + 2H_2O$: (IV) → (I) + NaSH; (IV) + NaSH → Na_2CS_3 + NH_2Ph; NH_2Ph + (I) → (II); $NH_2Ph + CS_2 \rightarrow NHPh·CS_2H$, $NH_2Ph \rightarrow$ (I) + $NH_2Ph + H_2S \rightarrow$ (II) + H_2S; $NHPh·CS_2NH_4 \rightarrow$ (III) + H_2S. R. T.

Action of phenylcarbimide on α-glycols and α-oxides. K. A. KRASUSKI and M. MOVSUM-ZADE (J. Gen. Chem. Russ., 1936, **6**, 1203—1207).—PhNCO (I) and $(CH_2·OH)_2$ (15 hr. at 100°) yield exclusively the diphenylurethane. (I) and $OH·CH_2·CMe_2·OH$ in Et_2O (100°; 40 hr.) afford $CO(NHPh)_2$ and *isobutylene glycol diphenylcarbamate*, m.p. 140·5°, whilst pinacone yields analogously the *diphenylcarbamate*, m.p. 215°. $(CH_2)_2O$ and (I) (100°; 18 hr.) yield Ph_3 *iso*cyanurate, whilst trimethylethylene oxide does not react after 30 hr. at 100°. R. T.

Action of iodine trichloride on acetanilide. E. CLEPAZ (Atti R. Ist. Veneto Sci., 1934—1935, **94**, 555—562; Chem. Zentr., 1936, i, 1411—1412).—KCl,ICl_3 in cold $CHCl_3$ reacts with NHPhAc to yield *N-dichloroiodacetanilide*, $NPhAcICl_2$, m.p. 127° (decomp.), which yields *p*-C_6H_4Cl·NHAc, m.p. 174°, with H_2O, dil. alkali, or when heated. HNO_3 affords 4-chloro-2-nitro-, m.p. 101°, and 4-nitro-acetanilide, m.p. 214°. H. N. R.

Rearrangement of *N*-chloroacetanilide in presence of radioactive hydrochloric acid.—See A., I, 87.

Electrochemical reduction of *N*-nitrosomethylaniline.—See A., I, 91.

Action of sodium nitrite on *p*-nitrodimethylaniline in hydrobromic acid. G. J. G. Milton and T. H. Reade (J.C.S., 1936, 1749—1750).—*p*-NO_2·C_6H_4·NMe_2 and $NaNO_2$ (4 mols.) in >4*N*-HBr at 0° give 2-*bromo*-4-*nitrodimethylaniline hydrobromide perbromide*, m.p. 157°, converted by hot aq. EtOH into 2-*bromo*-4-*nitrodimethylaniline*, m.p. 74°. This with $NaNO_2$ (3 mols.) in HCl at 0° gives 2-*bromo*-4-*nitrophenylmethylnitrosoamine*, m.p. 95°, hydrolysed by hot conc. HCl to 2-*bromo*-4-*nitromethylaniline*, m.p. 115°, which with warm conc. HNO_3 gives 2-*bromo*-4 : 6-*dinitrophenylnitroamine*, m.p. 126°, converted by hot PhOH into 4 : 6 : 2-$(NO_2)_2C_6H_2Br$·NHMe. The limiting [Br] for brominating action of HNO_2–HBr mixtures is 0·003 g.-mol. per litre as judged by formation of $NPhMe_3Br_3$; it is decreased by addition of NaBr. $NPhMe_3Br_3$ in H_2O slowly gives the *m*-Br-compound, Br, and BrO_3'. R. S. C.

2 : 4 : 6-Trichloro-*m*-toluidine and some derivatives. E. Bureš and M. Trpišovská (Časopis českoslov. Lék., 1935, **15**, 179—186; Chem. Zentr., 1936, i, 1209).—Chlorination of acet-*m*-toluidide in AcOH affords 2 : 4 : 6-trichloroacet-*m*-toluidide, m.p. 192°, hydrolysed (NaOH) to 2 : 4 : 6-trichloro-*m*-toluidine, m.p. 85° (*Bz*, m.p. 218°, and *Ac* derivative, m.p. 81—82°). 2 : 4 : 6-Trichloro-, m.p. 38°, and 2 : 3 : 4 : 6-tetrachloro-, m.p. 91·5—92°, -toluene are prepared from the appropriate amines by the diazo-reaction; on nitration they yield 2 : 4 : 6-trichloro-3-nitrotoluene, m.p. 50°, and 2 : 3 : 4 : 6-*tetrachloro*-5-*nitrotoluene*, m.p. 148—150°, respectively. 2 : 4 : 6-*Trichloro*-3-*bromo*-, m.p. 85°, and -2-*iodo*-, m.p. 63°, -*toluene* are obtained from the appropriate diazonium salts, Cu-bronze, and KBr or KI. H. N. R.

Nuclear alkylation of aromatic bases. III. Action of methyl alcohol on the hydrochlorides of α- and β-naphthylamine. D. H. Hey and E. R. B. Jackson (J.C.S., 1936, 1783—1788; cf. A., 1934, 764).—Nuclear alkylation occurs more readily with β- than with α-$C_{10}H_7$·NH_2, but the products are mainly phenolic, owing to ready fission of the C·N linking. α-$C_{10}H_6$·NH_2,HCl with 3 mols. of MeOH at 240—250° gives mainly α-$C_{10}H_7$·OH and tar, but at 220° also some α-$C_{10}H_7$·NMe_2; with 4 mols. at 230—250° much α-$C_{10}H_7$·OH, some 2 : 1-$C_{10}H_6Me$·OH, α-$C_{10}H_7$·NH_2, α-$C_{10}H_7$·NHMe, and α-$C_{10}H_7$·OMe, and less tar are formed. β-$C_{10}H_7$·NH_2,HCl with 3 mols. of MeOH at 200—220° gives β-$C_{10}H_7$·NMe_2, $NH(C_{10}H_7$-β$)_2$, β-$C_{10}H_7$·OH, β-$C_{10}H_7$·OMe, 3 : 4 : 6 : 7- and less 2 : 3 : 6 : 7-dibenzacridine; with 4 mols. at 240—250° mainly 1 : 2-$C_{10}H_6Me$·OH and NH_2Me are obtained with less of the other products (no β-$C_{10}H_7$·OH). In an attempt to circumvent the very ready hydrolysis of the α-base, α-$C_{10}H_7$·NMe_2,HCl (I) and MeOH were heated at 230—250°, but the main reaction was (I) → $C_{10}H_6Me$·NHMe + MeCl → $C_{10}H_6Me$·OH + NH_2Me. This is in line with the formation of NH_2Me and not $NHMe_2$ in the above experiments. It is highly probable that hydrolysis precedes methylation. The benzacridines are formed by condensation of β-$C_{10}H_7$·NH_2 and 1 : 2-$C_{10}H_6MeR$ (R = NH_2 or OH), the 1-position of the former taking part in preference to the 3-position. R. S. C.

Nitration of phthalonaphthylimides and the facile preparation of 8-nitro-α-naphthylamine. H. H. Hodgson and J. H. Crook (J.C.S., 1936, 1844—1848).—Nitration of α-$C_{10}H_7$·$N(CO)_2C_6H_4$-*o* occurs exclusively in the $C_{10}H_7$ nucleus, 60% in the 8-, 28% in the 5-, and 5% in the 4-position. These proportions are but little affected by substitution of the acyl group. 8 : 1-NO_2·$C_{10}H_6$·NH_2 is probably co-ordinated thus: $O_2N \leftarrow NH_2$. Phthalo-β-naphthylimide gives mainly 8 : 2- and 5 : 2-NO_2·$C_{10}H_6$·NH_2 [*picrate*, m.p. 208° (decomp.)]. The simpler diacyl derivatives are hydrolysed during nitration. The following are prepared: phthalo-α-naphthylimide, m.p. 185° (lit. 180—181°); 3-, m.p. 225°, and 4-*nitro*-, m.p. 212°, 3-*chloro*-, m.p. 191·5°, 3 : 4-, m.p. 170°, and 3 : 6-*dichloro*-, m.p. 217°, and *tetrachloro-phthalo-α-naphthylimide*, m.p. 244°; *succin*-α-, m.p. 153°, and -β-*naphthylimide*, m.p. 218°; NN-*dibenz*-, m.p. 198°, and -*di*-m-*nitrobenzenesulphon*-α-*naphthalide*, m.p. 252°; *malein*-α-*naphthylamic acid*, m.p. 150°; 8-*nitro*-α-*naphthylamine picrate*, m.p. 181°; m-*nitrobenzenesulphon*-, m.p. 200° (*Na* salt, +*x*H_2O, m.p. 190—200°, and anhyd., m.p. 265°), and *di*-m-*nitrobenzenesulphon*-8-*nitro*-α-*naphthalide*, m.p. 198—199°; *malein*-8-*nitro*-α-*naphthylamic acid*, m.p. 198° (decomp.). R. S. C.

Acylation of aromatic aminosulphonic acids. N. N. Voroschcov and A. I. Titov (J. Gen. Chem. Russ., 1936, **6**, 1298—1305).—The velocity of acylation of aminosulphonic acids by boiling AcOH or HCO_2H is small, owing to the low concn. of substrates in solution. Addition of NaOAc increases the solubility of 1 : 6- or 1 : 7-NH_2·$C_{10}H_6$·SO_3H (I), and raises the b.p. of the mixture, thus giving a max. yield of 75% of acetylated product in presence of 2·5 mols. of NaOAc per mol. of (I). Further addition of NaOAc to 4·5 mols. lowers the yield, as a result of salting-out of the Na salt of (I), but as more NaOAc is added the yields again rise, owing to the higher b.p., and to removal of the Na salt of the Ac derivative from the sphere of reaction by the salting-out action of the excess of Na ions. The efficacy of different cations in the reaction varies with the solubility of the salts formed, in the order K > Na > Mg > Zn, both for acetylation and formylation. R. T.

Elimination of halogen during the nitration of halogenonaphthylamines. H. H. Hodgson and R. L. Elliott (J.C.S., 1936, 1762—1764).—Electronic considerations applied to a static Erlenmeyer formula explain differences in basicity and mode of nitration of halogenonaphthylenediamines. 3-Chloro-2-nitro-1-acetnaphthalide and $SnCl_2$ in HCl–EtOH give 3-*chloro*-1-N-*acetyl*-1 : 2-*naphthylenediamine*, m.p. 161° (*stannichloride*); this with Ac_2O in 20% AcOH gives the NN'-Ac_2 compound, m.p. 317·5°, from which Cl is eliminated by cold HNO_3 (*d* 1·42) with formation of 3-*nitro*-NN'-*diacetylnaphthylenediamine*, m.p. 303°. 3-*Chloro*-1 : 2-*naphthylenediamine*, m.p. 136° (*dihydrochloride*), is obtained from 2 : 3 : 1-NO_2·$C_{10}H_5Cl$·NH_2 and $SnCl_2$. 4-Chloro-, -bromo-, or -iodo-1 : 2-naphthylenediamine with conc. HNO_3–AcOH at 90° gives 4-*nitro*-2-N-*acetyl*-1 : 2-*naphthylenediamine*, m.p. 245°, also obtained from the 4-halogeno-2-*N*-acetylnaphthylenediamines and warm aq. HNO_3. The 2-

halogeno-1-*N*-acetyl-1 : 4-diamines similarly lose the halogen when nitrated, giving 2-*nitro*-1-N-*acetyl*-1 : 4-*naphthylenediamine*, m.p. 164° [corresponding Ac_2 compound, m.p. 310·5° (cf. lit.)]. 4 : 1-NO_2·$C_{10}H_6$·NH_2 and $SnCl_2$ give 1 : 4-$C_{10}H_6(NH_2)_2$ [Ac_2 derivative, m.p. 319° (lit. 303—304°)]. 4 : 1-NO_2·$C_{10}H_6$·NHAc gives N-*acetyl*-1 : 4-*naphthylenediamine*, unstable (*stannichloride*). R. S. C.

New type of condensation of organic compounds by means of alkali metals. Amide condensation. G. V. Tschelincev and E. D. Osetrova (J. Gen. Chem. Russ., 1936, **6**, 1267—1277).—Na and NPh_2Ac in C_6H_6 (3 hr. at the b.p.) yield *acetoacetdiphenylamide* (I), m.p. 86—87° : NPh_2Ac + CH_2Na·CO·NPh_2 → NPh_2·CMe(ONa)·CH_2·CO·NPh_2 ⇌ (I) + $NaNPh_2$ ⇌ ONa·CMe:CH·CO·NPh_2 + $NHPh_2$. Na, NPh_2Ac, and COPhMe in Et_2O or C_6H_6 yield COMe·CH_2Bz. R. T.

***cis–trans*-Isomeric stilbenes. III. Stereochemistry of R. Pschorr's phenanthrene synthesis.** P. Ruggli and A. Staub (Helv. Chim. Acta, 1936, **19**, 1288—1291).—The Pschorr synthesis of phenanthrene (I) depends on the *cis* relation of the two Ph groups. *o*-NO_2·C_6H_4·C:CPh and H_2–Ni in aq. EtOH gives cis-2-*aminostilbene*, an oil, which yields (Pschorr) 34% of (I). Ordinary *o*-aminostilbene compounds are *trans* and give no derivatives of (I). C_6H_4R·CH:CPh·CO_2H (R = NO_2 or NH_2) are *cis*(Ph)-compounds by repulsion of the Ph and CO_2H, which accounts for the success of the ordinary Pschorr synthesis. R. S. C.

Flavin synthesis. Crystalline intermediate products. P. Karrer and H. Meerwein (Helv. Chem. Acta, 1936, **19**, 1190—1191).—Hydrogenation (Ni; 70—90°; 20 atm.) of crude 2-*l*-arabityl- or 2-*d*-ribityl-amino-4 : 5-dimethylazobenzene gives 50—55% yields of *N*-l-*arabityl*-, m.p. 138° (uncorr.), and N-d-*ribityl*-4 : 5-*dimethylphenylenediamine*, m.p. 128° (uncorr.), $[\alpha]_D$ −17·7°. R. S. C.

Special transformation of some phenylhydroxylamine derivatives. E. Jolles (Gazzetta, 1936, **66**, 717—723).—A further study of the interconversion of substituted succin- and malein-imides (cf. A., 1936, 459). Maleic anhydride and NHPh·NH_2 in boiling AcOH yield maleinphenylhydrazide, new m.p. 265°, or, on prolonged boiling in aq. AcOH, *phenylhydrazinosuccinphenylhydrazide*, m.p. 246°. *Malein*-p-*chlorophenyl*-, m.p. 288°, and -β-*naphthyl*-*hydrazide*, m.p. 269—270°, are prepared. Maleinanil and NHPh·OH in boiling C_5H_5N form *phenylhydroxylaminosuccinanil*, m.p. 189°; on prolonged heating of reactants or of product in C_5H_5N, *anilinomaleinanil*, m.p. 238°, is obtained. Similarly *phenylhydroxylaminosuccin*-p-*tolylimide*, m.p. 190°, gives rise to *anilinomalein*-p-*tolylimide*, m.p. 215—217°. Citraconanil forms α-*phenylhydroxylamino*-α′-*methylsuccinanil*, m.p. 175°, which does not lose H_2O, even in presence of $ZnCl_2$. α-*Phenylhydrazino*-α′-*methylsuccin*-α-*naphthylimide*, m.p. 175°, behaves similarly. Citraconphenylhydrazide with NHPh·OH yields α-*phenylhydrazino*-α′-*methylsuccinphenylhydrazide*, m.p. 191°. E. W. W.

Preparation of thymol from *m*-cresol. IV. Actions of phosphoric acid, zinc chloride, and acetic acid–sulphuric acid on *m*-tolyl *iso*propyl ether. K. Ono and M. Inoto (J. Soc. Chem. Ind. Japan, 1936, **39**, 361B).—*m*-C_6H_4Me·OPr^β (I) with H_3PO_4 (*d* 1·75) at 120—130° affords *m*-cresol and 4- and 6-*iso*propyl-*m*-tolyl Pr^β ether, but is largely unchanged. (I) with $ZnCl_2$ at 200° is almost unchanged, as it is with Niederl's reagent (cf. A., 1931, 838; 1932, 510) at 100° or when boiled. J. L. D.

Synthesis of dulcin by the Curtius reaction. P. P. T. Sah and K. S. Chang (Ber., 1936, **69**, [*B*], 2762—2764).—*p*-OEt·C_6H_4·CO_2Et and N_2H_4,H_2O in boiling H_2O yield p-*ethoxybenzhydrazide*, m.p. 126—127° (*benzaldehyde*-, m.p. 198—199°, and *acetophenone*-, m.p. 153—154°, -p-*ethoxybenzoylhydrazone*), converted by $NaNO_2$ and HCl into p-*ethoxybenzazide* which passes when boiled in C_6H_6 and then treated with EtOH–NH_3 into *p*-ethoxyphenylcarbamide (dulcin), m.p. 160—161°. Similarly *p*-OMe·C_6H_4·CO_2Et is transformed successively into p-*methoxybenzhydrazide*, m.p. 135—136°, p-*methoxybenzazide*, and p-*anisylcarbamide*, m.p. 164—165°. H. W.

Kinetics of reaction between allyl bromide and sodium phenoxide in dissociating solvents.—See A., I, 87.

Exchange reactions of heavy water with organic compounds. I. Phenol, acetanilide, and the formate ion.—See A., I, 87.

Oxidation of safrole and *iso*safrole by selenium dioxide. P. Wierzchowski (Rocz. Chem., 1936, **16**, 451—458).—Safrole is heated with SeO_2 in EtOH (3 hr. at the b.p.), the product is filtered from pptd. Se, EtOH is removed at 100°, and the residue is extracted with Et_2O. The following substances were identified in the extract : piperonylacraldehyde (I), α- and β-ketodihydrosafrole, and 1′-ethoxysafrole. *iso*Safrole (II) and SeO_2 yield (I) and *α-piperonylpropane αγ-oxide*, m.p. 39—40°. (II) and SeO_2 in xylene (1 hr. at the b.p.) afford a selenide, $C_{10}H_8O_2Se$, m.p. 122°. R. T.

***iso*Eugenol and its polymerides. I.** E. Puxeddu and (Signa.) A. Rattu (Gazzetta, 1936, **66**, 700—710).—*iso*Eugenol Me, Et, and Pr^α ethers are polymerised by $FeCl_3$ (cf. A., 1913, i, 460) to the corresponding di*iso*eugenol diethers (cf. A., 1912, i, 185), all of which form Br_1-derivatives (cf. A., 1912, i, 255). *Bromodiisoeugenol* Pr^α_2 *ether* has m.p. 70°. Di*iso*eugenol Me_2 ether (I) is oxidised by CrO_3 to a *substance*, m.p. 154°, and to tetramethoxyanthraquinone (cf. A., 1931, 954); this is, however, not considered to indicate an anthracene structure in (I). *iso*Eugenol Pr^α ether with HNO_2 yields *dioximinodihydroisoeugenol* Pr^α *ether peroxide*, m.p. 76°, converted by KOH into an *oxazolone oxime* (?), $C_{13}H_{16}O_4N_2$, m.p. 142°, and reduced (Sn–HCl) to a 1 : 2 : 5-*oxadiazole*, $C_{13}H_{16}O_3N_2$, m.p. 72°. E. W. W.

Anthracene and *cyclo*butane structures for polymerides of di*iso*eugenol. E. Puxeddu (Gazzetta, 1936, **66**, 710—717).—Theoretical; the *cyclo*butane is preferred to the anthracene structure (cf. A., 1931, 954). E. W. W.

Wandering of halogen atoms in carbon chains and rings. II. Halogen wandering in the

additive products of α-halogeno-ethers and olefines. C. D. Nenitzescu and V. Przemetzki (Ber., 1936, 69, [*B*], 2706—2707).—*cyclo*Hexene and $CH_2Cl{\cdot}OMe$ in CS_2 containing $ZnCl_2$ at 0° yield 2-*chloro*-1-*methoxymethyl*cyclo*hexane*, b.p. 88—91°/17 mm., converted by $AlCl_3$ in C_6H_6 at 60—65° into 4-*phenyl*-1-*methoxymethyl*cyclo*hexane*, b.p. 118—120°/2 mm., which is dehydrogenated by Pt at about 310° and then oxidised to p-$C_6H_4Ph{\cdot}CO_2H$. Wandering is therefore not a sp. effect of CO or CO_2H, but due to a general repelling action of O of any function.

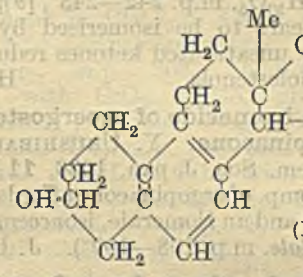
H. W.

Mesitylene derivatives. Formation of an ether from chloride [ω-chloro-derivatives] and methyl alcohol. W. T. Nauta and J. W. Dienske (Rec. trav. chim., 1936, 55, 1000—1006).—Me or CH_2Cl in the 2, 4, and 6 positions of CH_2PhCl increases the conductivity in liquid SO_2 and causes unusual reactivity. Mesitylene, aq. CH_2O (1 mol.), and HCl gas at 65° give 2 : 4 : 6-trimethylbenzyl chloride (I) m.p. 37°, b.p. 114—115°/10 mm., μ in SO_2 at −10° 0·013 (CH_2PhCl 0·0013; CPh_3Cl 7·7), and 2 : 4-*di*(*chloromethyl*)*mesitylene* (II), m.p. 105°; 2 mols. of CH_2O lead to much (II) and a little (I). (I) immediately ppts. AgCl from $AgNO_3$–EtOH; with AgOAc in AcOH at 100° it affords 2 : 4 : 6-*trimethylbenzyl acetate* (III), b.p. 136—137°/15 mm., hydrolysed by hot 15% aq. KOH to the alcohol, m.p. 88—89°; with hot *N*-KOH–MeOH or –EtOH it gives 2 : 4 : 6-*trimethylbenzyl Me* (IV), b.p. 109—110°/15 mm., and *Et ether*, b.p. 114—115°/14 mm., respectively. (III) and 2% HCl–MeOH give much (IV) and some (I). (IV) and *N*-HCl–MeOH slowly give (I). (I) itself slowly reacts with hot MeOH. $CH_2Ph{\cdot}OAc$ and HCl–MeOH give some CH_2PhCl, but no $CH_2Ph{\cdot}OMe$. (II) and AgOAc afford similarly 2 : 4-*diacetoxymethyl*-, m.p. 91—92°, and -*di*(*hydroxymethyl*)-*mesitylene*, m.p. 188—189°. (II) and *N*-KOH–MeOH or –EtOH give 2 : 4-*dimethoxy*-, m.p. 67·5—68·5°, and -*diethoxymesitylene*, m.p. 57—58°, respectively. R. S. C.

***cis*-*cyclo*-Hexanediol from *cyclo*hexene oxide.** R. Criegee and H. Stanger (Ber., 1936, 69, [*B*], 2753—2757).—The *mono*-p-*toluenesulphonate* of trans-cyclo*hexane*-1 : 2-*diol* (I), m.p. 96—96·4°, is obtained in 90% yield from *cyclo*hexene oxide (II) and p-$C_6H_4Me{\cdot}SO_3H$ in anhyd. Et_2O. It is also obtained (37% yield) accompanied by the corresponding acetate by addition of 30% H_2O_2 to *cyclo*hexene (III) and p-$C_6H_4Me{\cdot}SO_3H$ in AcOH, in 48% yield accompanied by *trans-cyclo*hexanediol (III) by gradual addition of H_2O_2–Et_2O to (III) and p-$C_6H_4Me{\cdot}SO_3H$ and from (IV) and p-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N. (III) and 2 : 5-$C_6H_3Cl_2{\cdot}SO_3H$ in AcOH containing AcO_2H afford trans-cyclo*hexane*-1 : 2-*diol* 2′ : 5′-*dichlorobenzenesulphonate*, m.p. 134° (corr.; decomp.) [*acetate*, m.p. 170° (corr.; decomp.)]. (II) and an excess of $CCl_3{\cdot}CO_2H$ in anhyd. Et_2O give trans-cyclo*hexane*-1 : 2-*diol monotrichloroacetate*, m.p. 76—77° (corr.). trans-cyclo*Hexane*-1 : 2-*diol di*-p-*toluenesulphonate*, m.p. 109° (corr.), from (I) and p-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N, is remarkably stable to acid and alkali. cis-cyclo-*Hexane*-1 : 2-*diol di*-p-*toluenesulphonate*, m.p. 128·5—129·5°, could not be partly hydrolysed. Treatment of (I) with KOAc in boiling MeOH yields $C_6H_4Me{\cdot}SO_3K$, (II), and a fraction of b.p. 118—120°/12 mm., which gives (IV) when hydrolysed; the first stage in the change appears to be the formation of (II), since a similar product is derived from (II), KOAc, AcOH, and EtOH. trans-cyclo*Hexane*-1 : 2-*diol acetate* p-*toluenesulphonate*, m.p. 78—79°, from (I) and Ac_2O containing a little conc. H_2SO_4, is transformed by KOAc in boiling EtOH with subsequent hydrolysis into *cis-cyclo*hexane-1 : 2-diol, m.p. 96—98° (yield 68%). Better yields (89%) are obtained in boiling AcOH. With AcOH alone the change is unimol.

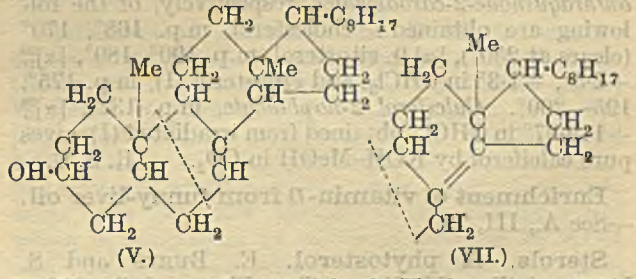
H. W.

7-Dehydrocholesterol. F. Schenck, K. Buchholz, and O. Wiese (Ber., 1936, 69, [*B*], 2696—2705).—The differences in the recorded m.p. of 7-dehydrocholesterol (I) are attributed to the presence of solvent of crystallisation. After separation from MeOH and desiccation at room temp. (I) has m.p. 143—144°, whereas if dried at 100°/vac. or crystallised from EtOAc it has m.p. 149° after softening at 148°. 7-Dehydrocholesteryl acetate (II) unites slowly with maleic anhydride in boiling xylene to the *adduct*, $C_{33}H_{48}O_5$, m.p. 178°. Exposure to sunlight of (I) in EtOH containing eosin leads to "7-*dehydrocholesterolpinacol*" (III), $C_{54}H_{86}O_2{,}1{\cdot}5H_2O$, m.p. 196—197° (decomp.), converted by Ac_2O in C_5H_5N into the corresponding *diacetate*, m.p. 201—202° (decomp.), $[\alpha]_D^{22}$ −161·2° in $CHCl_3$, also obtained by insolation of (II). (III) is decomposed when heated above its



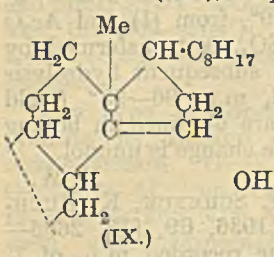
(IV.)

m.p. or boiled with Ac_2O and then hydrolysed into *norsterol* (IV), m.p. 111°, $[\alpha]_D^{22}$ +106° in $CHCl_3$ [3 : 5-*dinitrobenzoate*, m.p. 207° (decomp.), $[\alpha]_D^{22}$ −2·5° in $CHCl_3$]. Insolation of (I) in presence of eosin and O_2 gives 7-*dehydrocholesterol peroxide*, $C_{27}H_{44}O_3$, m.p. 152°, $[\alpha]_D^{15}$ +6·55° in $CHCl_3$, reduced by Zn dust in KOH–

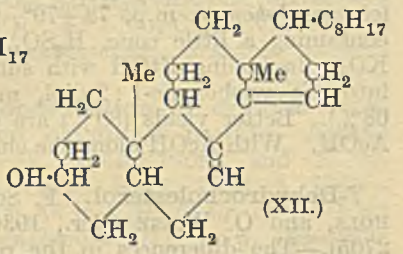


EtOH to a *cholestenetriol*, $C_{27}H_{46}O_3$, m.p. 211° (decomp.). (I) is reduced by Na and abs. EtOH to γ-*cholestenol* (V), m.p. 122—123°, $[\alpha]_D$ −13·5° [*acetate* (VI), m.p. 118—119°, $[\alpha]_D$ ±0°; *benzoate*, m.p. 157—158° becoming clear at 176°, $[\alpha]_D^{18}$ +7·14° in $CHCl_3$]. (V) is transformed by BzO_2H in $CHCl_3$ into *cholestane*-3 : 7 : 8-*triol*, m.p. 192°, converted by Ac_2O and C_5H_5N into the *diacetate*, m.p. 164—165°.

Contact of (VI) with Pt in cold EtOAc–Et_2O causes isomerisation to *α-cholestenyl acetate*, m.p. 77—78°, $[\alpha]_D^{21}$ +9·46° in $CHCl_3$, also obtained by hydrogenation (Pd sponge in EtOAc) of (II); it is hydrolysed to *α-cholestenol* (VII), m.p. 119—120°, $[\alpha]_D^{21}$ +20·36°



(IX.)



(XII.)

in $CHCl_2$ [*benzoate* (VIII), m.p. about 140° after becoming cloudy at about 115°, $[\alpha]_D^{20}$ +8·53° in $CHCl_3$]. (VIII) is isomerised by HCl in $CHCl_3$ to *β-cholestenyl benzoate*, m.p. 168°, $[\alpha]_D^{22}$ +32·54° in $CHCl_3$, whence *β-cholestenol* (IX), m.p. 130—131°, $[\alpha]_D^{22}$ +34° in $CHCl_3$ [*acetate* (X), m.p. 91—92°]. Hydrogenation (Pt sponge in EtOAc–Et_2O) of (X) yields cholestanyl acetate. 7-Dehydrocholesteryl benzoate is transformed by HCl in $CHCl_3$ at 0° into *dehydrocholesteryl*-B_2 *benzoate* (XI), m.p. 149—150°, $[\alpha]_D^{21}$ −115·1° in $CHCl_2$, hydrolysed by KOH in MeOH–Et_2O to *dehydrocholesterol*-B_3 (XII), m.p. 117—118°, $[\alpha]_D^{23}$ −145·5° in $CHCl_3$ (*acetate*, m.p. 86—87°, $[\alpha]_D^{21}$ −114·5° in $CHCl_3$). (XI) and maleic anhydride in boiling C_6H_6 give the *adduct*, $C_{38}H_{50}O_5$, m.p. 242—243°, $[\alpha]_D^{22}$ −17° in $CHCl_3$. (I) appears to be isomerised by finely divided Ni to singly unsaturated ketones reduced by Na and EtOH to cholestenols. H. W.

Formation of an isomeride of neoergosterol by pyrolysis of ergopinacone. Y. Urushibara and T. Ando (Bull. Chem. Soc. Japan, 1936, **11**, 757—758).—Thermal decomp. of ergopinacone affords a mixture of neoergosterol and an isomeride, *isoneoergosterol*, m.p. 138—139° (*acetate*, m.p. 108—109°). J. D. R.

2-Naphthoates and anthraquinone-2-carboxylates of vitamin-*D* and other sterols. M. Sumi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, **30**, 252—257).—By treatment of a hot C_5H_5N solution with 2-$C_{10}H_7$·COCl in C_6H_6 or anthraquinone-2-carboxyl chloride alone or in C_6H_6 2-*naphthoates* and *anthraquinone-2-carboxylates*, respectively, of the following are obtained: cholesterol, m.p. 168°, 170° (clears at 250°), [α] 0, sitosterol, m.p. 190°, 189°, $[\alpha]_D^{20}$ +2·5°, −1·3° in $CHCl_3$, and ergosterol (I), m.p. 175°, 195—200°. *Calciferol* 2-*naphthoate*, m.p. 132°, $[\alpha]_D^{20}$ +149·97° in $CHCl_3$, obtained from irradiated (I), gives pure calciferol by KOH–MeOH in CO_2. R. S. C.

Enrichment of vitamin-*D* from tunny-liver oil. —See A., III, 79.

Sterols. A phytosterol. E. Bureš and S. Lisicová (Rep. III Congr. Slav. Pharm., 1934, 213—220).—Repeated hydrolysis of the oil of the seeds of the black henbane (*Hyoscyamus niger*, L.) and extraction with Et_2O gave a *phytosterol* (I), $C_{28}H_{48}O,H_2O$, m.p. 119—120°, characterised by the Salkowski reaction and $[\alpha]_D^{20}$ −29·4° in $CHCl_3$ [*acetate* (II), m.p. 124°, $[\alpha]_D^{20}$ −26·5° in $CHCl_3$; *benzoate*, m.p. 123—124°], converted by PCl_5 into a mixture of Cl_1- and Cl_2-compounds. The I val. of (I) was 118·6 corresponding with two ethylenic linkings, whilst (II) with Br gave a *Br*-derivative. Reduction of (I) with H_2 (Ladenburg) gave the H_6-compound, I val. 52·68, no longer giving the Salkowski reaction and slowly absorbing Br. F. R.

Raphanosterol and some of its derivatives. E. Bureš and E. Sedlář (Rep. III Congr. Slav. Pharm., 1934, 221—227).—Repeated hydrolysis and extraction of the oil of the seeds of the wild radish (*Raphanus raphanistrum*, L.) gave a phytosterol, *raphanosterol* (I), $C_{27}H_{54}$·OH, m.p. 136°, $[\alpha]_D^{20}$ −32·19 in $CHCl_3$ [*acetate*, m.p. 125°, and *benzoate*, m.p. 139°, both converted by Cl_2 in $CHCl_3$ into the corresponding Cl_2-compounds, m.p. 160° and 124°, respectively]. (I) and PCl_5 gave the *chloride*, m.p. 103°, converted by Cl_2 in $CHCl_3$ into the Cl_2-compound, m.p. 113°, and reduction of (I) with Na and C_5H_{11}·OH gave a H_2-derivative, m.p. 155°. The OH is therefore alcoholic and (I) contains one ethylenic linking. F. R.

Œstriolglycuronide.—See A., III, 74.

Kinetics of thermal *cis–trans* isomerisation. VI. [β-Cyanostyrene].—See A., I, 86.

Tenacity of organic radicals and reactivity. III. Hydrolysis of esters and reduction of nitro-compounds. K. Kindler [with K. G. Ellinger, W. Fürst, and H. Schmidt] (Ber., 1936, **69**, [*B*], 2792—2810).—The rate of hydrolysis of esters, R·CO_2Et, and of addition of H_2S to nitriles, R·CN, increases as the firmness of the union of R to ·CO_2Et or ·CN diminishes. Further, compounds R·NO_2 are reduced more rapidly by $TiCl_3$ as the tenacity of R declines. Experimentally, the first and third methods are the most accurate. A general parallelism is observed in the data given by the three methods, but exact mathematical agreement is neither expected nor attained. The tenacity of alkyl radicals increases markedly from Me to Pr^a and then slowly. *n*-Alkyls are more loosely attached than those with branched chains. The unsaturated oleic residue is more firmly united than the saturated stearic group. *p*-Substituted aryls with negative substituents cling more loosely, those with positive substituents more strongly, than Ph. *p*-Me, -Et, or -Pr^a behaves very similarly to *p*-CO_2Et. Both position and nature influence the tenacity of aryls. Increase in the no. of NO_2 groups causes marked decline in tenacity. In general, aralkyl groups are less firmly united than the corresponding alkyl radicals. CHAr:CH· is much more firmly joined than CH_2Ar·CH_2·. 2-, 3-, and 4-Pyridyl, 2-, 3-, and 4-quinolyl, and 2-*iso*quinolyl are less firmly attached to ·CO_2Et than Ph. Me and OMe in quinolyl behave as when in the *p*-position in aryls. 2-Thienyl closely resembles Ph, but 2-furfuryl is much more loosely combined. The sequence of tenacity towards ·CO_2Et, ·CN, and ·NO_2 is the same as that observed previously towards halogens and now established by the rate of reaction of R·COCl and NaOEt. The following compounds appear new: *Et* p-n-*propylbenzoate*, b.p. 143°/18 mm. (corresponding acid, m.p. 142·5°); *Et* p-n-*propoxybenzoate*, b.p. 193—194°/9 mm.; *Et* p-iso*propoxybenzoate*, b.p. 157—160°/9

mm.; *Et* p-iso*octoxybenzoate*, b.p. 201—203°/9 mm.; *Et quinoline*-2-*carboxylate*, b.p. 186—188°/13 mm.; *Et quinoline*-3-*carboxylate*, b.p. 174°/10 mm., m.p. 66—67° [corresponding *acid*, m.p. 282—283° (decomp.)]; *Et* 4-*methylquinoline*-2-*carboxylate*, b.p. 198—200°/13 mm., m.p. 33—36°; *Et* 8-*methylquinoline*-2-*carboxylate*, b.p. 181—182°/12 mm. H. W.

Synthesis of diphenylyl acetates. N. N. Chatterjee (J. Indian Chem. Soc., 1936, **13**, 593—598; cf. A., 1935, 1496).—Et 4-methyl*cyclo*hexanone-2-carboxylate with $CH_2Cl{\cdot}CO_2Et$ and NaOEt–EtOH (or Na–C_6H_6) gives *Et*$_2$ 4-*methyl*cyclo*hexanone*-2-*carboxylate*-2-*acetate* (I), b.p. 165°/5 mm. (*semicarbazone*, m.p. 174°), hydrolysed by HCl–H_2O to 4-*methyl*cyclo*hexanone*-2-*acetic acid*, b.p. 160—165°/6 mm. [*Et* ester (II), b.p. 129°/8 mm. (*semicarbazone*, m.p. 210—211°)]. (II) with MgPhBr–Et_2O gives *Et* 1-*hydroxy*-4-*methylhexahydrodiphenyl*-2-*acetate*, b.p. 168—178°/8 mm., reduced by S (200—240°; 4—5 hr.) to *Et* 4-*methyldiphenyl*-2-*acetate*, b.p. 160—167°/6 mm., and converted by $SOCl_2$–C_5H_5N–Et_2O into *Et hexahydrodiphenyl*-2-*acetate*, b.p. 165—175°/7 mm., hydrolysed to the corresponding *acid*, m.p. 168—170°. (I) when treated with MgPhBr–Et_2O and then with H_2SO_4 gives the *lactone*, m.p. 112°, b.p. 200—220°/7 mm., of 1-hydroxy-2-carbethoxy-4-methylhexahydrodiphenyl-2-acetic acid. The following have been prepared by similar methods. Et$_2$ 5-, b.p. 163—166°/5 mm. (cf. lit.), and *Et*$_2$ 6-, b.p. 158—162°/8 mm., -*methyl*cyclo*hexanone*-2-*carboxylate*-2-*acetate*; 5-, m.p. 94—95°, b.p. 162°/4 mm. [Et ester, b.p. 127°/5 mm. (semicarbazone, m.p. 174—175°)] (cf. lit.), and 6-*methyl*cyclo*hexanone*-2-*acetic acid*, b.p. 162—166°/6 mm. (*Et* ester, b.p. 125—130°/8 mm.); *Et* 1-*hydroxy*-5-, b.p. 165—175°/7 mm., and -6-, b.p. 160—170°/7 mm., -*methylhexahydrodiphenyl*-2-*acetate*; *Et* 5-, b.p. 160—165°/6 mm., and *Et* 6-, b.p. 160—163°/9 mm., -*methyldiphenyl*-2-*acetate*; *lactone*, b.p. 210—220°/7 mm., of 1-hydroxy-2-carbethoxy-5-methylhexahydrodiphenyl-2-acetic acid and the *lactone*, b.p. 205—215°, of the corresponding -6-Me-compound. H. G. M.

Decomposition of methoxymethyl salicylate. Prismatic crystals of salicylic acid. V. A. Izmailski and B. M. Bogoslovski (J. Gen. Chem. Russ., 1936, **6**, 1193—1197).—A sample of methoxymethyl salicylate (I) had undergone decomp. after remaining for 8 years in a stoppered bottle, at room temp., to yield a mixture of products, of which salicylic acid (II), 2-hydroxy-3-aldehydobenzoic acid, 2-hydroxy*iso*phthalic acid, and 3-hydroxymethylsalicylic acid (III) were identified. The probable reactions are: (I) + H_2O → (II) + CH_2O + MeOH; (II) + CH_2O → (III). The (II) crystallises from the reaction mixture in the form of rectangular prisms. R. T.

Phenacylthiolacetic acid and related compounds. B. Holmberg (Arkiv Kemi, Min., Geol., 1936, **12**, A, No. 9, 11 pp.).—Interaction of $COPh{\cdot}CH_2Br$ (I) with $SH{\cdot}CH_2{\cdot}CO_2H$ (II) in NaOH affords $CH_2Bz{\cdot}S{\cdot}CH_2{\cdot}CO_2H$ (III) (Behagel *et al.*, A., 1935, 1237) (*oxime*, m.p. 125—127°, reduced by Na–Hg to a *substance*, $C_{18}H_{22}O_3N_2S$). When steam-distilled with *N*-NaOH, (III) gives COPhMe and $CH(CH_2Bz)_2{\cdot}CO_2H$ + C_6H_6, m.p. 133·5—134·5°, and solvent-free, identical with a specimen prepared by Bougault's method (A., 1909, i, 487). Condensation of (II) with either (III) or $COPh{\cdot}CH_2{\cdot}OH$ in presence of 5*N*-HCl at 100° affords ββ-*di*(*carboxymethylthiol*)-β-*phenylethylthiolacetic acid*, $CPh(S{\cdot}CH_2{\cdot}CO_2H)_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$ (IV), m.p. 147—150°, stable to *N*-NaOH at 100°. (I) and (II) in Et_2O afford (III) and the products of an oxidation–reduction reaction: (I) + 2(II) → COPhMe + HBr + $(S{\cdot}CH_2{\cdot}CO_2H)_2$, but since both products react with (II) the presence of this reagent in excess affords (IV) and an *oil*, seeming to be mainly $CPh(S{\cdot}CH_2{\cdot}CO_2H)_2{\cdot}CH_2{\cdot}OH$. Oxidation of (III) with aq. $K_2S_2O_8$ with cooling gives *phenacylthionylacetic acid*, two *forms*, m.p. 85—86°, m.p. 124—125° (decomp.), decomposed by alkali thus: $CH_2Bz{\cdot}SO{\cdot}CH_2{\cdot}CO_2Na$ + NaOH → COPhMe + $ONa{\cdot}SO{\cdot}CH_2{\cdot}CO_2Na$. J. W. B.

Introduction of double linkings into bile acids and sterols. I. Bromination of 3-ketocholanic acid and of cholestenone. E. Dane, Y. Wang, and W. Schulte (Z. physiol. Chem., 1936, **245**, 80—88).—3-Ketocholanic acid in AcOH with 2*N*-Br in AcOH gives a 35% yield of 4-bromo-3-ketocholanic acid (I), m.p. 179° (decomp.), which with KOH in MeOH gives 4-*hydroxy*-3-*ketocholanic acid*, m.p. 186°. (I) when boiled with C_5H_5N gives 3-keto-Δ^4-cholenic acid, m.p. 178°, in 49% yield (Me ester, m.p. 126°). Cholestenone in $CHCl_3$ + AcOH with Br in AcOH gives 2 : 4-*dibromocholestenone*, $C_{27}H_{42}OBr_2$ or $C_{24}H_{40}OBr_2$, m.p. 203°. 5 : 6-Dibromocholesterol oxidised with CrO_3 at 45° gives 5 : 6-dibromocholestanone (II) and with $KMnO_4$ 6-bromo-Δ^4-cholestenone (III), m.p. 132°, also obtained by boiling (II) in abs. EtOH for 1 hr. with NaOAc. (II) and (III) boiled for several hr. with HCl in MeOH give 3 : 6-cholestanedione, m.p. 170° [disemicarbazone, m.p. 203° (decomp.)]. (III) with 6% $AgNO_3$ in C_5H_5N at room temp. gives $\Delta^{4:6}$-*cholestadienone* [*semicarbazone*, m.p. 218° (decomp.)], with boiling C_5H_5N a *substance*, m.p. 276°, and cholestenone, m.p. 83° (*oxime*, m.p. 179°), and with KOH in MeOH in 3 hr. at room temp. followed by treatment with semicarbazide acetate the *semicarbazone*, m.p. 222° (decomp.), of 6-*hydroxy*-Δ^4-*cholestenone*. W. McC.

Syntheses of 2-amino- and 2-chloro-3-methoxy-4-ethoxybenzoic acid and attempted synthesis of 3-methoxy-4-ethoxy-o-phthalic acid. K. Feist, W. Awe, and W. Völksen (Ber., 1936, **69**, [*B*], 2743—2749).—2-Nitrovanillin is ethylated by KOH–Et_2SO_4 or *p*-$C_6H_4Me{\cdot}SO_3Et$ to 2-*nitro*-3-*methoxy*-4-*ethoxybenzaldehyde* (I), m.p. 112° [*semicarbazone*, m.p. 247—248° (decomp.)], the constitution of which is established by its transformation by KOH and $COMe_2$ into 7 : 7′-*dimethoxy*-6 : 6′-*diethoxyindigotin*, m.p. 290°. (I) is oxidised by a large excess of $KMnO_4$ to 2-*nitro*-3-*methoxy*-4-*ethoxybenzoic acid*, m.p. 190—191° [*Me* ester (II), m.p. 92°], reduced by NH_3–$FeSO_4$ to 2-*amino*-3-*methoxy*-4-*ethoxybenzoic acid* (III), m.p. 183° [*Me* ester (IV), m.p. 42°, obtained also by reduction of (II) with Sn and HCl]. Diazotisation of (III) in 2*N*-HCl followed by treatment with $K_3Cu(CN)_4$ unexpectedly leads to 2-*chloro*-3-*methoxy*-4-*ethoxy*-

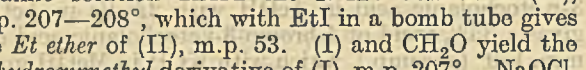
benzoic acid, m.p. 177° (non-cryst. *Me* ester). Analogously, 2-aminoveratric acid yields 2-*chloroveratric acid*, m.p. 169°, or 2-bromoveratric acid if HBr replaces HCl; in complete absence of halogen hemipinic acid is obtained in very small amount. Diazotisation of (III) in 2*N*-H_2SO_4 followed by hydrolysis of the nitrile yields small amounts of material, m.p. 155—157°, apparently a mixture of mono- and di-carboxylic acids; under more drastic conditions decarboxylation occurs with production of 3 : 4-OMe·C_6H_3(OEt)·CO_2H (V), m.p. 194°. Diazotisation of (IV) in 2*N*-H_2SO_4 and treatment of the product with $K_3Cu(CN)_4$ gives *Me* 2-*cyano*-3-*methoxy*-4-*ethoxybenzoate*, m.p. 107°, in good yield; it is unaffected by cold HCl–Et_2O but hydrolysed by 10—15% KOH–MeOH to (V). Possibly the dicarboxylic acid is obtained by use of 2% KOH at 100°. H. W.

Derivatives of hydroxyphenylmaleimide. V. Harlay (J. Pharm. Chim., 1936, [viii], **24**, 537—549).—α-Hydroxy-α′-phenylmaleimide (I) gives with 2*N*-NaOH $CH_2Ph·CO·NH_2$ and with *N*-NaOH, *phenylpyruvimide*, m.p. 156—157°. (I) and Me_2SO_4 in aq. alkaline solution afford the *N-Me* derivative (II), m.p. 207—208°, which with EtI in a bomb tube gives the *Et ether* of (II), m.p. 53. (I) and CH_2O yield the N-*hydroxymethyl* derivative of (I), m.p. 207°. NaOCl, NaOBr, and NaOI in the presence of insufficient alkali give lachrymatory oils; with excess they give $CHPhCl·CO·NH_2$, $CHPhBr·CO·NH_2$, and α-*iodophenylacetamide*, m.p. 150°. R. F. P.

Preparation of the ten dicyanonaphthalenes and the related naphthalenedicarboxylic acids. E. F. Bradbrook and R. P. Linstead (J.C.S., 1936, 1739—1744).—The following dicyanonaphthalenes are prepared in the yields stated from the pure alkali cyanonaphthalenesulphonates and $K_3Fe(CN)_6$ or KCN at 320—390° (occasionally only at higher temp.)/40 mm. in CO_2 or (usually) in lower yield from the crude sulphonates: 1 : 2-, m.p. 190° (75%), 1 : 3-*, m.p. 179° (17%), 1 : 4-, m.p. 208° (71%), 1 : 5-, m.p. 263° (53%), 1 : 6-, m.p. 211° (18%), 1 : 7-*, m.p. 167° (>31%), 1 : 8-*, m.p. 232° (9%), 2 : 6-, m.p. 293° (42%), and 2 : 7-, m.p. 267° (8%). *Substances* marked * are new. Regularities in the variations of yields are discussed; the SO_3H is activated by the CN if separated therefrom by an ethylenic linking or a conjugated system of such linkings. Hydrolysis by boiling aq. H_2SO_4–AcOH gives 1 : 2-, m.p. 168° (*Me H*, m.p. 145°, and Me_2 ester, m.p. 85°), 1 : 3-, m.p. 267—268°, 1 : 4-, m.p. >300° [Me_2 ester, m.p. 67° (lit. 64°)], 1 : 5-, m.p. >300° [Me_2 ester, m.p. 119° (cf. lit.)], 1 : 6- (Me_2 ester, m.p. 98°), 1 : 7- (Me_2 ester, m.p. 90°), 1 : 8- (Me_2 ester, m.p. 104°), 2 : 6-, m.p. >300° (Me_2 ester, m.p. 186°), and 2 : 7- (Me_2 ester, m.p. 135°) -naphthalenedicarboxylic acid. The following are incidentally described: *Na* 2-*cyanonaphthalene*-1-, -3-, -5-, and -8-*sulphonate*, *K* 1-*cyanonaphthalene*-4-*sulphonate*, *Na* 2-*cyanonaphthalene*-6- and -7-*sulphonate*.

[With A. R. Lowe.] 2 : 3-$NH_2·C_{10}H_6·CO_2H$ gives (Sandmeyer) 2 : 3-naphthalimide (cf. lit.), which, when passed in NH_3 over ThO_2 at 490°, gives 2 : 3-*dicyanonaphthalene*, m.p. 251°, and thence the Me_2 *dicarboxylate*, m.p. 47°. R. S. C.

***spiro*-Compounds. II. Ring transformation into *spiro*-compound from 4-methylcyclohexanone. New synthesis of cadalene.** N. N. Chatterjee (J. Indian Chem. Soc., 1936, **13**, 588—592; cf. this vol., 19).—4-Methylcyclohexanonecyanohydrin when treated with CN·CHNa·CO_2Et–EtOH (3 days) and then mixed with $CH_2Cl·CH_2·CO_2Et$ and boiled gives *Et*$_2$ 1-*cyano*-4-*methylcyclohexane*-1-*cyanoglutarate*, b.p. 208—215°/4 mm., hydrolysed by H_2SO_4 and then by NaOH to 1-*carboxy*-4-*methylcyclohexane*-1-α-*glutaric acid*, m.p. 155° [*Et*$_3$ ester (I), b.p. 175—180°/5 mm.; *Et* ester, m.p. 79°, obtained from the *anhydride* with EtOH–H_2SO_4]. (I) when heated with Na in C_6H_6 gives *Et*$_2$ 4-*methylcyclohexane*spiro-cyclo*pentan*-2′-*one*-3′ : 5′-*dicarboxylate*, b.p. 180—185°/4 mm., hydrolysed by dil. H_2SO_4 to 4-*methylcyclohexane*spiro-cyclo*pentan*-2′-*one*-5′-*carboxylic acid*, m.p. 130° [*semicarbazone*, m.p. 228°; *Et* ester (II), b.p. 133°/4 mm.], oxidised by HNO_3 to hexahydro-*p*-toluic acid. (II) with MgMeI–Et_2O gives the compound



which when heated with Se (290—300° for 20 hr. and then 330° for 30 hr.) gives cadalene (III). This result suggests that the formation of (III) or eudalene on S or Se dehydrogenation of certain sesquiterpenes is not trustworthy evidence for their naphthalene-like ring structure. H. G. M.

Synthetic experiments in the naphthalene and phenanthrene series. B. K. Menon (J.C.S., 1936, 1775—1777).—*p*-$C_6H_4Br·CH_2·CO_2Et$, NaOEt, and $OEt·CH:C(CO_2Et)_2$ first at 0° and then at 145—155° give *Et*$_2$ 7-*bromo*-1-*naphthol*-2 : 4-*dicarboxylate*, m.p. 105°, hydrolysed to the corresponding *acid*, m.p. 299° (decomp.) [*Me ether*, m.p. 261° (*dianilide*, m.p. 260°)]. *p*-$C_6H_4Cl·CH_2·CO_2Et$ gives similarly α-p-*chlorophenylglutaconic acid*, m.p. 175° (obtained from the impure *Et*$_2$ ester, b.p. about 192°/2 mm.), and *Et*$_2$ 7-*chloro*-1-*naphthol*-2 : 4-*dicarboxylate*, m.p. 102—103° {corresponding *acid*, m.p. 294° [*Me ether*, m.p. 228° (*dianilide*, m.p. 215°)]}. 1-$C_{10}H_7·CH_2·CO_2Et$ yields α-1-*naphthylglutaconic acid*, m.p. 171°, and 1-*phenanthrol*-2 : 4-*dicarboxylic acid*, m.p. 304° (*Me ether*, m.p. 228°). Decarboxylation of the acids gives only poor yields. R. S. C.

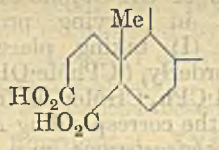
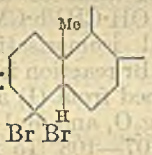
Synthesis of resorcylbutyrolactone mono- and di-methyl ethers. K. Susuki (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 71).—γ-Keto-γ-2-hydroxy-4-methoxy- and -2 : 4-dimethoxy-phenylbutyric acid with Na–Hg and dil. AcOH give γ-2-*hydroxy*-4-*methoxy*-, m.p. about 110—114°, and γ-2 : 4-*dimethoxy-phenylbutyrolactone*, m.p. 95—98°, respectively. R. S. C.

Enolic form of acid anhydrides in the Perkin synthesis. P. Kalnin (Ber., 1936, **69**, [*B*], 2843; cf. A., 1929, 63).—A claim for priority in the conception that Perkin's synthesis involves the condensation of the aldehyde with the enolic form of the acid anhydride. H. W.

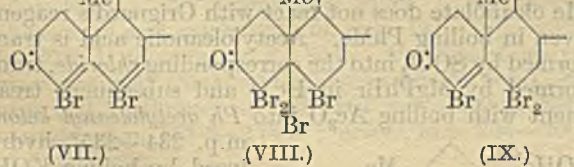
Action of hydrocyanic acid on active 3-methylcyclohexanone. M. Godchot and (Mlle.) G.

CAUQUIL (Compt. rend., 1936, **203**, 1042—1044).—The $NaHSO_3$ compound of 3-methyl*cyclo*hexanone ($[\alpha]_{589}$ +13·6°) with HCN at 100° yields 1-*cyano*-3-*methyl*cyclo*hexyl* 3′-*methyl*cyclo*hexyl ether*, m.p. 146°, $[\alpha]_{5461}$ −30·63° in C_6H_6, a *compound*, $C_{15}H_{26}O_3$, m.p. 96°, $[\alpha]_{5461}$ −25·73° in $COMe_2$, and mixed 3-methyl*cyclo*hexan-1-ol-1-carboxylic acids the *Me* esters (I) of which have b.p. 98—99°/16 mm., $[\alpha]_{5786}$ +29·73°, $[\alpha]_{5461}$ +34·17°, $[\alpha]_{4358}$ +62·12°, and b.p. 108°/16 mm., $[\alpha]_{5786}$ −7·93°, $[\alpha]_{5461}$ −8·52°, $[\alpha]_{4358}$ −14·27°, respectively. *l*-(I) with NH_3–EtOH yields the *amide*, m.p. 128°, $[\alpha]_{5461}$ −2·28°, $[\alpha]_{4358}$ −4·19° in $COMe_2$, from which is obtained the *acid*, m.p. 97—98°, $[\alpha]_{5461}$ −6·60°, $[\alpha]_{4358}$ −11·01° in $COMe_2$ (*anilide*, m.p. 109°, $[\alpha]_D$ −11·5° in C_6H_6). F. N. W.

Brominated sterol ketones. A. BUTENANDT, G. SCHRAMM, A. WOLFF, and H. KUDSZUS (Ber., 1936, **69**, [*B*], 2779—2783).—Cholestanone with Br (1 mol.) gives 2-bromocholestanone (I), transformed by further bromination into a Br_2-compound, m.p. 193—194°, also obtained from (I). Contrary to Ruzicka *et al.* (A., 1936, 1382) this is regarded as 2 : 4-*dibromocholestanone*, since it is transformed by KOAc in BuOH into *cholestane*-3 : 4-*dione* (II), m.p. 147—148°, characterised by marked absorption at 280 mμ, the formation

(III.)  (V.) 

of a dark red colour with $FeCl_3$, and the formation of a *monoenol acetate*, m.p. 100—101°, which shows strong absorption between 240 and 250 mμ. The *quinoxaline* derivative has m.p. 207—208°. The constitution of (II) follows further from its ready oxidation by H_2O_2 to the dihydro-Diels acid (III). Further, cholesterol hydrochloride is oxidised by CrO_3 to 5-*chlorocholestanone*, m.p. 102° or 135° (according as solvent of crystallisation is present or not), which with Br gives 5-*chloro*-4-*bromocholestanone* (IV), m.p. 122°, whence an αβ-unsaturated *Br*$_1$-*ketone*, m.p. 123°. (IV) with KOAc and AcOH gives (II) and cholestane-3 : 6-dione which is compatible only with the presence of the halogens at 4 and 5 in (IV).



(VII.) (VIII.) (IX.)

Dibromocoprostanone, m.p. 135—136° [Ruzicka (*loc. cit.*) gives m.p. 143°], is obtainable from 4-bromocoprostanone and its quinoxaline derivative is identical with that derived from (II). It is probably but not certainly (V).

Bromination of Δ^4-cholestenone (VI) under varied conditions gives a variety of products among which is a dibromide, m.p. 177°, or, occasionally, m.p. 183°, apparently identical with the 2 : 4-dibromo-Δ^4-cholestenone of Ruzicka (*loc. cit.*). This is regarded as (VII) for the following reasons. The absorption spectrum is similar to that of cholestenedione Et ether and indicates double conjugation to :CO. (VII) is obtained by direct bromination of (VI) or from the saturated tribromide $C_{27}H_{41}OBr_3$, m.p. about 182—183°, obtained by bromination of (VI) in presence of KOAc and readily converted by loss of HBr into (VII) thus establishing the empirical formula and degree of unsaturation. Further the Br_4-ketone (VIII), m.p. 128°, passes readily by loss of HBr into the αβ-unsaturated Br_3-ketone, m.p. 165°, which by further loss of HBr gives (VII) in good yield, also obtainable directly from (VIII). Br is therefore at $C_{(4)}$ and $C_{(6)}$ not at $C_{(2)}$, and the doubly unsaturated character is confirmed. Other products of the bromination of (VI) are a doubly unsaturated *Br*$_3$-*ketone*, $C_{27}H_{39}OBr_3$, m.p. 165—166°, $[\alpha]_D^{20}$ −22°, absorption max. at 313 mμ, and a trebly unsaturated *Br*$_2$-*ketone*, m.p. 203°, $[\alpha]_D$ −38° (*oxime*, m.p. 118°). H. W.

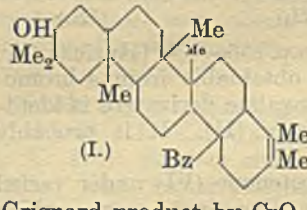
Sterol-œstrone group. I. Synthesis of 3-keto-3 : 4-dihydro-1 : 2-*cyclo*pentenophenanthrene. J. C. BARDHAN (J.C.S., 1936, 1848—1851).—$CHNaAc{\cdot}CO_2Me$ and $CO_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$ in Et_2O give *Me* γε-*diketo*-δ-*carbomethoxyheptoate*, b.p. 137°/0·5 mm., which with cold NH_3–Et_2O gives a good yield of *Me*$_2$ β-*ketoadipate* (I), b.p. 122°/0·5 mm. $CH_2Ac{\cdot}CO_2Et$ leads similarly to *Me* γε-*diketo*-δ-*carbethoxyheptoate*, b.p. 136°/0·6 mm., and *Me Et* β-*ketoadipate*, b.p. 123°/0·5 mm. (I) with hot dil. HCl gives lævulic acid, but with cold conc. HCl affords β-ketoadipic acid in good yield; this is remarkably stable. (I), NaOMe, and β1-$C_{10}H_7{\cdot}CH_2{\cdot}CH_2Br$ give *Me* γ-*keto*-δ-*carbomethoxy*-ζ-1-*naphthylheptoate*, b.p. about 195° (slight decomp.)/0·5 mm., which with cold H_2SO_4 gives an ester, hydrolysed (KOH–MeOH) to 2-*carboxy*-3 : 4-*dihydrophenanthrene*-1-β-*propionic acid*, m.p. 237—238° (*Me*$_2$ ester, m.p. 75°); with Ac_2O at 155—210°, this gives 3′-*keto*-3 : 4-*dihydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 210° (*semicarbazone*, m.p. >285°), which, when reduced (Zn–Hg) and then dehydrogenated (Se at 310—330°), affords 1 : 2-*cyclo*pentenophenanthrene. $CH_2Ph{\cdot}CH_2Br$ and (I) give *Me* γ-*keto*-δ-*carbomethoxy*-ζ-*phenylheptoate*, b.p. 185°/1 mm., which with NaOMe and MeI gives *Me* γ-*keto*-δ-*carbomethoxy*-ζ-*phenyl*-δ-*methylhepotate*, b.p. 189°/1 mm. Œstrone Me ether (II), HCO_2Et, and Na in C_6H_6 give the *formyl* derivative, m.p. 170—171°, the oxime of which with 33% KOH gives 2-*carboxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-1-β-*propionic acid*, m.p. 251—252°, which with Ac_2O regenerates only (II) and with Se gives a cryst. hydrocarbon. R. S. C.

Ketonic derivatives of acetylbenzoyl. K. VON AUWERS and H. LUDEWIG (Annalen, 1936, **526**, 130—143).—All ketonic reagents appear to attack first the aliphatic half of the AcBz mol. This appears to be true for homologous aliphatic-aromatic α-diketones unless exception is caused by very marked branching of the aliphatic chain. For derivatives of AcBz it is proposed to use *A* and *B* according as substitution occurs at the aliphatic or benzenoid portion of the mol. Acetylbenzoyloxime-*A* (I), m.p. 114—115°, is readily obtained from COPhEt, *iso*amyl nitrite, and HCl. The corresponding oxime

B (II), m.p. 166—167°, is not readily prepared from $CH_2Ph{\cdot}COMe$ and is best derived from $CMe_2{:}N{\cdot}OH$ and PhN_2Cl in acid solution. Both isomerides are readily converted into the dioxime, m.p. about 235° when rapidly heated. AcBz and $NHPh{\cdot}NH_2$ in EtOH afford *acetylbenzoylphenylhydrazone*-A (III), m.p. 144—145°, the structure of which is confirmed by its production from PhN_2Cl and the product of the alkaline hydrolysis of $CHMeBz{\cdot}CO_2Et$ or from PhN_2Cl and $OH{\cdot}CH{:}CEtBz$. Analogous methods lead to the corresponding p-*nitrophenylhydrazone*-A, m.p. 217—219° or m.p. 221° according to the mode of heating, and the 2 : 4-*dinitrophenylhydrazone*-A, m.p. 18·7° [accompanied by an orange-yellow (?) *variety* and the *osazone*, $C_{11}H_{16}O_8N_8$, m.p. 257°]. *Hydroxymethylenebenzyl Me ketone*, m.p. 73—74°, from $CH_2Ph{\cdot}COMe$ and HCO_2Et, and PhN_2Cl afford *acetylbenzoylphenylhydrazone*-B (IV), m.p. 124—125°. (I) and $NHPh{\cdot}NH_2$ in EtOH afford acetylbenzoylphenylhydrazone-*B*-oxime-*A*, m.p. 207° (acetate, m.p. 136°), also obtained from (IV) and NH_2OH,HCl in presence or absence of alkali or, as abnormal product, from (III) and NH_2OH,HCl in boiling EtOH, whereby a *substance*, $C_9H_{10}O_2N_2$, is also produced. Attempts to prepare a hydrazoneoxime from (II) were unsuccessful. The monosemicarbazone-*A* (V), m.p. 208—209°, is converted by NH_2OH into the *semicarbazone*-A-*oxime*-B, m.p. 203° (decomp.) according to the rate of heating, also obtained from (II), $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2,HCl$ and NaOAc in EtO–H_2O at 40—50°; application of the latter method to (I) leads to the *semicarbazone*-B-*oxime*-A, decomp. 217—218° after becoming discoloured at 210°. (V) and $NHPh{\cdot}NH_2$ in warm EtOH yield the *semicarbazone*-A-*phenylhydrazone*-B, m.p. 194—196° (decomp.), also derived from (IV) and $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, whilst the *semicarbazone*-B-*phenylhydrazone*-A, decomp. 228—229° after becoming discoloured at 225°, is obtained from (III). H. W.

αβ-Ketols. K. von Auwers, H. Ludewig, and A. Müller (Annalen, 1936, **526**, 143—172).—The optical behaviour of the supposed $OH{\cdot}CHMeBz$ (ketol-*B*), obtained by conversion of $CHBrMeBz$ into $OAc{\cdot}CHMeBz$ and hydrolysis of the latter with boiling H_2O containing $BaCO_3$, is traced to unchanged acetate. Prolonged hydrolysis, whether in quartz or SiO_2, leads mainly to $CHPhAc{\cdot}OH$ (ketol-*A*) (I). Treatment of the mixture with aq. $NaHSO_3$ has little effect on the optical properties of the dissolved portion and leaves only a small residue. The process cannot be applied preparatively, since $NaHSO_3$ unites with both ketones. Homogeneous (I) is obtained from $OH{\cdot}CHPh{\cdot}CO{\cdot}NH_2$ and MgMeI but much by-product is formed. Pure *benzoylmethylcarbinol* (II), b.p. 123°/14 mm., is not easily obtained from $COPh{\cdot}CHO$ and MgMeI and is best prepared from $COPh{\cdot}CHMeBr$ and HCO_2K in boiling MeOH. (I) and (II) are yellow liquids which reduce cold Fehling's solution. When treated successively with PCl_3 and Zn + AcOH (I) and (II) give $COMe{\cdot}CH_2Ph$ and COPhEt, respectively. (II) can be distilled unchanged under 14 mm., but becomes partly isomerised at its b.p./atm. pressure; prolonged boiling with H_2O–$BaCO_3$ converts it almost completely into (I). It is more stable towards acid, but hydrolysis of its acetate by H_2SO_4 gives mainly (I). Indications of the reverse change are not obtained apart from processes of esterification. The *oxime* of (II) has m.p. 133—134°, and that of (I) m.p. 112·5°. (II) is transformed by $NHPh{\cdot}NH_2$ into acetylbenzoylphenylhydrazone-*A*, m.p. 144—145°, whereas (II) yields only non-cryst. products. (I) gives a 2 : 4-*dinitrophenylhydrazone* (III), m.p. 126°, the constitution of which is confirmed by the formation of an *acetate*, m.p. 165—166°, and by its non-identity with acetylbenzoyldinitrophenylhydrazone; the structure of Hey's product, m.p. 170° (A., 1930, 935), is unexplained. In cold EtOH (II) and 2 : 4-$C_6H_3(NO_2)_2{\cdot}NH{\cdot}NH_2$ react very slowly, whereas in boiling EtOH (III) is produced; in AcOH at room temp. the product is *s*-acetyldinitrophenylhydrazine. (I) gives the corresponding *semicarbazone* characterised by oxidation to acetylbenzoylsemicarbazone-*A*. (II) reacts slowly with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ giving exclusively acetylbenzoyldisemicarbazone (II), m.p. about 240°, the production of which is never observed from (I) and is a certain sign of the presence of (II) in mixtures. Unexpectedly, (IV) is also derived from $COPh{\cdot}CHMeBr$ and $COPh{\cdot}CHMe{\cdot}OAc$. Treatment of (I) or (II) with MgMeI leads to mixtures of $OH{\cdot}CPhMe{\cdot}CHMe{\cdot}OH$ and $OH{\cdot}CHPh{\cdot}CMe_2{\cdot}OH$ in varying proportion, partial isomerisation of (I) taking place. With MgPhBr reaction is more orderly, $(\cdot CPhMe{\cdot}OH)_2$ being obtained from (I) and $OH{\cdot}CPh_2{\cdot}CHMe{\cdot}OH$ from (II). (I), Ag_2O, and MeI afford the corresponding *Me ether*, b.p. 107—108°/15 mm. (*semicarbazone*, m.p. 157·5—158·5°). (I) with boiling Ac_2O yields an incompletely homogeneous material, b.p. 136—140°/11 mm., the physical consts. of which show it to be derived mainly from (II). Benzoylation appears to be accompanied by a somewhat less pronounced isomerisation of (I) into (II). (II) and PhNCO unite rapidly to the phenylurethane, $NHPh{\cdot}CO{\cdot}O{\cdot}CHMeBz$, m.p. 144—145°, also obtained slowly and accompanied by $CO(NHPh)_2$ from (I). The transformations do not appear to occur through definite intermediate products, but, as with desmotropic compounds, to be due to the wandering of H atoms or radicals. H. W.

Phenyl acetyloleanyl ketone. H. Grasshof and E. Wedekind (Ber., 1936, **69**, [*B*], 2686—2688).—Me oleanolate does not react with Grignard's reagents even in boiling PhMe. Acetyloleanolic acid is transformed by $SOCl_2$ into the corresponding *chloride*, transformed by MgPhBr in Et_2O and subsequent treatment with boiling Ac_2O into *Ph acetyloleanyl ketone*, m.p. 234—235°, hydrolysed by boiling KOH–MeOH to *Ph oleanyl ketone* (I), m.p. 234—235°. Behenic acid is isolated in small amount from the products of the oxidation of the crude Grignard product by CrO_3 in boiling AcOH.



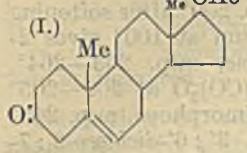
(I.)

H. W.

Δ⁵-Androsten-17-ol-3-one, an isomeride of testosterone. A. Butenandt and G. Hanisch (Ber., 1936, **69**, [*B*], 2773—2775).—Androstene-3 : 17-

diol 17-acetate is brominated in AcOH and then cautiously oxidised by CrO_3 to the Br_2-ketone, which is converted by Zn dust in boiling MeOH into Δ^5-*androsten*-17-*ol*-3-*one acetate*, (I), m.p. 147° after softening at 130°, $[\alpha]_D^{20}$ −30·5° in EtOH, and a *substance*, $C_{22}H_{30}O_4$ (? Me ether), m.p. 180° after softening at 165—170°. Attempts to hydrolyse (I) to the corresponding alcohol were unsuccessful on account of the ready displacement of the double linking towards Δ^4. It is isomerised by HCl in MeOH to testosterone acetate (II). Physiologically (I) is considerably more active than (II). H. W.

(I.)



Simple preparation of the chloroketone $C_{19}H_{27}OCl$ (dehydroandrosteryl chloride) isolated from male urine. A. Butenandt and W. Grosse (Ber., 1936, **69**, [*B*], 2776—2778).—Dehydroandrosterone is converted by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N into its p-*toluenesulphonate*, m.p. 157—158°, $[\alpha]_D^{20}$ −12·1° in dioxan, transformed by boiling MeOH into *dehydroandrosterone Me ether*, m.p. 140—142°, $[\alpha]$ ±0° in $CHCl_3$, and by KOAc in boiling MeOH into epi*dehydroandrosterone Me ether* (I), b.p. 100—110°/0·001 mm., $[\alpha]_D^{20}$ +111° in $CHCl_3$. (I) is smoothly transformed by conc. HCl in AcOH into dehydroandrosteryl chloride [3-chloro-Δ^5-ætiocholen-17-one], m.p. 155—157°, $[\alpha]_D^{21}$ +14° in $CHCl_3$, identical with the substance isolated from male urine. H. W.

Sex hormones. XVIII. Preparation of further enol-esters from ketones of the cholestane and androstene series. L. Ruzicka and W. F. Fischer. **XIX. Preparation of Δ^5-3-*epi*hydroxyandrosten-17-one (Δ^5-*epi*dehydroandrosterone).** L. Ruzicka and M. W. Goldberg (Helv. Chim. Acta, 1936, **19**, 1371—1375, 1407—1410; cf. A., 1936, 1382).—XVIII. The following enolic esters are prepared: *cholestanone benzoate*, m.p. 127—128°, Δ^4-*androstene*-3 : 17-*dione acetate* (I), m.p. 127—129°, and *testosterone di-benzoate*, m.p. 183—184° (decomp.), *-acetate* (II), m.p. 150—151°, and *-propionate*, m.p. 127—219°. [E. Tschopp.] (I) and the corresponding benzoate and (II) have powerful male, but no female, sex hormone activity.

XIX. Partial hydrogenation (Raney Ni) of Δ^5-cholestenone in *cyclo*hexane gives a mixture of cholesterol and *epi*cholesterol, m.p. 141°, $[\alpha]_D$ −37·5° in EtOH (*acetate*, m.p. 85°). Δ^5-Androstenedione gives similarly *trans*- and epi-*hydroxyandrosten*-17-*one*, m.p. 221°, sublimes at 140°/0·01 mm., α 0 in EtOH (*acetate*, m.p. 173·5—174·5°; *oxime*, m.p. 204—206°). M.p. are corr. R. S. C.

Halogenation of phenolic ethers and anilides. VIII. Alkoxy- and dialkoxy-benzophenones and dialkoxydiphenylsulphones. B. Jones (J.C.S., 1936, 1854—1862).—pp′-*Dihydroxydiphenyl sulphoxide*, m.p. 194°, with AcOH and H_2O_2 gave the *sulphone*, m.p. 239°, which with NaOEt and alkyl bromide gave the following 4 : 4′-*dialkoxydiphenylsulphones*: n- and iso-*dipropoxy*-, m.p. 142—143° and 157°, respectively, *di*-n-*butoxy*-, m.p. 92·5°, and *di*-n-*amyloxy*-, m.p. 86·5°. The following *benzophenones* were prepared: pp′-*di*-n-*propoxy*-, m.p. 127°, pp′-*di*iso-*propoxy*-, m.p. 72·5°, pp′-*di*-n-*butoxy*-, m.p. 118°, pp′-*di*-n-*amyloxy*-, m.p. 108°, p-*methoxy*-p′-*ethoxy*-, m.p. 111°, p-*methoxy*-p′-n-*butoxy*-, m.p. 105—106°, p-*methoxy*-p′-n-*amyloxy*-, m.p. 101°, p-*methoxy*-p′-β-*chloroethoxy*-, m.p. 106°, p-*ethoxy*-p′-n-*butoxy*-, m.p. 103°, p-*ethoxy*-p′-n-*amyloxy*-, m.p. 95°, 3′-*chloro*-4-*methoxy*-4′-*ethoxy*-, m.p. 108°; 3′-*chloro*-4 : 4′-*dimethoxy*-, m.p. 97·5°, 3′-*chloro*-4-*methoxy*-4′-n-*propoxy*-, m.p. 77°, p-n-*butoxy*-, m.p. 37°, p-n-*amyloxy*-, m.p. 41°, p-n-*heptoxy*-, m.p. 47°, 2′-, 3′-, and 4′-*fluoro*-4-*methoxy*-, m.p. 49°, 72°, and 95°, respectively, 2′- and 4′-*chloro*-4-*methoxy*-, m.p. 80° and 125·5°, respectively, 4′-*chloro*-4-*ethoxy*-, m.p. 121°, 2′-*chloro*-4-β-*chloroethoxy*-, m.p. 65°, 3′- and 4′-*bromo*-4-*methoxy*-, m.p. 80° and 154°, respectively, 4-*methoxy*-3′- and -4′-*methyl*-, m.p. 56° and 90—91°, respectively, 3′-*nitro*-4-*methoxy*-, m.p. 93°, and 3′-*nitro*-4-n-*butoxy*-, m.p. 73°.

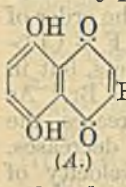
The velocities of chlorination were determined in 99% AcOH at 20°. In the series of symmetrical benzophenones (I) and diphenylsulphones (II) the same relative directive powers for the alkoxy-groups are found as for the simpler ethers $RO{\cdot}C_6H_4{\cdot}X$ (cf. A., 1936, 719) and the reactivities of analogous (I) and (II) are in the ratio 100 : 2·38. For polar groups X in ketones of the type p-$RO{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4X$ the order of reactivity for *p*-substituents is Me > H > F > Cl > Br > NO_2; *m*-F and Br have identical effects, but in the *o*-position the order of reactivity is F > Br. As the strength of the acid $C_6H_4X{\cdot}CO_2H$ increases, the reactivity of the corresponding ketone decreases. *p*-Alkoxybenzophenones, in respect of velocity of chlorination, are 2·87 times as reactive as the corresponding *p*-alkoxybenzoic acids. J. G. A. G.

Cyclitol series. IV. Inosose, a cyclose derivative of *meso*inositol. T. Posternak (Helv. Chim. Acta, 1936, **19**, 1333—1345; cf. A., 1936, 1376).—A "cyclose" (ketose with an isocyclic ring) is prepared and shown to have a free CO. It is converted in stages into phloroglucinol (I), a conversion which may have biogenetic significance. *meso*Inositol and HNO_3 (*d* 1·4) give *inosose* (II) (2 : 3 : 4 : 5 : 6-*pentahydroxy*cyclo*hexanone*), m.p. 198—200° [*phenyl*-, m.p. 220—222° (block), and 2 : 4-*dinitrophenyl-hydrazone*, m.p. 270° (block); *semicarbazone*, decomp. 207°; no osazone]. NaOBr gives, much less well, a similar *compound* (*phenylhydrazone*, m.p. 192—194°). (II) reduces cold Fehling's solution and $AgNO_3$–NH_3 at once and consumes 2 equivs. of alkaline NaOI. With Ac_2O–H_2SO_4 (little) (II) gives an Ac_5 (III), m.p. 106—108°, and with BzCl–$ZnCl_2$ at 110—130° a Bz_5 derivative (IV), m.p. 144°. The acyl derivatives are very sensitive to weak bases; *e.g.*, (III) with NaOAc or C_5H_5N gives 1 : 2 : 3 : 5-*tetra-acetoxybenzene* (V), m.p. 107—108°, which is also formed on attempted acetylation in presence of NaOAc or C_5H_5N. Hydrogenation (PtO_2) of (III) in abs. EtOH yields epi*inositol penta-acetate*, m.p. 153—154° (Ac_2O–$ZnCl_2$ gives the *hexa-acetate*, m.p. 188°), hydrolysed by $Ba(OH)_2$ in aq. MeOH to epi*inositol*, decomp. about 285° (Bz_6 derivative, m.p. 224°), also obtained similarly or by Na–Hg from (II). (IV) in hot NaOAc–AcOH or, less well, in cold C_5H_5N gives 2 : 3 : 5-*tribenzoyloxyphenol*, m.p. 167—168° (no $FeCl_3$ colour; BzCl gives 2 : 3 : 4 : 5-*tetrabenzoyloxybenzene*, m.p.

118°), the *Me ether*, m.p. 134°, of which is obtained by CH_2N_2 or from 2-hydroxy-6-methoxybenzoquinone by reduction with $Na_2S_2O_4$, followed by benzoylation. 1 : 2 : 3 : 5-$C_6H_2(OH)_4$ or $C_6(OH)_6$ with Na–Hg gives (I). R. S. C.

Oxidation of quinol by air in presence of methylammonium sulphite. Oxidation of quinolsulphonic acid in presence of methylamine. (Mlle.) Y. Garreau (Compt. rend., 1936, 203, 1073—1074; cf. A., 1935, 338).—*Bismethylaminobenzoquinonesulphonic acid* (*NH_2Me* salt + $4H_2O$, decomp. 105°; *glycine* salt + $1H_2O$, m.p. 235°) results from the action of air on a solution of quinolsulphonic acid in aq. NH_2Me in presence of $Cu(OH)_2$, or on quinol and SO_2 in aq. NH_2Me in presence of $Cu(OH)_2$. F. N. W.

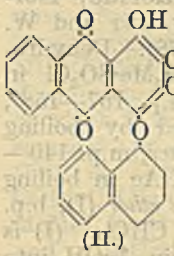
Constitution of shikonin. Syntheses of *iso*hexylnaphthazarin and related compounds. C. Kuroda and M. Wada (Proc. Imp. Acad. Tokyo, 1936, 12, 239—241).—When heated with $AlCl_3$ + NaCl, *p*-anisyl *iso*hexoate affords 2 : 5-*dihydroxyphenyl* iso*amyl ketone*, m.p. 68·5°, reduced by Zn–Hg to 2-iso*hexylquinol*, m.p. 100°, converted by heating with maleic anhydride–$AlCl_3$–NaCl into iso*hexylnaphthazarin*, m.p. 100° (*A*, R = $[CH_2]_2$·CH_2Pr^β), identical with the product obtained by catalytic reduction of shikonin Me ether. By similar methods are prepared 2 : 5-*dihydroxyphenyl* Pr^a, m.p. 91°, and Bu^β, m.p. 111°, *ketone*, reduced to 2-n-*butyl*-, m.p. 86°, and 2-iso*amyl*-, m.p. 96°, *-quinol*, from which *homologues* of *A*, R = *Et*, m.p. 126°, Bu^a, m.p. 118° and $\cdot CH_2 \cdot CH_2Pr^a$, m.p. 89°, are prepared. No details or analyses are given.


(A.)

J. W. B.

Effect of alkyl groups on the properties of anthraquinone and fluorescein dyes. R. M. Harris, G. J. Marriott, and J. C. Smith (J.C.S., 1936, 1838—1844).—Increasing the length of the alkyl group in 1-amino-2-alkylanthraquinones lowers the m.p., shifts and broadens the absorption band slightly, increases the extinction coeff., and, up to Bu rapidly and thereafter slowly, the general absorption. A similar change in Na 1-amino-4-anilino-2-alkylanthraquinone-*p*-sulphonates causes less marked changes in the absorption, but increases the rate of dyeing and, up to C_7, the covering power on wool. Alkyl groups in fluorescein dyes probably increase the absorption of red light and the covering power. Prep. of the following is described. 1-Amino-2-methylanthraquinone; PhBu^a, o-p′-n-*butyl-benzoyl*-, m.p. 99°, and (by Zn–Cu–NH_3) *-benzyl-benzoic acid*, m.p. 86°, 2-n-*butylanthraquinone*, m.p. 87·5° (1-*NO_2*-, m.p. 147·5°, and 1-*NH_2*-derivatives, m.p. 174—175°); COPh·C_6H_{13}, b.p. 140—150°/15 mm., m.p. 17°, *n*-C_7H_{15}Ph, o-p-n-*heptyl-benzoyl*-, m.p. 99—101°, and *-benzyl-benzoic acid*, m.p. 69—71°, b.p. 220°/0·2 mm., 2-n-*heptylanthraquinone*, m.p. 76° (1-*NO_2*-, m.p. 137°, and 1-*NH_2*-derivative, m.p. 138—139°); 1-*amino*-2-n-*dodecylanthraquinone*, m.p. 134—135°. 1-*Amino*-4-*anilino*-2-*methylanthraquinone*, m.p. 245·5°, is obtained from the 4-Br-compound, KOAc, $Cu(OAc)_2$, and NH_2Ph at 160°, and with oleum affords the *Na* p′-*sulphonate*; the 2-n-*heptyl*- and 2-n-*dodecyl*-dyes are also prepared. 3 : 6-Dichlorofluorescein has m.p. 285—286°. The structure of 4 : 5-dibromofluorescein, m.p. 283°, is confirmed by degradation by 50% NaOH at 120—130° to 2-bromoresorcinol and o-3-*bromo*-2 : 4-*dihydroxybenzoylbenzoic acid*, m.p. 200° after softening at 187°, which with H_3BO_3–oleum at 100° gives 2-*bromo*-1 : 3-*dihydroxyanthraquinone*, m.p. 263—264°. 4-*n*-Hexylresorcinol and *o*-$C_6H_4(CO)_2O$ at 200—205° give 2 : 7-*di*-n-*hexylfluorescein*, dimorphous, m.p. 245° (4 : 5-*Br_2*-derivative, m.p. 188°); 3′ : 6′-*dichloro*-2 : 7-*di*-n-*hexylfluorescein*, m.p. 228—229° (4 : 5-*Br_2*-derivative, m.p. 169—170°), is also prepared. R. S. C.

Intermediate products in dehydrogenations with quinones. R. Criegee (Ber., 1936, 69, [*B*], 2758—2761).—Dichloroquinizarinquinone (I) and 1 : 2 : 3 : 4-tetrahydronaphthalene at 100° yield *tetrahydronaphthyl dichloroquinizaryl ether* (II), in which the presence of OH is proved by Zerevitinov's method and by the production of the *acetate* (III), m.p. 160° (decomp.). (II) at 140—170° gives dichloroquinizarin (IV) and Δ^1-dihydronaphthalene (V). At 150°, (III) is decomposed into (V) and *dichloroquinizarin monoacetate*, m.p. 209—211°, thus showing that an initial decomp. into the parent substances does not occur. (I) and *cyclo*hexene at 125—135° afford cyclo*hexenyl dichloroquinizaryl ether* [*Ac* derivative, m.p. 130—132° (corr.; gradual decomp.)], which at 180—190° passes into (IV) and $\Delta^{1:3}$-*cyclo*hexadiene. During dehydrogenations, therefore, quinones do not invariably behave solely as acceptors, but may yield main valency, additive products with the substrate. H. W.

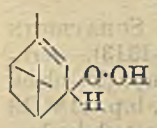

(II.)

Influence of solvent on the course of chemical reactions. IX. Kinetics of simple substitution reactions.—See A., I, 87.

Phellandrenes. IV. Comparison of the catalytic dehydrogenation of *l*-α-phellandrene and *l*-piperitone. J. Dewar and J. Read (J.C.S., 1936, 1781—1783).—Piperitone was practically unaffected by Pt–asbestos, Pt–C, or Pd–C at 300°, but it was converted almost quantitatively into thymol by Zelinski's Pt–C (CO_2; 300°). Rupe's porcelain–Ni catalyst similarly effected conversion (70%) into thymol at 250°, and at room temp. in H_2, piperitone was hydrogenated to menthones. *l*-α-Phellandrene, with an activated Ni catalyst in CO_2, gave a mixture (4 : 1) of *p*-cymene and *p*-menthane. F. R. S.

Synthesis of *trans*-s-homopinic acid. P. C. Guha and K. Ganapathi (Current Sci., 1936, 5, 244).—Reduction of either *cis*- or *trans*-Et norpinate with Na–abs. EtOH gives the *trans*-diol, the *dibromide*, b.p. 100—102°/4 mm., of which is converted by boiling NaCN–EtOH into the *dinitrile*, b.p. 142—145°/6 mm., hydrolysed by boiling 20% KOH to trans-2 : 2-*dimethyl*cyclo*butane*-1 : 3-*diacetic acid* (trans-s-*homopinic acid*), m.p. 120—121° (*dianilide*, m.p. 219—220°; *Et_2* ester, b.p. 131—132°/4 mm.), stable to distillation over $Ba(OH)_2$ and converted by Ac_2O only into the double anhydride. J. W. B.

Pinene peroxide. K. Susuki (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 70—71).—The α-pinene peroxide, d_4^{21} 0·9810, n_D^{21} 1·4885, $[\alpha]_D^{21}$ +21·22°, obtained by autoxidation of *d*-α-pinene, with H_2–PtO_2 gives some dihydroverbenol and with $KMnO_4$ pinononic acid. The annexed structure is suggested. R. S. C.



Oxidation of α-pinene with potassium permanganate in acetone solution. T. Kuwata (J. Soc. Chem. Ind. Japan, 1936, **39**, 394—395B).—*d*-α-Pinene (I) in 90% aq. $COMe_2$ containing $KMnO_4$ [2 O to 1 mol. of (I)] at 10—15° affords *d*-α-pinonic acid, m.p. 101—103°, and (d)-1-*hydroxy*-6-*keto*-1 : 3 : 3-*trimethyl*-2 : 4-*methylene*cyclo*hexane*, m.p. 35·5—36·5° [*semicarbazone*, m.p. about 230° (decomp.)]. J. L. D.

Catalytic action of Japanese acid clay on terpene compounds. V. Hydration of α-pinene with acetic acid. T. Kuwata (J. Soc. Chem. Ind. Japan, 1936, **39**, 392—394B).—α-Pinene with AcOH containing Ac_2O and clay free from acid-sol. material affords *d*-limonene (I), bornyl, *iso*bornyl, and terpinyl acetate, the last probably formed from (I). J. L. D.

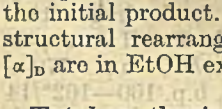
Terpene compounds. III. Synthesis of *iso*fenchocamphononic acid. J. C. Bardhan and N. C. Ganguly (J.C.S., 1936, 1852—1853).—Et αα-dimethyl-lævulate and $CN{\cdot}CH_2{\cdot}CO_2Et$ with $C_5H_{11}N$ give *Et* α-*cyano*-βδ-*dimethyl*-Δ^{α}-*pentene*-αδ-*dicarboxylate*, b.p. 165°/4 mm., which with KCN yields the *Et* ester (I), b.p. 161°/4 mm., of βδ-*dimethylpentane*-αβδ-*tricarboxylic acid*, m.p. 200—201° (*ester-imide*, m.p. 88—89°). (I) with Na in C_6H_6 affords *Et* 2 : 2 : 4-*trimethyl*cyclo*pentan*-1-*one*-4 : 5-*dicarboxylate*, b.p. 135°/4 mm., hydrolysed to 2 : 2 : 4-trimethylcyclopentan-1-one-4-carboxylic acid, m.p. 70—71° (*Et* ester, b.p. 96—97°/3 mm., and its *semicarbazone*, m.p. 180—181°), which must be identical with Aschan's *iso*fenchocamphononic acid. F. R. S.

Racemisation in the camphene rearrangement. A. I. Schavrigin (J. Gen. Chem. Russ., 1936, **6**, 1314—1324).—*tert.*-Methylfenchyl alcohol, $[\alpha]_D$ +9·04°, yields α-methylcamphene, $[\alpha]_D$ +14·87° to +31·85° in Et_2O, depending on the duration of heating with anhyd. K_2CO_3 or $NaHSO_4$, and this affords 4-methyl*iso*bornyl acetate (I), $[\alpha]_D$ +15·1°, from which 4-methyl*iso*borneol (II), $[\alpha]_D$ +9·84°, is obtained by hydrolysis. This is converted by heating with $NaHSO_4$ into β-mothylcamphene, $[\alpha]_D$ −6·45°, from which (I), $[\alpha]_D$ +4·21°, and (II), $[\alpha]_D$ +3·72°, are obtained as above. The camphene rearrangement of type I involves inversion of optical rotation in passing from camphene to *iso*borneol, or *vice versa*, whilst type II involves two successive inversions, yielding a final product with optical rotation of the same sign as the initial product. A no. of schemes explaining the structural rearrangements involved are given. All $[\alpha]_D$ are in EtOH except where stated otherwise. R. T.

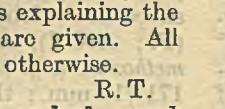
Total synthesis of camphenilone and of α- and β-fenchocamphorone. G. Komppa and O. Komppa (Ber., 1936, **69**, [*B*], 2606—2610).—$CMe_2{:}CH{\cdot}CO_2H$ is converted by protracted boiling with an excess of di*cyclo*pentadiene into 3 : 3-*dimethyltri*cyclo-[1 : 2 : 2]-Δ^5-*heptene*-2-*carboxylic acid*, b.p. 141—141·5°/12 mm., hydrogenated (Pd) to *iso*camphenilanic acid (I), m.p. 115—116°. (I) is transformed through the chloride and azide essentially into camphenilylamine; the alcohol obtained from this is a mixture oxidised by $KMnO_4$ to camphenilone, *apo*camphoric and *cis*-*apo*fenchocamphoric acid. The intermediate formation of *apo*cyclene is assumed. H. W.

Stereoisomeric camphenilols. W. Hückel and W. Tappe (Ber., 1936, **69**, [*B*], 2769—2772).—Camphene, b.p. 157·8°/742 mm., m.p. 49°, $[\alpha]_D$ −95·7°, from Siberian pine-needle oil, is oxidised to camphenilone (I), b.p. 193°/760 mm., m.p. 39°, $[\alpha]_D$ −60·8° in C_6H_6, reduced by Na and EtOH to *camphenilol* I, m.p. 76—77°, $[\alpha]_D^{20}$ −23·0° in EtOH (*H phthalate*, m.p. 146—147°, $[\alpha]_D^{19}$ −72·9° in C_6H_6; p-*nitrobenzoate*, m.p. 96—98°, $[\alpha]_D^{20}$ −42·1° in C_6H_6; p-*aminobenzoate*, m.p. 169°, $[\alpha]_D^{20}$ −60·4° in EtOH). Hydrogenation (Pt-sponge in AcOH saturated with HCl) of (I) leads (after purification) to *camphenilol* II, m.p. 98—101°, $[\alpha]_D^{23}$ +33·3° in EtOH (p-*aminobenzoate*, m.p. 161°, $[\alpha]_D^{19}$ +34·6° in EtOH). Alkaline or catalytic reduction of *r*-camphenilone*oxime* gives a mixture of *r*-camphenilylamines one of which yields *Bz* and *Ac* derivatives, m.p. 149—151° and 135—136°, respectively, whereas the other affords *Bz* and *Ac* compounds, m.p. 104° and m.p. 99—100°, respectively. H. W.

Supposed transition of camphor or campholenic acid into pinonic acid. Dehydration of dihydroxydihydro-α-campholenic acid. G. Komppa and S. Beckmann (Ber., 1936, **69**, [*B*], 2783—2789).—Repetition of Tiemann's work on the oxidation of campholenic acid shows that the amount of oily by-products (I) can be greatly suppressed by suitable choice of conditions and that dl-*dihydroxydihydro*-α-*campholenic acid* (II), m.p. 138—139°, is readily isolated. α-Campholonic acid [Tiemann's " pinonic acid " (III)] is not present in (I) and is a product of the dehydration of (II), which occurs partly when it is distilled under diminished pressure or, more completely, under atm. pressure. Under these conditions the distillate is a mixture of dl-α-*campholonic acid* (IV), b.p. 186°/9 mm. [*semicarbazone* (V), m.p. about 240° (decomp.) according to the rate of heating; *oxime*, m.p. 188°], and 2 : 6-diketocamphane (V), m.p. 189—190° [*dioxime*, m.p. 244—245°; *semicarbazone*, m.p. 290° (decomp.)]. (II) is converted into (IV) by boiling dil. H_2SO_4. (IV) is transformed into (VI) when heated at its b.p. and (VI) into (IV) by boiling dil. HCl. Treatment of (V) with NaOEt–EtOH at 160—170° leads to *dl*-α-campholanic acid (corresponding amide, m.p. 124—125°). (IV) is therefore regarded as 2 : 3 : 3-*trimethyl*cyclo*pentan*-1-*one*-4-*acetic acid* and (III) is either *A* or *B*. The



(*A*.)



(*B*.)

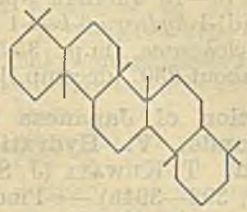
reported formation (Tiemann) of pinic acid from (III) and NaOBr is erroneous. The formation of $CHBr_3$ or CBr_4 is due to impurities and the product

is a cryst. *acid*, $C_{10}H_{14}O_6$, m.p. 212—213°, or an optically active *form*, m.p. 229—230°, which can be neither identical nor isomeric with pinic acid. H. W.

Isomeric 2 : 3-diaminocamphanes. H. Rupe and P. Bohny (Helv. Chim. Acta, 1936, **19**, 1305—1323).—With Na–EtOH camphorquinonedioxime gives a mixture of α- (I) and an isomeric (II) 2 : 3-diaminocamphane; it resists H_2–Ni, but with Al–Hg in Et_2O affords an isomeric β-*diamine* (III), which under acid conditions often gives derivatives of (I). (III), m.p. 148—149°, sublimes at 124°/12 mm., $[\alpha]_D^{20}$ +10·655° in C_6H_6, decomposes after some months in vac., gives a *mono-aurichloride*, decomp. 204—205°, *platinichloride*, decomp. 251°, *$HgCl_2$* double salt, *thiocyanate*, *di-hydrochloride*, cryst., *-perchlorate*, decomp. 267°, and *-picrate* (IV), m.p. 231° (decomp.), *oxalate*, m.p. 245°, *citrate*, decomp. 195°, *diurethane*, m.p. 139°, b.p. 158°/12 mm., *Ac_2* (V) (no methylglyoxaline obtained), m.p. 307°, $[\alpha]_D^{20}$ +17·6° in HCO_2H, *Bz_2* (VI), m.p. 276° (a *substance*, $C_8H_{14}<^{CH}_{CH}>NBz$, m.p. 148°, is also formed), *di*-p-*nitrobenzoyl* (VII), m.p. 276°, *diphenylthiocarbamide* (VIII), m.p. 187°, *phenylcarbamide*, m.p. >260°, and *dicarbamide*, m.p. >280°, *di*-p-*nitrobenzylidene*, m.p. 170°, -p-*anisylidene*, an oil, and *-benzylidene*, b.p. 212°/12 mm., derivatives. With benzil and isatin (III) gives the *substances* (IX), $C_8H_{14}<^{CH\cdot NR}_{CH\cdot NR'}$, R = COPh·CPh:, m.p. 19°, and o-$C_6H_4<^{NH}_{C}>CO$ (X), decomp. 234°, $[\alpha]_D^{20}$ +9·2° in dioxan. (III), Me_2SO_4, and aq. NaOH give 7% of NN′-*Me_2* (XI) [(*NO*)$_2$-derivative, m.p. 144—146°], and NN′-*Me_4* derivative, b.p. 126°/11 mm., d_4^{20} 0·9308, $[\alpha]_D^{20}$ +29·22° [*mono-picrate* (XII), m.p. 164° after sintering at 161°, *-methiodide* (XIII), decomp. 218°, $[\alpha]_D^{20}$ +3·3° in 50% EtOH, *-carbethoxymethoperchlorate* N′-*perchlorate*, m.p. 170°, decomp. 208°, and *-carbethoxymethobromide*, m.p. 170° after sintering at 159° (with Ag_2O gives the *carboxymethobetaine*, m.p. 177°, $[\alpha]_D^{20}$ +10·665° in H_2O); *diperchlorate*, decomp. 235°]. (I), b.p. 133—136°/12 mm., 246°/760 mm., and (II), b.p. 246°/760 mm., 125°/12 mm., are best separated by the *Ac_2* derivatives, m.p. 308—309°, $[\alpha]_D^{20}$ +17·9° in 80% HCO_2H [? = (V)], and m.p. 247·5—250°, $[\alpha]_D^{20}$ +19·5° in 80% HCO_2H, respectively, which cannot be hydrolysed, or, less well, by way of the *oxalates*, m.p. 255° and 230°, respectively (a fraction, m.p. 275°, was also obtained). The crude mixture of (I) and (II), containing mostly (I), gives (VI), (VII), a *picrate*, m.p. 227—232° [? = (IV)], *diphenylthiocarbamide* derivative, m.p. 178—179° [? = (VIII)], and a *substance* (IX) [R = (X)], decomp. 194°, $[\alpha]_D^{20}$ −14·65° in dioxan; with Me_2SO_4 it gives a little (XI) and much NN′-*Me_4* derivative, b.p. 122°/12 mm., $[\alpha]_D^{20}$ +16·75° [*picrate* = (XII); *methiodide*, m.p. 217° (decomp.), $[\alpha]_D^{20}$ +3·7°, ? = (XIII); *carbethoxymethobromide*, m.p. 170° (sinters at 155°), $[\alpha]_D^{20}$ +15·91° in H_2O, and corresponding *betaine*, m.p. 176°, hygroscopic, $[\alpha]_D^{20}$ +5·6° in H_2O], and a small amount of a *substance*, b.p. 165°/12 mm. (with MeI gives a *substance*, m.p. 96°, not a methiodide), which may be derived from (II). In both methylations some ? *Me methosulphate*, an oil, is obtained, which gives the *methoperchlorate perchlorate*, decomp. 225°, also obtained from (XIII). R. S. C.

***tert.*-Propylfenchyl alcohol.** A. I. Schavrigin (J. Gen. Chem. Russ., 1936, **6**, 1310—1313).—*tert.*-Allylfenchyl alcohol and H_2 at room temp. (Pt-black catalyst) yield tert.-*propylfenchyl alcohol*, b.p. 118°/13 mm., from which a mixture of unsaturated hydrocarbons is obtained by heating with anhyd. $KHSO_4$ at 120°. R. T.

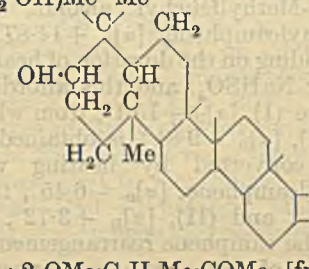
Structure of triterpenes. F. S. Spring (Chem. and Ind., 1936, 1050—1051).—The annexed skeleton is adopted for triterpenes.



R. S. C.

Novel interrelationship in the triterpene group. J. H. Beynon, I. M. Heilbron, and F. S. Spring (Nature, 1936, **138**, 1017).—The alcohol previously described (A., 1934, 1330), now named basseol, is readily cyclised by various reagents to β-amyrin, furnishing the first example of the conversion of a naturally-occurring tetracyclic into a naturally-occurring pentacyclic triterpene. L. S. T.

Polyterpenes and polyterpenoids. CVIII. Syntheses of the trimethylnaphthol obtained by dehydrogenation of pentacyclic terpenes. L. Ruzicka, K. Hofmann, and H. Schellenberg. **CIX. Glycyrrhetic acid.** L. Ruzicka and H. Leuenberger (Helv. Chim. Acta, 1936, **19**, 1391—1402, 1402—1405; cf. A., 1936, 1514).—CVIII. The Me_3 derivatives obtained by degradation of polyterpenes are 1 : 2 : 5-$C_{10}H_5Me_3$ and 2-*methoxy*-1 : 5 : 6-*trimethylnaphthalene* (I). Mixtures of styphnates, but not of picrates or $C_6H_3(NO_2)_3$ compounds, of isomeric $C_{10}H_5Me_3$ give definite depressions of the m.p. The



structure of triterpenes and the general principles to be used for determination thereof are discussed. The annexed structure is suggested, only that part given in full having been confirmed by degradative experiments. 3 : 1 : 2-OMe·C_6H_4Me·COMe [from the acid chloride (III) and ZnMeI], b.p. 131—132°/15 mm., with Mg (not Zn) and CHMeBr·CO_2Et give *Et* β-*hydroxy*-β-6-*methoxy*-o-*tolyl*-α-*methyl*-n-*butyrate*, converted by successive dehydrogenation by I, hydrogenation (Pt; AcOH), and reduction by Na–EtOH into γ-6-*methoxy*-o-*tolyl*-β-*methyl*-n-*butyl alcohol*, b.p. 170—171°/15 mm.; the derived *bromide*, b.p. 160—162°/14 mm., gives, by way of the nitrile, γ-6-*methoxy*-o-*tolyl*-β-*methylvaleric acid*, m.p. 120—121°, the *chloride* (prep. by $SOCl_2$–C_6H_6) of which with $AlCl_3$ in CS_2 gives 1-*keto*-6-*methoxy*-3 : 4 : 5-*trimethyl*-1 : 2 : 3 : 4-

tetrahydronaphthalene. Clemmensen reduction at 50° followed by dehydrogenation (Pd–C) at 300° gives 2-*methoxy*-1 : 7 : 8-*trimethylnaphthalene*, m.p. 74—75° [1 : 3 : 5-$C_6H_3(NO_2)_3$ *compound*, m.p. 128—129°]. (II) with CH_2N_2–Et_2O, followed by HCl gas, gives 6-*methoxytolyl* CH_2Cl *ketone*, m.p. 44—45°, which with $CHMe(CO_2Et)_2$ leads to γ-*keto*-γ-6-*methoxy*-o-*tolyl*-α-*methyl*-n-*butyric acid*, m.p. 140—141°, reduced (Clemmensen) to γ-6-*methoxy*-o-*tolyl*-α-*methyl*-n-*butyric acid*, b.p. 139—142°/0·1 mm., the chloride of which gives 1-*keto*-6-*methoxy*-2 : 5-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 112—113°. This with MgMeI gives 1-*hydroxy*-6-*methoxy*-1 : 2 : 5-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 83—84°, converted by Pd–C at 310° into (I), m.p. 89—90° [1 : 3 : 5-$C_6H_3(NO_2)_3$ *compound*, m.p. 146—147°]. The naphthol obtained by dehydrogenation of amyrin with Zn dust or by hydrogenation and subsequent dehydrogenation by Pd gives 1 : 2 : 5-$C_{10}H_5Me_2$ [*styphnate*, m.p. 128—129°; $C_6H_2Me(NO_2)_3$ *compound*, m.p. 90—90·5°].

CIX. Glycyrrhetic acid [purified by way of the *acetate*, m.p. 309—313°, $[\alpha]_D$ +145° in $CHCl_3$ (1 active H; *Me* ester, m.p. 299—300°)], $C_{30}H_{46}O_4$, dimorphic, m.p. 300—304° and 287—293°, $[\alpha]_D$ +161° (163°) in $CHCl_3$, gives a *Me* ester, m.p. 259° (1 active H). None of these compounds gives a colour with $C(NO_2)_4$.

R. S. C.

Constitution of resin phenols and their biogenetic relationships. V. Natural phenolic substances of the "dimeric coniferyl type." H. Erdtman (Svensk Kem. Tidskr., 1936, **48**, 250—257).—A general survey of the more or less completely established structures of compounds of this type indicates that many variants of the diphenylbutane or 1-$C_{10}H_7$Ph scheme occur naturally. The compounds appear to arise by dimerisation of simple components of the safrol, eugenol, and coniferyl alcohol types but the exact course of biogenesis is at present unknown.

H. W.

Lignin and related compounds. XXVIII. Behaviour of lignin towards activated hydrogen. R. G. D. Moore and H. Hibbert (Canad. J. Res., 1936, **14**, B, 404—407).—The absence of ethylenic linkings in lignin is suggested by observations that fully methylated lignin (from spruce wood-meal; 34—35% OMe) is not reduced catalytically using either Adams or Raney-Ni catalysts in EtOH or AcOH at 55—60°/45 lb. per sq. in. J. W. B.

[Dioxan lignin and the pigment of ebony wood.] E. Wedekind (Ber., 1936, **69**, [*B*], 2521—2522; cf. A., 1936, 207).—A reply to Hilpert *et al.* (A., 1936, 858). H. W.

3- and 6-Membered cyclic oxido-compounds. II. W. Madelung and M. E. Oberwegner (Annalen, 1936, **526**, 195—251; cf. A., 1932, 62).—The crude product (I) obtained from desyl chloride and NaOMe contains small amounts of *trans*-$(CH{\cdot}C_6H_4Bz)_2$ and (*cis*-)α-2 : 5-dimethoxy-2 : 3 : 5 : 6-tetraphenyldioxan (II), m.p. 223°, whereas that (III) derived from desyl bromide contains (II), CHPhBz·OH, and CHPhBz·OMe. Distillation of (I) under diminished pressure affords α-methoxy-αβ-diphenyloxan, b.p. 194—196°/16 mm. With minor amounts of the isomeric dibenzoylstilbenes (IV) whereas (III) yields OMe·CHPhBz, a little CHPhBz·OH, and tetraphenyldioxin, but no (IV). (I) and (III) behave similarly when treated with HCl in light petroleum except that (I) gives small amounts of (IV). The same products are formed from (I) or (III) and HCl–MeOH as from CHPhBz·OH. (II) passes at 250° into CHPhBz·OMe. An improved prep. of *trans*-2 : 5-dimethoxy-2 : 3 : 5 : 6-tetraphenyldioxan (V), m.p. 285° (cf. Irvine *et al.*, J.C.S., 1907, **91**, 1391; Bergmann *et al.*, A., 1930, 1438), and *trans*-methoxytetraphenyldioxen (VI), m.p. 185°, from CHPhBz·OH and HCl–MeOH is described. (II) in C_6H_6 is transformed by HCl into CHPhBz·OH and a little CHPhBz·OMe whereas (V) yields (VI) and (VI) is largely unchanged, but gives a little *cis*-stilbenediol dibenzoate and tetraphenyldioxadiene (VII); the latter is readily obtained by treating the crude product of the action of HCl–MeOH on CHPhBz·OH with boiling Ac_2O containing $ZnCl_2$ or $FeCl_3$. Treatment of (VII) with dry HCl in C_6H_6 yields cis-*chlorctetraphenyldioxen*, $C_{28}H_{21}O_2Cl$, converted by MeOH into cis-*methoxytetraphenyldioxen*, m.p. 155°; under similar conditions (VI) gives a mixture of ethers. With EtOH the *cis*-Et ether, m.p. 163°, is produced, isomerised by HCl–EtOH or boiling AcOH to the *trans*-compound, m.p. 192°. cis- (VIII), m.p. 156°, and trans- (IX) -*Acetoxytetraphenyldioxen*, m.p. 228°, are described. (VII) with Br in CS_2 affords 2 : 3-*dibromotetraphenyldioxen*, m.p. 226° (decomp.) after softening at 220°, converted by boiling MeOH into trans-, m.p. 292°, and cis-, m.p. 198°, -2 : 3-*dimethoxytetraphenyldioxen*; the corresponding *Et*$_2$ *ethers* have m.p. 248° and about 295°, respectively. 2 : 3-*Deacetoxytetraphenyldioxen*, m.p. 297°, is described. (VII) is transformed by conc. H_2SO_4 into the very hygroscopic green oxonium *salt*, formulated $\left[\begin{matrix}CPh{\cdot}O{:}CPh\\CPh{\cdot}O{:}CPh\end{matrix}\right]^{++}SO_4$ since SO_2 is also produced and gives (VII) and (?) H_2O_2 or (?) $H_2S_2O_8$ when treated with H_2O and the corresponding Me ether or acetate when treated with MeOH or NaOAc. When kept with H_2SO_4 the green salt passes into a red *compound* (corresponding *perchlorate*) in which only 1 O appears to participate in salt formation whereas the composition of the (not isolated) violet *oxonium* salts is indicated by the formation when (VII) is added to a solution of the green salt. The substance described as 2-acetoxy-2 : 3 : 5 : 6-tetraphenyl-Δ^5-dioxen, m.p. 174° (*loc. cit.*), is proved to be 2 : 3-*oxidotetraphenyldioxan*. (VIII) or (IV) is converted by boiling AcOH–H_2O into a mixture of cis- (X), m.p. 154°, and trans- (XI), m.p. 198° (decomp.), -2 : 3-*oxidotetraphenyldioxan*. (X) is partly converted into (XI) by boiling AcOH, yields *cis*-$(CH{\cdot}C_6H_4Bz)_2$, m.p. 211°, when treated with AcOH containing HCl or H_2SO_4, and gives $OH{\cdot}CPh_2{\cdot}CO_2K$ and CH_2PhBz when boiled with KOH–EtOH. The behaviour of (XI) is in the main similar. Hydrogenation (Pd in EtOAc) of (VII) gives cis-*tetraphenyldioxen* (X), m.p. 165°, which slowly reacts with Br in CS_2 giving benzil and α-stilbene dibromide, m.p. 239°, whereas reduction of (VII) with Na and amyl alcohol in C_6H_6 at 50—60° leads to trans-*tetraphenyldioxen* (XI), m.p. 245—247°, with small amounts of α-*tetraphenyldioxan*, m.p. 152°, and β-*tetraphenyl*-

dioxan (XII), m.p. 305°; the *tetraphenylethyl ether* $C_{28}H_{26}O$, m.p. 131°, is formed as by-product. Complete reduction of (XI) by Na and amyl alcohol gives only the dioxans, whereas that of (X) occurs very slowly, giving mainly unchanged material with a little of the same products. Catalytic hydrogenation of (XI) gives (XII), γ-, m.p. 285°, and δ-, m.p. 143°, *-tetraphenyldioxan*. CHPhBz·OH in $CHCl_3$ is converted by the successive action of 70% $HClO_4$ and H_2SO_4 into the *desyl ether* (XIII), $C_{28}H_{22}O_3$, m.p. 129° (*dioxime*, m.p. 198°), also obtained similarly from (VII); it is converted by cold KOH–EtOH into BzOH, benzil, and CH_2PhBz and by the hot reagent into CH_2PhBz, BzOH, and $OH·CPh_2·CO_2H$. Similar treatment of (VI) affords (XIII) and the *iso*desyl *ether*, m.p. 88° [*monoxime*, m.p. 152° (decomp.)], which resembles (XIII) in its behaviour towards acid and alkali. The conversion of CHPhBz·OH into *iso*benzoin and polymeric benzoin is described. H. W.

Velocity of reaction of furfuraldehyde with acetone, and its application to the determination of furfuraldehyde. E. K. Nikitin (J. Gen. Chem. Russ., 1936, **6**, 1278—1285).—5 ml. of 0·1% aq. $COMe_2$ and 5 ml. of H_2O are shaken with 5 ml. of solution containing approx. 0·02% of furfuraldehyde (I), 5 ml. of 60% aq. KOH are added, and the mixture is kept at 20° for 12 min. The turbidity developed is compared with that given by a similar mixture containing 5 ml. of 0·005% (I) in place of 5 ml. of H_2O. The concn. of (I) is given by $0·005/[\sqrt{(h_1/h_2)}-1]$, where h_1 and h_2 are the readings of the first and second solutions, respectively. R. T.

Syntheses in the pyran group. *cis*-Tetrahydropyran-2 : 6-dicarboxylic acid. W. Czornodola (Rocz. Chem., 1936, **16**, 459—465).—Pyran-2 : 6-dicarboxylic acid (I) or its Me_2 ester are readily hydrogenated (Pt catalyst) to *cis*-tetrahydropyran-2 : 6-dicarboxylic acid (II) (*anhydride*, m.p. 71°; *chloride*, an oil), or its *Me*$_2$ ester, m.p. 53—54°. Attempts to convert (II) into the *trans*-modification were unsuccessful. (I) in aq. Na_2CO_3 and Na–Hg, in a CO_2 atm., yield its *H*$_2$-derivative, m.p. 210°, which is further hydrogenated to (II) in presence of Pt. R. T.

Hydroxy-carbonyl compounds. XII. 5 : 7-Dihydroxycoumarin. R. G. Heyes and A. Robertson (J.C.S., 1936, 1831—1832).—2-Hydroxy-4 : 6-dimethoxybenzaldehyde, NaOH, and $CN·CH_2·CO_2H$, followed by HCl, give 5 : 7-*dimethoxycoumarin*-3-*carboxylic acid*, m.p. 249° (decomp.), which is decarboxylated to 5 : 7-dimethoxycoumarin (citropten) (cf. Malkin *et al.*, A., 1931, 353). Phloroglucinaldehyde or 2 : 4 : 6-triacetoxybenzylidene diacetate with NaOAc and Ac_2O similarly yields 5 : 7-diacetoxycoumarin. F. R. S.

Synthesis of rotenone and its derivatives. X. 6 : 7-Dimethoxychroman-4-one. H. F. Birch, A. Robertson, and T. S. Subramaniam (J.C.S., 1936, 1832—1834).—β-3 : 4-*Dimethoxyphenoxypropionic acid*, m.p. 136—137°, prepared from $CH_2Cl·CH_2·CO_2Na$ and 1 : 3 : 4-$OH·C_6H_3(OMe)_2$, with P_2O_5 gives 6 : 7-*dimethoxychroman*-4-*one*, m.p. 123—124°, identical with the product obtained by oxidation of netoric acid (Takei *et al.*, A., 1932, 400). The chromanone with veratraldehyde forms 6 : 7-*dimethoxy*-3-*veratrylidenechroman*-4-*one*, m.p. 156·5—157·5° (*-furfurylidene*-compound, m.p. 138—139°), and with 1 : 2 : 4-$CHO·C_6H_3(OH)·OMe$ yields 7 : 6 : 7′-*trimethoxychromeno*-4′ : 3′ : 2 : 3-*benzopyrylium ferrichloride*, m.p. 256—257° (decomp.). β-3 : 5-*Dimethoxyphenoxypropionic acid*, m.p. 128—129°, prepared from 1 : 3 : 5-$OH·C_6H_3(OMe_2)$ and $CH_2Cl·CH_2·CO_2Na$, is cyclised to 5 : 7-*dimethoxychroman*-4-*one*, m.p. 99°. F. R. S.

Usnic acid. IV. Synthesis of 4 : 6-dimethoxy-3 : 5-dimethylcoumarone-2-acetic acid. H. F. Birch, D. G. Flynn, and A. Robertson (J.C.S., 1936, 1834—1837).—α-3-*Methoxyphenoxypropionic acid*, m.p. 93—94° (*amide*, m.p. 102°), prepared from *m*-$OH·C_6H_4·OMe$ and $CHMeBr·CO_2Et$, is converted into the chloride, which with $AlCl_3$ yields 6-*methoxy*-2-*methyl*-3-*coumaranone*, b.p. 120—125°/1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 206°), and this with Zn and $CH_2Br·CO_2Et$ affords 6-*methoxy*-2-*methylcoumarone*-3-*acetic acid*, m.p. 115—116°. 1 : 3 : 5-$OH·C_6H_3(OMe)_2$ and $CH_2Br·CO_2Et$ yield the *Et* ester, b.p. 188—190°/16 mm., of α-3 : 5-*dimethoxyphenoxypropionic acid*, m.p. 115—116°, which is converted through the chloride with $AlCl_3$ into 4 : 6-*dimethoxy*-2-*methyl*-3-*coumaranone*, m.p. 74—75° (2 : 4-*dinitrophenylhydrazone*, m.p. 240°), mixed with some 4 : 6-*dimethoxy*-3-*phenyl*-2-*methylcoumarone*, m.p. 125°. The coumaranone with $CH_2Br·CO_2Et$ and Zn forms the *Et* ester, m.p. 55—57°, of 4 : 6-*dimethoxy*-2-*methylcoumarone*-3-*acetic acid*, m.p. 147—148°. Reduction (Pd–H_2) of 4-*benzyloxy*-2 : 6-*dimethoxybenzaldehyde*, m.p. 122—123°, affords C-*methylphloroglucinol* β-*Me*$_2$ *ether*, m.p. 148—149°, which with $CH_2Br·CO_2Et$ gives α-3 : 5-*dimethoxy*-4-*methylphenoxypropionic acid*, m.p. 123—123·5°. The corresponding chloride with $AlCl_3$ yields 4 : 6-*dimethoxy*-2 : 5-*dimethylcoumaranone*, m.p. 66—67°, which with Zn and $CH_2Br·CO_2Et$ gives 4 : 6-*dimethoxy*-2 : 5-*dimethylcoumarone*-3-*acetic acid*, m.p. 179—180°. This acid is isomeric and not identical with *O*-dimethylpyrousnic acid (cf. Asahina *et al.*, A., 1936, 1104). F. R. S.

Constitution of ayapanin. P. K. Bose and A. C. Roy (J. Indian Chem. Soc., 1936, **13**, 586—587).—Ayapanin, m.p. 114—115° (cf. Nag and Bose, A., 1934, 1421), isolated from the leaves of *Eupatorium ayapana*, is shown to be 7-methoxycoumarin. Two other *compounds*, m.p. 220—221° (termed *ayapin*) and m.p. 109°, have also been isolated. H. G. M.

Alpinone, a benzopyrone derivative. Y. Kimura and M. Hoshi (Proc. Imp. Acad. Tokyo, 1936, **12**, 285—288).—*Alpinone* (3 : 5-*dihydroxy*-7-*methoxy*-2-*phenyl*-2-*methyl*-2 : 3-*dihydrobenzo*-1 : 4-*pyrone*) (I), m.p. 178° [*Ac*$_2$, m.p. 108°, and *Bz*$_2$ derivatives, m.p. 208—209°; *Me*$_2$ ether (II), m.p. 115°; *oxime*, m.p. 203—204°; *semicarbazone anhydride*, m.p. 200—201°], with boiling MeI affords *noralpinone*, $C_{16}H_{14}O_5$, m.p. 136—137° (*Bz*$_3$ derivative, m.p. 203°). (I) with boiling 30—50% KOH (H_2 atm.) affords mainly izalpinin (III), whereas with hot 10—20% KOH (H_2 atm.), apo*alpinone* (3 : 5-*dihydroxy*-7-*methoxy*-2-*phenyl*-2 : 3-*dihydrobenzo*-1 : 4-*pyrone*) (IV), m.p. 148° [*Me*$_2$ ether (V), m.p. 108—109°], mainly is formed with loss of 1 CH_3; some (IV) is converted into (III). (II) with boiling 5%

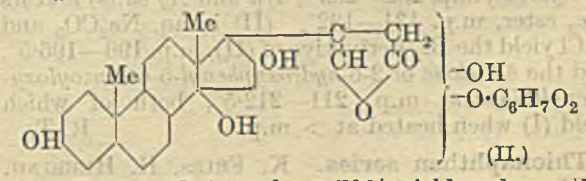
KOH affords 2-*hydroxy*-4 : 6-*dimethoxyphenyl* α-*methoxystyryl ketone*, m.p. 112° (also synthesised from 2-hydroxy-4 : 6-dimethoxy-ω-methoxyacetophenone and PhCHO), converted by boiling EtOH–HCl into the Me_1 ether of (IV) and thence into (V). (I) with 3% H_2O_2 in cold 3% KOH affords some COPhMe, which indicates that 1 Me is in position 2. The skeletons of (I), (IV), and fustin (cf. A., 1935, 757) are similar since their ultra-violet absorption spectra are almost identical. J. L. D.

Colouring matter of red cabbage. II. I. Chmielewska (Rocz. Chem., 1936, 16, 384—387).—*Rubrobrassicin chloride* (I), isolated from red cabbage, is a compound of an unidentified biose with methyl-7- or -5-sinapylcyanidin. (I) when warmed with MeOH–Et_2O yields rubrobrassin chloride, $C_{28}H_{33}O_{16}Cl$ (A., 1934, 336), and *Me sinapate*, m.p. 91—92°. R. T.

Colouring matter of *Hibiscus Sabdariffa*, L. (hiviscin). II. R. Yamamoto and Y. Osima (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 258—262; cf. A., 1932, 1296).—Pure hiviscin chloride, $C_{26}H_{29}O_{16}Cl,3H_2O$, m.p. 178°, with 17% HCl gives glucose, a (?aldo)pentose, and delphinidin chloride, identified by its colour reactions, absorption spectrum, and by conversion into αγ-2 : 4 : 6 : 3′ : 4′ : 5′-hexamethoxydiphenylpropane. R. S. C.

Synthesis of chrysin and other hydroxyflavones. R. Seka and G. Prosche (Monatsh., 1936, 69, 284—291).—Gradual addition of CPh:C·COCl in $PhNO_2$ to a well-cooled solution of 1 : 3 : 5-$C_6H_3(OH)_3$ and $AlCl_3$ in $PhNO_2$, followed by removal of the solvent with steam and sublimation of the dried, residual resin in a vac. gives 5 : 7-dihydroxyflavone (chrysin), m.p. 274—275°. Similarly 1 : 3-$C_6H_4(OH)_2$ and 1 : 2 : 3-$C_6H_3(OH)_3$ afford 7-hydroxyflavone, m.p. 240·8°, and 7 : 8-dihydroxyflavone, m.p. 240—241°, respectively. Attempts to condense CPh:C·COCl with 1 : 2- or 1 : 3-$C_6H_4(OH)_2$ were fruitless. 1 : 3 : 5-$C_6H_3(OH)_3$ and 3 : 4-$(OMe)_2C_6H_3$·C:C·COCl or 3 : 4-CH_2O_2:C_6H_3·C:C·COCl appear to give hydroxyflavones. The application of sublimation in a high vac. to the purification of natural and synthetic 3′ : 5 : 7-trihydroxy-4′-methoxyflavanone (hesperitin) and synthetic 4′ : 5 : 7-trihydroxy-3′-methoxyflavanone (homoeriodictyol) is described. H. W.

Calotropin, the African arrow poison. I. G. Hesse and F. Reichenedeer (Annalen, 1936, 526, 252—276).—Extraction of the dried leaves and stalks of *Calotropis procera* with 50% EtOH at 40—50° and treatment of the extract with $Pb(OAc)_2$ followed by concn. and extraction with $CHCl_3$ leaves a solution from which *calotropagenin* (I), m.p. 240°, is removed by charcoal. The $CHCl_3$ solution is washed with *N*-Na_2CO_3 and treated with light petroleum, thus giving the *compound*, $C_{29}H_{40}O_9,CHCl_3$, decomp. 221°, from which by treatment with boiling C_6H_6 followed by crystallisation from EtOH or EtOAc and desiccation at 120°/high vac. calotropin (II), $C_{29}H_{40}O_9$ (? $C_{29}H_{42}O_9$), m.p. 221° (decomp.) when rapidly heated, $[\alpha]_D$ +55·7° in MeOH (*monohydrate*), is obtained. (II) is very hygroscopic, stable to air, and gives a positive Legal test. The amorphous Me ether has m.p. about 165°. Fission of (II) with *N*-NaOH under N_2 gives *ψ-calotropaic acid* (III), $C_{23}H_{34}O_7$, decomp. 228° after marked softening at 190—195° (*Et* ester, m.p. 224°), *ψ-calotropagenin* (IV), $C_{23}H_{32}O_6$, m.p. 241° (decomp.), and a very strongly reducing substance (V). Similar treatment with $Ba(OH)_2$–MeOH gives an insol. *Ba* salt which, when dry, ignites spontaneously on exposure to air; (V) is not present in the mother-liquors. (II) in MeOH containing $Ba(OH)_2$ readily absorbs atm. O_2, whereby > one change appears to occur. The solution contains a *substance*, $C_{29}H_{42}O_{10}$, m.p. 154° which loses CO_2 at 100° giving the *compound*, $C_{28}H_{42}O_8$, m.p. 224°, whilst (V) is also present. When (II) is heated at 230°/high vac. it gives (V) as a cryst. sublimate whilst (I) is obtained by chromatographic analysis of the residue. Both fissions proceed similarly with regard to (V) but differently with respect to the other products owing to the action of alkali on (I) whereby (III) and (IV) are produced. To eliminate this effect (II) is heated with conc. $Na_2B_4O_7$ in absence of air, whereby (V) and the lactone iso*calotropagenin*, m.p. 251° (converted by cautious treatment with alkali into iso*calotropaic acid*, $C_{23}H_{34}O_7$, decomp. 156°), are produced, also formed from (I). (V), m.p. 84° [*dinitrophenylosazone* (VI), decomp. 230°], is *methylreductic acid*, $\begin{matrix}OH\cdot C\text{—}CO\\OH\cdot C\cdot CH_2\end{matrix}>CHMe$ (VI) or $\begin{matrix}OH\cdot C\text{—}CO\\OH\cdot C\cdot CHMe\end{matrix}>CH_2$. It reduces Tollens' reagent, neutral $AgNO_3$, acid I, cold Fehling's solution, and methylene-blue. $KMnO_4$, CrO_3, or H_2O_2–EtO_2 do not transform it into cryst. products. HNO_3 gives $H_2C_2O_4$ in good yield. Under defined conditions Ag_2O transforms (V) into methylsuccinic acid, the change following the course (VII) → $\begin{matrix}CO\text{—}CO\\CO\cdot CH_2\end{matrix}>CHMe$ [from which (VI) is derived] → $CHO\cdot CH_2\cdot CHMe\cdot CO\cdot CO_2H$ or $CO_2H\cdot CH_2\cdot CHMe\cdot CO\cdot CHO$ (which gives a *phenylhydrazidediphenylhydrazone*, $C_{24}H_{26}ON_6$, decomp. 148°) → $CO_2H\cdot CH_2\cdot CHMe\cdot CO\cdot CO_2H$ (the *dinitrophenylhydrazone*, decomp. 188°, differs from that of α-keto-α′-methylglutaric acid) → $CO_2H\cdot CH_2\cdot CHMe\cdot CO_2H$. Attempts to prepare (V) from rhamnose were unsuccessful; at 200°/0·5 mm. a reducing distillate is obtained which gives minimal amounts of a red compound with $(NO_2)_2C_6H_3\cdot NH\cdot NH_2$ but acidic hydrolysis does not afford reducing substances, which are produced in minor amount by alkaline treatment but not by $Na_2B_4O_7$. (I) is a new aglucon of the cardiac poisons class and is very closely related to strophanthidin. Of the 6 O 2 are present in the enol-lactone ring and 2 are in OH groups in the neighbourhood of the side-chain which give rise to two series of transformation products. The function of the remaining 2 O is not established but by analogy the presence of OH at $C_{(3)}$ may be assumed. Thermal decomp. of (II)



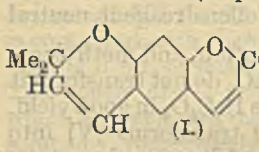
(II.)

gives (I) and (V) in at least 70% yield and no other volatile material is formed. In harmony the formula

of (II) is obtained by summation of (I) and (V). Towards boiling 1% H_2SO_4 (II) is stable and under more drastic conditions it gives *anhydrocalotropin*, m.p. 207°, which gives (V) when heated in vac. It therefore appears certain that (V) exists pre-formed in (II) and the annexed structure for (II) is suggested. H. W.

Compound of dioxan with perchloric acid. C. SMEETS (Natuurwetensch. Tijds., 1937, **19**, 12—15).—Dioxan forms a *perchlorate*, $C_4H_8O_2,HClO_4,H_2O$, m.p. 80—82°, and double *compounds*, $M(ClO_4)_2,12C_4H_8O_2,6H_2O$, in which M = Ni, Cu, Co, and Mn. Dioxan can be determined by oxidation with excess of $K_2Cr_2O_7$ in H_2SO_4. S. C.

Constituents of the bark of *Zanthoxylum americanum* (Mill). II. Xanthyletin. (MISS) J. C. BELL and A. ROBERTSON (J.C.S., 1936, 1828—1831).—From the mother-liquors left after removing xanthoxyletin, *xanthyletin* (I), $C_{14}H_{12}O_3$, m.p. 128—128·5°, has been isolated; (I) is reduced (Pd–H_2) to the H_2-derivative, m.p. 124—125°, which with Me_2SO_4–NaOH yields o-*methyldihydroxanthoxyletinic acid*, m.p. 141—142°, reduced to the *-tetrahydro*-acid, m.p. 99—100°, also obtained from o-*methylxanthyletinic acid*, m.p. 193—194° (decomp.), prepared from (I) and Me_2SO_4. NaOH converts (I) into $COMe_2$ and resorcinol (*di*-p-*nitrobenzoate*, m.p. 184—185°).



(I.)

Ozonolysis of (I) affords 7-*hydroxy*-6-*formylcoumarin*, m.p. 253° (decomp.) [*phenylhydrazone*, m.p. 255—257° (decomp.)], which is reduced (Pd–H_2) to 7-*hydroxy*-6-*methylcoumarin*, m.p. 248° (*acetate*, m.p. 145—146°), also obtained from 1 : 5 : 2 : 4-$CHO{\cdot}C_6H_2Me(OH)_2$, NaOAc, and Ac_2O. F. R. S.

Preparation of β-thiophenic [thiophen-3-carboxylic] acid. I. J. RINKES (Rec. trav. chim., 1936, **55**, 991—992).—Tetraiodothiophen, m.p. 199—200°, with Al–Hg gives 64% of 3-iodothiophen, b.p. 77—80°/11 mm., which with KCN and CuCN in aq. EtOH at 180° affords 62% of thiophen-3-carboxylic acid, m.p. 137—138°. R. S. C.

New thiophen derivative. J. SAWLEWICZ (Rocz. Chem., 1936, **16**, 470—478).—The product obtained by fusing coumarin with S (A., 1936, 997) is shown to be the δδ-*dilactone* (I), m.p. 331—331·5°, of 2 : 5-*di*-o-*hydroxyphenylthiophen*-3 : 4-*dicarboxylic acid* (II) (*dichloride*, decomp. 155°; *Me*$_2$ ester, m.p. 155·5—156°; *dianilide*, m.p. 264—264·5°). (I) is hydrolysed to (II) by aq. NaOH, and (II) readily regenerates (I) when heated at below the m.p. A solution of (II) in aq. NaOH and Me_2SO_4 afford a mixture of 2 : 5-*di*-o-*anisylthiophen*-3 : 4-*dicarboxylic acid* (*anhydride*, m.p. 232—233°; *Na* and *Ag* salts) and its *Me*$_2$ ester, m.p. 131—132°. (II) in aq. Na_2CO_3 and BzCl yield the *Bz*$_2$ derivative of (II), m.p. 196—196·5°, and the δ-*lactone* of 2-o-*hydroxyphenyl*-5-o-*benzoyloxyphenylthiophen*, m.p. 211—212·5°, both of which yield (I) when heated at > m.p. R. T.

Thionaphthen series. K. FRIES, H. HEERING, E. HEMMECKE, and G. SIEBERT (Annalen, 1936, **527**, 83—114).—The character of thionaphthen is definitely not benzenoid. In most of its reactions it appears naphthoid and when this is not so the changes appear to require further explanation.

Gradual addition of 33% KOH to $COPh{\cdot}CH_2Br$ and m-$OH{\cdot}C_6H_4{\cdot}SH$ in EtOH affords *phenacyl* m-*hydroxyphenyl sulphide*, m.p. 78·5° (*oxime*, m.p. 92°; *Me ether*, m.p. 47°), converted by conc. H_2SO_4 into 5-*hydroxy*-2-*phenylthionaphthen* (I), m.p. 81° [*Me ether* (II), m.p. 59°]. (I) is readily converted by Br (1 mol.) in $CHCl_3$ into 6-*bromo*-5-*hydroxy*-2-*phenylthionaphthen*, m.p. 102° [the *Me ether*, m.p. 113°, is obtained by use of Me_2SO_4 but not by direct bromination of (II)]. Further bromination readily leads to 1 : 6-*dibromo*-5-*hydroxy*-2-*phenylthionaphthen*, m.p. 128° [*Me ether*, m.p. 177°, obtained by bromination of (II), which then slowly gives 1 : 4 : 6-*tribromo*-5-*methoxy*-2-*phenylthionaphthen*, m.p. 164°]. Chlorination of (I) in $CHCl_3$ gives 1 : 6-*dichloro*-5-*hydroxy*-2-*phenylthionaphthen*, m.p. 99° (which is not a keto-chloride since it is sol. in alkali, unchanged by $SnCl_2$, and does not liberate I from KI), and then 1 : 4 : 6-*trichloro*-5-*hydroxy*-2-*phenylthionaphthen* (III), m.p. 113°. Treatment of (I) with a large excess of Cl_2 in $CHCl_3$ gives 1 : 3 : 4 : 4 : 6 : 6-*hexachloro*-5-*keto*-2-*phenyl*-3 : 4 : 5 : 6-*tetrahydrothionaphthen*, m.p. 167° (decomp.), which liberates I from KI and reacts with $SnCl_2$; it is reduced (Pd-sponge in anhyd. $CHCl_3$) to (III) or by $SnCl_2$ in excess of AcOH to 1 : 4-*dichloro*-5 : 6-*dihydroxy*-2-*phenylthionaphthen*, m.p. 160° (*diacetate*, m.p. 152°), oxidised by HNO_3 (*d* 1·4) in warm AcOH to 1 : 4-*dichloro*-2-*phenylthionaphthen*-5 : 6-*quinone*, m.p. 186°.

4 : 4′-Dinitro-2 : 2′-dialdehydodiphenyl disulphide is transformed by treatment with Na_2S–Na_2CO_3 in boiling EtOH–H_2O followed by $CH_2Cl{\cdot}CO_2Na$ into 4-*nitro*-2-*aldehydophenylthiolacetic acid*, m.p. 178°, transformed by boiling 2*N*-NaOH into 4-*nitrothionaphthen*-1-*carboxylic acid* (IV), m.p. 237° (*Et* ester, m.p. 166°, also obtained from 4 : 2-$(NO_2)(CHO)C_6H_3{\cdot}SBr$ and $CHAcNa{\cdot}CO_2Et$; corresponding *chloride*, m.p. 160°), obtained more readily by the successive treatment of 5 : 2-$NO_2{\cdot}C_6H_3Cl{\cdot}CHO$ in boiling EtOH with Na_2S–S, NaOH–Na_2S, and $CH_2Cl{\cdot}CO_2Na$. (IV) is reduced by $FeSO_4$ and NH_3 to 4-*aminothionaphthen*-1-*carboxylic acid* (V), m.p. 278° (decomp.), chlorinated in AcOH containing conc. HCl to 3 : 3 : 5 : 5 : 6-*pentachloro*-4-*keto*-3 : 4 : 5 : 6-*tetrahydrothionaphthen*-1-*carboxylic acid*, m.p. 172° (decomp.). This when heated at 170—180° or rapidly heated to boiling with AcOH containing NaOAc gives 3 : 3 : 5 : 6-*tetrachloro*-4-*keto*-3 : 4-*dihydrothionaphthen*-1-*carboxylic acid*, m.p. 213° (decomp.), and when reduced by $SnCl_2$ in AcOH containing NaOAc gives 3 : 5 : 6-*trichloro*-4-*hydroxythionaphthen*-1-*carboxylic acid*, m.p. 290°, oxidised by HNO_3 in AcOH to 5 : 6-*dichlorothionaphthen*-3 : 4-*quinone*-1-*carboxylic acid*, m.p. 225° (decomp.), also obtained by hydrolysis of the keto-chloride; it is converted by NH_2Ph in EtOH into 5-*chloro*-6-*anilo*-4-*hydroxy*-3-*keto*-3 : 6-*dihydrothionaphthen*-1-*carboxylic acid*, m.p. 255°. (V) is transformed through the *diazonium* compound into 4-*hydroxythionaphthen*-1-*carboxylic acid*, m.p. 264°. When heated with PbO at 280—290° (V) affords 4-*aminothionaphthen* (VI), m.p. 72° (*Ac* derivative, m.p. 106°), converted by Br in AcOH into

3-*bromo*-4-*aminothionaphthen*, m.p. 75° (*Ac* derivative, m.p. 143°), and by PhCHO into *benzylidenethionaphthyl*-4-*amine*, m.p. 98°. The latter and 4-*aminothionaphthen hydrochloride* at 180° and then at 200—205° give *di*-2′ : 3′ : 2″ : 3″-*thiopheno*-5-*phenyl*-5 : 10-*dihydro*-1 : 2 : 8 : 9-*acridine*, m.p. 269°. (VI) is transformed by Skraup's reaction into 2′ : 3′-*thiopheno*-5 : 6-*quinoline*, m.p. 88°. 8-*Bromo*-2′ : 3′-*thiopheno*-5 : 6-*quinoline*, m.p. 132°, is obtained similarly. (VI) couples with PhN_2Cl to 3-*benzeneazothionaphthyl*-4-*amine*, m.p. 103° (*Ac* derivative, m.p. 154°). Exhaustive chlorination of (VI) in AcOH containing HCl leads to 1 : 2 : 3 : 5 : 6-*pentachloro*-4-*hydroxythionaphthen*, m.p. 164°, oxidised by HNO_3 (*d* 1·4) in AcOH to 1 : 2 : 5 : 6-*tetrachlorothionaphthen*-3 : 4-*quinone*, m.p. 166°, whence 1 : 2 : 5-*trichloro*-4-*hydroxy*-3-*keto*-6-*anilo*-3 : 6-*dihydrothionaphthen*, m.p. 270°.

4-*Hydroxythionaphthen*, m.p. 103° (*Me ether*, m.p. 44°), obtained by diazotisation of (VI), is brominated in AcOH containing NaOAc to 3-*bromo*-4-*hydroxythionaphthen*, m.p. 112° [whence 3-*bromo*-2-*nitro*-4-*hydroxythionaphthen*, m.p. 173° (decomp.)], or 2 : 3-*dibromo*-4-*hydroxythionaphthen*, m.p. 103°. The latter is oxidised by HNO_3 (*d* 1·42) in $CHCl_3$ to 2-*bromothionaphthen*-3 : 4-*quinone*, sublimation, softening, and decomp. 130°, reduced by SO_2 to 2-*bromo*-3 : 4-*dihydroxythionaphthen*, m.p. 248° (also $+C_6H_6$) (*diacetate*, m.p. 140°). 2-*Bromo*-4-*hydroxy*-3-*keto*-6-*anilo*-3 : 6-*dihydrothionaphthen*, decomp. 213°, is described.

2-Nitrothionaphthen in H_2SO_4 is transformed by KNO_3 at $\not>$4° into 2 : 3 : 6-*trinitrothionaphthen*, m.p. 196°, or if less KNO_3 is used into 2 : 3-*dinitrothionaphthen* (VII), m.p. 199·5°, accompanied by *dinitrothionaphthen* B (labile α-*form*, m.p. 98—99°, and β-*variety*, m.p. 119—121°) and *dinitrothionaphthen* C, m.p. 171°, of unexplained constitution. Reduction of (VII) in EtOH by $SnCl_2$–HCl gives the very sensitive 2 : 3-*diaminothionaphthen* [*stannichloride* (VIII); Ac_2 derivative, m.p. 167°]; treatment of (VIII) with boiling 20% HCl followed by NaOH and $K_3Fe(CN)_6$ leads to (?) 4 : 4′-*diaminothioindigotin* in very small yield. (VII) is transformed by boiling EtOH–NH_3–H_2O followed by H_2S into 3-*nitrothionaphthen*, m.p. 88°, whence 3-*aminothionaphthen*, m.p. 59° (*Ac* derivative, m.p. 134°), which couples with $SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ to the *salt*, $C_{14}H_{10}O_3N_3S_2Na$, reduced by $Na_2S_2O_4$ to 3 : 6-*diaminothionaphthen*, m.p. 114° (decomp.) [*dihydrochloride*, m.p. 151° (decomp.); Ac_2 derivative, m.p. 287°], which does not react with benzil.

The following compounds are incidentally described: *di*-p-*hydroxyphenacyl disulphide*, m.p. 215°, which could not be converted into 2 : 5-dihydroxythionaphthen; *di*-p-*hydroxyphenacyl sulphide*, m.p. 190°; m-*methoxyphenylthiolacetic acid*, m.p. 64°, from which 2-hydroxy-5-methoxythionaphthen could not be obtained. H. W.

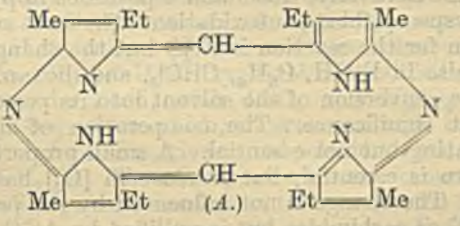
Curtius degradation in the pyrrole series. III. Autoxidation in the pyrrole series and a new synthesis of di-imidoporphyrins. W. METZGER and H. FISCHER (Annalen, 1936, 527, 1—37; cf. A., 1934, 1227).—4-Methyl-2-dichloromethyl-3-ethylpyrrole-5-carboxylazide (I) (improved prep.) is transformed by cold MeOH into 2-*aldehydo*-4-*methyl*-3-*ethylpyrrole*-5-*carboxylazide*, m.p. 67—68° (decomp.), which is unsuited for the methene condensation. It is transformed by boiling $CH_2Ph{\cdot}OH$–xylene into 2-*aldehydo*-4-*methyl*-3-*ethylpyrrole*-5-*benzylurethane*, m.p. 209° (decomp.) (corresponding *aldazine*, $C_{32}H_{36}O_4N_6$, m.p. 220°). 3-Bromo-4-methyl-2-dichloromethylpyrrole-5-carboxylazide is similarly transformed into 3-*bromo*-2-*aldehydo*-4-*methylpyrrole*-5-*benzylurethane* (II), m.p. 187° (decomp.) [*aldazine*, m.p. 254° (decomp.)], accompanied by the methene in considerable amount. (II) is transformed by 2 : 4-dimethylpyrrole (1 mol.) in HBr–AcOH into the two symmetrical *pyrromethenes*,

CH—CMe ⟩C·CH:C⟨ CMe═CH
CMe₂·NH ⟩ ⟨ N(HBr):CMe'

m.p. 251°, and

CH₂Ph CMe·CBr ⟩C·CH:C⟨ CBr:CMe
CO₂·NH·C——NH ⟩ ⟨ N═C·NH·CO₂·CH₂Ph,

m.p. 195° (decomp.), whereas with 2 mols. it gives 3-*bromo*-4 : 3′ : 5′-*trimethylpyrromethene*-5-*benzylurethane*, decomp. 158° (*picrate*, decomp. 165°). (I) is transformed by boiling EtOH (the liberated HCl acts as condensing agent) into 4 : 4′-*dimethyl*-3 : 3′-*diethylpyrromethene*-5 : 5′-*diethylurethane*, m.p. 147° [*mono*-, m.p. 179° (decomp.), and *di-hydrochloride*; Bz_2 derivative, m.p. 125° (decomp.); Ac_2 compound, decomp. 174°, and its *picrate*, m.p. 181° (decomp.)]. 4 : 4′-Dimethyl-3 : 3′-diethylpyrromethene-5 : 5′-diethylurethane (III) readily undergoes oxidative autocondensation in alkaline or acid

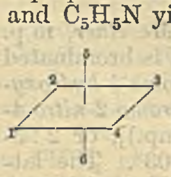


medium to the βδ-di-imidoætioporphyrin II (*A*), m.p. >300°, also obtained when (III) is heated with $(COCl)_2$ in Et_2O or with conc. HCl at 110° and, best, by treatment of it with $NHPh{\cdot}NH_2$ at 160—200°. 5-Carbethoxy-2 : 4-dimethylpyrrole-3-propionic acid is transformed by N_2H_4,H_2O at 130° into 2 : 4-*dimethylpyrrole*-5-*carboxylhydrazide*-3-*propionhydrazide*, m.p. 248° (decomp.) [*dihydrochloride*, decomp. 258°; p-*dimethylaminobenzylidene* derivative, $C_{28}H_{35}O_2N_7$, m.p. 242° (decomp.)]. Et 2 : 3 : 5-trimethylpyrrole-4-carboxylate is converted with difficulty into 2 : 3 : 5-*trimethylpyrrole*-4-*carboxylhydrazide*, m.p. 196° [:*CHPh* derivative, m.p. 230°; condensation *product*, $C_{16}H_{16}O_2N_4$, m.p. 283° (decomp.), with isatin], whence 2 : 3 : 5-*trimethylpyrrole*-4-*carboxylazide*, m.p. 108° (decomp.). 2 : 4-Dimethyl-3-ethylpyrrole-5-carboxylazide is transformed by boiling $CH_2Ph{\cdot}OH$–xylene into the *compound*, $C_{16}H_{20}O_3N_2$, m.p. 121° (instead of the expected urethane), hydrogenated (Pd-sponge–MeOH–AcOH) to the *substance*, $C_{18}H_{14}O_2N_2$, m.p. 180° (decomp.). 1-*Amino*-2 : 4-*dimethyl*-3-*ethylpyrrole* (?), m.p. 208°, is incidentally described. Autoxidation of pyrroles is conveniently studied by exposing the base in a suitable solvent in open or loosely-closed Erlenmeyer flasks to diffused daylight for several days. Thus 2 : 4-dimethyl-3-ethylpyrrole

affords the peroxide $\left(\begin{smallmatrix}CEt\cdot CMe\\ CMe\cdot NH\end{smallmatrix}\!>\!C\cdot O\cdot\right)_2$, m.p. 219—220°, also obtained as by-product of its oxidation by H_2O_2 in C_5H_5N or from cryptopyrrole ether and transformed by Br in AcOH into 4-*methyl*-2-*bromomethyl*-3-*ethylpyrrolen*-5-*one*, $\begin{smallmatrix}CEt\cdot C(CH_2Br)\\ CMe\text{———}CO\end{smallmatrix}\!>\!N$, m.p. 140—141°. *Di*-(2 : 3-*dimethyl*-4-*ethylpyrryl*) 5-*peroxide*, m.p. 228° (decomp.), and *di*-(2 : 3 : 4-*trimethylpyrryl*) 5-*peroxide*, m.p. 245°, are formed similarly. Cryptopyrroles with CO_2Et at 1 or 5 remain unchanged. Experiments with pyrrolepropionic acids were unsuccessful but Me 2 : 4-dimethylpyrrole-3-propionate readily yields the corresponding *peroxide*, m.p. 202° (decomp.), brominated at 100° to a *substance*, m.p. 172° (decomp.). Autoxidation of Me 2 : 3-dimethylpyrrole-4-propionate appears to yield Me 5 : 5-dihydroxy-2 : 3-dimethylpyrrolene-4-propionate, $\begin{smallmatrix}CMe\cdot CMe\\ N\cdot C(OH)_2\end{smallmatrix}\!>\!C\cdot CH_2\cdot CH_2\cdot CO_2Me$, m.p. 137° (decomp.), brominated mainly to *Me* 3-*methyl*-2-*dibromomethylpyrrolen*-5-*one*-4-*propionate*, m.p. 142° (decomp.). 2 : 4-Dimethylpyrrole (IV) in Et_2O is slowly autoxidised to 2 : 4-*dimethylpyrrolen*-5-*one hydrate*, m.p. 145°, decomp. 205°, converted by boiling Ac_2O containing KOAc into the *substance*, $C_{12}H_{18}ON_2$, m.p. 160°. *Di*-(3-*methyl*-4-*ethylpyrryl*) 2-*peroxide*, m.p. 281° (decomp.), and *di*-(*Me* 3-*methylpyrryl*-4-*propionate*) 2-*peroxide*, m.p. 193° (decomp.), are described. Generally, free 3 and 4 positions in pyrroles are not susceptible to autoxidation. The most suitable medium for the reaction is Et_2O but the change proceeds also in EtOH, C_6H_6, $CHCl_3$, and dioxan. The possible conversion of the solvent into its peroxide is without significance.. The co-operation of light is stimulating but not essential. A small proportion of moisture is essential, but increase in $[O_2]$ has little effect. The change is not influenced by the presence of HCN or carbimides but is nullified by Ac_2O. The peroxides do not liberate I from HI or decolorise indigotin in conc. H_2SO_4 and therefore do not contain active O. Ring fission occurs with boiling dil. NaOH. Oxidation of certain non-autoxidisable pyrroles with H_2O_2 is best effected in EtOH–Et_2O. Thus Et 2 : 4-dimethylpyrrole-3-carboxylate is converted into *Et* 5-*hydroxy*-2 : 4-*dimethylpyrrole*-3-*carboxylate*, m.p. 127°, and 5-*hydroxy*-2 : 4-*dimethylpyrrole*-3-*carboxylic acid*, m.p. 196° (decomp.), is obtained similarly; both are unstable to alkali. In hot EtOH (IV) is converted by H_2O_2 into 3 : 5-*dihydroxy*-2 : 4-*dimethylpyrrole*, m.p. 175°, whereas in cold solution the *product*, m.p. 130—131° (decomp.), is probably $\begin{smallmatrix}C(OH)\text{—}CMe\\ CMe\cdot C(OH)_2\end{smallmatrix}\!>\!N$, transformed by Br–AcOH at 100° into the *compound*, $C_6H_5O_3NBr_2$, decomp. 126°. 2- and 3-Methylpyrrole yield *compounds*, $C_5H_9O_3N$, m.p. 154° (decomp.), and $C_6H_{11}O_3N$, m.p. 143° (decomp.), respectively. The hydroxypyrroles do not give a coloration with $FeCl_3$ in EtOH. There appears to be no relationship between capability of autoxidation and behaviour towards H_2O_2. Substituents which impede the former are without action on the latter process. Autoxidisability of aminopyrroles and their carbamates exhibits the same regularities as that of other pyrroles. The process is linked with the basic nature of the pyrrole mol. and substituents which enhance this character increase the tendency towards autoxidation.
H. W.

Absorption spectra of dihydropyridine compounds.—See A., III, 68.

Pyridine complexes of quadrivalent platinum derivatives. A. M. RUBINSCHTEIN (Ann. Sect. Platine, 1936, 13, 21—57).—Cleve's salt and C_5H_5N at 100° give a ppt. of $Pt(C_5H_5NCl)_2Cl_2$, whilst the product with Gérard's salt is $[PtNH_3C_5H_5NNH_3ClC_5H_5NCl]Cl_2,4H_2O$ (I) (the substituents are given in the order shown in the figure). $[PtC_5H_5NNH_3C_5H_5NNH_3Cl_2]Cl_2,4H_2O$ (*oxalate*; *platini*- and *platino-chloride*) is obtained by heating aq. C_5H_5N with Reise's second salt, and treating with Cl_2 the $Pt(NH_3)_2(C_5H_5N)_2$ so formed. $[Pt(C_5H_5N)_2(NH_3)_2Cl_2]Cl_2$ is prepared analogously from Peyronne's salt. $Pt\,enCl_4$ and C_5H_5N yield $[Pt\,enCl_4](C_5H_5N)_2$ at room temp., whilst at the b.p. the product is a mixture of $[Pt\,enC_5H_5NCl_3]Cl$ and $[Pt\,enCl_2C_5H_5NCl]Cl$; these results contradict those of Schleicher *et al.* (A., 1923, i, 1120). $[Pt\,en(C_5H_5N)_2Cl_2]Cl_2$ is obtained by chlorinating the product



of reaction of $Pt\,enCl_2$ with aq. C_5H_5N. $Pt\,enCl_4$ and $(NH_2\cdot CH_2)_2$ in presence of C_5H_5N affords $Pt\,en_3Cl_4$. Blomstrand's salt (I) and C_5H_5N at 100° afford $[Pt(NH_3)_2(NO_2)_2C_5H_5NCl]Cl$ (*oxalate*). (I) and Reise's first salt, in aq. or C_5H_5N solution, give $[Pt(NH_3)_2(NO_2)_2Cl_2][Pt(NH_3)_4Cl_2]$. The above reactions are in accord with Tscherniaev's law of *trans*-substitution.
R. T.

Oxidation of *cis*- and *trans*-bivalent platinum non-electrolytes by nitric acid.—See A., I, 96.

Pyridine. XXIII. Derivatives of 3-aminopyridine. O. VON SCHICKH, A. BINZ, and A. SCHULZ (Ber., 1936, 69, [*B*], 2593—2605).—2-NH_2 in C_5H_5N directs the first new substituent mainly towards position 5 and to some extent towards 3; further substitution leads to 2-NH_2-3 : 5-derivatives. 3-NH_2 directs towards the 2 and 2 : 6 positions. Gradual addition of 15% H_2O_2 to 3-$C_5H_4N\cdot NH_2$ (I) in conc. HCl at 70—80° affords mainly 2-*chloro*-3-*aminopyridine* (II), b.p. 134—135°/15 mm., m.p. 79—80°, also obtained by reduction of 2-chloro-3-nitropyridine with Fe powder and AcOH. Similar chlorination of (I) at 110° affords also 2 : 6-*dichloro*- (III), b.p. 110°/0·2 mm., m.p. 119°, and 2 : 4 : 5 : 6-*tetrachloro*-, m.p. 143°, -3-*aminopyridine*. Passage of Cl_2 into a solution of (I) in boiling HCl gives small amounts of (II) and (III); the latter is also obtained by treating (II) or 6-chloro-3-aminopyridine with nascent Cl. (II) with cold Ac_2O gives 2-*chloro*-3-*acetamidopyridine*, m.p. 90—91°, whilst with boiling Et_2O 2-*chloro*-3-*diacetamidopyridine*, m.p. 67—68°, is ultimately obtained exclusively. 3-*Diacetamidopyridine*, m.p. 88°, is somewhat less readily prepared. (II), PhCHO, and anhyd. NaOAc at 80—100° yield 2-*chloro*-3-*benzylideneaminopyridine*, b.p. 162°/0·6 mm. 2-*Chloro*-3-*hydroxypyridine*, m.p. 163°, is obtained from (II) by the diazo-method or from 3-$C_5H_4N\cdot OH$ and H_2O_2 in boiling concn. HCl. 2-Chloro-3-cyanopyridine has m.p. 107—108°. (II), NaOMe or NaOH, and Cu powder in MeOH at 150° give 3-*amino*-2-

methoxypyridine, b.p. 116—118°/3 mm., m.p. 68° (*Ac* derivative, m.p. 163°), whence by the diazo-reaction, 3-*hydroxy*-2-*methoxypyridine* (IV), b.p. 82°/11 mm., m.p. 68—69°, also obtained from 2-halogeno-3-hydroxypyridines. (IV) and boiling 40% HBr or conc. HI yield 2 : 3-*dihydroxypyridine*, m.p. 246°, oxidised to pyridine-2 : 3-quinone. (I) is converted by 25% NH_3 containing $CuSO_4$ at 130° into 2 : 3-diaminopyridine, m.p. 112°; analogous reactions lead to 3-*amino*-2-*methylamino*-, m.p. 100—101°, and -2-*anilino*-, m.p. 141°, -*pyridine*. Gradual addition of H_2O–I–KI to 3-C_5H_4N·OH and Na_2CO_3 in H_2O at room temp. affords 2-*iodo*-, m.p. 192°, whereas at the b.p. *di-iodo*-, m.p. 198°, and *tri-iodo*-, m.p. 156—157°, -3-*hydroxypyridine* are formed. 2 : 3-*Dihydroxypyridine monoacetate* has m.p. 155°. 4-C_5H_4N·OH is converted by NaOH at 290—310° into 2 : 4-dihydroxypyridine, m.p. 260°. 3-C_5H_4N·NO_2, m.p. 35—36°, is obtained by gradual addition of (I) in conc. H_2SO_4 to a mixture of HNO_3 (*d* 1·93) and 30% H_2O_2 at room temp., less advantageously from (I) through the diazo-reaction; it is transformed by Cl_2 at 130—150° into *pentachloropyridine*, m.p. 124—125°. (I) with ICl in conc. HCl affords 3-*aminopyridine iodochloride hydrochloride*, m.p. 149°. Addition of H_2O_2 to (I) in aq. HI followed by treatment of the periodide with NaOH causes essentially oxidation with production of 3 : 3′-*azopyridine*, m.p. 138°. (I) with nascent Br at 80° or at room temp. appears to give exclusively 2 : 6-*dibromo*-3-*aminopyridine*, m.p. 145°. H. W.

3-Hydroxypyridine. I. Amination and sulphonation. E. Płażek (Rocz. Chem., 1936, **16**, 403—405).—3-Hydroxypyridine (I) and $NaNH_2$ in *p*-cymene at 130° yield 2 : 6-diaminopyridine. (I) and H_2SO_4 in presence of $(VO)_2(SO_4)_3$ at the b.p. afford 3-hydroxypyridine-2(6)-sulphonic acid, identical with that obtained from 3-diazopyridine-2(6)-sulphonic acid. R. T.

***N*-Hydroxyalkyl-2-pyridones.** J. A. Gautier (Compt. rend., 1936, **203**, 794—796; cf. A., 1933, 720; 1934, 663).—EtOH, Pr^{α}OH, Bu^{α}OH, and CH_2Pr^{β}·CH_2·OH with epichlorohydrin and H_2SO_4 afford Et, *Pr*$^{\alpha}$, b.p. 89°/13 mm., Bu$^{\alpha}$, and *iso*amyl γ-chloro-β-hydroxypropyl ether, respectively, which with hot C_5H_5N afford the hydrochlorides (very hygroscopic) of *N*-substituted pyridines, converted by $K_3Fe(CN)_6$ into 2-pyridones which are unstable in air and give red colours with $FeCl_3$. The following are prepared: N-γ-*ethoxy*-, b.p. 186°/14 mm. (*phenylcarbamate*, m.p. 117°), -*propoxy*-, b.p. 200°/17 mm. (*phenylcarbamate*, m.p. 115°), -*butoxy*-, b.p. 195—197°/12 mm. (*phenylcarbamate*, m.p. 98°), and -iso-*amyloxy*-β-*hydroxypropyl*-2-*pyridone*, b.p. 211—213°/12 mm. (*phenylcarbamate*, m.p. 126°). J. L. D.

***s*-Di-2-methyl-6-pyridylthiocarbamide.** K. Feist (Arch. Pharm., 1936, **274**, 547—548).—The identity of this substance, m.p. 209° (cf. Toptschiev, A., 1936, 612; Feist *et al.*, *ibid.*, 1519), is confirmed. R. S. C.

Preparation of aminoisatin and derivatives [therefrom]. M. Hartmann and L. Panizzon (Helv. Chim. Acta, 1936, **19**, 1327—1332).—5-Acetamido-oxindole (modified prep.; NO_2-derivative, m.p. 261°) with CrO_3 in aq. AcOH at 90—110° gives 5-*acetamidoisatin*, m.p. 286°, and +$2H_2O$, hydrolysed to 5-*aminoisatin*, m.p. >360° {*sulphate*; 5-N-*Me*$_2$-derivative (prep. by CH_2O in H_2O, not HCO_2H), m.p. 215° [*methiodide*, m.p. 247—249° (decomp.); *methochloride*, m.p. 250° (decomp.)]}, which with HNO_2 gives 5-*hydroxyisatin*, m.p. >360°. R. S. C.

Destructive hydrogenation of quinoline. I. B. Rapoport (J. Appl. Chem. Russ., 1936, **9**, 1456—1464).—Quinoline and H_2 (MoS_3 catalyst) at 220°/100—110 atm. yield tetrahydroquinoline, whilst at 420—450°/80 atm. the products are C_6H_6, PhMe, PhEt, xylene, naphthenes, CH_4, NH_3, NH_2Ph, NHPhEt, tetrahydroaniline, and dihydroethylaniline. R. T.

By-products of Skraup's quinoline synthesis. E. Sucharda and T. Mazonski (Ber., 1936, **69**, [*B*], 2719—2721).—*p*-NH_2·C_6H_4·OH, 6- and 8-hydroxyquinoline are obtained as by-products of Skraup's synthesis of quinoline with $PhNO_2$ as oxidising agent. $PhNO_2$ appears to be reduced to NHPh·OH which becomes isomerised or condenses with CH_2:CH·CHO. H. W.

[**Constitution of Knoevenagel's "acetone-anil."**] P. Kalnin (Ber., 1936, **69**, [*B*], 2843; cf. A., 1936, 1123).—A reply to von Auwers (A., 1936, 1522). H. W.

Quinone formation in the thalleioquinine reaction. Preparation of quinolyl-*o*-quinone. G. W. Hargreaves (J. Amer. Pharm. Assoc., 1936, **25**, 975—976).—6-Hydroxyquinoline (modified method of prep. described) with PbO_2 and H_2SO_4 yields quinolyl-*o*-quinone which, in common with oxidised solutions of quinine, gives a red solution when heated with NH_2Ph. The theory of quinone formation in the thalleioquinine reaction is thus supported (cf. A., 1926, 967). F. O. H.

Condensation of acetylene with aromatic amines. IV. Condensation with aniline and *p*-toluidine in presence of silver nitrate. N. Kozlov and E. Gimpelevitsch. V. Condensation with *o*- and *p*-anisidine in presence of CuCl and $HgCl_2$. N. Kozlov and R. Bogdanovskaja. VI. Condensation with aniline in presence of $HgCl_2$, HgCl, and $HgBr_2$. N. Kozlov, B. Dinaburskaja, and T. Rubina. VII. Condensation with aniline in presence of HgI_2. N. Kozlov and R. Patschanova (J. Gen. Chem. Russ., 1936, **6**, 1341—1345, 1346—1348, 1349—1351, 1352—1354).—IV. NH_2Ph and C_2H_2 in presence of $AgNO_3$ yield quinaldine (I) and tetrahydroquinaldine (II), whilst with *p*-toluidine the only identified product was 2 : 6-dimethylquinoline. The reaction consists probably of: $NH_2Ph + C_2H_2 \rightarrow$ NPh:CHMe (III) : 2(III) $\rightarrow$ NHPh·CHMe·CH:CH·NHPh (IV) $\rightarrow$ NH_2Ph + (I) + H_2; (I) + $2H_2 \rightarrow$ (II).

V. *o*- or *p*-Anisidine and C_2H_2 in PhMe and CuCl yield 8-, m.p. 123—125°, or 6-*methoxy*-2-*methylquinoline*, b.p. 176—179°/33 mm. (*methiodide*, m.p. 229—230°); in presence of $HgCl_2$ in place of CuCl the respective products are *diethylidene*-o-, m.p. 102—103°, and -p-*anisidine* (cis- and trans-), m.p. 89° and 169°, which yield the appropriate quinaldines when heated.

VI. NH_2Ph and C_2H_2 in presence of $HgCl$, $HgCl_2$, or $HgBr_2$ afford (IV), converted by heating into (I) and (II).

VII. The catalytic action of HgI_2 is identical with that of other Hg salts. R. T.

β-Hydroxyphenylethylamines and their transformations. IV. Synthesis of tetrahydro*iso*quinolinecarboxylic acids and the spontaneous decarboxylation of α-keto-acids under physiological conditions. G. Hahn and K. Stiehl (Ber., 1936, **69**, [*B*], 2627—2654).—The condensation of phenylethanolamines with α-CO-acids capable of enolisation to compounds, $C_6H_3X_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C(OH)(CH_2R){\cdot}CO_2H$ occurs very readily if the energy liberated by saturation of the double linking is equiv. to that required for the detachment of H and depends greatly on the p_H of the solution. Subsequent ring-closure to an *iso*quinoline takes place if a nuclear H is sufficiently loosened by a substituent in the *para*-position; otherwise, decarboxylation occurs. The changes are usually concurrent to some extent but their rates differ greatly. β-3 : 4-Dihydroxyphenylethylamine (I) and $CH_2Ph{\cdot}CO{\cdot}CO_2H$, best at p_H 6, yield 6 : 7-*dihydroxy*-1-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline-1-*carboxylic acid*, unstable to air (*hydrochloride*, decomp. about 240° after becoming yellow), converted by Me_2SO_4 and NaOH into *Me* 6 : 7-*dimethoxy*-1-*benzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline-1-*carboxylate* (II), m.p. 118°; the corresponding *acid* (III), decomp. 179—181° after shrinking at 100° (*hydrochloride*, m.p. 199—200°), loses CO_2 when kept in diffused light, more rapidly in sunlight, giving a yellow oil insol. in alkali. The mother-liquors from (II) when treated with 50% KOH evolve Me_2O and give the *methylbetaine*, m.p. 138—139° (*hydrochloride*, decomp. 167°), of (III). $AcCO_2H$ and (I) at about p_H 4 and 25° afford 6 : 7-*dihydroxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline-1-*carboxylic acid*, decomp. 230—235° when heated moderately rapidly. (I) and *p*-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$ at p_H 5 yield 6 : 7-*dihydroxy*-1-*p*-*hydroxybenzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline-1-*carboxylic acid* (*hydrochloride*, decomp. 260° after becoming discoloured at about 240°); at p_H 6·6 the reaction is greatly disturbed by atm. oxidation. 6 : 7-*Dihydroxy*-1-*m*-*hydroxybenzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline-1-*carboxylic acid* and its *hydrochloride*, decomp. 255° after becoming discoloured at 220°, are obtained similarly. 6 : 7-*Dihydroxy*-1-*o*-*hydroxybenzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline-1-*carboxylic acid*, decomp. >250° when heated moderately rapidly [*hydrochloride* (+$3H_2O$), m.p. 155°, decomp. >220°], is obtained at 100°. (I) and α-ketoglutaric acid do not react at 25° and p_H 3—6 and the *lactam*, decomp. 255—260° after darkening at 215°, of 6 : 7-dihydroxy-1-carbethoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline-1-carboxylic acid is best obtained from the reactants at 100° and p_H <1. 6 : 7-*Dihydroxy*-1-4′-*hydroxy*-3′-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline-1-*carboxylic acid* (+H_2O), decomp. 230° after becoming yellow, and its *hydrochloride* (+H_2O), decomp. 255—260°, are described. Reaction does not appear to take place between (I) and $BzCO_2H$ or between adrenaline and $AcCO_2H$, $AcCO_2Alk$, $(OMe)_2C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, MeCHO, or $CH_2Ph{\cdot}CHO$. If the OH of (I) are etherified, condensation with α-CO-acids proceeds only to the formation of Schiff's bases. $CH_2Ph{\cdot}CH_2{\cdot}NH_2$ (IV) and $AcCO_2H$ at 25° and p_H 4 readily evolve CO_2 (yield 65% calc. on amine) and give a red oil which could not be satisfactorily purified; the possibility that it is the Schiff's base from (IV) and MeCHO is strengthened by the anologous behaviour of these substances towards one another but the reaction is not simple. Under similar conditions, decarboxylation occurs, but at p_H ~4, but it is not immaterial whether this condition is secured by NaOH or NH_3 since the latter has a marked, proper decarboxylating action. The most favourable concn. of AcO_2H is 4*M*; the poorer results obtained at greater dilution are due to increased dissociation and consequently lessened enolisation. Higher temp. favours decarboxylation at the expense of possible side-reactions. In PhOH or glycerol reaction does not take place better than in H_2O; in contrast with the carboxylase models of Langenbeck which are active only in absolutely anhyd. media, H_2O is without harmful effect. Variation in the α-CO-acid appears to have little influence on the change if enolisation is possible; otherwise CO_2 is not evolved. All primary amines (NH_3, NH_2Me, NH_2Ph, $CH_2Ph{\cdot}NH_2$, $CH_2Ph{\cdot}CH_2{\cdot}NH_2$, and histamine) are active whereas *sec.*-amines and NH_2-acids (arginine, glutamic acid, tyrosine, tryptophan, Me clupeate) do not induce change. H. W.

Molecular compounds with sodium picrate. C. Schöpf, A. Hartmann, and K. Koch (Ber., 1936, **69**, [*B*], 2766—2769).—The Na salt of glutacondialdehyde (purification described) is converted by successive treatment with NH_2Ph in HCl and picric acid into the 1-phenylpyridinium *salt*, $C_{17}H_{12}O_7N_4{,}C_6H_2O_7N_3Na$, m.p. 191—193°, obtained also from its components in EtOH. 2-*Phenyl*isoquinolinium *picrate*, m.p. 125—127° after softening at 120° (prep. from homophthaldialdehyde described), does not give an additive compound whereas *iso*quinoline 2-oxide affords the *adduct*, $C_9H_7ON{,}C_6H_3O_7N_3{,}2C_6H_2O_7N_3Na$, m.p. 241—243°. H. W.

Polymembered cyclic compounds. IX. *cyclo*Ditridecamethylenedi-imine and tridecamethyleneimine. A. Müller and A. F. Schütz [with, in part, R. Treer] (Ber., 1936, **69**, [*B*], 2790—2792; cf. A., 1934, 419).—Attempts to oxidise *NN′*-dibenzoyl- (I) or *NN′*-dibenzenesulphonyl-*cyclo*ditridecamethylenedi-imine were unsuccessful. (I) passes when heated with PBr_5 in high vac. into α-dibromo-*n*-tridecane, identified by conversion into *αν-diphenoxy*-n-*tridecane*, m.p. 67—68° and, after re-solidification, m.p. 64·5—65°, and Me_2 *n*-tridecane-αν-dicarboxylate, m.p. 42·7—43° (corr.). *Tridecamethyleneimine aurichloride* has m.p. about 160°. H. W.

***iso*Carbamides and *iso*ureides. IV. Condensation of *iso*carbamides with ketones and ketonic esters.** S. Basterfield, A. E. Baughen, and I. Bergsteinsson (Trans. Roy. Soc. Canada, 1936, [iii], **30**, III, 115—127; cf. A., 1929, 329).—Ac_2 and Bz_2 (1 mol.) with ethyl*iso*carbamide (I) (2 mols.) afford *diethylureido-diacetyl*, m.p. 240°

(decomp.) (*dihydrochloride*), and *-dibenzoyl* (II), m.p. 245° (decomp.), respectively, converted through the hydrochlorides into the *diureides*, m.p. >300°. Equimol. amounts of (I) and Bz_2 in dry Et_2O afford an additive *compound*, m.p. 87°, converted at 90° into (II). (I) with $BzCO_2Et$ affords *benzoylformylethyl*-iso*carbamide*, m.p. 163° (decomp.) (*oxime*, m.p. 188°; *semicarbazone*, m.p. 238°), and with $CHPh(CO_2Me)_2$ at 50° affords 2-*ethoxy*-5-*phenylbarbituric acid*, m.p. 220° (*ethyl*iso*carbamate*, m.p. 237°), hydrolysed (dil. HCl) to 5-*phenylbarbituric acid*, m.p. 253°. (I) (2 mols.) with Et succinosuccinate (1 mol.) in anhyd. Et_2O at <0° affords an additive *compound*, m.p. 110° (decomp.), which when boiled in C_6H_6 is converted into 4 : 5′ : 5 : 4′-*dimethylene*-2 : 2′-*diethoxydiuracil*, decomp. at 305° (*dihydrochloride*, decomposed at 100° into EtCl and 4 : 5′ : 5 : 4′-*dimethylenediuracil*). (I) (2 mols.) with Me phenylformylacetate (III) (1 mol.) in dry Et_2O affords 2-*ethoxy*-5-*phenyluracil*, m.p. 211°, converted through an unstable hydrochloride at 100° into 5-*phenyluracil* (IV). Similarly, (III) with *cyclo*hexyliso*carbamide* (V) in Et_2O affords 2-*cyclohexyloxy*-5-*phenyluracil*, m.p. 171°, converted (HCl) into (IV). Me oxalacetate with (I) or (V) in dry Et_2O affords *Me ethyl*iso*carbamidodioxalacetate* (?), m.p. 140°, and *Me* cyclo*hexyl*iso*carbamido-oxalacetate* (?), m.p. 131°, respectively. Neither product is cyclised when heated. J. L. D.

Attempted synthesis of *gem*-substituted 6 : 6-dihydrouracils. E. Philippi, F. Hendgen, and F. Hernler (Monatsh., 1936, **69**, 270—283).—Treatment of the appropriate ketone with Mg and $CH_2Br{\cdot}CO_2Me$ in C_6H_6 affords *Me* β-*hydroxy*-β-*methyl*-n-*valerate*, b.p. 67°/10 mm. (yield 58—60%), *Me* β-*hydroxy*-β-*ethyl*-n-*valerate*, b.p. 80°/11 mm., and *Me* β-*hydroxy*-β-*methyl*-n-*hexoate*, b.p. 81°/12 mm., respectively. Cautious addition of the OH-esters in CCl_4 to PCl_5 in CCl_5 at >35° gives the following: *Me* β-*chloro*-β-*methyl*-n-*valerate*, b.p. 48°/16 mm. (yield 42%), *Me* β-*chloro*-β-*ethyl*-n-*valerate*, b.p. 58°/11 mm., *Me* β-*chloro*-β-*methyl*-n-*hexoate*, b.p. 59°/13 mm., Et β-*chloro*-β-*methyl*-n-*valerate*, b.p. 54°/14 mm., *Et* β-*chloro*-β-*ethyl*-n-*valerate*, b.p. 68°/12 mm., and *Et* β-*chloro*-β-*methyl*-n-*hexoate*, b.p. 67°/11 mm. Cautious treatment of these esters with NH_3 in cold EtOH gives *Me* β-*methyl*-Δ^{α}-*pentenoate*, b.p. 49·5°/11 mm., *Me* β-*ethyl*-Δ^{α}-*pentenoate*, b.p. 57°/11 mm., *Me* β-*methyl*-Δ^{α}-*hexenoate*, b.p. 57°/12 mm., *Et* β-*methyl*-Δ^{α}-*pentenoate*, b.p. 55°/11 mm., *Et* β-*ethyl*-Δ^{α}-*pentenoate* (I), b.p. 66°/11 mm., and *Et* β-*methyl*-Δ^{α}-*hexenoate*, b.p. 66°/11 mm. Treatment of Et β-methyl-Δ^{α}-butenoate with $CO(NH_2)_2$ in EtOH at 150° leads to 4 : 4-*dimethyldihydrouracil*, m.p. 202°, but the reaction cannot apparently be extended to other acrylates. (I) is transformed by NH_3–EtOH at 135—145° into a mixture of β-*ethyl*-Δ^{β}-*pentenoamide*, m.p. 115°, and *Et* β-*amino*-β-*ethylvalerate*, b.p. 96°/13 mm. (*hydrochloride*), and by prolonged action of liquid NH_3 at room temp. into β-*ethyl*-Δ^{α}-*pentenoamide*, m.p. 88°. Prolonged treatment of (I) with NH_2OH–EtOH at 100° leads to β-*amino*-β-*ethyl*-n-*valeric acid* (II), m.p. 184°. β-*Amino*-β-*methyl*-n-*hexoic acid* has m.p. 187°. (II) and PhNCO give β-*phenylureido*-β-*ethylvaleric acid*, m.p. 145°. (II) is converted by aq. KCNO at 100° into 4 : 4-*diethyldihydrouracil*, m.p. 188°, in minimal yield. 4-*Methyl*-4-*propyldihydrouracil* has m.p. 191°. H. W.

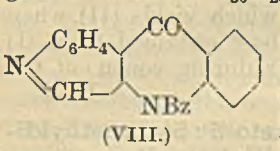
Active iron. IX. Reactions with 2 : 2′-dipyridyl and *o*-phenanthroline.—See A., I, 94.

Preparation of 2-pyridyl-*N*-pyridinium derivatives. Z. Rodewald and E. Płażek (Rocz. Chem., 1936, **16**, 444—450).—C_5H_5N,HCl and ClI are heated for 7 hr. at 250°, the mass is poured into aq. K_2CO_3, and steam-distilled. The residue is filtered and cooled, when 2-*pyridyl*-N-*pyridinium iodide* (I), m.p. 209° (*picrate*, m.p. 136°), is obtained. Alternatively, (I) is prepared from 2-iodopyridine and C_5H_5N,HCl (5 hr. at 240°). (I) and aq. NH_3 (8 hr. at 150°) afford 2-aminopyridine (II). (I) in H_2O and HI afford the *hydriodide* of 2-*pyridyl*-N-*iodopyridinium iodide*, m.p. 99°, which yields (II) when heated with aq. NH_3. The base obtained from (I) and Ag_2O rapidly decomposes during concn. of the solution. R. T.

Derivatives of 3 : 3′-diketo-5 : 5′-dimethyldihydro-2 : 2′-di-indolyl. A. Wróbel (Rocz. Chem., 1936, **16**, 416—423).—Diacetyltartaric anhydride and *p*-toluidine (I) (1—2 hr. at 150°) yield 3 : 3′-*diketo*-5 : 5′-*dimethyldihydro*-2 : 2′-*di-indolyl* (II), m.p. 260° (decomp.). (II) and Br in EtOH afford 2 : 2′ : 3′-*tribromo*-3′-*hydroxy*-3-*keto*-5 : 5′-*dimethyldihydro*-2 : 2′-*di-indolyl* (III), m.p. 221°, which eliminates Br when treated with H_2O, to yield the 2 : 2′-Br_2-derivative of (II), m.p. 74°. A by-product obtained together with (III) is αβ-*di*-p-*tolyliminosuccinyl bromide*, m.p. 227·5°, which with aq. KOH gives (I). Bromination of (II) in AcOH affords 2-(2′-*bromo*-3′-*keto*-5′-*methyl*-2 : 2′-*indolyl*)-3-*keto*-5-*methylindolenine*, m.p. 210°. (II) and HNO_3 afford 3 : 3′-*dinitro*-2 : 3 : 2′ : 3′-*tetrahydroxy*-5 : 5′-*dimethyldihydro*-2 : 2′-*di-indolyl*, decomp. at 230°. R. T.

Derivatives of *Py* : *Py*′-tetrahydrodiquinolyl. A. Wróbel (Rocz. Chem., 1936, **16**, 424—430).—Diacetyltartaric anhydride (I) and *o*-toluidine (2 hr. at 140—150°) afford 3 : 3′-*diketo*-1 : 1′ : 2 : 2′ : 3 : 3′ : 4 : 4′-*tetrahydro*-2 : 2′-*diquinolyl* (II), m.p. 130°, which yields 2 : 3 : 2′ : 3′-*tetrabromo*-3 : 3′-*dihydroxy*-1 : 1′ : 2 : 2′ : 3 : 3′ : 4 : 4′-*tetrahydro*-2 : 2′-*diquinolyl* (III), m.p. 225° (decomp.), when brominated in AcOH. (III) is converted by H_2O into the 2 : 2′-Br_2-derivative, m.p. 48°, of (II). (I) and *o*-4-xylidine (5 hr. at 150°) yield 3-*hydroxy*-3′-*keto*-4-*xylidino*-6 : 6′-*dimethyl*-1 : 1′ : 2 : 2′ : 3 : 3′ : 4 : 4′-*tetrahydro*-2 : 2′-*diquinolyl* (IV), m.p. 173°, which eliminates xylidine when heated with aq. KOH, to afford 3 : 4-*dihydroxy*-3′-*keto*-6 : 6′-*dimethyl*-1 : 1′ : 2 : 2′ : 3 : 3′ : 4 : 4′-*tetrahydro*-2 : 2′-*diquinolyl*, m.p. 221°. (IV) and BzCl (at the b.p.) yield 3 : 3′-*diketo*-6 : 6′-*dimethyl*-1 : 1′ : 2 : 2′ : 3 : 3′ : 4 : 4′-*tetrahydro*-2 : 2′-*diquinolyl*, m.p. 215°. (IV) and Br in EtOH afford 2 : 3 : 2′ : 3′-*tetrabromo*-3 : 3′-*dihydroxy*-4-*xylidino*-6 : 6′-*dimethyl*-1 : 1′ : 2 : 2′ : 3 : 3′ : 4 : 4′-*tetrahydro*-2 : 2′-*diquinolyl*, m.p. 228° (decomp.), converted by adding H_2O to its AcOH or EtOH solutions respectively into 2 : 2′-*dibromo*-3 : 4-*dihydroxy*-3′-*keto*-4-*xylidino*-, m.p. 43°, and 2 : 2′-*dibromo*-4-*hydroxy*-3 : 3′-*diketo*-6 : 6′-*dimethyl*-1 : 1′ : 2 : 2′ : 3 : 3′ : 4 : 4′-*tetrahydro*-2 : 2′-*diquinolyl*, m.p. 43°. R. T.

Benzoyl derivatives of indigotin. III. H. DE DIESBACH and T. DOBBELMAN (Helv. Chim. Acta, 1936, **19**, 1213—1222: cf. A., 1934, 306).—Evidence is adduced in favour of the view that the formation of Dessoulavy's compound (I), Höchst Yellow R (II) and U (III), and Indigo Yellow 3G Ciba (IV) from indigotin (V) and BzCl involves successive ring-closure between the Ph of BzCl and the median C of (V), formation of new rings under the influence of BzCl, and oxidation. Formation of (I) in boiling BzCl uses 4 mols. of BzCl. Di- (VI), but not tetra-benzoyl-indigotin (VII), m.p. 242—243° (modified prep.; 75% yield), gives (I) in boiling BzCl. (VI), BzCl, and a little Cu in $PhNO_2$ at 160° give (II). (VII), BzCl (or p-C_6H_4Cl·COCl or C_5H_{11}·COCl), and a little Cu in $PhNO_2$ or $C_6H_4(NO_2)_2$ (not $C_6H_3Cl_3$) at 160° (not 120°) give a *substance*, $C_{30}H_{20(18)}O_4N_4$, m.p. 384°, which is believed to be (VIII), because with NaOH at 300° it gives *o*-NH_2·C_6H_4·CO_2H (1 mol.) and BzOH (2 mols.), with hot KOH–EtOH it gives *o*-NHBz·C_6H_4·CO_2H and a *substance*, m.p. 190° (? an impure isomeride), with conc. HCl at 200° gives 2 mols. of BzOH and a small amount of another substance, is stable to H_2SO_4 at 200°, and with $AlCl_3$–NaCl at 170° affords (III). (II) and $AlCl_3$–NaCl at 170° give (III). (I), BzCl, and a little Cu in $PhNO_2$ at 150—160° give 20% of (IV), 4 mols. of BzCl being used; in the absence of Cu a mixture of (I) and (II) is obtained; in $C_6H_3Cl_3$ at 160° (II) is formed, but addition of a little $NaNO_2$ or passage of O_2 gives 21—27% of (IV) with little or no (II). R. S. C.


(VIII.)

3 : 4-Pyridopyrazine and a pyridylbenzotriazole. E. KOENIGS, H. BUEREN, and G. JUNG (Ber., 1936, **69**, [*B*], 2690—2695; cf. A., 1924, i, 988).—Reduction of 4-nitroaminopyridine in acid solution affords a complex mixture of bases from which 4-chloro-, 4-amino-, and 4-hydrazino-pyridine have been isolated; there is no evidence of the production of 3 : 4-diaminopyridine (I), m.p. 218—219° (*picrate*, m.p. 235—237°; *platinichloride*, gradual decomp. >200°; Bz_2 derivative, m.p. 222—223°, and its *picrate*, m.p. 251°), which is readily obtained by reduction of 3-nitro-4-aminopyridine by aq. Na_2S at 80°. (I) and glyoxal Na H sulphite (II) in aq. AcOH at 100° give a colourless compound which loses SO_2 when heated giving 3 : 4-pyridopyrazine, $C_5H_3N<^{N:CH}_{N:CH}$, m.p. 100—101° (*picrate*, decomp. 185° after blackening at >130°). (I) and phenanthraquinone in boiling AcOH afford *phenanthra*-3 : 4-*pyridopyrazine*, m.p. 254° after softening (*picrate*, decomp. 262—263° after softening and becoming discoloured). 6-*Chloro*-3 : 4-*pyridopyrazine*, m.p. 138—139° (*hydrochloride*, decomp. >250°), is obtained from (II) and 6-chloro-3 : 4-diaminopyridine. 4-Chloropyridine and p-OMe·C_6H_4·NH_2 at 180° give 4-p-*anisylaminopyridine*, m.p. 172° (*picrate*, m.p. 179°), converted by aq. HNO_3 containing HNO_2 at 100° into 4-2′-*nitro*-4′-*methoxyanilinopyridine*, m.p. 186°, reduced by aq. Na_2S at 70° to 4-2′-*amino*-4′-*methoxyanilinopyridine* (III), m.p. 138°. Diazotisation of (III) in 2*N*-H_2SO_4 leads to 5-*methoxy*-1-4′-*pyridylbenztriazole*, m.p. 165°. H. W.

Absorption of light and tautomerism of uric acids. H. BILTZ (Ber., 1936, **69**, [*B*], 2750—2752).—The optical investigations of Fromherz *et al.* (this vol., 36) do not afford any proof that the acid position of the uric acid ion is at $N_{(9)}$ and do not controvert the author's view, based on chemical observations, that it is at $C_{(8)}$. H. W.

Potentiometric study of flavins.—See A., I, 85.

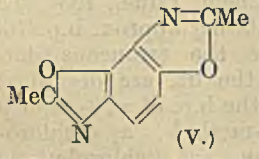
Phthalocyanines. VII. Phthalocyanine as a co-ordinating group. Metallic derivatives. VIII. 1 : 2-Naphthalocyanines. E. F. BRADBROOK and R. P. LINSTEAD (J.C.S., 1936, 1719—1736, 1744—1748).—VII. The prep. and properties of the following derivatives of phthalocyanine are described: *Na_2*, *K_2*, *Ca*, *Be* (+2H_2O), *Mg*, *Zn*, *Cd*, *Ni*, *Pb*, *Co*, *chloroaluminium*, *hydroxoaluminium* (+H_2O), *Sn^{II}* and *Sn^{IV}*, *dichloro-* and *di-iodo-tin*, *Pt^{II}*, *Fe^{II}*, *Mn^{II}*, and *V phthalocyanine*; *Zn*, *Co*, *chloroaluminium* (+2H_2O), *hydroxoaluminium*, and *dichlorotin chlorophthalocyanine*; *Al phthalocyanine oxide*; *K* salt of *dihydroxotin phthalocyanine*; *Sn^{II} phthalocyanine hydrochloride* and *dichlorotin chlorophthalocyanine*. Phthalocyanine acts throughout as a bivalent unit capable of occupying four positions in the co-ordination sphere of a metal. The changes undergone by metallic reagents in their efforts to accomplish the formation of phthalocyanine derivatives from N derivatives of phthalic acid are discussed.

VIII. Only 1 : 2- and 2 : 3-$C_{10}H_6(CN)_2$ yield phthalocyanine-like compounds. The 1 : 2-naphthalocyanines possess a general similarity to the corresponding phthalocyanines but isomerism occurs and isolation of cryst. compounds is difficult. The following are described: *Cu* and *Pb* 1 : 2-*naphthalocyanine*; *Cu chloro*-1 : 2-*naphthalocyanine*; α- and β-*Mg* 1 : 2-*naphthalocyanine* (+H_2O); α- and β-1 : 2-*naphthalocyanine*. F. R. S.

Stereochemistry of metallic phthalocyanines. R. P. LINSTEAD and J. M. ROBERTSON (J.C.S., 1936, 1736—1738).—*X*-Ray measurements on Be, Mn, Fe, and Co phthalocyanines are described. The crystals are closely isomorphous and their mol. dimensions are practically identical; all have centro-symmetrical mols. The stereochemical implications are discussed. F. R. S.

Benzoxazole series. K. FRIES and F. BEYERLEIN (Annalen, 1936, **527**, 71—83).—Benzoxazole, like benziminazole and benzthiazole, is intermediate in character between the benzenoid and naphthoid systems. Nitroresorcinol is heated in Ac_2O containing Co–Ni–Cu under H_2 at high pressure at 150°, the product is treated with anhyd. NaOAc, and the acetamidoresorcinol is heated until Ac_2O ceases to be evolved, thereby giving 5-hydroxy-1-methylbenzoxazole (I) in about 70% yield. Chlorination of (I) in AcOH at room temp. affords 6-*chloro*-5-*hydroxy*-1-*methylbenzoxazole* (II), m.p. 211°, or, if more Cl_2 is used, 4 : 6-*dichloro*-5-*hydroxy*-1-*methylbenzoxazole* (III), m.p. 185°; further chlorination causes separation of NH_4Cl. Even with >2 Br 4 : 6-*dibromo*-5-*hydroxy*-1-*methylbenzoxazole* (IV), m.p. 202°, is formed in AcOH containing NaOAc. Nitra-

tion of (I) in AcOH at room temp. yields 4 : 6-*dinitro*-5-*hydroxy*-1-*methylbenzoxazole*, m.p. 208° (decomp.). Nitration of (II) and (IV) proceeds in the same manner as with benzenoid systems, giving 6-*chloro*-4-*nitro*-5-*hydroxy*-1-*methylbenzoxazole*, m.p. 247° (decomp.) (*Na* salt), also obtained from (IV), and 6-*bromo*-4-*nitro*-5-*hydroxy*-1-*methylbenzoxazole*, m.p. 238°. (I) couples with diazotised *p*-$NH_2 \cdot C_6H_4 \cdot SO_3H$ to 5-*hydroxy*-1-*methylbenzoxazole*-6-*azobenzene*-p-*sulphonic acid* (*Na* salt), reduced by $Na_2S_2O_4$ in 2*N*-Na_2CO_3 to 6-*amino*-5-*hydroxy*-1-*methylbenzoxazole*, m.p. 163°. This is transformed by boiling Ac_2O and subsequent heating at 210° into 2′ : 2″-*dimethyl*-1 : 2 : 5 : 6-*benzo*-5′ : 4′ : 5″ : 4″-*dioxazole* (V), m.p. 109°. 4 : 6-Diacetamidoresorcinol diacetate passes at 320° into lin-2′ : 2″-*dimethyl*-1 : 2 : 4 : 5-*benzo*-5′ : 4′ : 4″ : 5″-*dioxazole* (VI), m.p. 143°. (VI) is more readily hydrolysed than (V) by dil. acids and the heat of combustion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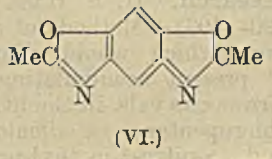
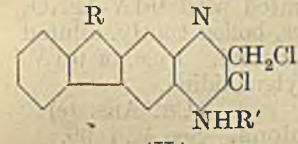
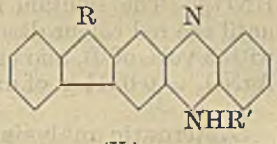

(VI.)

of (V) is about 1·3 kg.-cal. per mol. > that of (VI). Nitrohydroxyquinol triacetate is converted by treatment with H_2 under high pressure at 150° in Ac_2O containing Co–Ni–Cu followed by anhyd. NaOAc into the *Ac*$_4$, m.p. 188°, and *Ac*$_5$, m.p. 136°, derivatives of 2 : 4 : 5-trihydroxyaniline; the mixture passes at 250° into 4 : 5-*dihydroxy*-1-*methylbenzoxazole*, m.p. 231° after darkening at 225° (*diacetate*, m.p. 103°), which could not be oxidised to an *o*-quinone by HNO_3, CrO_3, PbO_2, or Ag_2O. 3 : 6-*Dibromo*-4 : 5-*dihydroxy*-1-*methylbenzoxazole*, m.p. 188° (*hydrobromide*), does not yield an *o*-quinone. H. W.

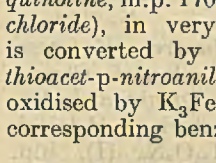
Synthesis of nitrogen-containing polycyclic compounds. I. C. Feldman (J. Gen. Chem. Russ., 1936, **6**, 1234—1242).—2-Aminodiphenylene oxide (I) and $CH_2Cl \cdot COCl$ yield 2-*chloroacetamido*-*diphenylene oxide* [-*dibenzfuran*], m.p. 162—164°, converted by treating with PCl_5 and $POCl_3$ into the *substance* (II) (R = O, R′ = 2-dibenzfuryl), m.p. 240—242°. The corresponding *substance* (II) (R = CH_2, R′ =


(II.)


(V.)

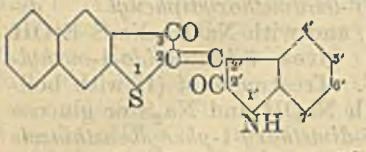
2-fluorenyl), m.p. 238—239°, is obtained similarly from 2-*chloroacetamidofluorene* (III), m.p. 183—185°. (I) and pimelyl dichloride (IV) yield the *di*-2-*diphenylene oxide* derivative of *pimelamide*, m.p. 264—265°, which is condensed as above to afford the *substance* (V) (R = O, R′ = 2-dibenzfuryl), m.p. >300°, and similarly the 2-*fluorenyl* derivative of *pimelamide*, m.p. >300° [from (III) and (IV)] gives the *substance* of formula (V) (R = CH_2, R′ = 2-fluorenyl). R. T.

Benzthiazole. K. Fries and A. Wolter (Annalen, 1936, **527**, 60—71).—Benzthiazole represents a transitional stage between a benzenoid and naphthoid system. 4-Bromo-5-nitroveratrole is converted by Na_2S–S in boiling EtOH into 2 : 2′-*dinitro*-4 : 4′ : 5 : 5′-*tetramethoxydiphenyl disulphide*, m.p. 227°, transformed by the successive action of Sn–HCl and BzCl into 5-*benzamido*-4-*benzoylthiolveratrole*, m.p. 153°, which with conc. H_2SO_4 at room temp. affords 2 : 2′-*dibenzamido*-4 : 4′ : 5 : 5′-*tetramethoxydiphenyl disulphide* (I), m.p. 175°, and with NaOH–Na_2S–EtOH followed by Me_2SO_4 gives 5-*benzamido*-4-*methylthiolveratrole*, m.p. 87°. Treatment of (I) with boiling HCl–AcOH or with NaOH and Na_2S or glucose in EtOH leads to 4 : 5-*dimethoxy*-1-*phenylbenzthiazole* (II), m.p. 152° [*monohydrochloride*, m.p. 180° (decomp.), decomposed by cold H_2O into (II); *trihydrochloride*, m.p. 244° (decomp.), which gives (II) by long treatment with boiling H_2O]. (II) is demethylated by boiling 60% H_2SO_4 to 4 : 5-*dihydroxy*-1-*phenylbenzthiazole*, m.p. 292° (*Ac*$_2$ derivative, m.p. 154°), which could not be oxidised to an *o*-quinone by HNO_3, CrO_3, PbO_2, Ag_2O, $Pb(OAc)_4$, or I and is converted by Br in boiling AcOH into 3 : 6-*dibromo*-4 : 5-*dihydroxy*-1-*phenylbenzthiazole*, m.p. 195° (*diacetate*, m.p. 214°), from which an *o*-quinone could not be derived. 4-Nitro-1-methylbenzthiazole, m.p. 139°, obtained from 4-nitro-2-aminothiophenol and Ac_2O or, preferably, by the action of Na_2S–S on 2-bromo-5-nitroacetanilide in boiling EtOH, is reduced by Sn and fuming HCl in presence of EtOH to 4-*amino*-1-*methylbenzthiazole* (III), m.p. 102° (*Ac* derivative, m.p. 157° or m.p. 125° and m.p. 156° after re-solidification if crystallised from EtOH), which could not be condensed with PhCHO. Chlorination of (III) in AcOH containing HCl followed by treatment with $SnCl_2$–AcOH leads to 3 : 5 : 6-*trichloro*-4-*hydroxy*-1-*methylbenzthiazole*, m.p. 158° (*acetate*, m.p. 92°), oxidised by HNO_3 (*d* 1·4) in AcOH at 100° to 5 : 6-*dichloro*-1-*methylbenzthiazole*-3 : 4-*quinone* (IV), m.p. 178°, which with *o*-$C_6H_4(NH_2)_2$ gives a *quinoxaline* derivative, m.p. 270°. (IV) is reduced by SO_2 to 5 : 6-*dichloro*-3 : 4-*dihydroxy*-1-*methylbenzthiazole*, m.p. 225° (*diacetate*, m.p. 176°). (III) passes by Skraup's reaction into 2′-*methyl*-4′ : 5′-*thiazolo*-5 : 6-*quinoline* (V), m.p. 108° (*sulphate*; *hydrochloride*; double *compound* with $HgCl_2$); the corresponding *methiodide*, decomp. 265° after darkening at 250°, is oxidised by $K_3Fe(CN)_6$ in alkaline solution to 2-*keto*-2′-*methyl*-4′ : 5′-*thiazolo*-1-*methyl*-1 : 2-*dihydro*-5 : 6-*quinoline*, m.p. 217°. 3-*Chloro*-4-*acetamido*-1-*methylbenzthiazole*, m.p. 154°, is hydrolysed by boiling conc. HCl to 3-*chloro*-4-*amino*-1-*methylbenzthiazole*, m.p. 124°, which is converted into 8-*chloro*-2′-*methyl*-4′ : 5′-*thiazolo*-6 : 7-*quinoline*, m.p. 170° (*hydrochloride*; unstable *mercurichloride*), in very small yield. Acet-*p*-nitroanilide is converted by P_2S_5–K_2S in boiling PhMe into *thioacet*-p-*nitroanilide*, m.p. 175°, which could not be oxidised by $K_3Fe(CN)_6$ in alkaline solution to the corresponding benzthiazole. H. W.


(V.)

Dyes derived from isatin. Azines and indigoid vat dyes. S. K. Guha and H. Basu-Mallick (J. Indian Chem. Soc., 1936, **13**, 571—574).—Isatin when boiled with 2 : 3-diaminoacenaphthene in AcOH yields *acenaphthenoindazine*, m.p. >310°. *Ace-*

naphtheno-5-nitro- and *-5 : 7-dinitro-indazine* (both sublime above 310°) were similarly prepared from the appropriate substituted isatin. These azines dye wool various shades of yellow. The following compounds were prepared by treating 4 : 5-benzo-oxythionaphthen and the appropriate substituted isatin in boiling AcOH with a little conc. HCl : *5-iodo-*, *5-bromo-7-nitro-*, and *5 : 7-dinitro-3-(4′ : 5′-benzo-oxythionaphthylidene)oxindole*. They melt above 395°, form deep yellow vats, and dye cotton various shades of violet. The general formula is annexed. H. G. M.



Tobacco alkaloids. IX. Syntheses of *l*- and *d*-nornicotine. E. Späth and F. Kesztler (Ber., 1936, **69**, [*B*], 2725—2727).—Successive treatments of *r*-nornicotine in MeOH with *l*- and *d*-6 : 6′-dinitro-2 : 2′-diphenic acid and purification of the crude optically active bases through their perchlorates lead to *l*- and *d*-nornicotine. H. W.

Synthesis of local anæsthetics from cytisine. H. R. Ing and R. P. Patel (J.C.S., 1936, 1774—1775).—Cytisine and $(CH_2)_2O$ give N-β-*hydroxyethylcytisine* (+H_2O), m.p. 73—74°, which with the appropriate reagent affords β-*cytisinoethyl benzoate*, m.p. 247—248° (decomp.), and *cinnamate hydrobromides*, m.p. 246—247° (decomp.). γ-Chloropropyl benzoate, NaI, and cytisine, followed by KBr, yield *γ-cytisinopropyl benzoate hydrobromide*, m.p. 232—233° (decomp.), and *hydrobromides* of the following have been similarly prepared: cinnamate, m.p. 224—225° (decomp.), phenylcarbamate, m.p. 225—226° (decomp.), α-naphthylcarbamate, m.p. 237—238°, *p*-nitrobenzoate, m.p. 255—256°, *p*-aminobenzoate (I), m.p. 236—237°. p-*Cytisinoethyl* p-*nitrobenzoate*, m.p. 103—104° (*hydrobromide*, m.p. 232—233°), and *γ-cytisinopropyl α-naphthylcarbamate*, m.p. 159°, are also described. All except (I) possess local anæsthetic properties. F. R. S.

Alkaloids of fumariaceous plants. XI. Two new alkaloids, corlumine and corlumidine, and their constitutions. R. H. F. Manske (Canad. J. Res., 1936, **14**, B, 325—327).—*Corydalis scouleri* (I) and *sibirica* and *Dicentra cucullaria* contain *corlumine* (II), m.p. 158°, which is stereoisomeric with adlumine, since it is hydrolysed to lodal and 3 : 4 : 2-CH_2O_2·$C_6H_2(CO_2H)$·CHO (best identified by conversion by aq. alkali into 3 : 4-methylenedioxy-phthalic acid and -phthalide). (I) contains also *corlumidine*, m.p. 236° [a phenolic base, converted into (II) by CH_2N_2], and 2 : 9-dihydroxy-3 : 10-dimethoxytetrahydroprotoberberine. R. S. C.

Alkaloid from *Equisetum palustre*. E. Glet, J. Gutschmidt, and P. Glet (Z. physiol. Chem., 1936, **244**, 229—234).—The plant yields a *hydrocarbon*, $C_{21}H_{42}$, m.p. 77° and a mixture of H_2O-sol. bases, including *palustrine*, $C_{12}H_{24}O_2N_2$ (I), b.p. 205—210°/0·1 mm. (*hydrochloride*, m.p. 181°). Shoots collected in June contain 0·95% of their dry wt. of (I). W. McC.

Solanidine-*t* and -*s*. H. Rochelmeyer (Arch. Pharm., 1936, **274**, 543—545).—Dehydrogenation of solanidine-*t* (cf. A., 1936, 216) and (probably) -*s* (Se; 320°) gives methyl*cyclo*pentanophenanthrene. R. S. C.

Organic magnesium compounds. III. Lead tris-*m*-tolyl. IV. Reaction between alkyl *p*-toluenesulphonates and RO·Mg·X. K. Mine (J. Chem. Soc. Japan, 1934, **55**, 1168—1173).—III. $Pb(C_6H_4Me\text{-}m)_3$ is prepared from *m*-C_6H_4Me·MgBr and $PbCl_2$.

IV. The reaction is $2C_6H_4Me\cdot SO_3R' + 2RO\cdot MgX \rightarrow (C_6H_4Me\cdot SO_3)_2Mg + (RO)_2Mg + 2R'X$. Ch. Abs. (*r*)

Base–protein–acid compounds.—See A., III, 56.

Estimation of b.p. as an aid in organic research. H. B. Hass (J. Chem. Educ., 1936, **13**, 490—493).—Methods of calculating approx. b.p./760 mm. which would eliminate the erroneous data at present accumulating in the lit. are described. Erroneous vals. in the lit. for the b.p. of α-, β-, and γ-chloropentane, αγ-dichloro-β-methyl-, αγ-dichloro-, and α-nitro-β-methyl-propane, αδ-dichlorobutane, and Δ^{α}-pentene are corr. L. S. T.

New heating vessel for the Pregl microdesiccator. Jenaer Glaswerk, Schott u. Gen. (Mikrochem., 1936, **21**, 131—132).—The heating reservoir of the apparatus is formed by an annular glass space, heating being carried out through the centre. J. W. S.

Determination of diphenylguanidine. S. Minatoya, T. Ebe, and I. Aoe (J. Soc. Rubber Ind. Japan, 1935, **8**, 328—337).—A 0·5-g. sample is heated on a water-bath under reflux for 20 hr. with 0·2 g. of CaO, 30 c.c. of abs. EtOH, and 3 c.c. of CS_2. The product is added to 250 c.c. of hot H_2O and evaporated to dryness. To the residue are added 30 c.c. of a solution (*A*) of 5 g. of Fe in 60 c.c. of conc. HNO_3, which has been evaporated to a syrup and diluted to 500 c.c. $Fe(CNS)_3$ is formed. The product is heated gently, and made up to 100 c.c. by solution *B* (500 c.c. of H_2O + 30 c.c. of solution *A* and 5 c.c. of conc. HNO_3). The solution is titrated with 0·1*N*-$AgNO_3$ until the red colour disappears, boiled gently, diluted with 3 vols. of *B*, and again titrated. 1 c.c. of 0·1*N*-$AgNO_3$ = 0·0211 g. of diphenylguanidine. Ch. Abs. (*e*)

Systematic analysis of anions.—See A., I, 96.

Reactions with nitroprusside of reduced glutathione, cysteine, acetone, and creatinine.—See A., III, 8.

Preparation of extremely pure liquids. W. Swientoslawski (Svensk Kem. Tidskr., 1936, **48**, 257—265).—The liquid is distilled up seven fractionating columns in cascade at a measured rate. The degree of purity is shown at each stage by the difference between the ebullition and condensation temp. The distribution of impurities is discussed. M. H. M. A.