BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1937.

Changes of configuration during reactions at singly and doubly bound carbon atoms. E. BERGMANN [with Y. SPRINZAK] (Helv. Chim. Acta, 1937, **20**, 590—621).—If a polar mol. C–X reacts with a negatively-charged ion Y the latter approaches the dipole C–X at the positive side and reacts with expulsion of X as negative ion: $Y' + CRR'R''\cdot X \rightarrow Y\cdot CRR'R'' + X'$. Spatially therefore Y occupies a position of the tetrahedron diametrically opposite to that of the substituent X; a Walden transformation occurs. Conversely a positive ion approaches the polar linking from the negative side, giving a neutral mol. and a positive carbonium radical which becomes stabilised with maintenance of configuration if the stability of the configuration within it is great and with partial or complete racemisation if the stability is small; a Walden inversion never occurs. From this viewpoint the following instances of racemisation have been investigated: CHMeBuBr by LiBr in abs. EtOH; $CO_2Me\cdot CHCl\cdot CH_2\cdot CO_2Me$ by LiCl in abs. $COMe_2$; $CO_2Me\cdot CHBr\cdot CH_2\cdot CO_2Me$ by LiBr in $COMe_2$; CHMeBuI by NaI in $COMe_2$ and binary solvents containing $COMe_2$. The conception of racemisation as a substitution process is strengthened by the similarity of the change with other bimol. reactions of the type $C–X + Y' \rightarrow CY + X'$, by analogy in the behaviour of I′ towards C·I and towards C·F, C·Cl, and C·Br, by the identity in the rate of substitution in the systems, org. iodide + radioactive I′ and optically active org. iodide + I′, and by the influence of the medium on the reaction. It follows, therefore, that the reaction between an optically active halide and the salt of an org. acid must be accompanied by a Walden inversion whereas the esterification of an optically active alcohol occurs without configurational change. Inversion also accompanies the reaction between optically active halide and sodiomalonic esters or metal alkyls. Instances of positive mechanism are discussed. The addition of halogen to the ethylenic linking is represented: $Br' + C{:}C \rightarrow Br\cdot C\cdot C^-$ and $Br\cdot C\cdot C^- + Br \rightarrow BrC\cdot CBr + Br'$... or $Br^+ + C{:}C \rightarrow BrC\cdot C^+$ and $BrC\cdot C^+ + Br_2 \rightarrow BrC\cdot CBr + Br^+$.... Reactions appear to occur according to both schemes; the negative mechanism converts *cis–trans* isomeric ethylenes into epimeric halides whereas positive mechanism leads either to one form of the additive product or to a mixture of both. Both mechanisms explain diene addition: $Br^- + C{:}C\cdot C{:}C \rightarrow BrC\cdot C^-\cdot C{:}C$ (I); (I) + $Br_2 \rightarrow CBr\cdot CBr\cdot C{:}C + Br^-$ and $Br^- + C{:}C\cdot C{:}C \rightarrow BrC\cdot C{:}C\cdot C^-$ (II), (II) + $Br_2 \rightarrow BrC\cdot C{:}C\cdot CBr + Br^-$. A third mechanism, $Br + C{:}C \rightarrow BrC\cdot C\cdots$ (III); (III) + $Br_2 \rightarrow CBr\cdot CBr + Br$, involves uncharged radicals and is applicable to the halogenation of gaseous ethylenes in light. All methods differ in the mechanism from catalytic hydrogenation, which is due to mol. H_2 and is characterised by *cis*-addition and 1 : 2 not 1 : 4 reaction in the case of dienes. Addition of halogen is never a mol. reaction; it does not take place by simple opening of a linking and addition at the liberated valency (*cis*-reaction) but is accompanied by isomerisation (*trans*-addition). Reduction of an ethylene with nascent H has the same characteristics as bromination with Br atoms; the intermediate product can be the carrier of a *cis–trans* isomerisation. The following compounds appear new: *α-methylamyl bromide*, b.p. 143—144°, and its optically active *isomeride*, $[\alpha]_D$ +20·1° in $COMe_2$; *Me*$_2$ (−)-*bromosuccinate*, b.p. 87°/2·5 mm., $[\alpha]_D$ −58·5° in $COMe_2$; *Et*$_2$ *α-phenylethylmalonate*, b.p. 138°/1·5 mm., $[\alpha]_D$ −6·55°; *α-phenylethylmalonic acid*, m.p. 142—143°; *β-phenylbutyric acid*, b.p. 140—141°/2 mm.; (+)-*phenylmethylcarbinyl acetate*, b.p. 104—105°/23 mm., $[\alpha]_D$ +6·44°, from (−)-CHPhMeCl and AgOAc or NaOAc; *phenylmethylcarbinyl Et ether*, b.p. 74—76°/23 mm., $[\alpha]_D$ −25·2° in $COMe_2$; (+)-*β-chloro-Δ*$^{\gamma}$*-pentene*, $[\alpha]_D$ +3·0° in Et_2O; (−)-*Δ*$^{\gamma}$*-penten-β-ol*, $[\alpha]_D$ −3·1°; (−)-*β-chloro-Δ*$^{\gamma}$*-pentene* (IV), $[\alpha]_D$ −5·4° in Et_2O; *αα-diphenyl-β-methyl-Δ*$^{\gamma}$*-pentene*, b.p. 174°/20 mm., $[\alpha]_D$ ±0° in Et_2O or EtOH [from (IV) and $CHPh_2Na$]; *β-benzhydrylpentane*, b.p. 160—162°/14 mm.; *Et*$_2$ *β-Δ*$^{\gamma}$*-pentenylmalonate*, b.p. 130°/20 mm., $[\alpha]_D$ ±0°; *β-methyl-Δ*$^{\gamma}$*-hexenoic acid*, b.p. 109—110°/15 mm.; *β-methylhexoic acid*, b.p. 116°/15 mm.

H. W.

Selectivity of iodic acid in the oxidation of organic compounds. R. J. WILLIAMS and M. A. WOODS (J. Amer. Chem. Soc., 1937, **59**, 1408—1409).—With KIO_3 in 40% H_2SO_4 (the liberated I being removed by steam and the remaining KIO_3 titrated), the following are oxidised (using <4 equivs. of KIO_3 per mol.): aliphatic alcohols (up to C_8) except MeOH, polyhydric alcohols with non-adjacent hydroxyls, aliphatic and aromatic aldehydes, $COMe_2$, COMeEt, and COPhMe, fructose, sorbose, sucrose, *d*-arabinose, *l*-xylose, and rhamnose, phenols and their ethers, and NH_2Ph derivatives. The following are unaffected: polyhydric alcohols with adjacent hydroxyls, $COPh_2$, benzil and benzoin, aliphatic and aromatic acids, unsaturated and α-OH-acids, protein NH_2-acids except cystine, tyrosine, and tryptophan, and aldohexoses.

A. LI.

Kinetics and mechanism of decomposition of hydrocarbons. IV. Influence of pressure on the velocity and direction of decomposition of

ethane. A. I. Dintzes, V. R. Sharkova, A. V. Sherko, and A. V. Frost (J. Gen. Chem. Russ., 1937, **7**, 1063—1070).—C_2H_6 decomposes at 635° as follows: $2H + 2C_2H_4 \leftarrow 2C_2H_6 \rightarrow 2CH_4 + C_2H_4$; the latter reaction is favoured by increasing pressure from 1 to 26 atm. R. T.

Pyrolysis of ethane.—See A., I, 466.

Unimolecular olefine formation from alkyl halides.—See A., I, 467.

Mechanism of substitution at a saturated carbon atom. VII—X.—See A., I, 467.

Dielectric constant and molecular size of duprene and rubber hydrochloride.—See A., I, 397.

Alkyl acetylenes and their addition compounds. XIX. Preparation and alkylation of metal acetylides in liquid ammonia. T. H. Vaughn, G. F. Hennion, R. R. Vogt, and J. A. Nieuwland (J. Org. Chem., 1937, **2**, 1—22).—Prep. of metal acetylides by passing C_2H_2 into a solution of the metal in liquid NH_3 is very slow. It is difficult to determine the end-point if the metal amide is used. C_2H_2 at 100—250 lb. per sq. in. acts rapidly but dangerously. The best method of prep. is to pre-cool the NH_3 by evaporation by a rapid stream of C_2H_2, thus obtaining a cold conc. solution, and to add thereto the metal in liquid NH_3 with stirring without allowing the bulk of the solution to become blue. 5 mols. of Na are thus converted into $NaHC_2$ in 40 min. KHC_2, CaH_2C_4, and BaH_2C_4 are similarly prepared. The Ca and, more so, Ba salts are unstable, the latter not being obtained pure. Thus prepared, the salts contain a little oxide and hydroxide and (?) traces of amide. The interaction of these salts with alkyl halides and sulphates at room temp./100—250 lb. per sq. in., about −34°/1 atm., and about −34°/25 lb. per sq. in., in 2, 12, and 30 g.-mol. batches is described and modifications of the methods are discussed. Yields varied from 0 to 100%, but were usually ≪ theoretical. Much of the loss is proved to be due to entrainment during removal of the solvent NH_3 and is avoidable by a modified procedure. For Me and Et, sulphates give the best crude yields of Δ^{α}-alkinenes, but bromides are generally preferable as they react more rapidly than chlorides and give smaller amounts of amines than do iodides or sulphates. The nature of the metal is relatively unimportant, but for the prep. of $C_5H_{11}\cdot C{:}CH$ under comparable conditions yields are K 54, Na 50, Ba 41, and Ca 31. The alkinene obtained is difficult to free from small amounts of halide, particularly the bromide. Other products formed and more easily removed are olefines (traces only of C_2H_4, 8—20% of Δ^{α}-pentene; *cyclo*hexyl bromide gives moderate yields of *cyclo*hexene and no $C_6H_{11}\cdot C{:}CH$), amines (formed particularly from the chlorides and at room temp.; removed by washing first with dil. HCl and then with H_2O), C_2H_2 (2—17%), alcohols (1—10%) and ethers (1—5%) (formed by traces of NaOH thus: $NaOH + RX \rightarrow ROH$; $ROH + NaHC_2 \rightarrow C_2H_2 + RONa$; $RONa + RX \rightarrow R_2O + NaX$), dialkylacetylenes R_2C_2, and probably $CH{:}C\cdot CMe_2\cdot OH$ (derived from $COMe_2$ in the C_2H_2). R_2C_2 are formed by way of $CR{:}CNa$, and not Na_2C_2; the isolation of $CR{:}CNa$ and its reaction with alkyl halides and sulphates to give $CR{:}CR'$ in fair yields are described. Δ^{ϵ}-*Decinene*, b.p. 105·2—105·8°/79 mm., 172°/745 mm., Δ^{ζ}-*dodecinene*, b.p. 97—98°/16 mm., 209°/745 mm., Δ^{β}-*heptinene*, b.p. 107—111°/750 mm., Δ^{δ}-, b.p. 130·4—130·6°/745 mm., Δ^{γ}-, b.p. 127—130°/750 mm., and Δ^{β}-*octinene*, b.p. 131—135°/750 mm., Δ^{δ}-, b.p. 150—154°/750 mm., and Δ^{γ}-*noninene*, b.p. 150—154°/750 mm., are described (*n* and *d* given). The possibility of wandering of the acetylenic linking, particularly at the higher temp., is discussed. R. S. C.

Dialkylacetylenes. E. A. Bried and G. F. Hennion (J. Amer. Chem. Soc., 1937, **59**, 1310—1311).—The following dialkylacetylenes were prepared by slowly adding the alkyl bromide to a well-stirred mixture of C_2Na_2, NH_2Na, and liquid NH_3: Et_2-, b.p. 81·5°/744 mm., Pr^{α}_2-, b.p. 130°/744 mm., Bu^{α}_2-, b.p. 115·9°/115 mm., *diamyl*-, b.p. 115°/30 mm.; and *ethylbutyl*-, b.p. 131·8°/737 mm., by successively adding BuBr, NH_2Na in liquid NH_3 (after 3 hr.), and EtBr (after ½ hr.) to a solution of C_2Na_2 in liquid NH_3. A. Li.

Rearrangements of polyacetylenes. X. Rearrangement product of hexa*tert.*-butylacetylenylethane. W. J. Sparks, W. J. Peppel, and C. S. Marvel (J. Amer. Chem. Soc., 1937, **59**, 1351—1352).—Hexa*tert.*-butylacetylenylethane, when heated in EtOH, isomerises to a compound (I) {*dibromide*, m.p. 169—170° [reconverted by KOH into (I)], *dichloride*, m.p. 161°}, rapidly reduced (PtO_2–Pt-black) to a viscous *hydrocarbon*, $C_{38}H_{70}$ (corresponding with a reduction of 4 triple linkings), which can absorb 8 Br per mol.; similar reduction of $(CBu^{\gamma}{:}C)_3C\cdot OH$ yields *tri*-(*γγγ-trimethyl*-n-*propyl*)-*carbinol*, m.p. 44—45°. Oxidation of (I) with O_3 followed by H_2O_2 affords $Bu^{\gamma}CO_2H$, whilst CrO_3 gives an oxidation product apparently identical with that of the dimeride of $(CBu^{\gamma}{:}C)_3CCl$. These facts suggest that (I) is the diallene $[(CBu^{\gamma}{:}C)_2C{:}C{:}CBu^{\gamma}\cdot]_2$. A. Li.

Hydrolysis and alcoholysis of alkyl halides.—See A., I, 417.

Fluorinated derivatives of methane. A. L. Henne (J. Amer. Chem. Soc., 1937, **59**, 1400).—The b.p. of the following have been accurately determined: $CHCl_2F$, 8·9—9·0°, $CHClF_2$, −40·8° to −40·6°, CH_2ClF, −9·0° to −9·1°, CH_2F_2, −51·6°. The difluorides are chemically and physiologically inert, but the monofluorides give the usual halide reactions (with difficulty) and are weak anæsthetics. A. Li.

Fluoroform. A. L. Henne (J. Amer. Chem. Soc., 1937, **59**, 1200—1202).—CHF_3, prepared by warming $CHBr_3$ with Br and excess of SbF_3 at 4 atm., and treating the resulting $CHBrF_2$, after purification, with HgF_2 (at 12 atm., cooled in solid CO_2), is chemically and physiologically inert, but reacts with F_2 at room temp., Cl_2 in bright sunlight, or CaO at red heat. A. Li.

Fluorocarbons. J. H. Simons and L. P. Block (J. Amer. Chem. Soc., 1937, **59**, 1407).—Fractionation of the reaction mixture of C and F_2 yields CF_4, C_2F_6, C_3F_8, f.p. −183°, b.p. −36°, C_4F_{10}, f.p. −84·5°, b.p.

4°, C_5F_{12}, f.p. −10°, b.p. 30°, and C_6F_{14}, f.p. −4°, b.p. 60°, identified by their mol. wts. A. Li.

Reaction kinetics and Walden inversion. I. Homogeneous hydrolysis and alcoholysis of β-*n*-octyl halides. E. D. Hughes, C. K. Ingold, and S. Masterman. **II. Homogeneous hydrolysis, alcoholysis, and ammonolysis of α-phenylethyl halides.** E. D. Hughes, C. K. Ingold, and A. D. Scott. **III. Homogeneous hydrolysis and alcoholysis of α-bromopropionic acid, its ester and anion.** W. A. Cowdrey, E. D. Hughes, and C. K. Ingold. **IV. Action of silver salts in hydroxylic solvents on β-*n*-octyl bromide and α-phenylethyl chloride.** E. D. Hughes, C. K. Ingold, and S. Masterman. **V. Action of silver salts in hydroxylic solvents on α-bromopropionic acid, its methyl ester, and sodium salt.** W. A. Cowdrey, E. D. Hughes, and C. K. Ingold. **VI. Relation of steric orientation to mechanism in substitutions involving halogen atoms and simple or substituted hydroxyl groups.** W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott (J.C.S., 1937, 1196—1201, 1201—1208, 1208—1236, 1236—1243, 1243—1252, 1252—1271).—I. Evidence showing that β-*n*-octyl alcohol, chloride, bromide, and iodide with the like sign of rotation have corresponding configurations is summarised. Hydrolysis of the bromide by *N*-KOH in 60 vol.-% aq. EtOH at the b.p. yields inverted alcohol of high optical purity, mainly by a bimol. reaction. In absence of KOH (0—0·3*N*-HBr) hydrolysis takes place exclusively by a unimol. mechanism ($RBr \rightarrow R^{\cdot} + Br'$), yielding an inverted product of lower optical purity. Inversion also occurs in the alcoholysis (with NaOEt) of both the bromide and chloride. The unimol. mechanism involves much more racemisation than does the bimol. Optically pure β-*n*-octyl bromide is calc. to have $[\alpha]_D^{20}$ 33·8°.

II. Hydrolysis of CHPhMeCl in H_2O or aq. $COMe_2$, whether in presence of KOH or of HCl, is exclusively unimol., and yields an inverted product of low optical purity. Alcoholysis by MeOH or EtOH gives a similar result, whereas if brought about by Na alkoxides the reaction is chiefly bimol. and gives an ether with inverted configuration and high optical purity. Inversion also occurs in ammonolysis. In the unimol. hydrolysis racemisation increases as the H_2O is diluted with inert $COMe_2$.

III. Hydrolysis of $CHMeBr{\cdot}CO_2H$ in dil. aq. H_2SO_4 is bimol. (though experimentally of first order) and yields an inverted product of high optical purity. A similar result is obtained in the methoxylation of the Me ester. Substitution of OH or OMe in the anion is bimol. when effected by OH′ or OMe′, but unimol. when effected by H_2O or MeOH. In the former case there is approx. complete inversion, whilst in the latter the original configuration is retained.

IV. Substitution of OH and OEt in $C_8H_{17}Br$ in aq. EtOH by means of Ag_2O, $AgNO_3$, or AgOAc, and of OH in CHPhMeCl by Ag_2O leads in every case to products with inverted configuration. The main difference is that in the heterogeneous reactions the retention of optical purity is > that in the homogeneous unimol. reactions. In hydrolysis of CHPhMeCl racemisation increases markedly on diluting the H_2O with $COMe_2$.

V. Experiments similar to those described in (III), but using Ag_2O, $AgNO_3$, and Ag_2CO_3, show inversion to be the predominant effect with the Me ester and a substituted amide of $CHMeBr{\cdot}CO_2H$, and retention of the original configuration with the anion. Racemisation occurs in all cases. In all these reactions, including those of (IV), the reagent is $Ag^{\cdot}$ adsorbed on AgBr, Ag_2O, or both.

VI. General principles relating to the orientation of substitution, in the case of reciprocal replacements of halogen and OR, are advanced. F. L. U.

Dehalogenation of organic iodo-compounds by hydrogenation in alkaline medium; simple determination of small quantities of organic iodine. J. A. Gautier (Bull. Soc. chim., 1937, [v], 4, 219—225).—Many org. I-compounds are readily and completely dehalogenated by boiling with Zn and about *N*-NaOH, or Zn and *N*-KOH–EtOH if insol. in aq. NaOH. On neutralisation the excess of Zn is pptd. as hydroxide which carries with it some of the decomp. products. The I (as ZnI_2) is best determined by the method of Bernier *et al.* (A., 1911, ii, 435). Good results are obtained with aliphatic and aromatic compounds, except with certain iodinated oils the hydrogenation products of which are difficult to filter, but heterocyclic I-compounds are not completely dehalogenated by this method. H. G. M.

Hydrolysis of carbon tetraiodide. M. S. Kharasch, W. G. Alsop, and F. R. Mayo (J. Org. Chem., 1937, 2, 76—83).—CI_4 is stable in EtOH, MeOH, Bu$^{\gamma}$OH, C_6H_6, $CHCl_3$, etc. in absence of O_2. In presence of O_2, it decomposes at various rates in these solvents, but, presumably because of its insolubility, not in H_2O or aq. KOH. KOH–MeOH decomposes both CI_4 and CHI_3. CaO– and NaOPh–MeOH decompose CI_4, but not CHI_3; with these reagents CI_4 gives I′, but no CHI_3, which is thus not a decomp. product of CI_4. CI_4 is destroyed by KOH–aq. MeOH–O_2; the amount of I formed depends on the amount of KOH, with 6 mols. of KOH no I, but much I′, and with 1 mol. much I and little I′, being obtained. There is thus no evidence for the existence of "positive I" in CI_4 or other iodomethanes; reports to the contrary are due either to the physical resemblance of CHI_3 and recovered CI_4 or to the fact, established by a series of experiments, that the presence of traces of CH_2O or MeCHO in aq. EtOH–KOH may lead to formation of large amounts of CHI_3. Exact duplication of results is not anticipated, as the rates of decomp. are probably affected also by the age and purity of the CI_4, peroxide content of the solvent and aldehyde, temp., illumination, and agitation. R. S. C.

Thermal decomposition of ethylene dibromide.—See A., I, 466.

Determination of unsaturation of chloroprene polymerides. II. A. L. Klebanski and M. Rachlina (J. Gen. Chem. Russ., 1937, 7, 1299—1305).—Theoretical vals. are obtained for the I vals. of chloroprene rubber in CCl_4, using a 140% excess of ClI, also in CCl_4. The I vals. fall with increasing complexity

of the polymerides (from α- to μ-). The chloroiodides do not undergo hydrolysis under the conditions of the determination, so that the acidity developed is ascribable to substitution. (Cf. A., 1936, 962.) R. T.

Hydrolysis of dichlorobutanes in presence of sodium carbonate and hydrogen carbonate, under pressure. A. F. Dobrianski, R. Gutner, and M. Schtschigelskaja (J. Gen. Chem. Russ., 1937, **7**, 1315—1320).—$(CHMeCl)_2$ and 6—12% $NaHCO_3$ or 8% Na_2CO_3 at 135—195° yield $CHMe{:}CMeCl$ (I), $(CHMe{\cdot}OH)_2$, $COMeEt$, $CH_2{:}CH{\cdot}CHMe{\cdot}OH$, and $CHMe{:}CH{\cdot}CH_2{\cdot}OH$. The products obtained analogously from $CH_2Cl{\cdot}CHEtCl$ are as above, except that the glycol is $OH{\cdot}CH_2{\cdot}CHEt{\cdot}OH$. $CH_2Cl{\cdot}CMe_2Cl$ yields $OH{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, $CHCl{:}CMe_2$ (II), and $Pr^{\beta}CHO$. The yield of glycol is inversely, and of (I) or (II) directly, $\propto [NaHCO_3]$. R. T.

Aliphatic chloro-derivatives. X. Action of chlorine on Δ^{α}- and Δ^{β}-pentenes. D. Tischtschenko and M. Schtschigelskaja (J. Gen. Chem. Russ., 1937, **7**, 1246—1248).—Δ^{β}-Pentene and Cl_2 yield a mixture of diastereoisomeric βγ-dichloropentanes, b.p. 140—141° and 143—144°; Δ^{α}-pentene similarly gives αβ-*dichloropentane*, b.p. 148·4—148·8°, with about 1% of a monochloropentene in both cases. The presence of substances binding HCl ($CaCO_3$, CaO, KOH) does not affect the result. R. T.

Higher ωω′-dihalogeno-compounds. II. αμ-Dibromododecane from adipic acid. J. von Braun and A. von Friedrich-Liebenberg (Ber., 1937, **70**, [*B*], 1598—1602; cf. this vol., 270).—The optimal conditions have been worked out for the scheme: $Br{\cdot}[CH_2]_6{\cdot}Br \rightarrow OPh{\cdot}[CH_2]_6{\cdot}Br \rightarrow OPh{\cdot}[CH_2]_{12}{\cdot}OPh \rightarrow C_6H_{11}{\cdot}O{\cdot}[CH_2]_{12}{\cdot}O{\cdot}C_6H_{11} \rightarrow Br{\cdot}[CH_2]_{12}{\cdot}Br$. In the first stage $Br{\cdot}[CH_2]_6{\cdot}Br$ and NaOPh (1·5 : 1) are allowed to interact in EtOH and the mixture of $OPh{\cdot}[CH_2]_6{\cdot}OPh$ and NaBr is filtered. The filtrate is distilled and the mixture of $Br{\cdot}[CH_2]_6{\cdot}Br$ and $Br{\cdot}[CH_2]_6{\cdot}OPh$ separated by a single fractionation. Fourfold treatment of the bromide rapidly gives an approx. 85% yield of the Br-ether. $OPh{\cdot}[CH_2]_{12}{\cdot}OPh$ containing $OPh{\cdot}[CH_2]_6{\cdot}OPh$ is not isolated by distillation but merely washed with EtOH, whereby $OPh{\cdot}[CH_2]_6{\cdot}OPh$ is not removed; this is best effected after hydrogenation, when a single distillation suffices. $C_6H_{11}{\cdot}O{\cdot}[CH_2]_{12}{\cdot}O{\cdot}C_6H_{11}$ is more conveniently converted into $Br{\cdot}[CH_2]_{12}{\cdot}Br$ by repeated treatment with boiling 48% HBr in open vessels than by use of fuming HBr under pressure. *αζ-Dicyclohexyloxyhexane*, b.p. 194°/13 mm., *ζ-phenoxyhexyl bromide*, b.p. 172—174°/13 mm., and *αμ-dicyclohexyloxydodecane*, b.p. about 260°/13 mm., appear new. H. W.

Preparation and reactions of α-halogenoalkinenes. P. A. McCusker and R. R. Vogt (J. Amer. Chem. Soc., 1937, **59**, 1307—1310).—α-Bromo-Δ^{α}-heptinene is prepared by refluxing MgEtBr with heptinene in Et_2O, adding Br at −32°, and hydrolysing with dil. HCl. α-Chloro-Δ^{α}-heptinene [prepared by adding heptinene to KNH_2 in liquid NH_3, replacing the NH_3 by Et_2O, passing in Cl_2 at −70°, and hydrolysing with H_2O] with KCN in aq. MeOH gives $C_5H_{11}{\cdot}C(OMe){:}CH{\cdot}CN$. Chloro- and bromo-heptinene add MeOH in presence of BF_3, giving *α-chloro-*, b.p. 80—82°/8 mm., and *α-bromo-*, b.p. 88°/5 mm., *-ββ-dimethoxyheptane*. A. Li.

Determination of ethyl alcohol in presence of acetone. C. R. Hoskins (Analyst, 1937, **62**, 530—533).—$COMe_2$ is removed by pptn. with excess of acid $HgSO_4$ in presence of HCO_2Na at 80°, excess of Hg pptd. by $K_2C_2O_4$, and the EtOH distilled. The loss of EtOH varies from 0·4 to 1·3%. E. C. S.

Diamagnetism of iodine solutions and the purity of alcohol.—See A., I, 459.

Exchange reactions in deuteroalcohol. M. S. Kharasch, W. A. Brown, and J. McNab (J. Org. Chem., 1937, **2**, 36—48).—EtOH, containing 9·1 mol.-% of EtOD, is obtained by treating abs. EtOH with D_2O and later heating with CaO and distilling. Exchange of H for D by various substances in this solvent under various conditions is investigated by burning 1 g. of the residual EtOH–EtOD and determining by flotation the *d* of the H_2O formed. No exchange takes place with acenaphthene, CH_2Ph_2, $CHPh_3$, or β-$C_{10}H_7{\cdot}OMe$. No exchange occurs with fluorene, $CHPh(C_6H_4{\cdot}OMe)_2$, *p*-$C_6H_4Me{\cdot}NO_2$, or 1 : 3 : 5-$C_6H_3(NO_2)_3$ unless 0·02*M*-NaOH is present. Exchange occurs with *o*-$C_6H_4Me{\cdot}NO_2$ and 7 : 8-benzoquinaldine, but more so in the presence of 0·02*M*-NaOH. Some exchange occurs with *m*-$C_6H_4Me{\cdot}NO_2$, but this is unaffected by NaOH and may be due to an impurity. Exchange occurs with $CH_2Ac{\cdot}CO_2Et$ (slightly >1H), succinimide (1H), and quinaldine (2H). Exchange occurs with $NPhMe_2$, unaffected by 0·02*M*-NaOH, but much increased by 0·01*M*-H_2SO_4. The results do not represent equilibrium vals.; they are discussed with particular reference to $NPhMe_2$, the result with which is held to be due to the high electro-negativity of *o*- and *p*-$C_6H_4{\cdot}NMe_2$. Possible mechanisms of the exchange are discussed. R. S. C.

Aluminium *iso*propoxide as reducing agent. General method for reduction of carbonyl. H. Lund (Ber., 1937, **70**, [*B*], 1520—1525).—Reduction of :CO to :C·OH is effected by $Al(OPr^{\beta})_3$ in boiling $Pr^{\beta}OH$ or C_6H_6 in an apparatus arranged so that the $COMe_2$ formed is volatilised without too great distillation of $Pr^{\beta}OH$; the end is reached when the distillate does not give a ppt. with 2 : 4′-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ in HCl. The method is widely adapted to the reduction of aldehydes and ketones to the corresponding alcohols, side reactions being seldom observed. It cannot be extended to ketones which readily become enolised (CH_2Bz_2, $CH_2Ac{\cdot}CO_2Et$, etc.) or to phenolic ketones or CO-acids which give Al salts insol. in $Al(OPr^{\beta})_3$. Examples are cited of the reduction of NO_2-ketones and -aldehydes to the corresponding NO_2-alcohols but the invariable non-reducibility of $\cdot NO_2$ is not established. Simply and multiply unsaturated ketones are normally reduced to the corresponding carbinols but their isolation is hampered by the facility with which they afford Pr^{β} ethers. $COPh{\cdot}CH_2Br$ is smoothly reduced to *phenylbromomethylcarbinol*, b.p. 133—134°/12 mm., and $CBr_3{\cdot}CHO$ to $CBr_3{\cdot}CH_2{\cdot}OH$ (yield 77%). *2-Naphthylmethylcarbinol*, m.p. 72°, *m-nitrophenylmethylcarbinol*, m.p. 62·5°, and *p-nitrobenzhydrol*, m.p. 74°, appear new. H. W.

Racemisation experiments with vapours of substances difficult to racemise. U. VON WEBER (Z. physikal. Chem., 1937, **179**, 295—306).—There is no racemisation when the vapour of *d*-amyl alcohol or *d*-CHMeEtPr under 0·5 atm. is heated even at temp. at which decomp. begins to be appreciable. The absence of reaction is probably due to the const. of action being very low. R. C.

Determination of sorbitol. J. JEANPRÊTRE (Mitt. Lebensm. Hyg., 1937, **28**, 87—91).—Litterscheid's method for the detection of sorbitol (B., 1932, 281) can be made approx. quant. in absence of excess of mannitol (I). (I) is largely removed by treatment of the mixture with hot EtOH, in which (I) is sparingly sol. The m.p. of the condensation product with *o*-$C_6H_4Cl{\cdot}CHO$ should be determined as a check on the identity of the alcohol. E. C. S.

Nitric oxide and alkyl ethers. M. W. TRAVERS (Nature, 1937, **140**, 107).—A discussion of the mechanism of the reaction occurring between Me_2O and NO (cf. A., 1937, I, 366). L. S. T.

Di*iso*thiocyanomethyl and di-α-*iso*thiocyanoethyl ethers. H. R. HENZE, A. J. HILL, and L. B. CROSS (J. Org. Chem., 1937, **2**, 29—35).—KSCN (4·1) and $(CH_2Cl)_2O$ (1 mol.) in dry C_6H_6 at 110° give 88% of *diisothiocyanomethyl ether*, b.p. 101·5—102°/2·5—3 mm., m.p. 18·5°, hydrolysed by H_2O to CH_2O and HNCS, and giving with NH_3–Et_2O *dithiocarbamidomethyl ether*, b.p. 147—149° (corr.), and with NH_2Ph or *o*-$C_6H_4Me{\cdot}NH_2$ in dry C_6H_6 *di-phenyl-*, m.p. 159·5°, and *-o-tolyl-thiocarbamidomethyl ether*, m.p. 169—169·5°, respectively; the two last-mentioned ethers with hot EtOH yield N-*ethoxyethyl*-N′-*phenyl-*, m.p. 135—136°, and *-o-tolyl-thiocarbamide*, m.p. 127·5—128·5°, respectively. $(CHMeCl)_2O$ with NaSCN (not KSCN) in C_6H_6 at 110° gives *di-α-isothiocyanoethyl ether* (I), b.p. 94·5°/2—3 mm., m.p. −7°, converted by NH_3–Et_2O into "diethylidenethiocarbamide," $NH<^{CHMe\cdot NH}_{CHMe\cdot NH}>CS$, m.p. 182—183·5° (*picrate*, m.p. 241—245°), and by NH_2Ph or *o*-$C_6H_4Me{\cdot}NH_2$ into phenyl- and *o*-tolyl-thiocarbamide, respectively. The reactions of (I) involve fission of the O linking. Both $(SCN)_2$-ethers are vesicants, unstable to O_2 and H_2O. R. S. C.

Thermal decomposition of ethylene oxide.—See A., I, 466.

Homologues of ethylene oxide and ethane-αβ-diol; mechanism of formation of chlorohydrins. H. MOUREU and M. DODÉ (Bull. Soc. chim., 1937, [v], **4**, 281—295).—The rates of the reactions of Cl_2–H_2O with C_2H_4, C_3H_6, $CHEt{:}CH_2$, and $CMe_2{:}CH_2$ with formation of the chlorohydrin are comparable with one another, but that with $(:CHMe)_2$ is much slower. This is considered to support the view that polarisation of the ethylene precedes the reaction and possibly determines its rate. The mechanism proposed by Frahm (A., 1931, 598) involving $(CH_2)_2O$ as an intermediate in the formation of epichlorohydrin (I) does not hold, since, under the conditions of experiment, the rate of reaction between HCl and $(CH_2)_2O$ is much slower than that between Cl_2, H_2O, and C_2H_2, and the ratio of Cl appearing as HCl to the total Cl appearing as (I) and HCl remains const. and ~ 0·5, as required by $Cl_2 + H_2O + C_2H_4 = CH_2Cl{\cdot}CH_2{\cdot}OH + HCl$. The above-mentioned ethylenes are best converted into the corresponding glycols through the chlorohydrins, which with boiling $Ca(OH)_2$–H_2O give the corresponding oxides. These being very volatile are readily separated, and are then hydrated to the glycol (cf. A., 1935, 63). H. G. M.

Preparation of αγ-dichaulmoogroylglycerol-β-phosphoric acid. T. WAGNER-JAUREGG and H. ARNOLD (Ber., 1937, **70**, [*B*], 1459—1462).—The acids obtained by hydrolysis of chaulmoogra oil and hence probably containing hydnocarpic acid are converted into the *Na*, m.p. 225° after softening at 210°, and *Pb*, m.p. 62—63°, salts, which with $OH{\cdot}CH(CH_2Br)_2$ in boiling xylene yield *αγ-dichaulmoogrin*, m.p. 47—48°. This is converted by the successive action of $POCl_3$ in C_5H_5N and ice into *αγ-dichaulmoogroylglycerol-β-phosphoric acid* (*Pb*, m.p. 175° after softening at 155°, *choline*, m.p. 160—165° after softening at 60°, and *Na*, m.p. 149—150°, salts). H. W.

Catalytic toxicity and chemical structure. II. Influence of chain length in the alkyl sulphide and thiol series.—See A., I, 418.

Structure of dihalogeno-dialkyl sulphides and selenides, and of their complexes with auric chloride and platinic bromide. P. SPINOGLIO (Gazzetta, 1937, **67**, 318—324).—SMe_2Br_2 presumably has the structure $[SMe_2Br]^+Br'$, since it forms *compounds* formulated as $[SMe_2Br]^+AuCl_3Br'$ and $[SMe_2Br]_2{}^{++}PtBr_6''$ (I). $[SeMe_2Br]^+Br'$ similarly gives a *compound*, $[SeMeBr]_2{}^{++}PtBr_6''$ (II). When (I) and (II) are washed with boiling H_2O, *compounds*, $[SMe_2]_2PtBr_4$ and $[SeMe_2]_2PtBr_4$, are obtained. E. W. W.

Methylenedisulphonic acid and its derivatives. J. C. BAUER and G. L. JENKINS (J. Amer. Pharm. Assoc., 1937, **26**, 485—493).—Modifications of the methods of Schroeter (A., 1905, i, 851; 1919, i, 516; 1928, 1216) for the prep. of $CH_2(SO_3H)_2$ are suggested. Attempts to prepare its cyclic ureide failed. F. O. H.

Constitution of formic acid. K. M. PANDALAI (J. Indian Chem. Soc., 1937, **14**, 172—175).—Biochemical evidence indicates that the activated acid is $:C(OH)_2$. It follows that the ordinary acid is HCO_2H. F. J. G.

Hydrolysis of esters and the Knoevenagel reaction.—See A., I, 417.

Enzymic dehydrogenation of trideuteroacetic acid. R. SONDERHOFF and H. THOMAS (Annalen, 1937, **530**, 195—213; cf. A., 1936, 1418).—The aerobic reaction of $CD_3{\cdot}CO_2Na$ is only slightly < that of NaOAc with yeast and $(\cdot CD_2{\cdot}CO_2Na)_2$ is dehydrogenated almost as readily as $(\cdot CH_2{\cdot}CO_2Na)_2$ in presence of an enzyme material from the horse heart. Dehydrogenation of $CD_3{\cdot}CO_2Na$ with 86 mol.-% of D gave $(\cdot CD_2{\cdot}CO_2Na)_2$ with 40·6 mol.-%. Similarly $(CD_3{\cdot}CO_2)_2Ba$ yielded citric acid (I) with 55·8 at.-% D. During the action cell material is formed by the yeast. Extraction of the latter with light petroleum yields a fat with 23% D and the

residue yields to Et_2O an acid fat with 23% D. There remains a carbohydrate with 1·6 mol.-% D which consequently cannot be the source of (I). The unsaponifiable matter of the fat contains 31·0% D. It appears therefore that both intermediate products of the degradation and the materials formed by the use of $CD_3{\cdot}CO_2Na$ as substrate have a considerable content of non-exchangeable D and also that unforeseen losses of D occur. It is possible to use D as indicator in investigating the fate of org. mols. or portions thereof but conclusions as to the course of the change can only be very cautiously drawn.

H. W.

Thermal and photochemical decomposition of acetyl peroxide.—See A., I, 471.

Esters of castor oil fatty acids. I—IV. Y. Toyama and T. Ishikawa (J. Soc. Chem. Ind. Japan, 1937, **40**, 172—174B).—The esters of ricinoleic, polyricinoleic (I), and oleic acids with glycerol, $(CH_2{\cdot}OH)_2$, MeOH, EtOH, BuOH, *iso*-$C_5H_{11}{\cdot}OH$, *cyclo*hexanol, and methyl*cyclo*hexanol have been prepared and their viscosities and m.p. are discussed. The influence of small quantities of these esters on the m.p. and η of castor oil is discussed. The esterification of (I) with the Me and Et esters of (I) is described and acid vals. and η of the products are discussed.

J. D. R.

Synthesis of stearic acid. R. Kuhn, C. Grundmann, and H. Trischmann (Z. physiol. Chem., 1937, **248**, IV—V).—Piperidine (I) salts with crotonaldehyde yield octatrienal, dodecapentaenal, and hexadecapentaenal (II), m.p. 217—218° (decomp.). (II) with $CH_2(CO_2H)_2$ and (I) gives *heptadecapentaene-αα-dicarboxylic acid*, which in AcOH with PtO_2–H_2 followed by distillation/0·0003 mm. gives stearic acid. Catalytic hydrogenation of (II) gives cetyl alcohol.

W. McC.

Conjugated dehydrogenation of ricinoleic acid. M. P. Belopolski and O. B. Maximov (Maslob. Shir. Delo., 1937, No. 2, 13—14).—λ-Ketostearic acid is obtained by heating castor oil at 250° with Ni, Cu (1 hr.; 40% yield), or Pd (30 min.; 60% yield).

R. T.

Syntheses from castor oil. II. C. H. Kao and W. S. Chang (Sci. Rep. Nat. Tsing Hua Univ., 1937, **4**, A, 35—39; cf. A., 1934, 753).—Octan-β-ol (I) is best (95%) obtained from castor oil by H_2SO_4 at 140°; it and *n*-$C_7H_{15}{\cdot}OH$ at 400—450° give an octene, b.p. 94—95°, and heptene, b.p. 121—122° (*n* and *d* given), and are hydrogenated to C_8H_{18} and C_7H_{16}, respectively. PBr_3 and (I) give $C_8H_{17}Br$ and thence (Cu–Zn) C_8H_{18} in 82% overall yield. A 66% yield of heptoic acid is obtained from (I) by $Na_2Cr_2O_7$.

R. S. C.

Ethyl orthohalogenoacetates and their reaction with zinc and magnesium. F. Beyerstedt and S. M. McElvain (J. Amer. Chem. Soc., 1937, **59**, 1273—1275).—*Et chloro-orthoacetate*, $CH_2Cl{\cdot}C(OEt)_3$, b.p. 74—75°/13 mm., from $CH_2Cl{\cdot}CN$ via $CH_2Cl{\cdot}C(OEt){:}NH,HCl$ (Sah, A., 1928, 394), does not react with Zn or Mg. The *bromo-orthoacetate*, b.p. 77—79°/9 mm., prepared (together with a trace of Br_2-compound, b.p. 102—104°/8 mm.) by brominating $CMe(OEt)_3$ in C_5H_5N at 10°, when heated with Zn or Mg in Bu_2O gives organometallic bromides which further yield non-volatile products by intermol. condensation. The iodo-orthoacetate (from the Br-compound by heating with NaI–EtOH in sealed tubes at 110° for 16 hr.) reacts similarly but more readily.

A. Li.

Abnormal acetoacetic ester synthesis. I. Reaction of sodium with allyl, benzhydryl, and cinnamyl acetate. H. F. Tseou and Y. T. Wang (J. Chinese Chem. Soc., 1937, **5**, 224—229).—In accordance with the author's electronic view of the acetoacetic ester synthesis, the action of Na on allyl acetate gives allyl Δ^{γ}-pentenoate whilst *benzhydryl acetate*, b.p. 152—153°/1 mm., m.p. 13°, and *cinnamyl acetate*, b.p. 114°/1 mm., afford $CHPh_2{\cdot}CHPh_2$ and αζ-diphenyl-$\Delta^{\alpha\epsilon}$-hexadiene with its dimeride, respectively.

H. W.

Mechanism of oxidative processes. XLVII. Induced reactions, particularly the "activation" of oxalic acid. H. Wieland and W. Zilg (Annalen, 1937, **530**, 257—273).—The activation of $H_2C_2O_4$ is caused by the reception of energy from the primary process of oxidation. The dehydrogenated residue of $H_2C_2O_4$, either C_2O_4 or CO_2, transmits a portion of the energy liberated during the oxidation to other $H_2C_2O_4$ mols. which thus become activated. If the loosened, reactive H finds a suitable acceptor ($HgCl_2$ or O_2) further transference of energy occurs with production of a reaction chain. Contrary to Oberhauser and Hensinger the formation of H_2O_2 when O_2 is bubbled through solutions in which $H_2C_2O_4$ has been partly oxidised by a dificiency of $KMnO_4$ is not due to the persistance of activated $H_2C_2O_4$ mols. since a similar behaviour is exhibited by solutions containing MnC_2O_4 and $H_2C_2O_4$ but not by $H_2C_2O_4$ or Mn^{II} salt and O_2; the production of HCO_2H or other volatile acid could not be detected. The reaction between $H_2C_2O_4$, $Fe^{\cdot\cdot}$, and H_2O_2 is very sensitive to light; with excess of H_2O_2 reaction ceases when all $Fe^{\cdot\cdot}$ has been oxidised to $Fe^{\cdot\cdot\cdot}$. The initial impulse follows very rapidly in light and in the dark. More CO_2 is formed in the light, the difference being due to a photochemical decomp. of $H_2C_2O_4$ comparable with Eder's reaction. In the reaction between $H_2C_2O_4$ activated by $Fe^{\cdot\cdot}$–H_2O_2 and $HgCl_2$, CO_2 and HgCl are produced in equiv. amounts. Dehydrogenation of $H_2C_2O_4$ occurs almost exclusively through the $HgCl_2$; $Fe^{\cdot\cdot}$ and H_2O_2 are involved only so far as is necessitated by the primary activation of $H_2C_2O_4$. If the reaction occurs in light, the Eder reaction which causes increase in the pptd. HgCl is accompanied by the dehydrogenation of $H_2C_2O_4$ by H_2O_2 in light. The incidence of the latter change is betrayed by the gradual disappearance of H_2O_2 and by the excess of CO_2 produced above the ratio $CO_2 : HgCl :: 1 : 1$. The reaction $H_2C_2O_4$–$Fe^{\cdot\cdot}$–H_2O_2–$HgCl_2$ is somewhat restricted by pyrogallol, resorcinol, and most appreciably by quinol but little by HCN. In the dark $H_2C_2O_4$ cannot be replaced by $CH_2(CO_2H)_2$, $(\cdot CH_2{\cdot}CO_2H)_2$, $OH{\cdot}CHMe{\cdot}CO_2H$, tartaric acid, malic acid, or HCO_2H whereas a slight pptn. of HgCl occurs in the light with all acids except $(\cdot CH_2{\cdot}CO_2H)_2$. The induction impulse, characteristic of $H_2C_2O_4$, is observed to a very slight degree only with HCO_2H and

in light. HCO_2H causes a slow separation of HgCl in amount dependent on the time of illumination; the HCO_2H is oxidised by H_2O_2 activated by Fe". Replacement of Fe" by Co or Ni gives formation of HgCl in the dark and of rather more thereof in the light. Fe"' is inactive in the dark. In the light Mn" behaves similarly to Fe". Et_2O_2, $OBz{\cdot}O{\cdot}SO_3K$ and Bz_2O_2 resemble H_2O_2 in their action whereas O_3 is ineffective. The activating effect of $K_2S_2O_8$ is described in detail, with the effect thereon of the acidity of the solution.

Maleic acid is quantitatively converted into fumaric acid when boiled with aq. $HgCl_2$ and a trace of $K_2S_2O_8$; the change occurs more slowly without $HgCl_2$. The conversions, citraconic to itaconic acid, *allo*cinnamic to cinnamic acid, oleic to elaidic acid are effected similarly. The changes are ascribed to an inductive impulse which acquires its energy from a primary, slight oxidation. Small amounts of $K_2S_2O_8$ are consumed in the change. H. W.

Preparation of malonic ester. C. H. Kao and K. H. Chen (J. Chinese Chem. Soc., 1937, **5**, 223).—Finely divided $CH_2(CO_2)_2Ca$ suspended in 95% EtOH is treated with HCl; after addition of C_6H_6 or CCl_4 the mixture is boiled for 3 hr. and the $CH_2(CO_2Et)_2$ is isolated as usual. The yield is about 70% calc. on the $CH_2Cl{\cdot}CO_2H$ used. H. W.

Halogenometric determination of fumaric acid in presence of those accompanying compounds common in biochemistry. E. Szegedy (Z. anal. Chem., 1937, **109**, 316—333).—Fumaric acid, in the presence of succinic, *l*-malic, pyruvic, oxalacetic, malonic, and arsenious acids, H_2SO_4, and phosphate buffer mixture, is separated as Hg fumarate (I) by pptn. with $Hg_2(NO_3)_2$ from solutions containing 5% of free HNO_3. (I) may be weighed as such or, better, is converted into Na fumarate by boiling with NaCl or NaOH, and is then determined bromometrically. WO_4', if present, is first separated by pptg. WO_3 with H_2SO_4. J. S. A.

Determination of tartaric acid as lead tartrate. C. H. Manley (Analyst, 1937, **62**, 526—530).—The Pb salt is pptd. by addition of $Pb(NO_3)_2$ to a solution of the tartrate previously made neutral to phenolphthalein. E. C. S.

Use of the name "racemic acid." A. Findlay (Nature, 1937, **140**, 22).—Historical. L. S. T.

Thermal decomposition of αα'-diethoxydicarboxylic acids. M. Meyer (Compt. rend., 1937, **204**, 1948—1949; cf. A., 1937, II, 246).—αα'-Diethoxypimelic acid when distilled at 760 mm. gives traces of aldehyde. αα'-Diethoxysuberic acid, treated similarly, gives Δ^1-cyclo*pentene*-1-*aldehyde*, b.p. 60—65°/15 mm. [semicarbazone, m.p. 222° (block) (lit., 208—209°)], and αα'-diethoxytetradecanedicarboxylic acid gives *decane-αι-dialdehyde*, b.p. 128—130°/4 mm. (*semicarbazone*, m.p. 202°). J. L. D.

Reactions of ascorbic acid. G. Woker and I. Antener (Helv. Chim. Acta, 1937, **20**, 732—741).—The determination of ascorbic acid (I) by reduction of picric acid–picrate also involves glutathione, cysteine (II), and creatinine (III); the iodate reduction method is more advantageous since it involves only acid reducing reagents. The blue colour with benzoquinone is given much more rapidly by (I) than by (II), whilst (III), xanthine, and uric acid are inactive. The conversion of (I) into furfuraldehyde and its treatment with orcinol or phloroglucinol are practicable but not very sensitive by reason of the discoloration of the controls by HCl alone. The reaction of (I) with α-$C_{10}H_7{\cdot}OH$ or thymol and the osazone reaction of dehydroascorbic acid are described. H. W.

Determination of total and of reduced ascorbic acid with methylene-blue.—See A., III, 327.

Production of peroxide during the auto-oxidation of ascorbic acid and of thiol compounds. P. Holtz and G. Triem (Z. physiol. Chem., 1937, **248**, 1—4; cf. Langenbeck, this vol., 167).—When O_2 is passed through a mixture of ascorbic acid (I) with a dil. solution of luminol in aq. Na_2CO_3 containing a trace of hæmin strong luminescence, not affected by addition of Cu", is observed. Weaker luminescence, strengthened by Cu", is observed when (I) is replaced by cysteine (II) or thiolacetic acid (III). (I) is much more rapidly oxidised than are (II) and (III), the increase in rate of oxidation produced by Cu" being insufficient to affect the strength of luminescence. Cu" very greatly increases the rate of oxidation of (II) and (III). Distillates from the mixtures contain H_2O_2 derived, presumably, from the labile org. peroxides produced by the oxidation. W. McC.

Preparation and properties of the osazone of dehydroascorbic acid. I. Antener (Helv. Chim. Acta, 1937, **20**, 742—746).—Air oxidation of ascorbic acid affords dehydroascorbic acid, isolated as the *osazone*, m.p. 218°. The absorption spectrum shows max. at 196, 266, 348, and 441 mμ. P. G. C.

Structure of pectin polygalacturonic acid. P. A. Levene and L. C. Kreider (Science, 1937, **85**, 610).—Degradation of the acid with HIO_4 yields *l*-tartaric acid. $C_{(4)}$ and $C_{(5)}$ are therefore engaged in the ring formation and in the condensation of each unit with its neighbouring unit. It is predicted that the OH of $C_{(4)}$ serves for condensation and that of $C_{(5)}$ for ring formation. L. S. T.

Photopolymerisation of formaldehyde to reducing sugars *in vitro*. A. Ram and N. R. Dhar (J. Indian Chem. Soc., 1937, **14**, 151—155).—Small yields of reducing sugars are obtained when aq. CH_2O in presence of $FeCl_3$ is exposed to sunlight. The yield is increased in presence of kieselguhr and is a max. at 30—40°. F. J. G.

Relation between velocity of the Cannizzaro reaction and the concentration of aldehyde. I. Cannizzaro reaction in formaldehyde solutions. E. K. Nikitin and I. I. Paul (J. Gen. Chem. Russ., 1937, **7**, 1292—1298).—Aq. CH_2O is determined as follows: 10 ml. of solution or H_2O are heated at 50—60° for 30—40 min. with 10 ml. of 50% KOH, the vol. is made up to 100 ml., and 10 ml. of each solution are titrated with 0·15*N*-H_2SO_4; the $[CH_2O] \propto$ difference between the two titrations. The velocity of the Cannizzaro reaction $\propto [CH_2O]$ and temp. R. T.

Direct method for the differentiation of acetals from ethers. H. F. Tseou and T. S. Chow (J. Chinese Chem. Soc., 1937, 5, 179—185).—The acetal (4 drops) is added to 0·5 c.c. of a solution of resorcinol, α- or β-$C_{10}H_7$·OH, or PhOH in EtOH and 1 c.c. of aq. H_2SO_4 (1 : 4) is slowly introduced down the side of the tube. A colour, usually red, is produced at the junction of the two layers. On shaking the mixture a coloured ppt. is formed which further changes in colour on addition of NaOH or NH_3. Results with the following acetals are tabulated: $CH_2(OMe)_2$, $CH_2(OEt)_2$, $CHMe(OMe)_2$, $CHMe(OEt)_2$, $CHMe(OPr^{\beta})_2$, $CHMe(OBu^{\beta})_2$, $CHPr^{\beta}(OPr^{\beta})_2$, $CHPr^{\beta}(O{\cdot}C_5H_{11})_2$, $CHPr^{\beta}(OMe)_2$, $CHPr^{\beta}(OEt)_2$, $CHPr^{\beta}(OBu^{\beta})_2$, $CHPh(OMe_2)$, $CHPh(OEt)_2$. Ethers do not give the reaction. H. W.

Kinetics of polymeric aldehydes. V. Polyoxymethylene dihydrates.—See A., I, 468.

Organic catalysts. XVII. Hydration of crotonaldehyde to aldol. W. Langenbeck and R. Sauerbier (Ber., 1937, 70, [*B*], 1540—1541).—Crotonaldehyde (I) is partly converted into aldol (II) when heated at 40° in aq. AcOH or EtOH containing sarcosine (III) or piperidine but not glycine. The change does not occur in absence of a catalyst. (II) is partly dehydrated to (I) when kept at 40° in aq. AcOH containing (III). H. W.

Mobility of halogens in αβ-dichlorocarbonyl derivatives. M. Naftali (Bull. Soc. chim., 1937, [v], 4, 333—342).—Acetals of αβ-dichloro-aldehydes with an α-H are converted by alkali alkoxides into the acetals of α-chloro-unsaturated aldehydes, but little or no reaction occurs, even in hot conc. solution, when the α-H has been replaced by alkyl. Thus $CH_2Cl{\cdot}CHCl{\cdot}CH(OMe)_2$, b.p. 78—82°/13 mm. (cf. lit.; prep. described), when treated with excess of NaOMe–MeOH (water-bath; 1 hr.) gives *α-chloro-Δ$^{\alpha}$-propenal Me$_2$ acetal*, b.p. 28°/12 mm., and similarly *αβ-dichlorobutanal Me$_2$ acetal*, b.p. 86—90°/13 mm., prepared from the aldehyde and MeOH in presence of 1% of HCl (4 hr. at the b.p.), gives *α-chloro-Δ$^{\alpha}$-butenal Me$_2$ acetal*, b.p. 58°/13 mm. *αβ-Dichloro-α-methylbutanal Me$_2$*, b.p. 88°/13 mm., and *Et$_2$*, b.p. 98—100°/12 mm., *acetal*, and *αβ-dichloro-α-methylhexanal Me$_2$*, b.p. 118°/13 mm., and *Et$_2$*, b.p. 127°/11 mm., *acetal* (preps. described) are very stable towards NaOMe, and even when boiled with conc. NaOMe–MeOH for 3 days give only small fractions of a composition close to that of the corresponding monochloride. $CMe_2Br{\cdot}CH(OMe)_2$, b.p. 54—55°/13 mm. (cf. A., 1910, i, 92), is unaffected when heated (water-bath) with 10, 20, and 30% aq. KOH during 8 hr., or during 3 hr. with KOH–EtOH, or with powdered KOH, but with powdered KOH at 120—140° a poor yield of $CH_2{:}CMe{\cdot}CH(OMe)_2$ is obtained. $CH_2Cl{\cdot}CHClAc$, b.p. 65—70°/16 mm., resinifies when treated with NaOMe–MeOH. Addition of Cl to $CHMe{:}CMeAc$ in $CHCl_3$ gives *Me αβ-dichloro-α-methylpropyl ketone*, b.p. 66°/13 mm., and a *compound*, b.p. 96—99°/13 mm., probably *Me αββ-trichloro-α-methylpropyl ketone*. The former, like the Cl-additive product of mesityl oxide, when treated with NaOMe–MeOH gives a mixture probably consisting chiefly of an unsaturated monoether. H. G. M.

Constitution and properties of dichloro- and dialkoxy-aldehydes. J. Lichtenberger and M. Naftali (Bull. Soc. chim., 1937, [v], 4, 325—333).—The following have been prepared by addition of Cl to the appropriate unsaturated aldehyde in $CHCl_3$ or CCl_4: *αβ-dichloro-α-methylbutanal* (I), b.p. 52—53°/12 mm., *αβ-dichloro-α-methylpentanal* (II), b.p. 67°/13 mm., and *αβ-dichloro-α-ethylhexanal*. The last two when treated with cold NaOAlk in excess of AlkOH give the corresponding αβ-alkoxy-compounds in good yield: *αβ-dimethoxy-* (III), b.p. 67°/12 mm., *-diethoxy-*, b.p. 81°/12 mm., and *-di-*n-*propoxy-*, b.p. 104°/12 mm., *-α-methylpentanal*; *αβ-dimethoxy-*, b.p. 87°/13 mm., *-diethoxy-*, b.p. 87—88°/4 mm., *-di-*n-*propoxy-*, b.p. 97°/3 mm., and *-di-*n-*butoxy-*, decomp. at about 70—80°/1 mm., *α-ethylhexanal*. (I) and its lower homologues when similarly treated with NaOAlk–AlkOH are completely decomposed and resinified. Mono-ethers corresponding with the above di-ethers cannot be obtained with half the quantities of NaOAlk previously used; there does not appear to be any difference in the mobility of the two Cl. Attempts to oxidise the foregoing dialkoxy-aldehydes to the corresponding acids, to reduce them to the corresponding alcohols, and to prepare solid derivatives (by means of $NaHSO_3$, $NHPh{\cdot}NH_2$, p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$, $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl, and NH_2OH) from them failed; and qual. tests for ·CHO gave positive indications only after some hr. The corresponding chloroaldehydes are also unreactive. The possibility of an alternative, *cyclo*semiacetal structure

$$CHMeX\langle\begin{matrix}CHEt\\CHX\end{matrix}\rangle O$$ (X = Cl, OMe) for (II) and (III),

respectively, is discussed. Oxidation of α-ethyl-β-*n*-propylacraldehyde with moist Ag_2O yields *α-ethyl-Δ$^{\alpha}$-hexenoic acid*, b.p. 107—108°/3 mm., which with Cl_2–$CHCl_3$ gives *αβ-dichloro-α-ethylhexoic acid*, b.p. 134°/3 mm., resinified by NaOMe. H. G. M.

Photo-decomposition of aldehydes and ketones.—See A., I, 471.

Accelerating action of ketones on the Cannizzaro–Tischtschenko reaction. I. M. N. Tlitschenko (J. Gen. Chem. Russ., 1937, 7, 1086—1092).—The activity of a no. of ketones in accelerating the Cannizzaro reaction of 10% CH_2O with 0·1*N*-KOH ∝ ketone concn., and inversely ∝ $[H_2O]$, and rises in the order pinacolin < valerone < $COPr_2$ < COMePr < COPhEt < $COMe_2$ < $COEt_2$ < COMeEt < COPhMe < *cyclo*hexanone. This order is, however, different for different $[CH_2O]$. R. T.

Determination of acetone by the reaction with salicylaldehyde. E. K. Nikitin and S. A. Verschinski (J. Appl. Chem. Russ., 1937, 10, 755—758).—1 ml. of 50% KOH and 0·5 ml. of 5% salicylaldehyde in EtOH are heated at 50° for 25 min. with 1 ml. of the solution (containing ≤0·001% $COMe_2$), and with 1 ml. of standard aq. $COMe_2$ (0·002—0·01%). 1 ml. portions of the resulting solutions are added to 10 ml. of 60% H_2SO_4, and the colorations are compared. The max. mean error is ±2%. R. T.

Glucofuranosides and thioglucofuranosides. I. Method of preparation and its application to galactose and glucose. J. W. Green and E.

Pacsu (J. Amer. Chem. Soc., 1937, **59**, 1205—1210).—Glucose alkyl (Et or CH_2Ph) mercaptals are converted by $HgCl_2$ in EtOH at 20° into α-ethylglucopyranoside, but under neutral conditions (excess of HgO) yield the (α + β) ethyl- (excess of $HgCl_2$) or α-alkylthio- (1 mol. of $HgCl_2$) -glucofuranosides. Hudson's rules, ready hydrolysis, and conversion by $HgCl_2$ (HgO) into the ethylfuranoside indicate that the latter is furanoid (cf. Schneider, A., 1916, i, 792; 1918, i, 252); HCl–EtOH converts β-ethylgalacto- or (α + β)-ethylgluco-furanoside into the (α + β)-pyranoside. With galactose, the intermediate thiogalactofuranoside cannot be isolated. A. Li.

Factors influencing the destruction of glucose and fructose by oxygen. M. Clinton, jun., and R. S. Hubbard (J. Biol. Chem., 1937, **119**, 467—472).—39·5% destruction of fructose occurs in PO_4''' buffer solutions at p_H 7·0 and 77·5° in presence of O_2, whilst only 5·7% of glucose is similarly destroyed. No destruction occurs in either case if O_2 is replaced by N_2. Only with PO_4''' and AsO_4''' buffers does destruction of fructose occur. Purification of the reagents shows that such destruction is catalysed by some unknown impurity. No hexose phosphate esters could be isolated. P. G. M.

Analysis of fructoside mixtures by means of invertase. VI. Methylated and acetylated derivatives of crystalline β-benzylfructopyranoside. C. B. Purves and C. S. Hudson (J. Amer. Chem. Soc., 1937, 59, 1170—1174).—CH_2Ph·OH–HCl slowly converts α-methyl- or α-benzyl-fructofuranoside into β-*benzylfructopyranoside* (I), m.p. 157°, $[\alpha]_D^{23}$ −130° in H_2O, acetylation of which with specially purified C_5H_5N and Ac_2O gives the *tetra-acetate*, m.p. 69—69·5°, $[\alpha]_D^{25}$ −128·4° in MeOH, whilst treatment with TlOEt followed by methylation yields the *Me*$_2$ *ether* (liquid), $[\alpha]_D^{20}$ −114° in dioxan, and further methylation the *Me*$_4$ *ether*, $[\alpha]_D^{20}$ −111·8° in dioxan. (I) is best prepared (30% yield) by shaking fructose with CH_2Ph·OH–HCl, evaporating, extracting with C_6H_6, and crystallising from H_2O; the C_6H_6 extract, after fermentation and acetylation, yields the tetra-acetyl-α-benzylfuranoside (5%). The rates of hydrolysis of (I) and β-methylfructopyranoside [prepared by the action of MeOH–HCl on (I)] with HCl are respectively 1·3 and 0·8 times that of sucrose. A. Li.

Direct demonstration of the sucrose linking in the oligosaccharides. H. W. Raybin (J. Amer. Chem. Soc., 1937, **59**, 1402—1403).—Gentianose and stachyose give the blue-green colour with diazouracil, characteristic of the sucrose linking (Raybin, A., 1933, 811). A. Li.

Fructose anhydrides. XVIII. Constitution of triticin. H. H. Schlubach and H. Peitzner (Annalen, 1937, **530**, 120—130; cf. A., 1936, 1096).—By a modified purification involving repeated fractional pptn., triticin (I) is obtained non-hygroscopic, colourless, and almost tasteless, with $[\alpha]_D^{20}$ −51·4° in H_2O and mol. wt. (cryoscopy in H_2O) 2600—2830 (16—17·5 fructose anhydride units). Exhaustive purification of the *Ac* derivative (43·5% Ac), $[\alpha]_D^{20}$ −15·6° in $CHCl_3$, *forms*, m.p. 115° and 191°, and subsequent hydrolysis gives an identical product. Quant. hydrolysis indicates that (I) contains only fructose anhydride units. Me_2SO_4–KOH–$COMe_2$ readily gives a *methyltriticin* (45—46% OMe), m.p. 141—151°, $[\alpha]_D^{20}$ −61·2° in $CHCl_3$, hydrolysed by $H_2C_2O_4$ in aq. EtOH to a 3 : 1 : 3 mixture of 1 : 3 : 4 : 6-tetra-, a new *tri*-, b.p. 86°/0·01 mm., $[\alpha]_D^{20}$ −10·5° → −13·8° in H_2O, +3° → −5·5° in MeOH, and +12·2° → +5·9° in $CHCl_3$ (*osazone*, m.p. 77·5°), and di-*methylfructose*, b.p. 132—136°/0·1 mm. (probably identical with that obtained from trimethylsinistrin). (I) probably contains a closed ring containing 7 fructose anhydride units repeated regularly. Staudinger's branched-chain formula for starch is rejected. R. S. C.

Floridoside, a *d*-monogalactoside of glycerol. H. Colin (Bull. Soc. chim., 1937, [v], 4, 277—281; cf. A., 1934, 121).—Floridoside, $C_9H_{18}O_8,H_2O$, m.p. 86—87°, $[\alpha]_D$ +151° in H_2O (optical and crystallographic data given), is hydrolysed to glycerol and galactose by acids, and also by the common moulds and bottom yeast, but not by invertase and emulsin. It is oxidised with difficulty by Br–H_2O and unaffected by acetobacteria capable of converting glycerol into dihydroxyacetone. It is therefore considered to be β-(α-*d*-galactosido)glycerol,

$$(OH\cdot CH_2)_2CH\cdot O\cdot \overline{CH\cdot[CH\cdot OH]_3\cdot CH\cdot CH_2\cdot OH}.$$

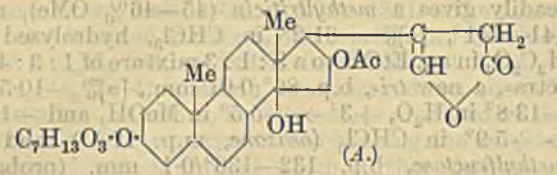
H. G. M.

Ericolin. H. Dieterle and O. Dorner (Arch. Pharm., 1937, **275**, 380—382).—Ericolin, from the leaves of *Arctophylos uva ursi*, is shown by hydrolysis to quinol and glucose and by purification to be impure arbutin. R. S. C.

Vegetable heart poisons. XV. Oleandrin. R. Tschesche (Ber., 1937, **70**, [*B*], 1554—1556).—The identity of folinerin with oleandrin is established. Cautious oxidation of oleandrigenin (I) with CrO_3 affords *oleandrigenone*, m.p. 250—252°, converted by cold, conc. H_2SO_4 into a dianhydro-oleandrigenone identical with dianhydrogitoxigenone (digitaligenone). This is possible only if OH at $C_{(3)}$ in (I) was free and has become oxidised to CO. Ac must therefore be attached to $C_{(16)}$ and the sugar, oleandrose, as in other heart glucosides is united through O to $C_{(3)}$. H. W.

Glucosides of the oleander. W. Neumann (Ber., 1937, **70**, [*B*], 1547—1554).—Oleandrin (I), m.p. 250° $[\alpha]_D^{18}$ −52·1° in MeOH, is identical with folinerin. It is hydrolysed by 0·1*N*-HCl in aq. MeOH to oleandrigenin (II), m.p. 223° after melting with decomp. at 110—115° and re-solidifying at 140—150°, $[\alpha]_D^{18}$ −8·5° in MeOH (which is identical with acetylgitoxigenin), and *oleandrose* (III), m.p. 68—70°, which at 60°/1 mm. passes into *anhydro-oleandrose*, $C_7H_{12}O_3$. (III) is probably a Me ether of a methyldeoxypentose; the OMe of (I) is proper to the sugar component. (I) is hydrolysed by boiling *N*-H_2SO_4 to *monoanhydro-oleandrigenin* $C_{25}H_{34}O_5$, m.p. 262°. Partial hydrolysis of (I) by NaOH yields *deacetyloleandrin*, m.p. 238—240°, $[\alpha]_D^{18}$ −24·9° in MeOH, obtained also from oleander leaves; it is hydrolysed by 0·1*N*-HCl to gitoxigenin (IV), $[\alpha]_D^{18}$ +35·2° in MeOH. Similar partial hydrolysis of (II) gives (IV) and AcOH, whilst treatment of (II) with

NaOAc and boiling Ac_2O yields diacetylgitoxigenin; this when partly hydrolysed gives a *monoacetyl-*



(*A*.)

gitoxigenin, m.p. 236—238°. (I) is probably therefore *A*. In addition to the two heart glucosides oleander leaves contain the pharmacologically inactive glucoside *adynerin* (?), $C_{23}H_{34}O_4,C_7H_{12}O_3$, m.p. 234° after softening at 228°. It appears to contain only one double linking (in the lactone group). It is hydrolysed by 0·1*N*-HCl in EtOH–H_2O to *adynerigenin*, $C_{23}H_{32}O_4$ or $C_{23}H_{34}O_4$, m.p. 238—242°, $[\alpha]_D^{18}$ +18° in C_5H_5N. H. W.

Araban of wheat flour.—See A., III, 332.

Fermentability of dextrins. Amylohexaose and different yeast species. H. Haehn, M. Glaubitz, and W. Gross (Ber., 1937, **70**, [*B*], 1492—1495).—Amylohexaose is not fermented by several species of yeast and it is therefore improbable that the larger dextrin mol. is attacked under similar conditions. H. W.

Starch as a starting material for the preparation of succinic acid and bromoform. C. H. Kao, H. C. Mou, and P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1937, **4**, A, 27—29).—1 kg. of starch gives 128 g. of lævulic acid and thence by NaOBr 62 g. of $CHBr_3$ and 40 g. of $(\cdot CH_2\cdot CO_2H)_2$. R. S. C.

Plant colloids. XLIV. Soluble starch from amyloses. M. Samec (Kolloid-Beih., 1937, **46**, 134—142; cf. A., 1932, 338).—Processes which result in the formation of sol. starch from native starch have been applied to the amyloses obtained by electrodialysis from potato starch. The resulting products are sol. in hot H_2O only when prepared by methods leading to mol. degradation, and in no case are the solutions stable when cold. An explanation is offered. F. L. U.

Aminated cellulose and starch. F. Pancirolli (Boll. R. Staz. Sperim. Ind. Carta, 1937, **32**, 314—316).—Alkali-cellulose combines with *p*-$NO_2\cdot C_6H_4\cdot CH_2Cl$ to give *p-nitrobenzylcellulose*, reduced to *p-aminobenzylcellulose*. This can be diazotised and coupled with β-naphthols to give coloured cellulose *azo-ethers*, which retain the ordinary fibrous structure of cellulose. Starch similarly gives *p-nitro-* and *p-amino-benzyl* derivatives, and thence coloured *azo*-compounds; these, however, have lost the adhesive properties of starch. E. W. W.

Methylation of polysaccharides. K. Freudenberg and H. Boppel (Ber., 1937, **70**, [*B*], 1542).—Ramie or cotton is treated with Me_2SO_4 until it contains 43—44% OMe and then suspended in liquid NH_3. Na is added, followed after 1·5 hr. by MeI. NH_3 is removed finally at 100°/vac. The methylcellulose is pure white, retains the fibrous structure, and is insol. in H_2O in absence of NaI. The loss of viscosity in $CHCl_3$ is remarkable. The difficulties of micro-determination of OMe are discussed. H. W.

Highly polymerised compounds. CLXV. Osmotic measurements with cellites in glacial acetic acid. H. Staudinger and G. V. Schulz (Ber., 1937, **70**, [*B*], 1577—1582).—Hess' hypothesis that cellite (I) in very dil. solution in AcOH is degraded to the $(C_6)_2$ stage is untenable since it does not diffuse through membranes which are permeable to cellobiose octa-acetate and biosan acetate. Osmotic measurements of cellite in AcOH and $COMe_2$ show that it exists in the same condition in all media and that independently of the concn. the macromols. have mol. wt. 20,000—90,000. Hess' observations are unexplained. H. W.

Highly polymerised compounds. CLXII. Hydrocelluloses. H. Staudinger and M. Sorkin (Ber., 1937, **70**, [*B*], 1565—1577).—Cotton wool is treated with 2% NaOH in absence of air and then extracted with EtOH and Et_2O; it has then degree of polymerisation about 1650. It is treated with various *N*-acids at 53°±0·5° and after defined intervals of time portions are washed free from acid, dried, and their viscosity is determined in Schweitzer's reagent. Degradation takes place much more rapidly with strong than with weak acids, HCl being particularly destructive. The various properties of cellulose as solid do not alter proportionately but only functionally with the degree of polymerisation. No sensible loss in these properties is experienced at a degree 700—800; subsequently diminution is rapid when the degree is <600. Similar observations have been recorded for artificial fibres so that it is not necessary that these should have the same high degree of polymerisation as the natural fibre. The mechanical behaviour is a macromol. property governed by the length of the macromols. and by their arrangement in the solid cellulose. By repeated freezing and thawing cellulose can be dissolved in 10% NaOH or 8% LiOH. Its viscosity is the same in these media and usually about 10—20% > in Schweitzer's reagent, showing that the state of dissolution of the material of degree of polymerisation up to 470 is the same in all three solvents and hence mol. since it is mol. in the last medium. H. W.

Individuality of cellulose micelles.—See A., I, 460.

Chelation of diamines with cupric salts.—See A., I, 420.

Glucosaminol, a reduction product of glucosamine. P. Karrer and J. Meyer (Helv. Chim. Acta, 1937, **20**, 626—627).—Glucosamine hydrochloride in H_2O is converted by H_2–Ni into *glucosaminol*, m.p. 131—132° (*Ac* derivative, by hydrogenation of the acetylglucosamine, m.p. 153°, $[\alpha]_D^{18}$ −11° in H_2O), isolated as the *hydrochloride*, m.p. 160—161°. P. G. C.

Configuration of glucosamine. Steric relations between α-amino- and α-hydroxy-acids. P. Pfeiffer and W. Christeleit (Z. physiol. Chem., 1937, **247**, 262—268; cf. this vol., 138; Karrer, *ibid.*, 234).—The configuration of *l*-alanine is not altered when NH_2 is replaced by OH (*l*-lactic acid). Curves showing the relation between α and light absorption indicate that the Cu salts of *d*-glucosamic

acid, *d*-gluconic acid, and *d*-galactonic acid have the same configuration which is that of the antipodes of the natural NH_2-acids. Hence glucosamine also has this configuration and cannot be regarded as a physiological intermediate between sugars and protein degradation products. W. McC.

Glucoproteins. IV. Determination of hexosamine. J. W. Palmer, E. M. Smyth, and K. Meyer (J. Biol. Chem., 1937, **119**, 491—499).—A modification of Elson and Morgan's method (A., 1934, 175) is the most satisfactory. P. G. M.

Aminoglucoside acetates and their rotatory power. M. Frerejacque (Compt. rend., 1937, **204**, 1480—1482).—It appears impossible to extend the rules of isorotation to this class of compounds. The following *substances* are obtained by treating the fully acetylated reducing sugar with the acetate of the requisite base in EtOH, the separation of the mixtures into the α- and β-forms being effected by crystallisation preferably after partial isomerisation by fusion or treatment with acid: α-, m.p. 143°, $[\alpha]_D^{22}$ +180° to +41·6° in $CHCl_3$, and β-, m.p. 97°, $[\alpha]_D^{22}$ −54·8° to +41·6° in $CHCl_3$, *-anilinoglucose tetra-acetate*; α-, m.p. 125°, $[\alpha]_D^{22}$ +119° to +34·2° in $CHCl_3$, and β-, m.p. 148°, $[\alpha]_D^{22}$ −47·6° to +34·2° in $CHCl_3$, -p-*toluidinoglucose tetra-acetate*; α-, m.p. 134°, $[\alpha]_D^{22}$ +93° to +59·4° in $CHCl_3$, and β-, m.p. 160°, $[\alpha]_D^{22}$ −48·8° to +59·4° in $CHCl_3$, -p-*bromoanilinoglucose tetra-acetate*; α-, m.p. 197°, $[\alpha]_D^{22}$ +101° to +21·2° in $CHCl_3$, and β-, m.p. 152°, $[\alpha]_D^{22}$ −31° to +21·2° in $CHCl_3$, *-anilinolactose hepta-acetate*; α-, m.p. 189°, $[\alpha]_D^{22}$ +82·3° to +24·8° in $CHCl_3$, and β-, m.p. 208°, $[\alpha]_D^{22}$ −29° to +24·8° in $CHCl_3$, -p-*toluidinolactose hepta-acetate*; α-, m.p. 209°, $[\alpha]_D^{22}$ +98·3° to +24·7° in $CHCl_3$, and β-, m.p. 192°, $[\alpha]_D^{22}$ −14·3° to +24·7° in $CHCl_3$, -p-*bromoanilinolactose hepta-acetate*; β-*anilinomaltose hepta-acetate*, m.p. 205°, $[\alpha]_D^{22}$ +37·5° to +92·5° in $CHCl_3$; β-p-*toluidinomaltose hepta-acetate*, m.p. 182°, $[\alpha]_D^{22}$ +39° to +94·4° in $CHCl_3$. H. W.

Absolute configuration of the naturally occurring α-amino-acids. R. C. Rainey (Nature, 1937, **140**, 150).—The probable abs. configuration of these acids has been deduced by the application of Boys' rule to lævorotatory β-aminohexane, the configuration of which is the same (this vol., 139). L. S. T.

Combinations of glycine and alanine with mercuric oxide. R. Truhaut (Compt. rend., 1937, **204**, 1484—1486).—Treatment of glycine with yellow HgO in H_2O gives the unstable *compound* $(NH_2{\cdot}CH_2{\cdot}CO_2H)_2,HgO$ (*picrate*, $[(NH_2{\cdot}CH_2{\cdot}CO_2H)_2HgO]_2C_6H_3O_7N_3$), in which NH_2 is determinable by Van Slyke's method but Hg appears partly masked. Similarly, alanine gives the *compound*, $2NH_2{\cdot}CHMe{\cdot}CO_2H,HgO$. H. W.

Action of ascorbic acid on amino-acids. I. Detection of histidine. II. E. Abderhalden (Fermentforsch., 1937, **15**, 285—290, 360—381; cf. A., 1936, 635).—I. Old but not fresh aq. ascorbic acid (I) acquires an orange to red colour on addition of aq. NaOH or KOH. Similar colours appear and NH_3 is slowly liberated when (I) is added to aq. NH_2-acids (and to related amines, *e.g.*, tyramine), the change being very rapid and the colour deep in the case of histidine (II). Hence (I) may be used to detect (II).

II. (I) catalyses, in varying degree, the deamination of *d*- and *l*-NH_2-acids, the action being accelerated by Fe^{II}, Cu, and Mn and by increasing the concn. of (I). The extent of deamination [which is large in the case of (II) only] is affected by [H·], temp., and concn. of O_2. CH_2O is produced on deamination of glycine (III) and MeCHO on that of alanine. Glycine anhydride is also slowly attacked by (I) with liberation of NH_3. Aq. (III) spontaneously decomposes, especially when very dil., with liberation of NH_3. The deamination of (III) by adrenaline is inhibited by (I) which prevents production of "omega." W. McC.

β-Hydroxyglutamic acid. E. Abderhalden and H. Murke (Z. physiol. Chem., 1937, **247**, 227—238).—The hydrochloride of the Et_2 ester of β-hydroxyglutamic acid (I) (*benzoate*), obtained by a modification of the procedure of Harington and Randall (A., 1932, 257), with NaOEt gives the free ester, m.p. 62—63°, which, on exposure to light and moisture, changes into the *Et* ester, m.p. 115°, of *hydroxypyrrolidinecarboxylic acid*, m.p. 176°. The prep. of the N-*carbobenzyloxy*-, m.p. 159° (*strychnine* salt; Et_2 ester, b.p. 215—225°/2—3 mm.; *anhydride*, m.p. 132—133°), dl-α-*bromoisohexoyl*, m.p. 158°, and dl-*leucyl* (II), m.p. 220—222° (decomp.) (Et_2 ester, m.p. 80—82°; *carbobenzyloxy*-derivative, m.p. 170°), derivatives of (I) and of the Et_2 ester, m.p. 49°, of carbobenzyloxyglutamic acid is described. α-Ketoglutaric acid, obtained from (I) by boiling with conc. HCl, gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 214°. The Et_2 ester of the diketopiperazine corresponding with (II) has m.p. 202°. W. McC.

Biuret reaction of the pentapeptide tetraglycylglycine. P. E. Wenaas (J. Amer. Chem. Soc., 1937, **59**, 1353—1354).—Tetraglycylglycine, when shaken in dil. NaOH with excess of $Cu(OH)_2$ and the product pptd. with EtOH–Et_2O, yields the pink *Na Cu* salt, $C_{10}H_{12}N_5O_6Na_3Cu$, decomp. 279—281°. A. Li.

Organic reactions of boron fluoride. XIV. Reaction of amides with acids and amines. XV. Alkylation of benzene with esters. F. J. Sowa and J. A. Nieuwland. **XV.** F. J. McKenna and F. J. Sowa (J. Amer. Chem. Soc., 1937, **59**, 1202—1203, 1204—1205).—XIV. The action of AcOH (or other acid) on the NH_2Ac–BF_3 additive compound gives MeCN in 95% yield, and $EtCO{\cdot}NH_2$ yields EtCN. The BF_3 is recovered from the residual BF_3,NH_3 by conc. H_2SO_4. Mono- and di-alkyl- and arylalkyl-substituted amides are prepared by boiling the amines with $R{\cdot}CO{\cdot}NH_2$–BF_3.

XV. Mixtures of mono-, di-, and poly-alkylbenzenes are formed by the action of org. or inorg. esters and BF_3 on C_6H_6; *n*- and *sec.*-Bu esters give *sec.*- whilst the Bu^β ester gives *tert.*-alkylbenzenes, thus showing the intermediate formation of olefines. A. Li.

Cacodyl compounds. R. Tiollais (Bull. Sci. Pharmacol., 1937, **44**, 7—35, 164—190).—A review.

Preparation of boron alkyls, B_2R_4. E. Wiberg and W. Ruschmann (Ber., 1937, **70**, [*B*], 1583—1591).—The partly methylated *compounds* $BMeCl_2$

and BMe_2Cl, obtained by the action of $ZnMe_2$ on BCl_3, are unstable and readily become disproportionated to BMe_3 and BCl_3. Consequently they are not obtainable from BMe_3 and $BeCl_3$. B_2Me_4 could not be isolated as such by the action of BMe_2Cl on Na but the products of its disproportionation B and BMe_3 are obtained. H. W.

Tetramethylammonium silicate. S. Glixelli and T. Krokowski (Rocz. Chem., 1937, **17**, 309—313).—SiO_2 gel is dissolved in aq. NMe_4OH at 100°, and the solution is conc. in vac., when *NMe_4 H meta-silicate*, $NMe_4HSiO_3,8H_2O$, m.p. 81—82°, separates. R. T.

Halogeno-organic lead compounds. M. Lesbre (Compt. rend., 1937, **204**, 1822—1824; cf. A., 1935, 611).—A nearly saturated solution of CsCl with boiling $PbCl_2$ in small excess affords $PbCl_2,CsCl$, which when anhyd. gives with EtI, $Pr^{\alpha}I$, and $Bu^{\alpha}I$ in the presence of a little I at room temp. *Pb Et*, *Pr^{α}*, and *Bu^{α} tri-iodide*, decomp. in each case >90°, respectively. These give additive *compounds*, $PbRI_3,2C_5H_5N$, with C_5H_5N and are easily hydrolysed. J. L. D.

Hydrogenation of acetylenic derivatives. XXVIII. Di*cyclo*hexenylacetylene and its hydrogenation. J. S. Salkind and N. N. Schuvalov (J. Gen. Chem. Russ., 1937, **7**, 1235—1245).—1 : 1′-Dihydroxydi*cyclo*hexylacetylene and $KHSO_4$ at 145—155° (2 hr.) yield *di*-Δ^1-cyclo*hexenylacetylene* (I), b.p. 158—159°/12 mm., which with Br gives unidentified products, and with I in $CHCl_3$ gives a *di-iodide*, m.p. 172—173°. (I) is hydrogenated to αβ-di*cyclo*hexylethane in presence of Pt, and to α-Δ^1-cyclo*hexenyl*-β-cyclo*hexylethane*, b.p. 136—137°, with Pd catalyst. R. T.

Reaction between inorganic complex compounds and hydrocarbons. G. D. Galpern (Bull. Acad. Sci. U.R.S.S., 1937, 435—442).—C_6H_6 or PhMe, but not other hydrocarbons, reacts with MX_2 in aq. NH_3 (M = Ni, Co, Cu, or Zn; X = CN or CNS), to yield complexes of the type $MX_2,C_6H_6,3NH_3$. The reaction is reversible, and ≯ a fraction of the C_6H_6 is combined. The complexes are decomposed by aq. NH_3, but quant. regeneration of the C_6H_6 was not achieved. Complexes are not formed when X_2 = Cl_2 or SO_4. R. T.

Formation of benzene in the radiochemical polymerisation of acetylene.—See A., I, 472.

5-Nitroso-*m*-xylene, m.p. 59°, *o*-, m.p. 61°, and *m*-nitrosoethylbenzene, m.p. 22°; Pr^{β} *p*-nitrosobenzoate, m.p. 61—62°; *o*-, m.p. 117°, and *m*-iodonitrosobenzene, m.p. 77°; *m*- and *p*-nitrosoethoxybenzene.—See A., I, 466.

Polymethylbenzenes. XIX. Jacobsen reaction. V. C. L. Moyle and L. I. Smith (J. Org. Chem., 1937, **2**, 112—137; cf. this vol., 338).—Recorded cases of the Jacobsen rearrangement of alkyl-, halogeno-, and halogenoalkyl-benzenes are collected. Except when halogen alone is present, only tetra- or penta-substituted derivatives rearrange. In the series C_6HMe_4Hal the relative ease of migration is Br > Me > Cl, but in the series $C_6H_2Me_3Hal$ it is Br > Cl > Me, and the ease of rearrangement is much influenced by the conditions and exact nature of the substituent. The effect of varying the nature of the reagent on the rearrangement of $C_6H_2Me_4$ is detailed. Ethyl-ψ-cumene and -mesitylene rearrange, losing the Et. Mechanisms hitherto postulated are shown to be incorrect, as also is that involving formation of CH_2Ph_2 derivatives (since C_6HMe_5 and ψ-cumene give only as much prehnitene as is obtained from C_6HMe_5 alone). *o*- or *p*-Addition of OH–SO_3H to give quinonoid compounds capable of rearrangement is possible, but of limited application. Decomp. into free radicals and rearrangement thereof is more probable; this would account also for the tarry material and SO_2 formed during slow rearrangements. With $AlCl_3$ 1 : 3 : 4-$C_6H_3Me_2Bu^{\gamma}$ gives 45% of 1 : 3 : 5-$C_6H_3Me_2Bu^{\gamma}$ as sole recognisable product. R. S. C.

Condensation of aromatic hydrocarbons with methyl chloromethyl ether. Alkylation of aromatic rings. G. Vavon and J. Bolle (Compt. rend., 1937, **204**, 1826—1828; cf. A., 1914, i, 156).—1 : 3 : 5-$C_6H_3Me_3$ (I mol.) with $CH_2Cl{\cdot}OMe$ (I) (1·1 mol.) in AcOH at 80° affords a $\cdot CH_2Cl$ derivative (II) which is determined by treating the reaction mixture with H_2O [when (I) is rapidly hydrolysed] and titrating free HCl. Many aromatic compounds react, more particularly those containing Me which orients the incoming group *o*-*p*. Chloromethylation greatly inhibits further reaction. (II) when reduced affords $C_6H_2Me_4$, which by a similar series of reactions is converted into C_6Me_6. J. L. D.

Tafel's rearrangement. III. Structural formula of the hydrocarbon $C_{12}H_{18}$ obtained by electrochemical reduction of ethyl benzylmethylacetoacetate. H. Stenzl and F. Fichter (Helv. Chim. Acta, 1937, **20**, 846—851; cf. A., 1934, 631; 1936, 604).—$CHMeEt{\cdot}CH_2{\cdot}COPh$ with Zn–Hg and HCl in AcOH affords *γ-methyl*-n-*amylbenzene*, b.p. 219°/740 mm., converted by Br at 150° into αβ-*dibromo-γ-methyl*-n-*amylbenzene*, m.p. 96°, and by way of the sulphonyl chloride into *γ-methyl*-n-*amylbenzene*-4-*sulphonamide*, m.p. 69·5°. $CHMePr^{\alpha}{\cdot}CHPh{\cdot}OH$ is converted by HI and P into β-*methyl*-n-*amylbenzene* (I), b.p. 214°/740 mm., which similarly affords β-*methyl*-n-*amylbenzene*-4-*sulphonamide* (II), m.p. 86°. $CH_2Ph{\cdot}CHEt_2$ affords β-*ethyl*-n-*butylbenzene*-4-*sulphonamide*, m.p. 89°. (II) is identical with the sulphonamide obtained from the product [which is therefore (I)] of cathodic reduction of $CH_2Ph{\cdot}CMeAc{\cdot}CO_2Et$. P. G. C.

Effect of a high-tension electrical discharge on the catalytic reduction of nitrobenzene.—See A., I, 470.

Applications of fractional distillation to intermediate products in the laboratory. F. R. Stahelin (Chem. Fabr., 1937, **10**, 315—321).—The use of packed and jacketed columns for laboratory-scale working is discussed with reference to the prep. and separation of *o*- and *p*-$C_6H_4Cl{\cdot}NO_2$ from PhCl, and of *m*-$C_6H_4Cl{\cdot}NO_2$ from $PhNO_2$. The latter reaction in presence of $FeCl_3$ gave a 72% yield on the $PhNO_2$ reacting. For nuclear chlorination in presence of Fe catalysts (*e.g.*, the prep. of PhCl from C_6H_6),

Cl_2 should be delivered below the surface of the liquid to avoid additive reaction in the gas phase. J. S. A.

Reaction of benzyl chloride with mercuric salts.—See A., I, 417.

Hexa-alkylphenylethanes. IV. Bromoalkylbenzenes. J. H. Brown and C. S. Marvel (J. Amer. Chem. Soc., 1937, **59**, 1176—1178).—Treatment of *p*-C_6H_4Br·CHO with MgRX yields a carbinol, which when heated with $KHSO_4$ at 150—180° for 2—5 hr. is partly oxidised to the ketone, but chiefly dehydrated to the olefine. This is reduced (PtO_2–Pt-black) to *p*-bromoalkylbenzene, better prepared by direct reduction of the carbinol with I and red P in glacial AcOH. The b.p. are: *n*-alkyl-*p*-bromophenylcarbinols, *Bu*- 122—127°/1 mm., *heptyl*- 149—150°/1 mm., *decyl*- 185—188°/2 mm., *dodecyl*- (m.p. 49—50°); *p*-bromo-*n*-alkenylbenzenes, *pentenyl*- 98—100°/1 mm., *octenyl*- 145—155°/1 mm., *undecenyl*- 166—169°/1 mm., *tridecenyl*- 198—200°/2 mm. (m.p. 28—30°); and *p*-bromo-*n*-alkylbenzenes, *amyl*- 113—115°/5 mm., *octyl*- 125—126°/1 mm., *undecyl*- 165—166°/2 mm., *tridecyl*- 182—185°/1 mm. (m.p. 31—32°). The *p*-bromophenyl *n*-alkyl ketones and their 2 : 4-dinitrophenylhydrazones respectively melt at: *heptyl*- 68—69° and 149—150°, *decyl*- 56—57° and 113—114°, *dodecyl*- 63—64° and 109—110° (*semicarbazone*, m.p. 107—108°). Similarly *m*-C_6H_4Br·CHO affords m-*bromo-phenylmethylcarbinol*, b.p. 136—140°/20 mm., *-styrene*, b.p. 90—94°/20 mm. (dehydration by P_2O_5), and *-ethylbenzene*, b.p. 85—86°/20 mm., also prepared from PhEt by nitration, reduction, acylation, bromination, hydrolysis, diazotisation, and replacement of N_2 by H. A. Li.

Peroxide effect in the halogenation of aromatic side chains. M. S. Kharasch, E. Margolis, P. C. White, and F. R. Mayo (J. Amer. Chem. Soc., 1937, **59**, 1405—1406).—The bromination and chlorination of PhMe are greatly accelerated by peroxides. In presence of ascaridole, PhMe (20 mol.) and Br (1 mol.) yield CH_2PhBr (0·83 mol.) in ½ hr. at 25°. A. Li.

Hexa-alkylphenylethanes. III. Hexa-*p*-cyclohexylphenylethane and hexa-*m*-tolylethane. J. H. Brown and C. S. Marvel (J. Amer. Chem. Soc., 1937, **59**, 1175—1176).—*p*-Bromo*cyclo*hexylbenzene, when treated in Et_2O with Mg followed by Et_2CO_3, and decomposed by cold saturated NH_4Cl, gives a carbinol which is converted by HCl and $CaCl_2$ in dry Et_2O into *tri*-p-cyclo*hexylphenylmethyl chloride*, m.p. 146—147°. This when shaken in PhMe with mol. Ag in absence of air and light affords a deep red solution of *hexa*-p-cyclo*hexylphenylethane* (the colour of which indicates less dissociation than of hexadiphenylylethane), rapidly oxidised by air to *tri*-p-cyclo*hexylphenylmethyl peroxide*, m.p. 151—152°. Similarly *tri*-m-*tolylmethyl chloride*, m.p. 84—85°, from *m*-C_6H_4MeBr, yields the orange *hexa*-m-*tolylethane* (dissociated to about the same extent as the *p*-compound), oxidised to *tri*-m-*tolylmethyl peroxide*, m.p. 158—159°. A. Li.

Structure and electronic interpretation of some optically active sulphoxides. P. Spinoglio (Gazzetta, 1937, **67**, 264—272).—It is suggested that the optical activity of mixed sulphoxides (A., 1936, 1031) may be due, not to a semipolar double linking, but to a tetrahedral structure. Optical activity of compounds of RR'S with Cl_2 is predicted. E. W. W.

Salts of sulphinic acids, R·SO_2H. J. V. Dubský and E. Oravec (Publ. Fac. Sci. Univ. Masaryk, 1937, No. 232, 10—16).—The following *salts* were pptd. and analysed: $Zn^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Ni^{\cdot\cdot}$ ($+2H_2O$ replaceable by $2NH_3$), $Co^{\cdot\cdot}$ ($+2H_2O$), and $Ag^{\cdot}$ salts of $PhSO_2H$; $Ag^{\cdot}$, $Hg^{\cdot\cdot}$, and $Fe^{\cdot\cdot\cdot}$ salts of *m*-$C_6H_4(SO_2H)_2$; $Mn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$ ($+3H_2O$), $Sn^{\cdot\cdot}$ (basic), $Zn^{\cdot\cdot}$ ($+3H_2O$), $Ag^{\cdot}$, and $Fe^{\cdot\cdot\cdot}$ salts of 1-$C_{10}H_7$·SO_2H; $Hg^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Ba^{\cdot\cdot}$ ($+H_2O$), $Ag^{\cdot}$, and $Fe^{\cdot\cdot\cdot}$ salts of 2-$C_{10}H_7$·SO_2H. F. R.

Molecular constitution of naphthalene. G. Oddo (Gazzetta, 1937, **67**, 216—217; cf. A., 1937, I, 224).—A claim of priority for the suggestion of displacement of $C_{10}H_8$ linkings during substitution reactions (cf. A., 1925, i, 804). E. W. W.

Formation of nitrobenzophenones during the nitration of diphenylmethane. J. F. Salellas (Anal. Asoc. Quím. Argentina, 1937, **25**, 39—43).—CH_2Ph_2 with commercial HNO_2 (*d* 1·35) gives, in addition to *pp'*- and *op'*-$CH_2(C_6H_4·NO_2)_2$, 2—3% of *pp'*- and *op'*-$CO(C_6H_4·NO_2)_2$. F. R. G.

Order of introduction of new substituents into the naphthalene nucleus. J. S. Joffe (J. Gen. Chem. Russ., 1937, **7**, 1106—1112).—Substituents are classified as "quinogenic" (OH, NH_2, etc.) or stabilising (NO_2, etc.), with halogens occupying an intermediate place. If an α-substituent of the first group is present, further substitution will take place preferentially in the order 2, 4, 5, and 6, whilst when it is at β the order will be 1, 3, 6, and 8. Substituents of the second group stabilise the nucleus into which they are introduced, so that further substitution takes place into the second ring. In addition, order of substitution depends on certain peculiarities of the $C_{10}H_8$ mol., viz., greater reactivity of the α-H atoms, absence of quinogenic tendency between $C_{(2)}$ and $C_{(3)}$, and the proximity of atoms in the *peri*-position. R. T.

Nitration of tetrahydronaphthalene. J. J. Makarov-Zemlianski and V. P. Bibischev (J. Gen. Chem. Russ., 1937, **7**, 1280—1283).—Tetrahydronaphthalene and conc. HNO_3 at 6—14° yield a mixture of 6 : 8- and 7 : 8-dinitro-1 : 2 : 3 : 4-tetrahydronaphthalene. R. T.

Action of aqueous bromine on 2-nitrofluorene. L. Gugliamelli and M. R. Franco (Anal. Asoc. Quím. Argentina, 1937, **25**, 1—38).—Bromination in absence of AcOH (see A., 1933, 401) yields mainly 2-bromo-7-nitro- and 5(or 6)-bromo-2-nitrofluorene (I), m.p. 135—136°, which in AcOH with $Na_2Cr_2O_7$ gives 5(or 6)-*bromo-2-nitrofluorenone*, m.p. 190° (*oxime*, m.p. 216°; *phenylhydrazone*, m.p. 177—178°; *semicarbazone*, m.p. 192°; p-*nitrophenylhydrazone*, m.p. 223°), reduced (in EtOH with NH_3 and H_2S) to 5(or 6)-*bromo-2-aminofluorenone*, m.p. 199°. (I) in EtOH with $SnCl_2$ in HCl yields 5(or 6)-*bromo-2-aminofluorene* (*Ac* derivative, m.p. 174°), which by diazotisation and bromination gives 2 : 5(or 2 : 6)-dibromofluorene. The following derivatives of 2-

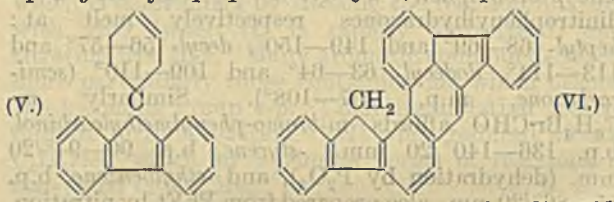
bromo-7-nitrofluorenone are described: *oxime*, m.p. 247° (decomp.); *semicarbazone*, m.p. >350°; *phenylhydrazone*, m.p. 210—212°; *p-nitrophenylhydrazone*, m.p. 300°; 2-*bromo*-7-*acetamidofluorenone*, m.p. 220°. F. R. G.

Dissociable oxides of anthracenes. 9-Phenylanthracene and its derivatives. C. Dufraisse, L. Velluz, and (Mme.) L. Velluz (Bull. Soc. chim., 1937, [v], 4, 1260—1264).—A more detailed account of work already noted (A., 1936, 1101). J. L. D.

Dissociable organic oxides. Photo-oxide of *meso*diphenylanthracene: formation, dissociation, and properties. C. Dufraisse and J. Le Bras (Bull. Soc. chim., 1937, [v], 4, 349—356; cf. A., 1935, 1233).—*meso*Diphenylanthracene (I) when insolated in C_6H_6, or better CS_2, absorbs 95% of the theoretical amount of O_2 (pure gas or from the air) for the formation of its photo-oxide (II), $C_{26}H_{18}O_2$, which when slowly heated to 180° dissociates into its components, 95% of the absorbed O being given up at the pure gas. The process has been repeated 7 times with the same sample of (I), but about 10% of it is decomposed each time. Decomp. of (II) begins at 150°, becoming rapid at 180°. Attempts to convert (I), including treatment with MgI_2, into a non-dissociable isomeride failed, such changes being considered possible only with the corresponding naphthacene compounds (cf. Enderlin, A., 1936, 1241). Attempts to form a monoxide of (I) failed; (II) with KI–AcOH liberates I corresponding with 2 O. H. G. M.

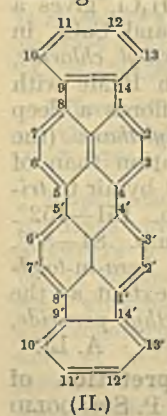
Synthesis of 1 : 4-dimethylphenanthrene. R. B. Akin, G. S. Stamatoff, and M. T. Bogert (J. Amer. Chem. Soc., 1937, 59, 1268—1272).—K *p*-xylylacetate (from *p*-xylene) with *o*-NO_2·C_6H_4·CHO and Ac_2O yields o-*nitro*-α-p-*xylylcinnamic acid*, m.p. 173·5—174°, reduced [ammoniacal $Fe(OH)_2$] to the NH_2-*acid*, m.p. 199—200·5°, which when diazotised and treated with Cu powder gives 1 : 4-*dimethylphenanthrene*-10-*carboxylic acid*, m.p. 199·7—200·2° (*semipicrate*, m.p. 148·5—149°). Heating with Cu in quinaldine converts this into 1 : 4-*dimethylphenanthrene* (I), m.p. 50—51° (*picrate*, m.p. 147—148°; *styphnate*, m.p. 135·5—136·5°), which on hydrogenation (Na + C_5H_{11}·OH) followed by oxidation ($K_2Cr_2O_7$) gives the *quinone*, m.p. 214—216°. (I) is not identical with the compound of Bardhan and Sengupta (A., 1932, 1241), which appears to be the 1 : 3-Me_2 compound (cf. Bogert and Stamatoff, A., 1933, 948), formed by migration of Me in the fusion with Se, although (I) is unchanged by similar fusion. All m.p. are corr. A. Li.

Fluorene series. IV. Reactions of diphenylene-ethylene. H. Wieland and O. Probst (Annalen, 1937, 530, 274—290).—Polymerisation of diphenylene-ethylene (I) $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$>C:$CH_2$ is accelerated by air, in the presence of which the polymeric hydrocarbon is accompanied by a higher peroxide $(C_{14}H_{10}O_2)_n$, fluorenone, and CH_2O. Polymerisation is the main reaction when a solution of the hydrocarbon is exposed to air in the dark. Autoxidation and polymerisation are restricted by the same substances, notably pyrogallol. (I) with Na in Et_2O gives an intensely red *compound*, which is converted by H_2O into αδ-*didiphenylenebutane* (II), m.p. 224—225°, and αγ-*didiphenylenebutane* (III), m.p. 171—171·5°. The production of (III) is indirect and due to reduction of (I) to Na 9-methylfluorene (owing to traces of moisture in the Et_2O), which then reacts with (I). The structure of (II) and (III) follows from the reaction of their Na derivatives with CO_2, whereby respectively αα′-*didiphenyleneadipic acid*, m.p. 253° (*Me*$_2$ ester, m.p. 250—251°), decarboxylated to (II) and αγ-*didiphenylenevaleric acid*, m.p. 211—212° (*Me* ester, m.p. 149—150°), decarboxylated to (III), are produced. Treatment of 9-methylfluorene (IV) with Na in Et_2O followed by CO_2 gives 9-*methylfluorene*-9-*carboxylic acid*, m.p. 168° (in a non-reproducible experiment a *substance*, $C_{28}H_{22}O_3$, m.p. 159·5°, was isolated). Hydrogenation (PtO_2 in Et_2O) of (I) affords βγ-*didiphenylenebutane*, m.p. 188°, with some (IV); in presence of Pd (IV) is the sole product. 2 : 7-*Dibromo*-9-*methylfluorene* has m.p. 141·5°. Addition of butadiene to (I) gives *diphenylene*cyclo*hexene* (V), m.p. 145·5°, hydrogenated to a *substance*, m.p. 80—80·5°. (I) and CHN_2·CO_2Et at 100° give *Et diphenylene*cyclo*propanecarboxylate*, m.p. 118·5°,



hydrolysed to *diphenylene*cyclo*propanecarboxylic acid*, m.p. 214—215°; this could not be decarboxylated but *diphenylene*cyclo*propane*, m.p. 73—73·5°, is readily obtained from (I) and CH_2N_2. CPh_2:CH_2 and CHN_2·CO_2Et do not readily yield the pure corresponding ester but 1 : 1-*diphenyl*cyclo*propanecarboxylic acid*, m.p. 171°, is readily purified; when heated with CaO at 300° it yields 1 : 1-*diphenyl*cyclo*propane*, b.p. 140° (bath)/12 mm., more readily obtained from CPh_2:CH_2 and CH_2N_2. Thermal depolymerisation of (I) is accompanied by the formation of fluorene, (IV), and a *hydrocarbon* (VI), m.p. 198—199°. H. W.

Fluoranthene and its derivatives. VI. J. von Braun and G. Manz (Ber., 1937, 70, [*B*], 1603—1610).—Treatment of fluoranthene (I) with $NaNH_2$ in boiling decahydronaphthalene yields *periflanthene*



(II.)

(II), m.p. >360°, which could not be obtained by use of NHPhNa, by heating with $AlCl_3$ at 200°, with $AlCl_3$ + NaCl, or with S or Se. It is converted by dil. HNO_3 in a sealed tube into non-homogeneous products, but is scarcely attacked by CrO_3 or by air in boiling $C_6H_3Cl_3$. It is unchanged by $Na_2S_2O_4$, metals, and acids or Na and amyl alcohol. Hydrogenation (Ni) of (II) at 270°/250 atm. readily gives the vitreous *compound*, $C_{32}H_{36}$, b.p. >320°/0·3 mm., which does not give recognisable products when boiled with dil. HNO_3 possibly by reason of simultaneous dehydrogenation to the *substance* (III), $C_{32}H_{32}$, m.p. 235—238°, also obtained accidentally by hydro-

genation of (II). (III) is dehydrogenated by S (8—9 atoms) to (II) and by Se (2 atoms) at 300° to the *compound*, $C_{32}H_{28}$, m.p. 314° after softening at 300°. 4-Bromofluoranthene is converted by Cu powder and NaI in N_2 at 300° into *difluoranthyl*, m.p. 327—329°, which gives (II) when heated with $NaNH_2$, thus supporting the constitution assigned to the latter. 4-Ketotetrahydrofluoranthene and MgMeI give a product converted by boiling 20% H_2SO_4 into 4-*methyldihydrofluoranthene*, b.p. 160—170°/0·2 mm., m.p. 127—128°, whence 4-*methylfluoranthene* (IV), m.p. 66° (*picrate*, m.p. 172°). 4-*Phenyldihydrofluoranthene*, b.p. 220—230°/0·3 mm., m.p. 148°, is dehydrogenated by Cu turnings in H_2 at about 600° to 4-*phenylfluoranthene* (V), m.p. 144°. Neither (IV) nor (V) resembles (I) in behaviour towards $NaNH_2$, thus leading further support to the constitution assigned to (II). Acenaphthene and acenaphthylene are not influenced by $NaNH_2$; tetrahydronaphthalene is largely resinified whilst stilbene is mainly converted into $CH_2Ph{\cdot}CH_2Ph$ with production of phenanthrene. (II) appears to be converted by fuming HNO_3 at −2° into an amorphous NO_2-derivative and to be sulphonated by conc. H_2SO_4 at 100°. It does not react with maleic anhydride. It gives a dark violet powder when heated with $AlCl_3$ + NaCl. H. W.

Synthesis of 1 : 2-benzanthracene derivatives related to 3 : 4-benzpyrene. M. S. Newman (J. Amer. Chem. Soc., 1937, **59**, 1003—1006).—5 : 9-*Dimethyl-* (I) and 9-*methyl*-1 : 2-*benzanthracene* (II) are synthesised. (I) is probably as carcinogenic as the 10-Me compound, but (II) appears to be less potent. In contrast to the course of the Friedel–Crafts reaction, 1-$C_{10}H_7{\cdot}MgBr$ and 3 : 1 : 2-$C_6H_3Me(CO)_2O$ (prep. from piperylene and maleic anhydride by way of the H_4-anhydride, m.p. 61—62°, b.p. 155—156°/12 mm., dehydrogenated by S at 250—260°), m.p. 115—116°, afford 52% of 3-α-*naphthoyl*-o-, m.p. 165·6—166·8°, and only 1·5% of 2-α-*naphthoyl*-m-*toluic acid*, m.p. 234—235° (sinters at 230°), the structures of which are proved by decarboxylation. The *o*-toluic derivative with MgMeBr gives 74% of the *lactone*, m.p. 131·6—132°, of 3-α-*hydroxy*-α-1′-*naphthylethyl*-o-*toluic acid*, reduced by Zn–Hg in HCl–AcOH to 3-α-1′-*naphthylethyl*-o-*toluic acid*, m.p. 162—162·6°, which by ring-closure with H_2SO_4 at 20°, followed by reduction by Zn–NaOH, gives a poor yield of (I), m.p. 135—135·5°. *o*-α-$C_{10}H_7{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$ affords similarly the *lactone*, m.p. 154·5—155°, of o-α-*hydroxy*-α-1′-*naphthylethylbenzoic acid*, o-α-1′-*naphthylethylbenzoic acid*, m.p. 169·4—170°, and a 26% yield of (II), m.p. 138·4—138·8°. *o*-$C_6H_4Me{\cdot}CO{\cdot}C_{10}H_7$-α exists in forms, m.p. 59—61° and (unstable) 51·5—52·5°. M.p. are corr. R. S. C.

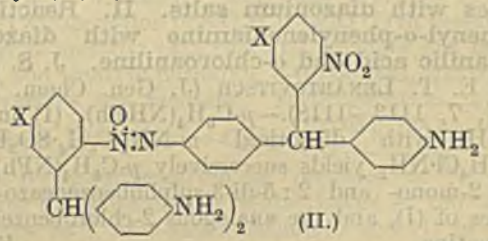
Condensation of acetylene with aromatic amines in presence of mercury salts. XII. N. Kozlov and D. Mitzkevitsch (J. Gen. Chem. Russ., 1937, **7**, 1082—1085).—The reaction is represented: $NH_2Ph + C_2H_2 + HgCl_2 \rightarrow$ $x NH_2Ph, y HgCl_2, z C_2H_2 \rightarrow$ 2NPh:CHMe → NHPh·CHMe·CH_2·CH:NPh → NHPh·CHMe·CH:CH·NHPh. The reaction is catalysed equally well by $HgCl_2$, $HgCl_2,2NH_2Ph$, $C_2H_2,3HgCl_2$, $3HgO$, or $C_2H_2,HgCl_2$. R. T.

Action of benzoyl chloride on sodium azide in contact with alkali. G. Labruto and A. Landi (Gazzetta, 1937, **67**, 213—216).—NaN_3, BzCl, and solid KOH give $CO(NHPh)_2$ (I), with traces of PhNCO, presumably by the reactions $NaN_3 \rightarrow BzN_3 \rightarrow PhNCO + N_2$; $PhNCO + KOH \rightarrow NH_2Ph + K_2CO_3$; $PhNCO + NH_2Ph \rightarrow$ (I). E. W. W.

Products of bromination of *d*-tartaric acid di-*p*-toluidide. H. Kuczyński (Rocz. Chem., 1937, **17**, 186—188; cf. this vol., 176).—The substance described by Wróbel (*ibid.*, 77) as 2 : 2′-dibromo-3 : 3′-diketo-5 : 5′-dimethyldihydro-2 : 2′-di-indolyl, m.p. 74°, is actually 2 : 6-dibromo-*p*-toluidine, and that described as 2-(2′-bromo-3′-keto-5′-methyl-2 : 2′-indolyl)-3-keto-5-methylindolenine, m.p. 210°, is probably tartaric acid di-2-bromo-*p*-toluidide. R. T.

Complex salts with *trans*-1 : 2-diamino*cyclo*hexane.—See A., I, 474.

Condensation of *o*-nitrobenzaldehydes with aniline. III. Photochemical behaviour of the anthranils and triphenylmethanes obtained. I. Tanasescu and (Mlle.) M. Suciu (Bull. Soc. chim., 1937, [v], **4**, 245—258; cf. A., 1936, 1509).—A mechanism involving tautomerism of the nitroaldehyde is proposed for the condensation of *o*-nitrobenzaldehydes with NH_2Ph sulphate in presence of $ZnCl_2$ to give a triphenylmethane and a *p*-aminophenylanthranil (cf. A., 1906, i, 515). 5-Chloro-2-nitro-4′ : 4″-diaminotriphenylmethane (I) when irradiated in C_6H_6 with sunlight gives a blue com-compound and a *compound*, $C_{38}H_{30}O_2N_6Cl_2$, m.p. 78—80° (*Ac* derivative; *Bz*$_3$ derivative, m.p. 157°), probably (II) (X = Cl), reduced by Sn–HCl to



(II.)

2 : 4′ : 4″-triaminotriphenylmethane. Similarly, 2-nitro-4′ : 4″-diaminotriphenylmethane (III) gives a blue compound and a *compound*, $C_{38}H_{32}O_2N_6$, m.p. 125°, considered to be (II) (X = H). The substances (II) (X = H and Cl) when irradiated in C_6H_6 with sunlight give the corresponding blue compounds, and like (I) and (III) slowly give a blue ppt. with H_2O_2–HCl in the cold and a brown ppt. when the solution is heated. *o*-Nitrobenzylidene chloride (IV) when treated with $AlCl_3$–CS_2 and PhCl gives 2-*nitro*-4′ : 4″-*dichlorotriphenylmethane* (V), m.p. 110°, also obtained (Sandmeyer) from (III), and converted by NH_3–H_2O–EtOH–$CuSO_4$ (sealed vessel; 15 hr.; 180°) into a *compound*, $C_{27}H_{23}ON_3$, m.p. 240—250°, probably 2-*diethylamino*-5-p-*diethylaminophenylacridine* N-*oxide*. Attempts to prepare 2-nitrotriphenylmethane-4′ : 4″-dicarboxylic acid from (V), KCN, $Cu_2(CN)_2$–H_2O–EtOH (sealed tube; 190—200°; 15 hr.), and from (IV), $AlCl_3$–CS_2, and PhCN, failed; the latter gave a *compound*, $C_{14}H_{11}O_4N_2Cl$, m.p. 180° (sublimes in vac. giving a *substance*, m.p. 225·5°), considered to be

m-NO_2·C_6H_4·CHCl·C_6H_4·CO·NH·OH-*p*. 2-Chloro-*p*-aminophenylanthranil (VI) is converted by the diazo-reaction into 2 : 4′-*dichlorophenylanthranil*, m.p. 202°, which with H_2SO_4–$NaNO_2$ at −10° gives 2 : 7-*dichloroacridone*, m.p. 416°. This when treated with NPhMe$_2$–$POCl_3$ (water-bath) gives 2 : 7-*dichloro*-5-*p*-*dimethylaminophenylacridine*, m.p. 240°. Attempts to prepare (VI) from *o*-NO_2·C_6H_4·CHO, NH_2Ph, and AcOH–$POCl_3$ failed, complex products being obtained. H. G. M.

Some nitro- and amino-derivatives of benzanilide, thiobenzanilide, and 1-phenylbenzthiazole, and the azoic colours derived from them. H. Rivier and J. Zeltner (Helv. Chim. Acta, 1937, **20**, 691—704).—Azo-compounds are prepared on cotton from β-$C_{10}H_7$·OH as coupling component, and NH_2-derivatives of NHPhBz, NHPh·CSPh, and 1-phenylbenzthiazole (I) as azo-components. It is concluded that the CO group increases the depth of colour slightly, the CS group greatly, but S is easily removed by acids; the effect of the thiazole group is intermediate. The dyes from H-acid and derivatives of NHPhBz and (I) as azo-components dye wool in red to blue-violet shades, but no correlation similar to that found with the dyes from β-$C_{10}H_7$·OH can be drawn. Dyes could not be prepared from H-acid and derivatives of NHPh·CSPh owing to loss of S under the acid conditions necessary for coupling. The following are described: m-, m.p. 134—134·5°, and p-*nitro*-, m.p. 154·5—155°, and m-*amino-thiobenzanilide*, m.p. 130—131°; *thiobenz*-m-*nitroanilide*, m.p. 150°; 3′-, m.p. 139°, 4′-, m.p. 156°, 4-, m.p. 206°, and 5-*amino*-1-*phenylbenzthiazole*, m.p. 205°. P. G. C.

Reaction of *p*-phenylenediamine and its derivatives with diazonium salts. II. Reaction of diphenyl-*o*-phenylenediamine with diazotised metanilic acid and *o*-chloroaniline. J. S. Joffe and E. T. Lenartovitsch (J. Gen. Chem. Russ., 1937, **7**, 1113—1118).—*p*-$C_6H_4(NHPh)_2$ (I) in 80% AcOH with diazotised *m*-NH_2·C_6H_4·SO_3H or *o*-C_6H_4Cl·NH_2 yields successively *p*-$C_6H_4(NPh)_2$ and the 2-mono- and 2 : 5-di-3-sulphobenzeneazo-derivatives of (I), and the analogous 2-chlorobenzeneazo-derivative. R. T.

Configurations of the isomeric diazocyanides. R. J. W. Le Fèvre and H. Vine (Chem. and Ind., 1937, 688).—Determination of the dipole moments of the two *p*-bromobenzene diazocyanides, m.p. 42° and 130°, respectively, indicates that the form of lower m.p. is the *trans*- and that of higher m.p. is the *cis*-variety. The conversion *trans* → *cis* proceeds spontaneously in C_6H_6 at room temp. It is probable that the structures assigned by Hantzsch to the diazocyanides should be interchanged and that these compounds are examples of geometrical isomerism, like that of $C_2H_2Cl_2$, in which the *trans*- is the less stable of the two isomerides. H. W.

Diazo-chemistry. H. A. J. Schoutissen (Chem. Weekblad, 1937, **34**, 506—515).—A review. S. C.

Diaryls and their derivatives. XIV. Ring-closure in 6 : 6′-dinitro-2 : 2′-dihydroxy-1 : 1′-dinaphthyl. J. S. Joffe and I. S. Gorelik (J. Gen. Chem. Russ., 1937, **7**, 1102—1105).—Attempted synthesis of 5 : 8-dinitro-1 : 12-dihydroxyperylene by heating 6 : 6′-dinitro-2 : 2′-dihydroxy-1 : 1′-dinaphthyl (I) or its Pb salt with $AlCl_3$ at 120—180° for 0·5—12 hr. was unsuccessful. (I) with H_2SO_4 at 40° (30 min.) gives 6 : 6′-*dinitro*-1 : 1′-*dinaphthylene* 2 : 2′-*oxide*. R. T.

Hydrogenation of αβ-dihydroxypropiophenone. Formation of two diasterioisomeric phenylglycerols. M. Cahnmann (Bull. Soc. chim., 1937, [v], **4**, 226—232; cf. A., 1936, 68).—CH_2:CH·COPh when treated with H_2O_2–MeOH–NaOH at 0—10° gives *epoxypropiophenone*, m.p. 53° (at higher temp. COPhMe is chiefly formed), which when refluxed (3—4 hr.) with 0·01*N*-HCl gives αβ-*dihydroxypropiophenone*, m.p. 81·5° (corr.). This when reduced by Al–Hg–H_2O or hydrogenated (Pd–C–H_2) gives a mixture of two diastereoisomerides, since on benzoylation it yields both α- and β-tribenzoates of α-phenylglycerol (cf. A., 1934, 649). H. G. M.

Sex hormones: their relationships with cholesterol. R. Delaby (J. Pharm. Chim., 1937, [viii], **26**, 136—165).—A lecture.

Cholesterol and the adrenal cortical hormone. —See A., III, 360.

Process of irradiation of compounds of the ergosterol type. K. Dimroth (Ber., 1937, **70**, [*B*], 1631—1636).—The comparative behaviour of ergosterol (I) and lumisterol (II) when subjected to very short irradiation shows that (II) is an essential intermediate in the conversion of (I) into trachysterol. Irradiation of 22-dihydroergosterol, 7-dehydrocholesterol, and 7-dehydrositosterol gives products with antirachitic activity. The changes in the spectra proceed analogously and it is therefore very probable that intermediate stages are passed through as with (I). All these sterols have two conjugated double linkings between $C_{(5)}$ and $C_{(6)}$ and between $C_{(7)}$ and $C_{(8)}$; this conjugated system is essential for the incidence of the photo-reaction. The course of irradiation of pyrocalciferol (III) and *iso*pyrocalciferol (IV) differs completely from that of (I) or (II) since there is no evidence of the formation of intermediate products with characteristic absorption between 248 and 320 mμ. The final products cannot contain conjugated double linkings. (III) gives *photopyrocalciferol* (V), m.p. 103—105° (indef.), $[\alpha]_D^{19}$ +50·8° in $CHCl_3$ (*dinitrobenzoate*, m.p. 162°, $[\alpha]_D^{19}$ +51·7° in $CHCl_3$; *isobutyrate*, m.p. 79—80°; non-cryst. *acetate*), which does not give a ppt. with digitonin (VI) in 90% EtOH and absorbs 2 H_2 when hydrogenated. (IV), as acetate, affords *photoisopyrocalciferol* (VII), m.p. (indef.), 76—80°, $[\alpha]_D^{20}$ −60·4° in $CHCl_3$, which does not give a ppt. with (VI) (*dinitrobenzoate*, m.p. 145—146°, $[\alpha]_D^{19}$ −11·2° in $CHCl_3$; *acetate*, m.p. 70°, $[\alpha]_D^{20}$ −56·3° in $CHCl_3$). When heated at 188° (V) is transformed into (III) and (VII) into (IV) so that it appears that only one double linking has wandered during irradiation. Under similar conditions suprasterol II and the irradiation product from dehydroergosterol are unchanged. Oxidation of (IV) or photo*iso*pyrocalciferyl acetate with conc. HNO_3 does not yield $C_6HMe(CO_2H)_4$. H. W.

Sex hormones. XXIII. Action of selenium dioxide on Δ^5-androstenediol. L. Ruzicka and P. A. Plattner (Helv. Chim. Acta, 1937, **20**, 809—811).—Δ^5-Androstene-3-*trans*-17-*trans*-diol with SeO_2 in H_2O–AcOH affords Δ^5-*androstene*-3 : 4 : 17-*triol*, m.p. 253—254° (*triacetate*, m.p. 156—156·5°). Catalytic reduction affords *androstane*-3 : 4 : 17-*triol*, m.p. 260—261° (*triacetate*, m.p. 222·5—223·5°).

P. G. C.

Synthetic experiments in the pinane group. III. Synthesis and configuration of pinic acid. P. C. Guha, K. Ganapathi, and U. K. Subramanian (Ber., 1937, **70**, [*B*], 1505—1512).—Pinonic acid obtained from Greek oil of turpentine appears to be a mixture of *cis*- and *trans*-forms. From Et pinonate, two semicarbazones, m.p. 154—155°, and m.p. 129—134°, are obtained; the former of these gives homogeneous Et pinonate, b.p. 127°/2—3 mm., the pinonic acid from which is oxidised to *trans*-pinic acid (I), b.p. 203°/4 mm. [Et_2 ester (II), b.p. 146°/10 mm.; *dianilide* (III), m.p. 204°; *diamide*, m.p. 222—223°]. The *trans*-nature of (I) follows from its production by the oxidation of trans-1-*hydroxymethyl*-3-β-*hydroxyethyl*-2 : 2-*dimethyl*cyclo*butane*, b.p. 145—146°/8 mm., obtained by reduction of (II) with Na and abs. EtOH. Reduction of *cis*-norpinic anhydride could not be effected by Na–Hg or by Zn with HCl or AcOH whereas Na and abs. EtOH gives *Et* 2 : 2-*dimethyl*-3-*hydroxymethyl*cyclo*butane*-1-*carboxylate* (IV), the *trans* nature of which is established by its oxidation by $KMnO_4$ to *trans*-norpinic acid. The acid from (IV) is converted by the successive action of PBr_3 and C_6H_6–EtOH into *Et* 2 : 2-*dimethyl*-3-*bromomethyl*-cyclo*butane*-1-*carboxylate*, b.p. 110°/5 mm., converted by NaCN in EtOH into *Et* 2 : 2-*dimethyl*-3-*cyanomethyl*cyclo*butane*-1-*carboxylate*, b.p. 125—126°/7 mm., hydrolysed by KOH–H_2O to (I). *cis*-Norpinic acid is converted by the successive action of $SOCl_2$ and NH_3–C_6H_6 into cis-*norpindiamide*, m.p. 188—189°.

H. W.

Polar and non-polar form of *o*-, *m*-, and *p*-aminobenzoic acids. P. Spinoglio (Gazzetta, 1937, **67**, 256—264).—The *compounds* (presumably thiocarbamides) from *o*- (I), *m*- (II), and *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (III) with $CH_2{:}CH{\cdot}CH_2{\cdot}NCS$ are prepared. That from (I) is obtained in EtOH at room temp., at which (I) is presumed to be in the non-ionised neutral form; (II) and (III) react when heated. The solubility of the three acids in H_2O increases to a max. with the addition of inorg. salts. The greatest increase is observed with (II), in which it is suggested that there is the greatest proportion of the double ion $NH_3{\cdot}C_6H_4{\cdot}CO_2'$, to which the solubility effect is ascribed.

E. W. W.

Friedel–Crafts reaction of lactones. II. Aromatic substituted fatty acids from δ-chloro-γ-valerolactone. H. Beyer (Ber., 1937, **70**, [*B*], 1482—1491).—The action of $AlCl_3$ on δ-chloro-γ-valerolactone and PhMe at 70—80° gives unchanged material, δ-p-*tolyl*-n-*valeric acid*, b.p. 146—148°/0·1 mm., m.p. 74° after softening at 71—73° (*amide*, m.p. 113—114°), γδ-*di*-p-*tolyl*-n-*valeric acid* (I), b.p. 195—197°/0·1 mm., a mixture of 2 : 6- and 2 : 7-dimethylanthracene [identified by ozonisation to 2 : 7-dimethylanthraquinone (II)], and 2 : 7-*dimethylanthracene*-10-*butyric acid* (III), m.p. 187—189° after softening at 185° (apparently accompanied by the isomeric 2 : 6-compound). (I) affords a *Me*, b.p. 169—171°/0·2 mm., and *Et*, b.p. 178—179°/0·1 mm., ester and is converted by PCl_5 followed by $AlCl_3$ in CS_2 into 1-*keto*-4-p-*xylyl*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 175—176°/0·1 mm. [*semicarbazone*, m.p. 208—210° (decomp.) after softening at 205° or m.p. 212—214° (decomp.) when rapidly heated]. (III) affords a *Me*, m.p. 116—118°, and an *Et*, m.p. 83—85° (decomp.), ester which could not be hydrogenated (PtO_2 in EtOH) and a *hydrazide*, m.p. 207—208°. It is reduced (H_2–PtO_2–AcOH) to 2 : 7 - *dimethyl* - 1 : 2 : 3 : 4 - *tetrahydroanthracene* - 10 - *butyric acid*, m.p. 143—154° after softening at 140°, which, unlike (III), does not fluoresce in solution. Ozonisation of (III) in $CHCl_3$ yields (II). Treatment of (III) with maleic anhydride at 120—150° gives the *adduct*, $C_{24}H_{22}O_5$, m.p. 221—223° (decomp.) after softening at 218°.

H. W.

Isolation of *p*-coumaric acid from green tea. M. Tsujimura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, **32**, 138—142).—Hot aq. $COMe_2$ extracts *p*-coumaric (*p*-hydroxycinnamic) acid [*Ac* derivative, m.p. 208°, *Me ether*, m.p. 171° (*Me* ester, m.p. 89°)]. These derivatives are identical with those prepared synthetically.

J. L. D.

Velocity of catalytic hydrogenations.—See A., I, 470.

Phthalide. I. Hydrogenation of phthalic anhydride. P. R. Austin, E. W. Bousquet, and W. A. Lazier (J. Amer. Chem. Soc., 1937, **59**, 864—866).—Hydrogenation of *o*-$C_6H_4(CO)_2O$ (I) in presence of different metallic catalysts and solvents has been studied, and yields of phthalide, *o*-toluic acid, and their H_6-derivatives are recorded. Hydrogenation probably occurs by way of *o*-$C_6H_4{<}\overset{C(OH)(OEt)}{CO}{>}O$ in EtOH. By hydrogenation in presence of Ni on kieselguhr 5-nitrophthalide in abs. EtOH at 150°/100 atm. gives 85% of 5-aminophthalide and (I) in aq. NaOH at 110°/100 atm. gives 80% of phthalide.

R. S. C.

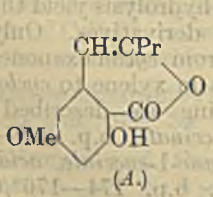
***spiro*-Compounds. III. Synthesis of *cyclo*hexane*spirocyclo*butane derivatives by the application of the Dieckmann reaction to esters of the tricarballylic series.** N. N. Chatterjee (J. Indian Chem. Soc., 1937, **14**, 127—132).—The cyanohydrins of $COMe_2$, *cyclo*pentanone, *cyclo*hexanone, 2-, 3-, and 4-methyl*cyclo*hexanone were condensed with Et sodiocyanoacetate and the Na salts of the Et cyanoacetates obtained treated with $CH_2Br{\cdot}CO_2Et$ to give cyanosuccinates, which on hydrolysis yield the corresponding carballylic acid derivatives. Only those carballylic acids derived from *cyclo*hexanones could be cyclised by means of Na in xylene to *cyclo*butane derivatives. The following are described: Et_2 1-*cyano*cyclo*hexane*-1-*cyanosuccinate*, b.p. 200—205°/7 mm.; 1-*carboxy*cyclo*hexane*-1-*succinic acid*, m.p. 187° (decomp.) (Et_3 ester, b.p. 174—176°/6 mm.); Et_2 cyclo*hexane*spirocyclo*butan*-2-*one*-3 : 4-*dicarboxylate*, b.p. 178—180°/6 mm.; Et_2 4-*methyl*-

cyclo*hexane*-1-*cyano*-1-*succinate*, m.p. 90°; 4-*methyl*-cyclo*hexane*-1-*carboxylic*-1-*succinic acid*, m.p. 188°; *Me*$_3$ 4-*methyl*cyclo*hexane*-1-*carboxylate*-1-*succinate*, b.p. 178—180°/5 mm.; 4′-*methyl*cyclo*hexane*spiro-cyclo*butan*-2-*one*-3 : 4-*dicarboxylate*, b.p. 177—185°/5 mm.; *Et*$_2$ 1-*cyano*-2-*methyl*cyclo*hexane*-1-*cyano*-*succinate*, b.p. 200—208°; 2-*methyl*cyclo*hexane*-1-*carboxylic*-1-*succinic acid* (*Et*$_3$ ester, b.p. 175—176°); *Et*$_2$ 1-*cyano*-3-*methyl*cyclo*hexane*-1-*cyanosuccinate*, b.p. 200—205°/6 mm.; 3-*methyl*cyclo*hexane*-1-*carboxylic*-1-*succinic acid* (*Et*$_3$ ester, b.p. 178°/5 mm.); *Et*$_2$ 1-*cyano*cyclo*pentane*-1-*cyanosuccinate*, b.p. 197—203°/7 mm.; cyclo*pentane*-1-*carboxylic*-1-*succinic acid*, m.p. 159° (*Et*$_3$ ester, b.p. 173—175°/7 mm.); Et$_2$ βγ-dicyano-β-methylbutane-γδ-dicarboxylate, b.p. 180—182°/6 mm.; αα-*dimethyltricarballylic acid*, m.p. 156° (*Et*$_3$ ester, b.p. 160°/5 mm.). D. J. B.

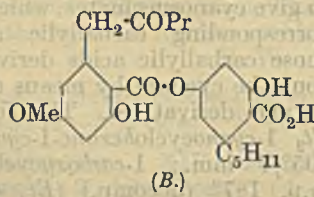
Attempted synthesis of αβ-dicinnamoylethane. W. Lampe, E. Blenderówna, and A. Bluman (Rocz. Chem., 1937, **17**, 216—225).—CHPh:CH·CO·CH$_2$·CH$_2$·CO$_2$Et and Ac$_2$O at 140° yield 5-keto-2-styryl-4 : 5-dihydrofuran (I), which with PhCHO in EtOH at 100° gives 5-*keto*-4-*benzylidene*-2-*styryl*-4 : 5-*dihydrofuran*, m.p. 164—165°. Attempted condensation of (I) with cinnamoyl chloride (II) was unsuccessful. Me sodioacetoacetate and (II) in Et$_2$O yield *Me* α-*cinnamoylacetoacetate* (III), m.p. 49—50°, and *Me* α-*cinnamoyl*-β-O-*cinnamoylacetoacetate*, m.p. 117—119°. (III) and aq. NH$_3$ at 50° afford *Me cinnamoylacetate*, m.p. 71—73°, which when treated successively with Na and I gives *Me*$_2$ αβ-*dicinnamoyl*-*succinate* (IV), m.p. 135—137°, hydrolysis of which (20% K$_2$CO$_3$ at 100°, 1% EtOH–KOH at the b.p., or autoclaving at 3 atm.) yields 4-*keto*-3-*carbomethoxy*-4-*cinnamoyl*-2-*styryl*-4 : 5-*dihydrofuran*, m.p. 240—245°, instead of the expected αβ-dicinnamoylsuccinic acid. (IV) in AcOH and H$_2$SO$_4$ at 100° yield 3 : 4-*dicarbomethoxy*-2 : 5-*distyrylfuran*, +H$_2$O, m.p. 293°. Sodiocinnamoylacetone and I in Et$_2$O yield αβ-*dicinnamoyl*-αβ-*diacetylethane*, m.p. 200°, converted by heating with aq. AcOH and H$_2$SO$_4$ into 3 : 4-*dicinnamoyl*-2 : 5-*dimethylfuran*, m.p. 135—136° [*dioxime*, m.p. 262—263° (decomp.)]. The synthesis of αβ-dicinnamoylethane by any of the above approaches was unsuccessful. R. T.

Reactions of rare earths and allied elements with pyrogallol, gallic acid, and morphine.—See A., I, 477.

Lichen substances. LXXXI. Glomelliferic acid. I. Y. Asahina and H. Nogami (Ber., 1937, **70**, [*B*], 1498—1499).—Extraction of the thalli of *Parmelia glomellifera*, Nyl, with Et$_2$O yields glomelliferic acid (I), m.p. 143—144°, which is $C_{25}H_{20}O_8$ since it is converted by cold 10% KOH into glomellin



(*A*.)



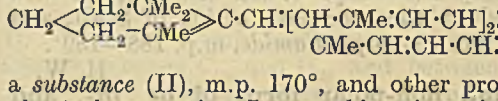
(*B*.)

(II), m.p. 85°, and olivetolcarboxylic acid. The inability of (I) to give a red colour with CaOCl$_2$, the absence of CO$_2$H from (II), and the similarity of (I) with microphyllic acid in behaviour towards alkali leads to the constitutions *A* and *B* for (II) and (I), respectively. H. W.

Lichen substances. LXXX. Components of so-called *Thamnolia vermicularis*, f. *taurica*. Y. Asahina and M. Yasue (Ber., 1937, **70**, [*B*] 1496—1497).—Thalli of *Thamnolia subvermicularis*, Y. Asahina, are extracted with Et$_2$O and COMe$_2$, and the extracts treated with NH$_2$Ph in COMe$_2$ and evaporated. The product after washing with dil. AcOH is extracted with Et$_2$O, whereby squamatic acid (I), m.p. 228° (decomp.), remains undissolved. The mother-liquors contain the *anil*, m.p. 211°, of baeomycessic acid from which the free acid, m.p. 223°, is obtained by treatment with 10% HCl. (I) (Me$_2$ ester, m.p. 183°) is isolated from *Cladonia squamosa*, f. *denticollis* from Europe. H. W.

Cannizzaro reaction. K. F. Bonhoeffer and H. Fredenhagen (Naturwiss., 1937, **25**, 459).—When the Cannizzaro reaction is carried out with PhCHO in alkaline solution containing D$_2$O, the CH$_2$ of the CH$_2$Ph·OH formed contains no D. This result indicates that the H is transported directly from the C of one CHO to the other and that the transport of H does not take place after hydration of one of the aldehyde mols. nor does the solvent play a part in its transference. W. O. K.

β-Carotenal, a degradation product of β-carotene. P. Karrer and U. Solmssen (Helv. Chim. Acta, 1937, **20**, 682—690).—The mixture obtained by oxidation of β-carotene with KMnO$_4$ contains chiefly β-*carotenal* (I), deep violet crystals, $C_{30}H_{40}O$, m.p. 139° [*oxime*, m.p. 180°; *semicarbazone*, m.p. 212° (sinters 205°)], to which is assigned the formula



a *substance* (II), m.p. 170°, and other products. In physical properties (I) resembles citraurin (III) (A., 1936, 1435), which, it is suggested, is the 3-OH-derivative of (I). The absorption max. of (I), (II), and (III) in various solvents are given. (I) shows vitamin-*A* activity. P. G. C.

Velocity of reaction of aldehydes with ketones. V. Reaction of vanillin with acetone. E. K. Nikitin and S. A. Verschinski (J. Gen. Chem. Russ., 1937, **7**, 1306—1314).—Vanillin in EtOH and aq. COMe$_2$ with 16% aq. KOH yield vanillylideneacetone; the velocity of the reaction ∝ concns. of vanillin and COMe$_2$. A method for determination of the substrates, based on the above reaction, is described. R. T.

Indones. XV. Chloro-derivatives of 3-phenyl-2-ethylindone. R. de Fazi and F. Pirrone (Gazzetta, 1937, **67**, 207—213; cf. this vol., 294).—3-*Phenyl*-2-*ethylindone* (crystal data recorded), with Cl$_2$ in CHCl$_3$ at −15°, gives 2 : 3-*dichloro*-3-*phenyl*-2-*ethylhydrindone* (I), m.p. 94—96°, with an *isomeride* (II), m.p. 115—116°, both of which have one labile Cl; also a *substance* $C_{17}H_{14}OCl$ (*sic*), m.p. 119—120°, and two *isomerides* of the last, m.p. 127—128° and 132—133°. Crystal data of the last two are recorded.

In CCl_4 at −5°, (I), (II), and two *substances*, $C_{17}H_{14}OCl$ (*sic*), m.p. 105—106° and 145—146°, are obtained. E. W. W.

Tautomerism of derivatives of acetomesitylene. E. P. Kohler and R. B. Thompson (J. Amer. Chem. Soc., 1937, **59**, 887—893).—The persistance of the enolic form of 2 : 4 : 6-$C_6H_2Me_3$·CO·CH_2·$CHPh_2$ (I) is proved by alkylation of the Mg derivative and other reactions; the amount of *O*-alkyl derivative formed from such systems is a measure of the persistence of the enol form. Reduction of CPh_2:CH·CO·$C_6H_2Me_3$ catalytically and by Zn–acid is proved to be a 1 : 4-addition, which is thus considered to be general both for reduction and for addition of MgRX to the system, C:C·CO. Addition first of CHPh:CH·COPh to MgPhBr in Et_2O and then of CH_2Cl·OMe gives 30% of *α-methoxymethoxy-γγ-diphenylpropenylbenzene*, m.p. 64—65° (formed from the enolic form), and 70% of β *methoxy-β′β′-diphenylisobutyrophenone* (II), m.p. 131—132°, with a little Ph_2 and CH_2Ph·OMe. (II) is stable to dil. acids and alkali, but with hot 50% HBr gives *β-bromo-γγ-diphenylisobutyrophenone*, m.p. 163°, converted by KOH–EtOH into *Ph α-benzhydrylvinyl ketone*, m.p. 115° (*dibromide*, m.p. 105°, debrominated by KI–MeOH), which does not polymerise or autoxidise, but is oxidised by $KMnO_4$ and is reduced by H_2–PtO_2 to $CHPh_2$·CHMe·COPh. With conc. NaOEt the Br-ketone gives a little *Ph ββ-diphenyl-α-methylvinyl ketone*, m.p. 114°, stable to $KMnO_4$. The Mg derivative of (I), however, prepared *in situ*, with CH_2Cl·OMe gives 77—80% of *α-methoxymethoxy-γγ-diphenylisopropenylmesitylene* (from the enolic form), m.p. 92°, and only 18—20% of *β-methoxy-β′β′-diphenyl-2 : 4 : 6-trimethylisobutyrophenone*, m.p. 155°; the last-mentioned ketone, in contrast to (II), is converted by 50% HBr or KOH–MeOH directly into *mesityl α-benzyhydrylvinyl ketone*, m.p. 109—110° (reduces $KMnO_4$; decolorises Br). Decomp. of the Mg derivative of (II) gives solutions, shown by Br-titration to contain 90—95% of enol; crystallisation gives only the keto-form, but the presence of the enol is confirmed by ready absorption of O_2 to form the *peroxide*, $CHPh_2$·CH·C(OH)·$C_6H_2Me_3$ (O—O), m.p. 116—117°, the cyclic nature of which is shown by absence of acidic properties; the peroxide decomposes when heated into $C_6H_2Me_3$·CO_2H and $CHPh_2$·CHO, and is reduced by H_2–PtO_2 or KI–AcOH to *α-hydroxy-ββ-diphenylpropionylmesitylene* (III), m.p. 76° (*acetate*, m.p. 89°; *benzoate*, m.p. 114—115°). The dienol (IV) from this OH-ketone, which is obtained from the Mg_2 derivative (2 mols. of CH_4 liberated), is an energetic reducing agent; it is persistent in solution, but could not be isolated as it autoxidises readily. Its existence is proved by reaction of its parent Mg_2 derivative with AcCl and BzCl to give *αβ-di-acet-, forms*, m.p. 127—128° and 149°, and *-benzoyl-oxy-γγ-diphenylpropenylmesitylene*, m.p. 157°; by promoting ketonisation by addition of a base or, better, by stopping oxidation by addition of a reducing agent (Zn–AcOH) it is converted into *α-hydroxy-β-keto-γγ-diphenylpropylmesitylene* (V), m.p. 77—78°, the isomeride of (III). (III) or (V) with CrO_3 gives *mesityl benzhydryl diketone*, m.p. 74—75°, also obtained with 3—4% of a *hydrocarbon*, (?) an indene derivative, m.p. 212°, by aërial oxidation of the dienol. The solid diketone is stable; it enolises very slowly, since its alcoholic solution barely absorbs O_2 except in the presence of alkali, which rapidly causes equilibration of the keto- and *enol* (VI), m.p. 117° (*phenylurethane*, m.p. 148°), forms. It is reduced by H_2–PtO_2 in MeOH or MgEtBr to the dienol (IV) and treatment with the latter reagent, followed by AcCl, affording the diacetate of the dienol; dissolution in 2% KOH–MeOH, followed by addition to an excess of 2*N*-HCl, gives a quant. yield of the enolic form (VI). The enol (VI) is only slowly oxidised when solid, but in solution absorbs O_2 more rapidly to yield $COPh_2$, $C_6H_2Me_3$·CO_2H, and $C_6H_2Me_3$·CO·CO_2H; it gives an O-*acetate*, m.p. 86—87°, and O-*benzoate*, m.p. 124°, reduced by Zn–AcOH to the esters of $CHPh_2$·CH(OH)·CO·$C_6H_2Me_3$. The diketone and its enol (VI) are substituted in the $C_6H_2Me_3$ by Cl_2, but with $SOCl_2$ and Br–$CHCl_3$ give *mesityl α-chloro-*, m.p. 134°, and *-bromo-ββ-diphenylvinyl ketone*, m.p. 152°, which are as reactive as CPh_3Hal; they yield the corresponding *methoxy-*, m.p. 60°, and *ethoxy-ketone*, m.p. 121°, and with metals, *e.g.*, Hg, give *γγδδ-tetraphenyl-αζ-dimesitylhexa-αβεζ-tetraone*, m.p. 194°, also obtained from the enol (VI) by $FeCl_3$.

CPh_2:CH·CO·$C_6H_2Me_3$ is hydrogenated (Pd–$CaCO_3$; less well, Pt) in EtOAc to a solution, which gives 10—12% of peroxide, this being the min. amount of enol present, but, when reduction is effected by Zn–AcOH, the yield of peroxide is 90%. R. S. C.

Biochemistry of micro-organisms. LIV. Molecular constitution of terrein, a metabolic product of *Aspergillus terreus*, Thom. P. W. Clutterbuck, H. Raistrick, and F. Reuter (Biochem. J., 1937, **31**, 987—1002).—Terrein (I), $C_8H_{10}O_3$, m.p. 127°, $[\alpha]_{5461}^{20}$ +185° in H_2O, is a colourless, powerfully reducing substance containing 1·39 active H atoms at 18° and 2·06 at 28° (in C_5H_5N), giving a p-*bromobenzoate*, m.p. 145—146°, a *mono-*, m.p. 211°, and a *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. >360°, one CO group, titrating with NH_2OH,HCl, being present as CO·CH(OH)·. (I) with Pd–C–H_2 rapidly absorbs 2 H_2 giving *tetrahydroterrein* (II), m.p. 84°, $[\alpha]_{5461}^{20}$ −280° in H_2O, which when warmed with dil. H_2SO_4 loses H_2O, giving 2-*keto*-4-*propyl*cyclo*pentanone* (III) (3 : 5-*dinitrobenzoate*, m.p. 116°; *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 241°). The latter was synthesised for comparison. (II) when treated with 3 : 5-dinitrobenzoyl chloride and with 2 : 4-dinitrophenylhydrazine hydrochloride gave the same two compounds respectively, H_2O being lost during their formation. (II) on distillation loses H_2O and gives a small amount of (III) together with a large yield of 3-*keto*-4-*propyl*cyclo*pentanone*, the mixture with Pd–C–H_2 giving a mixture of 2-*hydroxy-* (IV) and 3-*hydroxy*-4-*propyl*cyclo*pentanone* (V). Both (I) and (II) on exhaustive reduction with Pd–C–H_2 give a mixture of (IV) and (V), the latter having m.p. 124° (*dinitrophenylhydrazone*, m.p. 196°; *semicarbazone*, m.p. 157°). (II) with HIO_4 gives an *aldehydo-acid*, $C_7H_{12}O_3$ [*dinitrophenylhydrazone*, m.p. 157° (*Et* ester m.p. 86°)], which with alkaline I gives d-n-*propylsuccinic acid*, m.p. 103°, $[\alpha]_{5461}^{15}$ +26·6° in H_2O, which was prepared by resolution of the synthetic *dl*-acid

with strychnine. (I) with HIO_4 gives an *aldehydo-acid*, $C_7H_8O_3$, m.p. 82°, which with Pd–C–H_2 gives the lactone of *γ-hydroxy-β-propylbutyric acid*, b.p. 110—112°/20 mm. (*phenylhydrazide*, m.p. 115), which was synthesised for comparison. Decomp. of the ozonide of (I) gives MeCHO. (I) is probably 2-hydroxy-3 : 5-oxido-4-propenyl*cyclo*pentan-1-one. P. W. C.

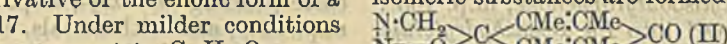
Constituents of the adrenal gland. IX. Function of the last oxygen atom. M. Steiger and T. Reichstein (Helv. Chim. Acta, 1937, **20**, 817—827).—Compounds already briefly described (cf. A., 1936, 473, 605, 704, 854, 1382; this vol., 105) are further examined. Hydrogenation of adrenosterone affords the triketone (I), m.p. 178—180°, identical with the "diketone" obtained from substances *A*, *C*, and *D* (*loc. cit.*) by CrO_3 oxidation. The monoketone (II), m.p. 231—235°, obtained from substance *A* by $Pb(OAc)_4$, or HIO_4 oxidation, is converted by Ac_2O–C_5H_5N into a *diacetate*, $C_{23}H_{34}O_5$, m.p. 156°, which reacts with Girard's reagent, and is therefore not the Ac derivative of the enolic form of a CO group in position 17. Under milder conditions (II) is converted into a *monoacetate*, $C_{21}H_{32}O_4$, m.p. 230—231°, which with CrO_3 in AcOH affords 11- or 12-keto*trans*-androsterone acetate, hydrolysed by KOH–MeOH to 11- or 12-keto*trans*-androsterone, m.p. 166·5—168°. This with CrO_3 affords (I), hydrogenated by (H_2, Raney Ni) to a *diol* (III), $C_{19}H_{30}O_3$, m.p. 247—248°; the *diacetate*, m.p. 162—163°, is not affected by CrO_3 at room temp., whereas (III) affords (I), and it is concluded that the 11- or 12-CO is not reduced in the prep. of (III). Removal of 2 H_2O from (III) by way of the xanthate affords an unsaturated ketone, m.p. 72—74°, hydrogenated to *androstan*-11(or 12)-*one*, m.p. 50—52°; it is not affected by CrO_3 at room temp. and does not give a semicarbazone. Androstane-3 : 17-diol is readily converted by the xanthate method, followed by hydrogenation, into androstane. P. G. C.

$\Delta^{3:5}$-Androstadiene-17-one.—See A., III, 321.

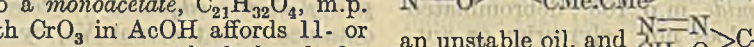
Syntheses of αβ-dicinnamoylethane and its *pp'*-dimethoxy-derivative. J. Świderski (Rocz. Chem., 1937, **17**, 226—232).—Et_2 sodiomalonate and cinnamoyl chloride in Et_2O yield *Et*$_2$ *cinnamoylmalonate*, m.p. 26° (*Cu* salt, m.p. 217°). Et cinnamoylacetate is converted by treatment successively with Na and I into *Et*$_2$ *αβ-dicinnamoylsuccinate*, m.p. 96°, from which *αβ-dicinnamoylethane* (I), m.p. 130° [*diphenylhydrazone*, m.p. 197° (decomp.)], is prepared by autoclaving (10 atm.: 4 hr.). *Et*$_2$ *p-methoxycinnamoylmalonate*, m.p. 60° (*Cu* salt, m.p. 201—202°), *αβ-di-p-methoxycinnamoylethane* (II), m.p. 156° [*diphenylhydrazone*, m.p. 200° (decomp.)], and *Et*$_2$ *αβ-di-p-methoxycinnamoylsuccinate*, m.p. 138—139°, have been prepared analogously. (I) and (II) differ from $CH_2(CO{\cdot}CH{:}CHPh)_2$ in having only a faint yellow colour, in not being substantive dyes for cotton, and in not giving colour reactions with $FeCl_3$. R. T.

Synthesis of αβ-di-(3 : 4-methylenedioxycinnamoyl)ethane. W. Lampe and J. Pohoska (Rocz. Chem., 1937, **17**, 233—236).—3 : 4-Methylenedioxycinnamoyl chloride and Me sodioacetoacetate in Et_2O, at the b.p., yield *Me α-3 : 4-methylenedioxycinnamoylacetoacetate*, m.p. 96—98°, converted by aq. NH_3 into *Me* 3 : 4-*methylenedioxycinnamoylacetate*. 3 : 4-Methylenedioxycinnamoylacetone when treated successively with Na and I yields *αβ-di-*(3 : 4-*methylenedioxycinnamoyl*)-*αβ-diacetylethane*, m.p. 200—202°, and this gives *αβ-di-*(3 : 4-*methylenedioxycinnamoyl*)-*ethane* (I), m.p. 199—200°, when boiled with aq. AcOH. (I) is a yellow substantive dye for cotton, and gives a colour reaction with $FeCl_3$. R. T.

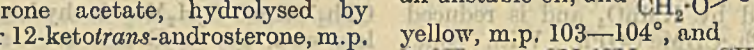
Action of diazomethane on duroquinone. L. I. Smith and W. B. Pings (J. Org. Chem., 1937, **2**, 95—111).—CH_2N_2 probably reacts with the CO of duroquinone (I); reaction with the C:C of (I) and reaction of (I) as 4-hydroxy-2-methylene-3 : 5 : 6-trimethyl-$\Delta^{3:5}$-*cyclo*hexadien-1-one are both excluded by the nature of the products. Structures assigned below, particularly (IV) and (V), are, however, uncertain, tautomeric variations being possible, although less probable. Reaction of CH_2N_2 and (I) is variable, except in MeOH; in general, two pairs of isomeric substances are formed, viz.,



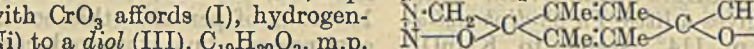
an unstable oil, and



yellow, m.p. 103—104°, and



colourless (IV), m.p. 124—125° (decomp.), and



(V), m.p. 143—144° (decomp.). Further reaction of (II) or (III) with CH_2N_2 gives (V), proving the mixed αβ'-ββ'-furodiazoline nature of (V). With $FeCl_3$, $KMnO_4$, Br, or Ac_2O–NaOAc (II) gives (I) and with Zn–Ac_2O–NaOAc duroquinol diacetate, as sole isolable products. When heated, (II) readily gives (?) 2 : 3 : 5 : 6-*tetramethyl*-$\Delta^{2:5}$-cyclo*heptadiene*-1 : 4-*dione*, m.p. 60—61° [*dioxime*, m.p. 241—242° (decomp. from 220°); no phenyl- or *p*-nitrophenyl-hydrazone], stable to Ac_2O, HCl, H_2SO_4, CrO_3, and dil. HNO_3, and giving with $KMnO_4$ and O_3 only traces of oily products. The instability of (II) is held to be due to its reaction as (II*a*). Even boiling, however, has no effect on (III); it cannot be sublimed, is odourless, gives (I) with $FeCl_3$ or, by an obscure mechanism, with Ac_2O followed by $NaHCO_3$; with NH_2OH it gives (?) an impure *oxime*, m.p. 201—203° (decomp.), with Br–$CHCl_3$ a *substance* (C 47·2, H 4·8, N 9·5%), m.p. 83—84°, with Zn–AcOH a *product*, m.p. 250—256° or 198—200° (decomp.) [the latter giving an (?) *Ac* derivative, m.p. 130—138°, and indefinite results with $FeCl_3$], and with $SnCl_2$ affords a N-free *substance*, m.p. 213—215°, which with $FeCl_3$ gives (I). In boiling PhCl (IV) gives 2 mols. of N_2 and (?) 2 : 3 : 6 : 7-*tetramethyl*-$\Delta^{2:6}$-cyclo*octadiene*-1 : 4- or -1 : 5-*dione*, m.p. 143—144° [*dioxime*, m.p. >260° (decomp. from 250°); no phenylhydrazone]. 1-$C_{10}H_7$·CNO has no action on (IV), but PhNCO yielded in one experiment (V) and in another a (?) *phenylurethane* (VI), m.p. 160—161°, and a *substance* (C 67·5, H 5·4, N 14·7%), m.p. 127—128° (decomp.); with NH_2OH (IV) gives only a red oil, with $NHPh{\cdot}NH_2$ a (?) *phenylhydrazone*, $C_{18}H_{22}ON_6$, m.p. 144—145° (decomp.), with Ac_2O

and a drop of H_2SO_4 a *diacetate*, $C_{16}H_{20}O_4N_4$, m.p. >260°, with $AgNO_3$ a *Ag* salt (Ag 34·5%), m.p. 128—129° (decomp.), with HCl a (?) *dihydrochloride*, (C 37·5, H 6·3%; mol. wt. 373), m.p. 112—114°, and with HBr a *substance*, m.p. 155—156° (decomp.), which in Et_2O–EtOH gives a (?) *dihydrobromide* (C 39—41, H 6·0—6·1, N 14·5%; mol. wt. 430), m.p. 139—140° (decomp.). Decomp. of the acid salts, which are similarly obtained from (V), by alkali or heat gives only (I), and their nature is obscure. Thermal decomp. of (V) at 155—180° gives only 1 mol. of N_2 and two unstable isomeric *substances*, $C_{12}H_{16}O_2N_2$, m.p. 103—113° and 125—129°, respectively, giving the same unstable (?) *Ac* derivative, m.p. 138—143°, and of which one may be $CH_2{\cdot}O{>}N{=}N{>}C{<}CMe{:}CMe{\cdot}CO{<}CMe{:}CMe{\cdot}CH_2$; the substance, m.p. 103—113°, gives no oxime, but with Zn–aq. AcOH yields its isomeride. No reaction occurs between (V) and 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$, NH_2OH, or semicarbazide; KCNO–AcOH gives a (?) *carbamide* (C 49·5, H 5·6, N 24·2%), m.p. 251° (decomp. from 245°); Me_2SO_4–NaOH destroys (V); PhNCO gives (VI); $KMnO_4$ gives AcOH; NaOI gives *substances* (C 63·6, H 7·9, N 24·8%), m.p. 144—145° and (C 49·9, H 5·95, N 21·5%) 107—108°; NH_2Ph in AcOH gives (I) as sole recognisable product; $AgNO_3$ gives a *Ag* salt (C 25·4—26·6, H 3·5—4·4, N 16·8, Ag 34·1—35·2%). The nature of both Ag salts is obscure. R. S. C.

New synthesis of 3-acetamido-β-naphthaquinone. H. Goldstein and P. Gardiol (Helv. Chim. Acta, 1937, **20**, 647—650).—2 : 3-OH·$C_{10}H_6$·NHAc in NaOH solution with $NaNO_2$ and H_2SO_4 affords 1-*nitroso*-3-*acetamido*-2-*naphthol* (I), m.p. 193° (decomp.), converted by $SnCl_2$–HCl into 1-*amino*-3-*acetamido*-2-*naphthol*, isolated as the *hydrochloride*; oxidation of the latter with $H_2Cr_2O_7$ affords 3-acetamido-β-naphthaquinone, identical with that prepared from β-naphthaquinone by nitration etc. (cf. A., 1892, 1229); treatment with NH_2OH affords (I). P. G. C.

Magnesium derivative of pinene hydrochloride. Action of phthalic anhydride followed by magnesium ethyl bromide. R. Bousset (Bull. Soc. chim., 1937, [v], **4**, 368—370).—Pinene hydrochloride with Mg–Et_2O yields its Mg derivative, which when condensed with *o*-$C_6H_4(CO)_2O$ and then treated with MgEtBr–Et_2O, all in an atm. of H_2, yields a product separated into an acid and a neutral fraction. The crude acid has m.p. 250—258° and resinifies in a few hr. From the neutral fraction bornylene and a *compound*, m.p. 193·5°, $[\alpha]_J$ +16·66°, $[\alpha]_V$ +17·5°, $[\alpha]_B$ +25°, have been isolated. The latter is unsaponifiable, does not form an oxime or semicarbazone or contain a reactive H (Zerevitinov). H. G. M.

Camphor series. IV. Synthesis of thiofenchone and two isomeric bis-thiocamphors and their derivatives. D. C. Sen (J. Indian Chem. Soc., 1937, **14**, 214—218).—Fenchone (I) in EtOH with H_2S–HCl affords thiofenchone (II) [which gives the oxime and semicarbazone of (I)], reduced by Al–Hg in moist Et_2O to *thiofenchol*, b.p. 95°/5 mm., 216—220°/762 mm.; this decolorises Br, I, and dil. aq. $KMnO_4$. *l*- (III) and *dl*-Thiocamphor with $NaNH_2$ in hot C_6H_6 afford, respectively, l-*bis-thiocamphor* (IV), m.p. 180°, $[M]_D^{20}$ −1109·5° in C_6H_6 [*dioxime*, m.p. 197°; *azine*, m.p. 200° (decomp.); *azine picrate*, m.p. 200° (decomp.)], and dl-*bis-thiocamphor* (V), m.p. 164° (*dioxime*, m.p. 199°; *azine*, m.p. 176°); these derivatives are of the corresponding bis-camphors, and their formation shows that (IV) and (V) contain CS groups and are not disulphides. Al–Hg in moist Et_2O converts (V) into dl-*bis-thioborneol*, m.p. 143°. In C_6H_6 (II), (III), and (IV) show an absorption band between 5270 and 4530 A. with centre at 4950 A. P. G. C.

Pyrolysis of myrtenyl selenide. G. Dupont, K. Sławinski, and W. Zacharewicz (Rocz. Chem., 1937, **17**, 154—160).—The same acids (norpinic and nopinic) are obtained by $KMnO_4$ oxidation of the products of pyrolysis (140—150°/15 mm.) of the non-volatile selenides obtained by oxidising pinene with SeO_2 and of myrtenyl selenide. The latter pyrolyses mainly to verbenene, which with H_2Se gives nopinene. R. T.

Sesquicryptol, a new crystalline sesquiterpene alcohol in the essential oil of Japanese sugi (*Cryptomeria japonica*, Don) leaves. S. Uchida and S. Murata (J. Soc. Chem. Ind. Japan, 1937, **40**, 159B).—Oil of sugi leaves yields 1% of a sesquiterpene *alcohol*, $C_{15}H_{26}O$, b.p. 172—174°/20 mm., m.p. 49—51°, $[\alpha]_D^{22}$ +22·72 in $CHCl_3$ (*tetrabromide*; *dihydrochloride*; *acetate*; *H phthalate*), for which the name "sesquicryptol" is proposed. When oxidised (H_2CrO_4), it yields an *aldehyde*, and with P_2O_5, a *sesquiterpene*, $C_{15}H_{24}$, b.p. 250—255°/760 mm., which yields a *dibromide*, and with S or Se a liquid *hydrocarbon*. J. D. R.

Biogenesis of the terpenes. K. Ganapathi (Current Sci., 1937, **6**, 19—20).—From a consideration of the distribution of the terpenes, it is suggested that the precursor of many of them is linalool, and a scheme of derivation is formulated F. R. S.

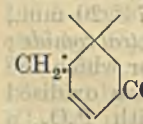
Polymerisation of terpenes. M. O. Carmody and W. H. Carmody (J. Amer. Chem. Soc., 1937, **59**, 1312).—Pinene, dipentene, and cedarwood oil are polymerised (75%) by $AlCl_3$ in C_6H_6, PhMe, xylene, or hexane at 10°, the whole of the solvent being recovered unchanged. A. Li.

Constitution of shonanic acid, one of the two characteristic volatile acids from the wood of *Libocedrus formosana*, Florin. IV. Dihydroshonanyl alcohol and the optical activity of shonanic acid and its derivatives. V. Oxidation of dihydroshonanyl alcohol and the ozonalysis of shonanic acid. VI. Oxidation of dihydroshonanic acid with ozone and potassium permanganate. N. Ichakawa (Bull. Chem. Soc. Japan, 1937, **12**, 253—257, 258—266, 267—275; cf. this vol., 108).—IV. Reduction (Na–EtOH) of Et, $[\alpha]_D^{25}$ −4·24°, or *Ph shonanate*, b.p. 153—155°/6 mm., $[\alpha]_D^{25}$ −2·40°, affords *dihydroshonanyl alcohol*. (I), b.p. 104°/7 mm., 228—230°/765 mm., $[\alpha]_D^{20}$ −2·24° (*H phthalate*, m.p. 124°), oxidised (CrO_3–AcOH) to a mixture of *dihydroshonanaldehyde*, b.p. 107—110°/18 mm. (*semicarbazone*, m.p. 149—150°), and dihydroshonanic acid (II), b.p. 132°/5 mm., whilst hydrogen-

ation (Pd) gives *tetrahydroshonanyl alcohol*, b.p. 100—101°/7 mm., $[\alpha]_D^{28}$ −1·64°, also obtained by reduction (Na–EtOH) of Et tetrahydroshonanate. Dehydration (H_3PO_4; 200—210°; 1 hr.) of (I) affords *dihydroshonanene*, b.p. 168—169°/759 mm., $[\alpha]_D$ 0, and interaction with PCl_5 affords *dihydroshonanyl chloride*, b.p. 87°/13 mm., $[\alpha]_D^{20}$ −2·00°, and a *compound*, b.p. 174°/757 mm.

V. Oxidation ($KMnO_4$–aq. NaOH) of (I) yields AcOH, $H_2C_2O_4$, *as*-dimethylsuccinic (III) and αα-dimethylglutaric acids (IV). Ozonolysis of shonanic acid (V) gives a *mono-ozonide*, m.p. 82° (decomp.), which with H_2O at 75° affords an unsaturated aldehydic *acid*, $C_9H_{14}O_3$ (?), oxidised (H_2O_2–aq. NaOH) to an *acid*, $C_7H_{12}(CO_2H)_2$ (?), the *Me* ester, b.p. 138—140°/7 mm., of which gives an *ozonide*, decomp. on removal of solvent, affording CO_2, CH_2O, HCO_2H, and an *acid*, which with HNO_3 (*d* 1·12) (5 hr.; 100°) gives (III) and (IV).

VI. Mild oxidation ($KMnO_4$–1% aq. NaOH) of (II) affords a dibasic ketonic *acid*, $C_{10}H_{16}O_5$ (VI) (*Et*$_2$ ester, b.p. 276°/758 mm., $[\alpha]_D^{28}$ −1·08°), and *dihydroxydihydroshonanic acid*, m.p. 161—161·5° [converted into (VI) by $Pb(OAc)_4$ followed by H_2O_2–aq. NaOH]. (VI) with aq. NaOCl affords a tribasic *acid*, $C_8H_{12}O_6$ (*Et*$_3$ ester, b.p. 135—149°/5 mm.), which is converted into (IV) by conc. HCl (0·5 hr.; 100°). Ozonolysis of (II) affords an *ozonide*, which with HNO_3 (*d* 1·12) (2 hr.; 100°) gives a dibasic ketonic *acid*, $C_8H_{12}O_5$ (*Et*$_2$ ester, b.p. 138—140°/6 mm., $[\alpha]_D$ 0), oxidised (H_2O_2) to (IV). The conclusion reached is that (II) has the annexed structure.



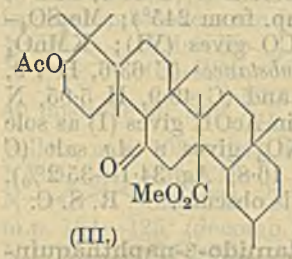
F. N. W.

Hydroxytriterpene acids from Somali incense. I. F. Trost (Annali Chim. Appl., 1937, **27**, 178—188).—The mixed acids, separated as Ba salts and fractionated with Ac_2O, followed by hydrolysis (EtOH–KOH) of the fractions, afford α- and β-boswellic acids (Winterstein and Stein, A., 1932, 856) and a third isomeride, *γ-boswellic acid*, $[\alpha]_D^{20}$ +279°. The β-acid is an α-hydroxy-acid, oxidation (CrO_3) yielding the corresponding *aldehyde*, $C_{28}H_{45}$·CHO, m.p. 200—202°, $[\alpha]_D^{20}$ +127° (*oxime*, m.p. 196—197°), whilst the Me ester yields the *Me* ester, m.p. 155—157° (*oxime*, m.p. 194—196°), of the keto-acid. High-vac. distillation of α-, β-, and γ-boswellic acids gives α-, β-, and *γ-boswelliene*, $C_{29}H_{46}$, m.p. 114—115°, 139—140°, 115—116°, $[\alpha]_D^{20}$ +180°, +329°, +159°, respectively, the α- having two reactive double linkings and the β- and γ-hydrocarbon one reactive and one difficultly reactive double linkings. All m.p. are corr., all rotations 1% in $CHCl_3$.

F. O. H.

Polyterpenes and polyterpenoids. CXII. Dehydrogenation in the amyrin group. L. Ruzicka, H. Schellenberg, and M. W. Goldberg. **CXIII. Oxidations in the oleanolic acid group without fission of the ring system. Nature of the fourth oxygen atom of glycyrrhetic acid.** L. Ruzicka and S. L. Cohen (Helv. Chim. Acta, 1937, **20**, 791—804, 804—808).—CXII. Se dehydrogenation of a mixture of α- and β-amyrin at 350° affords 1 : 2 : 3 : 4-$C_6H_2Me_4$, 2 : 7-$C_{10}H_6Me_2$, sapotalin (I), 1 : 2 : 5 : 6-$C_{10}H_4Me_4$ (II), 1 : 5 : 6 : 2-$C_{10}H_4Me_3$·OH, a *picene homologue*, $C_{25}H_{20}$, m.p. 302—304°, and a *hydroxypicene homologue*, $C_{24}H_{18}O$ or $C_{25}H_{20}O$, m.p. 331—332° (*Me ether*, m.p. 358—359°). β-Amyronesemicarbazone with NaOEt affords *β-amyrene*, m.p. 162—163°, $[\alpha]_D$ +50·7° in $CHCl_3$, which with Se at 340° is converted into 2 : 7-$C_{10}H_6Me_2$, 1 : 2 : 5-$C_{10}H_5Me_3$, (I), and two *substances*, $C_{30}H_{52}$ (amyrane ?), m.p. 226—227°, and $C_{25}H_{20}$ or $C_{24}H_{18}$, m.p. 304—305°; the latter does not depress the m.p. of the substance of m.p. 305—306° obtained from hederagenin or gypsogenin. α-Amyrone with MeMgI affords two substances, probably mixtures of stereoisomeric *methylamyrins*, m.p. 225—235° and 198—201°. The former with Se at 340—350° affords (I), (II), and a mixture probably containing chrysene and picene homologues. It is suggested that the formation of $C_{10}H_4Me_4$ is due to the elimination of H_2O and wandering of Me in the amyrins during the reaction with Se.

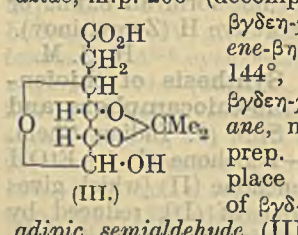
CXIII. Acetyloleanolic acid is converted by CrO_3 in AcOH into acetylketo-oleanolic lactone, m.p. 282—284°; the Me ester with H_2O_2–AcOH (or CrO_3; cf. A., 1934, 412) affords a substance, probably *Me acetylketodihydro-oleanolate* (III), m.p. 195—196°, $[\alpha]_D$ −10° in $CHCl_3$; the corresponding *acid* has m.p. 195—197°. Use of Bz_2O_2 in place of H_2O_2 affords an *isomeride* of (III), m.p. 201—204°, which does not possess the absorption band at 2900 A. ascribed to the CO group in (III). From a comparison of the absorption spectra of these substances it is suggested that glycyrrhetic acid is isomeric with keto-oleanolic acid.



(III.)

P. G. C.

Configuration of shikimic acid, and its degradation to glucodesonic acid. H. O. L. Fischer and G. Dangschat (Helv. Chim. Acta, 1937, **20**, 705—716).—Me *iso*propylideneshikimate is converted into its *Ac* derivative, m.p. 76—77°, which with $KMnO_4$ affords *Me* 1 : 4 : 5 : 6-*tetrahydroxy*-3-*acetoxy*-4 : 5-iso*propylidenehexahydrobenzoate*, m.p. 135°; this is converted by Ac_2O–C_5H_5N into *Me* 4 : 5-*dihydroxy*-1 : 3 : 6-*triacetoxy*-4 : 5-iso*propylidenehexahydrobenzoate*, m.p. 121—122°, and by 2*N*-NaOH at room temp. followed by HIO_4 and then NaOBr, into αβ*γ-trihydroxy*-αβ-iso*propylideneadipic lactone* (I), m.p. 129—130° [*Me* ester (II), m.p. 84—85°, and its *amide*, m.p. 122° (decomp.)]. (I) with 50% AcOH affords αβ*γ-trihydroxyadipic dilactone*, m.p. 141—143°, converted by NHPh·NH_2 into αβ*γ-trihydroxyadipic diphenylhydrazide*, m.p. 206° (decomp.). (II) with MeMgI affords βγδε*η-pentahydroxy*-γδ-iso*propylidene*-β*η-dimethyloctane*, m.p. 143—144°, converted by AcOH into βγδε*η-pentahydroxy*-β*η-dimethyloctane*, m.p. 108—109°. If, in the prep. of (I), Br–AcOH is used in place of NaOBr, the cyclic form of βγδ-*trihydroxy*-γδ-iso*propylideneadipic semialdehyde* (III), m.p. 154° (*acetyl nitrile*, m.p. 112°), is obtained. (III) with AcOH affords



(III.)

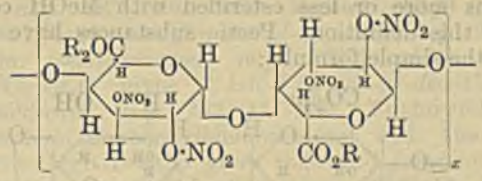
βγδ-trihydroxyadipic semialdehyde lactone (IV), m.p. 176° (decomp.) [*phenylhydrazone*, m.p. 154° (decomp.); *benzylphenylhydrazone*, m.p. 154—160° (decomp.)]. Reduction of (IV) (Ni) affords glucodesonic lactone, and this, its phenylhydrazone, and Me_5 ether are identical in m.p., mixed m.p., and $[\alpha]_D$ with the corresponding substances prepared from glucose. This fixes the structure of shikimic acid as 3 : 4 : 5-trihydroxy-2 : 3 : 4 : 5-tetrahydrobenzoic acid, and the spatial configuration of the OH at 3, 4, and 5 as the same as those at 3, 4, and 5 in *d*-glucose. The intermediate stage in the prep. of (I) is *α-keto-γδε-trihydroxy-δε-isopropylideneheptoic acid semialdehyde* [*dinitrophenylhydrazone*, m.p. 144° (decomp.); *p-nitrophenylhydrazone*, m.p. 180° (decomp.)]. P. G. C.

Crystalline components of Cortex Simaruba Amara. O. Glemser and E. Ott (Ber., 1937, **70**, [*B*], 1513—1519).—Treatment of the bark with H_2O at 80—90°, concn. of the aq. extract, and treatment with $CHCl_3$ affords simarubin (I), $C_{22}H_{30}O_9$, m.p. 230—231, $[\alpha]_D^{22}$ + 59·88° in MeOH, the tasteless simarubidin (II), $C_{22}H_{32}O_9$, m.p. 260°, $[\alpha]_D^{19}$ +48·1° in C_5H_5N, and a non-identified *substance*, m.p. 243—245°, $[\alpha]_D^{17}$ +14·0° in C_5H_5N. (I) is transformed by Ac_2O–C_5H_5N at room temp. into the *penta-acetate*, m.p. 169—170°, $[\alpha]_D^{17}$ +41·22° in C_5H_5N, whereas at 100° the *anhydro-penta-acetate*, m.p. 180°, is produced. (I) reduces hot Fehling's solution and gives a *phenylhydrazone*, m.p. 204° (decomp.) after softening at 161°, but a semicarbazone could not be prepared. With CH_2N_2 in Et_2O (I) yields a *Me_1 ether*, m.p. 280°, $[\alpha]_D^{17}$ −65·97° in C_5H_5N. (I) therefore contains 5 OH of which one is phenolic but does not react with $FeCl_3$. (I) rapidly decolorises aq. $KMnO_4$. Treatment of (I) with 2% or 5% HCl gives, in place of the expected hexose, a *compound*, m.p. 228° (decomp.), $[\alpha]_D^{17}$ +64·74°, mol. wt. 400 [*phenylhydrazone*, m.p. 139—140° (decomp.) after softening at 125°]. Oxidation of (I) by CrO_3 in AcOH + $KHSO_4$ gives *simarubaic acid*, $C_{12}H_{16}O_6$, m.p. 160° after softening at 143°, whilst ozonisation in EtOAc affords *simarubic acid*, m.p. 164—166° after softening at 143°, $[\alpha]_D^{18}$ +69·9° in MeOH (*phenylhydrazone*, m.p. 174—175°). Treatment of (I) with red P and HI (*d* 1·7) at 280° gives a fluorescent *oil*, b.p. 120—180°/40 mm. (II) yields a *penta-acetate*, m.p. 122°, and gives Selivanov's reaction for hexoses. Catalytic hydrogenation (Pd) gives an optically inactive *product*, m.p. 243°, with a bitter taste. Degradation with HI–red P gives the same products as are obtained with (I). Unlike (I) it does not contain phenolic OH or CO. The function of four of the nine O is unexplained. H. W.

Selenium dehydrogenation of α-tocopherol. C. S. McArthur and E. M. Watson (Science, 1937, **86**, 35).—Dehydrogenation (Se at 300—330°) yields a fluorescent oil and crystals, m.p. 106° (duroquinone ?). This probably corresponds with a side-chain, in α-tocopherol, consisting of two isoprene units. L. S. T.

Determination of the constitution of ammoresinol. H. Raudnitz (Ber., 1937, **70**, [*B*], 1582—1583).—Oxidation of hexahydroammoresinol by cold alkaline $KMnO_4$ and treatment of the crude product with CH_2N_2 yields an ester which according to analysis cannot be Me_2 γηλ-trimethyldodecylmalonate postulated by Späth (this vol., 38). When distilled in a high vac. it affords Me γηλ-trimethyltridecoate. H. W.

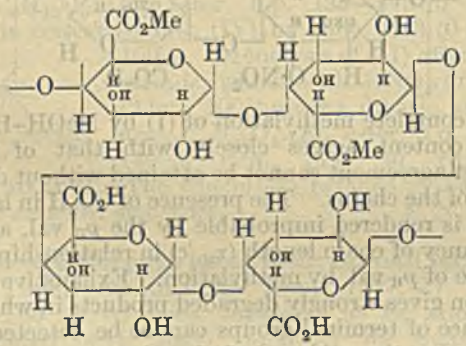
Esterification of pectin substances. IV. Determination of the constitution of pectin esters. G. G. Schneider and V. Frotschi (Ber., 1937, **70**, [*B*], 1611—1617).—Treatment of pectin nitrate (I) with 12% HCl gives HNO_3, MeOH, CO_2, and furfuraldehyde. It is oxidised by HNO_3 (*d* 1·15—1·10) to mucic acid and hydrolysed by non-oxidising acids (1—2%) to galacturonic acid. Since methylated mucic acid is not obtained by the oxidation of (I) and since the acidity of (I) increases as the OMe content decreases it follows that OMe is present in CO_2Me. Complete analyses, particularly determination of CO_2H, and measurement of the mol.-wt. of (I) from various sources show the impossibility of the presence of arabinose and galactose as integral components of (I) and hence of the pectin skeleton. The long pectin chains are formed essentially from galacturonic acid alone and since AcOH is absent the structure of (I) is



After complete methylation of (I) by MeOH–HCl the OMe content agrees closely with that of CO_2H. Perfect agreement cannot be attained without degradation of the chains. The presence of CO_2H in lactonic union is rendered improbable by the p_H val. and the constancy of chain length (η_{sp}/c) in relationship to the change of p_H val. by methylation. Exhaustive esterification gives strongly degraded products in which the presence of terminal groups cannot be detected, thus supporting the evidence of viscosimetric and osmotic methods that long mol. chains are present. H. W.

Constitution of pectin substances. G. G. Schneider and H. Bock (Ber., 1937, **70**, [*B*], 1617—1630).—It is proposed to use the term "pectin substances" to describe technical products containing ballast material and "pectin" to denote the corresponding homogeneous materials, *i.e.*, methylated polygalacturonic acids (I). "Pectic acid" denotes the strongly acidic (I) wholly or partly free from OMe whilst "hydropectin" analogously to "hydrocellulose" is the material obtained by partial degradation with acid. Ehrlich's formula is criticised. The conception of a "tetragalacturonic acid" is not in harmony with determinations of mol. wt., and complete methylation and determination of terminal groups show that the polygalacturonic acid contains $\lessapprox$10 galacturonic units. This is also true for pectolic and pectolactonic acid. Further *X*-ray evidence is against the presence of a "cyclic tetragalacturonic acid" and indicates the presence of extended mols. According to Ehrlich the hydrolysis of "primary pectic acid" proceeds: $C_{41}H_{60}O_{38} + 9H_2O = 4C_6H_{10}O_7 + 2MeOH + 2AcOH + C_5H_{10}O_5$ (*l*-arabinose) $+ C_6H_{12}O_6$ (*d*-galactose). In the author's experience, however, it is impossible to obtain a pectic acid from natural

sources which does not have a much higher content of MeOH etc. than that required by this scheme. Treatment with 70% EtOH of pectic acid obtained from citrus, orange, or apple by boiling H_2O removes only the simpler pentosans; this is the reason for the complexity of Ehrlich's formula. A more dil. EtOH removes the more complex pentosans but with increasing purification there is increased divergence from Ehrlich's conception and the analytical vals. approach more closely those required by a highly methylated polygalacturonic acid. There is no fixed relationship between pentosans and pectic acid and there is no reason for involving the pentosans or other hemicelluloses in the formula of pectic substances. Pectin substances can be degraded by decarboxylation to pentosan chains but there is no justification for unnecessarily complicating the pectin formula by inclusion of arabinoses etc. Pectin substances are complex, carbohydrate-like, vegetable materials which have the ability of forming gels with sugars under certain conditions. All substances isolated from fruits which have been found to consist of galacturonic acid chains more or less esterified with MeOH comply with this definition. Pectic substances have therefore the simple formula :



Ehrlich's assumption of the presence of Ac rests on the Ac vals. obtained after hydrolysis with 0·2% NaOH at 100° during 5 hr. With completely purified, authentic products Ac cannot be detected by mild methods (use of p-$C_6H_4Me{\cdot}SO_3H$ in abs. EtOH or with p-$C_6H_4Me{\cdot}SO_3H$, 2·5% or 5% H_2SO_4). More drastic methods cause decomp. of galacturonic acid with production of HCO_2H. The properties of pectin substances depend (*a*) on the mol. size which is fundamental for the formation of threads, films and gels, (*b*) on the degree of esterification of polygalacturonic acid by MeOH which affects the solubility, and (*c*) on the ballast material such as the pentosans which are invariably present. The peculiar inability of beet pectin to gelatinise is due to its small mol. size. It appears to be much more firmly attached to the cell wall than is fruit pectin so that only a small proportion is extracted by H_2O. H. W.

Bee poison.—See A., III, 341.

Lignin. VII. Nitration and fission of pine wood. H. Friese and H. Fürst (Ber., 1937, **70**, [*B*], 1463—1473).—Treatment of the finely-divided wood with HNO_3–H_2SO_4 results in considerable degradation with production of much material sol. in the nitrating acid. Better results are obtained by use of HNO_3–AcOH–H_3PO_4 and these are improved when AcOH is replaced by Ac_2O. $AcNO_3$ in Ac_2O offers no further advantage. The best results are obtained with HNO_3 (*d* 1·52) and cryst. H_3PO_4. With this reagent wood is converted into a NO_2-derivative with retention of structure and avoidance of oxidative degradation; the OH groups are esterified by HNO_3 and the lignin component suffers direct nitration. Under mild conditions hydrolysis and simultaneous fission of the material take place whereby it becomes completely sol. in H_2O. The mechanism of the reaction is not explained but with aid of ultra-filtration it enables a considerable proportion of the material to be isolated as a complex lignin derivative. HNO_3 may act by direct nitration or by addition of NO_2 and OH at a double linking. Catalytic hydrolysis of nitro-wood cannot be effected with NaOMe (Zemplén); the ester-N is retained and production of $MeNO_2$ is not observed. $Ba(OMe)_2$ is ineffective even in boiling solution. H. W.

Lignin. VIII. Preparation and sulphonation of lignin from beech wood. H. Friese and H. Glassner (Ber., 1937, **70**, [*B*], 1473—1477).—The reaction between red beech wood and H_2SO_4–AcOH–Ac_2O proceeds in much the same manner as with pine wood or rye straw, giving α-cellobiose acetate and ligninsulphonic acids isolated as the Ba salts, divided by ultrafiltration into various fractions closely resembling those obtained previously. Analyses of these indicate a fundamental composition $C_{36}H_{37}O_{13}$ on the assumption that H_2SO_4 behaves additively with introduction of OH and SO_3H. This agrees with Freudenberg's assumption of a fundamental unit $C_9H_{10}O_{3\text{-}4}$. The hypothesis that H_2SO_4 acts by sulphonation leads to less probable conceptions. H. W.

Constituents of *Verbena officinalis*, L. II. Constitution of cornin. B. Reichert and W. Hoffmann (Arch. Pharm., 1937, **275**, 474—477; cf. A., 1935, 1041).—Cornin gives a Ac_4 or Ac_5 derivative, m.p. 133°, which yields an *oxime*, m.p. 175—176°, converted by cold Ac_2O into the Ac_5 or Ac_6 *oxime*, m.p. 184°. As cornin is a reducing agent, it is thus probably an α-keto-alcohol. Ac determinations give indefinite results. R. S. C.

Paprika pigment. X. Citraurin from capsanthin. L. Zechmeister and L. von Cholnoky (Annalen, 1937, **530**, 291—300).—The product $C_{30}H_{40}O_2$ obtained by the action of KOH–EtOH–H_2 on capsanthin (I) is identified as citraurin. In general, polyenes containing at least 1 CO conjugated with the chromophor do not appear completely stable towards alkali. Chromatographic analysis of (I) in C_6H_6 by $CaCO_3$ gives two zones probably due to enolisation of (I) favoured by C_6H_6. H. W.

Constituents of ch'an su and the constitution of cinobufagin and cinobufotalin.—See A., III, 341.

Saponins of Chinese drug, San-ch'i, *Aralia bipinnatifida*. T. Q. Chou and J. H. Chu (Chinese J. Physiol., 1937, **12**, 59—66).—The drug contains sucrose, *arasaponin*-A, $C_{30}H_{52}O_{10}$, m.p. 195—210°, [α] +23° in EtOH (*hepta-acetate*, m.p. 256°), and *arasaponin*-B, $C_{23}H_{38}O_{10}$, m.p. 190—200°, [α] +8°

in EtOH. Hydrolysis of -*A* with 3% H_2SO_4 gives *arasapogenin*-A, $C_{17}H_{30}O_5$, m.p. 180—188° (*tetra-acetate*, m.p. 140—150°), glucose, a *substance*, $C_{24}H_{43}(?)O_4$, m.p. 244°, and another *substance*, m.p. 252°. J. N. A.

Tautomerism of gossypol. A. Zamischlaeva (Maslob. Shir. Delo, 1937, No. 2, 9).—The no. of OH in gossypol (I), as determined by the Tschugaev–Zerevitinov method, varies from 3·4 to 8·8, according to the conditions. Solutions of (I) in C_5H_{11}·OH become coloured or turbid after 24 hr., in presence or absence of light or air. This effect is not observed with solutions in xylene. R. T.

Biochemistry of micro-organisms. LV. Molecular constitution of geodin and erdin, two chlorine-containing metabolic products of *Aspergillus terreus*, Thom. I. Constitutional relationship of geodin and erdin. P. W. Clutterbuck, W. Koerber, and H. Raistrick (Biochem. J., 1937, **31**, 1089—1092; cf. Raistrick and Smith, A., 1936, 1116).—Methylation (CH_2N_2) of geodin, the *d*-form of a Me_1 ether of *dl*-erdin, and of *dl*-erdin gives products of the same empirical formula but each depresses the m.p. of the other. Methylation (CH_2N_2) of optically inactive dihydrogeodin and dihydroerdin gives a *product*, $C_{15}H_5O_2Cl_2(OMe)_5$, m.p. 108°, which with dil. NaOH in EtOH loses OMe to give a monobasic *acid*, $C_{15}H_6O_3Cl_2(OMe)_4$, m.p. 168°. Me_2SO_4–alkali converts geodin and *dl*-erdin into the same *product*, m.p. 147°; H_2O is added to each mol., the first becoming inactive and "adding" 4, and the second "adding" 5, OMe. This product loses 1 OMe with dil. NaOH–EtOH, giving a monobasic *acid*, $C_{15}H_5O_3Cl_2(OMe)_5$, m.p. 163°. Acetylation of geodin, involving addition of H_2O, gives a *tetra-acetate*, m.p. 209—210°, whilst acetylation of dihydroerdin to the *triacetate*, m.p. 154°, occurs simply. E. A. H. R.

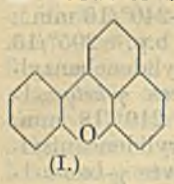
Action of furfuryl bromide on sodium phenoxide; *o*-furfurylphenol and furfuryl phenyl ether. R. Paul and H. Normant (Compt. rend., 1937, **204**, 1482—1484).—Interaction of furfuryl bromide with NaOPh in Et_2O–EtOH gives *furfuryl Ph ether* (I), b.p. 133—135°/13 mm. [hydrogenated (Raney Ni) to *tetrahydrofurfuryl Ph ether*, b.p. 144—145°/17 mm.)], and some *o-furfurylphenol* (II), b.p. 151—153°/14 mm. (*phenylurethane*, m.p. 99—100°; *o-tetrahydrofurfurylphenol*, b.p. 154—156°/15 mm.). It is improbable that (II) results from rearrangement of (I). Furfuryl, like CH_2Ph, renders Br mobile but its effect is insufficient to cause the production of substituted phenols by the action of bromides on phenoxides in slightly ionising media. H. W.

Action of mixed organomagnesium compounds on furyl ketones with two conjugated double linkings. N. Maxim and (Mlle.) M. Popescu (Bull. Soc. chim., 1937, [v], **4**, 265—277).—Furyl ketones (C_4H_3O·CH:CH·CO·CH:CHAr; Ar = aryl) with two double linkings react with mixed organo-Mg compounds (MgRX) to give the compounds C_4H_3O·CH:CH·CO·CH_2·CHRAr, the double linking attached to Ar being more reactive than that attached to C_4H_3O. The resulting compounds with MgRX give saturated ββ′-disubstituted ketones. Thus difurfurylideneacetone gives the following with the appropriate MgRX: *γ-keto-αε-di-1-furyl-*Δ^{α}*-heptene*, b.p. 199°/20 mm. (*semicarbazone*, m.p. 76°); *γ-keto-αε-di-1-furyl-*Δ^{α}*-octene* (I), m.p. 31°, b.p. 200°/16 mm. (*oxime*, m.p. 90°); *γ-keto-αε-di-1-furyl-ε-phenyl-*Δ^{α}*-pentene*, m.p. 102°, b.p. 220—240°/16 mm.; *γ-keto-αε-di-1-furyl-η-methyl-*Δ^{α}*-octene*, b.p. 205°/15 mm. (*semicarbazone*, m.p. 65°). Furfurylidenebenzylideneacetone with $MgPrBr–Et_2O$ gives *γ-keto-α-1-furyl-ε-phenyl-*Δ^{α}*-octene*, m.p. 33°, b.p. 219°/18 mm. (*semicarbazone*, m.p. 42°), and furfurylideneanisylideneacetone (II) with $MgEtI–Et_2O$ gives *γ-keto-α-1-furyl-ε-anisyl-*Δ^{α}*-heptene* (III), m.p. 55°, b.p. 241°/22 mm. (*semicarbazone*, m.p. 66°), also obtained by condensing furfuraldehyde with *β-keto-δ-anisylhexane*, b.p. 170°/21 mm. (*semicarbazone*, m.p. 144°), prepared from anisylideneacetone and $MgEtBr–Et_2O$. This establishes the constitution of (III). *γ-Keto-ε-1-furyl-α-anisyl-*Δ^{α}*-heptene*, b.p. 265°/33 mm. (*semicarbazone*, m.p. 188°), is similarly obtained from β-keto-δ-furylhexane. With $MgPrBr–Et_2O$ (II) gives *γ-keto-α-1-furyl-ε-anisyl-*Δ^{α}*-octene*, b.p. 232°/18 mm. (*semicarbazone*, m.p. 68°), and with $MgBu^{\beta}Cl–Et_2O$ gives *γ-keto-α-1-furyl-ε-anisyl-η-methyl-*Δ^{α}*-octene*, b.p. 239°/18 mm. (*semicarbazone*, m.p. 163°), which with $MgBu^{\beta}Cl–Et_2O$ gives *ζ-keto-δ-1-furyl-βκ-dimethyl-θ-anisylundecane*, b.p. 242°/17 mm. Furfurylidene-(*p*-dimethylaminobenzylidene)acetone with the appropriate MgRX–Et_2O gives *γ-keto-α-1-furyl-ε-*(p-*dimethylaminophenyl*)-Δ^{α}*-heptene*, b.p. 253°/13 mm. (*semicarbazone*, m.p. 66°), *γ-keto-α-1-furyl-ε-*(p-*dimethylaminophenyl*)*-η-methyl-*Δ^{α}*-octene*, m.p. 59°, b.p. 266°/18 mm. (*semicarbazone*, m.p. 192°), and *γ-keto-α-1-furyl-ε-*(p-*dimethylaminophenyl*)*-θ-methyl-*Δ^{α}*-nonene*, b.p. 266°/13 mm. (*semicarbazone*, m.p. 60°). With $MgPrBr–Et_2O$ (I) gives *ζ-keto-δθ-di-1-furylundecane*, b.p. 200°/18 mm. H. G. M.

Molecular resonance systems. IV. Absorption spectra of sulphonephthaleins. H. Mohler, H. Forster, and G. Schwarzenbach (Helv. Chim. Acta, 1937, **20**, 654—658).—If in a compound XH_n·T·XH_n in which T is a sulphonated triphenylcarbonium and XH_n and auxochromic group the H ions are systematically replaced, symmetrical and unsymmetrical compounds are alternately obtained. With fourteen sulphonephthaleins a very close resemblance is found in the absorption spectra of all the symmetrical forms on the one hand and of all the unsymmetrical forms on the other hand. The form of the graphs is discussed. H. W.

New constituents of coal-tar pitch. O. Kruber (Ber., 1937, **70**, [*B*], 1556—1564).—Removal of the black pigment from pitch by treatment with naphtha is difficult but by use of superheated steam in a vac. or by distillation at 2—6 mm. > half the material can be volatilised without decomp. A residue, b.p. 395—400°, from the pyrene fraction is freed from acidic (0·5%) and basic (6%) components, treated with Na at 150—155° and then with cold H_2O, and distilled. The main fraction of hydrocarbons thus isolated is a mixture of 2 : 3- and 1 : 2-benzofluorene, best separated from one another by use of AcOH. The latter is more readily isolated if the fraction is heated with KOH instead of Na. For the extraction

of compounds containing O, a pyrene residue fraction, b.p. 392—397°, is employed; from this phenylene 2 : 3-naphthylene oxide (brasan), m.p. 205—206°, is readily isolated after partial oxidation with $Na_2Cr_2O_7$ in AcOH or by use of molten KOH. The residues afford 1 : 9-*benzoxanthen* [7-*oxabenzanthrene*] (I), b.p. 395°/758 mm. (*picrate*, m.p. 124°), reduced (Na and EtOH) to 1 : 9-*tetrahydrobenzoxanthen*, b.p. 204—206°/15 mm., m.p. 58°, which is oxidised by $Na_2Cr_2O_7$ in AcOH at room temp. to β-1-*xanthonepropionic acid*, m.p. 169—170°; this is further oxidised by $KMnO_4$ to 1-*xanthoneglyoxylic acid* (II), m.p. 187—188°, and 1-*xanthoneacetic acid*, m.p. 176—177°. Treatment of (II) with NaOH–10% H_2O_2 affords *xanthone*-1-*carboxylic acid*, m.p. 229—230°, decarboxylated to xanthone. A *dihydrobrasan*, m.p. 157°, is incidentally described. H. W.


(I.)

Dimerisation of pyruvic anilide. J. V. Scudi (J. Amer. Chem. Soc., 1937, **59**, 1403—1404).—Treatment of pyruvanilide (I) with $NHEt_2$ in $COMe_2$ yields a dimeride (II), which reacts with NH_2OH,HCl in cold dil. NaOH giving the oxime of (I), and is hydrolysed by boiling dil. NaOH to $NHPh_2$ (extracted with Et_2O) and $BzCO_2H$ (pptd. as phenylhydrazone). The formation from (II) of an *OEt*-derivative, m.p. 198°, with EtOH and HCl, and an *Ac* derivative, m.p. 148—150°, with conc. H_2SO_4 in boiling Ac_2O shows that (II) is unsymmetrical, whilst its stability to acids indicates the structure $OH\cdot CMe\cdot CH_2\diagdown CO—NPh\diagup C(OH)\cdot CO\cdot NHPh$. A. Li.

Mechanism of closure of the pyrrole ring in the dry distillation of ammonium mucate. E. S. Chotinski (Trav. Inst. Chim. Charkov, 1935, **1**, 19—32).—It is concluded from a review of the lit. that pyrrole and pyrrolecarboxylamide are formed respectively from $(NH_4)_2$ mucate (I) and NH_4 mucinamate (II), and that conversion of (I) into (II) precedes ring-closure. R. T.

Pyrrole derivatives. V. B. Toi and S. Akabori (Bull. Chem. Soc. Japan, 1937, **12**, 316—318).—The following compounds are obtained by condensing $CH_2Ac\cdot CO_2Et$ with the appropriate β-aminoaldehyde obtained by the reduction (Na–Hg, EtOH–H_2O, —10°) of the corresponding β-substituted aminoacetic ester: Et 2-methyl-, Et 2 : 5-dimethyl-, and *Et* 2-*methyl*-5-iso*butyl*-*pyrrole*-3-*carboxylate*, m.p. 66·5—67·5°, and β-2-*methyl*-3-*carbethoxy*-5-*pyrrylpropionic acid*, m.p. 176—177°. F. N. W.

***N*-Arylbarbituric acids. III.** J. S. Buck (J. Amer. Chem. Soc., 1937, **59**, 1249—1251).—Nitration of 1-phenyl-5 : 5-diethylbarbituric acid yields equal quantities of m-, m.p. 189°, and p-*nitro*-, m.p. 208°, reduced (PtO_2) to m-, m.p. 226° [*hydrochloride*, m.p. 242° (decomp.)], and p-*amino*-, m.p. 234° [*hydrochloride*, m.p. 256° (decomp.)], -*phenyl*-5 : 5-*diethylbarbituric acid*. Acetylation (Ac_2O) of the last two gives the m-, m.p. 285°, and p-*NHAc*-compound, m.p. 174°, identical with those prepared by condensing *m*- and *p*-$NHAc\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2$ respectively with $CEt_2(CO_2Et)_2$, whilst treatment of the amines with nitrocarbamide in EtOH yields m-, m.p. about 206°, and p-*carbamidophenyl*-5 : 5-*diethylbarbituric acid*, m.p. about 221°. These condense (NaOEt) with $CEt_2(CO_2Et)_2$ to give m-, m.p. about 345°, and p-*phenylene*-NN′-*bis*-(5 : 5-*diethylbarbituric acid*), m.p. about 352°. $ClCO_2Et$ and NaOH convert the NH_2-compounds into the m-, m.p. 242°, and p-*carbethoxylamino*-compounds, m.p. 203·5°. *o*-, *m*-, and *p*-$C_6H_4Cl\cdot NH\cdot CO\cdot NH_2$ with $CEt_2(CO_2Et)_2$ afford respectively 1-o-, m.p. 169°, 1-m-, m.p. 152·5°, and 1-p-*chlorophenyl*-5 : 5-*diethylbarbituric acid*, m.p. 181°, the last two identical with those prepared by diazotisation of the NH_2-compounds. The diazonium salts are converted by boiling 40% H_2SO_4 into the m-, m.p. 222·5°, and p-*OH*-compounds, m.p. 191°, and couple with appropriate amines or phenols yielding the azo dyes 1-m- and 1-p-(4-*aminobenzeneazo*)-, -(4-*aminonaphthaleneazo*)-, -(4-*hydroxynaphthaleneazo*)-, and -(2-*azo*-α-*naphthol*-5-*sulphonic acid*)-*phenyl*-5 : 5-*diethylbarbituric acid*. o-*Acetamidophenylcarbamide*, m.p. 188° (decomp.), obtained by reducing *o*-$NO_2\cdot C_6H_4\cdot NHAc$ (Adams method) and treating the amine with nitrocarbamide in EtOH, does not condense with $CEt_2(CO_2Et)_2$. All m.p. are corr. A. Li.

Enol-betaines. Derivatives of 3 : 5-diketopiperidine. C. Gustafsson (Ber., 1937, **70**, [*B*], 1591—1598).—Sarcosine Et ester is converted by $CH_2Cl\cdot COMe$ and anhyd. Na_2CO_3 in abs. EtOH into *Et methylacetonylaminoacetate*, b.p. 95—96°/6 mm., the *methiodide*, m.p. 131—134° (decomp.), of which is transformed by NaOEt in warm EtOH into the *compound*, $C_{28}H_{44}O_8N_4,NaI$ (I), m.p. 236—239° (decomp.), which with Ag_2O affords 3 : 5-*diketo*-1 : 1-*dimethylpiperidiniumbetaine monohydrate* (II), m.p. >300° after gradual decomp. at 240°; this passes at 120°/vac. into the anhyd. *betaine*, $CH\langle\begin{matrix}C(\bar{O})\cdot CH_2\\ CO—CH_2\end{matrix}\rangle\overset{+}{N}Me_2$. Oxidation of (II) with $KMnO_4$ in dil. HCl gives methyliminodiacetic acid methochloride, m.p. 207—208° (decomp.), also obtained from *Et*$_2$ *methyliminodiacetate methiodide*, m.p. 118—120°. (II) is converted by aq. NaI into (I) and by $SrBr_2$ into the *compound*, $C_{14}H_{22}O_4N_2,SrBr_2$, also $+1H_2O$. (II) is transformed into the corresponding *chloride*, m.p. 213—214° (decomp.), and *nitrate*, m.p. 179—181° (decomp.), and into the abnormal *iodide*, $C_{14}H_{23}O_4N_2I$, m.p. 209—210° (decomp.). (I) is converted by NaOMe and an excess of MeI in MeOH into 5-*keto*-3-*methoxy*-1 : 1-*dimethyl*-Δ^3-*piperidinium iodide*, m.p. 169—171° (decomp.); the corresponding 3-*OEt*-compound has m.p. 175—176° (decomp.). (II) in MeOH immediately decolorises Br and in conc. solution 4-*bromo*-3 : 5-*diketo*-1 : 1-*dimethylpiperidinium bromide*, m.p. 203—204° (decomp.), is pptd.; if this is neutralised with NaOH, 4-*bromo*-3 : 5-*diketo*-1 : 1-*dimethylpiperidiniumbetaine*, m.p. 229—231° (decomp.), is produced. Treatment of (I) with I in presence of $NaHCO_3$ leads to 4-*iodo*-3 : 5-*diketo*-1 : 1-*dimethylpiperidiniumbetaine*, m.p. 213—214° (decomp.). H. W.

Synthesis of new local anæsthetics. II. K. N. Gaind, A. W. Khan, and J. N. Ray (J. Indian Chem. Soc., 1937, **14**, 237—240; cf. this vol., 243).—Esters

of $CH_2Cl{\cdot}CMe(OH){\cdot}CO_2H$ are heated under pressure with piperidine in C_6H_6, and the products benzoylated or *p*-nitrobenzoylated to $C_5H_{11}N{\cdot}CH_2{\cdot}CMe(CO_2R){\cdot}O{\cdot}CO{\cdot}R'$. The following new local anæsthetics are described: *Pr*$^{\alpha}$ β-*chloro*-α-*hydroxy*isobutyrate, b.p. 120°/15 mm. *Pr* α-*benzoyloxy*-β-*piperidino*isobutyrate (*hydrochloride*, m.p. 115°). *Et* α-*benzoyloxy*-β-*piperidino*isobutyrate (*hydrochloride*, m.p. 128°). *Et* α-p-*nitrobenzoyloxy*-β-*piperidino*isobutyrate (*hydrochloride*, +1COMe$_2$, m.p. 76°); the free base on reduction affords *Et* α-p-*aminobenzoyloxy*-β-*piperidino*isobutyrate *hydrochloride*, m.p. 102°. *Pr*$^{\beta}$ α-*hydroxy*-β-*piperidino*isobutyrate *hydrochloride*, m.p. 115° (O-*Bz* derivative *hydrochloride*, m.p. 156°; O-p-*nitrobenzoyl* derivative *hydrochloride*, m.p. 61°). *Benzyl* α-*benzoyloxy*-β-*piperidino*isobutyrate (*hydrochloride*, m.p. 195—197°). The $NaHSO_3$ compound of piperidinoacetone with aq. KCN affords α-*hydroxy*-β-*piperidino*isobutyronitrile, which on conversion into the Et ester hydrochloride of the acid and treatment with Na_2CO_3 is decomposed. P. G. C.

Hydroxylamine pyridine compounds of bivalent platinum.—See A., I, 475.

Phenoxypyridine. R. R. Renshaw (J. Amer. Chem. Soc., 1937, **59**, 1406—1407).—Errors in an earlier paper (this vol., 165) are corr. A. Li.

Modification of the Guareschi pyridine synthesis. I. N. Palit (J. Indian Chem. Soc., 1937, **14**, 219—224).—In contrast to the results of Guareschi (cf. A., 1898, i, 274), the reaction between PhCHO, $CN{\cdot}CH_2{\cdot}CO_2Et$, $CHMe{:}CAc{\cdot}CO_2Et$, and NH_3 affords only two products, the known $CO_2Et{\cdot}CHAc{\cdot}CHPh{\cdot}CH(CN){\cdot}CO{\cdot}NH_2$, m.p. 225—226°, and *Et* 6-*hydroxy*-3-*cyano*-4-*phenyl*-6-*methyl*-2-*piperidone*-5-*carboxylate* (I), m.p. 222—223°; the latter is also obtained from $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ (II) and $CHPh{:}CAc{\cdot}CO_2Et$ in presence of a little $NHEt_2$. With dil. HCl (I) affords $CH_2Ac{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, and in alkaline solution with Me_2SO_4 gives *Et* 6-*hydroxy*-2-*methoxy*-3-*cyano*-4-*phenyl*-3 : 5-*dimethyl*-Δ^1-*tetrahydropyridine*-5-*carboxylate*, m.p. 162°. Ac_2O in C_5H_5N converts (I) into 6-*hydroxy*-2-*acetoxy*-4-*phenyl*-6-*methyl*-Δ^1-*tetrahydropyridine*, m.p. 145—146°, which is insol. in NaOH solution but suffers ring fission by hot aq. NaOH. From (I) and PCl_3 in C_6H_6, *Et* 2-*hydroxy*-3-*cyano*-4-*phenyl*-6-*methyl*-$\Delta^{1:5}$-*dihydropyridine*-5-*carboxylate*, m.p. 142°, is obtained (*Me ether*, m.p. 149°). Condensation of (II) with $CHPh{:}C(CN){\cdot}CO_2Et$ in presence of $NHEt_2$ for 4—5 days affords 6-hydroxy-3 : 5-dicyano-4-phenyl-$\Delta^{3:6}$-dihydro-2-pyridone (J.C.S., 1920, **117**, 1465), whereas the initial product of the reaction is a *NHEt*$_2$ salt, m.p. 266—268°. P. G. C.

Preparation of amino-3-pyridylmethane. H. Erlenmeyer and A. Epprecht (Helv. Chim. Acta, 1937, **20**, 690—691).—Et nicotinate is converted by way of the amide into the nitrile, which with $Cr(OAc)_2$ affords 3-*pyridylmethylamine*, isolated as the *dihydrochloride*, m.p. 224°; *picrate*, m.p. 193°. P. G. C.

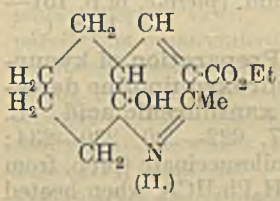
Reducing action of *N*-glucosido-*o*-dihydronicotinic amide and analogous compounds. P. Karrer and B. H. Ringier (Helv. Chim. Acta, 1937, **20**, 622—625).—Preparative methods are given for the conversion of *N*-*d*-glucosido-*o*-dihydronicotinamide (I) and its *O*-Ac$_4$ derivative into *N*-*d*-glucosidopyridinium-3-carboxylamide iodide and its *O*-Ac$_4$ derivative, respectively. In slightly acid solution (I) reduces 78% of dichlorophenol-indophenol in 1 hr., reduces aq. Ag salts, and converts *o*-$C_6H_4(NO_2)_2$ into *o*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}OH$, but in each case more slowly than ascorbic acid. P. G. C.

Manufacture of substituted pyridine-*o*-dicarboxylic amides.—See B., 1937, 842.

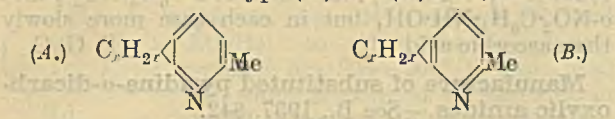
Transformation of indolyl methyl ketones into indole homologues. C. Alberti (Gazzetta, 1937, **67**, 238—243).—3-Indolyl Me ketone (I) and NaOMe at 210—220° give 3-methylindole and unchanged (I); similarly 2-methyl-3-indolyl Me ketone (II) gives 2 : 3-dimethylindole. With NaOEt, (I) gives 3-ethylindole, and (II) gives 2-methyl-3-ethylindole. Boiling 20—20% H_2SO_4 scarcely attacks (I) or 3-methyl-2-indolyl Me ketone, but converts (II) into 2-methylindole. E. W. W.

Catalytic dehydrogenation of *trans*-decahydroquinoline. J. K. Juriev and G. I. Mironenko (Sci. Rep. Moscow State Univ., 1936, No. 6, 277—279).—Quinoline is obtained in 35% yield from *trans*-decahydroquinoline in presence of C–Pt catalyst at 330°. R. T.

Synthesis of *Bz*-tetrahydroquinolines. III. U. Basu (Annalen, 1937, **530**, 131—141; cf. A., 1935, 222).—2-Hydroxymethylene*cyclo*hexanone and $NH_2{\cdot}CMe{:}CH{\cdot}CO_2Et$ (I) at −5° give *Et* 10-*hydroxy*-5 : 6 : 7 : 8 : 9 : 10-*hexahydroquinaldine*-3-*carboxylate* (II), m.p. 200—201°, stable at 105°, but dehydrated above the m.p. or by boiling with picric acid in EtOH to Et *Bz*-tetrahydroquinaldine-3-carboxylate and simultaneously dehydrated and hydrolysed by boiling 15% KOH. 2-Et oxalo*cyclo*hexanone and (I) at 28° give similarly *Et*$_2$ 10-*hydroxy*-5 : 6 : 7 : 8 : 9 : 10-*hexahydroquinaldine*-3 : 4-*dicarboxylate*, b.p. 191°/5 mm. (*picrate*, m.p. 134°) (with a small amount of a non-basic, nitrogenous *substance*, m.p. 212°), and thence the corresponding *acid*, m.p. 257° (decomp.), which loses CO_2 only with difficulty when heated, but when distilled in vac. with 2 parts of soda-lime gives 10-*hydroxy*-4 : 6 : 7 : 8 : 9 : 10-*hexahydroquinaldine*, b.p. 232—234°/754 mm. (*picrate*, m.p. 191°), partly converted by distillation with PbO into *Bz*-tetrahydroquinaldine. 2-Et oxalo-6-, -5-, and -4-methyl*cyclo*hexanone and (I) give similarly *Et*$_2$ 10-*hydroxy*-2 : 8-, b.p. 191—192°/12 mm. (*picrate*, m.p. 144°) (and a *substance*, m.p. 236°), -2 : 7-, b.p. 206°/12 mm. (*picrate*, m.p. 87°) (and a *substance*, m.p. 217°), and -2 : 6-*dimethyl*-5 : 6 : 7 : 8 : 9 : 10-*hexahydroquinoline*-3 : 4-*dicarboxylate*, b.p. 205°/15 mm. (*picrate*, m.p. 128°) (and a *substance*, m.p. 230°), the corresponding *acids*, m.p. 210—211° (decomp.), 238—239° (decomp.), and 236° (decomp.), and 10-*hydroxy*-2 : 8-, b.p. 241—243°/755 mm. (*picrate*, m.p. 177°), -2 : 7-, b.p. 248—249°/757 mm. (*picrate*, m.p. 194—195°), and -2 : 6-


(II.)

dimethyl-5 : 6 : 7 : 8 : 9 : 10-*hexahydroquinoline*, b.p. 251—253°/754 mm. (*picrate*, m.p. 180—181°), respectively. *Bz*-Tetrahydroquinaldine and 6-methyl-2 : 3-dihydro-β-pyridindene (5 : 6-trimethylene-α-picoline) derivatives condense with aldehydes to 2-styryl derivatives; this method of distinguishing between formulæ of type (*A*) and (*B*) fails, since from



considerations of valency angles (*B*) should be favoured in the quinaldine and (*A*) in the pyridindene series. The author prefers a centric formula. The following are described, m.p. in parentheses being those of the *hydrochlorides*: *Et* 2-m-, m.p. 141° (170°), and -p-*nitro*-, m.p. 119°, and -p-*methoxy*-, m.p. 96° (173°; *methosulphate*, m.p. 214°), and -p-*dimethylamino-styryl*-Bz-*tetrahydroquinoline*-3-*carboxylate*, m.p. 120°; 2-p-*dimethylamino*-, m.p. 160°, 2-p-, m.p. 203°, and -m-*nitro-styryl*-Bz-*tetrahydroquinoline*, m.p. 217°; 3-*acetyl*-, m.p. 163—164°, and 3-*benzoyl*-2-p-*nitro-styryl*-Bz-*tetrahydroquinoline*, m.p. 181—182° (210°); 3-*acetyl*-2-p-*nitro*-, m.p. 213° (207°), and -2-p-*methoxy-styryl*-6-*methyl*-Bz-*tetrahydroquinoline*, m.p. 173°; 3-*benzoyl*-2-p-*nitrostyryl*-6-, cryst., and -7-*methyl*-Bz-*tetrahydroquinoline*, m.p. 186—187°. 2-Hydroxymethylene*cyclo*heptanone and (I) at 100° give *Et* 6-*methyl*-2 : 3-*dihydro*-β-*pyridindene*-7-[5 : 6-*trimethylene*-α-*picoline*-3-]*carboxylate*, b.p. 178—180°/25 mm. (*picrate*, m.p. 134°; p-*nitrobenzylidene* derivative, m.p. 210°), hydrolysed by 15% KOH to the corresponding *acid*, m.p. 208° (decomp.), which, when distilled with soda-lime, gives 6-*methyl*-2 : 3-*dihydro*-β-*pyridindene* [5 : 6-*trimethylene*-α-*picoline*], b.p. 78—80°/20 mm., 195—196°/750 mm. (*picrate*, m.p. 151—152°). R. S. C.

Xanthurenic acid. V. Preparation of kynurenic acid and of other 4-hydroxyquinoline derivatives. VI. Synthesis of xanthurenic acid. L. Musajo (Gazzetta, 1937, 67, 222—230, 230—234; cf. this vol., 305).—V. Et_2 anilosuccinate (prep. from Et_2 sodio-oxalacetate and NH_2Ph,HCl), when heated in petroleum jelly at 280°, yields Et kynurenate (Et 4-hydroxyquinoline-2-carboxylate); this, and the acid, are identical with products from natural sources. *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ and $NO_2{\cdot}CH_2{\cdot}CH{:}N{\cdot}OH$ condense in aq. HCl to form o-β-*nitroethylideneaminobenzoic acid*, m.p. 196° (decomp.) (G.P., 347,375; B., 1922, 522), converted by NaOAc–Ac_2O into 3-*nitro*-4-*hydroxyquinoline*, m.p. >300° (*loc. cit.*) (*K* salt; *Bz* derivative, m.p. 144—145°). This is reduced (Sn and HCl) to 3-*amino*-4-*hydroxyquinoline*, m.p. >300° (*Bz* derivative, m.p. 289°).

VI. 4-Hydroxy-2-methylquinoline with KOH at 240—300° furnishes xanthurenic acid, m.p. 285° (after purification through the Me ester). E. W. W.

Synthesis of 2 : 4-dihydroxyquinoline and its derivatives. Their constitution. P. Heimann (Diss., Dijon, 1937, 60 pp.).—The halogenation, nitrosation, and diazonium coupling of 4-hydroxycarbostyril (I) and its Br-derivatives and a new synthesis of these compounds are described. Tautomerism between the diphenolic and diketo-forms is indicated by the varied modes of reaction. Purification of (I) is readily effected by crystallisation of its *Na* salt. With 1 mol. of Br in cold HCO_2H or with 2 mols. in conc. H_2SO_4 (I) gives the yellow α-(5- or 8-)*Br*-derivative (II), m.p. 199°; with an excess of Br in cold or with 2 mols. in hot HCO_2H it gives the 3-*Br*-derivative (III), m.p. 281°; with 2 mols. of Br in C_6H_6 it gives the 6-*Br*-derivative (IV), m.p. 241° (*NO*-derivative, m.p. 256°). With PBr_5 (I) gives 2 : 4-*di*-, m.p. 265°, (II) gives 2 : 4 : 5- or 2 : 4 : 8-*tri*-, m.p. 276°, and (III) gives 2 : 3 : 4-*tri-bromoquinoline*, m.p. 288°. PCl_5 converts (II) into 2 : 4-*dichloro*-5- or -8-, m.p. 174·5°, and (III) into 2 : 4-*dichloro*-3-*bromoquinoline*, m.p. 99°. *m*-$C_6H_4Br{\cdot}CO_2H$ (modified prep.), b.p. 280°, gives, by way of 5-bromo-2-nitrobenzoyl chloride, m.p. 142°, *Et*$_2$ 5-*bromo*-2-*nitrobenzoylmalonate*, cyclised by Sn–HCl to (IV). $KMnO_4$ oxidises (I) or (II) to 4 : 6-*dihydroxypyridine*-2 : 3-*dicarboxylic acid*, m.p. 261° (*Ag* and *Pb* salts), which proves that the Br of (II) is in the *Bz* ring; this is confirmed by formation of a *NO*-derivative, m.p. 200°. The orientation of (III) follows from its oxidation to 5-*bromo*-4 : 6-*dihydroxypyridine*-2 : 3-*dicarboxylic acid*, m.p. 240° (also obtained from the preceding acid by Br), and from its diazo-synthesis from 3-amino-2 : 4-dihydroxyquinoline. The NO-derivative (V) of (I) crystallises from H_2O at 15° or from EtOH in a yellow, thermolabile *form*, m.p. 208°, which gives the red form at >100°; from H_2O at >40° it gives a thermostable, yellow *monohydrate*, m.p. 251°. It gives a green solution of the Na and a reddish-brown solution of the Na_2 salt; by use of <1 NaOH the green, cryst. *Na* salt is isolated, which with $CoCl_2$ gives a brown *salt*, $Co^{II}(OH)_2,C_9H_5O_3N_2$, converted by HCl into $CoCl_2$, Cl_2, and a red *salt*, $Co^{III}(C_9H_5O_3N_2)_2$, also obtained directly from (V) by $CoCl_2$ in AcOH; $NiCl_2$ and (V) in AcOH, however, give the green *salt*, $Ni^{II}(C_9H_5O_3N_2)_2$. Me_2SO_4 and (I) give 4-*methoxycarbostyril*, m.p. 271° (*NO*-derivative, m.p. 220°). *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ affords 6- and 5-(or 8-)*bromo*-2 : 4-*dihydroxy*-3-p-*nitrobenzeneazoquinoline*, m.p. >370°. Diazotised 3-amino-4-hydroxycarbostyril and (I) give *azo*-4-*hydroxycarbostyril*, m.p. 218°. Long treatment with the appropriate amine converts $CH_2(CO_2R)_2$ into *malondi*-o-, m.p. 171°, and -p-*chloroanilide*, m.p. 261°, and -o-*anisidide*, m.p. 163°; *ethylmalondi*-p-*chloroanilide*, m.p. 258°, is similarly obtained; boiling for only 0·5 hr. gives *carbomethoxyacet*-o-, m.p. 70·5°, and -p-*chloro-anilide*, m.p. 84°, *carbethoxyacet*-o-*chloroanilide* (VI), m.p. 176°, and -o-*anisidide*, m.p. 66°, and α-*carbethoxypropion*-p-*chloroanilide* (VII), m.p. 93°. By passing steam into the mono-esters in aq. Na_2CO_3 are obtained *malonmono*-p- (VIII), m.p. 168°, and -o-*chloroanilide*, m.p. 158°, and -o-*anisidide* (IX), m.p. 154°. Addition of $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4R$-*p* (R = Me or Cl) in small portions to paraffin at 250° gives 4-*ethoxy*-6-*methyl*-, m.p. 138° [oxidised to 4 : 6-*dihydroxynicotinic acid* (*Ag* and *Pb* salts)], and -6-*chloro-carbostyril*, m.p. 91°, with a little diamide; $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$-*o* gives only a little 4-*ethoxy*-8-*methylcarbostyril*, m.p. 190°, and much ditoluidide. $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ and $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4X$-*o* (X = Cl or OMe) give

the diamide and no carbostyril; (VII) loses EtOH instead of H_2O and yields 5-*chloro*-4-*hydroxycarbostyril*, m.p. 264°, and $CO_2Et{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$-*o* gives similarly 4-*hydroxy*-8-*methyl*-3-*ethylcarbostyril*, m.p. 218°. Hot Ac_2O converts *o*- and *p*-$C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ into *o*- and *p*-$C_6H_4Me{\cdot}NHAc$, respectively. PCl_5 converts (VI) and its *p*-analogue into 2 : 3 : 8-*trichloro*-4-*ethoxy*-, m.p. 63·5° and 4 : 6-*dichloro*-2-*hydroxy-carbostyril*, m.p. 138°, respectively. P_2O_5 converts the anilidoesters into dianilides. PCl_5 converts the anilido-acids (VIII) and (IX) into 2 : 3 : 4 : 6-*tetrachloro*-, m.p. 127°, and 2 : 4-*dichloro*-8-*methoxyquinoline*, m.p. 92°, respectively. R. S. C.

Salts and complex derivatives of 4-hydroxy-2 : 6- and -2 : 8-dimethylquinoline. A. Meyer and H. Drutel (Compt. rend., 1937, **204**, 1824—1826; cf. A., 1935, 758, 1506).—The following derivatives of 4-hydroxy-2 : 6-dimethylquinoline are prepared: *sulphate*, m.p. 240°; *H sulphate*, m.p. 207—208°; *hydrochloride*, m.p. 184—185°; *K* derivative, m.p. 313—315°; *picrate*, m.p. 192°; *picrolonate*, m.p. 230°; *bismuthi-iodide*, m.p. 222° (decomp.); *mercuri-iodide*, m.p. 202°, and *-chloride*; 4-*OMe*- and *-OEt*-derivatives, m.p. 107° (+*MeI*, m.p. 214°; +*EtI*, m.p. 187°) and 75—76° (+*MeI*, m.p. 220°; +*EtI*, m.p. 208—209°), respectively; *ethiodide*, m.p. 208°. The following derivatives of 4-hydroxy-2 : 8-dimethylquinoline are prepared: *sulphate*, m.p. 222°; *hydrochloride*, m.p. 220°; *picrate*, m.p. 188°; *picrolonate*, m.p. 227—228°; *bismuthi-iodide*, m.p. 217° (decomp.); *mercuri-iodide*, m.p. 180—181° and *-chloride*; 4-*OMe*- and *-OEt*-derivatives, m.p. 103·5° (+*MeI*, m.p. 148—149°) and 77·5° (+*EtI*, m.p. 200°), respectively; *ethiodide*, m.p. 174—175°. J. L. D.

Production of aldehydes [indoles, carbazoles, quinolines etc.].—See B., 1937, 761.

Dipolar complex salts. A. Ablov (Bull. Soc. chim., 1937, [v], **4**, 1220—1229).—The following *substances* have been prepared: *Cu quinoline*-5-*carboxylate* (I), (I)$2C_5H_5N$, *Ni* and *Co quinoline*-5-*carboxylate* +$8H_2O$, *Cu quinoline*-8-*sulphonate* +$2H_2O$, *Cu tetrapyridylquinoline*-8-*sulphonate* $(C_9H_6N{\cdot}SO_3)_2[Cu(C_5H_5N)_4]$, *Cu quinoline*-6-*sulphonate* +$6H_2O$, $(C_9H_6N{\cdot}SO_3)[Cu(C_5H_5N)_4]$, $(C_9H_6N{\cdot}SO_3)CuOH$ + $1{\cdot}5H_2O$ (II), and *Cu quinoline*-5-*sulphonate* +$4H_2O$. Acetoxycupric quinoline-5-carboxylate and (II) are probably dipolar complex salts. J. G. A. G.

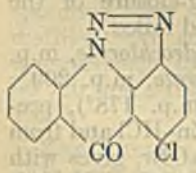
Tautomerism of ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate. H. V. Heeramaneck and R. C. Shah (Proc. Indian Acad. Sci., 1937, **5**, **A**, 442—446).—Et 4-hydroxy-2-phenylquinoline-3-carboxylate (I) (*H sulphate*, m.p. 212—215°; *picrate*, m.p. 247—250°) is shown to react both in the enol and keto-forms. *Et* 2-*phenyl*-3-*methyl*-3 : 4-*dihydroquinoline*-3-*carboxylate*, m.p. 164—166° [*carboxylic acid*, m.p. 221—222° (evolution of CO_2)], is obtained by the interaction of (I) and MeI in EtOH–NaOEt. The corresponding 3-*Et* compound, m.p. 226—228°, is obtained similarly, or by condensing benzanilide imidochloride with $CH_2(CO_2Et)_2$. Clemmensen reduction of (I) affords *Et* 2-*phenyl*-3 : 4-*dihydroquinoline*-3-*carboxylate*, m.p. 125° (decomp.), but more drastic reduction (EtOH–HCl–Sn; 4—5 hr.; reflux) gives *Et* 2-*phenyltetrahydroquinoline*-3-*carboxylate* (?), m.p. 245°, whilst interaction with PCl_5 affords *Et* 4-*chloro*-2-*phenylquinoline*-3-*carboxylate*, m.p. 101—103°. Decarboxylation (H_2O; 210—220°; 6 hr.) of 4-hydroxy-2-phenylquinoline-3-carboxylic acid is described. F. N. W.

***iso*Quinoline series. I. Attempted synthesis of *iso*quinoline derivatives from substituted benzylamines.** B. B. Dey and T. R. Govindachari. **II. *iso*Quinolines from opianylmethylamine.** B. B. Dey and T. K. Srinivasan (Arch. Pharm., 1937, **275**, 383—397, 397—405).—I. $CHAc{:}N{\cdot}OH$ with NH_2Ph, $NH_2{\cdot}CH_2Ph$, or piperonylamine (I) in C_6H_6 gives β-phenyl-, m.p. 174°, β-*benzyl*-, m.p. 131°, and β-*piperonyl-iminopropaldoxime*, m.p. 128°, respectively. Reduction of the CH_2O_2-compound could not be effected. $CMeAc{:}N{\cdot}OH$, (I), and a little K_2CO_3 in hot EtOH give *Me* α-*piperonyliminoethyl ketone*, m.p. 105°. $(CHO)_2$ and (I) give a resin, which did not give an *iso*quinoline derivative with dehydrating agents. BzCHO and (I) in EtOH give a poor yield of ω-*piperonylamino*-ω-*hydroxyacetophenone*, m.p. 121°, which resists ring-closure; AcCHO gives a resin; $OH{\cdot}CHMe{\cdot}CO_2H$ and $OAc{\cdot}CHMe{\cdot}CO_2H$ give products, from which no basic product is obtained by dehydration. Aq. CH_2O–$NaHSO_3$ with (I) or 3 : 4-$(OMe)_2C_6H_3{\cdot}CH_2{\cdot}NH_2$ gives *piperonyl*-, an oil (*hydrochloride*, m.p. 185°), and 3 : 4-*dimethoxybenzyl-aminoacetonitrile*, m.p. 64° (*hydrochloride*, m.p. 188°), respectively; attempted ring-closure of the former product by the Hoesch method failed.

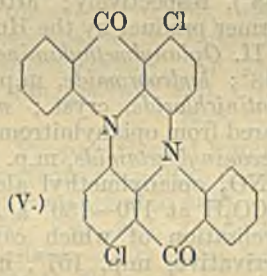
II. *Opianylmethylamine*, an oil (*hydrochloride*, m.p. 248°; *hydrobromide*, m.p. 235°; *picrate*, m.p. 209°; *platinichloride*, cryst.; *methiodide*, m.p. 178°), prepared from opianylnitromethane by Zn–HCl and from *meconinylacetamide*, m.p. 224°, by NaOBr, gives with HNO_2 opianylmethyl alcohol, m.p. 115°, and with HCO_2H at 170—180° a *HCO* derivative, m.p. 147°, cyclisation of which cannot be effected; the *Ac* derivative, m.p. 157°, however, with P_2O_5 in hot xylene gives the tricyclic *lactone*, an oil (*picrate*, m.p. 242°; *methiodide*, m.p. 207°), of 4-*hydroxy*-6 : 7-*dimethoxy*-1-*methyl*-3 : 4-*dihydro*isoquinoline-5-*carboxylic acid*, reduced by Zn–HCl to the corresponding H_4-*lactone*, an oil (*picrate*, m.p. 230—232°; *methiodide*, m.p. 242° after sintering from 176°; *Ac* derivative, m.p. 167° after sintering from 100°; with HNO_2 gives an oil); the *Bz* derivative, m.p. 158°, gives similarly the *lactone*, an oil (*picrate*, m.p. 158°), of 4-*hydroxy*-6 : 7-*dimethoxy*-1-*phenyl*isoquinoline-5-*carboxylic acid*. *o*-$CO_2H{\cdot}C_6H_4{\cdot}CHO$ and $MeNO_2$ give α-*nitromethylphthalide*, m.p. 130°, reduced by Zn–HCl to α-*aminomethylphthalide*, an oil [*hydrochloride*, m.p. 253°; *hydrobromide*, m.p. 245°; *picrate*, m.p. 192°; (?) *methiodide* of the N-Me_2 derivative, m.p. 240°]; attempts to cyclise the oily *HCO* and *Ac* and *Bz*, m.p. 169—170°, derivatives failed. R. S. C.

Acridine. XVII. Syntheses in the acridone series. K. Lehmstedt and K. Schrader (Ber., 1937, **70**, [*B*], 1526—1538).—2 : 6-$C_6H_3Cl_2{\cdot}CO_2H$ (I), m.p. 139—140° (prep. from 1 : 2 : 6-$C_6H_3MeCl{\cdot}NO_2$

described), is converted by NH_2Ph, Cu-bronze, and K_2CO_3 in boiling amyl alcohol into diphenylamine-2-carboxylic acid and BzOH. Similar slow change occurs in presence of Na but in absence of catalyst there is no reaction. $NPhMe_2$ behaves similarly to NH_2Ph. (I) is transformed by conc. H_2SO_4–HNO_3 (*d* 1·52) into 2 : 6-*dichloro*-3-*nitrobenzoic acid*, m.p. 152°, which is converted by NH_2Ph at 135—140° into 3-*chloro*-6-*nitrodiphenylamine*-2-*carboxylic acid* (II), m.p. 206°, and 4-*nitro*-1 : 3-*dianilinobenzene*, m.p. 178°, and by boiling NH_2Ph and anhyd. Na_2CO_3 into 3-*nitro*-2 : 6-*dianilinobenzoic acid*, m.p. 167—169° (decomp.). NO_2 cannot be removed from (II) in the usual manner since reduction and diazotisation lead to 6-*chloro*-1-*phenylbenztriazole*-7-*carboxylic acid*, m.p. 230°. Treatment of (II) with $POCl_3$ followed by H_2O or by conc. H_2SO_4 at 100° leads to 4-*chloro*-1-*nitroacridone* (III), decomp. 249°, nitrated [conc. H_2SO_4–HNO_3 (*d* 1·5)–AcOH] to 4-*chloro*-1 : 7-*dinitroacridone*, m.p. 275—277°, which couples with 4-aminodiphenylamine-2-sulphonic acid in $PhNO_2$ to 1 : 7-*dinitro*-4-*acridonylaminodiphenylamine*-2-*sulphonic acid* (*Na* salt), which gives brown-red shades on wool. Cl in (III) is very reactive. Short boiling with NH_2Ph converts (III) into 1-*nitro*-4-*anilinoacridone*, m.p. 224°, and treatment of (III) with 1-aminoanthraquinone and K_2CO_3 in $PhNO_2$ at 206° affords 1-*nitro*-4-1′-*anthraquinonylaminoacridone* of very high m.p. Reduction of (III) by $SnCl_2$–conc. HCl gives 4-*chloro*-1-*aminoacridone*, m.p. 224—227° (decomp.) when placed in bath preheated to 220°, converted by $NaNO_2$ and HCl into 4-*chloro*-1 : 10-*azoacridone* (IV), decomp. 218°. 1-Aminoacridone similarly yields



(IV.)



(V.)

1 : 10-*azoacridone*, decomp. 258—259°. Both compounds evolve N when heated by themselves or in solvents of high b.p. Under these conditions (IV) gives the *compound* (V), m.p. 369—371° after darkening when placed in bath preheated to 350°. (IV), 1-aminoanthraquinone, N_3H, NaOAc, and CuCl in boiling tetrahydronaphthalene give the *compound*, $C_{54}H_{28}O_6N_4$; the corresponding 5- and 8-*NHBz*-derivatives are obtained similarly. 1 : 2 : 6-$C_6H_3MeCl{\cdot}NO_2$ is converted into 2-chloro-6-nitrobenzoic acid, the K salt of which is transformed by NH_2Ph, K_2CO_3, and Cu powder in boiling amyl alcohol into 3-*nitrodiphenylamine*-2-*carboxylic acid*, m.p. 172°, from which 4-nitroacridone could not be prepared. K 2-chloro-4-nitrobenzoate, *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2K$, K_2CO_3, and Cu powder in boiling amyl alcohol afford 5-*nitrodiphenylamine*-2 : 2′-*dicarboxylic acid*, decomp. 323° after darkening, which is transformed by $POCl_3$ into 2-*nitroacridone*-9-*carboxylic acid*, m.p. 331—333°, decarboxylated by mol. Ag at 290—300°/high vac. to 2-nitroacridone. H. W.

Manufacture of acridine derivatives.—See B., 1937, 842.

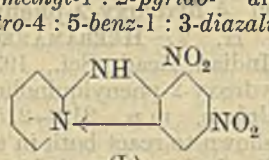
Acridones. XI. Condensation of 5-chloro-2-nitrobenzaldehyde with chloro- and bromobenzene by means of concentrated sulphuric acid. I. Tanasescu and M. Macarovici (Bull. Soc. chim., 1937, [v], **4**, 240—245).—2 : 5 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}CHO$ (I) with PhCl and H_2SO_4 gives 2 : 7-*dichloro*-5-*hydroxyacridine* 10-*oxide* (II), m.p. >300° (*Na* salt; *Bz* derivative, m.p. 258—260°), hydrolysed by HCl–EtOH–H_2O to 2 : 7-*dichloroacridone*, m.p. >300°, also obtained from (II) by reduction with Zn–$CaCl_2$–EtOH–H_2O, and converted by $POCl_3$–$NPhMe_2$ into 2 : 7-*dichloro*-5-p-*dimethylaminophenylacridine*, m.p. 240—241°. In addition to (II) a *compound*, m.p. about 100°, is also obtained. Reduction of (II) with Na–Hg–NaOH–H_2O gives 2 : 7-*dichloroacridine* 10-*oxide*, m.p. 220°. Similarly, (I) with PhBr and H_2SO_4 gives 2-*chloro*-7-*bromo*-5-*hydroxyacridine* 10-*oxide*, m.p. 396° (*Bz* derivative, m.p. 293°), hydrolysed to 2-*chloro*-7-*bromoacridine* 10-*oxide*, m.p. 290—295°, and converted by $POCl_3$–$NPhMe_2$ into 2-*chloro*-7-*bromo*-5-p-*dimethylaminophenylacridine*, m.p. about 225°. H. G. M.

Preparation of hydantoin from glycine and nitrocarbamide. P. P. T. Sah and T. F. Liu (Sci. Rep. Nat. Tsing Hua Univ., 1937, **4**, A, 31—33).—Details are given for the prep. of hydantoic acid and thence of hydantoin from glycine and $NH_2{\cdot}CO{\cdot}NH{\cdot}NO_2$, each in 90% yield. R. S. C.

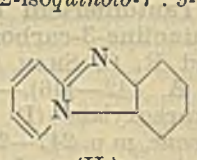
Resistance of diketopiperazinepropionic acid to fission by proteinases. S. Akabori and S. Maeda (Proc. Imp. Acad. Tokyo, 1937, **13**, 213—216).—The complete resistance of l- and dl-*diketopiperazinepropionic acid* (prep. from *dl*-glutamic acid), m.p. 130°, to even large amounts of trypsin and papain is proved by the Sasaki colour reaction (measured in a step-photometer) and by recovery of large amounts of unchanged acid. R. S. C.

Preparation of 1-phenyl-2 : 3-dimethylpyrazol-5-on-4-yl *iso*pentyl [α-ethylpropyl] ketone.—See B., 1937, 843.

Cyclic 1 : 3-diazalines. (Sir) G. T. Morgan and (Miss) J. Stewart (Chem. and Ind., 1937, 670).—2-Aminopyridine and picryl chloride give a picryl derivative, which when heated forms a $(NO_2)_2$-compound (I) (?). Reduction and elimination of NH_2 leads to 1 : 2-*pyrido*-4 : 5-*benz*-1 : 3-*diazaline* (II), isomeric with 3-carboline. 2-Amino-3-methylpyridine and 1-amino*iso*quinoline similarly afford 3′-*methyl*-1 : 2-*pyrido*- and 1 : 2-iso*quinolo*-7 : 9-*dinitro*-4 : 5-*benz*-1 : 3-*diazaline*.



(I.)

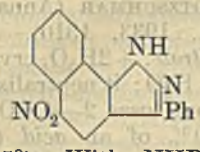
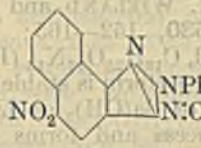


(II.)

F. R. S.

Aromatic nitro-derivatives. XII. Action of certain hydrazines on 1-chloro-2 : 4-dinitronaphthalene. A. Mangini (Atti R. Accad. Lincei, 1937, [vi], **25**, 326—332).—1 : 2 : 4-$C_{10}H_5Cl(NO_2)_2$ (I) with N_2H_4,H_2O in EtOH at 20° for 3 days gives

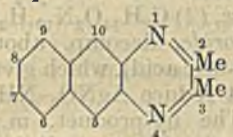
4 : 4′-dinitro-2 : 2′-azoxynaphthalene, with some 5-nitro-3-hydroxynaphthotriazole (A., 1926, 163). With NH_2·N:CHPh, (I) gives *benzaldehyde*-2 : 4-*dinitro*-α-*naphthylhydrazone*, m.p. 204—204·5°, converted by NaOH into 5-*nitro*-3-*phenyl*-βα-*naphthopyrazole* (II), m.p. 289—290° (decomp.) (*Ac* derivative, m.p. 175—

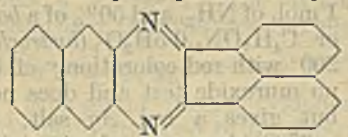
(II.)  (III.) 

176·5°). With NHPh·NH_2, (I) yields directly 5-*nitro*-2-*phenyl*-βα-*naphthotriazole* 3-*oxide* (III), m.p. 182·5—183·5°. *p*-NO_2·C_6H_4·NH·NH_2 gives N-2 : 4-*dinitro*-α-*naphthyl*-N′-p-*nitrophenylhydrazine*, converted by AcOH into 5-*nitro*-2-p-*nitrophenyl*-βα-*naphthotriazole* 3-*oxide*, m.p. 288—289° (decomp.).

E. W. W.

Derivatives of *lin.*-benzoquinoxaline. H. Goldstein and M. Streuli (Helv. Chim. Acta, 1937, **20**, 650—653).—Condensation of 2 : 3-$C_{10}H_6(NH_2)_2$ with the appropriate *o*-diketone affords the following *lin.*-quinoxalines: 2 : 3-*dimethyl*- [2 : 3-*dimethyl*-


(I.)


(II.)

6′ : 7′-*benzoquinoxaline*] (I), m.p. 211°, and 2 : 3-*diphenyl*-lin.-*benzoquinoxaline*, m.p. 192°; *phenanthro*-lin.-*naphthazine* [1′ : 2′ : 3′ : 4′ : 7′ : 8′-*tribenzophenazine*], m.p. 302°; 2-*hydroxy*-3-*methyl*-, m.p. 290° (decomp.), and 2 : 3-peri*naphthylene*-lin.-*benzoquinoxaline* (II), m.p. 360°.

P. G. C.

Compounds of cinnamaldehyde with skatole. V. Dostál (Chem. Listy, 1937, **31**, 250—252).—Skatole and cinnamaldehyde in EtOH with H_2SO_4 yield colourless 3 : 3′-*dimethyl*-2 : 2′-*di-indolylstyrylmethane*, m.p. 73°, converted by oxidation ($FeCl_3$ in EtOH–H_2SO_4) into blue 3 : 3′-*dimethyl*-2 : 2′-*di-indolylstyrylcarbinol* (I), m.p. 117°. Evaporation of Et_2O solutions of (I) yields a red *substance*, $C_{27}H_{28}ON_2$ or $C_{27}H_{26}ON_2$, m.p. 105°, converted into a yellow *substance*, $C_{27}H_{26}N_2$, m.p. 142—145°, when shaken with aq. alkalis; the red and yellow substances regenerate (I) when treated with aq. acids.

R. T.

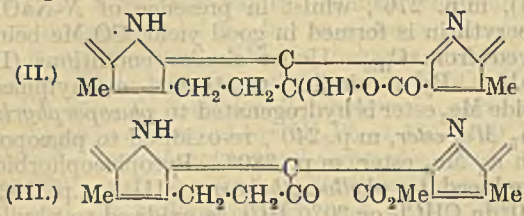
Manufacture of polyamino-1 : 9-anthrapyrimidines.—See B., 1937, 764.

Chlorophyll. LXXVII. Phæoporphyrinogen a_5, phylloerythrinogen, and attempted inactivation of chlorophyll and its derivatives. H. Fischer and K. Bub (Annalen, 1937, **530**, 213—230).—Inactivation of chlorophyll can probably be achieved only by synthetic means. Isomerisation processes which are not clearly understood give an appearance of racemisation; achievement of the latter is complicated by the no. of asymmetric centres. Hydrogenation (Pd-sponge in AcOH) of phæophorbide *a* gives *phæoporphyrinogen* a_5 (I), $C_{35}H_{42}O_5N_4$, m.p. 242°, [α] ±0° in $COMe_2$ or 20% HCl. Reduction proceeds in the same manner as with HI in that 2 H from nucleus III wander to the vinyl group of nucleus II. Re-oxidation of (I) gives exclusively phæoporphyrin a_5 (II), m.p. 276°, whilst in presence of *N*-NaOH phylloerythrin is formed in good yield, CO_2Me being removed from $C_{(10)}$. Under similar conditions (II) is stable. By a similar treatment, methylphæophorbide Me_2 ester is hydrogenated to *phæoporphyrinogen* a_5 *Me*$_2$ *ester*, m.p. 240°, re-oxidised to phæoporphyrin a_5 Me_2 ester, m.p. 280°. Pyrophæophorbide *a* is reduced to *phylloerythrinogen* (III), m.p. 202°, [α] +0° in $CHCl_3$ or 20% HCl, re-oxidised to phylloerythrin; an oxime of (III) could not be obtained. Hydrogenation of mesophæophorbide *a* in $COMe_2$ gives an apparently optically inactive product after absorption of 5 H; the leuco-compound could not be obtained cryst. but oxidation of it leads to optically inactive *mesophæophorbide* a (III), m.p. 218°. It is converted by boiling C_5H_5N–KOH–MeOH into *mesochlorin* e_6 [*Me* ester (IV), m.p. 184°, [α] ±0° in $COMe_2$], further transformed by prolonged boiling with C_5H_5N into *mesochlorin* e_4, m.p. 195°, $[\alpha]_D$ ±0° in $COMe_2$. Treatment of (III) with boiling C_5H_5N affords mesopyrophæophorbide *a*, [α] −230° in $COMe_2$. (IV) is transformed by C_5H_5N–KOH–MeOH into "ring-synthetic" mesophæophorbide *a* [α] ±0° in $COMe_2$. (III) is converted by KOH–PrOH into mesopurin 7. The transformations of (III) into mesopurpurin 18, m.p. 262°, [α] +222° in 20% HCl, mesochlorin p_6 Me ester, $[\alpha]_D$ +135° in 20% HCl, and meso-ψ-chlorin, m.p. 188°, [α] −149° in $COMe_2$, are recorded. Mesochlorin e_6 Me_2 ester, [α] −48° in $COMe_2$, as Na salt is transformed by BzCl in C_5H_5N at 0° into the *anhydride*, $C_{43}H_{46}O_7N_4$, m.p. 195°, [α] ±0° in $COMe_2$, which with boiling glycol gives the *glycol ether*, m.p. 168°, [α] −180° in $COMe_2$; this with anhyd. Na_2CO_3 in boiling C_5H_5N affords mesopyrophæophorbide *a*, m.p. 232°, [α] −350° in $COMe_2$. Inactive mesophæophorbide *a* is converted into mesochlorin e_6 Me_2 ester–Bz_2O and thence by C_5H_5N at 100° into mesochlorin e_6 Me_2 ester, m.p. 205°, [α] −48° in $COMe_2$; this with BzCl gives a compound with [α] ±0° in $COMe_2$ transformed by boiling C_5H_5N into the di-ester with [α] −77° in $COMe_2$. Phæopurpurin 7 ester (V) is hydrogenated (Pd-sponge in $COMe_2$) to the leuco-compound, [α] +235° in $COMe_2$, re-oxidised to (V) with [α] +201° in $COMe_2$. Similarly phæopurpurin 18 (VI) is hydrogenated to a substance, [α] +259° in $COMe_2$, re-oxidised to (VI) with [α] +628° in $COMe_2$. Chlorin p_6 ester (VII) yields a hydro-compound, [α] ±0°, from which (VII) is regenerated with [α] +129° in $COMe_2$. ψ-Chlorin p_6 ester (VIII) yields a leuco-compound with [α] ±0° in $COMe_2$, re-oxidised to (VIII) with [α] −133° in $COMe_2$. Attempts are described to racemise pyrophæophorbide *a* in $PhNO_2$ and chlorin-e_6 in NaOH.

H. W.

Chlorophyll. LXXIX. Anhydrochlorins, rhodorhodin, and catalytic reduction of porphyrins to chlorins. H. Fischer and K. Herrle (Annalen, 1937, **530**, 230—256).—Mesorhodochlorin (I) is converted by P_2O_5 at 100° into *rhodorhodin* (II), m.p. >330°, which is somewhat unstable and is almost completely decomposed by BzCl in C_5H_5N or HCl–MeOH. It is converted by boiling glacial AcOH into

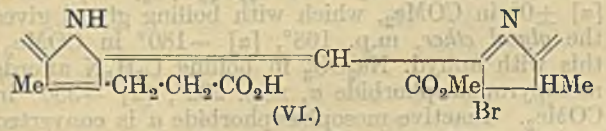
rhodoporphyrin-γ-carboxylic anhydride and by CH_2N_2 in Et_2O into *rhodorhodin Me ester* (III), m.p. 298°.



(II.)

(III.)

Oxidation of rhodoporphyrin dihydrazide with $KMnO_4$ affords rhodoporphyrin and (II). Similarly oxidation of rhodoporphyrin monohydrazide Me ester yields (III). Treatment of (I) with oleum at room temp. and of the product with CH_2N_2 gives *anhydromesorhodochlorin Me ester*, m.p. 279° (*salt*, $C_{33}H_{34}O_3N_4Cu$, m.p. 308°; *anhydromesorhodochlorin*, m.p. 257°), attempted oximation of which gives a dye identical with that obtained similarly from (II). Mesopyrrochlorin is transformed by P_2O_5 and sand or, preferably, by oleum into *anhydromesopyrrochlorin* (IV), m.p. 270° (*salt*, $C_{31}H_{32}ON_4Cu$, m.p. 292°), which is degraded to pyrrorhodin (V) by HI or by AgOAc and AcOH. (IV) is converted by NH_2OH,HCl in boiling C_5H_5N into the *oxime*, m.p. 265°. Pyrrochlorin is dehydrated to *anhydropyrrochlorin*, $C_{31}H_{32}ON_4$, m.p. 246°, which is degraded by HI to (V), and gives an additive *product* with $CHN_2{\cdot}CO_2Et$. Vinylpyrroporphyrin Me ester in $CHCl_3$ is converted by $Fe(OAc)_2$ and NaCl in AcOH into the corresponding *hæmin*, which with resorcinol at 180° gives *2-de-ethylpyrroporphyrin Me ester*, m.p. 230°. Meso-



(VI.)

rhodochlorin Me ester is readily brominated in $CHCl_3$ to the *compound* (VI), m.p. 165° after softening, the constitution of which follows from its conversion by KOH–MeOH into rhodoporphyrin and by AgOAc in AcOH into a dye of the type of the dihydroxychlorins. Pyrroporphyrin (VII) is hydrogenated (Raney Ni in dioxan at 60°) to leuco-compounds which could not be caused to crystallise and are re-oxidised by air, thus giving the original material and mesopyrrochlorin, m.p. 240—250°, also obtained by hydrogenation in BuOH or $NPhMe_2$ and converted by AgOAc–AcOH into (VII). Similar hydrogenation of phylloporphyrin gives a chlorin which is not spectroscopically identical with mesophyllochlorin and the product derived from porphyrinmonocarboxylic acid 7 differs from the synthetic material. Hydrogenation (Pd) of pyrroporphyrin Me ester Zn salt yields a chlorin complex. H. W.

Highly coloured condensation products from benzamidine and glyoxal. I. J. B. Ekeley and A. R. Ronzio (J. Amer. Chem. Soc., 1937, **59**, 1313—1316).—The action of NaOEt and EtOH under various conditions on benzamidine-glyoxal (A., 1935, 1133) yields glyoxaline-red, and the *compounds*, $(C_{20}H_{17}O_3N_4)_2O$ (deep purple), m.p. 326°, $C_{42}H_{30}O_6N_8$ (green), m.p. 264°, and $C_{22}H_{20}O_3N_4$ (orange), m.p. 249° (structures suggested). The benzamidine-glyoxal mother-liquors yield a *compound*, $C_{20}H_{18}O_4N_4$ (dark red), m.p. 183°, possibly 1 : 3-dibenzamidyl-4 : 6-dihydroxyquinol. A. Li.

Wing pigments of common white butterflies. III. H. Wieland and A. Kotzschmar (Annalen, 1937, **530**, 152—165; cf. A., 1933, 1310).—The triglycol, $C_{19}H_{25}O_{17}N_{15}$ (I) (*trinitrate*, $+2H_2O$, cryst.), from leucopterin is stable to hot H_2O; it neutralises 3 equivs. of $Ba(OH)_2$ or LiOH, but loses 2—4 CO_2 in the process and forms 40—50% of an *acid* (II), $C_{14}H_{18}O_{13}N_{10}$, about 15% of a *base*, $C_{15}H_{21}O_{11}N_{13}$, cryst. [(?*tri*)*hydrochloride*, m.p. 227—230° (decomp.), loses HCl when kept], and 0·1 mol. of $H_2C_2O_4$ [not a by-product of the formation of (II), but possibly of the base]. (II) titrates as a tribasic acid, but gives a hydrochloride, gives no murexide test, and does not reduce ammoniacal $AgNO_3$; it is stable to $Pb(OAc)_4$, as also is uric acid glycol; with $Ba(OH)_2$ at 90° it gives 6 mols. of NH_3, 3 of CO_2, and 3 of $H_2C_2O_4$; with dil. HCl at 30—40° it gives a little NH_4Cl and $H_2C_2O_4$ and a monobasic *acid*, $C_{13}H_{18}O_{11}N_{10}$, decomp. 260—270°; with 25% HCl at 70° it gives 2 mols. of $H_2C_2O_4$, 1 mol. of NH_3, and 50% of a *base*, (?) $C_8H_{14}O_2N_{10}$,H_2O or $C_4H_7ON_5$,$0{\cdot}5H_2O$ (*hydrochloride*, decomp. about 200° with red coloration; cf. ψ-uric acid), which gives no murexide test and does not reduce $AgNO_3$–NH_3, but gives a red *Ag* salt. The by-product, m.p. >370° (decomp.), obtained in the prep. of (I) is a weak base, $C_{11}H_{20}O_{11}N_{10}$, stable to hot H_2O, giving no CO_2 with HCl, and liberating NH_3 and a little CO_2 with alkali. This base is also formed along with much (I) by the action of 0·2*N*-HCl on anhydroleucopterin, the relations of which to leucopterin are discussed. The H_2O-sol. dye of the wings is fractionated by $(NH_4)_2SO_4$ into a blue and a green component; the mixture readily liberates its albumin, which gives Gmelin's reaction for gallic dyes; the dye resembles oocyanin in many respects and is probably of the same type. The Et_2O-extract of the wings yields, after hydrolysis by KOH, cholesterol, palmitic, oleic, and linolenic acid. R. S. C.

Manufacture of amide derivatives of *iso*oxazolecarboxylic acids.—See B., 1937, 843.

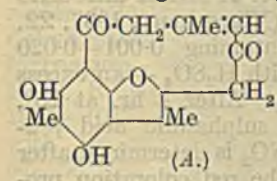
Preparation of 1-methylbenzoxazole. B. Beilenson (J.S.C.I., 1937, **56**, 302T).—*o*-$OH{\cdot}C_6H_4{\cdot}NH_2$ and Ac_2O in aq. suspension give *o*-$OH{\cdot}C_6H_4{\cdot}NHAc$, converted by P_2O_5 (75% yield) into 1-methylbenzoxazole.

Condensation of aromatic aldoximes with esters of β-ketonic acids. R. Fusco and C. Musante (Gazzetta, 1937, **67**, 248—256).—The products from CHR:N·OH (R = Ph or *p*-$OMe{\cdot}C_6H_4$), regarded by Minunni and D'Urso as α-benzylidene- (A., 1928, 1245) and α-anisylidene-aminocrotono-β-lactone (A., 1929, 555), are actually 4-benzylidene- and 4-anisylidene-3-methyl-5-*iso*oxazolone. Similarly "α-benzylidene-" (A., 1928, 1245) and "α-anisylidene-aminocinnamo-β-lactone" (A., 1929, 555) are 3-phenyl-4-benzylidene- and -4-anisylidene-5-*iso*oxazolone (I), also prepared from CHR:N·OH and CPh:C·CO_2Et. The product from (I) and NH_2OH is not aminocinnamo-β-lactone (A., 1929, 556), but

3-phenyl-5-*iso*oxazolone. Araldoximes when heated with $ZnCl_2$ are partly isomerised to amides. E. W. W.

Quinoline derivatives. II. T. N. Ghosh (J. Indian Chem. Soc., 1937, **14**, 123—126; cf. this vol., 309).—Attempts have been made to prepare new quinoline derivatives with anti-malarial properties. 1-*Phenyl*-3-*methylpyrazolino*-4 : 5-(2′ : 3′)-4′-*hydroxyquinoline*, m.p. 175—176°, results by condensing 1-phenyl-3-methylpyrazolone with anthranilic acid. Et α-urethanylacetate with *o*-NO_2·C_6H_4·CHO gives *Et α-urethano-o-nitrocinnamate*, m.p. 227—228°, reduced to *o*-aminocinnamic acid and not 2-hydroxy-3-urethanoquinoline. Condensation of hippuric acid with anthranilic acid gives 1-*keto*-3-*benzamidomethyl*-5 : 6-*benz*-2 : 4-*oxazine*, m.p. 205—207° (*o-nitrobenzylidene* derivative, m.p. 234—235°). D. J. B.

Lichen substances. LXXXII. Usnic acid. III. Y. Asahina and M. Yanagita [with S. Kawamura] (Ber., 1937, **70**, [*B*], 1500—1505).—At room temp. usnic acid (I) has 2 active H (Zerevitinov) whilst at higher temp. 3 active H are present; decarbousnic acid (II) has 3 active H. The oxime anhydride of (II) is oxidised by H_2O_2 to the dicarboxylic acid, $CO_2H·C(=O)·C(CO_2H)(CMe)>C·CH_2·C<(O—N=)CH·CMe$, decomp. 202° after softening at 180°, thus giving further evidence of the 1 : 3-diketone side-chain attached to the furan nucleus. The *iso*decarbousnic acid, m.p. 197°, of Widman is also obtained by the action of EtOH or (II) at 170°; it is not an isomeride of (II) but is *deacetylcarbousnic acid*, $C_{15}H_{16}O_5$ (*dihydrazone*, decomp. 196—197°). (I) is transformed by conc. H_2SO_4 at 50—60° into usnolic acid (III), m.p. 230—231° (decomp.) after softening at about 210°; this is a true carboxylic acid since it is converted by HCl–EtOH into an ester and by warm NH_2Ph into *decarbousnanilide*, m.p. 235—236°. Similar treatment of (II) with conc. H_2SO_4 yields *decarbousnol* (IV), $C_{17}H_{16}O_5$, m.p. 209°, which gives a very pronounced Ehrlich reaction; it is also formed from (III) and Cu-bronze. (IV) is unimol. and therefore an internal condensation product of (II). Since loss of H_2O cannot occur from the 1 : 3-diketone side chain it follows that Ac of the phloroglucinol nucleus must be involved so that (V) is very probably *A*. H. W.



(*A*.)

β-Naphthothiazine (thio-β-naphthylamine) and its derivatives. H. Y. Fang, C. L. Liu, and P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1937, **4**, A, 21—26).—$NH(C_{10}H_7$-β$)_2$ and S (2 atoms) at 190° give β-*naphthothiazine*, 2 : 3-$C_{10}H_7<(NH>S)>C_{10}H_7$-2 : 3, m.p. 222—223° [*dipicrate*, m.p. 250—251° (decomp.); *styphnate*, m.p. 262—263° (decomp.)]. R. S. C.

Anthrylthiocarbimides, anthrathiazoles, and thiolanthrathiazoles. M. Battegay and P. Boehler (Compt. rend., 1937, **204**, 1477—1479).—The aromatic nature of α- (I) and β- (II) -anthramine is illustrated further. CS_2 almost quantitatively converts (I) in C_5H_5N into *di*-1-*anthrylthiocarbamide* (III), m.p. 234°, giving with warm Ac_2O 1-*anthrylthiocarbimide*, m.p. 99°, from which (III) is regenerated by the action of (I) in PhMe. Similarly (II) gives *di*-2-*anthrylthiocarbamide*, m.p. 262°, and 2-*anthrylthiocarbimide*, m.p. 196°. S, (I), and $HCO·NH_2$ at 200° give 1′ : 2′-*anthra*-4 : 5-*thiazole*, m.p. 132°, the constitution of which is established by its oxidation by HNO_3 to an anthraquinone derivative containing S. 1′ : 2′-*Anthra*-5 : 4-*thiazole*, m.p. 166°, is obtained from (II). Di-2-aminodianthryl disulphide is converted into 2-*thiol*-1′ : 2′-*anthra*-5 : 4-*thiazole*, m.p. 300°. H. W.

Manufacture of dyes [thiazole derivatives etc.].—See B., 1937, 764.

Indigoid vat dyes of the isatin series. II. 3-Indole-1′-(5′-methyl)thionaphthenindigos. S. K. Guha (J. Indian Chem. Soc., 1937, **14**, 240—244; cf. A., 1934, 1013).—The 5-*Cl*-, 5-*Br*-, 5 : 7-*Br*$_2$-, 5-*bromo*-7-*nitro*-, and 5 : 7-(*NO*$_2$)$_2$-derivatives of 3-indole-1′-(5′-methyl)thionaphthenindigo are prepared from isatin or a derivative and the appropriate 3-hydroxythionaphthen derivative in AcOH in presence of HCl. They dye wool (acid bath) and cotton (vat) in red shades lighter than those given by the corresponding 5′-Me derivatives, in conformity with Martinet's rule. P. G. C.

Alkaloid from the Equisetaceæ family. E. Glet and J. Gutschmidt (Apoth.-Ztg., 1937, **52**, 265—266).—*Equisetum palustre* contains a *hydrocarbon*, $C_{21}H_{42}$, m.p. 77°, and a mixture of alkaloids, mainly *palustrine*, $C_{12}H_{24}O_2N_2$, b.p. 205—210°/0·1 mm. (*hydrochloride*, m.p. 181°, [α] 0). R. S. C.

Microscopical examination of ergot alkaloids. II. Ergotinine, ergotoxine, and sensibamine. A. Kofler (Arch. Pharm., 1937, **275**, 455—467; cf. A., 1936, 1527).—The crystallo-optical properties (photomicrographs) of ergotinine (3 forms), m.p. 220° (decomp. from 210—215°), ergotoxinine, m.p. 165° (decomp. from 100°), and sensibamine, m.p. 180—182°, are detailed. R. S. C.

Presence in the bark of *Corynanthe paniculata*, Welwitsch, of a lævorotatory isomeride of yohimbine. Raymond-Hamet (Bull. Sci. Pharmacol., 1937, **44**, 54—59).—*Paniculatine*, $C_{21}H_{20}O_3N_2 + 1·5H_2O$ (I), $[\alpha]_D$ −42° in EtOH, hygroscopic, an isomeride of yohimbine (II), is isolated with it from the bark of *C. paniculata*, separation being effected by fractional crystallisation of the more sol. *hydrochloride*, $[\alpha]_D$ +45·95° in H_2O, of (I). The colour tests of (II) are also given by (I); the latter is more sol. in MeOH at 50°. R. F. P.

Cotarnine series. IX. Attempts to synthesise alkaloids of the cryptopine types. B. B. Dey and (Miss) P. L. Kantam (J. Indian Chem. Soc., 1937, **14**, 144—150).—*o-Toluoylcotarnine*, m.p. 99—100° (*oxime*, m.p. 170°; *semicarbazone*, m.p. 200°; *hydrazone*, m.p. 211°), and its p-*NO*$_2$-derivative, m.p. 124—125° (*semicarbazone*, m.p. 219—220°; *oxime*, m.p. 175°; *hydrazone*, m.p. 215°), prepared by benzoylation could not be cyclised to compounds containing two *iso*quinoline rings. Interaction of homophthalonitrile with Ac_2O was likewise un-

successful. 5-Nitrophthalide and cotarnine in Ac_2O give *anhydroacetylcotarnino-5-nitrophthalide*, m.p. 165°. *Anhydrocotarnino-methyl anthranilate*, m.p. 136°, was made by condensing Me anthranilate with cotarnine. D. J. B.

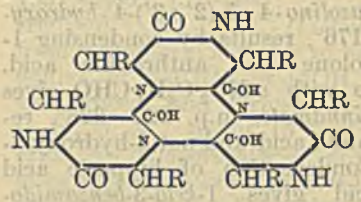
Isomerism of norcoralydine. E. Späth and W. Gruber (Ber., 1937, **70**, [*B*], 1538—1540).—Norcoralydine, isolated from the hydrochloride obtained by the condensation of tetrahydropapaverine with 40% CH_2O and 2*N*-HCl at 100°, exists in two forms, (I), m.p. 151·5—152° (vac.), and (II), m.p. 160—161° (vac.). Apparently the base is dimorphous since either (I) or (II) can be caused to separate at will from solutions of either form if a seed is available. The difference is not due to the presence of solvent of crystallisation and there appears no reason to assume a new type of stereoisomerism. H. W.

Alkaloids of *Veratrum album*. I. Preparation of the alkaloids and their distribution amongst rhizomes, roots, and leaf base. Germerine, a new alkaloid of *V. album*. W. Poethke (Arch. Pharm., 1937, **375**, 357—379).—Complex, new methods of extracting and separating the alkaloids of *V. album* are detailed. The crude alkaloids (50) from the rhizomes from Jugoslavia contained *germerine* (I), $C_{36}H_{57}O_{11}N,H_2O$, m.p. 193—195° (corr.) (7), protoveratridine (II) (0·7), jervine (III) (0·25), rubijervine (IV) (0·2), and amorphous alkaloids (25 g.). Material collected in summer in the Bavarian Alps contained in the roots protoveratrine (V) >0·8, (III) 0·2, (IV), and (I), in the rhizomes (V) 1·33, (I) 1·25, (IV) 0·04, (III) 0·94, and ψ-jervine 0·6, and in the leaf base (IV) 0·54, (I) >0·8, and (III) 0·03 g. per kg. Treatment with $Ba(OH)_2$ converts (I) into (II), but simultaneously destroys all the (V) present. The constituents vary according to the origin of the plant. R. S. C.

Alkaloids of *Salsola Richteri*. III. Optically active salsoline, and the isolation of two new alkaloids. N. Proskurnina and A. Orekhov (Bull. Soc. chim., 1937, [v], **4**, 1265—1274; cf. A., 1934, 907).—$C_2H_4Cl_2$ extracts salsoline (cf. A., 1933, 727), *salsolidine*, m.p. 71—73° (*hydrochloride*, m.p. 233—235°; *dihydrate*, m.p. 60—62°; *picrate*, m.p. 194—195°; *picrolonate*, m.p. 220—221°; *Bz* derivative, m.p. 124—125°), and *salsamine*, m.p. 155—157° (decomp.) [*hydrochloride*, m.p. 255—260° (decomp.); *picrate*, m.p. 213—214°; *picrolonate*, m.p. 220—221°], from the leaves and young shoots. Salsoline, a mixture of the *d*- and *dl*-forms, affords a *d*-tartrate from which, after repeated crystallisation, d-*salsoline* d-*tartrate*, m.p. 215—216° [d-*base*, m.p. 215—216° (*hydrochloride*, m.p. 171—172°, $[\alpha]_D$ +40·1° in H_2O)], is isolated. The mother-liquors afford l-*salsoline*, m.p. 214—215° (*hydrochloride*, $[\alpha]_D$ −39·2° in H_2O; *picrate*, m.p. 214—215°; *picrolonate*, m.p. 238—240°), which with CH_2N_2 gives salsolidine. Equimol. parts of the *d*- and *l*-forms gives a product identical with naturally occurring salsoline. J. L. D.

New salt of emetine. E. Caserio (Boll. Chim. farm., 1937, **76**, 365—368).—The *dicamphorsulphonate* is described. F. O. H.

Pattern of proteins. D. M. Wrinch (Proc. Roy. Soc., 1937, **A**, **160**, 59—86; cf. A., 1936, 1528, 1535).—A geometrical theory of the structure of proteins, based on the assumed existence of double and triple peptide linkings, suggests that the mol. is a ring structure produced by the "cyclisation" of polypeptides. Complex mols. are built up from "cyclol 6" mols. (see annexed formula); the resulting laminar mol. has a "front" surface from which side-chains emerge and a "back" surface free from side-chains, explaining the stability on a H_2O–air interface of proteins one residue thick. The hypothesis allows the construction of laminar mols. with the right order of density, *i.e.*, residue wt. per sq. cm., and explains why chemically different proteins share many properties in common. G. D. P.



Casein. E. Cherbuliez and J. Jeannerat (Arch. Sci. phys. nat., 1937, [v], **19**, Suppl., 51—52).—Casein has three distinct components (α_1, γ, and δ); α_2 (cf. A., 1933, 843) is $\alpha_1 + \gamma$. Paracasein is $\alpha_1 + \gamma$. Thus Hammarsten's proteose is present in milk. J. L. D.

Apparatus for centigram elementary analysis.—See A., I, 480.

V.p. of saturated gaseous hydrocarbons.—See A., I, 453.

Modification of the method of Nicloux for the micro-determination of ethyl alcohol. A. Ionesco-Matiu and C. Popesco (Bull. Soc. Chim. biol., 1937, **19**, 911—914).—The titration with aq. $K_2Cr_2O_7$ is used, with leuco-methylene-blue as external indicator. Satisfactory results are obtained with 0·025—0·5% of EtOH. A. L.

Colorimetric determination of small amounts of carbamide. W. Brandt (Mikrochem., 1937, **22**, 181—186).—The solution [containing 0·001—0·020 mg. of $CO(NH_2)_2$] is treated with H_2SO_4 + an excess of 0·02% standard aq. KNO_2. After 4 hr. at 25°, NaOAc is added, and then sulphanilic acid + α-$C_{10}H_7{\cdot}NH_2$. The excess of KNO_2 is determined after 24 hr. from the intensity of the red coloration produced. Albumin, creatine, uric acid, and glycine do not interfere with the applicability of the method. J. S. A.

Determination of arginine.—See A., III, 334.

Micro-determination of creatine and creatinine.—See A., III, 344.

Analysis of mixtures of furfuraldehyde and methylfurfuraldehyde. (Miss) E. E. Hughes and S. F. Acree (Ind. Eng. Chem. [Anal.], 1937, **9**, 318—321).—Use is made of the difference in rates of interaction of furfuraldehyde and methylfurfuraldehyde with Br in *N*-HCl at 0° to determine the composition of a mixture, the second mol. of Br reacting more rapidly with the Me derivative. The mean error is 0·5 mg. on 3—50 mg. F. N. W.