BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1939.

Photochemical autoxidation of iodoform.—See A., 1939, I, 89.

Hydrolysis of ethyl chloride by alkalis.—See A., 1939, I, 85.

Preparation of alkene and alkine halides of high mol. wt. A. P. Oskerko (Mem. Inst. Chem. Ukrain. Acad. Sci., 1938, **5**, 251—270).—Bu^{β} oleate, b.p. 212—217°/7 mm., is reduced with Na in EtOH to Δ⁴-octadecenyl alcohol (I), from which α-chloro- or α-bromo-Δ⁴-octadecene are obtained (impure) in small yields by PCl_5 in Et_2O, in presence or absence of $ZnCl_2$, by PBr_3 in Et_2O in presence of C_5H_5N, or by SO_2Cl_2 in $NPhMe_2$ at 140°. HBr passed into a solution of Br in (I) at 110—135° yields *α-bromo-Δ⁴-octadecene*, b.p. 192—194°/4 mm. R. T.

ααβγδδ-Hexachlorobutane, principal end-product of the distillation of technical tetrachloroethane.—See B., 1939, 14.

Preparation of crotyl halides. R. Voigt (J. pr. Chem., 1938, [ii], **151**, 307—311).—Crotyl bromide (I), b.p. 101—104°, is obtained in 81·5% yield by passing butadiene through well-stirred 66% HBr at 30°. Crotyl iodide, b.p. 35°/12 mm., results similarly from 57% HI at 20° whereas crotyl chloride is prepared by means of HCl (*d* 1·19) containing $FeCl_2$, $FeCl_3$, $HgCl_2$, and HgCl at 0—10°. (I) obtained as above or from $CHMe{:}CH{\cdot}CH_2{\cdot}OH$ gives the same *dinitrobenzoate*, m.p. 54°. H. W.

Photolysis of β-chloro-β-nitrosobutane.—See A., 1939, I, 89.

Epichlorohydrin and hydrogen sulphide.—See A., 1939, I, 86.

Pinacol–pinacolone rearrangement: preparation and rearrangement of tetramethylethylene bromohydrin. G. W. Ayers, jun. (J. Amer. Chem. Soc., 1938, **60**, 2957—2960).—Whitmore's mechanism (A., 1932, 1016) of this rearrangement is supported by the following results. Anhyd. pinacol (I) (prep. from the hydrate by heating in vac.) and dry HBr–Et_2O give 21—27% of *tetramethylethylene bromohydrin* [*β-bromo-βγ-dimethyl-n-butan-γ-ol*] (II), m.p. 70·5°, volatile, lachrymatory. HBr–$CHCl_3$ and (I) at 0° give *pinacol hydrobromide*, $[OH{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH_2^+]Br^-$, cryst., converted by moist air into (II). HBr and (I) in light petroleum (b.p. 30—50°) or CCl_4 give *dipinacol hydrobromide*, $(C_6H_{14}O_2)_2,HBr$, m.p. 52—54°, able, also obtained as a by-product in Et_2O. Pinacolone is formed when (II) is heated in a closed tube at 100° or 150° or in air at 110° or when (II) is treated in Et_2O with aq. $AgNO_3$, $Na_2S_2O_3$, or Ag_2O. R. S. C.

Electrolysis of magnesium chloride hexahydrate and -alcoholate in methyl and ethyl alcohol.—See A., 1939, I, 35.

Syntheses of terpenes from acetylene. A. E. Favorski and A. I. Lebedeva (J. Gen. Chem. Russ., 1938, **8**, 879—883).—$OH{\cdot}CMe_2{\cdot}CH{:}CH_2$ and 20% H_2SO_4 (4—5 days at room temp.) yield a mixture of $OH{\cdot}CH_2{\cdot}CH{:}CMe_2$, $OH{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, linalool, and geraniol (traces). R. T.

Identification of methyl*iso*propylcarbinol in Sharples [commercial] diethylcarbinol. F. A. Karnatz and F. C. Whitmore (J. Amer. Chem. Soc., 1938, **60**, 3082).—Commercial $CHEt_2{\cdot}OH$ contains $CHMePr^{\beta}{\cdot}OH$, showing that rearrangement is not complete during hydrolysis of $CHMePr^{\beta}Cl$, although it is complete when the chloride is prepared from the alcohol. R. S. C.

Resolution of *n*-propylallylcarbinol. R. Consden, D. I. Duveen, and J. Kenyon (J.C.S., 1938, 2104—2106).—*dl-n*-Propylallylcarbinol with *o*-$C_6H_4(CO_2)O$ in C_5H_5N yields the *H phthalate*, m.p. 39—40°, which is resolved by its *brucine* salt, only the (−)-*salt* being obtained pure, m.p. 137—140° (decomp.), $[\alpha]_{5780}$ −22·0° in $CHCl_3$. This gives (−)-*n-propylallylcarbinyl H phthalate*, m.p. 39—40° ([α] for various λλ in EtOH, C_6H_6, C_5H_5N, $CHCl_3$, and CS_2 at room temp. are recorded), which is hydrolysed by NaOH to the (−)-*n-propylallylcarbinol*, b.p. 59—60°/20 mm. ([α] for various λλ alone at various temp. and in EtOH, C_6H_8, Et_2O, and CS_2 at room temp. are recorded) [*benzoate*, b.p. 147—148°/19 mm., α^{18}_{5893} −5·85° (*l* = 0·5); *acetate*, b.p. 71°/23 mm., α^{19}_{5893} −14·35° (*l* = 0·5)]. J. D. R.

Mechanism of replacement reactions in allyl compounds: reactions of (+)-*n*-propylpropenylcarbinol and its derivatives. C. L. Arcus and J. Kenyon (J.C.S., **1938**, 1912—1920).—In replacement reactions of $CHR{:}CH{\cdot}CHR'X$ (*A*) which involve loss of optical activity the product may be $CHR{:}CH{\cdot}CHR'Y$ (*B*) or $CHRY{\cdot}CH{:}CHR'$ (*C*), which cannot be distinguished if R = R′ = Me. Replacement in (+)-*n*-propylpropenylcarbinyl H phthalate (I) (*A*; R = Me, R′ = Pr^{α}) is therefore studied. From the results, and those with (II) (below), and previous observations (A., 1938, II, 215, 231), it is concluded that the planar ion $(CHMe{\cdot}CH{\cdot}CHPr^{\alpha})^{\oplus}$ is formed, permitting entry at either C^{α} or C^{γ}. Possible mechanisms of inversion of configuration are discussed. With (I) and HCO_2H or BzOH, the *dl*-formate or -benzoate is obtained. With (I) (69% optically pure) and AcOH there is inversion of configuration, and a product of 0·2% max. rotation is

formed; when this is reduced it becomes inactive, and thus no asymmetry has been transmitted to C$^{\gamma}$ (cf. *C*). Similarly (−)-Δ$^{\beta}$-δ-*chloroheptene* (II) (*A*; R = Me, R′ = Pr$^{\alpha}$, X = Cl), b.p. 44°/14 mm., α_{5461}^{22} −1·68°, obtained from the (+)-carbinol (III) and PCl_3 in C_5H_5N, and thus of opposite configuration to (III), with aq. Na_2CO_3 gives the carbinol, of 2% max. (+)-rotation. With MeOH–K_2CO_3, (II) from a carbinol of 30% optical purity gives the Me ether of 0·4% max. (+)-rotation. With AcOH–KOH, the *dl*-acetate is formed. All these are reduced to inactive products. Similarly dl-Δ$^{\beta}$-δ-*chloroheptene* (IV), b.p. 49°/21 mm., prepared from the *dl*-form of (III) yields inactive replacement products. When, catalytically, (IV) has absorbed 1H_2, the product contains residual (IV), some of the H_2 having attacked the C·Cl linking; reduction thus cannot be used to determine the optical purity of (II). The following are prepared: dl-n-*propylpropenylcarbinyl* p-*nitrobenzoate*, m.p. 40—41°, p-*xenylurethane*, m.p. 103·5°, *formate*, b.p. 53—54°/11 mm., and p-*toluenesulphinate* (V), decomp. 150°/<0·1 mm., n_D^{20} 1·5273. (+)-n-*Propylpropenylcarbinyl* p-*toluenesulphinate* (VI), α_{5461}^{17} +2·27°, is prepared from the (−)-carbinol. When (V) or (VI) is kept at 32°, a non-saponifiable product (sulphone?) is formed, α falling concurrently with ester content.

E. W. W.

Substituted acetylenes. XXIX. Preparation of acetylenic carbinols. K. N. Campbell, (Miss) B. K. Campbell, and L. T. Eby (J. Amer. Chem. Soc., 1938, **60**, 2882—2884; cf. A., 1938, II, 388).—CH:C·CMe$_2$·OH, CH:C·CMeEt·OH (I), CH:C·CMePr$^{\alpha}$·OH, CH:C·CMe(C$_5$H$_{11}$-*n*)·OH, 1-acetylenyl*cyclo*hexan-1-*ol*, CH:C·CPhMe·OH, *γ-phenyl-*Δ$^{\alpha}$-*propinen-γ-ol*, b.p. 114°/12 mm., *γ-methyl-*Δ$^{\delta}$-*noninen-γ-ol*, b.p. 96°/18 mm., Δ$^{\delta}$-*noninen-γ-ol*, b.p. 88°/40 mm., *δ-methyl-*Δ$^{\epsilon}$-*decinen-δ-ol*, b.p. 106°/20 mm., and *δ-methyl-*Δ$^{\epsilon}$-*undecinen-δ-ol*, b.p. 120°/19 mm., are obtained conveniently and in >50% yield from CH:CNa or CR:CNa and CORR′ in liquid NH_3, while excess of the acetylene is passed into the solution (omission of this reduces the yield and more of the glycol is formed from C_2H_2). A reaction mechanism is postulated. Conc. HCl and (I) give 40% of β-*chloro-*β-*methyl-*Δ$^{\alpha}$-*butinene*, b.p. 51—52°/135 mm.

R. S. C.

Production of butane-αγ-diol.—See B., 1939, 16.

Formation of βε-dimethyl-Δ$^{\gamma}$-hexine-βε-diol. A. T. Babajan (J. Gen. Chem. Russ., 1938, **8**, 602—607).—The following mechanism is proposed for Kazarian's reaction (A., 1935, 729): $COMe_2 + KOH \rightarrow OH\cdot CMe_2\cdot OK \xrightarrow{+CaO} (OK\cdot CMe_2\cdot C:)_2 + Ca(OH)_2$.

R. T.

Photochemical reactions in the *o*-nitrobenzylideneacetal series. XII. Mono- and di-*o*-nitrobenzylidenepentaerythritol, tri-*o*-nitrobenzylidenedulcitol, and di-*o*-nitrobenzylideneadonitol. I. Tanasescu and I. Iliescu (Bull. Soc. chim., 1938, [v], **5**, 1446—1457; cf. A., 1933, 275; 1936, 1234).—Extraction of *o*-nitrosobenzoyl-*o*-nitrobenzylidenepentaerythritol, m.p. 135° (I) (obtained by insolation of di-*o*-nitrobenzylidenepentaerythritol), with cold EtO_2 gives a more labile *isomeride*, m.p. 85—90° (II) (formulæ discussed), which when slowly heated passes into (I). With BzCl–C_5H_5N, (I) and (II) give the same *Bz* derivative, m.p. 83—84°, and with HCl–EtOH–H_2O afford the same o-*nitrobenzylidenepentaerythritol* (III), m.p. 144—145° (*dibenzoate*, m.p. 111°). (I) and NH_2Ph–EtOH for 1 hr. form a *monoazo*-derivative, $C_{25}H_{23}O_7N_3$, m.p. 110° (previous shrinking), thus proving the presence of 1 NO only. (III) and *p*-$NO_2\cdot C_6H_4\cdot CHO$ (excess) with H_2SO_4 or P_2O_5 give di-*p*-nitrobenzylidenepentaerythritol, m.p. 234—235°. Insolation of (III) in $CHCl_3$ gives o-*nitrosobenzoylpentaerythritol*, m.p. 95° (? 105°) (*tribenzoate*, m.p. 86—88°). Dulcitol and *o*-$NO_2\cdot C_6H_4\cdot CHO$–$P_2O_5$ at 50° for 4—5 hr. give *tri*-o-*nitrobenzylidenedulcitol*, m.p. 92—94°, converted (in $CHCl_3$) by light into βε-*di*-o-*nitrosobenzoyl-γδ-*o-*nitrobenzylidenedulcitol*, m.p. 138—140° (*αζ-dibenzoate*, m.p. 125°; *αζ-dibenzenesulphonate*, m.p. 116°). Adonitol and *o*-$NO_2\cdot C_6H_4\cdot CHO$ in H_2SO_4 (1 : 1) give *αβδε-di-o-nitrobenzylideneadonitol*, m.p. 183—185°, insolated ($CHCl_3$) to δ-o-*nitrosobenzoyl-*αβ-o-*nitrobenzylideneadonitol*, m.p. 100° [*γε-dibenzoate*, m.p. 104° (previous shrinking); *γε-dibenzenesulphonate*, m.p. 87°; NH_2Ph–EtOH gives the *monoazo*-compound, $C_{25}H_{23}O_8N_3$, m.p. 175°].

A. T. P.

Synthesis of *r*-arabitol and adonitol. R. Lespieau (Bull. Soc. chim., 1938, [v], **5**, 1638—1641).—Mainly a detailed account of work already reported (A., 1936, 1229; 1938, II, 346).

CH:C·[CH·OAc]$_2$·CH$_2$·OAc is obtained from CH:C·[CH·OH]$_2$·CH$_2$Cl. CH(CH:CH$_2$)$_2$·OH with $AgClO_4$ and a little OsO_4 gives a syrup, acetylation of which yields some *r*-arabitol penta-acetate.

R. S. C.

Explosions and other dangers in using ether, and their prevention. J. Stamm (Chem.-Ztg., 1939, **63**, 11—13).—Published work on the explosion of mixtures containing Et_2O and its auto-oxidation products, the purification of Et_2O, and tests for its purity, especially with reference to H_2O_2, are reviewed.

C. R. H.

Isomerisation of dimethylvinylethylene oxide into αα-dimethyl-Δ$^{\beta}$-butenal. Migration of vinyl. Y. Deux (Compt. rend., 1938, **207**, 920—921).—Mesityl oxide with $Al_2(OPr^{\beta})_3$ affords CMe_2:CH·CHMe·OH which when distilled over H_2SO_4 (pumice) gives *dimethylvinylethylene*, b.p. 75—76°/760 mm., converted into a chlorohydrin, which with K in dry Et_2O gives *dimethylvinylethylene oxide* (I), b.p. 80—81°/60 mm. When (I) is passed over fuller's earth at 250°, or when it is treated with $MgBr_2$–Et_2O, it affords *αα-dimethyl-*Δ$^{\beta}$-*butenal*, b.p. 87—88°/70 mm., reduced to ββ-*dimethylbutyl alcohol*, b.p. 135—137°/760 mm. (*Ph carbamate*, m.p. 63—64°) [identical with the alcohol obtained by interaction of $CMe_2Et\cdot MgCl$ (II) and HCO_2Et], oxidised to *αα-dimethylbutyric acid*, b.p. 113—114°/53 mm. (*amide*, m.p. 102—103°; *anilide*, m.p. 92—93°), identical with the acid prepared from (II) and CO_2.

J. L. D.

Methylene dinitrate. G. Travagli (Gazzetta, 1938, **68**, 718—721).—$(CH_2O)_3$ and HNO_3 (*d* 1·52) in H_2SO_4 at 3—5° give *methylene dinitrate* (I), $CH_2(O\cdot NO_2)_2$, b.p. 75—77°/20 mm., hydrolysed by KOH to KNO_2, KNO_3, CH_2O, and some HCO_2H and MeOH. In the products from C_2H_4 and HNO_3, (I) is not detected.

E. W. W.

Acid catalysis in liquid ammonia. III. Effect of α-substituents on the ammonolysis of esters. L. F. AUDRIETH and J. KLEINBERG (J. Org. Chem., 1938, **3**, 312—316; cf. A., 1938, I, 258).—Conversion of esters into amides by liquid NH_3 is shown to be always (8 examples) very greatly accelerated by NH_4Cl, in accordance with the view that NH_4Cl acts as an acid in NH_3. The effect of R in $CH_2R{\cdot}CO_2Et$ is shown by the following relative reaction rates: $CN>CO{\cdot}NH_2>CO_2Et>OEt>Ph>H$; the rates for $OH{\cdot}CHPh{\cdot}CO_2Et>OH{\cdot}CHMe{\cdot}CO_2Et$ are intermediate between those of $CH_2(CO_2Et)_2$ and $OEt{\cdot}CH_2{\cdot}CO_2Et$. Prep. of $OH{\cdot}CHPh{\cdot}CO{\cdot}NH_2$ and $OH{\cdot}CHMe{\cdot}CO{\cdot}NH_2$ in 80·5 and 74—76% yield, respectively, is described. R. S. C.

β-Alkoxyethyl esters of chlorocarbonic and carbamic acids. H. G. ASHBURN, A. R. COLLETT, and C. L. LAZZELL (J. Amer. Chem. Soc., 1938, **60**, 2933—2934).—The appropriate alkoxyethyl chloroformate (prep. by $COCl_2$ at <0°) with aq. NH_3 gives β-*methoxy*-, m.p. 46·8°, -*ethoxy*-, m.p. 62·2°, -n-, b.p. 132·2—132·5°/7 mm., and -iso-*propoxy*-, m.p. 53°, -n-, b.p. 132·2—132·4°/2·5 mm., -iso-, b.p. 133—134°/5 mm., and -sec.-*butoxy*-, b.p. 135·4°/3 mm., -n-, b.p. 142·2°/3 mm., and -iso-*amyloxy*-, b.p. 131·4°/1·5 mm., -β′-*methyl*-n-*butoxy*-, b.p. 129—130°/2 mm., -α′-*ethyl*-n-*propoxy*-, b.p. 133—134°/2·5 mm., and -α′-*methyl*-n-*butoxy-ethyl carbamate*, b.p. 137—138°/3·5 mm. Urethane is more active and less toxic than the OEt-esters, equal to the Pr esters, but less active and less toxic than the Bu and $O{\cdot}C_5H_{11}$ esters. β-n-*Propoxy*-, b.p. 78·3°/13 mm., β-n-*butoxy*-, b.p. 93—93·5°/14 mm., and β-n-*amyloxy-ethyl chloroformate*, b.p. 104·3°/12 mm., are described. B.p., n_D^{25}, d^{25}, and γ^{25} are given for all the chloroformates. R. S. C.

Neutral and basic lead monochloroacetates. E. GRILLOT (Compt. rend., 1938, **207**, 996—998; cf. A., 1935, 1089; 1937, II, 440).—$(CH_2Cl{\cdot}CO_2)_2Pb$ (I) when boiled with H_2O or N-aq. NH_3 affords a basic salt (II), $(CH_2Cl{\cdot}CO_2)_2Pb,PbO$, together with small but variable amounts of $(OH{\cdot}CH_2{\cdot}CO_2)_2Pb,PbO$. (II) dissolves easily in hot aq. (I) to give $[(CH_2Cl{\cdot}CO_2)_3Pb_2]OH$, which has a strongly alkaline reaction. J. L. D.

Uranyl salts of substituted organic acids. J. H. KŘEPELKA and Z. RÉSÖ (Coll. Czech. Chem. Comm., 1938, **11**, 559—581).—The prep. and properties of the following UO_2 *salts* are described: α-*chloro*-, β-*chloro*-, α-*bromo*-, β-*bromo*-, β-*iodo-propionate*, *dibromosuccinate*, *thiolacetate*, α-*thiolpropionate*, o-*chlorobenzoate* (I). The salts decompose slowly in daylight and more rapidly in ultra-violet light, decomp. being catalysed by Et_2O. The aliphatic salts, of which the β-compounds are more stable, give CO_2, basic salts, and U_3O_8 in ultra-violet light; in daylight more U_3O_8 and less of the basic salts are obtained, and CO_2 is evolved only near the end of the decomp. (I), the most stable salt prepared, gives UO_2 salicylate and HCl in ultra-violet light. F. H.

Action of sodium ethoxide on γ-halogeno-crotonic esters. R. RAMBAUD (Bull. Soc. chim., 1938, [v], **5**, 1552—1564; cf. A., 1935, 1105).—$CH_2Cl{\cdot}CH{:}CH{\cdot}CO_2Et$ (I) and NaOEt–EtOH at 50° give Et γ-chloro-β-ethoxybutyrate (II), b.p. 108—108·3°/20 mm. From $CH_2Br{\cdot}CH{:}CH{\cdot}CO_2Et$, the analogous γ-Br-compound (III), b.p. 112—114°/15 mm., can be isolated, but usually there is loss of HBr, probably through (III), with formation of Et 2-ethoxy*cyclo*propanecarboxylate (IV), b.p. 74—75·5°/13 mm., also obtained from (II) by distillation with dry KOH [some succinic acid (V) is also formed] or from (I) and NaOEt in very low yield, or from (III) and NaOEt. (IV) and CrO_3 or H_2O_2 give traces of (V); (IV) and NaOH in a sealed tube give 2-ethoxy*cyclo*propane-1-carboxylic acid, b.p. 122°/14 mm., converted by CrO_3, or more slowly by air, into (V). The mechanism of formation of (IV) is discussed. $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$ distilled with dry KOH gives *cyclo*propanecarboxylic acid and its Et ester. A. T. P.

Diene syntheses with derivatives of sorbic acid. T. WAGNER-JAUREGG and E. HELMERT (Ber., 1938, **71**, [*B*], 2535—2543).—$CH_2Cl{\cdot}CH_2{\cdot}OH$ and sorbyl chloride (I) at 0° and subsequently at 110° afford β-*chloroethyl sorbate*, b.p. 115°/15 mm., converted by $NHEt_2$ at 100—120° into β-*diethylaminoethyl sorbate*, b.p. 109°/0·45 mm. (*hydrochloride*), also obtained from sorbic acid (II), $NEt_2{\cdot}[CH_2]_2{\cdot}OH$ (III) and HCl at 100° or from (I) and (III). (II) and (III) when heated in N_2 at 200° afford mainly a *product*, $C_{12}H_{21}O_2N$, b.p. 190—200°/0·15 mm. Acrylyl chloride and (I) in boiling xylene give 4-*methyl*-Δ^5-*tetrahydroisophthalyl chloride* (IV), b.p. 118—122°/0·3 mm., hydrolysed to the corresponding *acid*, m.p. 282·5—283°, which is dehydrogenated by Br at 150° to 4-methyl*iso*phthalic acid (V), m.p. 330—331° (corr.). (IV) is converted by $NHEt_2$ at 0° and then at 40° into 4-*methyl*-Δ^5-*tetrahydroisophthalbisdiethylamide*, b.p. 190—194°/0·2 mm. 4-*Methylisophthalbisdiethylamide* has b.p. 200—203°/0·1 mm., m.p. 74—74·5° (corr.). 3-*Carb*-β-*chloroethoxy*-6-*methyl*-Δ^4-cyclo*hexene*-1-*carboxyl chloride*, b.p. 150—154°/2 mm. [degraded by Br to (V)], is converted by $NHEt_2$ at 110° into 3-*carb*-β-*diethylaminoethoxy*-6-*methyl*-Δ^4-cyclo*hexene*-1-*carboxyldiethylamide*, b.p. 198°/0·3 mm. Maleic anhydride and $CHMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2{\cdot}C_2H_4Cl$ give 3-*carb*-β-*chloroethoxy*-6-*methyl*-Δ^4-*tetrahydrophthalic anhydride*, m.p. 124° (corr.), degraded by $K_3Fe(CN)_6$ in alkaline solution to p-$C_6H_4Me{\cdot}CO_2H$ and dehydrogenated and hydrolysed by Br to 3-*carboxy*-6-*methylphthalic anhydride*, m.p. 180°. Similarly with $(:C{\cdot}CO_2Me)_2$ *Me*$_2$ 3-*carb*-β-*chloroethoxy*-6-*methyl*-3 : 6-*dihydrophthalate*, b.p. 190—194°/0·25 mm. (slight decomp.), is produced. H. W.

Relative stability of aromatic and aliphatic monoglycerides. B. F. DAUBERT and C. G. KING (J. Amer. Chem. Soc., 1938, **60**, 3003—3004).—*Glyceryl* β-p-*bromobenzoate* (I), m.p. 95·2°, and β-palmitate (II) are rapidly converted into the α-esters by 0·1N-HCl or -NH_3 in EtOH, but for (II) 0·0067N-HCl or 0·0125N-NH_3 is as effective as is 0·05N-HCl or 0·067N-NH_3 for (I). No shift occurs with (I) or (II) at 7° above the m.p. R. S. C.

Transformations of stearic acid in the solid state.—See A., 1939, I, 13.

Intermolecular oxidation of oleic acid. M. BRAMBILLA (Annali Chim. Appl., 1938, **28**, 444—454).—Oleic acid, heated to 325° in N_2, yields CO_2, octoic

and sebacic acid, and an unsaponifiable residue which, on fractionation, affords C_8H_{16} and $C_{10}H_{20}$ on distillation at normal pressures and $C_{16}H_{32}$ at 20 mm. The mechanism of the degradation is discussed. F. O. H.

Lipins of tubercle bacilli. LIV. Mycolic acid. LV. Wax fractions of human tubercle bacillus. LVI. Wax of the bovine tubercle bacillus. F. H. Stodola, A. Lesuk, and R. J. Anderson. C. W. Wieghard and R. J. Anderson. J. Cason and R. J. Anderson (J. Biol. Chem., 1938, **126**, 505—513, 515—526, 527—541).—LIV (cf. A., 1936, 1028). Hydrolysis of the "unsaponifiable wax" of human tubercle bacilli with C_6H_6–MeOH–KOH for 80 hr. removes traces of fatty acids and phthiocerol, leaving *mycolic acid*, $C_{86}H_{167}(OH)(OMe)_{0\cdot6}\cdot CO_2H$, m.p. 54—56° (corr.), $[\alpha]_D^{25}$ +1·8° in $CHCl_3$ [*Me* ester (CH_2N_2), m.p. 43—45°], a saturated acid which with HI and PhOH gives l-acids of varying composition, and when heated at 280—350°/0·5 mm. yields *n*-hexacosoic acid and a non-acidic residue.

LV (cf. A., 1936, 899). The wax-like material from EtOH–Et_2O extracts of the bacilli, insol. in cold $COMe_2$, has been separated into three fractions by pptn. from EtOAc by cooling, and by addition of $COMe_2$. The least sol. fraction when hydrolysed (C_6H_6–MeOH–KOH) yielded H_2O-sol. substances, glycerol (I), mannose, and inositol, phthiocerol (II), and acids which were separated by pptn. from EtOH with $Pb(OAc)_2$: palmitic, stearic, *n*-hexacosoic (III), tuberculostearic, mycolic, and an acid, $C_{31}H_{62}O_2$(?), m.p. 37—38°, $[\alpha]_D^{20}$ −10·4° in Et_2O. The more sol. fractions contained (I), carbohydrates, (II), fatty acids, phthioic acid, unsaturated acids hydrogenated to (III), and acids similar to mycolic but of lower mol. wt.

LVI. The $CHCl_3$-sol. wax from bovine tubercle bacilli, purified by repeated pptn. from Et_2O by MeOH, has been hydrolysed (EtOH–KOH) and the products separated into four fractions: (*a*) H_2O-sol. substances, (I), glycerylphosphoric acid, a disaccharidemonophosphoric acid giving a positive Scherer test for inositol, and a neutral polysaccharide containing N, hydrolysed (dil. H_2SO_4) to inositolmonophosphoric acid, mannose, inositol, and another reducing sugar; (*b*) Et_2O–EtOH-insol. acids containing OH and OMe groups, of mean mol. wt. 1200, including bovine mycolic acid, m.p. 56—58°, $[\alpha]_D$ +2·7° in $CHCl_3$, which when heated at 250—300° under reduced pressure yields (III); (*c*) Et_2O–EtOH-sol. acids, palmitic, an inactive branched-chain (?) *acid*, $C_{24}H_{48}O_2$, m.p. 76—77° (*Me* ester, m.p. 39—42°), an inactive branched-chain *acid*, $C_{18}H_{36}O_2$, m.p. 29—30° (*Me* ester, b.p. 112—114°/0·006 mm.; 2 : 4 : 6-*tribromoanilide*, m.p. 96—96·5°), unsaturated acids, and a mixture of saturated *l*-acids of mean mol. wt. 430; and (*d*) neutral substances, (II), and an unknown non-cryst. substance A. Li.

Condensation of formaldehyde with α-methylacetoacetic ester. J. Burkhard (Bull. Soc. chim., 1938, [v], **5**, 1664—1669).—$CHMeAc\cdot CO_2Et$, CH_2O (1·5 mols.), and a little aq. K_2CO_3 at −10° give *Et α-methyl-α-hydroxymethylacetoacetate*, b.p. 96° (slight decomp.)/1·5 mm. (*acetate*, b.p. 94—96°/0·2 mm.; *oxime*, m.p. 165°; does not react with PhNCO), which decomposes slowly at 80° and rapidly at 140° or when distilled at 14 mm. R. S. C.

Potentiometric titration of complex compounds with several oxidisable components.—See A., 1939, I, 103.

Introduction of substituted vinyl groups. II. (1-Methylpropenyl)alkylmalonic esters. III. (Dialkylvinyl)alkylcyanoacetic esters. A. C. Cope and (Miss) E. M. Hancock (J. Amer. Chem. Soc., 1938, **60**, 2901—2902, 2903—2906; cf. A., 1939, II, 5).—II. *Et α-carbethoxy-γ-methyl-Δ$^\beta$-pentenoate* [*Et$_2$ α-methylpropylidenemalonate*] [prep. from $CH_2(CO_2Et)_2$, COMeEt, and $ZnCl_2$ in Ac_2O at 110°], b.p. 119—120°/9 mm., with $NaNH_2$ or, less well, NaOEt–EtOH, followed by RHal or R_2SO_4, gives good yields of *Et$_2$ methyl-*, b.p. 126—127°/15 mm., *ethyl-*, b.p. 124—124·5°/9 mm., *propyl-*, b.p. 128—131°/9 mm., *allyl-*, b.p. 124—129°/9 mm., and *butyl-*, b.p. 159—160°/22 mm., *-α-methyl-Δ$^\alpha$-propenylmalonate*, $CHMe{:}CMe\cdot CR(CO_2Et)_2$. The structure of the products follows because O_3 gives MeCHO with only traces of CH_2O. The wide b.p. of some of the products is due to *cis–trans* isomerism.

III. If $CH_2R\cdot CR'{:}C(CN)\cdot CO_2R''$ is treated with $NaNH_2$ in liquid NH_3 and then with Alk_2SO_4 in PhMe, cleavage and polymerisation occur. Use of Na in Et_2O causes partial reduction. NaOR''' in a R'''OH, followed by AlkBr or Alk_2SO_4 gives $CHR{:}CR'\cdot CAlk(CN)\cdot CO_2R''$, the structure being proved by production of RCHO by O_3. The order of preference is R''' = Pr$^\beta$ > Et > Me, the yield being related inversely to the ease of alcoholysis by the solvent. The following are prepared, those marked * being mixed Et–Pr esters: *Et α-cyano-β-methyl-α-ethyl-*, b.p. 117—117·5°/12 mm., *-α-n-propyl-**, b.p. 120—122·5°/9 mm., and *-α-butyl-Δ$^\beta$-pentenoate*, b.p. 134—134·5°/9 mm.; *Et α-cyano-αβ-dimethyl-Δ$^\beta$-hexenoate**, b.p. 124—126°/16 mm.; *Et α-cyano-β-methyl-α-ethyl-**, b.p. 135—136°/17 mm., *-α-n-**, b.p. 128—129°/9 mm., and *-α-iso-propyl-**, b.p. 133—134°/13 mm., and *-α-allyl-Δ$^\beta$-hexenoate**, b.p. 130—133°/9 mm.; *Et α-cyano-α-methyl-β-ethyl-*, b.p. 112—113°/8 mm., *α-cyano-αβ-diethyl-**, b.p. 141—143°/22 mm., *α-cyano-β-ethyl-α-n-propyl-**, b.p. 132—133·5°/10 mm., and *α-cyano-β-ethyl-α-isopropyl-**, b.p. 129—130°/12 mm., *-Δ$^\beta$-pentenoate*; *Et α-cyano-αβ-dimethyl-*, b.p. 138—139°/17 mm., and *α-cyano-β-methyl-α-ethyl-Δ$^\beta$-heptenoate*, b.p. 145—146°/17 mm.; *Me α-cyano-αβ-dimethyl-**, b.p. 150—152°/22 mm., *α-cyano-β-methyl-α-ethyl-*, b.p. 158—159°/22 mm., *-Δ$^\beta$-octenoate*; *Me α-cyano-αβδ-trimethyl-*, b.p. 130—133°/22 mm., and *α-cyano-βδ-dimethyl-α-ethyl-*, b.p. 137—139°/22 mm., and *α-cyano-α-ethyl-β-propyl-Δ$^\beta$-hexenoate*. $CH_2R\cdot CR'{:}C(CN)\cdot CO_2R''$ are best prepared in PrOH, but some interchange of R'' and Pr$^\beta$ occurs. R. S. C.

Chemically catalysed *cis–trans* isomerisation. C. C. Price and R. S. Thorpe (J. Amer. Chem. Soc., 1936, **60**, 2839—2841).—In light or in the presence of anthracene in the dark, Br isomerises Et_2 maleate to Et_2 fumarate. Br^+ is probably the catalyst, which functions by a long chain reaction. *cis–trans* Changes are thus not confined to Br atoms. R. S. C.

Accelerating action of ketones on the Cannizzaro–Tischtschenko reaction. II. Dependence of the accelerating action of ketones on the magnitude of the ketone : CH_2O ratio. M. N. Tilitschenko (J. Gen. Chem. Russ., 1938, **8**, 766—773; cf. A., 1937, II, 368).—The accelerating effect of ketones on the Cannizzaro reaction of CH_2O in aq. or aq. alcoholic NaOH rises with increasing ketone concn., to a max., corresponding with the no. of CH_2O mols. bound by the given ketone under given conditions ($COMe_2$ 6, *cyclo*hexanone 4, COPhMe 3); this part of the activation–ketone concn. curve is rectilinear. Further increase in ketone concn. inhibits the Cannizzaro reaction, owing to lowering of the effective $[CH_2O]$. R. T.

Formation of formaldehyde from percarbonate. A. Režek (Ber., 1938, **71**, [*B*], 2486—2487).—Baur's observation (A., 1938, I, 319) of the formation of CH_2O from percarbonate is confirmed by use of dimethylhydroresorcinol in its detection. H. W.

Rate of formation of oximes, phenylhydrazones, and semicarbazones of hydroxy-aldehydes. G. Vavon and P. Montheard (Compt. rend., 1938, **207**, 926—927; cf. A., 1938, II, 101).—Interaction of the aldehyde or ketone (1 mol.) with NH_2OH,HCl, $NHPh{\cdot}NH_2,HCl$, or $NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2,HCl$ (2 mols.) in 70% EtOH at 0° (aldehydes) or 30° (ketones) is followed by determining the HCl liberated in the first two cases and the unaltered $NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$ in the last. Many aldehydes and ketones show a marked decrease in the time of half reaction when OH or OMe is *o*- to CHO or CO. The effect is found at different p_H vals. *o*-$OH{\cdot}C_6H_4{\cdot}COMe$ reacts more slowly than COPhMe, which indicates that chelation occurs between the H of CHO and the O of OH, and not vice versa. J. L. D.

Synthesis of glycollic and glyceric aldehydes. A. Kuzin (J. Gen. Chem. Russ., 1938, **8**, 592—595).—0·25% glucose and 1% $Ca(OH)_2$ in 4% CH_2O are incubated at 37° until the reducing power (Fehling's solution at 20°) is max., when the solution is neutralised with H_2SO_4, made slightly acid with AcOH, and evaporated in vac. to a syrup, from which glyoxal is isolated (4% yield). Glyoxal and aq. CH_2O in presence of $Ca(OH)_2$ give *dl*-glyceraldehyde in 75% yield. R. T.

Photochemical oxidation of acetone.—See A., 1939, I, 89.

Analyses of mixtures of acetone, *n*-butyl alcohol, and ethyl alcohol.—See B., 1939, 14.

Condensation of ketones with acid chlorides in presence of metallic chlorides. J. Colonge and K. Mostafavi (Bull. Soc. chim., 1938, [v], **5**, 1478—1486; cf. Descudé, A., 1903, i, 735; A., 1930, 713).—$COMeEt$–AcCl–$ZnCl_2$ (amounts varied) at 15—20° for 24 hr. give a mixture, b.p. 155—158°, probably of $CHMe{:}CMe{\cdot}CH_2Ac$ and $CMeEt{:}CHAc$; the two respective semicarbazones have m.p. 182—183° and 131° (cf. Kon *et al.*, A., 1928, 1218). $COMePr$ affords a mixture, b.p. 196—199°/750 mm., of $CHEt{:}CMe{\cdot}CHEtAc$ and $CMePr{:}CEtAc$ (semicarbazone, m.p. 153—154°, probably of the former). Me amyl and hexyl ketone give products, b.p. 150—153°/30 mm., and 160—162°/16 mm., respectively. Reactions of $COEt_2$–$ZnCl_2$ and AcCl, BzCl, $SOCl_2$, SO_2Cl_2, $POCl_3$ (best), PCl_3, and *p*-$C_6H_4Me{\cdot}SO_2Cl$ at 15—20° for 48 hr. are examined. The mixed product, b.p. 186—190°/757 mm., gives a semicarbazone, m.p. 108—109°, probably from $CEt_2{:}CMe{\cdot}COEt$ (cf. Kon *et al.*, A., 1931, 1274). The interaction of $COEt_2$ and $POCl_3$ at 20° for 48 hr. with various metallic chlorides shows that $ZnCl_2$ and $SnCl_4$ are best. $COMePr^{\beta}$, $COMeBu^{\gamma}$, or $COPr^{\beta}_2$ does not react with $POCl_3$–$ZnCl_2$. Mechanisms of reactions are discussed. A. T. P.

Hydrogenation of higher ketones with catalysts consisting mainly of nickel or copper. K. Kino (J. Soc. Chem. Ind. Japan, 1938, **41**, 259—260B).—The quantities of hydrocarbon and *sec.* alcohol produced in the hydrogenation of ketones at 300° have been determined, using catalysts consisting of Ni or Cu and various other metals. A. Li.

Acid- and alkali-resisting properties of higher ketones, and their solubilities in some organic solvents. K. Kino (J. Soc. Chem. Ind. Japan, 1938, **41**, 259B).—When left in contact with the reagent for 142 days, mixed ketones (C_{31}—C_{35}) are appreciably attacked by conc. H_2SO_4, slightly by conc. HCl, conc. HNO_3, and 30% KOH, but not at all by 30% NaOH or dil. acids. The solubility of stearone in org. solvents at three temp. is recorded. A. Li.

Degradation reaction in organic chemistry. A. Schönberg (Nature, 1938, **142**, 997).—Examples of the conversion of $\cdot CO{\cdot}CO{\cdot}CO\cdot$ or $\cdot CO{\cdot}CH_2{\cdot}CO\cdot$ into $\cdot CO{\cdot}CO\cdot$ are given. L. S. T.

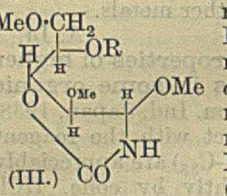
Modern results in the chemistry of carbohydrates. F. Micheel (Angew. Chem., 1939, **52**, 6—17).—A review in which the following are discussed; configuration, prep. of monosaccharides, reduction products, oxidation products, compounds involving interaction of the CO group, glucosides and ethers, aldehydic and ketonic derivatives, esters, syntheses, position of ring and configuration, oligosaccharides, cellulose, starch, glycogen, Schardinger dextrin, mannans, xylan, agar-agar, pectins, biologically important carbohydrate derivatives, carbohydrate–protein compounds, transition from carbohydrates to the carbocyclic compounds. H. W.

Synthesis of sugars from formaldehyde. VI. Mechanism of the reaction. A. Kuzin (J. Gen. Chem. Russ., 1938, **8**, 759—765).—Balezin's dilatometric studies of the reaction of condensation of CH_2O in presence of $Ca(OH)_2$ (A., 1938, II, 43) are criticised on the grounds that variations in the temp. of the systems were not taken into account. The following reaction mechanism is advanced, as being more in accord with the facts : $OH{\cdot}CR{:}CR{\cdot}OH$ (I) + $CH_2(OH)_2$ (II) → $OH{\cdot}CH_2{\cdot}CR(OH){\cdot}CR(OH)_2$ → (+MOH) $OH{\cdot}CH_2{\cdot}CR(OM){\cdot}CR(OH)_2$ → $OH{\cdot}CH{:}CR{\cdot}COR$ → [+ (II)] $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CR(OH){\cdot}COR$ → (I) + $OH{\cdot}CH_2{\cdot}CH(OH)_2$ (III); (III) → $OH{\cdot}CH{:}CH{\cdot}OH$ (IV) → [+ (II)] $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH)_2$. In this reaction M = 0·5Ca, (IV) functions as an autocatalyst, and (I) is a monose having the $\cdot C(OH){:}C(OH)\cdot$

group, and functioning as a catalyst. Under conditions of biosynthesis (I) may be fructose or ascorbic acid. R. T.

Production of *l*-erythrulose by the action of *Acetobacter suboxydans* on erythritol.—See A., 1938, III, 102.

Descent of the series of methylated sugars by the Weerman reaction. W. N. HAWORTH, S. PEAT, and J. WHETSTONE (J.C.S., 1938, 1975—1980).—3 : 5 : 6-Trimethylglucofuranose is oxidised by Br to 3 : 5 : 6-*trimethyl-γ-gluconolactone*, m.p. 44—45°, $[\alpha]_D^{20}$ +51·8° → +14·1° in H_2O in 860 hr., which is converted by liquid NH_3 into 3 : 5 : 6-*trimethylgluconamide* (I), m.p. 144°, $[\alpha]_D^{20}$ +34·0° in H_2O. Me pentamethylgluconate with NH_3–MeOH yields *pentamethylgluconamide* (II), m.p. 66°, $[\alpha]_D^{18}$ +51·1° in H_2O. 2 : 3 : 5 : 6-Tetramethylgluconamide at 0° with aq. NaOCl yields a *cyclic urethane* (IV) [(III), R = Me],



(III.)

m.p. 110°, $[\alpha]_D^{14·5}$ +99·3° in H_2O, whilst 2 : 3 : 6-trimethylgluconamide yields the *cyclic urethane* [(III), R = H], m.p. 157°, $[\alpha]_D^{17}$ +103° in H_2O, methylated by MeI–Ag_2O in MeOH to the N-*Me derivative* of (IV), m.p. 99°, $[\alpha]_D^{17}$ +65·8° in H_2O, also obtained by methylation of (IV). Similar treatment of 2 : 3 : 4 : 6-tetramethylgluconamide yields the cyclic urethane described by Irvine and Pryde (J.C.S., 1924, **125**, 1045), 2 : 3 : 4- and 2 : 3 : 5-trimethyl-*l*-arabonamide yield the urethanes described by Humphreys *et al.* (A., 1931, 1403), whilst (II) yields *tetramethyl*-aldehydo-d-*arabinose*, b.p. 85° (bath)/0·01 mm., $[\alpha]_D^{17·5}$ +16·6° in H_2O, and (I) gives 3 : 4 : 5-*trimethyl*-d-*arabinose* (a syrup), $[\alpha]_D^{17}$ +18·4° in H_2O, and NaCNO (identified as hydrazodicarbonamide) which is not formed from any other amide (cf. A., 1935, 72). J. D. R.

Mechanism of carbohydrate oxidation. XXIV. Action of *aldehydo-d*-glucose and of *aldehydo-d*-galactose in alkaline solutions. R. J. PLUNKETT and W. L. EVANS (J. Amer. Chem. Soc., 1938, **60**, 2847—2852; cf. A., 1937, II, 57).—The amounts of lactic (I) and saccharic (II) acids obtained by 0·5—6N-KOH from *aldehydo-d*-glucose and β-*d*-glucopyranose penta-acetates at 25°, 37·4°, 50°, and 62·5°, and from *aldehydo-d*-galactose and β-*d*-galactopyranose penta-acetates at 25° and 50° are determined. With 3N-KOH they are very similar, but in more conc. KOH the *aldehydo*-sugars give more (II). The results support the view that pyranoses form *aldehydo*-sugars before fission to (I). It is postulated that (I) and (II) are obtained by different, but analogous, changes, the rates of which depend on the exact conditions. Susceptibility to alkali usually is a max. at 37·5° and increases only slightly with >3N-KOH. R. S. C.

Mutarotation of *d*-galactose. B. C. HENDRICKS and R. E. RUNDLE (J. Amer. Chem. Soc., 1938, **60**, 3007—3009).—The rate of mutarotation of tetramethyl-α-*d*-galactopyranose at 0°, but not at 25°, decreases as equilibrium is approached; $k_1 + k_2$ for "thermal dissociation" from 25° to 0° (Isbell *et al.*, A., 1936, 1209) decreases similarly. Thus, conversion of pyranose into furanose forms is not a general cause of complex mutarotation. R. S. C.

Isolation of an anhydro-*l*-galactose derivative from agar. S. HANDS and S. PEAT (Nature, 1938, **142**, 797).—Methylation of agar with Me_2SO_4–NaOH, followed by hydrolysis (MeOH–HCl), fractionation of the glycosides, and methylation (MeI), yields 2 : 4-*dimethyl*-3 : 6-*anhydromethyl*-1-*galacto-pyranoside*, m.p. 82—83°, $[\alpha]_D$ +85·3° in $CHCl_3$, +73° in H_2O, and +77·8° → 21° in dil. aq. H_2SO_4, hydrolysed to 2 : 4-dimethyl-3 : 6-anhydro-*l*-galactose, m.p. 114°. J. D. R.

Hydrogenating fission of sucrose. R. WEIDENHAGEN and H. WEGNER (Ber., 1938, **71**, [*B*], 2712—2716).—At 170—180°/50 atm., neutral solutions of sucrose (I) in presence of a Ni–Mo catalyst rapidly absorb 4 H_2, after which the rate of absorption diminishes greatly but reaction does not cease. The solution contains acetol (II) due to the intermediate production of AcCHO. The absorption graph indicates that the change is $C_{12}H_{22}O_{11}$ → 4AcCHO → 4(II). The neutral character of the solution appears to prevent the further reduction of (II), which is probably present in the desmotropic ethylene oxide form $CH_2<O>CMe\cdot OH$. Attempts to obtain $OH\cdot CH_2\cdot CHMe\cdot OH$ (III) in a single operation by hydrogenative fission of (I) in presence of $Ca(OH)_2$ gave mainly $(OH\cdot CHMe\cdot CO_2)_2Ca$ with a little (III) but no (II). Stronger alkali causes an increase in the amount of $OH\cdot CHMe\cdot CO_2H$ whereas weaker alkali [K_2HPO_4, $Zn(OH)_2$, $Mg(OH)_2$] is unable to convert (II) into the reducible CO form. Good yields of (III) can be obtained by hydrogenating (I) in a neutral medium until the quantity of H necessary for the formation of (II) has been absorbed. (II) is distilled and the hydrogenation is completed in the distillate made alkaline, preferably with $Ca(OH)_2$. Addition of alkali to the initial solution at the appropriate stage does not lead to satisfactory results. It appears that at 170°, possibly owing to CO_2 formed as a by-product, (I) is hydrolysed to monosaccharides which at the relatively high temp. rapidly pass into C_3 sugars which lose H_2O to form AcCHO. H. W.

Preparation of rutinose from rutin without aid of enzymes. G. ZEMPLÉN and A. GERECS (Ber., 1938, **71**, [*B*], 2520).—Rutin is hydrolysed by boiling 10% AcOH and rutinose is isolated as the β-hepta-acetate, m.p. 169—170°, $[\alpha]_D^{20}$ −27·7° in $CHCl_3$. H. W.

Bioses of hesperidin and of neohesperidin. G. ZEMPLÉN and A. K. TETTAMANTI (Ber., 1938, **71**, [*B*], 2511—2520).—Hesperidin (I) is completely methylated by Me_2SO_4–NaOH followed by Ag_2O–MeI to *nonamethylhesperidin*, m.p. 180—181°, $[\alpha]_D^{27}$ −40·0° in $CHCl_3$, which is hydrolysed by acid to methylated monoses identical in optical activity and reducing power with those derived from completely methylated rutin or methylated rutinose (II). The biose of (I) is therefore identical with (II). Further, fission of (I) with $Ba(OH)_2$ leads to non-cryst. β-*phloroglucinolrutinoside* [this gives a non-cryst.

acetate (III), $[\alpha]_D^{19}$ −44·05° in $CHCl_3$, also obtained from phloroglucinol and acetobromorutinose]. The sp. rotation of (III) agrees with that calc. from observation of β-*phloroglucinolcellobioside acetate*, $[\alpha]_D^{20}$ −36·0° in $CHCl_3$, thus showing that (I) is hesperitin-β-rutinoside.

[With, in part, S. FARAGO.] Neohesperidin (IV), m.p. 244°, is hydrolysed to hesperitin, *d*-glucose, and *l*-rhamnose. The restricted action of 0·5% H_2SO_4 leads to a hesperitinglucoside, whereby (IV) is sharply differentiated from (I). The successive action of Me_2SO_4–NaOH and MeI–Ag_2O on (IV) gives *monomethylneohesperidin*, $[\alpha]_D^{21}$ −59·4° in EtOH. This is hydrolysed to a mixture of methylated monoses, the reducing power of which is considerably > that of the similar substances obtained from (I) or from rutin. (II) is therefore not present in (IV), which contains a new biose for which the term neohesperidose is proposed. It is probably 1-*l*-rhamnosido-4-*d*-glucose, although the possibility of a 3- or 2-glucose union is not completely excluded. The point of union of the biose to the flavanone is not established. *Decamethylrutin*, $[\alpha]_D^{19}$ −32·8° in EtOH, is described. H. W.

Arbuscoloside (myricetyl-*d*-galactoside), m.p. 208°.—See A., 1939, III, 219.

Emulsin. XXXV. Glucosides of phenolcarboxylic acids, their enzymic fission and autodecomposition. B. HELFERICH and H. LUTZMANN (Annalen, 1938, **537**, 11—21).—Me tetra-acetyl-β-*d*-glucosidosalicylate, m.p. 160·5° (corr.), $[\alpha]_D^{20}$ −29·3° in $CHCl_3$, −34° in $COMe_2$, is deacetylated by NaOMe in boiling MeOH to Me β-*d*-glucosidosalicylate, m.p. 107° (corr.), $[\alpha]_D^{20}$ −64·4° in H_2O, which is hydrolysed by aq. $Ba(OH)_2$ at room temp. to β-*d*-glucosidosalicylic acid (I) (+0·5H_2O), m.p. 136—137° (corr.), $[\alpha]_D^{20}$ −59·6° in H_2O, $[\alpha]_D^{21}$ −37·0° in 7% aq. K_2CO_3. Treatment of *m*-ONa·C_6H_4·CO_2Me with acetobromoglucose and of the product with Ac_2O and C_5H_5N yields *Me tetra-acetyl*-β-d-*glucosido*-m-*oxybenzoate*, m.p. 111—112° (corr.), $[\alpha]_D^{20}$ −28·6° in $CHCl_3$, whence *Me* β-d-*glucosido*-m-*oxybenzoate*, m.p. 153—154° (corr.), $[\alpha]_D^{20}$ −74·1°, and the free acid. β-d-*Glucosido*-p-*oxybenzoic acid* has m.p. 211—212° (corr.), $[\alpha]_D^{21}$ −81·4° in H_2O. β-*d*-Glucosido-*o*-coumaric acid (+1H_2O), m.p. 245° (corr.; decomp.), $[\alpha]_D^{21}$ −76·5° in 50 vol.-% EtOH [*tetra-acetate*, m.p. 187—188° (corr.), $[\alpha]_D^{17}$ −56·3° in $CHCl_3$], is converted by CH_2N_2 into its *Me* ester, m.p. 189—190° (corr.), $[\alpha]_D^{20}$ −72·2° in 50 vol.-% EtOH [*tetra-acetate*, m.p. 125—126° (corr.), $[\alpha]_D^{21}$ −53·5° in $CHCl_3$]. Coumarin is converted by 2N-NaOH and acetobromoglucose into *tetra-acetyl*-β-d-*glucosidocoumarinic acid*, m.p. 155—156° (corr.), $[\alpha]_D^{18}$ +14·5° in $CHCl_3$. The corresponding *Me* ester, m.p. 110° (corr.), $[\alpha]_D^{21}$ +7·3° in $CHCl_3$, is hydrolysed to *Me* β-d-*glucosidocoumarinate*, m.p. 98—99° (corr.), $[\alpha]_D^{22}$ −63·6° in H_2O, which yields a non-cryst. acid (II). Among the free acids the derivative of *o*-OH·C_6H_4·CO_2H is most rapidly hydrolysed by enzymes whilst there is practically no difference in the case of fission of the esters of the simple phenolcarboxylic acids. There appears to be no parallelism between the possibility of lactone formation and the rate of hydrolysis. Provided that a neutral or alkaline solution is assured by buffering there is no evidence of autodecomp. at 60°. Solutions of the free acids (p_H 2·4—2·9) are also stable with the exception of that of (I) which is affected even at room temp. On the other hand the possibility of lactone formation does not induce the autodecomp of (II). H. W.

Determination of uronic anhydride residues in polysaccharides. W. G. CAMPBELL, E. L. HIRST, and G. T. YOUNG (Nature, 1938, **142**, 912—913; cf. A., 1938, III, 545).—Glucose, fructose, sucrose, maltose, mannose, and xylose, potato, rice, and wheat starches, etc., but not mannitol, give small amounts of CO_2 (0·2—1%) when heated with aq. HCl. For starches, no structural significance can be attached to these small yields of CO_2, whilst for other polysaccharides yields >1% may be untrustworthy as an indication of the presence of uronic anhydride. The claim advanced previously (A., 1935, 797) that certain wood starch preps. contain uronic anhydride is not invalidated; only the numerical results are affected. L. S. T.

Significance of "end-group" determination in polysaccharides. E. HUSEMANN (Papier-Fabr., 1938, **36**, 51, 559—563).—A discussion of relevant literature. A. T. P.

Action of chlorine water on β-amyloses. H. H. FLETCHER and T. C. TAYLOR (J. Amer. Chem. Soc., 1938, **60**, 3018—3025).—β-Amylose is treated with Cl_2 at p_H <10 and the reaction stopped by C_2H_4 at different times; the reducing power and "alkali-labile val." (Taylor *et al.*, A., 1935, 1064) decrease gradually, but η remains const.; this is due to oxidation of terminal CHO to CO_2H. In neutral or acid solution, there is at first only slight change, then a sudden, large rise in reducing power and alkali-labile val. and a large decrease in η; thereafter, alkali-labile val. slowly decreases, but the reducing power and η remain const. In these cases the first action is penetration of H_2O into the micelle, catalysed by HOCl; then the micelles suddenly disrupt (lower η) and thus expose CHO which was previously masked. During reaction the p_H decreases and even partial prevention of this change by buffering increases the final decreases in alkali-labile val. and reducing power. Tapioca, potato, and maize starches behave similarly, but not identically. Longer grinding increases the rates of change. The reducing power and alkali-labile val., but not η, of glucose are decreased by Cl_2, but the reaction is not quite analogous to that of starch. R. S. C.

Polysaccharide produced from sucrose by *Betabacterium vermiforme*.—See A., 1939, III, 102.

Dextran produced from sucrose by *Betacoccus arabinosaceous hæmolyticus*.—See A., 1939, III, 102.

Methylated starch. K. FREUDENBERG and H. BOPPEL (Ber., 1938, **71**, [*B*], 2505—2511).—Starch is readily methylated with Na, NH_3, and MeI if the mixture is kept heterogeneous. It is necessary to remove NaI periodically and to reach at least a 20% OMe content during the first operation; otherwise gel formation

or, possibly, dissolution results. The product is purified by hot H_2O, whereby the final val. (45·6% OMe) is readily attained. Alternatively, after a certain OMe content has been reached the formation of slime can be avoided by operating in solution in $NHMe_2$, $NHEt_2$, or, preferably, NH_3. Amylose and amylopectin are methylated similarly and the products cannot be distinguished from one another. Terminal group determinations of the Me_3 ethers of the three compounds yield 3·2—3·4% of tetramethylglucose (I), 1·8—2·2% of dimethylglucose (II), 91% of trimethylglucose (III) (calc. as anhydride), and 4% of distillation residue. 5% of terminal groups appear to be present and (II) and (III) are present in the ratio 1 : 1. (I) is identified as such. Trimethylglucoses other than (III) do not appear to be present.

H. W.

Cellulose hydrolysis by ethyl mercaptan. III. M. L. Wolfram and J. C. Sowden (J. Amer. Chem. Soc., 1938, **60**, 3009—3013; cf. A., 1938, II, 265).—Cotton linters is hydrolysed by 41% HCl with and without EtSH, and the degree of polymerisation is calc. by η and the S content of the product at various times. η gives consistently the higher mol. wts.

R. S. C.

Methylation of cellulose. K. Freudenberg, E. Plankenhorn, and H. Boppel (Ber., 1938, **71**, [*B*], 2435—2438; cf. A., 1937, II, 370).—Cellulose (I) can be completely methylated by repeated treatment with Na and MeI in liquid NH_3. The methylation of (I), which contains 40% OMe introduced by the action of cold Me_2SO_4 and KOH, can be rapidly completed by this method. Such an incompletely methylated (I) gives a very viscous solution in $CHCl_3$ but after treatment with Na–MeI–liquid NH_3 the viscosity (η) diminishes markedly. Methylcellulose, prepared exclusively in NH_3, has invariably a low η. Treatment of highly viscous (I) at —70° under NH_3 with Na or $NaNH_2$ is sufficient to diminish η. Treatment of 2 : 3 : 6-trimethylglucose (II) with cold MeOH–3% HCl and of the product with Ag_2CO_3 gives, after distillation, a glucoside mixture with nearly the expected $[\alpha]_D$ in H_2SO_4. If the mixture is warmed before removing the HCl the val. of $[\alpha]_D$ increases with the temp. employed and with the duration of heating. Products derived from methyl-cellulose or -starch show precisely similar behaviour. If the glucoside mixtures of highest $[\alpha]_D$ are hydrolysed with dil. HCl the product is essentially (II). Glucosides with varying final $[\alpha]_D$ do not differ from one another essentially in b.p. The phenomena are not explained but it is advocated that treatment of polysaccharides with MeOH–HCl should be used with caution and that prolonged heating during glucosidation should be avoided as far as possible.

H. W.

Constitution of organic salts of hexamethylenetetramine. P. Bouchereau (J. Pharm. Chim., 1938, [viii], **28**, 484—489).—When alcoholic solutions of $(CH_2)_6N_4$ and org. acids are mixed at or below 80° the corresponding salts are obtained, whilst if aq. solutions and higher temp. are used then double NH_4 $(CH_2)_6N_4$ salts are formed. The following salts of $(CH_2)_6N_4$ are described: *salicylate* and double NH_4 *salicylate*, *citrate* and double NH_4 *citrate*, *benzoate*, m.p. 132°, and double NH_4 *benzoate*, m.p. 125°, *diethylbarbiturate*, m.p. 163—164°, and double NH_4 *methylenecitrate*, m.p. 163°.

J. N. A.

Chemical, physiological, and neutralising action of hexamethylenetetramine on dichlorodiethyl sulphide (Ypérite or Lost). P. Bruère and P. Bouchereau (J. Pharm. Chim., 1938, [viii], **28**, 490—492).—Aq. $(CH_2)_6N_4$ rapidly diffuses into tissues, and can be used to counteract the effects of mustard gas, with which it reacts in presence of H_2O forming NH_4Cl, the corresponding glycol, and trace of CH_2O.

J. N. A.

Crystalline triethanolamine iodomercurate. H. Griffon (Bull. Soc. chim., 1938, [v], **5**, 1694—1699).—$N(CH_2{\cdot}CH_2{\cdot}OH)_3$ gives no ppt. with Mayer's reagent, but with Valser's more conc. reagent in neutral or slightly acid solution (>0·03N.) gives the *salt*, *B*,HI,HgI_2 (photomicrograph).

R. S. C.

Aminopentane-polyols. J. Barbiere and J. Matti (Bull. Soc. chim., 1938, [v], **5**, 1565—1567).—$C(CH_2{\cdot}OH)_4$ and HBr (*d* 1·78) at 120° for 15 hr. afford $C(CH_2Br)_2(CH_2{\cdot}OH)_2$ and *β-bromomethyl-β-hydroxymethylpropane-αγ-diol*, m.p. 76°, converted by $NPhMe_2$–C_6H_6 at 150° for 15 hr. into *β-dimethylaminoethyl-β-hydroxymethylpropane-αγ-diol*, m.p. 51—52°, b.p. 178—182°/4 mm. (*hydrochloride*, m.p. 125·5°). Similarly, $CMe(CH_2{\cdot}OH)_3$ and HBr at 100° for 15 hr. give *β-methyl-β-bromomethylpropane-αγ-diol*, m.p. 71°, b.p. 151—152°/15 mm., converted (140°) into the corresponding β-NMe_2-compound, b.p. 128°/15 mm. (hygroscopic hydrochloride) (corresponding β-NEt_2-compound, b.p. 174°/2·3 mm.).

A. T. P.

Affinity of amino-acids and polypeptides for acids, bases, and zwitterions.—See A., 1939, I, 80.

Reversible action of oxidised phenols in the deamination of certain amino-acids. S. S. Hubard (J. Biol. Chem., 1938, **126**, 489—492).—The amount of deamination of glycine by tyrosinase and *p*-cresol (I) in aërated buffer solutions at p_H 7·8 shows that (I) functions reversibly to a limited extent. It probably combines with the end-products, since the NH_3 recovered is < that corresponding with the amount of deamination. Data of Robinson *et al.* (A., 1925, i, 745) are consistent with this theory.

A. Li.

Optically active amino-acids. VII. S. Berlingozzi and (Signa.) R. Lenoci (Gazzetta, 1938, **68**, 721—728).—*l*-α-Bromo*iso*valeryl-*l*-asparagine (I) (A., 1926, 819) with boiling 25% HCl gives *l*-α-bromo*iso*valeric acid (II) and aspartic acid. Similarly the *d*-isomeride of (I) gives the *d*-isomeride of (II). With boiling 4N-HCl, however, (I) gives mainly l-α-*bromoisovalerylaspartic acid* (III), m.p. 167°, $[\alpha]_D^{20}$ −10·2° (Na_2 salt in H_2O), with some (II). d-α-*Bromoisovalerylaspartic acid*, m.p. 158—159°, $[\alpha]_D^{20}$ +12·1° (Na_2 salt in H_2O), is obtained similarly. *l*-Aspartic acid and *r*-α-bromo*iso*valeryl-*l*-asparagine yield a product from which impure (III) is fractionated.

E. W. W.

S-Cysteinosuccinic acid. E. J. Morgan and E. Friedmann (Biochem. J., 1938, **32**, 2296—2298; cf. A., 1938, III, 614).—The amorphous reaction

product from *l*-cysteine and maleic acid (cf. A., 1938, II, 216) separates from MeOH to give *S-cysteinosuccinic acid*, m.p. 134—135° (decomp.) after softening at 102°, $[\alpha]_D$ −29·8° in H_2O, racemised by boiling AcOH. *S*-Glutathionosuccinic acid (*loc. cit.*) with boiling 25% H_2SO_4 gives partly racemised *S*-cysteinosuccinic acid. The inhibition by maleic acid of enzyme reactions induced by SH-compounds may be due to the above type of reaction. J. L. D.

Synthesis of natural creatinephosphoric acid. K. Zeile and G. Fawaz (Z. physiol. Chem., 1938, **256**, 193—196; cf. A., 1939, II, 11).—Creatine at 0° in aq. NaOH with $POCl_3$ gives a 28% yield of creatinephosphoric acid (separated as Ca salt, $C_4H_8O_5N_3PCa,4H_2O$) identical with the natural acid. W. McC.

New derivatives of the silyl radical. H. J. Emeléus and N. Miller (Nature, 1938, **142**, 996—997).—SiH_3Cl reacts spontaneously with NH_2Me or NH_2Et to give *methyl-*, $NMe(SiH_3)_2$, b.p. 32·3°, or *ethyl-disilylamine*, b.p. 65·9°, which are stable in air, but are quantitatively hydrolysed by alkali, and decomposed by HCl. Cold NMe_3 and SiH_3Cl yield a stable *solid*, NMe_3,SiH_3Cl (I), decomposed by H_2O to disiloxane and NMe_3,HCl. In moist air the final products are silicic acid and NMe_3,HCl, but the intermediate products give solutions with strong reducing properties. (I) is hydrolysed $NMe_3,SiH_3Cl + 3NaOH = Na_2SiO_3 + NaCl + NMe_3 + 3H_2$. (I) is a convenient silylating agent; *e.g.*, with alcohols it forms volatile silyl alkyl ethers, which can easily be isolated. At room temp. SiH_3Cl and $NHMe_2$ give the *compound*, $NSiH_3Me_2$, which appears to form an unstable quaternary salt with excess of SiH_3Cl. L. S. T.

Alkyl and aryl esters of orthosilicic acid. III. Synthesis of triethoxyallylmonosilane. K. Andrianov and M. Kamenskaja (J. Gen. Chem. Russ., 1938, **8**, 969—971).—CH_2:CH·CH_2Br, Mg, and $Si(OEt)_4$ yield *triethoxyallylmonosilane*, b.p. 172—178°. R. T.

Course of reaction giving rise to acetylenebismagnesium bromide.—See A., 1939, I, 85.

Complexes of magnesium chloride with organic oxygen compounds. A. S. Osokin (J. Gen. Chem. Russ., 1938, **8**, 583—587).—The following *compounds* are obtained by heating anhyd. $MgCl_2$ with anhyd. org. compounds containing O in C_6H_6 or light petroleum: $MgCl_2,6C_5H_{11}$·OH, $MgCl_2,2COMe_2$, $MgCl_2$,furfuraldehyde, $MgCl_2,10Bu^aCO_2H$, $MgCl_2,2C_5H_{11}$·OAc, $MgCl_2,12Ac_2O$. R. T.

Action of magnesium *tert.*-butyl chloride with acetyl chloride. F. C. Whitmore and W. R. Wheeler (J. Amer. Chem. Soc., 1938, **60**, 2899—2900).—Addition of $MgBu^\gamma Cl$ to an excess of AcCl in Et_2O gives $COMeBu^\gamma$ (I) 17, $CHMeBu^\gamma$·OAc 8, EtOAc 9, *iso*-C_4H_8 6·6, mesityl oxide (II) (origin unknown) 6·6, and *iso*-C_4H_{10} [probably derived by reaction of (I) and (II) with $MgBu^\gamma Cl$] 23·6%. The EtOAc is proved to be formed from the AcCl and Et_2O under the influence of the anhyd. $MgCl_2$ formed. R. S. C.

Activity of cadmium ion in organic salts of cadmium.—See A., 1939, I, 80.

Mechanism of oxidation of organic substances with selenium dioxide. III. Oxidation of metallo-organic compounds. N. N. Melnikov and M. S. Rokitzkaja (J. Gen. Chem. Russ., 1938, **8**, 834—838).—SeO_2 and HgR_2 yield $(HgR)_2SeO_3$ (R = Et; R = *Pr*, decomp. 220—230°; R = *Bu*, decomp. 172°; R = iso-C_5H_{11}, decomp. 240—250°). MPh_3 (M = P, As, Sb) reacts: $3MPh_3 + SeO_2 \rightarrow 2MPhO + MPh_2Se$. R. T.

Tetramethylplatinum and hexamethyldiplatinum. H. Gilman and M. Lichtenwalter (J. Amer. Chem. Soc., 1938, **60**, 3085—3086).—*Tetramethylplatinum*, cryst., obtained in 46% yield from $PtMe_3I$ and NaMe or as a by-product from $PtCl_4$ and MgMeI, is converted into $PtMe_3Cl$ by HCl. *Hexamethyldiplatinum*, cryst., obtained in 60% yield from $PtMe_3I$ and K in C_6H_6, is converted by I in Et_2O into $PtMe_3I$. R. S. C.

Isomerism of platinum ethylene chlorides.—See A., 1939, I, 94.

Compounds of rhodium and iridium with dimethylglyoxime.—See A., 1939, I, 93.

Catalytic transformations of 2-methyl-1 : 2 : 2-di*cyclo*-Δ^5-heptene and of 2-methyl-1 : 2 : 2-di*cyclo*heptane. B. A. Kazanski and N. G. Tschernova (J. Gen. Chem. Russ., 1938, **8**, 651—653).—2-Methyl-[1 : 2 : 2]-di*cyclo*-Δ^5-heptene is converted into unidentified substances of high mol. wt. when passed over C–Pt at 300°; the catalyst is thereby inactivated. 2-Methyl-[1 : 2 : 2]-di*cyclo*heptane and H_2 yield when passed over C–Pt at 310° a mixture of paraffins and *cyclo*pentanes, together with small amounts of PhMe and *m*-xylene. R. T.

Hydrogenation of aromatic hydrocarbons by the action of calcium–ammonia. II. B. A. Kazanski and N. F. Gluschnev (J. Gen. Chem. Russ., 1938, **8**, 642—650; cf. A., 1937, II, 489).—$Ca(NH_3)_6$ reduces PhMe, PhEt, *o*-, *m*-, and *p*-xylene, *s*-$C_6H_3Me_3$, tetrahydronaphthalene, or $\Delta^{1:4}$-*cyclo*hexadiene at room temp. to 1-methyl-, 1-ethyl-, 1 : 2-(+1 : 6-), 1 : 3-, and 1 : 4-dimethyl-, and 1 : 3 : 5-trimethyl-Δ^1-*cyclo*hexene, $\Delta^{1:9}$- and $\Delta^{9:10}$-octahydronaphthalene, or *cyclo*hexene, respectively. R. T.

Possibility of existence of cyclic systems having a triple linking. II. Synthesis of *cyclo*octinene. N. A. Domnin (J. Gen. Chem. Russ., 1938, **8**, 851—868).—*cyclo*Octanone and PCl_5 in light petroleum at >40° yield 1-*chloro*-Δ^1-cyclo*octene*, b.p. 64—68°/10 mm., the dibromide of which when heated with 20% KOH in EtOH gives 1-*chloro*-2-*bromo*-Δ^1-cyclo*octene*, b.p. 96—100°/3 mm. This with Na in Et_2O (6 days at room temp.) affords cyclo*octinene* (I), b.p. 72—76°/100 mm.; small amounts of a *dimeride*, b.p. 100—105°/3 mm., of (I), and of tri(hexamethylene)-benzene are also formed. R. T.

Compound of aluminium bromide with benzene.—See A., 1939, I, 81.

Kinetics of cracking of aromatic hydrocarbons under pressure.—See A., 1939, I, 85.

Photochemical addition of bromine to bromobenzene.—See A., 1939, I, 89.

New aromatic fluoro-derivatives. (Mme.) A. C. de Degiorgi and E. V. Zappi (Bull. Soc. chim., 1938, [v], **5**, 1441—1446).—An account of work previously reviewed (A., 1938, II, 482). A. T. P.

Dehydrogenation of 1-vinyl-Δ³-*cyclo*hexene. J. M. Slobodin and P. N. Krasnobaeva (J. Gen. Chem. Russ., 1938, **8**, 738—739).—1-Vinyl-Δ³-*cyclo*hexene passed over a Ni–Al_2O_3 catalyst at 300—320° yields chiefly PhEt with traces of styrene. R. T.

Hydrogen fluoride as condensing agent. II. Alkylation of benzene by olefines. III. Alkylation of aromatic [compounds] with aliphatic halides. J. H. Simon and S. Archer. **IV. Reaction of *cyclo*propane with benzene.** J. H. Simons, S. Archer, and (Miss) E. Adams. **V. Reactions of compounds containing oxygen and reactions of tertiary halides with olefines.** J. H. Simons, S. Archer, and H. J. Passino (J. Amer. Chem. Soc., 1938, **60**, 2952—2953, 2953—2954, 2955—2956, 2956—2957; cf. A., 1938, II, 225).—II. C_6H_6 with "relatively dry" HF and C_3H_6, $CH_2{:}CMe_2$, $CHMe{:}CHEt$, $CHMe{:}CMe_2$, or *cyclo*hexene gives $PhPr^{\beta}$ (84), $PhBu^{\gamma}$ (44) + $C_6H_4Bu^{\gamma}_2$ (41), m.p. 77—78°, (?β- + γ-)$C_5H_{11}Ph$ (47), $CPhMe_2Et$ (21) + $C_6H_4(CMe_2Et)_2$ (60), and *cyclo*hexylbenzene (62%), respectively. Polymerisation and addition of HF may also occur, but were not detected.

III. With $Bu^{\gamma}Cl$ or CMe_2EtCl and HF at 0°/1 atm. C_6H_6 gives $PhBu^{\gamma}$ (10) + $C_6H_4Bu^{\gamma}_2$ (60) and $CPhMe_2Et$ (41·5) + $C_6H_4(CMe_2Et)_2$ (21·5%), respectively. $C_{10}H_8$ in CCl_4 gives similarly $C_{10}H_7Bu^{\gamma}$, b.p. 142—143°/14 mm. (46%), and two $C_{10}H_6Bu^{\gamma}_2$, m.p. 148° (8%) and m.p. 80—81° (28%). PhMe, $Bu^{\gamma}Cl$, and HF give 75% of *p*-$C_6H_4MeBu^{\gamma}$. $Pr^{\beta}Cl$, C_6H_6, and HF react at 25°, giving a small yield of poly*iso*propylbenzenes, b.p. 155—175°/740 mm. $Pr^{\alpha}Br$, HF, and C_6H_6 react only at 80°, giving 48% of a mixture of $PhPr^{\alpha}$ (12%) and $PhPr^{\beta}$ (88%).

IV. C_6H_6, *cyclo*propane, and HF give $PhPr^{\alpha}$ (42), $C_6H_4Pr^{\alpha}_2$ (20), and $C_6H_3Pr^{\alpha}_3$ (3%). Pr^{β} derivatives are not formed, which indicates that the reaction mechanism is ionic. $PhPr^{\alpha}$ and $PhPr^{\beta}$ are distinguished by their sulphonamides, m.p. 102·5° and 98°, respectively (eutectic, 57 : 43, m.p. 73°).

V. $Bu^{\gamma}Cl$, $CHMe{:}CMe_2$, and HF give a mixture, including 18% of an olefinic product, b.p. 63—65°/19 mm. $Bu^{\gamma}Cl$, *cyclo*hexene, and HF give 31% of an unsaturated product, b.p. 40—42°/18 mm., 141·5—142°/739 mm., and <10% of tri*iso*butene. With much HF, C_6H_6 and $Bu^{\gamma}OH$ give 3% of $PhBu^{\gamma}$ and 8% of $C_6H_4Bu^{\gamma}_2$, m.p. 78—78·5°. $Bu^{\gamma}Cl$ and PhOH give 85% of *p*-$C_6H_4Bu^{\gamma}{\cdot}OH$, and $Bu^{\gamma}Cl$ and Et furoate give 54% of Et 5-*tert.*-butyl-2-furoate, b.p. 116—117°/16 mm. HF owes its catalytic ability to (*a*) its proton-donating properties, (*b*) its ability to add to org. compounds to give complexes, and (*c*) loss of F from C–F owing to the high energy of formation of HF. R. S. C.

Condensation of aliphatic alcohols with aromatic compounds in the presence of aluminium chloride. II. Tertiary aliphatic alcohols and benzene. R. C. Huston, W. B. Fox, and M. N. Binder (J. Org. Chem., 1938, **3**, 251—260; cf. A., 1936, 602).—Aliphatic *tert.* alcohols condense readily with C_6H_6 in presence of $AlCl_3$ to give *tert.*-alkylbenzenes, but, if branching of the chain occurs at the C next to the C·OH, the yield is lowered owing to the tendency to form olefines and chlorides. The reaction was studied with $Bu^{\gamma}OH$, $CMe_2Et{\cdot}OH$, three *tert.*-$C_6H_{13}{\cdot}OH$, and seven *tert.*-$C_7H_{15}{\cdot}OH$. B.p., [*M*], *d*, and parachors are reported for all the products; relationships are discussed; in general they follow accepted rules. The following are new. β-*Phenyl*-β*γ-dimethyl*-, b.p. 86—87°/15 mm., and -β*γγ-trimethyl*-n-*butane*, b.p. 105—108°/20 mm.; β-*phenyl*-β*γ-dimethyl*-n-*pentane*, b.p. 105—107°/20 mm.; β-*phenyl*-β-*methyl*-n-*hexane*, b.p. 106—109°/20 mm. β-Phenyl-β-ethyl- and γ-phenyl-γ-ethyl-*n*-pentane have b.p. 106—107°/20 mm. and 107—108°/20 mm. (225—226°/745 mm.), respectively (cf. lit.). R. S. C.

Products of condensation of benzene with *cyclo*pentene in presence of aluminium chloride. S. S. Nametkin and E. S. Pokrovskaja (J. Gen. Chem. Russ., 1938, **8**, 699—713).—*cyclo*Pentene (I) and C_6H_6 in presence of $AlCl_3$ yield *cyclo*pentyl- (II), p- (III), m.p. 42—43°, and m-*dicyclopentyl*- (IV), b.p. 154—156°/4 mm., and 1 : 3 : 5-*tricyclopentylbenzene* (V), m.p. 60—61°. (III) and (IV) are also prepared from (I) and (II), and (V) from (I) and (IV), a liquid *isomeride* of (V), b.p. 191—193°/4 mm., also being formed. (II) and excess of (I) yield *tetracyclopentylbenzene*, m.p. 200—201°. Hydrogenation of the products (active C catalyst, at 180°) yields: from (II) *cyclo*pentyl*cyclo*hexane, and from (III), (IV), and (V) respectively 1 : 4-, m.p. 86—86·5°, and 1 : 3-*di*-, b.p. 146—148°/4 mm. m.p. 28—29°, and 1 : 3 : 5-*tri*-*cyclopentyl*cyclo*hexane*, b.p. 194—195°/4 mm., m.p. 20—21°. The solubilities of the above products in H_2SO_4 of different concns., lævulic acid, light petroleum, and $C_2H_4Cl_2$ are determined. R. T.

Action of aromatic diazo-compounds on unsaturated compounds. IV. Aromatic and aromatic-aliphatic hydrocarbons. A. P. Terentiev and L. L. Gomberg (J. Gen. Chem. Russ., 1938, **8**, 662—668).—Styrene and dimethylstyrene do not react with diazotised *p*- or 2 : 4-di-nitroaniline; the latter gives a *compound*, m.p. 110—112° (decomp.), with indene. R. T.

Structure and absorption spectra of polymerides of aromatic compounds having a propenyl or *iso*propenyl side-chain.—See A., 1939, I, 7.

Isomeric change in stilbenes.—See A., 1939, I, 86.

Application of the electronic theory to organic chemistry. IX. Mechanism of the reaction of formation of naphthalene from 1-nitronaphthalene. A. M. Berkenheim and M. P. Filimonov (J. Gen. Chem. Russ., 1938, **8**, 608—624).—The reaction between 1-$C_{10}H_7{\cdot}NO_2$ (I) and $(NH_4)_2SO_3$ (II) is shown, on theoretical grounds, to proceed thus: (I) + (II) → 1-$C_{10}H_7{\cdot}SO_3NH_4$ (III) + NH_4NO_2; (III) + H_2O → $C_{10}H_8$ + NH_4HSO_4; (I) + (II) → α-$C_{10}H_7{\cdot}NH{\cdot}SO_3NH_4$ (IV) → 1 : 4-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3NH_4$ (V) → (+H_2O) $C_{10}H_7{\cdot}NH_2$ (VI) + NH_4HSO_4. This mechanism is confirmed by the following observations: the yield of (IV) falls from 60% to nil from the 2nd to the 22nd hr. of heating the reaction mixture; over

the same period that of (V) rises from 7 to a max. of 50%, thereafter falling at the same rate as that of (VI) rises. Max. production of $C_{10}H_8$ takes place between the 12th and 15th hr. of reaction, while (I) and (II) are still present in significant amounts. $C_{10}H_8$ is not obtained from 1-$C_{10}H_7$·NO or α-$C_{10}H_7$·NH·OH and (II) under the conditions of the above reaction. Each of the above constituent reactions was realised experimentally, with the exception of the rearrangement of (IV) to (V). R. T.

Spectrographic studies by means of corrected Hartley figures. *meso*-Derivatives of anthracene. C. Dufraisse and J. Houpillart (Bull. Soc. chim., 1938, [v], **5**, 1633—1637; cf. A., 1938, I, 373).—Data are recorded for the 9 : 10-Br_2-, -$(NO_2)_2$-, and -$(OMe)_2$-, and 10-iodo-9-phenyl derivatives, and for 9-phenylanthracene-10-carboxylic acid and its Me ester. C. R. H.

Spectrographic investigation of the "active" forms of 9 : 10-diphenylanthracene. C. Dufraisse and J. Houpillart (Bull. Soc. chim., 1938, [v], **5**, 1628—1633).—The yellow colour obtained by heating solutions of the compound is not due to radical formation (cf. Ingold and Marshall, A., 1927, 141), but to an increase in absorptive power with rise in temp. If new mols. are formed they are insufficient to affect the visible spectrum. C. R. H.

Phenanthrene series. XX. Nitration of 9 : 10-dihydrophenanthrene. J. W. Krueger and E. Mosettig (J. Org. Chem., 1938, **3**, 340—346).—9 : 10-Dihydrophenanthrene and HNO_3 (*d* 1·5) in AcOH at 29—33° give 65% of the 2-, m.p. 81—82°, and 3—4% of the 4-NO_2-derivative, m.p. 97—98° (resistant to CrO_3). H_2–PtO_2 in EtOH then yields the 2-, m.p. 49—52° (converted into the known 2-OH-compound), and 4-NH_2-derivative (I), m.p. 53—54° (corr.) [*hydrochloride*, m.p. 270—273° (decomp.; vac.; corr.)]. With NO·SO_4H (I) yields the diazonium sulphate, converted by hot H_2O into 4-*hydroxy*-9 : 10-*dihydrophenanthrene*, m.p. 72—74° (corr.), the oily Me ether of which with Pd-black at 300° in N_2 gives only a little phenanthrene. The Ac_2 derivative, m.p. 100—103°, of (I) with Pd-black in N_2 gives 4-*acetamidophenanthrene*, m.p. 196—197°, hydrolysed to 4-aminophenanthrene, m.p. 62·5—63·5° (lit., 104—105°) [Bz derivative, m.p. 216—218° (corr.)], which yields the known 4-OH- and 4-OMe-derivatives. Attempts to prepare a naphthoquinoline from (I) by the Skraup reaction failed. R. S. C.

Mechanism of aromatic bromination. C. C. Price and C. E. Arntzen (J. Amer. Chem. Soc., 1938, **60**, 2835—2837).—Determination of Br and acid shows that bromination of phenanthrene (I), when catalysed by I in the dark, follows the equation, $d[C_{14}H_9Br]/dt = k[C_{14}H_{10}][Br]^{1\cdot5}[I_2]^{2\cdot5}$, *k* being 6·7—5·4 × 10^{-6}. Bromination of (I) thus exactly resembles that of C_6H_6 (cf. A., 1937, II, 12). Both involve addition of Br^+, followed by elimination of H· under the influence of the catalyst (cf. *loc. cit.*). The reaction rate decreases with larger amounts of I, probably due to removal of Br by the reaction, $Br_2 + 2I \rightleftharpoons 2BrI$; this assumption leads to K_{IBr} = 15—30, in good agreement with the val. (19·9) calc. by extrapolation from Bodenstein and Schmidt's expression (A., 1926, 1100). R. S. C.

Reaction of bromine with various samples of phenanthrene. C. C. Price, C. E. Arntzen, and C. Weaver (J. Amer. Chem. Soc., 1938, **60**, 2837—2839).—Pure phenanthrene (*A*), m.p. 99—99·5°, is readily obtained from crude material by conversion into the dibromide and treatment thereof with Zn dust in EtOH at 50—60°. With Se at 300—320° this gives a material (*B*), m.p. 99·5—100°. With Br (at. reaction) (*B*) reacts only very slowly [cf. the synthetic material of Fieser *et al.* (A., 1936, 203), also prepared by Se]. In presence of anthracene in the dark 1 mol. of Br reacts with (*A*) or (*B*) for each mol. reacting with the anthracene. (*B*) inhibits the at. chain reaction of Br with other samples. Thus, Se treatment introduces an inhibitor, which breaks the chain. R. S. C.

Synthesis of phenanthrene derivatives. I. 9-Phenyl- and 9-*p*-tolyl-phenanthrene. C. K. Bradsher and A. K. Schneider (J. Amer. Chem. Soc., 1938, **60**, 2960—2962).—9-Substituted phenanthrenes are prepared by elimination of H_2O + ROH from *o*-C_6H_4Ph·CAr(OH)·CH_2·OR. *o*-C_6H_4Ph·MgI (I) and OMe·CH_2·CN in Et_2O–C_6H_6 give 2-ω-*methoxyacetyldiphenyl*, b.p. 159—162°/4 mm., converted by MgArBr into 2-α-*hydroxy*-β-*methoxy*-α-*phenyl*- and -α-p-*tolyl*-*ethyldiphenyl*, oils, which in conc. H_2SO_4 at room temp. give 9-phenyl- (II), m.p. 104—105° (picrate, m.p. 114°), and 9-p-*tolyl*-*phenanthrene*, m.p. 90—91° (*picrate*, m.p. 126—127°). COPh·CH_2·OPh and (I) in Et_2O–C_6H_6 give 2-α-*hydroxy*-β-*phenoxy*-α-*phenylethyldiphenyl*, m.p. 94—95°, converted into (II) by HBr–AcOH, but by conc. H_2SO_4 at 100° into a *substance*, $C_{26}H_{20}O$, m.p. 150—152°. R. S. C.

Preparation of $\Delta^{3:5}$-cholestadiene. K. Hattori (J. Amer. Chem. Soc., 1938, **60**, 3082).—ψ-Cholestene dibromide and $AgNO_3$ in C_5H_5N give $\Delta^{3:5}$-cholestadiene, m.p. 79—80°, $[\alpha]_D^{25}$ −68·7° (cf. Stavely *et al.*, A., 1937, II, 289). R. S. C.

Synthesis of 2 : 6 : 8 : 12-tetraphenyl-5 : 11-di-*p*-diphenylylnaphthacene and its photo-oxide. D. Duveen and A. Willemart (Compt. rend., 1938, **207**, 1226—1227; cf. A., 1936, 1499).—*p*-LiC_6H_4Ph with CPh:C·CO_2Me affords γ-*phenyl*-αα-*di*-p-*diphenylylpropargyl alcohol*, m.p. 143°, converted by PCl_3 into an unstable chloride which, when heated, loses HCl and dimerises to form 2 : 6 : 8 : 12-*tetraphenyl*-5 : 11-*di*-p-*diphenylylnaphthacene* (I), m.p. 320° and 380° after solidification. This is thermochromic in the solid state, shows absorption max. (in C_6H_6) at 5450, 5100, and 4800 A., and when insolated in solution forms a *photo*-5 : 12-*oxide*, $C_{66}H_{44}O_2$, which when heated loses O_2 (70%) and regenerates (I). J. L. D.

Synthesis of chrysene derivatives. M. S. Newman (J. Amer. Chem. Soc., 1938, **60**, 2947—2951).—General methods of preparing 2-substituted chrysene derivatives are described. Prep. of CH_2Bz·CHPh·CN from COPh·CH:CHPh and KCN is improved. CH_2Bz·CH_2·CO_2H, prepared therefrom by way of the Me ester, is reduced (Zn–Hg–HCl) to Ph·$[CH_2]_2$·CHPh·CO_2H, the chloride (prep. by PCl_5) of which with $AlCl_3$–C_6H_6 gives 87% of 1-*keto*-2-

phenyl-1 : 2 : 3 : 4-*tetrahydronaphthalene* (I), m.p. 76·2—77° [*semicarbazone*, m.p. 250—251·4° (decomp.; sinters at 245°)], converted by Zn–$CH_2Br·CO_2Et$ in C_6H_6 into 2-*phenyl*-3 : 4-*dihydro*-1-*naphthylacetic acid* (II), m.p. 156·2—156·8° [does not give (I) with O_3]. H_2–Pt or –Pd, Zn–Hg–HCl, and HI–P do not affect (II), but cis-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid* (III), m.p. 172—172·8° (and its isomeride), is obtained in 62% yield by 2% Na–Hg in aq. EtOH if the (II) used was recovered from an unsuccessful catalytic hydrogenation, but not otherwise. With PCl_5, followed by $AlCl_3$–C_6H_6, (III) gives cis-8-*keto*-1 : 2 : 7 : 8 : 1*a* : 7*a*-*hexahydrochrysene* (IV), m.p. 75·8—76·8° [*semicarbazone*, m.p. 255—258° (decomp.; sinters at 251°)], reduced (Clemmensen) to the known *cis*-hexahydrochrysene, m.p. 74·4—75·8° (Ramage *et al.*, A., 1933, 828). This proves the *cis*-structure of (III) and (IV). With MgMeBr, (IV) gives a carbinol, dehydrated at 220°, and then dehydrogenated by S at 230° to 2-*methylchrysene* (V) (82% yield), m.p. 161—161·4° (*picrate*, m.p. 170—170·6°). $Na_2Cr_2O_7$–AcOH then gives 2-*methylchrysene*-7 : 8-*quinone*, m.p. variable between 210—212° (decomp.) and 218—220° [not depressed by admixture with chrysenequinone (VI)], which with *o*-$C_6H_4(NH_2)_2$ yields a *phenazine* derivative, m.p. 220—221° [depressed by admixture with the *phenazine* derivative, m.p. 215—216°, from (VI)]. Sen-Gupta's (V) (A., 1937, II, 94; described as 6-derivative) may have been 3-methyl-1 : 2-benzanthracene. MgEtBr and (IV) yield similarly 2-ethylchrysene, m.p. 126·4—126·8° (*picrate*, m.p. 136·2—136·8°). S at 220—225° dehydrogenates (II) to 2-*phenyl*-1-*naphthylacetic acid*, m.p. 192—193°, which with a little $ZnCl_2$ in AcOH–Ac_2O gives 2-*chrysenyl acetate* (VII), m.p. 158·6—159·2°, hydrolysed by KOH–EtOH to 2-chrysenol, m.p. 248—250° (decomp. and sinters at 240°; lit., 240—242°) [Me ether, m.p. 127·2—127·8° (lit., 126°)]. With $ZnCl_2$–Ac_2O–AcOH (II) gives 7 : 8-*dihydro*-2-*chrysenyl acetate*, m.p. 95·6—96·2°, dehydrogenated to (VII) and hydrolysed to 7 : 8-*dihydro*-2-*chrysenol*, m.p. 156·2—156·6°. M.p. are corr. R. S. C.

Action of mixed organo-magnesium compounds on benzylimines. Preparation of secondary amines of the type CHRAr·NH·CH_2Ph. P. Grammaticakis (Compt. rend., 1938, **207**, 1224—1225; cf. A., 1905, i, 519).—Equimol. amounts of PhCHO and $CH_2Ph·NH_2$ in C_6H_6 afford *benzylidenebenzylamine*, b.p. 183°/10 mm., which with MgEtBr and MgPhBr affords *benzyl*-α-*phenylpropylamine* (I), b.p. 135°/<1 mm. [*hydrochloride*, m.p. ~168° (decomp.); *nitrate*, m.p. 146°; *sulphate*, m.p. 188°; *phenylcarbamyl* derivative, m.p. 89°], and *benzylbenzhydrylamine*, b.p. 181°/<1 mm. [*hydrochloride*, m.p. ~230° (decomp.); *nitrate*, m.p. 206°; *phenylcarbamyl*, m.p. 175°, and *Ac* derivative, m.p. 140°], respectively. p-*Tolylidene*-, b.p. 162°/<1 mm., and p-*anisylidene*-*benzylamine*, m.p. 40°, b.p. 204°/<1 mm., with MgEtBr afford *benzyl*-α-p-*tolylpropylamine* (II), b.p. 143°/<1 mm. [*hydrochloride*, m.p. ~204° (decomp.); *phenylcarbamyl* derivative, m.p. 100°], and *benzyl*-α-p-*anisylpropylamine* (III), b.p. 176°/<1 mm. [*hydrochloride*, m.p. ~191° (decomp.); *nitrate*, m.p. 129°; *sulphate*, m.p. 140°; *phenylcarbamyl* derivative, m.p. 124°], respectively. $CH_2Ph·N{:}CHEt$ with MgPhBr, *p*-$C_6H_4Me·MgBr$, and *p*-$OMe·C_6H_4·MgBr$ affords (I), (II), and (III), respectively. J. L. D.

Action of dimethylamine on 1 : 2-dibromo-1-methyl*cyclo*hexane. J. Gutman (Compt. rend., 1938, **207**, 1103—1104).—1 : 2-Dibromo-1-methyl*cyclo*hexane with $NHMe_2$ in C_6H_6 at room temp. or under pressure at 120—130° affords 2-*dimethylamino*-1-*methyl*-Δ⁶-cyclo*hexene* (I), b.p. 85°/90 mm. (*picrate*, m.p. 162—163°; *hydrochloride*, m.p. 134—135°), which with H_2–Ni-Cr gives *cis*- (II) (picrate, m.p. 218°) and *trans*-2-dimethylamino-1-methyl*cyclo*hexane (picrate, m.p. 156°). Electrolytic reduction of 2-methyl-Δ²-*cyclo*hexenoneoxime in H_2SO_4 affords a mixture of 2-amino-1-methyl-Δ⁶-*cyclo*hexene and *cis*-2-amino-1-methyl*cyclo*hexane which when methylated affords (I) and (II). J. L. D.

Sulphanilamide.—See B., 1939, 101.

Ethylenic isomerisation. IV. Stereoisomeric and chromoisomeric nitro- and amino-stilbenes. C. Weygand and R. Gabler (Ber., 1938, **71**, [*B*], 2474—2478).—Decarboxylation of *p*-$NO_2·C_6H_4·CH{:}CPh·CO_2H$ in quinoline containing Cu chromite at 230° gave, in a first instance, yellow *cis*-*p*-nitrostilbene (I), m.p. 65°. Three successive repetitions of the experiment, in which a possibly less highly purified quinoline was used, gave a red modification (II), m.p. 65° to a yellow liquid. (II) gives a pure yellow solution in light petroleum, Et_2O, $COMe_2$, or C_6H_6 and an orange solution in EtOH or $CHCl_3$. Irradiation of (II) as solid or in C_6H_6 causes a rapid and extensive isomerisation to the yellow *trans*-form. When isomerised by I in $PhNO_2$ at 200—210° (I) gives a yellow (III) and (II) affords (III) and a green (IV) *trans*-*p*-nitrostilbene, both of m.p. 155—156°, but giving solutions of different colour and having different solubilities. (III) and (IV) behave as true chemical isomerides rather than as chromoisomerides. A solution of (IV) in C_6H_6 becomes brownish-yellow when irradiated and leaves (III) when the solvent is removed. Solid (IV) is unchanged by light. Reduction of (I) or (II) by $FeSO_4$–NH_3 gives *cis*-*p*-aminostilbene (V), b.p. 147—150°/0·2 mm., isomerised by I in C_6H_6 into the *trans*-compound (VI). (V) and (VI) are condensed with 1 : 4-$OEt·C_{10}H_6·CHO$ to the corresponding Schiff's bases; only that derived from (VI) gives a cryst. liquid phase, thereby establishing its *trans*-structure. H. W.

Nitrosation of primary aromatic amines. L. Blangey (Helv. Chim. Acta, 1938, **21**, 1579—1608).—NH_2Ar which do not contain strongly negative substituents are not usually diazotised by $NO·SO_4H$ in conc. H_2SO_4. Those which couple directly with N_2-compounds to *p*-aminoazo-dyes are usually converted into *p*-nitrosoamines. The corresponding *sec.*-amines (*e.g.*, α-$C_{10}H_7·NHEt$) can be nitrosated in the nucleus in this manner. Addition of $NaNO_2$ to conc. H_2SO_4 at >10° followed by heating of the mixture to 60°, cooling to 0—5°, and addition of α-$C_{10}H_7·NH_2$ in CO_2 gives mainly 4-nitroso-α-naphthylamine (I), not quite pure, m.p. ~144—145° (decomp.), with 4 : 4′-di-

amino-1:1′-dinaphthyl and possibly $(NH_2)_2$-derivatives of 1:2′- or 2:2′-dinaphthyl. (I) is characterised by its reduction to 1:4-$C_{10}H_6(NH_2)_2$ and by the hydrolysis (dil. NaOH) of its salts to 4:1-$NH_2{\cdot}C_{10}H_6{\cdot}OH$. 1:6- and 1:7-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ similarly yield the corresponding 4-NO-derivatives, converted by boiling H_2O into the respective $NO{\cdot}C_{10}H_5(OH){\cdot}SO_3H$ and reduced to 1:4:6-$(NH_2)_2C_{10}H_5{\cdot}SO_3H$. 1:2- and 1:8-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ react similarly but less smoothly since the former undergoes more marked oxidation to naphthidine-3:3′-disulphonic acid and the latter is diazotised (on dilution) to some extent. 1:3- and 1:5-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ are not nitrosated but are diazotised to some extent. 1:4-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ loses SO_3H and gives 4:1-$NO{\cdot}C_{10}H_6{\cdot}NH_2$ in good yield. β-$C_{10}H_7{\cdot}NH_2$ is neither nitrosated nor diazotised and the gradual consumption of $NO{\cdot}SO_4H$ is unexplained. NH_2Ph is probably transformed into *p*-$NO{\cdot}C_6H_4{\cdot}NH_2$ which immediately undergoes further change. *o*-$C_6H_4Me{\cdot}NH_2$ behaves similarly whereas *p*-$C_6H_4Me{\cdot}NH_2$ resembles β-$C_{10}H_7{\cdot}NH_2$. Nitrosation occurs particularly smoothly with *p*-xylidine (from which small amounts of *p*-xyloquinone are formed by oxidation), *m*-$OMe{\cdot}C_6H_4{\cdot}NH_2$, and 2:1:4-$NH_2{\cdot}C_6H_3Me{\cdot}OMe$, less readily with *m*-$C_6H_4Me{\cdot}NH_2$ and 3:1:4-$NH_2{\cdot}C_6H_3Me{\cdot}OMe$. *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$ appears to afford a NO-derivative. 2:1:4-$NH_2{\cdot}C_6H_3Me{\cdot}NHAc$ is smoothly diazotised without giving a trace of NO-derivative. The mechanism of the reaction is not elucidated but an intermediate production of *N*-NO-derivatives is excluded.

H. W.

Action of ammonia and aromatic amines on ω-nitro-4-methylstyrene and related compounds. D. E. Worrall (J. Amer. Chem. Soc., 1938, **60**, 2841—2844).—Alkyl in the ring of ω-nitrostyrenes prevents addition of NH_3 or primary bases (*A*), but does not stop polymerisation. Alkyl or halogen in the side-chain hinders addition and stops polymerisation. Ph in the side-chain stops both reactions. NO_2 in the ring partly restores ability for addition without affecting polymerisation. ω-*Nitro*-p-*methylstyrene* (I), m.p. 102° (from *p*-$C_6H_4Me{\cdot}CHO$, $MeNO_2$, and $C_5H_{11}{\cdot}NH_2$), with NH_3 or (*A*) in warm EtOH gives a *polymeride*, decomp. >230°, but does not react in dry C_6H_6; with *p*-$C_6H_4(NH_2)_2$ in warm EtOH (not in C_6H_6) it gives the Schiff *base*, $C_{22}H_{20}N_2$, m.p. 188—189° (owing to hydrolysis), and with $C_5H_{11}{\cdot}NH_2$ alone it gives a tar, containing *p*-$C_6H_4Me{\cdot}CH{:}NC_5H_{11}$ and $MeNO_2$. The *dibromide*, m.p. 79—80°, of (I) is converted by KOAc–EtOH into (?) ω-*bromo*-ω-*nitro*-p-*methylstyrene* (II), m.p. 67—67·5° (2-, m.p. 82—83°, and 3-NO_2-, m.p. 105°, derivatives); the corresponding (?) ω-*Cl*-compound, m.p. 78—78·5° (3-NO_2-derivative, m.p. 107—108°), is similarly prepared. With fuming HNO_3 at <20° (I) gives 3:ω- (III), m.p. 121—122° (lit., 117—118°), and 2:ω-*dinitro*-4-*methylstyrene*, m.p. 96—97°. With NH_2Ph or $C_6H_4Me{\cdot}NH_2$ in EtOH (III) gives β-*nitro*-α-*anilino*-, m.p. 98—99°, or -α-p-*toluidino*-α-2-*nitro*-p-*tolylethane*, m.p. 135—136° (decomp.), respectively; *p*-$C_6H_4(NH_2)_2$ gives NN′-*di*-(β-*nitro*-α-2-*nitro*-p-*tolylethyl*)-p-*phenylenediamine*, m.p. 152—153° (decomp.). With NH_3 in dry C_6H_6 (III) gives *di*-(2:β-*dinitro*-α-p-*tolylethyl*)*amine*, m.p. 147° (decomp.). β-*Nitro*-α-p-*tolyl*-Δ$^{\alpha}$-*propene* [prep. using $EtNO_2$ as (I)], m.p. 55°, is nitrated to β:2-*dinitro*-α-p-*tolyl*-Δ$^{\alpha}$-*propene*, m.p. 72—73°, which with *p*-$C_6H_4Me{\cdot}NH_2$ affords β-*nitro*-α-p-*toluidino*-α-2-*nitro*-p-*tolylpropane*, m.p. 109—110° (decomp.), and with *p*-$C_6H_4(NH_2)_2$ gives a product, m.p. 254—255°, stable to alkali. *p*-$C_6H_4Me{\cdot}CH{:}CPh{\cdot}NO_2$ (?) and NH_3–EtOH followed by hydrolysis (HCl) give 3:5-*diphenyl*-4-p-*tolyl*isooxazolone *oxide* (IV), m.p. 171—172° (converted by KOH–EtOH into the iso*oxazole*, m.p. 198°), and a small amount of *dibenzoyl*-p-*tolylmethane* *monooxime*, m.p. 160—161°. With *p*-$C_6H_4Br{\cdot}CH_2{\cdot}NO_2$ and NH_3 in EtOH, (IV) yields 3-*phenyl*-5-p-*bromophenyl*-4-p-*tolyl*isooxazolone *oxide*, m.p. 182—183°, and thence the derived iso*oxazole*, m.p. 175. R. S. C.

Action of *p*-toluidine and *p*-phenylenediamine on substituted nitrostyrenes. D. E. Worrall and F. Benington (J. Amer. Chem. Soc., 1938, **60**, 2844—2845).—OH, OMe, or CH_2O_2 in the ring stops reaction of ω-nitrostyrenes with *p*-$C_6H_4Me{\cdot}NH_2$ or *p*-$C_6H_4(NH_2)_2$ (I), unless (sometimes) NO_2 is also present. Halogen in the ring also aids addition. ω-*Nitro*-o-*methoxystyrene* (obtained from $OMe{\cdot}C_6H_4{\cdot}CHO$, $MeNO_2$, and NEt_3 in EtOH), m.p. 50°, with fuming HNO_3 gives α:4-*dinitro*-β-o-*anisylethylene*, m.p. 175—176°. α:2-*Dinitro*-β-p-*anisylethylene*, m.p. 145—146°, is similarly prepared. Condensation with (I) yields NN′-*di*-(β-*nitro*-α-o-, m.p. 147°, -α-m-, m.p. 168°, and -α-p-*nitro*-, m.p. 172°, -α-4-*nitro*-2-*methoxy*-, m.p. 157—158°, and -α-4-*chloro*-2-*nitro*-*phenylethyl*)-p-*phenylenediamine*, m.p. 156—157°. β-*Nitro*-α-p-*toluidino*-α-4-*chloro*-2-*nitrophenylethane*, m.p. 136—137° (decomp.), is also prepared. R. S. C.

Action of aromatic amines on 2-chloro-4:ω-dinitrostyrene. D. E. Worrall (J. Amer. Chem. Soc., 1938, **60**, 2845—2846).—4:2:1-$NO_2{\cdot}C_6H_3Cl{\cdot}CH{:}CH{\cdot}NO_2$ adds bases more readily than does the 2:4:1-isomeride; in many cases it is more reactive than is $CHPh{:}CH{\cdot}NO_2$, but the oxidising effect due to the NO_2-groups prevents reaction with NH_2Ph or β-$C_{10}H_7{\cdot}NH{\cdot}NH_2$, causes tars to be formed with N_2H_4 or NH_2OH, and leads to destruction of the NH_3-addition product by EtOH. o-*Chloro*-ω-*nitrostyrene* (prep. by use of NEt_3), m.p. 48°, gives 2-*chloro*-4:ω-*dinitrostyrene*, m.p. 149—150°; addition of Br and subsequent elimination of HBr by KOAc–EtOH converts these compounds into α-*bromo*-α-*nitro*-β-o-*chloro*-, m.p. 132—133°, and -β-2-*chloro*-4-*nitro*-*phenylethylene*, m.p. 60—61°, respectively. Condensation with the appropriate base leads to α-*nitro*-β-o-, m.p. 117—118°, -m-, m.p. 127—128°, and -p-*toluidino*-, m.p. 130—131°, -β-p-*anisidino*-, m.p. 88—89°, -β-*phenylhydrazino*-, m.p. 133—134°, and -β-p-*tolylhydrazino*-, m.p. 127—128°, -β-2-*chloro*-4-*nitrophenylethane*, α-*bromo*-α-*nitro*-β-p-*toluidino*-β-2-*chloro*-4-*nitrophenylethane*, m.p. 138° (decomp.), NN′-*di*-(β-*nitro*-α-o-*chlorophenylethyl*)-p-*phenylenediamine*, m.p. 147—148° (decomp.), *di*-(β-*nitro*-α-2-*chloro*-4-*nitrophenylethyl*)*amine*, m.p. 118—119°, and NN′-*di*-(β-*nitro*-α-2-*chloro*-4-*nitrophenylethyl*)-p-*phenylenediamine*, m.p. 201—202°, and -*benzidine*, m.p. 137—138°. R. S. C.

Structure and mechanism of formation of the Bandrowski base. W. M. Lauer and C. J. Sunde

(J. Org. Chem., 1938, **3**, 261—264).—Bandrowski's base (A., 1894, i, 236), prepared by oxidation of *p*-$C_6H_4(NH_2)_2$, is 2 : 5-di-(*p*-aminoanilo)-1 : 4-phenylenediamine (cf. Green, J.C.S., 1913, **103**, 933), because with hot 10% HCl it gives 1·74 mols. of *p*-$C_6H_4(NH_2)_2$ and because its *diacetate*, m.p. 310—311° (converted by Ac_2O at 100° into the known tetra-acetate), is obtained from *p*-$C_6H_4(:NH)_2$ and *p*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$ (best 0·66 mol.) in H_2O or H_2O–MeOH–Et_2O–HCl at 0°. It is held to be formed by addition to give 2 : 1 : 4-(*p*-$NHAc{\cdot}C_6H_4{\cdot}NH)C_6H_3(NH_2)_2$, oxidation thereof to the di-imine, and further addition; formation of the base from *p*-$C_6H_4(NH_2)_2$ follows a similar route. R. S. C.

Stability of dithizone solutions.—See A., 1939, I, 98.

Synthesis of dinaphthylthiocarbazone, and formation of its intra-complex salts with heavy metals. I. B. Suprunovitsch (J. Gen. Chem. Russ., 1938, **8**, 839—843).—Naphthylhydrazine naphthylthiocarbazinate heated in CO_2 at 135° yields dinaphthylthiocarbazide, which with 5% KOH in EtOH gives the K salt of dinaphthylthiocarbazone (I). Solutions of (I) in $COMe_2$ give coloured ppts. with heavy metals (Cu, Ag, Au, Zn, Cd, Hg, Pb, Mn, Co, Ni); 0·06 μg. of Pb in 1 ml. of solution may be thus detected, as compared with 3 μg. with dithizone. R. T.

Diazotation, decomposition of diazo-compounds, and coupling of isomeric xylidines with *p*-nitrobenzenediazonium salts. V. R. Fedorov, A. A. Spriskov, and E. I. Scheludjakova (J. Gen. Chem. Russ., 1938, **8**, 844—850).—The velocity of diazotation at 0° rises in the series 1 : 3 : 4- < 1 : 2 : 4- < 1 : 4 : 2-$C_6H_3Me_2{\cdot}NH_2$; that of 1 : 3 : 2-$C_6H_3Me_2{\cdot}NH_2$ could not be measured, owing to decomp. of the diazonium salt at 0°. The velocity of decomp. of the diazo-compounds at 40° rises in the order 1 : 3 : 4- < 1 : 2 : 4- < 1 : 3 : 2- < 1 : 4 : 2-$C_6H_3Me_2{\cdot}NH_2$. 1 : 3 : 2- and 1 : 4 : 2-, but not 1 : 3 : 4- and 1 : 2 : 4-$C_6H_3Me_2{\cdot}NH_2$, can be coupled with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ in HCl at 18°. R. T.

Condensation of phenols with formaldehyde. E. Bureš and A. Masárek (Časopis českoslov. Lék., 1936, **16**, 177—188; Chem. Zentr., 1937, i, 1291).—The rate of reaction of the following ArOH (mol. amounts) with 40% CH_2O at 100° (bath) in presence of 1% of catalyst is: *m*- > *o*-cresol = PhOH (technical > pure) > *p*-cresol. The strongest bases and acids are the most active catalysts. PhOH and 40% CH_2O at 100° (bath)/50 hr. in absence of catalyst give resinous material from which H_2O extracts 2 : 4′-(I) (*dibenzoate*, m.p. 115°) and 4 : 4′-dihydroxydiphenylmethane (II) [*dibenzoate*, m.p. 156°; compound, m.p. 150° (decomp.), with $(CH_2)_6N_4$] and *o*-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$. (II) reacts slowly and (I) somewhat more quickly with CH_2O; alkaline catalysts lead to resins. Oxidation (air; alkaline $KMnO_4$) of (I), (II), and products therefrom (all of which couple with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$) gives brown, amorphous, alkali-sol. material. Nitration (method: Staedel, A., 1895, i, 232) of CH_2Ph_2 gives the 2 : 4′- and (mainly) 4 : 4′-$(NO_2)_2$-derivatives; the respective $(NH_2)_2$-compounds are converted (diazo-method) into (I) and (II). Saturated solutions of PhOH and $(CH_2)_6N_4$ in H_2O and EtOH afford the *compounds*, $(CH_2)_6N_4$,3PhOH, m.p. 124° (decomp.), and $(CH_2)_6N_4$,PhOH, m.p. 176·5° (decomp.), respectively; in $COMe_2$, cryst. compounds, m.p. 80°, 112°, 125°, and 160—161°, are formed. H. B.

Action of gaseous hydrogen chloride on 4-nitroso-α-naphthol and 4-nitrosoguaiacol. A. Angeletti and M. Pirona (Atti R. Accad. Sci. Torino, Cl. Sci. fis. mat. nat., 1936, **71**, I, 602—606; Chem. Zentr., 1937, i, 1138).—4 : 1-$NO{\cdot}C_{10}H_6{\cdot}OH$ (reacting as quinoneoxime) in cold Et_2O saturated with dry HCl gives NH_2OH and 2 : 3-dichloro-1 : 4-naphthaquinone. 4-Nitrosoguaiacol (OH = 1), however, similarly yields 3-*chloro*-4-*nitrosoguaiacol* (I), decomp. 255° (darkens 213°), and an amorphous violet substance, but no NH_2OH. Reduction ($SnCl_2$, conc. HCl) of (I) affords the 4-NH_2-compound, decomp. 160° (darkens 154°), the diazonium salt of which with cold conc. NaOH gives 3-*chloroguaiacol*, m.p. 32—33°. H. B.

Synthesis of derivatives of quinol related to dihydroflavoglaucin. J. H. Cruickshank and R. Robinson (J.C.S., 1938, 2064—2071).—Bu^aCOCl and *p*-$OMe{\cdot}C_6H_4{\cdot}OH$–$C_5H_5N$–$Et_2O$ give p-*anisyl valerate*, b.p. 150—152°/10 mm., converted by $AlCl_3$ at 100° (bath) into 2-*hydroxy*-5-*methoxy*-n-*valerophenone* (I), m.p. 62° (2 : 4-*dinitrophenylhydrazone*, m.p. 186°), also obtained from Bu^aCOCl–$AlCl_3$–CS_2 and *p*-$C_6H_4(OMe)_2$–CS_2. (I) and Zn–Hg in 20% HCl, boiled for 4 hr., afford 2-*hydroxy*-5-*methoxy*-n-*amylbenzene* (II), m.p. 44°, which with *n*-octoyl chloride (III) in C_5H_5N–Et_2O gives 4-*methoxy*-2-n-*amylphenyl octoate*, b.p. 167—171°/0·1 mm. This and $AlCl_3$ in H_2 at 100° (bath) afford 2-hydroxy-5-methoxy-3-*n*-amyloctophenone, b.p. 180—190°/0·1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 103°), attempted demethylation ($AlBr_3$, HBr, HI) of which gives only *n*-amylquinol. (II) and Me_2SO_4–20% NaOH–$COMe_2$ yield 2 : 5-*dimethoxy*-n-*amylbenzene*, b.p. 144—146°/12 mm., which with (III) and $AlCl_3$–CS_2 first at 0° and finally at the b.p. gives 2-*hydroxy*-5-*methoxy*-4-n-*amyloctophenone* (IV), m.p. 42° (2 : 4-*dinitrophenylhydrazone*, m.p. 117°), demethylated readily by $AlBr_3$–C_6H_6 to the 2 : 5-$(OH)_2$-derivative, m.p. 94° (2 : 4-*dinitrophenylhydrazone*, m.p. 112°). Successive reduction (Clemmensen), methylation (Me_2SO_4), and oxidation (AcOH–HNO_3) of (IV) gives 2-n-*amyl*-5-n-*octyl*-p-*benzoquinone* (V), m.p. 65°. The corresponding quinol is prepared from (V) and EtOH–$Na_2S_2O_4$. Quinol and $Bu^\beta COCl$ in C_5H_5N–Et_2O at 0°—room temp., give *quinol diiso-valerate*, m.p. 55°, which with quinol and $AlCl_3$ at 150—160° affords 2 : 5-*dihydroxy*isovalerophenone, m.p. 110°. The latter and CH_2PhCl–NaOEt–EtOH at 100° (bath) give 2-*hydroxy*-5-*benzyloxy*isovalerophenone, m.p. 60° ($NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$,HCl–$C_5H_5N$ or excess of N_2H_4,H_2O–AcOH gives the *ketazine*, m.p. 174°). *p*-$C_6H_4(OMe)_2$ and $Bu^\beta COCl$ with $AlCl_3$–CS_2 afford 2-hydroxy-5-methoxy- [*semicarbazone* (VI), m.p. 171°] and 2 : 5-*dimethoxy*-isovalerophenone (VII), b.p. 124—126°/1 mm. The latter is prepared pure from the crude reaction product and Me_2SO_4–10% NaOH–$COMe_2$. (VI) and NaOEt–EtOH at 180—185° give the corresponding *ketazine*, m.p. 144°. (VII) is

reduced (Clemmensen) to 2 : 5-*dimethoxyisoamylbenzene*, b.p. 100—102°/2 mm., converted by (III) and $AlCl_3$–CS_2 into 2-hydroxy-5-methoxy-4-*iso*amyloctophenone (2 : 4-*dinitrophenylhydrazone*, m.p. 146°). Heating of 2-hydroxy-5-allyloxyacetophenone, b.p. 123—125°/2 mm. (cf. Baker *et al.*, A., 1936, 474), gives 2 : 5-dihydroxy-6-allylacetophenone, which with H_2 (2—3 atm.) and Pd–$SrCO_3$ in EtOAc affords 2 : 5-*dihydroxy*-6-n-*propylacetophenone* (+H_2O), m.p. 88°, the CO of which is inert. 2 : 5-Dimethoxy-6-allylphenyl styryl ketone and $KMnO_4$ in boiling aq. NaOH give 3 : 6-dimethoxyphthalic anhydride. EtCOCl and p-$C_6H_4(OMe)_2$ give (Friedel–Crafts) an oil, reduced (Clemmensen) to 2 : 5-dihydroxy-*n*-propylbenzene, m.p. 87°; the corresponding 2 : 5-$(OMe)_2$-compound, b.p. 128—130°/20 mm. (NO_2-derivative, m.p. 64°), with AcCl–$AlCl_3$–CS_2 at 0° —100° (bath) gives 2-hydroxy-5-methoxy-4-*n*-propylacetophenone, b.p. 150—155°/1 mm., which with $AlBr_3$–C_6H_6 affords the corresponding 2 : 5-(OH)$_2$-compound, m.p. 85° (2 : 4-*dinitrophenylhydrazone*, m.p. 216°), and *n*-propylquinol. p-$C_6H_4(OMe)_2$ and (III) in CS_2–$AlCl_3$ at 0—100° (bath) afford *2-hydroxy-5-methoxyoctophenone*, m.p. 45° (2 : 4-*dinitrophenylhydrazone*, m.p. 134°), demethylated by $AlBr_3$–C_6H_6 to the 2 : 5-(OH)$_2$-compound (VIII), m.p. 86° (2 : 4-*dinitrophenylhydrazone*, m.p. 186°), converted by *n*-amyl bromide and NaOEt–EtOH into 2-hydroxy-5-*n*-amyloxyoctophenone, b.p. 190—195°/1·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 121°); the latter and $AlCl_3$–CS_2 at room temp. for 3 days give (VIII). A. T. P.

Synthesis of αβ-dichloro-α-*p*-anisylethane; conversion into β- and α-chloro-α-*p*-anisylethylene. R. Quelet and J. Allard (Compt. rend., 1938, **207**, 1109—1111; cf. A., 1936, 719).—PhOMe with $CH_2Cl{\cdot}CH(OEt)_2$ in conc. HCl saturated with HCl at 70° affords αβ-dichloro-α-*p*-anisylethane (I) and β-chloro-αα-di-*p*-anisylethane (II). The crude prep. when rapidly distilled at 100° (bath)/vac. and then treated with C_5H_5N at 115° affords β-chloro-α-*p*-anisylethylene [from (I)] and *s*-di-*p*-anisylethylene [from (II)]; with NaOEt or KOH–EtOH mainly α-*chloro*-α-p-*anisylethylene* (III), m.p. 35°, and some αα-di-*p*-anisylethylene result. (III) is easily hydrolysed to p-OMe·C_6H_4·COMe and readily oxidises in air to a red substance. J. L. D.

Natural ethers of phenols with prenologous alcohols. VIII. Constitution and synthesis of foeniculin. E. Späth and J. Bruck (Ber., 1938, **71**, [*B*], 2708—2711).—The occurrence of the residues $CMe_2{:}CH{\cdot}CH_2{\cdot}$ (I), $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}$, and Me·[$CMe{:}CH{\cdot}CH_2{\cdot}CH_2$]$_2$·$CMe{:}CH{\cdot}CH_2{\cdot}$ as side-chains of natural coumarins is noted and for (I) the name "prenyl" is suggested to indicate the close relationship to isoprene. Foeniculin (II), b.p. 147°/5 mm., m.p. (vac.) 23·5—24·5°, obtained by Takens (B., 1929, 910) from fennel and star anise oils, is $C_{14}H_{18}O$. It passes at 260° into *p*-anol (*p*-OH·C_6H_4·CH:CHMe) (III). It is hydrogenated (Pd sponge in MeOH) to *tetrahydrofoeniculin*, b.p. 100—110° (bath)/0·03 mm., converted by distillation with HI (*d* 1·7) into dihydro-*p*-anol (p-$C_6H_4Pr^{\alpha}$·OH) and *iso*amyl iodide. (II) is p-Δ^{α}-*propenylphenyl* γ-*methyl*-Δ^{β}-*butenyl ether* since it is obtained from (III) and $CMe_2{:}CH{\cdot}CH_2Br$. The ready hydrolysis of (II) by AcOH containing a little conc. H_2SO_4 is remarkable as is its instability to heat, whereby either migration of the prenyl residue from O to C occurs or elimination of isoprene is observed. H. W.

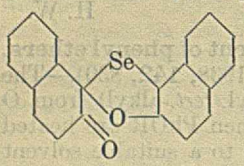
Mechanism of rearrangement of phenyl ethers. W. J. Hickinbottom (Nature, 1938, **142**, 830).—The migration of R (= CH_2Ph, allyl, *tert.*-alkyl) from O to the nucleus which occurs when PhOR are heated at the b.p., and its transference to a suitable solvent can be explained by assuming that R is first eliminated as a free radical. L. S. T.

Identification of naphthyl ethers as picrates. V. H. Dermer and O. C. Dermer (J. Org. Chem., 1938, **3**, 289—293).—The following, prepared from $C_{10}H_7$·OH, ROH, and H_2SO_4, or $C_{10}H_7$·ONa and RHal in EtOH, are purified by way of the picrates, the m.p. of which are given in parentheses (italics for new picrates). α-$C_{10}H_7$ Me, b.p. 271° (129·5—130·5°), Et, b.p. 280·5° (118·5—119°), Pr^{β}, b.p. 282·5° (*104·5—105·5°*), Pr^{α}, b.p. 293·5° (*99·5—100°*), *CHMeEt*, b.p. 293·5° (*100·5—101°*), Bu^{β}, b.p. 301·5° (*104·5—105·5°*), Bu^{α}, b.p. 308·5° (*85°*), *iso*amyl, b.p. 317·5° (*96—97°*), *n*-amyl, b.p. 322°, m.p. 30° (*75—75·5°*), CH_2Ph, m.p. 77—77·5° (decomp. *85—100°*), *$CH_2Ph{\cdot}CH_2$*, m.p. 72—72·5° (*117·5—118·5°*), and *allyl* (*100·5—101°*) *ether*; β-$C_{10}H_7$ Me, b.p. 273°, m.p. 72·5—73° (116·5—117°), Et, b.p. 282°, m.p. 35·5—36° (101—101·5°), Pr^{β}, b.p. 285°, m.p. 40° (95—95·5°), Pr^{α}, b.p. 297°, m.p. 39·5—40° (80·5—81·5°), CHMeEt, b.p. 298·5° (86—86·5°), Bu^{β}, b.p. 304·5°, m.p. 33—33·5° (84—85°), Bu^{α}, b.p. 309° (67—67·5°), *iso*amyl, b.p. 321°, m.p. 28—28·5° (93·5—94°), *n*-amyl, b.p. 327·5°, m.p. 24·5° (66·5—67°), CH_2Ph, m.p. 101·5—102° (123°), *$CH_2Ph{\cdot}CH_2$*, m.p. 70—70·5° [*83—84°* (sinters and turns red at 67·5°)], and *allyl*, m.p. 16° (*98·5—99°*), *ether*. Di-β-naphthyl methylene and ethylene ethers give no picrates. M.p., if not given, are <—10°. The picrates give satisfactory mixed m.p. depressions. Temp. are corr. R. S. C.

Derivatives of *o*-aminophenol. II. L. Galatis (J. pr. Chem., 1938, [ii], **151**, 331—341; cf. A., 1934, 183).—*N*-Acetyl-2-phenylbenzoxazoline (*loc. cit.*) with conc. HCl at room temp. gives 3 : 3′-*diacetamido*-4 : 4′-*dihydroxytriphenylmethane* (I), m.p. ~265° (decomp.) after darkening, which rapidly darkens on exposure to air; under precisely similar conditions it is obtained from *o*-NHAc·C_6H_4·OH and PhCHO. (I) is transformed by hot Ac_2O containing a little conc. H_2SO_4 into its *diacetate*, m.p. 240°, and by Me_2SO_4–10% NaOH into the *Me_4* derivative, $C_{27}H_{30}O_4N_2$, m.p. 220°. Boiling 20% HCl hydrolyses (I) to the 3 : 3′-(NH_2)$_2$-derivative, m.p. 193°. The presence of p-OH in (I) is established by the production of a dye when (I) is oxidised. H. W.

Covalent alkaline derivatives of di-2-hydroxy-1-naphthyl selenide and allied substances. V. Dvorkovitz and S. Smiles (J.C.S., 1938, 2022—2028; cf. A., 1937, II, 336).—Di-2-hydroxy-1-naphthyl selenide (I) [*Me ether*, m.p. 148°, from (II) (below) and MeOH–Me_2SO_4 at 35°] and N-NaOH (2 mols.) afford the yellow *Na* derivative (II) (+$4H_2O$), m.p. 270° (previous loss of H_2O); boiling $CHCl_3$ then gives the

colourless anhyd. *Na* salt, no m.p. KOH and LiOH similarly afford a yellow *K* derivative (which when dried at 15° forms a paler *dihydrate*, m.p. 170°), and a *Li* derivative ($+4H_2O$), no m.p., respectively. (I) (1 mol.) and $K_3Fe(CN)_6$ (2·2 mols.) in aq. KOH afford the *dehydro-selenide* (*A*), m.p. 145°. (I) or the corresponding sulphide forms unstable Cu derivatives. Covalent mono-alkali derivatives could not be obtained from di-2-hydroxy-1-naphthyl sulphoxide, sulphone, or di-sulphide (cf. *loc. cit.*). Di-2-chloro-5-hydroxy-*m*-4-xylyl sulphide (III) similarly gives *Na* ($+2H_2O$), *K* ($+2H_2O$), and *Li* ($+2H_2O$) derivatives; (III) and hot 1·5% aq. NaOH (1·1 mols.) afford an "*acid*" *Na* salt, $C_{16}H_{15}O_2Cl_2SNa$,$C_{16}H_{16}O_2ClS$. Under similar conditions, di-2-hydroxy-1-naphthyl sulphide (IV) or -naphthylmethane give the normal Na derivatives ($+4H_2O$), but (IV) and hot aq. KOH (1·2 mols.) give the *acid K* salt ($+2H_2O$), m.p. 200°. Di-6-chloro-3-hydroxy-2-*p*-xylyl sulphide affords *Na* ($+4H_2O$, m.p. 255°; $+2H_2O$, m.p. 255°, and anhyd.), *K* ($+2H_2O$), m.p. 260°, and *Li* derivatives ($+4H_2O$, m.p. 200°; converted in N_2 at 26° into the *dihydrate*). Di-5-hydroxy-6-*ψ*-cumyl sulphide similarly affords *Na* [$+4H_2O$, m.p. 245° (previous loss of H_2O), and $+2H_2O$], *Li* ($+4H_2O$ and $+2H_2O$, m.p. ~150°), and an *acid K* salt ($+2H_2O$), m.p. 223°. The *Li* derivative ($+4H_2O$) of di-5-hydroxy-6-*ψ*-cumylmethane is more stable than that of the sulphide. Di-6-chloro-3-hydroxy-2-cymyl sulphide affords *Na* ($+2H_2O$, m.p. 125°; unstable tetrahydrate), *K* ($+2H_2O$), m.p. 206°, and *Li* ($+2H_2O$), m.p. 95°, derivatives. 5-Chloro-*o*-4-xylenol and S_2Cl_2–$AlCl_3$–CS_2 for 24 hr. at 16° afford *di-5-chloro-4-hydroxy-o-3-xylyl sulphide*, m.p. 154° [*Na* derivative ($+4H_2O$)], converted by 2% aq. NaOCl–NaOH into the *dehydro*-derivative, m.p. ~115°. *o*-4-Xylenol and S_2Cl_2–$CHCl_3$ give *di-4-hydroxy-o-5-xylyl sulphide*, m.p. 157°, converted by SO_2Cl_2 in $CHCl_3$ at 15° into *di-3-chloro-4-hydroxy-o-5-xylyl sulphide*, m.p. 145°; neither sulphide affords a covalent Na or dehydro-derivative. *m*-5-Xylenol and S_2Cl_2–$CHCl_3$ give *di-5-hydroxy-m-2-xylyl sulphide*, m.p. 265°, and *-m-6-xylyl sulphide*, m.p. 149° (*acid Na* salt). Salicylideneacetophenone (1 mol.) also affords covalent *Na* ($+2H_2O$) (1 : 1 *adduct* with salicylaldehyde; the Na derivative of *p*-hydroxybenzylideneacetophenone does not yield an analogous adduct), *K* ($+2H_2O$), m.p. 175°, and *Li* ($+2H_2O$), m.p. 250° (decomp.), derivatives. Salicylideneacetone and NaOEt–EtOH–Et_2O afford the *Na* salt ($+4H_2O$) (1 : 1 *adduct* with salicylaldehyde). 2-Salicylidene-5-methyl*cyclo*hexanone affords *Na* ($+4H_2O$), m.p. 190° (after loss of some H_2O), *K* ($+xH_2O$), m.p. ~95° (also $+2H_2O$), and *Li* ($+4H_2O$) derivatives, m.p. ~235°.



(*A*.)

A. T. P.

Diene syntheses. X. Diene syntheses with αβ-unsaturated nitro-derivatives, sulphones, and thioethers. K. Alder, H. F. Rickert, and E. Windemuth (Ber., 1938, **71**, [*B*], 2451—2461).—CH_2:$CH{\cdot}NO_2$ behaves in diene additions in the same manner as CH_2:$CH{\cdot}CHO$ or CH_2:$CH{\cdot}CO_2H$ giving with *cyclo*pentadiene (I), in abs. Et_2O at 105—110°, 2-nitronorbornylene, hydrogenated (PtO_2 in AcOH) to 2-nitronorbornylane, which is reduced (Fe powder) to *endo*norbornylamine. Similarly (I) and $CHMe$:$CH{\cdot}NO_2$ in AcOH at 103° afford 2-nitro-3-methyl-Δ^5-norbornylene, b.p. 94—95°/14 mm., whence 2-nitro-, b.p. 101—102°/15 mm., 2-amino- (hydrochloride, m.p. 269°; picrate, m.p. 202—203°), and 2-*carbamido*-3-*methylnorbornylane*, m.p. 203°. α-Nitro-Δ^α-pentene (II) yields successively 2-nitro-3-*n*-propyl-Δ^5-norbornylene, b.p. 122—125°/14 mm., -norbornylane, b.p. 126°/14 mm., and 2-amino-3-*n*-propylnorbornylane (hydrochloride, m.p. 223°; *picrate*, m.p. 176°). 1-Nitro-2-*n*-propyl-Δ^4-*cyclo*hexene, b.p. 118°/11 mm., is derived from (II) and $(CH_2$:$CH{\cdot})_2$ (III) containing a little quinol at 100—110°, whilst $(CH_2$:$CMe{\cdot})_2$ (IV) affords 1-nitro-4 : 5-dimethyl-2-*n*-propyl-Δ^4-*cyclo*hexene, b.p. 146—147°/12 mm. αβ-Unsaturated sulphones at 140—150° add dienes according to the scheme of a diene synthesis. Thus *p*-tolyl vinyl sulphone and (IV) give 3 : 4-*dimethyl*-Δ^3-cyclo*hexenyl* p-*tolyl sulphone*, m.p. 82—83°. Δ^2-Butadienesulphone (V) is transformed by (III) into 1 : 2 : 3 : 6 : 7 : 8-*hexahydrothionaphthensulphone*, b.p. 131—133°/0·1 mm., m.p. 94—95°, by (IV) into 4 : 5-*dimethyl*-1 : 2 : 3 : 6 : 7 : 8-*hexahydrothionaphthensulphone*, m.p. 96°, and by (I) into 3 : 6-endo*methylene*-1 : 2 : 3 : 6 : 7 : 8-*hexahydrothionaphthensulphone* (VI), m.p. 141—142°, with the *compound*, $C_{14}H_{18}O_2S$, m.p. 218°, formed from 2 mols. of (I) and one of (V). PhN_3 and (VI) give isomeric *hydrotriazoles*, $C_{15}H_{17}O_2N_3S$, m.p. 187—188° and 200° (decomp.). *p*-$C_6H_4Me{\cdot}S{\cdot}CH$:$CH_2$ and (I) at 180—190° yield 2 : 5-endo*methylene*-Δ^3-cyclo*hexenyl* p-*tolyl sulphide*, b.p. 175—178°/11 mm.

H. W.

Magnesium pentamethylphenyl bromide. H. Clément (Compt. rend., 1938, **207**, 864—866; cf. A., 1937, II, 331; 1938, II, 275).—$C_6Me_5{\cdot}MgBr$ with MeCHO, CH_2O, and EtOBz affords some *pentamethylphenylmethylcarbinol*, m.p. 141° (*acetate*, m.p. 157°), *pentamethylbenzyl alcohol*, m.p. 136—137°, and pentamethylbenzophenone, m.p. 125°, respectively.

J. L. D

Reactions of epoxy-compounds with reagents. I. Interaction of epoxyphenylethane (styrene oxide) and magnesium aryl halides. M. S. Kharasch and H. G. Clapp (J. Org. Chem., 1938, **3**, 355—360).—Addition of epoxyphenylethane (I) to MgPhBr gives ββ-diphenylethyl alcohol (II), b.p. 125—135° (*oxalate*, m.p. 160·5°; 3 : 5-*dinitrobenzoate*, m.p. 135°), but addition of MgPhBr to (I) gives $CH_2Ph{\cdot}CHPh{\cdot}OH$; oxidation of the product to $COPh_2$ or BzOH indicates formation of a small amount of the isomeride in each case. *p*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ reacts similarly. (II) is synthesised by the following reactions (not detailed): $OH{\cdot}CH_2{\cdot}CO_2Et + 3MgPhBr \rightarrow C_6H_6 + OH{\cdot}CPh_2{\cdot}CH_2{\cdot}OH$ (III) + EtOH + 3MgBrOH; (III) in hot 0·5N-HCl gives $CHPh_2{\cdot}CHO$, hydrogenated (Pt) to (II). With P_2O_5 in C_6H_6, (II) gives $(CHPh$:$)_2$.

R. S. C.

Synthesis of alcoholic derivatives of the fatty series. I. Catalytic hydrogenation of phenylstearic acid under pressure. W. Kimura, T. Omura, and H. Taniguchi (Ber., 1938, **71**, [*B*], 2686—2687).—Oleic acid is converted by $AlCl_3$ and

C_6H_6 (free from S compounds) into ι-phenylstearic acid, reduced (300—310°/25—100 atm., Cu–Cr–Ba oxide catalyst) to κ-phenylstearyl alcohol, identified as the urethane. H. W.

Action of magnesium halide etherates on epoxides. M. Tiffeneau and B. Tchoubar (Compt. rend., 1938, **207**, 918—919).—βγ-Epoxypentane with $MgBr_2$ etherate in the cold (and decomp. with H_2O; general method) affords a mixture, b.p. 67—68°/15 mm., of CHMeBr·CHEt·OH and CHEtBr·CHMe·OH (preponderates); in the hot $COEt_2$ and $COMePr^{\alpha}$ (preponderates) are formed. Similarly, 1 : 2-epoxy-*cyclo*hexane with $MgHal_2$ in the cold affords trans-2-*bromo*-, b.p. 90—91°/13 mm. (p-*nitrobenzoate*, m.p. 59—60°; 3 : 5-*dinitrobenzoate*, m.p. 155°), and trans-2-*iodo*-cyclo*hexanol*, m.p. 40° (p-*nitrobenzoate*, m.p. 74—75°; 3 : 5-*dinitrobenzoate*, m.p. 157°); when it is heated, *cyclo*pentylformaldehyde is formed. 1-Methyl-1 : 2-epoxy*cyclo*hexane and $MgBr_2$ in the cold yield the stable trans-2-*bromo*-1-*methyl*-, b.p. 100—101°/16 mm. (p-*nitrobenzoate*, m.p. 130°; 3 : 5-*dinitrobenzoate*, m.p. 120°), and *trans*-2-bromo-2-methyl-*cyclo*hexanol which easily loses Br; in the hot *cyclo*pentyl Me ketone (*semicarbazone*, m.p. 145°), 2-methyl*cyclo*pentylformaldehyde (*semicarbazone*, m.p. 168°), and some 2-methyl*cyclo*hexanone (*semicarbazone*, m.p. 198°) result. Methylene*cyclo*hexane oxide with $MgBr_2$ gives 1-*bromo*-1-*hydroxymethyl*cyclo*hexane*, m.p. 82° (3 : 5-*dinitrobenzoate*, m.p. 133°) (cold), or hexahydrobenzaldehyde (hot). Styrene oxide with $MgHal_2$ (cold) forms β-*bromo*-, b.p. 131—132°/19 mm. (p-*nitrobenzoate*, m.p. 56—57°; 3 : 5-*dinitrobenzoate*, m.p. 103°), and β-iodo-β-phenylethyl alcohol (p-*nitrobenzoate*, m.p. 76°; 3 : 5-*dinitrobenzoate*, m.p. 110°); when this is heated $CH_2Ph·CHO$ is formed. The above results show that $\overbrace{CHR·O·CHR'}$ react with, *e.g.*, $MgBr_2$ in the cold to give CHRBr·CHR'·O·MgBr (or the isomeride); when heated, the latter loses $MgBr_2$ affording $CH_2R·COR'$ (with or without transposition). J. L. D.

Catalytic hydrogenation of hydroxymethylene-*cyclo*hexanone. H. Rupe and O. Klemm (Helv. Chim. Acta, 1938, **21**, 1538—1541).—Hydrogenation (Ni–aq. EtOH; atm. pressure) of hydroxymethylene-*cyclo*hexanone (I) gives 2-*hydroxymethyl*cyclo*hexanol* (II), b.p. 135—137°/9 mm. (*diacetate*, b.p. 133°/13 mm.; *di*-p-*nitrobenzoate*, m.p. 134°). With this on a SiO_2 gel catalyst uniform products are not obtained if hydrogenation is interrupted after the absorption of 1 H_2. Na–Hg and AcOH reduce (I) to (II) accompanied by much resin. Cu chromite appears inactive under 150 atm. Gradual addition of 20% H_2SO_4 to (II) in EtOH through which steam is passing gives the corresponding *oxide*, b.p. 54°/11 mm., in poor yield. H. W.

Reduction of α-halogeno-ketones. Synthesis of *dl*-ψ-ephedrine. P. G. Stevens (J. Amer. Chem. Soc., 1938, **60**, 3089).—$Al(OPr^{\beta})_3$ partly removes Br in the α-position to CO if H is available on the adjacent C. COPh·CHMeBr and $Al(OPr^{\beta})_3$ give only 35% of OH·CHPh·CHMeBr, b.p. 73—75%/0·1 mm., which with NH_2Me yields a mixture containing *dl*-ψ-ephedrine, but no *dl*-ephedrine. R. S. C.

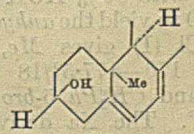
Reactions of benzhydryl chloride with hydroxylic solvents.—See A., 1939, I, 86.

Reactivity of *p*-fluorine in triarylmethyl chlorides. F. Bacon [with J. H. Gardner] (J. Org. Chem., 1938, **3**, 281—286).—*p*-F in CAr_3Cl reacts in the same way as, but less readily than, *p*-Br or *p*-Cl. *p*-C_6H_4F·COPh and MgPhBr, followed by HCl–C_6H_6 on the purified product, give *p*-$C_6H_4F·CPh_2Cl$ (I), m.p. 90—91° (lit., 87°). $(p\text{-}C_6H_4F)_2CPh·OH$ (from *p*-C_6H_4F·MgBr and MeOBz) and HCl in light petroleum give pp'-*difluorotriphenylmethyl chloride* (II) (14%), m.p. 56—57°. $(p\text{-}C_6H_4F)_3C·OH$ (from *p*-C_6H_4F·MgBr and *p*-$C_6H_4F·CO_2Me$) gives similarly impure *tri*-p-*fluorophenylmethyl chloride* (III) (4%), m.p. 81—82°. In liquid SO_2, with or without AgCl, small amounts of F′ are formed by rearrangement of (I), (II), or (III). With Ag in C_6H_6 under CO_2 reaction to radicals of the type, *p*-$CAr_3·C_6H_4·CAr_2$, occurs slowly. R. S. C.

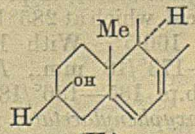
Separation of sterols by chromatographic adsorption. K. Ladenburg, E. Fernholz, and E. S. Wallis (J. Org. Chem., 1938, **3**, 294—299).—*Cholesteryl* (I), m.p. 188—189°, *stigmasteryl*, m.p. 191—192°, and *ergosteryl*, m.p. 200—201°, *azobenzene*-4-*carboxylate* are separated by adsorption from C_6H_6 on anhyd. Al_2O_3 and development of the chromatogram by light petroleum or, less well, a mixture thereof with C_6H_6. Presence of the β-*sitosteryl* ester (II), m.p. 173—174°, prevents the separation, although some pure (II) is obtained from the portion least adsorbed unless (I) is also present. *p*-$COCl·C_6H_4·N{:}NPh$, m.p. 93—94°, is obtained from the acid by $SOCl_2$ only in presence of an excess of anhyd. Na_2CO_3. The esters are prepared in C_5H_5N at 100°. R. S. C.

Structure of lumisterol. F. S. Spring (J. Amer. Chem. Soc., 1938, **60**, 3088—3089).—Misquotations of Weizmann *et al.* (A., 1938, II, 348) are corr. R. S. C.

Pyrovitamins-D_3 and their dehydro-derivatives. A. Windaus, M. Deppe, and C. Roosen-Runge (Annalen, 1938, **537**, 1—10; cf. A., 1938, II, 58).—Vitamin-D_3 passes at 205° in vac. into non-cryst. *pyrovitamin*-D_3 (I) and non-cryst. iso-*pyrovitamin*-D_3 (II). (I) gives a cryst. 3 : 5-*dinitro*-



(I.)



(II.)

benzoate (III), m.p. 142°, $[\alpha]_D^{19}$ +221° in $CHCl_3$, a p-*nitrobenzoate*, m.p. 93°, $[\alpha]_D^{18}$ +212° in $CHCl_3$, and an *acetate*, (IV), m.p. 121°, $[\alpha]_D^{19}$ +428° in $CHCl_3$, whereas (II) affords a 3 : 5-*dinitrobenzoate* (V), m.p. 170°, $[\alpha]_D^{18}$ +318° in $CHCl_3$, a p-*nitrobenzoate*, m.p. 150°, $[\alpha]_D^{19}$ +332° in $CHCl_3$, and a non-cryst. acetate. Dehydrogenation of 7-dehydrocholesterol [$\Delta^{5:7}$-cholestadien-3-ol] (VI) with $Hg(OAc)_2$ in $CHCl_3$–AcOH at room temp. yields *tetradehydrocholesterol* [$\Delta^{5:7:9:11}$-*cholestatrien*-3-*ol*] (VII), m.p. 112°, $[\alpha]_D^{20}$ +146° in $CHCl_3$; reaction proceeds somewhat more smoothly with its acetate and yields *tetradehydro-*

cholesteryl acetate (VIII), m.p. 88—89°, $[\alpha]_D^{20}$ +220° in $CHCl_3$, also obtained by acetylation of (VII). 7-Dehydrocholesteryl dinitrobenzoate is more slowly transformed into *tetrahydrocholesteryl dinitrobenzoate* (IX), m.p. 205°, $[\alpha]_D^{18}$ +166° in $CHCl_3$, also obtained from (VII) and $(NO_2)_2C_6H_3{\cdot}COCl$ in C_5H_5N. (V) is slowly converted by $Hg(OAc)_2$ in $CHCl_3$–AcOH at room temp. into (IX), the identity of which is confirmed by hydrolysis and transformation into (VIII). (VI) and (II) differ therefore only in the steric arrangement of the substituents at $C_{(9)}$. Dehydrogenation of lumisterol-3 (and its derivatives) is relatively difficult since it is scarcely attacked at room temp. and does not give cryst. compounds when the temp. is raised. Its dinitrobenzoate is slowly converted into *dehydrolumisteryl-3 dinitrobenzoate* (X), m.p. 120°, $[\alpha]_D^{20}$ +16° in $CHCl_3$, also obtained by dehydrogenation of (III). (IV) is transformed by $Hg(OAc)_2$ into *dehydrolumisteryl-3* (*dehydropyrovitamin-*D_3) *acetate*, m.p. 103—104°, $[\alpha]_D^{20}$ +252° in $CHCl_3$, which has the same spectrum as dehydroergosterol. Lumisterol-3 and (I) differ therefore solely in the steric arrangement of the substituents at $C_{(9)}$. H. W.

Sterols. XLVII. Reduction products of œstrone. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1938, **60**, 2927—2928).—α-Œstradiol [obtained with β-œstradiol in good yield from œstrone by $Al(OPr^{\beta})_3$] with H_2–PtO_2 and a little HCl in EtOH gives œstrane-3 : 17(α)-diol (I), m.p. 204° (A., 1938, II, 407), and a mol. *compound* (II), $C_{18}H_{30}O_2$,$C_{18}H_{30}O$, m.p. 175°. With CrO_3–AcOH at room temp. (I) and (II) give œstranedione, m.p. 170°. $C_{(17)}$ of (I) has the α configuration since it is obtained also (Dirscherl, A., 1936, 472) by catalytic reduction of œstrone. R. S. C.

Derivatives of œstradiol.—See B., 1939, 104.

5-Bromo-2-methoxyphenylacetonitrile and its derivatives. M. Paty (Bull. Soc. chim., 1938, [v], **5**, 1676—1685).—2 : 5 : 1-$OMe{\cdot}C_6H_3Br{\cdot}CH_2{\cdot}CN$ (I), b.p. 182·5—183°/13 mm., m.p. 65°, best (96% yield) obtained from the chloride and KCN in aq. EtOH, with H_2SO_4–H_2O (5 : 1) gives *5-bromo-2-methoxyphenylacetamide*, m.p. 170°, or with 50% KOH gives the acid, which at 285° loses H_2O to yield the *anhydride*, m.p. 166·5°. With ROH–HCl (I) gives *Me*, b.p. 171—173°/18 mm., *Et*, b.p. 176—177·5°/18 mm., *Pr*, b.p. 185—186°/18 mm., and *CH_2Ph* *5-bromo-2-methoxyphenylacetate*, m.p. 50°. The Na derivative of (I), prepared by $NaNH_2$ in Et_2O, with RHal gives α-*5-bromo-2-methoxyphenyl-propio-*, b.p. 174—176°/14 mm., -n-*butyro-* (II), b.p. 179—181°/14 mm., and -n-*valero-nitrile*, b.p. 186—187·5°/14 mm., whence α-*5-bromo-2-methoxyphenyl-α-ethyl*-n-*butyronitrile*, m.p. 58°, b.p. 189—191·5°/14 mm., and -α-*methyl*-n-*valeronitrile*, b.p. 191—193·5°/17 mm., are similarly, but more slowly, obtained. With H_2SO_4–H_2O (2 : 1) (II) gives α-*5-bromo-2-methoxyphenylbutyramide*, m.p. 101°, and with KOH in 95% EtOH gives this amide and the corresponding *acid* (75%), m.p. 98·5°. 2 : 5 : 1-$OMe{\cdot}C_6H_3Me{\cdot}CHNa{\cdot}CN$ reacts with MeI (to give α-*4-methoxy*-m-*tolylpropionitrile*, b.p. 142—144°/15 mm.) as rapidly as does $CHPhNa{\cdot}CN$, and the slower reaction of (I) must be due to the nuclear Br. R. S. C.

Preparation of substituted mandelic acids and their bacteriological effects. II. J. L. Riebsomer, R. Baldwin, J. Buchanan, and H. Burkett (J. Amer. Chem. Soc., 1938, **60**, 2974—2976).—*Et_2 hydroxy*-p-n-*propyl-*, b.p. 170—175°/4—5 mm. (40%), -p-n-*butyl-*, b.p. 176—177°/4—5 mm. (59%), -p-n-*amyl-*, b.p. 199—204°/4—5 mm. (51%), -p-tert.-*amyl-*, b.p. 178—179°/4—5 mm. (95%), and -2 : 3 : 5 : 6-*tetramethyl-phenylmalonate*, b.p. 195—210°/27 mm., p-n-*propyl-*, m.p. 126—126·5° (20%), p-n-*butyl-*, m.p. 116·5—117° (25%), p-n-, m.p. 112·5° (8%), p-iso-, m.p. 87—87·5° (16%), and p-tert.-*amyl-*, m.p. 73—74° (53%), *pentamethyl-*, m.p. 180—181° (9%), 2 : 3 : 5 : 6-*tetramethyl-*, m.p. 163° (1·3%), *p*-bromo-, m.p. 117·5° (8·8%), and *p*-iodo-, m.p. 135—136° (7·2% yield), *-mandelic acid* are prepared (method : A., 1938, II, 278). Only the Br- and I-acids have greater effect on *B. coli in vitro* than has $OH{\cdot}CHPh{\cdot}CO_2H$. PhMe, $CO(CO_2Et)_2$ (I), and $SnCl_4$ give a 1 : 1 : 1 additive *compound*. $SnCl_4$ and (I) give an unstable compound. R. S. C.

Acid amides as hypnotics. I. Acylcarbamides. II. Acetamides. F. F. Blicke and A. P. Centolella (J. Amer. Chem. Soc., 1938, **60**, 2923—2924, 2924—2926).—I. The following are prepared, but none of the carbamides has noteworthy hypnotic activity when injected peritoneally into white rats. β-*Phenylethyl-propyl-*, m.p. 123—124° (*Et_2* ester, b.p. 190—195°/14 mm.), -iso*propyl-*, m.p. 129—130° (*Et_2* ester, b.p. 204—206°/24 mm.), -iso*butyl-*, m.p. 136—137° (*Et_2* ester, b.p. 205—208°/20 mm.), *-allyl-*, m.p. 128—129° (*Et_2* ester, b.p. 205—208°/20 mm.), and -β′-cyclo*hexylethyl-malonic acid*, m.p. 134—135° (*Et_2* ester, b.p. 255—260°/30 mm.); *ethyl-γ-phenylpropyl-*, m.p. 148—149° (*Et_2* ester, b.p. 195—200°/18 mm.), -δ-*phenylbutyl-*, m.p. 114—115° (*Et_2* ester, b.p. 216—220°/22 mm.), -ε-*phenylamyl-*, m.p. 106—107° (*Et_2* ester, b.p. 230—235°/25 mm.), -ζ-*phenylhexyl-*, m.p. 67—68° (*Et_2* ester, b.p. 227—233°/18 mm.), and *-cinnamyl-malonic acid*, m.p. 133—134° (*Et_2* ester, b.p. 215—220°/30 mm.). α-β′-*Phenylethyl*-n-, b.p. 195—200°/20 mm. (*chloride*, b.p. 164—169°/19 mm.), and -iso-*valeric*, b.p. 198—204°/35 mm., -Δ^{γ}-*pentenoic*, b.p. 196—199°/22 mm. (*chloride*, b.p. 205—210°/15 mm.), and -γ-cyclo*hexyl*-n-*butyric acid*, b.p. 245—250°/19 mm. (*chloride*, b.p. 220—225°/25 mm.); α-β′-*phenylethyl-γ-methyl*-n-*valeric acid*, b.p. 200—203°/20 mm. (*chloride*, b.p. 216—222°/18 mm.); α-*ethyl-δ-phenyl*-n-*valeric*, b.p. 193—196°/18 mm. (*chloride*, b.p. 217—220°/30 mm.), -ε-*phenyl*-n-*hexoic*, b.p. 227—230°/50 mm. (*chloride*, b.p. 190—194°/22 mm.), -ζ-*phenyl*-n-*heptoic*, b.p. 213—219°/20 mm. (*chloride*, b.p. 199—204°/20 mm.), -η-*phenyl*-n-*octoic*, b.p. 218—222°/17 mm. (*chloride*, b.p. 206—210°/21 mm.), and -δ-*phenyl*-Δ^{γ}-n-*pentenoic acid*, b.p. 215—220°/35 mm. (*chloride*, b.p. 184—190°/20 mm.). α-*Ethyl*-n-*butyryl*-N-*methylcarbamide*, m.p. 93—95°; α-*ethyl*-n-*valeryl-*, m.p. 200—201°, -n-*heptoyl-*, m.p. 138—139°, -n-*octoyl-*, m.p. 126—127°, -γ-cyclo*hexyl*-n-*butyryl-*, m.p. 176—177°, -β-*phenylpropionyl-*, m.p. 141—142°, -γ-*phenyl*-n-*butyryl-*, m.p. 152—153°,

-δ-*phenyl*-n-*valeryl*-, m.p. 143—145°, -ε-*phenyl*-n-*hexoyl*-, m.p. 137—138°, -ζ-*phenyl*-n-*heptoyl*-, m.p. 120—121°, -η-*phenyl*-n-*octoyl*-, m.p. 122—123°, and -δ-*phenyl*-Δ^{γ}-n-*pentenoyl*-, m.p. 139—140°, -*carbamide*; α-*ethyl*-n-*hexoyl*-N-*methyl*-, m.p. 77—78°, α-*bromo*-α-*ethyl*-n-*hexoyl*-, m.p. 84—85°, α-β′-cyclo*hexylethyl*-γ-cyclo*hexyl*-n-*butyryl*-, m.p. 175—176°, γ-*phenyl*-n-*butyryl*-, m.p. 174—175°, and γ-*phenyl*-α-β′-*phenylethyl*-n-*butyryl*-, m.p. 149—150°, -*carbamide*; α-β′-*phenylethyl*-n-, m.p. 148—150°, and -iso-*valeryl*-, m.p. 157—158°, -Δ^{γ}-n-*pentenoyl*-, m.p. 115—116°, -n-*hexoyl*-, m.p. 117—118°, and -γ-cyclo*hexyl*-n-*butyryl*-, m.p. 148—149°, -*carbamide*; γ-*methyl*-α-β′-*phenylethyl*-n-*valerylcarbamide*, m.p. 149—150°.

II. The following are prepared, those marked * being strong hypnotics when injected as above. α-*Ethyl*-n-*butyr-thioamide**, m.p. 80—81°, -N-*ethyl-amide*, m.p. 79—80°, and -*butylamide*, m.p. 34—35°; α-ethyl-*n*-hexo-amide*, m.p. 106—107° (lit., 101—102°), -*methylamide**, m.p. 69—70°, -*ethylamide*, m.p. 58—59°, -β′-*hydroxyethylamide*, m.p. 47—49°, b.p. 199—200°/15 mm., and -*butylamide*, b.p. 177—178°/5 mm.; α-ethyl-*n*-heptoamide*, m.p. 102—103° (lit., 96°), and -n-*octoamide**, m.p. 106—107°; γ-cyclo*hexyl*-α-*ethyl*-n-*butyr-amide*, m.p. 134—135°, -*methyl-amide*, m.p. 111—112°, -*ethylamide*, m.p. 96—97°, -β′-*hydroxyethylamide**, m.p. 90—91°, and -*butylamide*, m.p. 61—62°; γ-cyclo*hexyl*-α-β′-cyclo*hexylethyl*-n-*butyr-amide*, m.p. 173—174°, -*methylamide*, m.p. 164—165°, and -*ethylamide*, m.p. 137—138°; α-β′-cyclo*hexylethyl*-n-*hexo-amide*, m.p. 140—141°, -*methyl-amide*, m.p. 110—111°, -*ethylamide*, m.p. 94—95°, and -β″-*hydroxyethylamide*, m.p. 92—93°; N-α-*ethyl*-n-*butyryl*-, b.p. 159—160°/9 mm., and N-α-*ethyl*-n-*hexoyl-morpholine*, b.p. 185—186°/9 mm.; NN′-*di*-(α-*ethyl*-n-*butyr*)*ethylenediamide*, m.p. 230—231°; α-*benzyl*-n-*butyramide*, m.p. 117—118°; α-β′-phenylethyl-*n*-butyr-amide*, m.p. 105—106° (lit., 104°), -*methylamide*, m.p. 98—99°, and -*ethylamide**, m.p. 72—73°; γ-*phenyl*-α-β′-*phenylethyl*-n-*butyr-amide*, m.p. 162—163°, -*methylamide*, m.p. 124—125°, and -*butylamide*, m.p. 86—87°; γ-cyclo*hexyl*-α-β′-*phenylethyl*-n-*butyramide*, m.p. 170—171°; α-β′-*phenylethyl*-n-*valer-amide**, m.p. 109—110°, -*methylamide*, m.p. 93—94°, -*ethylamide**, m.p. 84—85°, -β″-*hydroxyethylamide**, m.p. 74—75°, and -*butylamide*, m.p. 69—70°; α-β′-*phenylethyl*iso*valer-amide**, m.p. 121—122°, and -β″-*hydroxyethylamide*, m.p. 83—84°; α-β′-*phenylethyl*-Δ^{γ}-*pentenoamide**, m.p. 90—91°; α-β′-*phenylethyl*-n-*hexo-amide*, m.p. 124—125°, -*methyl-amide*, m.p. 108—109°, -*ethylamide*, m.p. 71—72°, -β″-*hydroxyethylamide*, m.p. 66—67°, and -*butylamide*, m.p. 59—60°; α-β′-*phenylethyl*-γ-*methyl*-n-*valeramide**, m.p. 89—90°; α-*ethyl*-δ-*phenylvaler*-, m.p. 118—119°, -ε-*phenyl*-n-*hexo*-, m.p. 107—108°, -ζ-*phenyl*-n-*hepto*-*, m.p. 98—99°, -η-*phenyl*-n-*octo*-, m.p. 113—114°, and -δ-*phenyl*-Δ^{γ}-n-*penteno-amide*, m.p. 94—96°.

R. S. C.

Constituents of natural phenolic resins. XIII. Synthesis of *dl*-, *d*-, and *l*-hinokinin. R. D. Haworth and D. Woodcock (J.C.S., 1938, 1985—1989; cf. A., 1938, II, 323; Keimatsu *et al.*, A., 1936, 1247; 1937, II, 21).—Piperonal and Et succinate in NaOEt–Et_2O at 0° for 7 days afford αβ-di-(3 : 4-methylenedioxybenzylidene)succinic acid, m.p. 207—208° (+2AcOH), 228° ("anhyd.") (anhydride, m.p. 212—213°) (cf. Stobbe *et al.*, A., 1911, i, 373). The acid and Na–Hg in 1% NaOH at 80—90° (CO_2) give *meso*-αβ-di-(3 : 4-methylenedioxybenzyl)succinic acid (I), m.p. 240—241°, not resolvable by strychnine, brucine, or cinchonine. (I) and Ac_2O give *dl*(*trans*)-αβ-di-(3 : 4-methylenedioxybenzyl)succinic anhydride (II), m.p. 160—161°, hydrolysed by aq. NaOH to the *dl*-acid, m.p. 201° (decomp.). The latter is resolved by strychnine into the l-*acid*, m.p. 174—175°, $[\alpha]_D^{17}$ −12·4° in $COMe_2$ [*strychnine* salt (+9·5H_2O), decomp. 260° (softens ~140°)], and the d-*acid*, m.p. 174—175°, $[\alpha]_D^{17}$ +12·1° in $COMe_2$ [*strychnine* salt (+4H_2O), decomp. ~240° (softens at 140°)]. These with Ac_2O give the l(+)- (III), m.p. 143—144°, $[\alpha]_D^{17}$ +21·5° in $COMe_2$, and d(−)- (IV), m.p. 143—144°, $[\alpha]_D^{17}$ −21·4° in $COMe_2$, *-anhydrides*, respectively. (II) and Al–Hg in C_6H_6–Et_2O–H_2O afford *dl*(*trans*)-αβ-di-(3 : 4-methylenedioxybenzyl)butyrolactone, m.p. 108° [Br_2-, m.p. 160°, and $(NO_2)_2$-, m.p. 172°, derivatives]. (III) similarly affords *l*(*trans*)-αβ-di-(3 : 4-methylenedioxybenzyl)butyrolactone (V), m.p. 65—66°, $[\alpha]_D^{17}$ −34° in $CHCl_3$ [Br_2-, m.p. 136°, and $(NO_2)_2$-derivative, dimorphous, m.p. 163—164° and 184—185°], identical with *l*-hinokinin (=*l*-cubebinolide). (IV) similarly affords the d(trans)-*isomeride* of (V), m.p. 64—65°, $[\alpha]_D^{17}$ +33·8° in $CHCl_3$ [Br_2-, m.p. 136°, and $(NO_2)_2$-derivative, dimorphous, m.p. 161—162° and 183—184°]. Measurements of the rates of hydrolysis of the lactones and of lactonisation of the corresponding OH-acids confirm the identity of synthetic *l*-hinokonin; the natural lactone possesses probably the *trans*-configuration. A. T. P.

Action of erepsin and trypsin on tetrapeptides derived from two molecules of glycine, one molecule of *l*(+)-alanine, and one molecule of *l*(−)-tyrosine. E. Abderhalden, R. Abderhalden, H. Weidle, E. Baertich, and W. Morneweg (Fermentforsch., 1938, **16**, 98—124; cf. Bergmann *et al.*, A., 1934, 809).—Carbobenzyloxy-*l*-alanyl chloride (I) (free acid, new m.p. 91—92°) in Et_2O and glycyl-*l*-tyrosine [from chloroacetyl-*l*-tyrosine, m.p. 153° (Et ester, m.p. 86—87°), and NH_3] in cold approx. 0·5N-NaOH give 60% of *carbobenzyloxy*-l-*alanylglycyl*-l-*tyrosine*, m.p. 128°, $[\alpha]_D^{20}$ +6·9° in EtOH, converted by H_2+Pd-black in MeOH into *l*-alanylglycyl-*l*-tyrosine, also obtained in poor yield from *d*-α-bromopropionylglycyl-*l*-tyrosine, new m.p. 164°, and EtOH–NH_3. The tripeptide and carbobenzyloxyglycyl chloride (II) similarly give the *carbobenzyloxy*-derivative, $[\alpha]_D^{20}$ +24·18° in EtOH, of glycyl-*l*-alanylglycyl-*l*-tyrosine, $[\alpha]_D^{20}$ +18·44° in H_2O (cf. lit.). *O*-Acetyl-*N*-carbobenzyloxy-*l*-tyrosyl chloride (III) and $NH_2{\cdot}CH_2{\cdot}CO_2Et$ in $CHCl_3$ afford O-*acetyl*-N-*carbobenzyloxy*-l-*tyrosylglycine Et* ester, m.p. 116°, hydrolysed (N-NaOH at room temp.) to N-*carbobenzyloxy*-l-*tyrosylglycine* (+2H_2O), decomp. 111° (sinters at 90°), which is hydrogenated (Pd–$BaSO_4$, aq. MeOH) to *l*-tyrosylglycine, m.p. 266° (decomp.) (darkens 232° and sinters 262°), also prepared (cf. A., 1933, 1063) by hydrogenation of its dicarbobenzyloxy-derivative. *Dicarbobenzyloxy*-l-*tyrosine* has m.p. 97—99°. *l*-Tyrosylglycine and (II) afford *carbobenzyloxyglycyl*-l-*tyrosylglycine*, m.p. 134°, $[\alpha]_D^{20}$

+5·35° in EtOH, converted (H_2+Pd) into *glycyl*-l-*tyrosylglycine*, $[\alpha]_D^{20}$ +24·12° in H_2O, which with (I) gives *carbobenzyloxyalanylglycyl*-l-*tyrosylglycine* and thence l-*alanylglycyl*-l-*tyrosylglycine*, $[\alpha]_D^{20}$ −8·5° in H_2O. *Carbobenzyloxy*-l-*alanyl*-l-*tyrosylglycine*, m.p. 146° [from *l*-tyrosylglycine and (I)], is converted (H_2+Pd) into l-*alanyl*-l-*tyrosylglycine*, which with (II) affords the *carbobenzyloxy*-derivative, m.p. 99° of *glycyl*-l-*alanyl*-l-*tyrosylglycine*, $[\alpha]_D^{20}$ +21·6° in H_2O. Dicarbobenzyloxy-*l*-tyrosyl chloride (IV) with glycylglycine yields *dicarbobenzyloxy*-l-*tyrosylglycylglycine*, m.p. 154—155°, whence l-*tyrosylglycylglycine*, decomp. 199° (darkens at 192°), $[\alpha]_D^{20}$ +42·8° in 20% HCl, also obtained by hydrolysis (N-NaOH–MeOH) of O-*acetyl*-N-*carbobenzyloxy*-l-*tyrosylglycylglycine Et* ester, m.p. 141° [from glycylglycine Et ester and (III)], to N-*carbobenzyloxy*-l-*tyrosylglycylglycine*, m.p. 215° (sinters 213°), and subsequent hydrogenation. l-*Alanyl*-l-*tyrosylglycylglycine*, $[\alpha]_D^{20}$ +35·58° in H_2O, is obtained from its *carbobenzyloxy*-derivative, m.p. 113—114°, $[\alpha]_D^{20}$ +7·24° in EtOH [prep. from (I) and the tripeptide]. d-α-*Bromopropionylglycylglycine*, m.p. 171°, $[\alpha]_D^{20}$ +30·22° in 0·1N-NaOH, and 25% aq. NH_3 give l-*alanylglycylglycine* (+H_2O), m.p. 227° {*Et* ester (V) [*hydrochloride*, m.p. 129° (turbid), froths 154°, decomp. 211°]}, which with (IV) affords *dicarbobenzyloxy*-l-*tyrosyl*-l-*alanylglycylglycine*, froths 127°, clear melt at 154°, decomp. 181° (*monocarbobenzyloxy*-derivative, froths 144°, decomp. 178°), whence l-*tyrosyl*-l-*alanylglycylglycine*, froths ~184°, decomp. 197°, $[\alpha]_D^{20}$ +23·39° in dil. EtOH, also obtained (less pure) by hydrogenation of the reaction product from (III) and (V) in EtOAc. *Chloroacetylglycyl*-l-*tyrosine*, decomp. 184°, $[\alpha]_D^{20}$ +44·75° in EtOH, with 25% aq. NH_3 at 37° gives *glycyl*-l-*tyrosine anhydride*, m.p. 296° (by loss of CH_2Cl·CO), and *glycylglycyl*-l-*tyrosine*, m.p. 218—220° (decomp.); the last and *d*-CHMeBr·COCl in 2N-NaOH afford d-α-*bromopropionyl*- and thence l-*alanyl*-*glycylglycyl*-l-*tyrosine*, decomp. ~194°, $[\alpha]_D^{20}$ +28·19° in H_2O (corresponding dl-*alanyl* compound, decomp. 197°). *l*-Tyrosyl-*l*-tyrosine, m.p. >260°, $[\alpha]_D^{20}$ +32·5° in H_2O, is prepared by Bergmann's method (*loc. cit.*) and by hydrolysis (approx. 0·5N-NaOH) of *l*-tyrosine anhydride (from tyrosine Me ester, m.p. 137°, at 140°).

The above tri- and tetra-peptides are hydrolysed by trypsin (carboxypolypeptidase) (from pig pancreas) or, better, by erepsin (aminopolypeptidase) (from pig's small intestine) or rabbit serum, but not by acylase. The changes in $[\alpha]_D^{37}$ confirm the view that aminopolypeptidase attacks the residue containing free NH_2, and that carboxypolypeptidase attacks the residue containing CO_2H. The *N*-carbobenzyloxy-derivatives are generally hydrolysed by trypsin but not by erepsin or acylase (except for *N*-carbobenzyloxy-*l*-tyrosyl-*l*-tyrosine which undergoes 15% fission). W. McC.

Syntheses in the carane group. III. Synthesis of carane. P. C. Guha and D. K. Sankaran (Ber., 1938, **71**, [*B*], 2673—2675).—A fuller account of work already reported (A., 1938, II, 371). 4-Methyl-Δ^1-*cyclo*hexene-1-carboxylic acid gives an *anilide*, m.p. 106—107°, an *amide*, m.p. 148°, and a *p-toluidide*, m.p. 127—128°. The *anilide*, *amide*, and *p-toluidide* of trimethyl*dicyclo*-[0 : 1 : 4]-heptanecarboxylic acid, $\begin{matrix}CHMe\cdot CH_2\cdot CH\text{——}\\ CH_2\text{—}CH_2\text{—}C(CO_2H)\end{matrix}>CMe_2$, have m.p. 98—99°, 124—125°, and 113—114°, respectively. H. W.

Re-esterification of phenolic esters of carboxylic acids in presence of inorganic salts. G. A. Varvoglis (Ber., 1938, **71**, [*B*], 2488—2492).—Most of the experiments are performed with *p*-$C_6H_4(OBz)_2$ (I) but *o*- and *m*-$C_6H_4(OBz)_2$ and 2 : 1 : 4-$C_6H_3Cl(OBz)_2$ behave similarly. In the absence of catalysts little reaction occurs between (I) and *iso*amyl alcohol (II) the products being *iso*amyl benzoate, *p*-OH·C_6H_4·OBz (III), and very little *p*-$C_6H_4(OH)_2$ (IV). $ZnCl_2$ and $AlCl_3$ are very effective giving exclusively (IV) and the alkyl benzoate (V). $ZnSO_4$, $CaCl_2$, and $MgCl_2$ are less active, the change proceeding only to (III) and (V); (IV) is formed in traces or not at all. $SnCl_2$ and Cu salts are still less efficient, the slight change which occurs resulting in (IV) and (V). NaCl has no appreciable effect. Among alcohols [MeOH, EtOH, (II), CH_2Ph·OH, $(CH_2$·$OH)_2$] the best yields are obtained from those of relatively high b.p. Boiling MeOH and EtOH cause no appreciable change but at 130° under pressure the re-esterification is complete. Reaction, however, proceeds more slowly than with (II) under similar conditions. Extensive re-esterification takes place with CH_2Ph·OH and $(CH_2$·$OH)_2$ in the absence of a catalyst if the experiment is sufficiently prolonged. In presence of catalysts ($ZnCl_2$) CH_2Ph·OH give intractible brown resins. H. W.

Transformation products of 2-chloro-4 : 5-dinitrobenzoic acid. H. Goldstein and W. Glauser (Helv. Chim. Acta, 1938, **21**, 1513—1518; cf. A., 1938, II, 13).—Further examples of the mobility of NO_2 at $C_{(4)}$ in 4 : 5 : 2-$(NO_2)_2C_6H_2Cl$·CO_2H (I) are cited. 33% NH_2Me converts (I) at 100° into 2-*chloro*-5-*nitro*-4-*methylaminobenzoic acid*, m.p. 280° (decomp.). 2-*Chloro*-5-*nitro*-4-*dimethylamino*-, m.p. 238—239° (decomp.), -4-*ethylamino*-, m.p. 242°, and -4-*diethylamino*-, m.p. 167°, -*benzoic acid* are obtained similarly. (I) and EtOH–N_2H_4,H_2O give the unstable 2-*chloro*-5-*nitro*-4-*hydrazinobenzoic acid* (N_2H_4 salt, m.p. 186—187°; *Ac* derivative, m.p. 265°), which with $COMe_2$ yields *acetone*-5-*chloro*-2-*nitro*-4-*carboxyphenylhydrazone*, m.p. 247°, and is converted by 2N-Na_2CO_3 at 100° into 6-*chloro*-3-*hydroxybenztriazole*-5-*carboxylic acid*, decomp. 234·5°. (I) and NHPh·NH_2 in boiling EtOH afford 2-*chloro*-5-*nitro*-4-*phenylhydrazinobenzoic acid*, m.p. 190—200° (very rapidly heated) or 246° after changing from red to yellow at 190—200°, transformed by glacial AcOH into 6-*chloro*-3-*oxido*-2-*phenylbenztriazole*-5-*carboxylic acid*, m.p. 255·5°. (I) and Na_2S_2 in boiling EtOH yield 4 : 4′-*dithiodi*-2-*chloro*-5-*nitrobenzoic acid*, m.p. 316° (decomp.). 2-*Chloro*-4-*iodo*-5-*nitrobenzoic acid*, m.p. 210—211°, is obtained from 5 : 2 : 4-NO_2·$C_6H_3Cl(NH_2)$·CO_2H by the diazo-method; boiling 2N-NaOH transforms it into 5 : 2 : 4-NO_2·$C_6H_3Cl(OH)$·CO_2H. It does not appear to be affected by conc. aq. NH_3 or by NH_2Ph in presence of anhyd. K_2CO_3. With NH_2Ph–catalytic Cu it loses Cl and I. All m.p. are corr. H. W.

Schiff bases from 4-amino-o-tolunitrile. C. Candea and E. Macovski (Bull. Soc. chim., 1938, [v], **5**, 1487—1489; cf. A., 1938, II, 491).—The

CHPh:, m.p. 80°, *vanillylidene*, m.p. 132°, *piperonylidene*, m.p. 127°, and o-, m.p. 134° (sensitive to light), m-, m.p. 160°, and p-, m.p. 168° (best for identification) *-nitrobenzylidene* derivatives of 4 : 1 : 2-NH_2·C_6H_3Me·CN (*loc. cit.*) are described. A. T. P.

Rearrangement of *o*-carbamyl derivatives of diphenyl ether. B. T. Tozer and S. Smiles (J.C.S., 1938, 2052—2056; cf. A., 1939, II, 20).—Rearrangement of the amides is by NaOH (1·25 mols., 0·2N) in H_2O–$COMe_2$ (1 : 4) (unless stated otherwise), and is studied with regard to substituents in the phenoxy-nucleus and the character of the amide-N (theory discussed). 2-p-*Nitrophenoxy-benzamide*, m.p. 167° (50°; 1 hr.), *-benzanilide*, m.p. 127° (18°), and *-benz-m-nitroanilide*, m.p. 141° (18°) (also by piperidine or C_5H_5N at 18°), give salicyl-4′-nitroanilide, *-4′-nitrodiphenylamide*, m.p. 134°, and *-3′ : 4″-dinitrodiphenylamide*, m.p. 168°, respectively. The last is hydrolysed to *o*-OH·C_6H_4·CO_2H and 3 : 4′-*dinitrodiphenylamine*, m.p. 217°, also synthesised from *m*-NO_2·C_6H_4·NH_2 and *p*-C_6H_4Br·NO_2 (method: Eckert *et al.*, A., 1915, i, 596). 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and *o*-OH·C_6H_4·CO_2Me in MeOH–NaOMe at 18° (6 hr.) give *Me* o-2′ : 4′-*dinitrophenoxybenzoate*, m.p. 88°. The corresponding *acid*, m.p. 164°, affords the *amide*, m.p. 121°, converted (18°) into *salicyl-2′ : 4′-dinitroanilide*, m.p. 213°, also prepared by heating the amide at 200°, or synthesised from salicylamide and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ in NaOEt–EtOH. 4-Nitrophenoxy-acetyl chloride and NH_2Ph give *4-nitrophenoxy-acetanilide*, m.p. 172°, which affords [in N-NaOH (1·25 mols.) at 100°, through (?) glycollo-4-nitrodiphenylamide (not isolable)], 4-nitrodiphenylamine. 4-o-*Nitrophenoxytoluene-3-sulphonamide*, m.p. 159°, and *-sulphonmethylamide*, m.p. 145° (the -sulphonanilide does not react), and N-NaOH (2·5 mols.) at 100° give *4-hydroxytoluene-3-sulphon-o-nitroanilide*, m.p. 160°, and *-o-nitromethylanilide*, m.p. 135°, respectively; both anilides with Me_2SO_4 in alkali afford *4-methoxytoluene-3-sulphon-o-nitromethylanilide*, m.p. 140°, also prepared by methylation of *4-methoxytoluene-3-sulphon-o-nitroanilide*, m.p. 116°. 2 : 4-*Bismethylsulphonylphenyl* o-*nitrobenzoate*, m.p. 186°, and $SnCl_2$–AcOH (saturated with HCl) at 16° afford 2 : 4-*bismethylsulphonylphenyl anthranilate*, m.p. 204°, not rearranged by alkali. 2 : 4 : 6 : 1-$C_6H_2Cl_3$·OH, *o*-NO_2·C_6H_4·SO_2Cl, and K_2CO_3 in boiling $COMe_2$, give 2 : 4 : 6-*trichlorophenyl* o-*nitrobenzenesulphonate*, m.p. 142°, converted by $SnCl_2$–AcOH into the o-*aminobenzenesulphonate*, m.p. 153°, unchanged or partly hydrolysed by boiling N-NaOH. 2 : 4 : 1-$(MeSO_2)_2C_6H_3$·OH and *o*-NO_2·C_6H_4·SO_2Cl–K_2CO_3 give a product, reduced by $SnCl_2$–AcOH at 18° to 2 : 4-*bismethylsulphonylphenyl* o-*aminobenzenesulphonate*, m.p. 169°, unchanged by N-NaOH at 80°. o-*Nitrobenzenesulphonacetamide*, m.p. 190°, and $SnCl_2$–AcOH at 18°, or alkaline $Na_2S_2O_4$, give *3-methylbenz*-1 : 2 : 4-*thiadiazine* 1 : 1-*dioxide*, m.p. 268°, also obtained by heating o-*acetamidobenzenesulphonamide*, m.p. 164°, (from the Na salt of the *o*-NH_2-compound and AcCl in C_6H_6) at 290°, or from *o*-NH_2·C_6H_4·SO_2·NH_2 and Ac_2O–C_5H_5N at 18°. A. T. P.

Chlorination of *o*-thiolbenzoic acid. L. E. Hart, E. W. McClelland, and (in part) F. S. Fowkes (J.C.S., 1938, 2114—2117; cf. Price and Smiles, A., 1929, 62).—*o*-SH·C_6H_4·CO_2H or (*o*-CO_2H·C_6H_4·S)$_2$ and Cl_2 in CCl_4 give the *S*-dichloro-anhydride, $\left[C_6H_4<\begin{matrix}SCl\\CO\end{matrix}>O\right]Cl$ (I) (mechanism discussed), which with $PhSO_2$·NH_2–C_5H_5N affords 2-*keto*-1-*benzenesulphonyl*-1 : 2-*dihydrobenzisothiazole* S-*oxide* (II), m.p. 182°, converted by H_2O_2–AcOH at 100° into *N*-benzenesulphonyl-*o*-benzoicsulphinide and $PhSO_2$·NH_2. (II) and 2N-NaOH give *o*-$PhSO_2$·NH·CO·C_6H_4·SO_2H, converted by boiling aq. $HgCl_2$ followed by HCl–EtOH into $PhSO_2$·NHBz. (I) with *p*-C_6H_4Me·SO_2·NH_2 and NH_2Ac, respectively, affords 2-*keto*-1-p-*toluenesulphonyl*-, m.p. 179°, and -1-*acetyl*-, m.p. 150°, -1 : 2-*dihydrobenzisothiazole* S-*oxide*. The latter substance, with H_2O_2–AcOH at 100°, gives *o*-benzoicsulphinide, with 2N-NaOH or HCl affords *o*-CO_2H·C_6H_4·SO_2H and 2 : 2′-dithiobenzoic acid, and with H_2O at 100° gives 2-*keto*-1 : 2-*dihydrobenzisothiazole* S-*oxide*, m.p. 159°, converted by Zn–AcOH–HCl into *o*-thiolbenzamide, identified as disulphide. *o*-SH·C_6H_4·CO_2H and Cl_2 in anhyd. $FeCl_3$–CCl_4 give a product (*A*) which with H_2O yields *m*-chloro- and 3 : 5-dichloro-benzoic acid, and 5 : 5′-*dichloro*-2 : 2′-*dithiobenzoic acid* (III), m.p. 316—320° (decomp.) (mechanism of reaction discussed), but in boiling solution, 3 : 5 : 3′ : 5′-*tetrachloro*-2 : 2′-*dithiobenzoic acid*, m.p. 263°, is formed. (III) and Zn–AcOH–HCl give 5-*chloro*-2-*thiolbenzoic acid*, m.p. 193° (cf. Krishna and Singh, A., 1928, 173), and (III) and CH_2Ac·CO_2Et–H_2SO_4 at 55° afford 5-chloro-3-hydroxy-1-thionaphthen. Dry NH_3 and (*A*) (not isolated) yield 4-*chloro*-2-*keto*-1 : 2-*dihydrobenzisothiazole* (IV), m.p. 259—261°, and 5-*chloro*-2-*aminothiolbenzoic acid*, m.p. 199°; NH_2Ac–C_5H_5N afford (IV) and 4-*chloro*-2-*keto*-1-*acetyl*-1 : 2-*dihydrobenzisothiazole*, m.p. 175—176° [also obtained from (IV) and Ac_2O]. The Ag salt of *o*-benzoicsulphinide (V), with $PhSO_2Cl$ at 180° affords N-*benzenesulphonyl*-o-*benzoicsulphinide*, m.p. 202°, which with boiling 2N-NaOH gives N-*benzenesulphonyl*-o-*sulphobenzamide*, m.p. 209—212°. (V) and $PhSO_2Cl$ or *p*-C_6H_4Me·SO_2Cl in C_5H_5N at room temp. give O-*benzene*-, m.p. 249°, and O-p-*toluene*-, m.p. 252°, *-sulphonyl*-o-*benzoicsulphinide*, respectively, converted by NaOH into (V). A. T. P.

7-Halogeno-1-naphthoic acids. H. Goldstein and H. A. Fischer (Helv. Chim. Acta, 1938, **21**, 1519—1523).—7 : 1-NH_2·$C_{10}H_6$·CO_2H (modified prep.) is converted (diazo-method) into 7-*chloro*-1-*naphthoic acid*, m.p. 243° (*Me* ester, m.p. 54°; *chloride*, m.p. 106°; *amide*, m.p. 237°; *anilide*, m.p. 185°), 7-*bromo*-1-*naphthoic acid*, m.p. 237° (*Me*, m.p. 55°, and *Et* ester, m.p. 46°; *chloride*, m.p. 106°; *amide*, m.p. 247°; *anilide*, m.p. 202°), and 7-*iodo*-1-*naphthoic acid*, m.p. 223° (*Me*, m.p. 88°, and *Et*, m.p. 64°, ester; *chloride*, m.p. 108°; *amide*, m.p. 248°; *anilide*, m.p. 217°). All m.p. are corr. H. W.

Hydrolysis of the amide and nitrile of 4-nitro-1-naphthoic acid. S. I. Sergievskaja and V. V. Nesvadba (J. Gen. Chem. Russ., 1938, **8**, 934—936).—4 : 1-NO_2·$C_{10}H_6$·CO_2H is obtained by hydrolysis of its amide with conc. H_3PO_4 (5 hr. at 120—125°) or by the action of $NaNO_2$ in 50% H_2SO_4, or by hydrolysis of 4 : 1-NO_2·$C_{10}H_6$·CN with conc. HCl

(6 hr. at 134—140°) or H_2SO_4–AcOH (18 hr. at 125—135°). R. T.

Anæsthetics of the naphthalene series. I. 4-Amino-1-naphthoic acid esters. S. I. Sergievskaja and V. V. Nesvadba (J. Gen. Chem. Russ., 1938, **8**, 924—933).—4 : 1-NO_2·$C_{10}H_6$·CO_2Et in EtOH is reduced (H_2–Pt) to *Et* 4-*amino*-1-*naphthoate*, m.p. 81° (*hydrochloride*; N-*Ac* derivative, m.p. 183°). The *Pr*$^{\alpha}$, b.p. 181—182°/4 mm., *Pr*$^{\beta}$, m.p. 71—72°, β-*diethylaminoethyl*, an oil (*hydrochloride*, m.p. 189·8—190°), γ-*diethylamino*-ββ-*dimethylpropyl* [*hydrochloride*, m.p. 153—155° (decomp.)], β-*diethylamino*iso*propyl* [*hydrochloride*, m.p. 194—195° (decomp.)], and γ-*diethylamino*-αβ-*dimethylpropyl* ester (*hydrochloride*, m.p. 177—179°), and the *chloride*, m.p. 95—96°, of 4 : 1-NO_2·$C_{10}H_6$·CO_2H, and the *Pr*$^{\alpha}$, m.p. 82—82·5°, *Pr*$^{\beta}$, m.p. 68·5—69·5°, β-*diethylaminoethyl* (*hydrochloride*, m.p. 212°; *citrate*, decomp. 114—116°), γ-*diethylamino*-ββ-*dimethylpropyl* [*hydrochloride*, m.p. 187—188° (decomp.); *citrate*, decomp. 146—147°], β-*diethylamino*iso*propyl* (*hydrochloride*, m.p. 208°), and γ-*diethylamino*-αβ-*dimethylpropyl* ester [*hydrochloride*, m.p. 210—212° (decomp.)], of 4 : 1-NH_2·$C_{10}H_6$·CO_2H, are prepared similarly. The diethylaminoalkyl esters have pronounced local anæsthetic properties, being in many respects superior to cocaine and novocaine. R. T.

Kolbe–Schmidt synthesis. I. Mechanism of formation of 2 : 3-hydroxynaphthoic acid. N. F. Silin and N. K. Moschtschinskaja (J. Gen. Chem. Russ., 1938, **8**, 810—823).—The reaction β-$C_{10}H_7$·ONa (I) + CO_2 → $C_{10}H_7$·O·CO_2Na (II) is reversed at higher temp. (140—160°). (II) rearranges to 2 : 1-ONa·$C_{10}H_6$·CO_2H (III), which reacts at 145—160° as follows: (III) → (I) + CO_2; (III) + (I) → 2 : 1-ONa·$C_{10}H_6$·CO_2Na (IV) + $C_{10}H_7$·OH; at 200—250° (IV) → 2 : 3-ONa·$C_{10}H_6$·CO_2Na (V). The max. possible yield of (V) is thus 50% on the (I) taken. The reactions leading to production of (IV) take place practically simultaneously at 150—160°, at which temp. the amount of CO_2 absorbed is half of that at 40—50°, and the same applies to direct production of (V) at 230°. Increasing the pressure to 45 atm. does not inhibit the reaction (III) → (I) + CO_2. The Na_2CO_3 content of the melt from which (V) is obtained is approx. ∝ its content of tarry substances. R. T.

Determination of the fine structure of aromatic compounds. E. Bergmann and T. Berlin (J. Org. Chem., 1938, **3**, 246—250).—2 : 3-OH·$C_{10}H_6$·COMe, new m.p. 121°, contains an ethylenic linking stabilised in position 2 : 3, since its *oxime*, m.p. 151°, gives an insol. *Cu* derivative; 2 : 3-OH·$C_{10}H_6$·CO_2H is probably similarly constituted. 2 : 3-OH·$C_{10}H_6$·CO_2Me with CH_2:CH·CH_2Br or CHPh:CH·CH_2Br and NaOH in $COMe_2$, and distillation of the product in a vac., gives respectively *Me* 2-*hydroxy*-1-*allyl*-, m.p. 60° (*acetate*, b.p. 170°/0·3 mm.), and -1-*cinnamyl*-3-*naphthoate*, m.p. 132°, thus proving that the double linking in 2 : 3-CH_2:CH·CH_2·O·$C_{10}H_6$·CO_2Me is in the 1 : 2 position. With basic Cu carbonate in quinoline 2-*hydroxy*-1-*allyl*-3-*naphthoic acid*, m.p. 203°, or 1 : 2-CH_2:CH·CH_2·$C_{10}H_6$·OH gives 2-*methyl*-4 : 5-1′ : 2′-*naphth*-2 : 3-*dihydrofuran*, b.p. 125°/2 mm. R. S. C.

3-Hydroxyfluorene-2-carboxylic acid and arylamides.—See B., 1939, 17.

Syntheses in the pinane group. V. Configuration of bromo- and hydroxy-pinic acids. P. C. Guha and P. L. N. Rao (Ber., 1938, **71**, [*B*], 2663—2665).—*dl*-Bromopinic acid (I), m.p. 154—155°, is converted by Zn dust and AcOH into the *trans*-pinic acid (II) (diamide, new m.p. 192°) from which it is derived and therefore has the *trans*-configuration. Since *dl*-hydroxypinic acid (III), m.p. 193—194°, is converted by PBr_3 into (I) it is a *trans*-compound. The change of configuration in the sequence (II) → (I) → (III) → *cis*-norpinic acid must occur during the last stage. H. W.

Syntheses in the thujane group. VII. Complete synthesis of thujone. P. C. Guha and M. S. Muthanna (Ber., 1938, **71**, [*B*], 2671—2672).—Thujadicarboxylic [2-*iso*propyl*cyclo*propane-1-carboxylic-2-acetic] acid (I) is converted by Ac_2O into its anhydride, which with MgMeI yields thujaketonic [1-acetyl-2-*iso*propyl*cyclo*propane-2-acetic] acid. The still missing link in the complete synthesis of thujone is the conversion of umbellularic acid into (I). H. W.

Syntheses in the thujane group. VI. New synthesis of umbellularic acid. Attempted preparation of thujadicarboxylic and thujaketonic acid. P. C. Guha and M. S. Muthanna (Ber., 1938, **71**, [*B*], 2668—2671).—Partly an account of work previously abstracted (A., 1938, II, 364). The following appears new. *trans*-Umbellularic [1-*iso*propyl*cyclo*propane-1 : 2-dicarboxylic acid] acid, m.p. 191—192°, is converted by the successive action of AcCl at 180° and boiling H_2O into the corresponding *cis*-acid (monohydrate, m.p. 94—95°). Et γ-methyl-Δ^{α}-pentenoate and $CHNa(CO_2Et)_2$ afford *Et*$_2$ α-*carbethoxy*-β-iso*propylglutarate*, b.p. 135—140°/4 mm. [whence α-*carboxy*-β-iso*propyl*-, m.p. 160—162°, and β-iso*propyl*-*glutaric acid* (I), m.p. 101—102°], converted by Br in CCl_4 at 50° into *Et*$_2$ α-*bromo*-α-*carbethoxy*-β-iso*propylglutarate*, b.p. 175—176°/3 mm. This when treated with $NPhEt_2$, quinoline, C_5H_5N, KOH–EtOH, or powdered KOH suspended in PhMe gives a debrominated compound which when treated with CH_2N_2 and hydrolysed yields (I) instead of the expected thujadicarboxylic acid. Et α-bromo*iso*hexoate and CHNaAc·CO_2Et appear to yield the semisolid *Et* 2 : 4-*diketo*-6-iso*propyl*cyclo*hexane*-1-*carboxylate*. H. W.

Strainless monocyclic rings. III. Synthesis of 2-methyl*cyclo*hexane-1-carboxylic-1-acetic acid and separation of its isomerides. M. Qudrat-i-Khuda, A. A. Mallick, and (in part) A. Mukherji (J. Indian Chem. Soc., 1938, **15**, 489—497; cf. A., 1938, II, 491).—2-Methyl*cyclo*hexanone, CN·CH_2·CO_2Et, and a little piperidine give *Et* 2-*methyl*cyclo*hexylidenecyanoacetate*, b.p. 165—167°/41 mm., converted by KCN into Et 1-cyano-2-methyl-*cyclo*hexane-1-cyanoacetate, hydrolysed (50 hr.) to 2-*methyl*cyclo*hexane*-1-*carboxylic*-1-*acetic acid*, separated into *isomerides*, viz., *A*, m.p. 162° [*anhydride* (I),

b.p. 202°/24 mm.; *imide*, m.p. 107°; *anilic acid*, m.p. 150°; p-*toluidinic acid*, m.p. 179°; p-*tolylimide*, m.p. 140°; p-*naphthylamic acid*, m.p. 163°; β-*naphthylimide*, m.p. 169°] [hydrolysis of (I) with H_2O (8 hr.) gives an *isomeride B*, m.p. 155° (*anhydride*, b.p. 157°/12 mm.; *imide*, m.p. 110—111°; *anilic acid*, m.p. 143°)]; more sol. in C_6H_6 are the acids *C*, m.p. 153° (Et_2 ester, b.p. 147—148°/18 mm.; *anhydride*, b.p. 142°/8 mm.; *imide*, m.p. 98°; *anilic acid*, m.p. 140°; *phenylimide*, m.p. 105°; p-*toluidinic acid*, m.p. 187°; p-*tolylimide*, m.p. 130°), and *D*, m.p. 142° (*anhydride*, b.p. 160—162°/8 mm.; *imide*, m.p. 105°), which affords the same anilic and *p*-toluidinic acid derivatives as does *C*. The anhydride of *C* is hydrolysed to *D*. The evidence supports the multiplanar configuration of the methyl*cyclo*hexane ring. A. T. P.

Lichen substances. XC. Orcinoldicarboxylic acid monomethyl ethers and the non-existence of the so-called *iso*squamatic acid. Y. Asahina, Z. Simosato, and (in part) V. Sakurai (Ber., 1938, **71**, [*B*], 2561—2568; cf. A., 1933, 159, 504).—Me_2 orcinoldicarboxylate Me ether from thamnolic and squamatic (I) acid has m.p. 125° and the m.p. of (I) is raised by suitable purification to 228°. There is therefore no difference between (I) and "*iso*squamatic" acid. Microchemical observation shows the complete absence of any depside from *Cladonia Boryi* (*loc. cit.*), in the examined specimens of which there must have been some *C. uncialis*. Successive treatments of Me *iso*evernate with anhyd. HCN and HCl at −5° and with H_2O at 100° give *Me* 5-*hydroxy*-6-*aldehydo*-3-*methoxy*-o-*toluate*, m.p. 135° (*anil*, m.p. 138°), hydrolysed to the corresponding *acid*, m.p. 163—164°, which yields evernaldehyde, m.p. 64°, when dry-distilled. Me *p*-orsellinate Me_1 ether, HCl, $AlCl_3$, and HCN in Et_2O at 0° give exclusively Me 3-hydroxy-2-aldehydo-5-methoxy-*p*-toluate, m.p. 136°. Me hæmatommate (II), $ClCO_2Et$, and N-NaOH at 0° yield *Me* 2-O-*carbethoxyhæmatommate*, m.p. 96·5° (together with the 2 : 4-*di*-O-*carbethoxy*-derivative, m.p. 80°), converted by Ag_2CO_3 and MeI in $COMe_2$ into the corresponding *Me ether*, m.p. 144·5°, whence Me hæmatommate 4-Me ether (III), m.p. 87—88°, also obtained by partial demethylation of Me hæmatommate Me_2 ether. (II), CH_2PhCl, NaI, and K_2CO_3 in boiling $COMe_2$ afford, according to conditions, the corresponding $(CH_2Ph)_2$, m.p. 79°, or 2-CH_2Ph (IV), m.p. 112·5° (p-*nitrophenylhydrazone*, m.p. 278°), and 4-CH_2Ph *ether* (V), m.p. 91° (p-*nitrophenylhydrazone*, m.p. 249°; condensation *product*, m.p. 143·5°, with *o*-$C_6H_4Me{\cdot}NH_2$). (IV) and (V) are converted by MeI and K_2CO_3 in boiling $COMe_2$ into *Me hæmatommate* 2-CH_2Ph 4-*Me ether* (VI), m.p. 65·5°, and 4-CH_2Ph 2-*Me ether* (VII), m.p. 80°, respectively. Debenzylation of (VI) gives (III) and of (VII) yields *Me hæmatommate* 2-*Me ether*, m.p. 64° (*anil*, m.p. 101°). Reduction (Pd–C in AcOH) of (VI) and (VII) leads to Me rhizonate and *iso*rhizonate respectively. (VI) is oxidised ($KMnO_4$ in $COMe_2$) and then methylated to *Me*$_2$ *orcinol*-1 : 3-*dicarboxylate* 2-CH_2Ph 4-*Me ether* (VIII), m.p. 51°, whilst (VII) correspondingly gives 1-*Me H orcinol*-1 : 3-*dicarboxylate* 4-CH_2Ph 2-*Me ether*, m.p. 136°, converted by CH_2N_2 into the *Me*$_2$ ester (IX), m.p. 76°. Reductive debenzylation (Pd–C in AcOH) of (VIII) gives Me_2 orcinol-1 : 3-dicarboxylate 4-Me ether, m.p. 125°, identical with that derived from (I). (IX) similarly yields *Me*$_2$ *orcinol*-1 : 3-*dicarboxylate* 2-*Me ether*, m.p. 52·5°, hydrolysed to the corresponding dicarboxylic *acid*, m.p. 158° (decomp.) or (+H_2O) m.p. 158° after softening at about 100°, with a little unidentified material, m.p. 168°. H. W.

Action of organo-magnesium compounds on 1-bromo*cyclo*hexanealdehyde. B. Tchoubar and O. Sackur (Compt. rend., 1938, **207**, 1105—1106; cf. Bartlett and Rosenwald, A., 1934, 1221).—1-Bromo*cyclo*hexanealdehyde (I) with MgPhBr in Et_2O at 0° affords 1-phenyl*cyclo*hexanealdehyde (A., 1935, 1240). Similarly (I) with MgMeI and MgEtBr affords *cyclo*hexyl Me and Et ketone, respectively. Reaction of (I) with MgRX involves migration of either H (R = alkyl) or R (R = aryl) in the intermediate $C_5H_{10}{>}CBr{\cdot}CHR{\cdot}OMgX$. J. L. D.

Nitrones. III. *cis–trans*-Isomerism of anils? F. Kröhnke (Ber., 1938, **71**, [*B*], 2593—2595).—Repetition of the work of Sachs *et al.* (A., 1902, i, 377), Barrow and Griffith (J.C.S., 1921, **119**, 212), and Bergmann and Hervey (A., 1929, 695) on the interaction of *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$ and *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ (I) shows that the assumed existence (A., 1929, 695) of *cis–trans* isomeric anils is erroneous. Aldehydes can be obtained from benzyl halides in manner other than through the nitrones. Thus CH_2PhCl, CH_2PhBr, or CH_2PhI and (I) in EtOH containing NaOH at 20° give much PhCHO, a little azoxydimethylaniline, but no nitrone. The same compounds are obtained from CH_2PhBr or CH_2PhI and (I) in EtOH without alkali; nitrone cannot be isolated although it is stable under these conditions. H. W.

Nitrones. II. F. Kröhnke (Ber., 1938, **71**, [*B*], 2583—2593; cf. A., 1936, 1510).—Nitrone formation with 1 mol. of a NO-compound occurs if the group >CHHal, >CH·OH, or >CH·NC_5H_5,X is present and the methine-H is sufficiently activated by the other residues; pyridinium can be replaced by quinolinium or *iso*quinolinium. The important factor is the presence of the N:C double linking in a ring since this has a very activating effect on neighbouring CH_2 or CH groups in alkaline solution. CHPh:CH·CH_2Br and C_5H_5N in C_6H_6 at 20° followed by 2N-$HClO_4$ give *cinnamylpyridinium perchlorate*, m.p. 73—74°, transformed by *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ (I) and NaOH in EtOH at 0—20° into N-p-*dimethylaminophenylstyrylnitrone*, m.p. 180°. The following benzylpyridinium halides are obtained by heating the benzyl halide with about a 20% excess of C_5H_5N in EtOH at 100°. The nitrones are prepared from the pyridinium salt and the NO-compound in EtOH with the calc. amount of N-NaOH at 20—30°. The following new or revised data are given. phenyl-*N*-*p*'-dimethylaminophenylnitrone, m.p. 144°, from benzylpyridinium bromide and (I); *p*-nitrobenzylpyridinium bromide, m.p. 219°, whence *p*-nitrophenyl-*N*-*p*'-dimethylaminophenylnitrone, m.p. 206°; *p*-nitrobenzylidene-*p*'-dimethylaminoanil, m.p. 219—220°; *o-nitrobenzylpyridinium chloride* (+H_2O), m.p. 183—184° (corresponding *perchlorate*, m.p. 161—162°),

whence o-*nitrophenyl*-N-p′-*dimethylaminophenylnitrone*, m.p. 134·5°; m-*nitrobenzylpyridinium chloride*, m.p. 191°, and m-*nitrophenyl*-N-p′-*dimethylaminophenylnitrone*, m.p. 168·5°; p-*chlorobenzylpyridinium bromide*, m.p. 172—173°, and p-*chlorophenyl*-N-p′-*dimethylaminophenylnitrone*, m.p. 178°; p-*chlorobenzylidene*-p′-*dimethylaminoanil*, m.p. 165·5°; m-*chlorobenzylpyridinium chloride*, m.p. 180°, and m-*chlorophenyl*-N-p′-*dimethylaminophenylnitrone*, m.p. 118° (corresponding *anil*, m.p. 104°); p-*bromobenzylpyridinium bromide*, m.p. 150—151°, and p-*bromophenyl*-N-p′-*dimethylaminophenylnitrone*, m.p. 193°; p-*methoxybenzylpyridinium bromide*, m.p. 164°, and p-*anisyl*-N-p′-*dimethylaminophenylnitrone*, m.p. 146—147°; p-*methoxybenzylidene*-p′-*dimethylaminoanil*, m.p. 145°; 1-naphthylmethylpyridinium bromide, m.p. 135° after softening at 114°, and 1-*naphthyl*-N-p′-*dimethylaminophenylnitrone*, m.p. 127—129° after softening; S-p-*xylylenedipyridinium bromide* (+$2H_2O$), m.p. 281—282° (corresponding *perchlorate*), and the *dinitrone*, decomp. >225°, converted by N-NaOH into *p*-$C_6H_4(CHO)_2$ in 77% yield; s-m-*xylylenedipyridinium bromide*, m.p. 221° (*perchlorate*), and the *dinitrone*, m.p. 193°, whence *m*-$C_6H_4(CHO)_2$ in 40% yield; s-o-*xylylenedipyridinium bromide* which undergoes side reactions with (I) and ultimately gives *o*-$C_6H_4(CHO)_2$ in only very modest yield; *benzhydrylpyridinium bromide*, m.p. 185° (corresponding *perchlorate*, m.p. 206—207°), and *diphenyl*-N-p′-*dimethylaminophenylnitrone*, m.p. 135° (decomp.), which with 2N-HCl gives $COPh_2$ in 95% yield; *phenylcarbethoxy*-N-p′-*dimethylaminophenylnitrone*, m.p. 133·5°. NPh:CPh·CN, m.p. 72°, is obtained in 62% yield by the addition of PhNO in EtOH to CH_2Ph·CN and N-NaOH in EtOH. H. W.

Preparation of aromatic aldehydes. B. Helferich, R. Streeck, and E. Günther (J. pr. Chem., 1938, [ii], **151**, 251—256).—Gradual addition of 6 : 3 : 1-OH·C_6H_3(CH_2·OH)·CHO to HNO_3 (*d* 1·4) at >80° gives 4-hydroxy*iso*phthalaldehyde, m.p. 108—109° (corr.) (*bisphenylhydrazone*), in 70% yield. Similarly *o*- and *p*-NO_2·C_6H_4·CH_2·OH give the corresponding aldehyde in 85% or 80% yield, respectively. *p*-$C_6H_4(CHO)_2$ is obtained in 80% yield from *p*-$C_6H_4(CH_2$·$OH)_2$. 4 : 6 : 1 : 3-$C_6H_2Me_2(CH_2$·$OH)_2$ affords 4 : 6-*dimethylisophthalaldehyde*, m.p. 107—108° [*bisphenylhydrazone*, m.p. 195° (decomp.)]. H. W.

Syntheses in the thujane group. VI. Synthesis of umbellulonic [2-acetyl-1-*iso*propyl-*cyclo*propane-1-carboxylic] acid. P. C. Guha and M. S. Muthanna (Ber., 1938, **71**, [*B*], 2665—2667).—An account of work previously reviewed (A., 1938, II, 336). H. W.

Preparation of R-methyl ketones from keten. I. Preparation of acetophenone. B. N. Daschkevitsch (J. Gen. Chem. Russ., 1938, **8**, 779—782).—MgPhBr in Et_2O and keten at >30° yield a complex, which with H_2O at 50° gives COPhMe (30—35%). R. T.

Condensation of paraformaldehyde with aromatic ketones. R. C. Fuson, W. E. Ross, and C. H. McKeever (J. Amer. Chem. Soc., 1938, **60**, 2935—2936).—COPhMe, paraformaldehyde (I) (all proportions), and a little K_2CO_3 in MeOH at room temp. (7 days) give β-*benzoylpropane*-α*γ*-*diol* CH_2 *ether* (II), b.p. 124—126°/3 mm., converted by conc. HCl at room temp. into CH_2O and α*γ*-*dichloro*-β-*benzoylpropane*, m.p. 56—57°, and thence by C_6H_6–$AlCl_3$ into COPh·CH(CH_2Ph)$_2$. H_2SO_4 hydrolyses (II) (CH_2O liberated), but the $(OH)_2$-ketone could not be isolated; an unstable, lachrymatory oil, b.p. 101—105°/3 mm., was obtained. COPhEt, (I), and K_2CO_3 in MeOH give β-*benzoyl*-n-*propyl alcohol*, b.p. 143—145°/5 mm. (*phenylurethane*, m.p. 86—87°), converted by cold H_2SO_4 into 2-methyl-α-hydrindone, b.p. 88—90°/3 mm. (2-Br-derivative, m.p. 72—73°), oxidised by HNO_3 to *o*-$C_6H_4(CO_2H)_2$. R. S. C.

β-Benzoyl-αβ-diphenylpropionic [*γ*-keto-αβ*γ*-triphenylbutyric] acid. (Miss) H. M. Crawford (J. Amer. Chem. Soc., 1938, **60**, 3078—3079).—COPh·CHPhNa (prep. by Na in Et_2O) and CHPhBr·CO_2Et give COPh·CHPh·CHPh·CO_2Et, hydrolysed by KOH–EtOH to *γ-keto*-αβ*γ-triphenylbutyric acid*, m.p. 201—202° (*Me*, m.p. 147—148°, and *Et* ester, m.p. 147·5—148°), with a little of the form, m.p. 211—212° (Me, m.p. 158·5—159°, and *Et* ester, m.p. 138—139°) (Reimer *et al.*, A., 1908, i, 989). With 65% H_2SO_4 both acids give the *lactone*, m.p. 124—125°, of *γ*-hydroxy-αβ*γ*-triphenyl-Δ^{β}-butenoic acid, from which they are both recovered by KOH–EtOH. CO-derivatives could not be obtained. R. S. C.

Regulation of the catalytic reduction of unsaturated compounds and the ageing phenomena of platinum contacts. C. Weygand and A. Werner (Ber., 1938, **71**, [*B*], 2469—2474).—Hydrogenation (pure Pt-black from PtO_2) of CHPh:CH·CO·C_6H_4Me-*p* yields α-*cyclo*hexyl-*γ*-*p*-methyl*cyclo*hexylpropane. Addition of a very small amount of $FeCl_3$ causes a somewhat more rapid but otherwise similar hydrogenation, whereas if a much larger proportion of $FeCl_3$ is used the reaction ceases after absorption of 2 H_2 with formation of CH_2Ph·CH_2·CH(OH)·C_6H_4Me. $FeCl_2$ and H_2O are necessary for the sp. restriction. The reaction is similar for several substances (CHPh:CHPh; diphenylbutadiene; CHPh:CH·COPh; *cis*- and *trans*-CHPh:CH·CO_2H); >CO is unchanged or is converted into >CH·OH whilst aromatic residues are unaffected. With the restricted catalyst it is readily possible to convert *trans*-(CHBz:)$_2$ into (CH_2Bz·)$_2$; this cannot be achieved otherwise even when the experiment is discontinued after absorption of 1 H_2. A difference in the absorptive capacity of *cis*- and *trans*-(CHBz:)$_2$ is noted in the presence or absence of the restricting agent. With mg. quantities the experiments are readily reproducible but considerable variations are observed when higher concns. are used. It is suggested that the activity of Fe^{II} salts depends on the removal of the last traces of O from the catalyst by Fe" ions. The activity of the catalyst diminishes with keeping. H. W.

αβ-Unsaturated ketones obtained from acetophenone and their reaction with phenylhydrazine. L. C. Raiford and G. V. Gundy (J. Org. Chem., 1938, **3**, 265—272).—Br_1- and Cl_1-derivatives of vanillin

with C_6H_4X·COMe and NaOH give only monoacetophenone derivatives (cf. A., 1932, 515). *o*-NO_2·C_6H_4·COMe does not react with 5-, nor *p*-C_6H_4Cl·COMe with 2-bromovanillin. The following are obtained: ω-2′-*nitro*-, m.p. 175—178°, and ω-5′-*bromo*-2′-*nitro*-*vanillylideneacetophenone*, m.p. 185—187° (decomp.); ω-5′-*bromovanillylidene*-p-*methyl*-, m.p. 146—147°, -p-*methoxy*- (also +AcOH), m.p. 138—140°, -p-*hydroxy*-, m.p. 229—230°, -m-*nitro*-, m.p. 270° (decomp.), -p-*bromo*-, m.p. 154—155°, -o-*chloro*-, m.p. 120—121°, and -p-*chloro*-, m.p. 164—167°, -*acetophenone*. 5-Nitrovanillin gives ω-5′-*nitrovanillylideneacetophenone*, m.p. 139—140°, and αε-*diphenyl*-γ-5-*nitro*-4-*hydroxy*-3-*methoxyphenylpentane*-αε-*dione*, m.p. 150—151°, and 2 : 5-dichlorovanillin gives ω-2′ : 5′-*dichlorovanillylideneacetophenone*, m.p. 139—141°, and αε-*diphenyl*-γ-2 : 5-*dichloro*-4-*hydroxy*-3-*methoxyphenylpentane*-αε-*dione*, m.p. 160—161°. With NHPh·NH_2 or *p*-NO_2·C_6H_4·NH·NH_2 under all conditions tried the products, CHAr:CH·COAr, give pyrazolines directly, as judged by failure to obtain NH_2Ph on reduction. The following are described. 1 : 3-*Diphenyl*- (I), m.p. 139—141°, 1-*phenyl*-3-p-*bromophenyl*- (II), m.p. 195—197°, 3-*phenyl*-1-p-*nitrophenyl*-, m.p. 211—213°, 3-p-*chlorophenyl*-1-p-*nitrophenyl*-, m.p. 214—215°, 1-p-*nitrophenyl*-3-p-*tolyl*-, m.p. 231—232°, and 1-p-*nitrophenyl*-3-p-*hydroxyphenyl*-, m.p. 255—256°, -5-5′-*bromo*-4′-*hydroxy*-3′-*methoxyphenylpyrazoline*; 3-*phenyl*-, m.p. 210—212°, and 3-m-*nitrophenyl*-, m.p. 237—238°, -1-p-*nitrophenyl*-5-6′-*bromo*-4′-*hydroxy*-3′-*methoxyphenylpyrazoline*; 3-*phenyl*-1-p-*nitrophenyl*-5-5′-*bromo*-2′-*nitro*-4′-*hydroxy*-3′-*methoxyphenylpyrazoline*, m.p. 220° (decomp.). With Na–EtOH 1 : 5-diphenyl-3-*p*-bromophenylpyrazoline gives 12% of 1 : 3 : 5-triphenylpyrazoline, and (II) gives 10% of (I), much starting material being recovered in both cases.

R. S. C.

Rearrangement in the benzoin series. F. L. James [with R. E. Lyons] (J. Org. Chem., 1938, **3**, 273—280).—Decomp. of benzoin to CH_2Ph_2 and CO_2 by H_3PO_4 at elevated temp. is largely prevented by catalysts. The best yield (53·9%) of $CHPh_2$·CO_2H is obtained by the use of 60% H_3PO_4 and SiO_2 gel at 270°/24 hr. 4 : 4′-Dimethyl- and -*iso*propyl-benzoin give similarly only 25% of $(p\text{-}C_6H_4Me)_2CH\cdot CO_2H$ and <5% of $(p\text{-}C_6H_4Pr^{\beta})_2CH\cdot CO_2H$, respectively, both without decomp., but OH·CPh_2·COPh is unchanged and *p*-methoxy-, *p*-dimethylamino-, *pp*′-dimethoxy-, and *o*′-chloro-*p*-methoxy-benzoin decompose. The reaction mechanism is discussed. R. S. C.

Relative proportions of stereoisomeric oximes formed by oximation of unsymmetrical ketones. W. E. Bachmann and (Miss) M. X. Barton (J. Org. Chem., 1938, **3**, 300—311).—In naming ketoximes the prefix *syn* or *anti* refers to the relative positions of the OH and the radical named first. COPh·C_6H_4-*p*, NH_2OH,HCl, and C_5H_5N in abs. EtOH give the *syn*- (I), m.p. 173°, and *anti*- (II), m.p. 200°, -oximes, a similar mixture being also obtained under Koller's conditions (A., 1892, 186). Conversion of the crude product, best by PCl_5 in thiophen-free C_6H_6, into the amide, hydrolysis thereof, and separation of the acids shows the mixture to contain 49% of (I) and 51% of (II). Under the conditions of oximation pure (I) or (II) is equilibrated to the same mixture. The same method of analysis shows the following yields of *syn*-oxime to be formed: COPhR, R = *p*- 48, *m*- 50, and *o*-tolyl 23, *p*-anisyl 51, *p*-C_6H_4Cl 44, and 2-fluorenyl 46; *o*- 66, *m*- 47, and *p*-tolyl *p*-C_6H_4Ph ketone 34; α- or β-$C_{10}H_7$ or *p*-C_6H_4Ph Me ketone 99%. Ph mesityl and 9-anthranyl ketones do not form oximes. 1-Acetylanthracene, m.p. 106·5—108° (lit., 103—105°), partly decomposes during oximation. Analogous results are discussed. The following are incidentally prepared. p-*Phenylbenz-methyl*-, m.p. 167°, -o-, m.p. 179·5—180°, -m-, m.p. 165—166°, and -p-*tolyl*-, m.p. 230—231°, -*amide*; o-, m.p. 256°, m-, m.p. 270°, and p-*tolu*-p′-*diphenylylamide*, m.p. 236—237°; 1-, m.p. 159—160°, and 2-*naphthomethylamide*, m.p. 108—109·5°; m-*toluanilide*, m.p. 125—125·5°; 2-*benzamidofluorene*, m.p. 215°; *fluorene*-2-*carboxyanilide*, m.p. 255—256°.

R. S. C.

Local anæsthetics derived from benzoylbenzoic acids. B. Samdahl and T. Christiansen (Bull. Soc. chim., 1938, [v], **5**, 1573—1580).—*o*-C_6H_4Bz·COCl (I) (prep. with $SOCl_2$) and NEt_2·$[CH_2]_2$·OH in C_6H_6 at 100° (bath)/20 min. give β-diethylaminoethyl *o*-benzoylbenzoate [*hydrochloride* (II), m.p. 95—130°, which is probably mainly the lactone form]. One experiment, viz., (I) left in a desiccator for 3 weeks before use, and reaction for 2½ hr., gave the ketonic *hydrochloride*, m.p. 137—138°, also obtained in poor yield from (I) (prep. with PCl_5). The *hydrochlorides* of β-diethylaminoethyl *m*- and *p*-benzoylbenzoates have m.p. 143·5—144·5° and 138—139°, respectively. (II) only is a good anæsthetic, but is toxic.

A. T. P.

Partition principle as applied to the structures of enolic sodium derivatives of β-diketones and β-keto-esters. III. A. Michael and N. Weiner (J. Org. Chem., 1938, **3**, 372—384; cf. A., 1932, 254).—COPh·CH:CPh·ONa (prepared by $NaNH_2$ or NaOMe) with $ClCO_2Me$ (1 mol.) in dioxan at room temp. gives *Me dibenzoylacetate* (I), m.p. 116—117° (*Cu* derivative, m.p. 240°), some CHBz:CPh·O·CO_2Me (II), and, by further reaction [from (I)], CO_2Me·CBz:CPh·O·CO_2Me (III) (not isolated pure), b.p. ~204—208° (slight decomp.)/2 mm.; 20—25% of CH_2Bz_2 is recovered. MeOH–NaOH converts (III) into (I) and CH_2Bz_2. With 0·5 mol. of $ClCO_2Me$ in dioxan 25·1% of (I) and 17·2% of (II) are formed; in Et_2O, however, 7% of (I) and 13·8% of (II) are obtained, the difference being ascribed to a "solvent effect." Sodiobenzoylacetone with 0·5 mol. of $ClCO_2Me$ in Et_2O or dioxan gives mainly CHBz:CMe·O·CO_2Me with less *Me* α-*benzoylacetoacetate* (IV), b.p. 136—137°/2 mm. (*Cu* derivative, m.p. 226—228°; obtained also from CHAcNa·CO_2Me and BzCl). If an excess of $ClCO_2Me$ is used, about equal amounts of γ-*keto*-α-*carbomethoxyoxy*-β-*acetyl*-α-*phenyl*-Δ^{α}-*butene*, m.p. 87°, and *Me* β-*carbomethoxyoxy*-α-*benzoylcrotonate*, m.p. 97°, are formed (cf. A., 1931, 1035); these products are also obtained from $ClCO_2Me$ and the Na derivative of (IV), and their structure is proved by hydrogenation, followed by hydrolysis to Ph·$[CH_2]_2$·COMe and COPhPr^{α}, respectively. Thus, (IV) enolises in both possible ways.

The product, m.p. 166°, obtained from $CO_2Me{\cdot}O{\cdot}CMe{:}CH{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$ by dil. AcOH (A., 1931, 1035) is the *semicarbazone*, $CH_2Ac{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$. R. S. C.

The "two forms" of symmetrical tetrabenzoylethane. H. KLEINFELLER and H. TROMMSDORFF (Ber., 1938, **71**, [*B*], 2448—2450).—The product of the action of $CHNaBz_2$ on I (Abell, J.C.S., 1912, **101**, 997) is ααββ-tetrabenzoylethane (I), m.p. 212°, accompanied by $(:CBz_2)_2$ (identified by its photochemical behaviour and conversion into $C_2H_2AcBz_3$). Hydrolysis of (I) gives $(\cdot CH_2Bz)_2$. The "tetrabenzoylethane of lower m.p." obtained by Wesenberg (Diss., Leipzig, 1898) from CH_2Bz_2, NaOEt, and I is identified as *ααβ-tribenzoylethane*, m.p. 155°, obtained also from CH_2BzI and $CHNaBz_2$ in $COMe_2$. It is converted by Cl_2 in boiling AcOH into *β-chloro-ααβ-tribenzoylethylene*, m.p. 90—91°, and by HCl in boiling AcOH into *3-benzoyl-2 : 5-diphenylfuran*, m.p. 77—78° (*oxime*, m.p. 170—172°). H. W.

Stereochemistry of cyclanes. V. Stereoisomeric dibenzylidene derivatives. R. CORNUBERT, M. DE DEMO, R. JOLY, P. LOUIS, and A. STRÉBEL. **VI. Stereoisomeric dibenzylidene-*cyclo*heptanones. Action of ultra-violet rays on diarylidenecyclanones.** R. CORNUBERT, R. JOLY, and A. STRÉBEL (Bull. Soc. chim., 1938, [v], **5**, 1490—1501, 1501—1505; cf. A., 1938, II, 235).—V. When 2 : 5-dibenzylidene*cyclo*pentanone (I), m.p. 190°, is heated at near the b.p./15—20 mm. for 10—15 min., a *stereoisomeride* (II), m.p. 141°, is obtained (amongst other products). (I) and (II) are hydrogenated to the same 2 : 5-dibenzyl*cyclo*pentanone. (II) and Br give (method : Vorländer and Hobohm, A., 1896, i, 603) the tetrabromide of (I), together with a little of an (?) *isomeride*, m.p. 80—85°. *cyclo*Pentanone (III) and PhCHO with various condensing agents give (I) (best by NaOEt) and no (II) is isolated; with Na_2CO_3 or NMe_3, some *2 : 5-di-(α-hydroxybenzyl)*cyclo*pentanone*, m.p. 178° [converted partly by heating in EtOH into an *isomeride*, m.p. 158°, also obtained from (III)–PhCHO–NEt_3], is also formed. Dehydration of either diol gives only (I) (cf. A., 1930, 474). (III) and *p*-$C_6H_4Me{\cdot}CHO$ in NaOEt–EtOH give the corresponding *di-p-tolylidene*cyclo*pentanone* (IV), m.p. 235—236°; after heating at ~b.p. for ½ hr., distillation gives a *stereoisomeride*, m.p. 115°. A stereoisomeride is not obtained from dibenzylidene*cyclo*hexanone (V), m.p. 118°, or by dehydration of the corresponding di-α-hydroxybenzyl derivatives, m.p. 160—163° and 153—156° (cf. Vorländer and Kunze, A., 1926, 1144). *cyclo*Octanone and PhCHO (2 mols.) (as below) give a *hydroxybenzylbenzylidene* derivative, m.p. 134—135°, dehydrated (Ac_2O) to a liquid *product*, $C_{22}H_{22}O$ [? $(CHPh:)_2$ derivative].

VI. *cyclo*Heptanone and PhCHO in MeOH–NaOMe at 60—65° give the dibenzylidene derivative (VI), m.p. 108°, hydrogenated (Ni formate, EtOH, at 75°) to the *dibenzyl* compound (VII), b.p. 248—249°/20 mm. (*oxime*, m.p. 112°). (VI) at ~b.p./18 mm. and distilled gives a stereoisomeric *dibenzylidene*cyclo*heptanone* (VIII), m.p. 107°, also reduced to (VII). Irradiation (ultra-violet) experiments are recorded : (VI) (520 hr.) and (V) are unaltered, but (VIII) gives some (VI); (II) is little affected but (I) and (IV) undergo some oxidation. The ketonic reactivity [with PhCHO to give tetrahydropyrones] of dibenzyl-*cyclo*-pentanone, -hexanone, and -heptanone (does not react) diminishes in the order quoted. A. T. P.

Synthesis of substances related to the sterols. XXV. K. H. LIN and R. ROBINSON (J.C.S., 1938, 2005—2008; cf. A., 1937, II, 196).—$CMeNa(CO_2Et)_2$ and $Ac{\cdot}[CH_2]_2{\cdot}Cl$–$Et_2O$ give *Et methyl-β-acetylethylmalonate*, b.p. 114—116°/0·4 mm., which when refluxed with NaOEt–EtOH affords *1-carbethoxy-1-methyl*cyclo*hexane-2 : 4-dione* (I), m.p. 81·5—82·5°. *m*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$ and anhyd. $SnCl_2$–Et_2O–HCl at 0° afford the aldimine stannichloride, decomp. (neutral PO_4''' buffer) to *m-methoxyphenylacetaldehyde*, b.p. 117—119°/13 mm. (*semicarbazone*, m.p. 130—131°); no CO-compound is isolated on condensation with (I). Dimethyldihydroresorcinol (dimedone) (II) and $CH_2Ph{\cdot}CHO$ in piperidine–EtOH give *ββ-bis-(2′ : 6′-diketo-4′ : 4′-dimethyl*cyclo*hexyl)ethylbenzene*, m.p. 164—165°, converted by boiling Ac_2O or P_2O_5–C_6H_6 into *9-benzyl-3 : 3 : 6 : 6-tetramethyloctahydroxanthen-1 : 8-dione*, m.p. 125—126°. Piperonylacetaldehyde and (II) at 160—165° give a product containing some (?) *6 : 7-methylenedioxy-2-acetyl-1-methylnaphthalene* [*2 : 4-dinitrophenylhydrazone*, m.p. 299—300° (decomp.)], probably formed from CH_2Ac_2 [by loss of $:CMe_2$ from (II)]. *γ-3 : 4-Dimethoxyphenylbutyryl* chloride and Et sodioacetylsuccinate in Et_2O give a product, which with aq. KOH–EtOH affords mixed acids. Esterification (CH_2N_2) gives Me dimethoxyphenylbutyrate and Me *γ-keto-ζ-3′ : 4′-dimethoxyphenylheptoate*, b.p. 195—198°/0·3 mm. [free *acid*, m.p. 69—70° (*semicarbazone*, m.p. 158—159°)]. The *lactone*, b.p. 203—208°/0·22 mm., of *γ-hydroxy-ζ-3′ : 4′-dimethoxyphenylheptoic acid* is synthesised (method : *loc. cit.*). Air and HBr passed into eugenol Me ether in C_6H_6–BzO_2H give a *hydroxymethoxybromopropylbenzene*, b.p. 160—163°/10 mm. Safrole and HBr with BzO_2H–C_6H_6 or in presence of $FeCl_3$ or α-heptenylheptaldehyde give only β-bromodihydrosafrole. A. T. P.

Attempted synthesis of the antirachitic vitamin. III. K. DIMROTH and H. JONSSON (Ber., 1938, **71**, [*B*], 2658—2662; cf. A., 1938, II, 326, 327).—*cyclo*Hexylideneacetaldehyde condenses with *p*-methoxy*cyclo*hexanone to *α-cyclohexylidene-β-2-keto-5-methoxycyclohexylidene-ethane*, m.p. 84°, which is stable to air. Similarly *cyclo*hexanone and 1-decahydronaphthylideneacetaldehyde afford *α-1-decahydronaphthylidene-β-2-keto*cyclo*hexylidene-ethane*, m.p. 82—83° [*2 : 4-dinitrophenylhydrazone*, m.p. 232—236° (decomp.)], or, under different conditions, *2 : 6-di-(1′-decahydronaphthylidene-ethylidene)*cyclo*hexanone*, m.p. 196°. The absorption spectra of the ketones are discussed. Reduction $[Al(OPr^\beta)_3$ in $Pr^\beta OH]$ of *α-cyclo*hexylidene-β-2-keto*cyclo*hexylidene-ethane gives *α-cyclohexylidene-β-2-hydroxy*cyclo*hexylidene-ethane*, m.p. 124—125°. The following substances are incidentally described : 1-ethyldecahydro-1-naphthol, b.p. 124—126°/12·5 mm. (*p-nitrobenzoate*, m.p. 114°); *1-hydroxydecahydronaphthalene-1-acetic acid*, m.p. 147° (from 1-ketodecahydronaphthalene, Zn, and $CH_2Br{\cdot}CO_2Et$ in C_6H_6, and subsequent hydrolysis),

converted by boiling Ac_2O into decahydronaphthylideneacetic acid, m.p. 185°, which is oxidised to *trans*-1-ketodecahydronaphthalene, m.p. 230°.

H. W.

(A) Tertiary amino-alcohols and enols from carvone. (B) Optically active zwitterions and enol-betaines. H. Rupe and H. Gysin (Helv. Chim. Acta, 1938, **21**, 1413—1432, 1433—1449; cf. A., 1931, 1300; 1934, 1224).—(A) Carvone oxide (improved prep.; cf. Treibs, A., 1932, 398, 1139) is converted by 30% $NHMe_2$ at 95—105° into (mainly) 2-*dimethylamino*-3-*hydroxy*-2-*methyl*-5-iso*propenyl*cyclo*hexanone* (I), b.p. 70—72°/0·008 mm., $[\alpha]_D^{20}$ —55·16°, 3-*dimethylamino*-2-*hydroxy*-2-*methyl*-5-iso*propenyl*cyclo*hexanone* (II), b.p. 90°/0·006 mm., 156° (slight decomp.)/11 mm., $[\alpha]_D$ —40·85°, and a little 3-*dimethylamino*-2-*methyl*-5-iso*propenyl*-Δ^2-cyclo*hexenone* (III), b.p. 60—61°/0·006 mm., $[\alpha]_D$ +30·77° (separated from one another partly by distillation under diminished pressure and partly through their perchlorates), with unchanged material and hydroxycarvone, m.p. 185° (semicarbazone, m.p. 222°). (I) gives a *perchlorate*, m.p. 173—174°, $[\alpha]_D^{20}$ —12·78° in H_2O, *semicarbazone*, m.p. 164°, *oxime*, m.p. 136°, a somewhat unstable *acetate*, b.p. 144—146°/10·5 mm., and a *methiodide*, m.p. 163°. Partial hydrogenation (Ni in EtOH) of (I) yields 2-*dimethylamino*-3-*hydroxy*-2-*methyl*-5-iso*propyl*cyclo*hexanone*, b.p. 132—134°/12·5 mm. $[\alpha]_D^{20}$ —47·42° in C_6H_6 (*perchlorate*, m.p. 156°; *semicarbazone*, m.p. 134°; *methiodide*, m.p. 180—181°), whereas complete hydrogenation gives the (?) diastereoisomeric 2-*dimethylamino*-2-*methyl*-5-iso*propyl*cyclo*hexane*-1 : 3-*diols*, (IV), b.p. 139—141°/11 mm., $[\alpha]_D^{20}$ —38·89° in substance, —41·38° in C_6H_6 (*methiodide*, m.p. 175—176°; *aurichloride*, m.p. 124°), and (V), b.p. 149—151°/11 mm., $[\alpha]_D^{20}$ —37·13° in C_6H_6, which does not yield a methiodide or aurichloride. The relative position of the OH in (I) is established by the observation that (IV) absorbs 6 O when oxidised by $Pb(OAc)_4$. (II) affords a *perchlorate*, m.p. 143—144°, $[\alpha]_D^{20}$ +9·86° in H_2O, and a *methiodide*, m.p. 140—141°, but does not appear to yield an oxime or a semicarbazone. It is partly hydrogenated (Ni in 50% EtOH) to 3-*dimethylamino*-2-*hydroxy*-2-*methyl*-5-iso*propyl*cyclo*hexanone*, b.p. 157—159°/13 mm., $[\alpha]_D^{20}$ —39·16° in C_6H_6, which does not give cryst. derivatives, is not further hydrogenated by Pd–H_2 at 75°/115 atm. but yields a mobile *Me ether*, and is completely hydrogenated (Ni in EtOH at room temp. and then at 60°) to 6-*dimethylamino*-1-*methyl*-4-iso*propyl*cyclo*hexane*-1 : 2-*diol* (VI), b.p. 163—165°/11 mm., $[\alpha]_D^{20}$ —41·79° in C_6H_6 (*methiodide*, m.p. 181° after softening at 179°); this absorbs 1 O when treated with $Pb(OAc)_4$ but does not react with $COMe_2$ in presence of anhyd. $ZnCl_2$. (III) forms a *perchlorate*, m.p. 164°, $[\alpha]_D^{20}$ —40·1° in H_2O, and a *methiodide*, m.p. 154—155° to a turbid melt. It does not give a semicarbazone. (I) is transformed by MgMeI into 2-*dimethylamino*-1 : 2-*dimethyl*-5-iso*propenyl*cyclo*hexane*-1 : 3-*diol*, b.p. 139—139·5°/10·5 mm., m.p. 42°, $[\alpha]_D^{20}$ —25·85° in C_6H_6 (*perchlorate*, m.p. 163°). Similarly (II) affords 6-*dimethylamino*-1 : 2-*dimethyl*-4-iso*propenyl*cyclo*hexane*-1 : 2-*diol*, b.p. 158—159°/11·5 mm., $[\alpha]_D^{20}$ —2·92° in C_6H_6 (*perchlorate*, m.p. 125—126°), and (III) yields 3-*dimethylamino*-1 : 2-*dimethyl*-5-iso*propenyl*-Δ^2-cyclo*hexenol*, b.p. 122—124°/12·5 mm., $[\alpha]_D^{20}$ —3·16° in C_6H_6, from which cryst. derivatives could not be prepared. Reduction of (I) with Na and boiling EtOH gives two bases, m.p. 166° and 103—104°. When heated at 140—145°/12 mm. with a little $ZnCl_2$, (I) loses H_2O and passes into 6-*dimethylamino*-6-*methyl*-3-iso*propenyl*-$\Delta^{1:4}$-cyclo*hexadienol* (VII), b.p. 116—118°/11 mm., $[\alpha]_D^{20}$ —10·81° [*perchlorate*, m.p. 141°; *acetate*, b.p. 142·5—143·5°/11 mm.; Me ether (*perchlorate*, m.p. 131°) not obtainable by Purdie's method or with CH_2N_2 but with Me_2SO_4 and 30% NaOH; *methiodide*, m.p. 163°].

(B) (I) is converted by $CH_2Br{\cdot}CO_2Et$ into 6-*hydroxy*-2-*keto*-1-*methyl*-4-iso*propenyl*-1-cyclo*hexyldimethylcarbethoxymethylammonium bromide* (VIII), which has m.p. 165° (partial decomp.) $[\alpha]_D$ +7·81° in H_2O (mutarotation) if obtained in presence of H_2O and $[\alpha]_D$ —9·56° in EtOH if prepared in the complete absence of H_2O. The aq. solution (0·01N.) of (VIII) is strongly acidic (p_H ~3) whereas in EtOH it is only weakly acidic. The *perchlorate* has m.p. 159° after softening at 152°. Addition of $CH_2Br{\cdot}CO_2Et$ to the Ac derivative of (I) gives the corresponding *ester hydrobromide*, $C_{18}H_{30}O_5NBr$, m.p. 129—131°, $[\alpha]_D^{20}$ +13·81° in EtOH, +16·24° in H_2O (no mutarotation); the corresponding non-cryst. *betaine* gives a *perchlorate*, m.p. 125° (decomp.) after softening at 115°, $[\alpha]_D^{20}$ —1·7° in H_2O. The mutarotation of (VIII) is therefore ascribed to the production of the zwitterion

$$CH_2{:}CMe{\cdot}CH\!<\!\begin{matrix}CH_2{\cdot}CH(O^-)\\ CH_2\!\!-\!\!-\!\!-\!\!CO\end{matrix}\!>\!CMe{\cdot}\overset{+}{N}Me_2{\cdot}CH_2{\cdot}CO_2Et$$

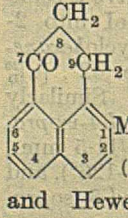
(IX). Ag_2O transforms (VIII) into the neutral, amorphous *betaine*, $[\alpha]_D^{20}$ —12·0° in H_2O, characterised as the *perchlorate*, $C_{14}H_{23}O_8NCl$, m.p. 162° after softening at 157°; attempts to isolate (IX) by using Ag_2CO_3 or $MgCO_3$ in place of Ag_2O were unsuccessful. (II) and $CH_2Br{\cdot}CO_2Et$ slowly and incompletely give 2-*hydroxy*-3-*keto*-2-*methyl*-5-iso*propenyl*-1-cyclo*hexyldimethylcarbethoxymethylammonium bromide*, m.p. 166°, $[\alpha]_D^{20}$ +5·86° in H_2O, the aq. solution of which has p_H ~6; it is transformed by TlOH but not by Ag_2O into the corresponding *betaine*, $[\alpha]_D^{20}$ —11·8° in H_2O, which is neutral in H_2O and does not give a well-defined perchlorate. (IV) unites rapidly with $CH_2Br{\cdot}CO_2Et$ to 2 : 6-*dihydroxy*-1-*methyl*-4-iso*propyl*cyclo*hexyldimethylcarbethoxymethylammonium bromide*, m.p. 218—220°, $[\alpha]_D^{20}$ —10·3° in H_2O (*perchlorate*, m.p. 196—199°), whereas the isomeric *bromide* from (V) has m.p. 201°, $[\alpha]_D^{20}$ +15·4° in H_2O; the corresponding, very hygroscopic *betaine*, $[\alpha]_D^{20}$ +7·5° in H_2O, gives a *perchlorate*, m.p. 201° after softening at 194°. (VI) and $CH_2Br{\cdot}CO_2Et$ slowly give 2 : 3-*dihydroxy*-2-*methyl*-5-iso*propyl*-1-cyclo*hexyldimethylcarbethoxymethylammonium bromide*, m.p. 187°, $[\alpha]_D^{20}$ —8·38° in H_2O (*perchlorate*, m.p. 233°), which has p_H ~5 in H_2O; the corresponding *betaine*, $C_{14}H_{27}O_4N$, m.p. 168—169°, $[\alpha]_D^{20}$ —29·3° in H_2O (*perchlorate*, m.p. 245°), is described. (VII) and $CH_2Br{\cdot}CO_2Et$ give 2-*hydroxy*-1-*methyl*-4-iso*propenyl*-$\Delta^{2:5}$-cyclo*hexadienyldimethylcarbethoxymethylammonium bromide*, m.p. 129°, $[\alpha]_D$ ±0° (*perchlorate*, m.p. 238—239°), which in H_2O has p_H 3—4; with TlOH it yields the true *enol-betaine*, m.p. 199—200°, $[\alpha]_D$ ±0° (*perchlorate*, m.p. 242—243°), which has p_H 6 in H_2O. 3-*Keto*-2-*methyl*-5-iso*propenyl*-Δ^1-cyclo*hexenyldimethylcarbethoxymethyl*-

ammonium bromide, $[\alpha]_D^{20}$ —10·7° in H_2O, is too hygroscopic to permit crystallisation and does not give a cryst. perchlorate. 6-*Hydroxy*-2-*keto*-1-*methyl*-4-iso*propenyl*-1-cyclo*hexyltrimethylammonium hydroxide*, $[\alpha]_D^{20}$ —38·8° in H_2O, has p_H ~11 in H_2O and gives an unstable *perchlorate*, m.p. 114° after softening at 108°. 2-*Hydroxy*-1-*methyl*-4-iso*propenyl*-$\Delta^{2:5}$-cyclo*hexadienyltrimethylammonium hydroxide*, m.p. 168° (*perchlorate*, m.p. 138—139°), is not a strong base, does not absorb CO_2 from the air, and is stable; it is also obtained from the enol base with Me_2SO_4 and NaOH. (I) and $CH_2Cl{\cdot}CH_2{\cdot}OH$ at 100° give 6-*hydroxy*-2-*keto*-1-*methyl*-4-iso*propenyl*-1-cyclo*hexyldimethyl*-β-*hydroxyethylammonium chloride*, m.p. 105°, which is neutral in H_2O; the corresponding betaine base is amorphous and does not give cryst. salts. H. W.

Properties of conjugated compounds. XX. Diphenylketen as an addendum. E. H. Farmer and M. O. Farooq (J.C.S., 1938, 1925—1930).—$CPh_2{:}CO$ (I) and $\Delta^{1:3}$-*cyclo*hexadiene at room temp. form the anticipated 7-*keto*-8 : 8-*diphenyl*-Δ^2-dicyclo-[4 : 2 : 0]-*octene* (II), m.p. 132—133°, the H_2-derivative (III), m.p. 130°, of which is identical with the adduct obtained by prolonged heating of (I) and *cyclo*hexene (cf. Staudinger and Suter, A., 1920, i, 556). (II) refluxed with KOH–MeOH for 70 min. gives (? trans)-2-*benzhydryl*-Δ^3-*tetrahydrobenzoic acid* (IV), m.p. 148—149°, and the (?) cis-*isomeride*, m.p. 112°; both forms with $KMnO_4$ in H_2O or $COMe_2$ afford αε-*diphenylpentane*-αγδ-*tricarboxylic acid* (V), m.p. 210° (rapid heating, 228°); with the *cis*-form, a (?) stereoisomeride is also obtained. (III) refluxed with MeOH–NaOMe and a little H_2O affords 2-*benzhydrylhexahydrobenzoic acid*, m.p. 151—152° [also by hydrogenation of (IV)], and an impure *stereoisomeride*, m.p. 123°. Oxidation ($KMnO_4$–$COMe_2$) of (II) gives 2 : 2-*diphenyl*cyclo*butanone*-3-*carboxylic*-4-β-*propionic acid*, m.p. 205—206°, converted by NaOH–MeOH into (V). Et α-bromoglutarate and $CHNa(CO_2Et)_2$–C_6H_6 (steam-bath) give *Et butane*-ααβδ-*tetracarboxylate*, b.p. 168—170°/0·5 mm., which with Na followed by $CHPh_2Br$ in C_6H_6 affords $(CHPh_2)_2$ and an ester, b.p. 252°/1 mm.; the latter and KOH–EtOH yield a cryst. product, m.p. 90—150°, which loses CO_2 with boiling dil. H_2SO_4 to yield (V) and a (?) stereoisomeride (cf. above). *cyclo*Pentadiene and (I) form the adduct, $CH\begin{matrix}CH{-}CH{\cdot}CPh_2\\ CH_2{\cdot}CH{\cdot}CO\end{matrix}$ (VI), m.p. 89—90°, hydrolysed with a very slight excess of KOH–MeOH to two isomeric *forms*, m.p. 148—149°, and 121—122°, of 2-*benzhydryl*-Δ^3-cyclo*pentene*-1-*carboxylic acid*, which with $KMnO_4$–$COMe_2$ give isomerides, m.p. 186—187° and 208—209° (VII), respectively, of δδ-diphenylbutane-αβγ-tricarboxylic acid (cf. Simonsen *et al.*, A., 1938, II, 20). (VI) and $KMnO_4$–$COMe_2$ give an acid, hydrolysed by NaOH–MeOH to (VII). The polarised form of the ketens is discussed. A. T. P.

Experiments on the synthesis of substances related to the sterols. XXIV. Some derivatives of 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. P. G. Crowley and R. Robinson (J.C.S., 1938, 2001—2005).—Et 3 : 4-dihydro-β-naphthoate, N_2H_4,H_2O and EtOH, at 120° (bath) for 6 hr. give the *hydrazide*, m.p. 141°, converted through the azide into the urethane, which when stirred with 0·33N-H_2SO_4 at 100° yields $NH_2{\cdot}CO_2Et$ and 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 140°/18 mm. (phenylhydrazone, m.p. 108°). Et γ-*m*-anisylbutyrate, b.p. 170—171°/20 mm., *iso*amyl formate, and EtOH-free NaOEt in Et_2O at 0°—room temp. afford Et and *iso*amyl α-formyl-γ-*m*-anisylbutyrates, cyclised by H_2SO_4–H_3PO_3 (*d* 1·75) at —10°, or by heating alone at 230—240°/30 mm., to mixed crude esters (*A*), b.p. 162—170°/0·3 mm., hydrolysed (20% NaOH) to 6-*methoxy*-3 : 4-*dihydro*-β-*naphthoic acid*, m.p. 176° (*Et* ester, b.p. 148°/0·5 mm.). N_2H_4,H_2O–EtOH at 115° (bath) converts (*A*) into the corresponding *hydrazide*, m.p. 145°, converted through the azide into *Et* 6-*methoxy*-3 : 4-*dihydro*-β-*naphthylcarbamate* (I), m.p. 116°. (I) and *o*-$C_6H_4(CO)_2O$ at 220° yield *phthal*-6′-*methoxy*-3′ : 4′-*dihydro*-β-*naphthylimide*, m.p. 195°. (I) and 0·6N-H_2SO_4 at 100° afford 2-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (II), m.p. 36°, b.p. 164°/11 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 132°), and $NH_2{\cdot}CO_2Et$. (II) and $NaNH_2$–Et_2O in N_2, followed by $COMe{\cdot}[CH_2]_2{\cdot}NEt_2,MeI$ (III) in EtOH, yield 2-keto-7-methoxy-2 : 3 : 4 : 9 : 10 : 12-hexahydrophenanthrene, b.p. 178—181°/0·3 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 186—187°), and a (?) dehydrogenated *dimethoxytetrylidenetetralone*, $C_{22}H_{18}O_3$, m.p. 247°. When excess of (III) is used, a *substance*, $(C_6H_8O)_n$, m.p. 228° (no ketonic properties), is also formed. Et γ-1-naphthylbutyrate (IV), b.p. 209—210°/13 mm. (cf. Fieser *et al.*, A., 1935, 1495), and $HCO_2CH_2Bu^\beta$–NaOEt–Et_2O afford a formyl derivative, which with H_2SO_4–H_3PO_3 (*d* 1·75) at —5° for 3 hr., then hydrolysis (aq. NaOH), gives 3 : 4-*dihydrophenanthrene*-2-*carboxylic acid*, m.p. 234° (*Et* ester, b.p. 192—193°/0·4 mm.). The Et ester, b.p. 169°/0·2 mm. (cf. Cohen *et al.*, A., 1936, 326), of γ-6-methoxy-1-naphthylbutyric acid (prep. by dehydrogenation of its 3 : 4-H_2-derivative with S) similarly yields 7-*methoxy*-3 : 4-*dihydrophenanthrene*-2-*carboxylic acid*, m.p. 242°. Et γ-*m*-anisylbutyrate and KOEt–Et_2O–$(CO_2Et)_2$ give a product, converted by 96% H_2SO_4 at —15° (at —5° the anhydride is formed) into *Et*$_2$ 6-*methoxy*-3 : 4-*dihydronaphthalene*-1 : 2-*dicarboxylate* (V), b.p. 189—190°/0·7 mm. Hydrolysis with 20% aq. KOH gives acid + anhydride; boiling $CHCl_3$ then affords the *anhydride*, m.p. 166°, b.p. 193—195°/0·6 mm. (*imide*, m.p. 263°). (V) and H_2–Pd–$SrCO_3$ in EtOH give, through the *Et*$_2$ ester, b.p. 192°/0·66 mm., 6-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic acid*, m.p. 191° (*methylimide*, m.p. 126°). A. T. P.

Derivatives of phenalene. W. Klyne and R. Robinson (J.C.S., 1938, 1991—1994; cf. Koelsch *et al.*, A., 1938, II, 19).—2 : 1-$C_{10}H_6Me{\cdot}CH_2Cl$ and $CHNa(CO_2Et)_2$ in dry C_6H_6 give *Et* 2-*methyl*-1-*naphthylmethylmalonate*, b.p. 190—195°/2—3 mm.; the *acid*, m.p. 172° (decomp.), loses CO_2 at 170—180°, to give β-2-*methyl*-1-*naphthylpropionic acid*, m.p. 93°, the chloride of which with $AlCl_3$ in light petroleum gives 1-*methyldihydrophenalen*-7-*one* (I), m.p. 54—55° (yellow sample, m.p. 49—50°, is probably contaminated with methylphenalenone) [2 : 4-*dinitrophenylhydrazone*, m.p. 250° (decomp.)] (cf. Cook and Hewett, A., 1934, 519). The *oxime*, m.p.



(I.)

147—149°, of (I) in AcOH–EtOH at 55°, with 3% Na–Hg, gives 7-amino-1-methyldihydrophenalene [*hydrochloride*, m.p. 264—268° (decomp.) (sinters at 258°)]. (I) and *o*-NH_2·C_6H_4·CHO–EtOH–KOH afford *methylperinaphthacridine*, m.p. 134—137°. Reduction [$Al(OPr^\beta)_3$–$Pr^\beta OH$ at 110—115°] of (I) gives 7-*hydroxy*-1-*methyldihydrophenalene*, m.p. 126—127·5°, converted by the successive action of Na (in PhMe), CS_2, and MeI into a hydrocarbon (*picrate*, m.p. 128—129·5°). A. T. P.

Syntheses in the hexahydrofluorene series. S. Fujise (Ber., 1938, 71, [*B*], 2461—2468; cf. A., 1936, 1380).—*o*-Phenylhexahydrobenzoic acid (I), m.p. 105—106°, b.p. 120—123°/0·02—0·03 mm. (*l*-menthylamine salt, m.p. 118—122·5°, $[\alpha]_D^{17}$ —23·3° in EtOH), obtained by reduction of *o*-C_6H_4Ph·CO_2H by Na and amyl alcohol, is not isomerised by HCl–AcOH at 130—135°. Catalytic reduction of *o*-C_6H_4Ph·CO_2H gives an *o-cyclo*hexylbenzoic acid, m.p. 97·5—99·5°. (I) is converted (method: Cook and Hewett, A., 1936, 321) into 1 : 2 : 3 : 4 : 10 : 11-hexahydrofluorenone (II), m.p. 43·5—44°, b.p. 126—129°/0·8 mm., 98—103°/0·007 mm., which becomes pale yellow when kept or heated. When treated by different methods (II) gives an apparently non-homogeneous oxime (III), m.p. 101—108° or 106—116°; the product, m.p. 183—185°, of Cook and Hewett (*loc. cit.*) appears impure. Reduction of (III) catalytically (PtO_2 in AcOH), by Na–abs. EtOH, or by Na–Hg in abs. EtOH–AcOH affords a mixture of much β- (IV) and little α- (V) -hexahydrofluorenylamine (cf. Nakamura, A., 1930, 466); a similar mixture is obtained by the hydrogenation (PtO_2 in AcOH) of fluorenoneoxime. (IV) and (V) are separated through their acetates or benzoates (α, m.p. 146—147°; β, m.p. 183°). NaOAc and boiling Ac_2O convert (V) mainly into the α-N-*Ac* derivative, m.p. 148°, with a product, m.p. 215—218°, whilst (IV) gives a homogeneous Ac compound, new m.p. 258—259°. Benzoylation (Schotten–Baumann) of (IV) gives a homogeneous Bz derivative, m.p. 224—225°, also obtained from (V) with the α-Bz compound, new m.p. 168—170°. 2-Phenyl-4 : 5-dimethylhexahydrobenzoic acid affords 2 : 3-*dimethylhexahydrofluorenone* (VI), m.p. 68°, which becomes partly liquid on exposure to air. The *oxime*, m.p. 159—160°, obtained therefrom is essentially a single form; it is catalytically reduced to 2 : 3-dimethylhexahydrofluorenylamine (*acetate*, m.p. 172—173°; *hydrochloride*, m.p. 254—256°). Dehydrogenation (Se at 280° and then at 310°) of (VI) yields 2 : 3-dimethyl-fluorene and -fluorenone. (II) behaves similarly. H. W.

Preparation of amines from partly hydrogenated phenanthrols. G. Haberland, G. Kleinert, and H. J. Siegert (Ber., 1938, 71, [*B*], 2623—2626). —3 : 4-OMe·$C_{10}H_6$·CO·CHN_2 and Ag_2O in boiling MeOH give 30% of 3-*methoxy*-2-*naphthylacetic acid*, b.p. 210°/1 mm., m.p. 183°. 3 : 2-OH·$C_{10}H_6$·CO_2H in dry C_6H_6 is converted by the successive action of $SOCl_2$ and Et_2 sodioacetosuccinate followed by hydrolysis into β-3-*hydroxy*-2-*naphthoylpropionic acid*, m.p. 200° (*Me* ester, m.p. 104°), reduced (Clemmensen) to γ-3-*hydroxy*-2-*naphthyl*-n-*butyric acid*, m.p. 133°, which is cyclised by P_2O_5 in hot C_6H_6 to 10-hydroxy-4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (I), m.p. 226°. 3 : 7 : 2-$(OH)_2C_{10}H_5$·CO_2H, is transformed by Ac_2O at 100° into 3 : 7-*diacetoxy*-2-*naphthoic acid*, m.p. 178°, converted by the successive action of $SOCl_2$ and CH_2N_2 in Et_2O into 3 : 7-*diacetoxy*-2-*diazoacetonaphthalene*, m.p. 157°. 10-*Hydroxy*-4-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II), m.p. 218°, is best obtained by partial demethylation (boiling 48% HBr–AcOH) of the corresponding $(OMe)_2$-compound. The OH of (I) is not advantageously replaced by NH_2 by Bucherer's method and 10-*acetamido*-4-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 240°, is best obtained from (I), NaOAc, NH_4Cl, and AcOH at 210—215°; it is hydrolysed by 20% HCl at 100° to the *NH*$_2$-*ketone*, m.p. 133° [2 : 4-*dinitrophenylhydrazone*, m.p. 230—235° (decomp.)]. (II) is converted into 10-*acetamido*-4-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 175°. H. W.

Experiments on the synthesis of substances related to the sterols. XXVI. R. Robinson and J. M. C. Thompson (J.C.S., 1938, 2009—2012; cf. A., 1938, II, 144).—CN·CH_2·CO_2Et (I) and Ph·$[CH_2]_2$·Br in EtOH–NaOEt afford *Et* α-*cyano*-γ-*phenylbutyrate*, b.p. 182—183°/17 mm. (free *acid*, m.p. 74·5°), which with Me Δ^β-dihydromuconate (II) in Et_2O–KOEt–EtOH gives an adduct (III), b.p. 220—225°/0·5 mm. (b.p. 225—230°/0·4 mm., from Et Δ^β-dihydromuconate). (I) and (II) in NaOEt–EtOH afford a compound which with K–PhMe–Ph·$[CH_2]_2$·Br gives (III), hydrolysed (20% aq. EtOH–KOH followed by conc. HCl) to δ-*carboxy*-γ-*carboxymethyl*-ζ-*phenylheptoic acid*, m.p. 139—140° [when purified through its Me ester (CH_2N_2), b.p. 200—205°/0·7 mm.], which with H_2SO_4 at 0° affords β-(1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthyl*)*adipic acid*, m.p. 158—159°; the CO is inert. The chloride, b.p. 124—127°/0·5 mm., of Et H methronate and CHNaAc·CO_2Et give an ester, hydrolysed (method: Claisen, A., 1896, i, 557) to *Et* 4-*carbethoxy*-5-*methylfuran*-2-*acetoacetate*, b.p. 153—156°/14 mm. Me γ-(6-methoxy-1-naphthyl)-butyrate (IV) and CO_2Me·$[CH_2]_2$·COCl (V) in $AlCl_3$–$PhNO_2$ at <0°, then at room temp. for 36 hr., give a product which is methylated (*loc. cit.*) to γ-(6-methoxy-5-succinoyl-1-naphthyl)butyric acid (converted by boiling HI into 7-hydroxy-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene) and γ-(6-*methoxy*-2- or -4-*succinoyl*-1-*naphthyl*)*butyric acid*, m.p. 201—202°. (IV) and PCl_5 afford the 5-*Cl*-ester, m.p. 76·5° [does not react with (V)], hydrolysed to γ-(5-*chloro*-6-*methoxy*-1-*naphthyl*)*butyric acid*, m.p. 189—190°, which with H_2SO_4–H_2O (3 : 1) at 100° for ½ hr. yields 8-*chloro*-1-*keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 219—220°. 1 : 2-$C_{10}H_6Cl$·OMe, (V), and $AlCl_3$–$PhNO_2$, afford β-(5-*chloro*-6-*methoxy*-2-*naphthoyl*)*propionic acid* (VI), m.p. 199—200° (*Me ester*, m.p. 156°), converted by refluxing with HI (*d* 1·7)–AcOH and a little H_2O, for 18 hr., into β-(6-*hydroxy*-2-*naphthoyl*)*propionic acid*, m.p. 235° (decomp.), and by boiling dil. NaOCl–NaOH into approx. equal amounts of 5-*chloro*-6-*methoxy*-2-*naphthoic acid* (VII), m.p. 305° (boiling HI–AcOH gives 6 : 2-OH·$C_{10}H_6$·CO_2H) and -2-*naphthaldehyde* (VIII), m.p. 141° [2 : 4-*dinitrophenylhydrazone*, m.p. 315° (decomp.)], oxidised by $KMnO_4$–NaOH to (VII).

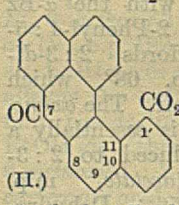
(VIII), $CH_2(CO_2H)_2$, and C_5H_5N + piperidine afford β-(5-*chloro*-6-*methoxy*-2-*naphthyl*)*acrylic acid*, m.p. 310°. Clemmensen reduction of (VI) gives γ-(5-*chloro*-6-*methoxy*-2-*naphthyl*)*butyric acid*, m.p. 137—138°, converted by H_2SO_4–H_2O at 100° into 8-*chloro*-4-*keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 169—170°. A. T. P.

Synthesis of 4-keto-6 : 10-dimethoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene. G. Haberland and H. J. Siegert (Ber., 1938, **71**, [*B*], 2619—2622; cf. A., 1938, ii, 144).—3 : 7 : 2-$(OH)_2C_{10}H_5{\cdot}CO_2H$ is converted by Me_2SO_4 and NaOH into 3 : 7-*dimethoxy*-2-*naphthoic acid*, m.p. 140° (*Me* ester, m.p. 113°), the *chloride* (I), m.p. 88—90° (whence the *amide*, m.p. 218°), of which is transformed by CH_2N_2 in Et_2O into 3 : 7-*dimethoxy*-2-*diazoacetonaphthalene*, m.p. 115°; in hot AcOH this passes into 3-*keto*-6′-*methoxynaphth*-[2′ : 3′-4 : 5]-2 : 3-*dihydrofuran*, m.p. 172°. Et_2 sodioacetosuccinate and (I) in Et_2O give (after hydrolysis) β-3 : 7-*dimethoxy*-2-*naphthoylpropionic acid* (II), m.p. 170° (*Me* ester, m.p. 107°), in very varying yield and *Et*$_2$ α-3 : 7-*dimethoxy*-2-*naphthoyl*-α-*acetylsuccinate*, m.p. 120°. 3 : 7-*Dimethoxy*-2-*naphthoic anhydride* has m.p. 189°. 3 : 7-*Dimethoxy*-2-*naphthyl Me ketone*, m.p. 94°, and its 2 : 4-*dinitrophenylhydrazone*, m.p. 209°, are described. (II) is hydrogenated (Pd–C in $Pr^{\beta}OH$ containing a little conc. HCl) to γ-3 : 7-*dimethoxy*-2-*naphthyl*-n-*butyric acid*, m.p. 157° (*Me* ester, m.p. 89°), cyclised by P_2O_5 in boiling C_6H_6 to 4-*keto*-6 : 10-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 89° (*oxime*, m.p. 162°; 2 : 4-*dinitrophenylhydrazone*, m.p. 102°). H. W.

Oxidative degradation of *meso*benzanthrone and of its substitution derivatives. G. Charrier (Chim. e l'Ind., 1938, **20**, 658—663).—A review, in which varying types of oxidation are discussed. The easier oxidation of the *meso*benzanthrone system under alkaline conditions is ascribed to oxidation at $C_{(4)}$ and $C_{(6)}$, giving a phenanthrene system known to be sensitive to alkaline oxidation. E. W. W.

Sulphonation of *meso*benzanthrone and some of its derivatives. R. R. Pritchard and J. L. Simonsen (J.C.S., 1938, 2047—2052; cf. Lauer and Irie, A., 1936, 1381).—Benzanthrone-7 (I) and 5% oleum at 145—150° (bath) or 18% oleum (Hg catalyst) at room temp., give (mainly) the 9-sulpho-derivative (II) [Na salt (+$2H_2O$)] (cf. *loc. cit.*). A homogeneous chlorobenzanthrone-7 could not be obtained from the Na or K sulphonate and PCl_5 at 100° (bath). Crude (II) contains some 3-sulpho-derivative (III), as treatment with PCl_5 affords some 3-chlorobenzanthrone-7. It is improbable that (III) is the primary sulphonation product. The Na salt of (?) crude (II) with $KClO_3$–HCl at 95° affords 3 : 9-dichloro- and (?) 9-chloro-benzanthrone; with NaOH–KOH at 220—230° followed by Me_2SO_4 + anhyd. Na_2CO_3 in *o*-$C_6H_4Cl_2$, 9 : 9′-*dimethoxydibenzanthrone* is obtained. Oxidation (CrO_3–AcOH–H_2O) of (II) affords 6-*sulphoanthraquinone*-1-*carboxylic acid* (IV), m.p. 271—274°, decomp. >275° [$(NH_4)_2$ salt (V)], purified through the *Ba* salt (+H_2O). (V) and $KClO_3$ in aq. HCl at 95° give 6-chloroanthraquinone-1-carboxylic acid, m.p. 305—306° (Me ester, m.p. 190—191°). (V), freshly prepared MnO_2, and aq. NH_3 at 200° give 6-*aminoanthraquinone*-1-*carboxylic acid*, m.p. 247—249° (sinters at 245°), and crude (?) 2-aminoanthraquinone, m.p. 295—297° (Ac derivative, m.p. 257—258°). (I) and 10% oleum at 165—170° give (?) benzanthrone-3 : 9-disulphonic acid; the *Na* salt and PCl_5 give a *substance*, m.p. 247—248°. 3-Chlorobenzanthrone and 5% oleum at 165—170° (bath) give the 9-SO_3H derivative [*Na* salt, oxidised (CrO_3) to (IV)], but 10% oleum at 145—150° gives the 9 : ?-disulphonic acid (*Na* salt; impure *dichloride*, m.p. 230—255°). 9 : 10-Dichlorobenzanthrone (VI) and 5% oleum at 165—170° give the 3-SO_3H derivative [*Na* salt (VII), with PCl_5 at 100° gives 3 : 9 : 10-*trichlorobenzanthrone*, m.p. 349—350°, also prepared from (VI) and Cl_2–AcOH at 100°]. (VI) and CrO_3–AcOH give 6 : 7-*dichloroanthraquinone*-1-*carboxylic acid*, m.p. 275—276° (*Me* ester, m.p. 197—198°), similarly obtained from (VII). 3-Bromobenzanthrone (VIII) and 5% oleum at 125—130° give the 9-SO_3H derivative; the *Na* salt [oxidised (CrO_3) to (IV)] and PBr_5 at 100° (bath) yield the sulphonyl bromide, which in xylene at 155—160° gives 3 : 9-dibromobenzanthrone (IX), m.p. 255—256°, also obtained from (VIII) and Br–H_2O at 40—100°. (IX) and CrO_3–aq. AcOH afford 6-*bromoanthraquinone*-1-*carboxylic acid*, m.p. 298—299° (*Me* ester, m.p. 198—199°). 3-Nitrobenzanthrone and 5% oleum at 125—130° give the 9-sulphonic acid [the *Na* salt and CrO_3–AcOH give (IV)]. A. T. P.

Anthanthrone and derivatives. V. Oxidation of 1′-carboxy-10 : 11-benzbenzanthrone-7. A. Corbellini and F. Steffenoni. **VI. Alkali fusion of anthanthrone.** A. Corbellini and D. Crespi (R. Ist. lombardo Sci. Lett. Rend., 1936, [ii], **69**, 429—438, 580—586; Chem. Zentr., 1937, i, 1420—1421).—V. 1 : 1′-Dinaphthyl-8 : 8′-dicarboxylic acid (I) is converted by Ac_2O at 150—160° (bath) into 1′-*carboxy*-10 : 11-*benzbenzanthrone*-7 (II), m.p. 280—281° [*Me* ester (III), m.p. 155·5—156·5°, also obtained from the Me_2 ester of (I) and conc. H_2SO_4], together with a little anthanthrone (IV). Hot dil. NaOH–$Na_2S_2O_4$ converts (III) into dihydroanthanthrone, oxidised (air) to (IV). Distillation of the *Ba* salt of (II) with $Ba(OH)_2$ in N_2 gives small amounts of unidentified products, m.p. 170° and 230°, whilst the Ba salt of (I) similarly affords perylene and 1 : 1′-dinaphthyl. Distillation of the NH_4 and *Ag* salts of (II) yields mainly (IV), also obtained by fusion of (II) with alkali. Oxidation ($Na_2Cr_2O_7$, dil. H_2SO_4) of (II) gives some *hydroxyanthanthrone* (V), m.p. 304° (*benzoate*, m.p. 299°; *Me ether*, m.p. 299—300°), which when distilled with Zn dust affords anthanthrene.

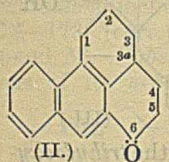


(II.)

VI. Fusion of (IV) with KOH–H_2O, $KClO_3$, and $CuCl_2$ at 150—250° gives a *dihydroxyanthanthrone*, decomp. >360° (*dibenzoate*, m.p. >350°; *Me*$_2$ *ether*, m.p. >350°), which is not obtained from (V) and is reduced (Zn dust) to anthanthrene. A similar compound is also obtained in the absence of oxidising agents. Molten alkali first reduces (IV) to dihydroanthanthrone [*dibenzoate*, m.p. 321—324° (blackens ~310°)]. H. B.

Enolic ethers of keto*cyclo*pentanopolyhydrophenanthrene compounds.—See B., 1939, 104.

Œstrogenic substances. Synthesis of keto-1 : 2-*cyclo*pentenophenanthrenes. J. Hoch (Compt. rend., 1938, **207**, 921—923; cf. Bachmann and Kloetzel, A., 1938, II, 17).—1 : 2-*cyclo*Pentenophenanthrene with CrO_3 in cold AcOH affords ~50% of 1′-keto-1 : 2-*cyclo*pentenophenanthrene (cf. *loc. cit.*). 1-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene, $CH_2Br{\cdot}CO_2Et$, and Zn–Hg in C_6H_6 afford *Et* (3 : 4-*dihydro*-1-*phenanthryl*)*acetate*, b.p. 215—220°/2 mm., reduced (Na–EtOH) to β-(1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthryl*)*ethyl alcohol*, b.p. 225—230°/15 mm., which with PBr_3 gives a bromide (I) which after condensation with $CH_2(CO_2Et)_2$, hydrolysis, and fusion gives γ-(1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthryl*)*butyric acid*, m.p. 94—95°, dehydrogenated (S at 230°) to γ-1-*phenanthrylbutyric acid*, m.p. 152°. This is cyclised by $SnCl_4$ at 110° to 3-*keto*-3 : 4 : 5 : 6-*tetrahydrochrysene*, m.p. 222° (*phenylhydrazone*, m.p. 244—246°). (I) with KCN affords a nitrile, hydrolysed (EtOH–KOH) to β-(1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthryl*)*propionic acid*, m.p. 115°, cyclised with $SnCl_4$ to 1 : 2 : 3 : 3a : 4 : 5-*hexahydrobenzanthrone*-6 (II), m.p. 115°.


(II.)

J. L. D.

Ketone from vitamin-D_2. A. Windaus and K. Buchholz (Z. physiol. Chem., 1938, **256**, 273—276).—Vitamin-D_2 (I) boiled for 12 hr. with $COMe_2$, C_6H_6, and $Al(OBu^{\gamma})_3$ gives a non-cryst. ketone (II) (alternative structures suggested) [*semicarbazone* (III), $C_{29}H_{45}ON_3$, m.p. 218—222° (decomp.); absorption max. at 293 mμ.] which has an absorption max. at 265 mμ. and an antirachitic action on rats ~300-fold inferior to that of (I). (II) is obtained from (III) by treatment with PhCHO; decomp. with boiling AcOH–$H_2C_2O_4$ gives, however, an isomeride [*semicarbazone*, m.p. 225—227° (decomp.); absorption max. at ~340 and 425 mμ.] of (II). Reduction [$Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$] of (II) gives a poor yield of (I).

W. McC.

Experiments on the synthesis of substances related to the sterols. XXIII. Formation of œstrone from a dicarboxylic acid obtained by degradation of œstrone methyl ether. F. Litvan and R. Robinson (J.C.S., 1938, 1997—2001; cf. A., 1938, II, 144).—$CH_2Ph{\cdot}CH_2{\cdot}COCl$ and KOH-free CH_2N_2 in Et_2O at −10° give a diazoketone, which in dioxan with Ag_2O–aq. $Na_2S_2O_3$ at 70° (Arndt–Eistert reaction; cf. A., 1936, 844) affords γ-phenylbutyric acid, m.p. 49—50°. *d*-Homocamphoric acid (I) and H_2SO_4–EtOH afford the Et_2 ester, b.p. 128—130°/1 mm., converted by KOH into Et H *d*-homocamphorate (II), m.p. 78°, b.p. 145—147°/0·44 mm. (cf. Haller, A., 1889, i, 1205), better prepared from (I)–C_6H_6–H_2SO_4–EtOH (limited amount) [the product obtained has m.p. 58·5—59·5°, $[\alpha]_D^{15}$ +57·5° in EtOH, and submitted to the Arndt–Eistert reaction gives, after hydrolysis, (I)]. The chloride of (II) submitted to the Arndt–Eistert reaction gives a product hydrolysed by excess of HBr (*d* 1·5) to hydrocamphorylacetic acid, m.p. 137°, converted (Blanc's Ac_2O method) into homocamphor, m.p. 189·5—190·5° (2 : 4-dinitrophenylhydrazone, m.p. 232°). *O*-Methylœstrone with *iso*amyl nitrite in $Bu^{\gamma}OH$–$KOBu^{\gamma}$ and N_2 gives 16-*oximino*-O-*methylœstrone*, m.p. 161—162° (decomp.), converted by PCl_5–AcCl at room temp. into a product, hydrolysed (EtOH–KOH for 14 days with subsequent addition of Zn dust) to O-*methylœstric acid* (III), m.p. 189—190° (mechanism discussed). Oximinocamphor and PCl_5 in AcCl give mainly the α-mononitrile of camphoric acid, m.p. 151—152°, but with *iso*amyl ether as solvent, the main product is the α-monoamide, m.p. 174—175°. (III) and CH_2N_2–Et_2O give the Me_2 ester, hydrolysed (aq. KOH–MeOH) to the α-Me H ester, which is converted (Arndt–Eistert reaction) into *O*-methylhomo-œstric acid (IV) (Me_2 ester, m.p. 85°). The work of Bardhan (A., 1937, II, 63) is fully confirmed. Hydroxymethylene-*O*-methylœstrone gives Bardhan's acid, *i.e.*, (IV), and an (?) *iso*oxazole derivative. (IV) and $PbCO_3$ heated in a rotated tube give *O*-methylœstrone, demethylated [HI (*d* 1·9)–AcOH] to œstrone.

A. T. P.

Two derivatives of œstrone. F. Bergel and A. R. Todd (Biochem. J., 1938, **32**, 2145—2146).—*Œstrone* β-*naphthoate*, m.p. 262—264°, produces prolonged œstrus in rats, although the onset is delayed longer than with œstrone. *Œstrone diethylaminoethyl ether*, m.p. 76—77° (*hydrochloride*, m.p. 190—191°), yields H_2O-sol. salts but has no œstrogenic activity.

H. G. R.

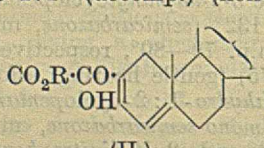
Hydroxyketo-œstrin, m.p. 258—260°, and its benzoate, m.p. 205—207°.—See B., 1939, 104.

Experiments on the synthesis of substances related to the sterols. XXII. Synthesis of *x*-norequilenin methyl ether. A. Koebner and R. Robinson (J.C.S., 1938, 1994—1997; cf. A., 1938, II, 496).—3-β-Naphthyl-Δ²-*cyclo*pentenone-2-acetic acid and its *Me* ester, m.p. 100°, with H_2 and Pd–$SrCO_3$ in MeOH at 40°, give 3-β-*naphthyl*cyclo*pentanone*-2-*acetic acid* (I), m.p. 132° (*semicarbazone*, m.p. 217°), and its *Me* ester, m.p. 79—80°, respectively. (I) and P_2O_5–H_3PO_3 (*d* 1·75) (gentle heating) afford 3′ : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentanophenanthrene*, m.p. 115° (*mono-semicarbazone*, m.p. 245°, *-hydrazone*, m.p. 156°, and *-2 : 4-dinitrophenylhydrazone*, m.p. 240°), the constitution of which is confirmed by Clemmensen reduction to an oil, b.p. 200°/1 mm., dehydrogenated (Pd–C at 330°) to *cyclo*pentenophenanthrene. The mixed methoxy- and hydroxy-naphthyl*cyclo*pentenoneacetic acids (*loc. cit.*) afford *Me* 3-β-6′-*methoxy*- (II), m.p. 115—116°, and *-hydroxy*-, m.p. 164—165°, *-naphthyl*-Δ²-cyclo*pentenone*-2-*acetate*, respectively, but (II) is obtained best by methylating the crude acids before esterification. (II) is hydrogenated to 3-β-6′-*methoxynaphthyl*cyclo*pentanone*-2-*acetic acid*, m.p. 146—147° (*Me* ester, m.p. 61—62°), which gives [as for (I)] 20% of 3′ : 4-*diketo*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentanophenanthrene*, m.p. 126—127° [2 : 4-*dinitrophenylhydrazone*, m.p. 143° (decomp.)]. The latter is reduced (H_2, Pt–C, $PdCl_2$, EtOH at room temp.) to 3′-*keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentanophenanthrene*, m.p. 116—117° [2 : 4-*dinitrophenylhydrazone*, m.p. 246—247° (decomp.)]. Qual. experiments with the CHPh: and piperonylidene derivatives of the latter support the conclusion that

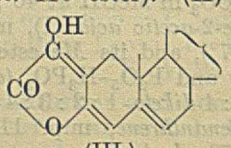
it is *x*-norequilenin Me ether (*x* indicating undetermined stereochemical configuration). A. T. P.

***iso*Equilin-*A*.** H. Hirschmann and O. Wintersteiner (J. Biol. Chem., 1938, **126**, 737—748).—Equilin with boiling AcOH–conc. HCl in CO_2 yields iso*equilin*-A (I), m.p. 231° (incipient decomp. at 227°), $[\alpha]_D^{25}$ +222° in EtOH [*semicarbazone* (+0·5H_2O), decomp. 230° (turns brown at 180°)], the *acetate*, m.p. 95° (softens at 83°), of which with OsO_4 in Et_2O, followed by Na_2SO_3 in 20% EtOH, yields (?) 14-epi-$\Delta^{9\text{-}11}$-8-*hydroxyequilin*, m.p. 204° (decomp.). With Ac_2O in C_5H_5N this gives only a *monoacetate* (an oil); hence the new OH is probably *tert*. (I) is dehydrogenated (Pd-black) to a *compound* (? 14-*epi*-equilenin), $C_{18}H_{18}O_2$, m.p. 262°, $[\alpha]_D^{30}$ +160° in EtOH, differing from equilenin but having a similar absorption spectrum. From these facts and the nature of the absorption spectrum of (I) and its derivatives, it is concluded that (I) is 14-*epi*-$\Delta^{8\text{-}9}$-equilin, which with OsO_4 gives an osmic ester breaking down with the elimination of H_2O. (I) differs from the diol isolated (A., 1938, III, 299) from the urine of pregnant mares and has about one fifth of the activity of œstrone. All m.p. are corr. A. Li.

Steroids and sex hormones. XLVII. Condensation of cholestenone with oxalic ester. L. Ruzicka and P. A. Plattner (Helv. Chim. Acta, 1938, **21**, 1717—1725).—Condensation of cholestenone (I) with $Et_2C_2O_4$ by NaOEt–EtOH and hydrolysis of the product gives *cholestenoneoxalic acid* [(II) R = H], m.p. 150—151°, $[\alpha]_D$ +38·6° in $CHCl_3$; this gives a dark red colour with $FeCl_3$ and at 250°/vac. gives (I) in 95% yield. Analogously the non-cryst. *Me* and *Et* esters give a large proportion of (I) when heated. With N_2H_4,H_2O in AcOH (II) yields $\Delta^{4'}$-*cholesteno*-2′ : 3′-4 : 5-*pyrazole*-3-*carboxylic acid*, m.p. 273–274° (decomp.) (non-cryst. *Me* ester). (II) is



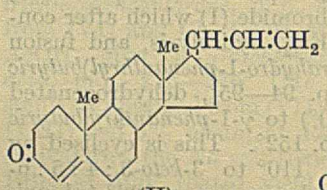
(II.)



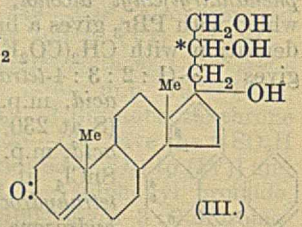
(III.)

transformed by HBr in boiling AcOH into *cholestenoneoxalolactone* (III), m.p. 202° (decomp.), $[\alpha]_D$ −177° in $CHCl_3$, which is readily autoxidised, does not give a colour with $FeCl_3$ in EtOH or Et_2O, is completely decomposed when heated, and yields with CH_2N_2 a *Me ether*, m.p. 137—138°, $[\alpha]_D$ −214° in $CHCl_3$. Hydrogenation (Pd-sponge in Et_2O) of (II) and treatment of the product with HBr–AcOH gives *dihydrocholestenoneoxalolactone*, m.p. 200° (decomp.), $[\alpha]_D$ +15·4° in $CHCl_3$ (*Me ether*, m.p. 137—138°; *Ac* derivative). (III) is hydrogenated (Pd-sponge in Et_2O) to *tetrahydrocholestenoneoxalolactone*, m.p. 242° (decomp.), $[\alpha]_D$ −45·8° in $CHCl_3$ [*Me ether*, m.p. 133°; *acetate*, m.p. 183° (decomp.)], oxidised to the acid, $C_{27}H_{46}O_4$, obtained by Windaus and Uibrig (A., 1914, i, 1066) from cholestanol. (II) and Br react in $CHCl_3$ to a colourless, non-cryst. product transformed by HBr–AcOH into the *bromolactone*, $C_{29}H_{41}O_3Br$, m.p. 194° (decomp.) [*pyridinium* compound, $C_{34}H_{46}O_3NBr$, m.p. 155° (decomp.)], also obtained by the direct bromination of (III). H. W.

17-Allyltestosterone and its transformation products. A. Butenandt and D. Peters (Ber., 1938, **71**, [*B*], 2688—2695).—Dehydroandrosterone acetate is converted by Mg and CH_2:$CH{\cdot}CH_2Br$ in Et_2O into 17-allyl-Δ^5-androstene-3 : 17-diol, m.p. 151°, $[\alpha]_D^{20}$ −42·2° in EtOH (3-*monoacetate*, m.p. 154°), transformed by $Al(OPr^\beta)_3$ and *cyclo*hexanone in boiling PhMe into 17-*allyltestosterone* (I) (+0·5H_2O), m.p. 105—107·5° or 93° [*oxime* (+0·5H_2O), m.p. 144—146°]. This is dehydrated by $POCl_3$ in boiling C_5H_5N to the *triene-ketone* (II), m.p. 172—174° (*semicarbazone*, m.p. >365°; darkens slightly ~250°), oxidised by OsO_4 in Et_2O to the corresponding *tetrahydroxy-ketone*,

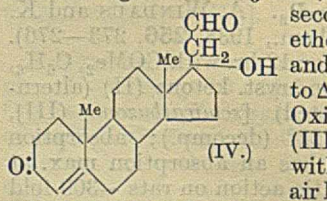


(II).



(III.)

m.p. 237·5°. (I) is similarly oxidised to the *trihydroxy-ketone* (III), m.p. 224—225°, $[\alpha]_D^{20}$ +53·9°, or m.p. 198° (also in a labile form, m.p. 168°), $[\alpha]_D^{20}$ +48·3° (the forms differ from one another only in the steric arrangement around the new asymmetric C*). The first form gives a *CPh$_3$ ether*, m.p. 197·5°, whereas the second form does not; the ether is oxidised [$Al(OPr^\beta)_3$ and *cyclo*hexanone in PhMe] to Δ^4-androstene-3 : 17-dione. Oxidation of either form of (III) by $Pb(OAc)_4$ in C_6H_6 with complete exclusion of air leads to the *aldehyde* (IV), m.p. 142—143° [*dioxime* (+1H_2O), m.p. 141° (decomp.) and 208—210° (decomp.) after re-solidifying at about 175—185°]; if air is not excluded the corresponding *acid*, m.p. 162° (decomp.), is obtained. H. W.



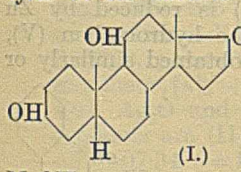
(IV.)

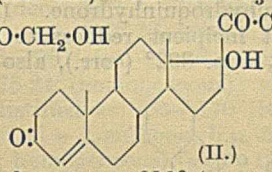
Biochemical transformation of dehydroandrosterone into testosterone.—See A., 1939, III, 55.

Steroids and sex hormones. XLVIII. Conversion of 17-acetylenylandrostene derivatives into pregnenone derivatives. Preparation of 17-hydroxyprogesterone. L. Ruzicka and H. F. Meldahl (Helv. Chim. Acta, 1938, **21**, 1760—1770; cf. A., 1938, II, 413).—Addition of 3-*trans*-17(α)-dihydroxy-17-acetylenyl-Δ^5-androstene, its 3-acetate (I), or diacetate followed by BF_3–Et_2O to HgO in anhyd. AcOH–Ac_2O gives 3-trans-17(α)-*diacetoxy*-Δ^5-*pregnen*-20-*one* (II), m.p. 190—192°, $[\alpha]_D^{18}$ −54° in dioxan. (II) does not react with NH_2OH or Girard reagent *T*; it is hydrolysed (KOH–MeOH) to 3-trans-17(α)-*dihydroxy*-Δ^5-*pregnen*-20-*one*, m.p. 275—277°, $[\alpha]_D^{18}$ −110° in dioxan [*oxime*, m.p. 243—244° (decomp.)], converted by Ac_2O in C_5H_5N at room temp. into the 3-*acetate*, m.p. 270—272°, which could not be acetylated further. (I) is transformed by BzCl in C_5H_5N at 100° into 17(α)-*benzoyloxy*-3-trans-*acetoxy*-17-*acetylenyl*-Δ^5-*androstene*, m.p. 209—211°, converted by HgO–AcOH–Ac_2O–BF_3–Et_2O at room temp. into 17(α)-*benzoyloxy*-3-trans-*acetoxy*-Δ^5-*pregnen*-20-*one*, m.p. 217—217·5°. Partial hydrolysis (K_2CO_3–

MeOH at room temp.) of (II) and subsequent oxidation (Oppenauer) gives 17-*acetoxyprogesterone*, m.p. 198—200°, $[\alpha]_D^{18}$ +68·5° in dioxan, hydrolysed to 17-*hydroxyprogesterone*, m.p. 284—288°, $[\alpha]_D^{18}$ +54° in dioxan (*oxime*, m.p. 268—270°), also obtained (HgO–AcOH–Ac_2O–BF_3–Et_2O followed by hydrolysis) from 17(α)-acetylenyltestosterone (*acetate*, m.p. 167—168°). Hydrogenation (PtO_2 in AcOH at room temp.) of (II) gives (?) 3-trans-17(α)-*diacetoxypregnan*-20-*one*, m.p. 225·5—227°, $[\alpha]_D^{18}$ −4° in dioxan, which does not give a yellow colour with $C(NO_2)_4$. H. W.

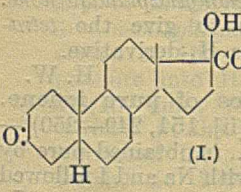
Constituents of the adrenal gland. XXI. Constitution of the substances *R* and *S*. T. Reichstein (Helv. Chim. Acta, 1938, **21**, 1490—1497; cf. A., 1938, II, 498).—Substance *R* is (I) since it is oxidised by CrO_3 in AcOH at room temp. to 3 : 11-diketo*allo*ætiocholanic acid and its diacetate, m.p. 172—173° (corr.), is oxidised to the diacetate of compound *N*. *Substance* S, obtained by cautious hydrolysis of its acetate (*loc. cit.*) with $KHCO_3$ in aq.


(I.)


(II.)

MeOH at room temp., has m.p. ~210° (corr.; slight decomp.) greatly dependent on the rate of heating and the degree of previous trituration. It is strongly reducing and shows in the ultra-violet absorption spectrum the bands typical of αβ-unsaturated ketones. Oxidation of it with CrO_3 in AcOH at room temp. yields Δ^4-androstene-3 : 17-dione. *S* is therefore (II) if the possibility of the presence of the group :C(OH)·CH(OH)·CHO is disregarded. The sole uncertainty is the configuration at $C_{(17)}$. H. W.

Constituents of the adrenal gland. XXII. Constitution of substance *L*. T. Reichstein and K. Gätzi (Helv. Chim. Acta, 1938, **21**, 1497—1505; cf. A., 1936, 1382).—Substance *L*, m.p. 264—266° (corr.), $[\alpha]_D^{21}$ +30·6°±3° in abs. EtOH, as obtained by various enrichment processes, is best purified by taking advantage of its sparing solubility in boiling C_6H_6 and then through the acetate. Ac_2O and C_5H_5N at room temp. transform crude *L* into the *L*-acetate, m.p. 191—192° (corr.), $[\alpha]_D^{21}$ +14·8°±2° in $COMe_2$, which appears to be a mixture of Ac_1 and Ac_2 derivatives, and a second *acetate*, m.p. 182—182·5° (corr.), $[\alpha]_D^{18}$ +19·3°±2° in $COMe_2$ [*semicarbazone*, m.p. 255—259° (corr.)], which appears to be the Ac_2 derivative of a compound, $C_{21}H_{34}O_3$. *L* does not reduce Ag_2O solution and does not give the absorption bands typical of αβ-unsaturated ketones. It is oxidised by CrO_3 in AcOH at room temp. to a *substance* (I), m.p. 270—272° (corr.), and androstane-3 : 17-dione. Reduction (Raney Ni) of *L* gives a mixture of two stereoisomeric triols readily separated through their diacetates and recognised as substances *J* and *O*. *L* is therefore (I) with CO=CH·OH. *L*, *J*, and *O* have therefore the same configuration at $C_{(17)}$ and the main difference between *J* and *O* is due to the different spatial arrangement of OH at $C_{(20)}$. H. W.

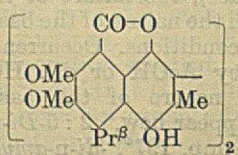

(I.)

[Interaction of] phenols and sulphites. (Mlle.) Y. Garreau (Ann. Chim., 1938, [xi], **10**, 485—558).—Mainly a comprehensive account of work already reported (A., 1935, 245, 348; 1936, 337, 721; 1937, II, 66, 251, 338; 1938, II, 96, 136, 237).—When quinol (0·2 mol.) is shaken in air with aq. SO_2 (1 mol.), NH_3 or NH_2Alk (3 mols.), and $Cu(OH)_2$ (0·05 mol.) (indispensible for good yields), there are obtained 2 : 5-diamino-1 : 4-benzoquinone-3- and -3 : 6-disulphonic acids and 2(or 5)-amino-5(or 2)-hydroxy-1 : 4-benzoquinone-4-imine-3- and -3 : 6-di-sulphonic acids (or their alkylamino-homologues), the nature of the product(s) depending mainly on the nature of the base, but in some cases also on the conditions. Occurrence of hydrolysis of the SO_3H by AcOH or dil. HCl depends remarkably on the nature of the basic substituents. The following appear new. 2 : 5-*Di*-n-*butyl*-, m.p. 160°, -*diisobutyl*-, m.p. 197°, -*di*-n-*amyl*-, m.p. 143°, and -*diisoamyl*-*amino*-1 : 4-*benzoquinone*, m.p. 170°. *Diisobutylammonium* 2 : 5-*diisobutyl*-, *di*-n-*amylammonium* 2 : 5-*di*-n-*amyl*-, and *diisoamylammonium* 2 : 5-*diisoamyl*-*amino*-1 : 4-*benzoquinone*-3 : 6-*disulphonate*. β-*Hydroxyethylammonium* (?2 : 5-) *di*-(β-*hydroxyethylamino*)-1 : 4-*benzoquinone*-3-*sulphonate*, $+2H_2O$. R. S. C.

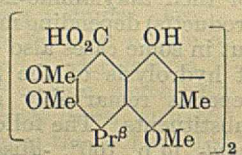
Action of diazonium compounds on 2-hydroxy-1 : 4-naphthaquinone. O. Neunhoeffer and J. Weise (Ber., 1938, **71**, [*B*], 2703—2707).—In AcOH 2-hydroxy-1 : 4-naphthaquinone (I) couples with diazo-compounds exclusively to azo-dyes, whereas in alkaline solution N_2 is eliminated with production of an arylated hydroxynaphthaquinone. Addition of *o*-$C_6H_4Me{\cdot}N_2Cl$ to a solution of (I) in 5% KOH at 45° gives 2-*hydroxy*-3-o-*tolyl*-1 : 4-*naphthaquinone*, m.p. 127° (*monoacetate*, m.p. 76°), converted by heating with Zn dust and Ac_2O containing a trace of H_2SO_4 into 1 : 2 : 4-*triacetoxy*-3-o-*tolylnaphthalene*, m.p. 132°. The following compounds are obtained analogously: 2-hydroxy-3-phenyl-1 : 4-naphthaquinone m.p. 146°, and 1 : 2 : 4-triacetoxy-3-phenylnaphthalene, m.p. 168°; 2-*hydroxy*-3-*p*-*tolyl*-1 : 4-*naphthaquinone*, m.p. 168° (*acetate*, m.p. 138—139°), and 1 : 2 : 4-triacetoxy-3-*p*-tolylnaphthalene, m.p. 188°; 2-*hydroxy*-3-β-*naphthyl*-1 : 4 *naphthaquinone*, m.p. 195° (*monoacetate*, m.p. 156°); 2-*hydroxy*-3-*p*-*anisyl*-1 : 4-*naphthaquinone*, m.p. 127°, and its *acetate*, m.p. 121·5°; 2-*hydroxy*-3-o-*carboxyphenyl*-1 : 4-*naphthaquinone*, m.p. 248°, and the corresponding *lactone*, $C_{17}H_8O_4$, m.p. 253° (decomp.); 2-*hydroxy*-3-p-*carboxyphenyl*-1 : 4-*naphthaquinone*, m.p. 288° [*monoacetate* ($+0{\cdot}5H_2O$)]; the *K* salt ($+0{\cdot}5H_2O$) of 2-hydroxy-3-*p*-sulphophenyl-1 : 4-naphthaquinone. H. W.

Structure of gossypol. XVI. Reduction products of gossypolone tetramethyl ether and gossypolonic acid tetramethyl ether. XVII. Nitration of gossypol hexamethyl ether, gossypolone tetramethyl ether, and gossypolonic acid tetramethyl ether. R. Adams, T. A. Geissman, and R. C. Morris. **XVIII. Synthesis of 3 : 4-dimethoxy-5-*iso*propylaniline.** R. Adams, M. Hunt,

and R. C. Morris (J. Amer. Chem. Soc., 1938, **60**, 2967—2970, 2970—2972, 2972—2974).—XVI. The quinone structure of gossypolonic acid Me_4 ether (I) and gossypolone Me_4 ether (II) (A., 1938, II, 452) is proved by reduction. With Zn dust in boiling AcOH (I) gives *hydroxygossylolactone* Me_4 *ether* (III), m.p. 320° (block), and in Ac_2O its Ac_2 derivative, m.p. 231—233°, also obtained from (III) by Ac_2O–C_5H_5N. With Me_2SO_4 in KOH–MeOH (III) gives its Me_2 [*hydroxygossylolactone* Me_6] *ether*, m.p. 273—274°, hydrolysed by warm KOH–MeOH in presence of a little Zn dust to *methoxygossylic acid* Me_4 *ether* (IV), m.p. 250° (preheated bath), which is reconverted into the lactone at the m.p. or by warm Ac_2O. Reduction of (II) is difficult owing to the

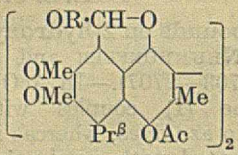


(III.)

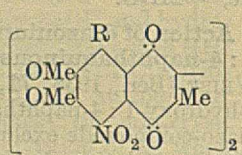


(IV.)

instability of the product, but $Na_2S_2O_4$ in hot abs. EtOH, followed by Ac_2O–C_5H_5N, gives the *acetal* [(V) R = Et], m.p. 264—265°, and in MeOH the *compound*, [(V) R = Me], m.p. 266—267°, is formed. CrO_3 oxidises [(V) R = Me or Et] to (II). In MeOH–



(V.)



(VII.)

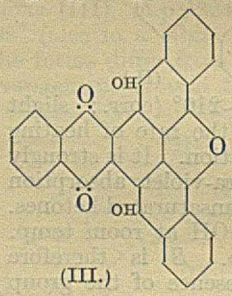
KOH (III) is hydrolysed, oxidised, and then degraded. Prep. of gossypol Me_6 ether (VI) is improved.

XVII. With HNO_3 (*d* 1·5) at −5° (VI) or (II) suffers replacement of Pr$^\beta$ by NO_2, giving the *compound* [(VII) R = CHO], decomp. 257—262° (darkens at 220°) (*dianil*, darkens at ~210°, chars at ~260°). With HNO_3 (*d* 1·5) (I) gives similarly the *acid* [(VII) R = CO_2H], darkens 260—270° (begins at ~220°), m.p. >320° (block), also obtained from [(VII) R = CHO] by HNO_3.

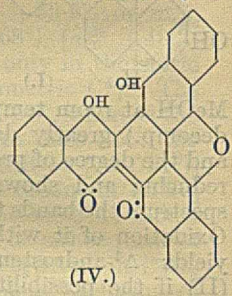
XVIII. 3 : 4 : 5 : 1-$(OMe)_2C_6H_2Pr^\beta$·NH_2 is synthesised. Its identity with the base obtained by degradation of gossypol (*loc. cit.*) proves the presence of Pr$^\beta$, the position of the OH relative thereto, and thus, in conjunction with other evidence, the 1-, 5-, 6-, 7-, and 8-substituents. Dry *o*-OMe·C_6H_4·ONa and CO_2 at 115° give 33% of 3 : 2 : 1-OMe·C_6H_3(OH)·CO_2H, m.p. 150°, the Me ester, m.p. 61° (lit., 63°), b.p. 134—136°/2 mm., of which with MgMeCl gives 2-*hydroxy*-3-*methoxyphenyldimethylcarbinol*, m.p. 126°, dehydrated at 195—200° to 2-*hydroxy*-3-*methoxy*isopropenylbenzene, b.p. 122—124°/14 mm. H_2–Raney Ni in 95% EtOH at 2—3 atm. then gives 2-*hydroxy*-3-*methoxy*isopropylbenzene, b.p. 123—125°/8 mm., converted (Me_2SO_4) into 2 : 3-*dimethoxy*isopropylbenzene, b.p. 119—121°/24 mm., which with HNO_3 (*d* 1·5) in AcOH yields the 5-NO_2-, m.p. 53°, or $(NO_2)_2$-derivative, m.p. 106°, and thence (H_2, Raney Ni, EtOH) 3 : 4-*dimethoxy*-5-isopropylaniline, m.p. 75° (Ac_2 derivative, m.p. 86°), and a $(NH_2)_2$-derivative, m.p. 75°, respectively. M.p. (all parts) are corr.

R. S. C.

Polymerisation processes. Condensation of 1 : 4-naphthaquinone to triphthalylbenzene by pyridine. R. Pummerer, A. Lüttringhaus, R. Fick, A. Pfaff, G. Riegelbauer, and E. Rosenhauer (Ber., 1938, **71**, [*B*], 2569—2583; cf. A., 1938, II, 65).—The yellow condensation product from 1 : 4-naphthaquinone (*loc. cit.*; G.P. 350,783) is not dinaphthylenediquinone but triphthalylbenzene (I). It is converted by the successive action of NaOH–$Na_2S_2O_4$ and *o*-C_6H_4Cl·COCl into *hexahydrotriphthalylbenzene hexa-o-chlorobenzoate* (II), m.p. 240—242° (decomp.) after softening at 180°. The green anhydroquinhydrone of (I) is (III) or (IV) since it yields a *diacetate*, m.p. 325° (decomp.), a *di-o-chlorobenzoate*, m.p. 317°, and is converted by $Na_2S_2O_4$–NaOH followed by *o*-C_6H_4Cl·COCl into the *tetra-o-chlorobenzoate*, m.p. 325—330° after softening, of the dihydroanhydroquinhydrone. (I) is reduced by Zn dust at incipient redness to the hydrocarbon (V), $C_{30}H_{18}$, m.p. 392° (corr.), also obtained similarly or



(III.)



(IV.)

by use of 48% HI at 200° from (III) or (IV). (I) is oxidised by 91% HNO_3 at 130° to mellitic acid. (I) is transformed by NaOH–$Na_2S_2O_4$ and treatment of the product by air into a red substance, oxidised (65% HNO_3 at 160—165°) to *o*-$C_6H_4(CO_2H)_2$.

The constitution of (V) as tri-2 : 3-naphthylene is confirmed by the determination of its mol. wt. in boiling PhCl; its picrate (cf. *loc. cit.*) therefore has its components in the ratio 1 : 1, not 3 : 2. The mol. wt. of (II) has been determined similarly. The substance obtained by reduction of (I) with HI and red P is identified as *tetracosihydrotrinaphthylene*, m.p. 360—362° after softening.

The "triphthalylbenzene" of Scholl *et al.* (A., 1937, II, 34), obtained in minimal yield by heating 2 : 3-dichloro-1 : 4-naphthaquinone with Cu powder, is very probably *di*-2-*naphthaquinonylnaphthaquinone*. Reductive acetylation appears to give the *tetra-acetate*, m.p. 325° (decomp.), of a H_4-derivative.

H. W.

Preparation and properties of pure ionene. A. Müller (J. pr. Chem., 1938, [ii], **151**, 249—250).—Ionene, b.p. 238—239°/730 mm., is obtained pure by threefold treatment of α-ionone with Na and I followed by distillation over Na under atm. pressure. In contrast with β-ionone it does not give an intensely-coloured condensation product with the usual *p*-NMe_2·C_6H_4·CHO reagent but yields a yellow-red to Bordeaux-red colour if the [H_3PO_4] is increased.

H. W.

Preparation of *N*-methylmenthylamines by a new method of *N*-alkylation. J. READ and J. A. HENDRY (Ber., 1938, **71**, [*B*], 2544—2552).—Reactions follow the scheme: $NH_2R + CH_2Cl{\cdot}CO_2Et \rightarrow NHR{\cdot}CH_2{\cdot}CO_2Et \rightarrow NHR{\cdot}CH_2{\cdot}CO_2H \rightarrow NHRMe + CO_2$. *sec.* Amines can be used similarly. Thus *l*-menthylaminoacetic acid gives N-*methyl*-l-*menthylamine* (I), b.p. 87°/12 mm., $[\alpha]_D^{17}$ −78·27° (homogeneous), $[\alpha]_D^{17}$ −69·2° in $CHCl_3$ (*hydrochloride*, m.p. 168°, $[\alpha]_D^{17}$ −52·75° in H_2O; *Bz*, m.p. 65°, $[\alpha]_D^{17}$ −32·4° in $CHCl_3$, and p-$C_6H_4Me{\cdot}SO_2$, m.p. 61°, $[\alpha]_D^{17}$ −37·5° in $CHCl_3$, derivatives; N-*methyl*-l-*menthylnitrosoamine*, m.p. 30·5°, $[\alpha]_D^{17}$ −39·5° in $CHCl_3$, −54·0° in C_6H_6), with some 2 : 5-*diketo*-1 : 4-*di*-l-*menthylpiperazine*, m.p. 201—202° (decomp.), $[\alpha]_D^{17}$ −106·3° in $CHCl_3$. (I) is transformed by $CH_2Cl{\cdot}CO_2Et$ and subsequent hydrolysis into l-*menthylmethylaminoacetic acid* (+1H_2O), m.p. 148°, $[\alpha]_D^{17}$ −51·5° in H_2O, whence l-*menthyldimethylamine* (II), b.p. 90·5°/10 mm., $[\alpha]_D^{17}$ −60·50° (homogeneous), $[\alpha]_D^{17}$ −59·7° in $CHCl_3$ [*platinichloride*, m.p. 205—206° (decomp.)]. *l*-Menthyltrimethylammonium iodide, m.p. 190° (decomp.), $[\alpha]_D^{17}$ −39·3° in H_2O, passes at 190°/atm. pressure into (II) and menthene, $[\alpha]_D^{17}$ +75·24° (homogeneous); when treated with Ag_2O and distilled at 165—170°/10 mm., the products are (II) and a menthene, b.p. 56°/10 mm., α_D^{17} +107·34° (*l* = 1; homogeneous), $[\alpha]_D^{17}$ +131·7° (homogeneous), $[\alpha]_D^{17}$ +149·7° in abs. EtOH, +149·2° in Et_2O. Et neomenthylaminoacetate is hydrolysed to d-*neomenthylaminoacetic acid*, m.p. 182°, $[\alpha]_D^{17}$ +28·1° in H_2O, +32·2° in abs. EtOH, which passes when heated into 2 : 5-*diketo*-1 : 4-*di*-d-*neomenthylpiperazine*, m.p. 63°, $[\alpha]_D^{17}$ +43·9° in $CHCl_3$ (*hydrochloride*, m.p. 242°, $[\alpha]_D^{17}$ +42·9° in $CHCl_3$), and N-*methyl*-d-*neomenthylamine*, b.p. 87°/12 mm., $[\alpha]_D^{17}$ +20·44° (homogeneous), +26·4° in $CHCl_3$ (*hydrochloride*, m.p. 196°, $[\alpha]_D^{17}$ +16·7° in H_2O; *Bz*, m.p. 67°, $[\alpha]_D^{17}$ +5·7° in $CHCl_3$, and p-$C_6H_4Me{\cdot}SO_2$, m.p. 49°, $[\alpha]_D^{17}$ +18·5° in $CHCl_3$, derivatives; N-*methyl*-d-*neomenthylnitrosoamine*, m.p. 62°, $[\alpha]_D^{17}$ +19·9° in $CHCl_3$). N-*Methyl*-d-*neomenthylaminoacetic acid*, m.p. 98° or (+2H_2O) m.p. 55°, $[\alpha]_D^{17}$ +28·5° in H_2O, passes at 200° into CO_2, $NHMe_2$, *d*-Δ³-menthene, b.p. 70°/15 mm., $[\alpha]_D^{16}$ +102·2° (homogeneous), and d-*neomenthyldimethylamine*, b.p. 93°/12 mm., $[\alpha]_D^{17}$ +42·69° (homogeneous), +40·7° in $CHCl_3$ [*platinichloride*, m.p. 196° (decomp.); *hydrochloride*, $[\alpha]_D^{17}$ +15·3° in H_2O]. d-*Neomenthyltrimethylammonium iodide*, m.p. 160·5° (decomp.), $[\alpha]_D^{17}$ −19·5° in H_2O (corresponding *tri-iodide*, m.p. 107°), passes at 155—160°/20 mm. into NMe_3, HI, and *d*-Δ³-menthene, b.p. 59°/10 mm., α_D^{16} +80·66° (*l* = 1; homogeneous). The cryst., very hygroscopic d-*neomenthyltrimethylammonium hydroxide* is converted at 150—160°/15 mm. or at 175—180°/atm. pressure into H_2O, NMe_3, and *d*-Δ³-menthene, b.p. 57°/10 mm., $[\alpha]_D^{20}$ +112·9° (homogeneous), $[\alpha]_D^{20}$ +108·5° in abs. EtOH, +112·9° in Et_2O. NH_2Ph is converted into anilinoacetic acid, m.p. 126—127°, which, at 200°, gives mainly 2 : 5-diketo-1 : 4-diphenylpiperazine, m.p. 263°, with a smaller proportion of NHPhMe. $NPhMe{\cdot}CH_2{\cdot}CO_2H$ readily decomposes when heated into $NPhMe_2$ and CO_2. Addition of Na_2CO_3, NaOAc, C_5H_5N, quinoline, or $NPhMe_2$ to the mixture of $CH_2Cl{\cdot}CO_2Et$ and amine (to absorb the liberated HCl) is disadvantageous. H. W.

***l*-Menthyl dialkylbetaine acetates.** (MME.) Y. RIGHETTI (Bull. Soc. chim., 1938, [v], **5**, 1463—1472; cf. (Mme.) Guaisnet-Pilaud, A., 1936, 196).—l-*Menthyl-dimethylamino*-, (I), b.p. 140·5—141°/14—15 mm., *-methylethylamino*- (II), b.p. 151—155°/17 mm., *-methylpropylamino*- (III), b.p. 166°/20 mm., and *-dipropylamino*-, b.p. 172·5—173·5°/13 mm., *-acetate* are prepared from *l*-menthyl bromoacetate (IV) and the corresponding amine in Et_2O. (I) and (IV) afford *bis*-(l-*menthyl acetate*)*dimethylammonium bromide*, $N(CH_2{\cdot}CO_2C_{10}H_{19})_2Me_2Br$, in a form converted at 80° or slowly by H_2O into a form, m.p. 127—128° (decomp.); each with Ag_2O–EtOH gives the *betaine*, $CO\langle{}^{CH_2}_{O}\rangle NRR'{\cdot}CH_2{\cdot}CO_2C_{10}H_{19}$ [(*A*), R = R′ = Me] (+3H_2O, lost at 100°); anhyd., m.p. 198—199° (decomp.), $[\alpha]_D^{18}$ −50·43° in EtOH. The cryst. quaternary bromides from *l*-menthyl-diethyl- and -dipropylaminoacetates and (IV)–Ag_2O give the corresponding *betaines*. The stable quaternary bromide from (II) and (IV), or from (II) and $CH_2Br{\cdot}CO_2Et$ (in this case a little inactive Ag salt of the betaine is isolated), or from (IV) and Et methylethylaminoacetate, give *betaines* [(*A*); R = Me, R′ = Et], a *monohydrate*, m.p. 162° (V), $[\alpha]_D$ −42·4° in EtOH, and a geometrical *isomeride* in anhyd. form (VI), m.p. 175°, $[\alpha]_D$ −50° in EtOH. (VI) and dil. HCl–Ag_2O give (V). The stable quaternary bromides from (III) or the benzylmethyl analogue, with (IV), give betaines with difficulty. A. T. P.

Mixed ethyl *l*-menthyl dilactylates [oxidodi-αα′-propionic acid derivatives]; attempt to prepare an optically active diester. M. GODCHOT and P. VIÈLES (Bull. Soc. chim., 1938, [v], **5**, 1535—1539; cf. A., 1932, 253; 1935, 474).—CHMeBr·COBr and *l*-menthol in Et_2O give l-*menthyl* (d + l-)α-*bromopropionate*, b.p. 156—160°/15 mm., which with (*d* + *l*-)*Et* lactate, α_{5468} −0·04°, gives a mixture, b.p. 134—138°/20 mm., $[\alpha]_{5468}^{26}$ −11·2°, of (*d* + *l*-) and (*i*-)dilactylates of Et and *l*-menthyl, hydrolysed, with isomerisation of latter, by excess of NaOH–EtOH to a Na_2 dilactylate, α 0°. A. T. P.

Terpene ethers.—See B., 1939, 18.

Addition reactions to conjugated systems. β-Phellandrene and maleic anhydride. N. F. GOODWAY and T. F. WEST (J.C.S., 1938, 2028—2031).—Pure *l*-β-phellandrene and maleic anhydride (I) give a resinous product, containing a small quantity of adduct identical with that obtained from *l*-α-phellandrene. The available evidence indicates that the *l*-β-phellandrene–(I) adduct is derived from β-phellandrene and (I) by thermal decomp. of the primary resinous product. The bearing of this result on the stereochemistry of more complex structures is discussed. F. R. S.

Thujone series. I. Thujones and some thujyl alcohols and thujylamines. A. G. SHORT and J. READ (J.C.S., 1938, 2016—2021).—The stereochemical relationship of the so-called " α-thujone " of thuja oil to " β-thujone " of tansy oil is similar to that of *l*- to *d-iso*-menthone. *l*-Thujone, obtained by oxidation (CrO_3) of *l*-thujyl alcohol, has b.p. 74·5°/9 mm., α_D^{18} −19·94° (*l* = 1), and forms a 2 : 4-*dinitrophenyl*-

hydrazone, m.p. 117°, $[\alpha]_D^{16}$ +44·0° in $CHCl_3$. *d-iso*-Thujone, similarly prepared from *d-iso*thujyl alcohol, has b.p. 76°/10 mm., $[\alpha]_D^{15}$ +72·46°, and gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 116°, $[\alpha]_D^{16}$ +161° in $CHCl_3$. In presence of NaOEt–EtOH, the isomerides undergo interconversion, the equilibrium mixture containing 35% of *l*-thujone. Hydrogenation of "α-" or "β-thujone" in C_6H_{12} with a catalyst yields *l-thujyl alcohol*, m.p. 66—67°, $[\alpha]_D^{16}$ −20·5° in MeOH (p-*nitrobenzoate*, m.p. 101°, $[\alpha]_D^{15}$ −32·25° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 106°, $[\alpha]_D^{19}$ −24·5° in $CHCl_3$). Reduction of "α-" or "β-thujone" with Na–EtOH gives d-iso*thujyl alcohol*, b.p. 103°/16 mm., α_D^{14} +106·70° (3 : 5-*dinitrobenzoate*, m.p. 92°, $[\alpha]_D^{17}$ +96·75° in $CHCl_3$; p-*nitrobenzoate*, m.p. 78°, $[\alpha]_D^{13}$ +107·0° in $CHCl_3$). Crude *l*-thujone oxime is reduced (Na–EtOH) to *l*-thujylamine, b.p. 81·5°/15·5 mm., α_D^{17} −24·32° [hydrochloride, m.p. 248—249° (decomp.), $[\alpha]_D^{16}$ −15·75° in H_2O; p-*nitrobenzoyl*, m.p. 146·5°, $[\alpha]_D^{15}$ −51·25° in $CHCl_3$, and *salicylidene* derivatives, m.p. 66°, $[\alpha]_D^{15}$ −7·03° in $CHCl_3$; *l-thujyltrimethylammonium iodide*, m.p. 269° (decomp.), $[\alpha]_D^{15\cdot5}$ −30·75° in $CHCl_3$; *picrate* of *N*-dimethyl-*l*-thujylamine, m.p. 137—138°, $[\alpha]_D^{18}$ −40·5° in $CHCl_3$]. Similarly *d-iso*thujylamine has b.p. 75·5°/11 mm., α_D^{13} +94·82°, and forms *benzoyl*, m.p. 131·5°, $[\alpha]_D^{15}$ +90·5° in $CHCl_3$ and p-*nitrobenzoyl* derivatives, m.p. 147°, $[\alpha]_D^{15}$ +77·0° in $CHCl_3$, d-iso*thujyltrimethylammonium iodide*, m.p. 260° (decomp.), $[\alpha]_D^{15}$ +47·0° in $CHCl_3$, and the *platinichloride* of *N*-dimethyl-*d-iso*thujylamine, m.p. 173—174° (decomp.). A mixture of *dithujylamines*, b.p. 181—182°/9 mm., α_D^{14} +23·5°, is obtained from "α-thujone" and HCO_2NH_4, followed by MeOH–HCl. A similar mixture of *dimenthylamines*, b.p. 176°/10 mm., α_D^{15} −9·96°, is obtained from *l*-menthone and HCO_2NH_4. F. R. S.

Triterpene group. IV. Triterpene alcohols of *Taraxacum* root. S. Burrows and J. C. E. Simpson (J.C.S., 1938, 2042—2047).—Al_2O_3 adsorption of the non-saponifiable matter of the root shows the complexity of the mixture. The "homotaraxasterol" of Power and Browning (J.C.S., 1912, **101**, 2411) is a mixture. Seven compounds have been isolated: taraxasterol (p-*nitrobenzoate*, m.p. 277—278°, $[\alpha]_D^{17}$ +98·3°) is a chemical individual, and is oxidised (CrO_3–AcOH) to a *product*, $C_{30}H_{48}O$, m.p. 175—176°, $[\alpha]_D^{18}$ +109·5°; β-amyrin, isolated as the acetate; stigmasterol; β-sitosterol; *taraxol*, $C_{30}H_{46}O_3$, m.p. >360°, $[\alpha]_D^{14}$ +78·6° [*acetate*, m.p. 299—301° (decomp.), $[\alpha]_D^{14}$ +93·9°; *oxide acetate*, m.p. 294—297°; *oxide*, m.p. 261—261·5°]; *taraxerol*, $C_{30}H_{50}O$, m.p. 269—271° (*benzoate*, m.p. 282—284°, $[\alpha]_D^{11}$ +35·0°; *acetate*, m.p. 296—297°, $[\alpha]_D^{18}$ +8·4°); and *ψ-taraxasterol*, m.p. 198—200°, $[\alpha]_D^{18}$ +47·1° (*benzoate*, m.p. 274—276°, $[\alpha]_D^{21}$ +72·3°; *acetate*, m.p. 234—235·5°, $[\alpha]_D^{20}$ +53·2°). The physical consts. of taraxasterol, the three new alcohols, and their derivatives indicate their probable triterpenoid nature. All rotations are in $CHCl_3$. F. R. S.

Structure of triterpenes. L. Ruzicka and W. J. Smith (Chem. and Ind., 1938, 1210—1211).—The hydrocarbon, m.p. 128—129° (picrate, m.p. 167—168°; quinone, m.p. 207—208°; quinoxaline derivative, m.p. 182—183°), obtained from hederagenin or basseol by Se, is shown by synthesis (not detailed) to be 1 : 2 : 6-trimethylphenanthrene. This confirms Ruzicka's structure for basseol (A., 1934, 530) and is in line with various formulæ proposed for β-amyrin. R. S. C.

Lignin. XIX. Derivatives of pine lignin containing mercury and iodine. K. Freudenberg and H. F. Müller (Ber., 1938, **71**, [*B*], 2500—2504).—In reply to the criticism of Hilpert *et al.* (A., 1937, II, 205) on the work of Freudenberg *et al.* (A., 1931, 1278), the mercuration of methyl-lignin (I) has been effected with addition of AcOH during the boiling and with washing of the products with the acid. The observation that a limiting val. for the entering Hg is attained and cannot be exceeded is proof that there is a true reaction between (I) and $Hg(OAc)_2$. Contrary to Hilpert, the differences in the reactivity of the metal in the Hg compounds of (I), vanillin, and homoveratrole are not such as to justify the assumption that it is in different types of union. Observations on the iodo-compounds, readily obtained from the Hg compound by I–KI, show that Hg is contained in large amount in (I) and that the reaction is concerned with substituents in C_6H_6 nuclei; I is retained with a firmness which with infrequent exceptions is found only in derivatives of PhI. H. W.

Chlorine–sodium sulphite reaction of woody tissues and the constitution of hardwood lignin. —See A., 1939, III, 217.

Methylation of ursolic acid. H. M. Sell and R. E. Kremers (J. Biol. Chem., 1938, **126**, 501—503; cf. Jacobs *et al.*, A., 1931, 1154).—Pure ursolic acid with CH_2N_2 or Me_2SO_4, or Ag ursolate with MeI, gives (good yield) only one Me ester, m.p. 170—171°. A. Li.

Ether-soluble constituents of sarsaparilla root. II. J. C. E. Simpson and N. E. Williams (J.C.S., 1938, 2040—2042; cf. A., 1937, II, 289).—The liquid fraction of the unsaponifiable matter obtained from the Et_2O-sol. material consists of a highly complex mixture of unsaturated alcohols and hydrocarbons, probably containing azulene. Treatment of two of the more volatile fractions with 3 : 5-$(NO_2)_2C_6H_3$·COCl gives traces of a *substance*, $C_{15}H_{11}O_6N_2$, m.p. 111°. An alcohol, $C_6H_{12}O$, has been isolated as its *pyruvic ester semicarbazone*, m.p. 114—115°, and also an alcohol, $C_{18}H_{36}O$, as the *pyruvic ester semicarbazone*, m.p. 137—137·5°. F. R. S.

Egonol. V. Nature of the hydroxyl group of egonol and the oxidation of acetylegonol by selenium dioxide. S. Kawai and K. Yamagami. **VI. Optical activity and active hydrogen atoms of egonol.** S. Kawai and N. Sugiyama (Ber., 1938, **71**, [*B*], 2438—2443, 2443—2447; cf. A., 1938, II, 501; 1939, II, 32).—V. Egonol (I) and *o*-$C_6H_4(CO)_2O$ in boiling PhMe yield *egonol H phthalate* (II), m.p. 153—153·5° (*Ag* salt, m.p. 177°); the OH of (I) is very probably primary. Oxidation of acetylegonol by SeO_2 in Ac_2O yields *α-di(acetylegonolyl) selenide* (III), $C_{42}H_{38}O_{12}Se$, m.p. 159—160°, noregonolonidine acetate, m.p. 180—180·5°, and *β-di(acetylegonolyl) selenide* (IV), m.p. 150—150·5°. (III) is hydrolysed (KOH–MeOH) to *α-diegonolyl selenide*,

m.p. 224—225° (*di*-p-*nitrobenzoate*, m.p. 186—188°). (IV) gives β-*diegonolyl selenide*, m.p. 174—175°.

VI. Egonoké oil, obtained by cold pressing, is hydrolysed by the requisite amount of KOH in cold OH·$[CH_2]_2$·OMe and (I) thus obtained is crystallised repeatedly from aq. $COMe_2$ and then from aq. MeOH, whereby an optically inactive product is ultimately obtained; this does not give a ppt. with digitonin. The optical activity of the oil is due to the presence of phytosterol. (II) does not give well-cryst. salts with brucine, strychnine, or cinchonine. l-*Brucine styraxinolate*, decomp. 212·5—213°, $[\alpha]_D^{20}$ +16·97° in $CHCl_3$, give optically inactive styraxinolic acid (IV) when decomposed by NH_3. It cannot be maintained that (I) and (IV) do not contain an asymmetric C since H at $C_{(4)}$ is readily mobile and hence asymmetric $C_{(4)}$ would be readily racemised. By use of MgMeI in C_5H_5N it is shown that (I) and its Ac derivative contain 2 and one active H respectively. Under similar conditions the expected no. of active H are found in *o*-OH·C_6H_4·CO_2H, xanthhydrol, and *p*-OH·C_6H_4·Ac whereas 2 active H are present in $CH_2(CO_2Et)_2$ and there is none in CH_2Ph_2. Since the use of MgMeI or MgEtBr shows the presence of 1 active H in *cyclo*pentadiene, indene, or fluorene, it must be admitted that (I) contains 2 active H of which one is united directly to C. H. W.

Catuabol obtained from the bark of catuabach (*Trichilia* spec.). M. M. Janot and E. Cionga (Compt. rend., 1938, **207**, 798—799).—Cold EtOH extracts a material from which C_6H_6 removes a substance, m.p. 115—116°, and *catuabol* (I), $C_{25}H_{40}O$, m.p. 200—201° (block), $[\alpha]_D^{15}$ +88·4° in $CHCl_3$ (*formyl*, *Ac*, and *Bz* derivatives, m.p. 242—243°, 242—243°, and 235—236°, respectively), which does not react with Br, $KMnO_4$–$COMe_2$, $C(NO_2)_4$–$CHCl_3$, or $FeCl_3$. (I) contains a labile H but no OMe or OEt. (I) with CrO_3–AcOH affords a ketone (*oxime*, m.p. 238—240°). J. L. D.

African arrow poisons. II. Heart poisons in *Calotropis* sap. G. Hesse, F. Reichenեder, and H. Eysenbach (Annalen, 1938, **537**, 67—86; cf. A., 1937, II, 71).—Coagulation of the sap by EtOH and treatment of the aq.-alcoholic serum by the method used previously (*loc. cit.*) does not yield calotropin (I) but a no. of new poisons, of which *uscharin* (II), *calotoxin* (III), and *calactin* (IV) are described. (II), decomp. 265° or higher if heating is rapid, $[\alpha]_D$ +29·0° in $CHCl_3$, is $C_{31}H_{41}O_8NS$. It gives *compounds* +1H_2O, +1EtOH, and +1 or 2 mols. of dioxan. It gives a positive Legal test and darkens boiling plumbite solution. (II) is readily decomposed by boiling dil. acids to NH_3, volatile org. compounds containing S, and *uscharidin* (V), $C_{29}H_{40}O_9$, decomp. 290° (also *monohydrate*). It is isomeric with (I). It is converted by NH_2OH,HCl and NaOAc in boiling EtOH into *uscharidinoxime*, decomp. 257°, also obtained similarly from (II). With CH_2N_2 in MeOH–Et_2O (V) gives *methyluscharidin*, decomp. 224°. Catalytic hydrogenation (Pb in EtOH) of (V) slowly gives *dihydrouscharidin*, decomp. 200°, which gives a positive Legal reaction. Hydrogenation (PtO_2 in AcOH) of (V) causes absorption of nearly 2 H_2 but leads to non-cryst. products. Hydrolysis of (V) by aq. $Na_2B_4O_7$ gives a substance very similar to but not identical with methylreductic acid (*loc. cit.*) and *iso*anhydrocalotropagenin, $C_{23}H_{32}O_6$, decomp. 251° after softening at 247°, obtained previously (*loc. cit.*) from (I). (V) and (I) are therefore derived from the same fundamental substance. (III), decomp. 244°, $[\alpha]_D$ +74°±4° in $CHCl_3$, is $C_{29}H_{40}O_{10}$ (also +1H_2O and +1EtOH); it is therefore a hydroxycalotropin. Physiologically it resembles strophanthin-*g*. Like (I) and (II) it is very resistant towards acids and only in presence of $(NO_2)_2C_6H_3$·NH·NH_2 or other osazone-formers are dil. acids effective. It is rapidly hydrolysed by alkali to ψ-anhydrocalotropagenin, decomp. 241°, obtained previously from (I). (I) and (III) are therefore derived from the same fundamental substance. The mother-liquors from the hydrolysis give the *phenylosazone*, decomp. 151—152°, of a substance, $C_6H_8O_4$, and with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 the *derivative*, $C_{18}H_{14}O_9N_8$, decomp. 214—217°, of an anhydro-compound, $C_6H_6O_3$. Thermal decomp. of (III) gives the *compound*, $C_6H_8O_4$, which shows the strong reducing action of enediols towards neutral $AgNO_3$, I, and $FeCl_3$; it is probably a hydroxymethylreductic acid. (IV) is not invariably found in the sap and appears to be more abundantly present as the content of (II) diminishes. It is possible that it is an after-formation due to some fermentative process. It is very similar to (I), giving on hydrolysis methylreductic acid with a genin which is not identical with calotropagenin. The pure poisons show marked differences in the ultra-violet fluorescence colours when the Liebermann reaction is effected with H_3PO_4 instead of H_2SO_4 or when in the Kiliani reaction $FeCl_3$ is replaced by $MnCl_2$ or $SbCl_5$. The reactions are very sensitive to impurities and hence unsuitable for crude fractions. (II) can be detected by alkali plumbite but the change is not very sensitive. Janus-red is decolorised in warm solution in a short time by *Calotropis* poisons but not by normal glucosides (antiarin gives 50% decolorisation). Most *Calotropis* poisons with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2,HCl give an orange-red ppt. within a few hr.; this dissolves in alcoholic alkali to an intensely blue or violet-blue solution whereas other glucosides give only a blood-red to yellow colour and, frequently, no ppt. H. W.

Melanoidins and their relation to humic acids. C. Enders and K. Theis (Brennstoff-Chem., 1938, **19**, 360—365, 402—407, 439—449).—Melanoidin (I), prepared by heating glucose with glycine in aq. solution, was sol. in aq. alkali, slightly sol. in H_2O, and insol. in org. solvents. The kinetics of formation was studied, the (I) being determined colorimetrically; the rate of formation increased with rising temp. and increasing p_H. The composition and mol. wt. of the (I) corresponded with $C_{67}H_{76}O_{32}N_5$; the mol. contained 8 alcoholic and 3 phenolic OH, 3 CO, and 5 CO_2H. In properties and reactions (I) closely resembled Merck's humic acid. At 150° it "coalified" with the loss principally of CO_2 and H_2O and with decreasing solubility in aq. alkali. During coalification the N at first increased but passed through a max. and then decreased; the CO decreased whilst the phenolic OH remained const. The changes are

similar to those that occur on heating humic acid except that they occur somewhat more readily and can be correlated with the natural coalification series humic acid–brown coal–bituminous coal–anthracite. Oxidation of (I) led through the formation of some unidentified intermediate products (one of which, $C_5H_{12}O_2N_4$, had m.p. 156°) to oxalic, glycollic, succinic, and picric acids, and a dihydroxybenzenedicarboxylic acid. A. B. M.

Chemistry of *Aspergillus* colouring matters. II. J. H. Cruickshank, H. Raistrick, and R. Robinson (J.C.S., 1938, 2056—2064).—Auroglaucin (I) forms (K_2CO_3–MeI) a *Me ether*, m.p. 100° [*oxime*, m.p. 117° (decomp.)], which shows a $Fe^{...}$ reaction; a Me_2 ether could not be obtained. Flavoglaucin (II) is reduced (Pd–H_2) to *dihydroflavoglaucin* (III), m.p. 98° (2 : 4-*dinitrophenylhydrazone*, m.p. 203°), which condenses with *o*-$C_6H_4(NH_2)_2$ to a *substance*, m.p. 150°, and is oxidised ($KMnO_4$) to *n*-octoic acid. Reduction (Pd–H_2) of the Me ether of (I) gives dihydroflavoglaucin Me ether (2 : 4-*dinitrophenylhydrazone*, m.p. 193°), which is oxidised (NaOH–H_2O_2) to *n*-octoic acid. Further reduction of (I) affords *decahydroauroglaucin* (*tetrahydroflavoglaucin*), m.p. 85°, which forms a Ac_3 derivative, m.p. 70°, and a Me_2 *ether*, m.p. 79°. Zn–AcOH with (III) yields tetrahydrodeoxyflavoglaucin (*Me_2 ether*, b.p. 175—180°/0·02 mm.). Comparative diazo-coupling and bromination tests of (I) and (II) and their derivatives with synthetic substances indicate resemblance to 4-*n*-amylquinoctophenone. These results confirm and extend the deductions arrived at for the structure of (I) and (II) (A., 1937, II, 106); (II) is regarded as an *n*-octoyl*iso*pentenylquinol or an *n*-octoylvinyl*iso*propylquinol and (I) has the same skeleton with three more double linkings. 3 : 6-$(OMe)_2C_6H_2(CO)_2O$, *o*-C_6H_5Me·OMe, and $AlCl_3$ give 3 : 6 : 6′-*trimethoxy*-2-*m*-*toluoylbenzoic acid*, m.p. 218°, which with H_2SO_4 yields 5 : 8-*dihydroxy*-3-*methoxy*-2-*methylanthraquinone*, m.p. 194—195°, methylated to the 3 : 5 : 8-(*OMe*)$_3$-compound, m.p. 231°. This substance is demethylated to the 3 : 5 : 8-(*OH*)$_3$-derivative (+0·6H_2O), m.p. 254° (*Ac_3* derivative, m.p. 196°). F. R. S.

Synthesis of substances with morphine-like action. H. Henecka (Med. u. Chem., 1936, **3**, 403—407; Chem. Zentr., 1937, i, 1146—1147).—NEt_2·[CH_2]$_3$·COMe (I), C_2H_2, and $NaNH_2$ in Et_2O give α-*diethylamino*-δ-*hydroxy*-δ-*methyl*-Δ$^{\epsilon}$-*hexinene*, b.p. 84—85°/3 mm., the Na salt (II) of which with $COMe_2$ + $NaNH_2$ affords α-*diethylamino*-δη-*dihydroxy*-δη-*dimethyl*-Δ$^{\epsilon}$-*octinene*, b.p. 126°/1 mm. This is converted ($HgSO_4$ in 10% H_2SO_4 at 80°/48 hr.) into 4(or 3)-*keto*-2 : 5 : 5-*trimethyl*-2-γ-*diethylaminopropyltetrahydrofuran*, b.p. 110—111°/4 mm., reduced (Na, EtOH) to the 4(or 3)-*OH*-derivative, b.p. 126—128°/3 mm. ακ-*Bisdiethylamino*-δη-*dihydroxy*-δη-*dimethyl*-Δ$^{\epsilon}$-*decinene*, b.p. 175—180°/1 mm. [from (I), (II), and $NaNH_2$ in Et_2O], similarly gives 3-*keto*-2 : 5-*dimethyl*-2 : 5-*bis*-γ-*diethylaminopropyltetrahydrofuran*, b.p. 162—164°/2·5 mm., and thence the 3-*OH*-derivative, b.p. 165—168°/1 mm. The furans have no morphine-like action. H. B.

Constitution of usnic acid. C. Schöpf and F. Ross (Naturwiss., 1938, **26**, 772—773; cf. A., 1937, II, 347; 1938, II, 198; 1939, II, 32).—Usnic acid diacetate (I) with O_3 in CCl_4 affords an *ozonide* (II), $C_{22}H_{20}O_{12}$, decomp. 152°, catalytic hydrogenation of which removes 1 H_2O to give a non-cryst. product. When heated with EtOH (II) affords Et α*γ*-diketovalerate and 1-*keto*-3 : 5-*diacetoxy*-6-*acetyl*-2 : 4-*dimethyl*-1 : 2-*dihydrobenzfuran* (III), m.p. 132°, which gives no $FeCl_3$ reaction, but contains the methylphloroglucinol ring and both Ac groups of (I). With conc. H_2SO_4 or HCl–EtOH, (III) affords a *substance*, $C_{12}H_{12}O_5$, m.p. 223° after sintering at 195°, re-acetylated to an *isomeride*, m.p. 132°, of (III). *d*-Diacetoxyusnic acid with O_3 gives, in solution, a strongly dextrorotatory ozonide which when decomposed affords (III). J. L. D.

Syntheses of chroman derivatives with the ring system of α-tocopherol. I. W. John, P. Günther, and M. Schmeil (Ber., 1938, **71**, [*B*], 2637—2649).—Gradual addition of trimethylquinol (I) and CHMeAc·CO_2Me in MeOH to P_2O_5 at 0° and heating of the mixture to 120—140° gives 6-*hydroxy*-2 : 3 : 5 : 7 : 8-*pentamethylchromone*, m.p. 201°, hydrogenated (Pd sponge in AcOH) to 6-*hydroxy*-2 : 3 : 5 : 7 : 8-*pentamethylchroman*, m.p. 108°. Analogously, CH_2Ac·CO_2Et affords 6-hydroxy-2 : 5 : 7 : 8-tetramethyl-chromone and -chroman, m.p. 145° [*allophanate*, m.p. about 220° (decomp.)]. With COPr$^{\alpha}$·CH_2·CO_2Et a *compound*, $C_{17}H_{22}O_5$, m.p. 141°, results, hydrogenated to a *substance*, $C_{17}H_{26}O_5$, m.p. 112°, which is not a chroman derivative. P_2O_5 and (I) do not appear to react with *Me* α-*cetylacetoacetate*, b.p. 170°/0·25 mm., m.p. 36—37°, obtained from CH_2Ac·CO_2Me, cetyl bromide, and NaOMe in MeOH. (I) is converted by dimethylacrylyl chloride and $AlCl_3$ in $PhNO_2$ at 75—80° into 6-*hydroxy*-2 : 2 : 5 : 7 : 8-*pentamethylchromanone* (II), m.p. 162°; in CS_2 the reaction follows a different course, giving a *compound* (III), $C_{14}H_{18}O_3$, m.p. 109°, isomeric with (II) but not containing an aromatic system and a *substance* (IV), $C_{14}H_{18}O_3$, m.p. 117°, possibly a dihydrocoumarin derivative. In $PhNO_2$ at room temp. (III) and (IV) are obtained. (II) is reduced (Clemmensen) to 6-*hydroxy*-2 : 2 : 5 : 7 : 8-*pentamethylchroman* (V), m.p. 93—94° (*allophanate*, m.p. 230°). The most successful syntheses in the series are effected by Grignard's reagents. Thus, 6-hydroxy-5 : 7 : 8-trimethyl-3 : 4-dihydrocoumarin (VI) is transformed by MgMeI into (V) (*p*-*bromobenzoate*, m.p. 159°). Similarly (VI) and (VII) in Et_2O–C_6H_6–PhOMe yield 6-*hydroxy*-5 : 7 : 8-*trimethyl*-2 : 2-*didodecylchroman*, m.p. about 28° (*allophanate*, m.p. 116°). 6-*Hydroxy*-2 : 5 : 7 : 8-*tetramethyl*-2-*dodecylchroman*, m.p. 60—61° (*allophanate*, m.p. 180°), is obtained by the simultaneous action of MgMeI and (VII) on (VI). *Dodecyl allophanate*, m.p. 150°, and *dodecylurethane*, m.p. 84°, are described incidentally. H. W.

Synthesis of chromones. F. von Werder and F. Jung (Ber., 1938, **71**, [*B*], 2650—2652).—Trimethylquinol, CH_2Ac·CO_2Et, and P_2O_5 in EtOH at 140° give 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethylchromone* (I), m.p. 224°, converted by boiling Ac_2O into its *acetate* (II), m.p. 172°. Trimethylquinol diacetate is transformed by $AlCl_3$ at 220° into (II), (I) (possibly formed during the working up of the product), and 2 : 5-*dihydroxy*-

3 : 4 : 6-*trimethylacetophenone*, m.p. 152° (*monoacetate*, m.p. 113°), which does not react with NH_2·CO·NH·NH_2, NH_2OH, or *p*-NO_2·C_6H_4·NH·NH_2 but is reduced (Clemmensen) to 3 : 6-*dihydroxy*-1 : 2 : 4-*trimethyl*-5-*ethylbenzene*, m.p. 165°. H. W.

Aminobenzylidenechromanones. P. PFEIFFER and G. VON BANK (J. pr. Chem., 1938, [ii], **151**, 319—326).—Addition of NaOMe–MeOH to 7-methoxychromanone (I) and *m*-NO_2·C_6H_4·CHO gives 7-*methoxy*-3-m-*nitrobenzylidenechromanone*, m.p. 147—148°, reduced ($SnCl_2$ and HCl in AcOH) to 7-*methoxy*-3-m-*aminobenzylidenechromanone*, m.p. 106° (*hydrochloride*, m.p. (indef.) 230°; *Bz* derivative, m.p. 165°), which, in conc. H_2SO_4, gives a colourless solution with very pale, blue-green fluorescence. Similarly, 7-hydroxychromanone affords 7-*hydroxy*-3-m-*nitrobenzylidenechromanone*, m.p. 242·5° after becoming brown at 230° (*acetate*, m.p. 138·5°), whence 7-*hydroxy*-3-m-*aminobenzylidenechromanone*, m.p. 241·5° after softening at 238° (*hydrochloride*, m.p. 185°, decomp. 205°). *p*-NO_2·C_6H_4·CHO and (I) yield 7-*methoxy*-3-p-*nitrobenzylidenechromanone*, m.p. 174—175° after softening at 170°. *p*-NHBz·C_6H_4·CHO and (I) in EtOH saturated with HCl at 0° give 7-*methoxy*-3-p-*benzamidobenzylidenechromanone*, m.p. 209° (slight decomp.). 7-*Hydroxy*-3-p-*nitro*-, m.p. 211° (decomp.) (*acetate*, m.p. 207—208°), and 7-*hydroxy*-3-p-*benzamido*- (*acetate*, m.p. 205°) -*benzylidenechromanone* are described. H. W.

Magnetochemical investigation of organic compounds. XV. Constitution and magnetic behaviour of metallic ketyls. E. MÜLLER and W. WIESEMANN (Annalen, 1938, **537**, 86—112).—The metal compounds are divided into actual radicals, "holoradicals," meriradical, and non-radical substances. Previously reported, non-radical compounds all belong to the 4-pyrone series. In extension it is shown that the K compounds of chromone and 2-phenylchromone are diamagnetic. The former contains 2 CO per K whereas all other compounds have CO : K = 1 : 1. There is therefore no relationship between radical structure and K content per CO. The constitution of the non-radicals is investigated with Li methylchromone (I), which is readily obtained from LiBu and methylchromone (II). It is diamagnetic. With BzBr, Br, or MeI it gives resins from which a cryst. material cannot be isolated. Hydrogenation (Pd–$CaCO_3$ in C_6H_6) of (I) and hydrolytic removal of Li leads to a non-cryst. mixture of 2-*methylchromanone* (III) and 2-*methylchromanol* (IV). [Hydrogenation (Pd–$CaCO_3$–C_6H_6) of 2-methylchromone gives (III) (p-*nitrophenylhydrazone*, m.p. 253°), further hydrogenated (Pt-black in C_6H_6) to (IV) (benzoate, m.p. 70°).] (I) must therefore be formulated either as a quinhydrone or as a pinacolate; the latter is preferred since the production of (II) cannot be observed when (I) is cautiously decomposed with dil. acids. An electronic structure is also discussed. The meriradical compounds formed by addition of alkali metals to non-enolisable ketones are to be regarded as mol. compounds of complex structure. Their common characteristic is that one atom of metal is invariably added for 2 CO of the initial ketone. The alkali metal compounds so produced are mol. compounds of the radical–quinhydrone or pinaconate–quinhydrone the composition of which depends on the temp. Investigations with K benzil or K phenanthraquinone show that with spatially proximate CO groups the second CO which does not add metal can function as an internal quinhydrone. In the case of K *p*-dibenzoylbenzene a pinaconate–quinhydrone is not formed but a diamagnetic "quinonoid" dimetallic compound results. Peculiarities in the constitution of the initial ketone are therefore operative. Since paramagnetism decreases with decreasing temp. there is a displacement towards the non-radical form even in the solid state. The magnitude of this displacement over the range, room temp. to liquid air, depends on the constitution of the initial material. The radical condition of most of these meriradical substances can be stabilised only when the lone electron can be merged into a large cloud of π electrons. If the electron cloud of the unimol. compound is inadequate, as in these cases, further mols. are brought in. Thus two xanthone mols. add 1 K atom and hence a π electron in common. At low temp. there is partial compensation between two vicinal adducts. The holoradical compound from K and COPh·C_6H_4Ph contains 77—74% of radical; the content sinks to about 60% of the solution is cooled from room temp. to that of liquid air. The effect appears general. H. W.

Chalkones. Synthesis of 1-*p*-alkoxyarylidene-5 : 6-benzocoumaran-2-ones. A. P. KHANOLKAR and T. S. WHEELER (J.C.S., 1938, 2118—2119).—1-Hydroxy-2-naphthyl *p*-alkoxystyryl ketone dibromides, which normally yield flavones with alcoholic alkali, give β-alkoxy-compounds and then arylidenecoumaranones, if the solubility of the dibromide in alcohols is increased by addition of $CHCl_3$. With aq. alkali and $COMe_2$ the dibromides give the corresponding naphthaflavones. The following are described: 4-*bromo*-1-*hydroxy*-2-*naphthyl* αβ-*dibromo*-, m.p. 173°, α-*bromo*-β-*ethoxy*-, m.p. 169—171°, and α-*bromo*-β-*methoxy*-β-3 : 4-*methylenedioxyphenylethyl ketone*, m.p. 169—170°; 6-*bromo*-3′ : 4′-*methylenedioxy*-α-*naphthaflavone*, m.p. 276°; 4-*bromo*-1-*hydroxy*-2-*naphthyl* αβ-*dibromo*-, m.p. 157—158°, α-*bromo*-β-*ethoxy*-, m.p. 155—156°, and α-*bromo*-β-*methoxy*-β-p-*anisylethyl ketone*, m.p. 146—147°; 4-*bromo*-1-*hydroxy*-2-*naphthyl* p-*methoxystyryl ketone*, m.p. 184°; 6-*bromo*-4′-*methoxy*-α-*naphthaflavone*, m.p. 240—241°; and 4-*bromo*-1-*anisylidene*-5 : 6-*benzocoumaran*-2-*one*, m.p. 219—220°. F. R. S.

Pyrylium salts from acid anhydrides and acid chlorides. P. P. HOPF and R. J. W. LE FÈVRE (J.C.S., 1938, 1989—1991).—By the interaction of COPhMe (2 mols.) or dypnone with various acid anhydrides or chlorides (1 mol.), in the presence of $FeCl_3$, a no. of 2-substituted 4 : 6-diphenylpyrylium ferrichlorides have been prepared. No marked condensation occurs in the absence of $FeCl_3$ and the effective intermediates may be of the type RCOCl + $FeCl_3$. The following are new: 4 : 6-*diphenyl*-2-*ethyl*-, m.p. 166°, -n-*propyl*-, m.p. 198°, -iso*propyl*-, m.p. 258°, -iso*butyl*-, m.p. 162°, -n-*amyl*-, m.p. 144°, -*hexyl*-, m.p. 88°, -*styryl*-, m.p. 257°, and -*benzyl*-*pyrylium ferrichloride*, m.p. 203°. F. R. S.

Melting point of psoralen (ficusin). K. Okahara (Bull. Chem. Soc. Japan, 1938, **13**, 653—655; cf. A., 1936, 861, 1121; 1937, II, 112).—Carefully purified natural psoralen and the synthetic product (method of Späth *et al.*) both melt at 161—162°.

A. Li.

Preparation and properties of pure dioxan. K. Hess and H. Frahm (Ber., 1938, **71**, [*B*], 2627—2636).—The changes which occur in dioxan (I) when kept are due to union with atm. O_2 to form a peroxide; the change is accelerated by impurities and by the consequential products. In absence of air pure (I) can be kept unchanged at will. It may be advisable to remove ethylene acetal, $\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}>CHMe$, from crude (I) by boiling with 10% of N-HCl but if it is present only in small amount, a prolonged heating with Na is adequate. Subsequent operations included careful fractionation and repeated freezing, which require the complete absence of atm. moisture. The physical methods used in controlling the purity of (I) are constancy of m.p. when fractionally frozen, equality of the temp. of boiling and condensation, and equality of the vapour tension of the liquid itself and of that produced by condensing its vapour. Peroxide is detected by Rieche's benzidine reaction or by the (very sensitive) conversion of Hg into black Hg_2O. Aldehyde is detected by Schiff's reagent. Pure (I) has m.p. 11·80°±0·01° (corr.), b.p. 101·31° (corr.)/760 mm., d^{20} 1·03375±1 × 10^{-5} g./c.c., n_D^{20} 1·42241±1 × 10^{-5}. At room temp. pure (I) has very little action on O_2 so that it can be kept in contact with air but a comparatively rapid change occurs at the b.p. It appears that the changes occur in the sequence: (I) → oxonium peroxide → aldehyde → peroxide.

H. W.

Synthesis of β-2-thienylalanine and of β-2-thienylethylamine. G. Barger and A. P. T. Easson (J.C.S., 1938, 2100—2104).—Thiophen (improved prep. from C_2H_2 and FeS_2) is converted, through 2-thienyl Me ketone and 2-thienylglyoxylic acid, into thiophen-2-aldehyde. This with hippuric acid gives the *azlactone* of *α-benzamido-β-2-thienylacrylic acid*, m.p. 175°, the free *acid*, m.p. 238—240°, from which is reduced (Na–Hg) to the *-propionic acid*, m.p. 176—180°, hydrolysed to *β-2-thienylalanine*, m.p. 274—275°. This compound is more readily prepared from the aldehyde with hydantoin through *acetyl-2-thienylidenehydantoin*, m.p. 214—216°, *2-thienylidenehydantoin*, m.p. 253—255°, and *2-thienylmethylhydantoin*, m.p. 188—190°. *β-2-Thienylpropionamide*, m.p. 99—100°, obtained from the corresponding acid, with Cl_2–KOH gives *β-2-thienylethylamine*, b.p. 200—201°/750 mm. (*hydrochloride*, m.p. 200—202°). This amine has a pressor action qualitatively and quantitatively indistinguishable from that of $Ph\cdot[CH_2]_2\cdot NH_2$, a finding attributed to the similarity in physical properties of the two bases. Oximinoacetothienone is reduced ($SnCl_2$) to *2-thienylaminomethyl ketone hydrochloride*, m.p. 215—218°.

F. R. S.

Highly arylated compounds. VIII. Derivatives of tetraphenylthiophen. W. Dilthey and E. Graef (J. pr. Chem., 1938, [ii], **151**, 257—278).—Gradual addition of rather > the calc. amount of conc. H_2SO_4 to tetraphenylthiophen (I) and the calc. amount of KNO_3 in AcOH at 100° affords 3 : 4 : 5-*triphenyl-2-p-nitrophenylthiophen* (II), m.p. 179—180°, in 60% yield. It gives *p*-$NO_2\cdot C_6H_4\cdot CO_2H$ when oxidised. Reduction ($SnCl_2$–HCl–AcOH) of (II) gives 3 : 4 : 5-*triphenyl-2-p-aminophenylthiophen*, m.p. 204—205° (*Ac* derivative, m.p. 258°; corresponding *diazonium perchlorate*; *anisylidene* derivative, m.p. 201°). (II) is oxidised by H_2O_2 to the corresponding *sulphone*, m.p. 250°, which gives an intense violet-red halochromism with NaOMe in C_5H_5N and affords only BzOH and *p*-$NO_2\cdot C_6H_4\cdot CO_2H$ when degraded with O_3. Gradual addition of conc. HNO_3–AcOH to (I) suspended in AcOH at 100° leads to 3 : 4-*diphenyl*-2 : 5-*di-p-nitrophenylthiophen* (III), m.p. 217—218°, with a smaller proportion of 4 : 5-*diphenyl*-2 : 3-*di-p-nitrophenylthiophen* (IV), m.p. 169—170°, either of which gives exclusively *p*-$NO_2\cdot C_6H_4\cdot CO_2H$ when oxidised. (III) is reduced ($SnCl_2$–HCl–AcOH) to 3 : 4-*diphenyl*-2 : 5-*di-p-aminophenylthiophen*, m.p. 273° [*Ac*, m.p. 324—325°, *Bz*, m.p. 320°, and *dianyslidene*, m.p. 243°, derivatives; *compound*, $C_{48}H_{32}O_2N_4S$, m.p. 267°, obtained by coupling diazotised (III) with 2-$C_{10}H_7\cdot OH$]. Oxidation of (III) by H_2O_2 in AcOH or sulphoacetic acid affords the corresponding *sulphone* (V), m.p. 294°, oxidised by H_2O_2, O_3, or CrO_3 exclusively to *p*-$NO_2\cdot C_6H_4\cdot CO_2H$; it appears to add 1 NaOMe. (IV) is reduced to 4 : 5-*diphenyl*-2 : 3-*di-p-aminophenylthiophen*, m.p. 220°, which gives a weak yellow-orange halochromism in conc. H_2SO_4, and is oxidised by H_2O_2 to 4 : 5-*diphenyl*-2 : 3-*di-p-nitrophenylthiophen dioxide* (VI), m.p. 194°, which shows a violet-red halochromism with NaOMe in C_6H_5N. Fuming HNO_3 at >0° transforms (I) into *hexanitrotetraphenylthiophen*, m.p. 284°, probably identical with the $(NO_2)_4$-derivative described by Fleischer. Nitration of (II) gives a mixture of (III) and (IV). Nitration of (III) by fuming HNO_3 in AcOH at 100° gives *tetranitrotetraphenylthiophen*, m.p. 302°, in small amount; the main product appears to be a mixture of several NO_2-compounds. *pp'*-Dinitrodibenzyl sulphide is oxidised by H_2O_2 to *pp'-dinitrodibenzyl sulphone*, m.p. 259°, the colour reactions of which closely resemble those of (V) and (VI). The choice of formulæ for (III) and (IV) is dictated by this consideration, by analogies of m.p., and by the isolation of small amounts of benzil by the oxidation of (IV).

H. W.

Attempted preparation of an optically active 4 : 4'-dithioxanthyl. W. Steinkopf and L. Garbe (J. pr. Chem., 1938, [ii], **151**, 327—330).—2 : 2'-Diiododiphenyl, *o*-$SH\cdot C_6H_4\cdot CO_2H$, anhyd. K_2CO_3, and $Cu(OAc)_2$ in amyl alcohol under CO_2 at 220° give *2 : 2'-di-o-carboxyphenylthioldiphenyl* (I), m.p. 254°. This gives two *quinine* salts, $C_{26}H_{18}O_4S_2$,$C_{20}H_{24}O_2N_2$, m.p. 228° and 222°, respectively, from which the optically active *acids*, m.p. 259°, $[\alpha]_D^{22}$ +194·3° in abs. EtOH, and m.p. 265°, $[\alpha]_D^{19}$ −62·3° in abs. EtOH, are isolated. Conc. H_2SO_4 at 90° transforms (I) into (?) 4 : 4'-*dithioxanthyl*, which becomes dark brown without melting at 350°; the solubility of the analogous product obtained from the optically active acids is so small that possible optical activity could not be investigated.

H. W.

Extension of Knorr's pyrrole synthesis. D. DAVIDSON (J. Org. Chem., 1938, **3**, 361—364).—Amarone and Zn dust in AcOH give tetraphenylpyrrole (I) (cf. A., 1938, II, 114). With $COPh{\cdot}CH_2Ph$ and NH_4OAc, $COPh{\cdot}CHPh{\cdot}NH_2$ or benzoin gives 74% of (I); in absence of NH_4OAc, $COPh{\cdot}CHPh{\cdot}NH_2$ gives only 33% of (I). 50% of (I) is also obtained from benzoin, NH_4OAc, and Zn dust (to produce $COPh{\cdot}CH_2Ph$) in AcOH. With benzoin and NH_4OAc in AcOH, $COMe{\cdot}CH_2Ph$, $CO(CH_2Ph)_2$, and $CH_2Ac{\cdot}CO_2Et$ give 3 : 4 : 5-*triphenyl*-2-*methyl*-, m.p. 164° (corr.), and -2-*benzyl*-*pyrrole*, m.p. 151° (corr.), and *Et* 4 : 5-*diphenyl*-2-*methylpyrrole*-3-*carboxylate*, m.p. 203° (corr.), but COPhMe does not react.

R. S. C.

Oxidation products of pyrrole amines. II. T. AJELLO and G. SIGILLÒ (Gazzetta, 1938, **68**, 681—688).—The substance, m.p. 170°, obtained from 4-amino-2 : 3 : 5-triphenylpyrrole and $K_3Fe(CN)_6$ or PbO_2 (cf. A., 1939, II, 35) is identified (mol. wt.) as 4-*imino*-2 : 3 : 5-*triphenylpyrrole*, which is converted by dil. AcOH into triphenylpyrrylhydroxylamine and the substance of m.p. 290° (*loc. cit.*), and by dil. HCl or H_2SO_4 in aq. EtOH into a substance, m.p. 188°.

E. W. W.

Pyridine-*N*-oxide-*O*-sulphonic acid betaine.—See A., 1939, I, 91.

Condensation products of (A) acetylisatic acid, (B) isatin. M. YOKOYAMA (J. Chem. Soc. Japan, 1936, **57**, 247—250, 251—254).—(A) Acetylisatic acid [(?) quinoline salt (I), m.p. 177·5°, decomposes when kept in EtOH giving isatin, quinoline, and AcOH] with hydantoin and AcOH–NaOAc at 107° affords acetyloxindolylidenehydantoin (II), m.p. 290° (decomp.), similarly prepared from (I) in presence of saturated aq. NaCl at 105—110°. Hydrolysis (aq. NH_3) of (II) gives oxindolylidenehydantoin, m.p. >310°, reduced (Na–Hg, dil. NaOH) to oxindolylhydantoin ($+H_2O$), m.p. 204—205°, which is hydrolysed [$Ba(OH)_2$] to NH_3 and 2 : 3-dihydroxy-3 : 4-dihydroquinoline-4-carboxylic acid, m.p. >300° (Ag salt when slowly heated gives a sublimate of 2-hydroxyquinoline).

(B) Isatin (1 mol.) with 1 and 2 mols. of $CN{\cdot}CH_2{\cdot}CO_2Et$ in EtOH–piperidine gives Et oxindolylidenecyanoacetate (III), m.p. 202°, and Et_2 indole-2 : 3-dicyanoacetate ($+H_2O$), m.p. 99—100°, respectively. EtOH–conc. H_2SO_4 converts (III) into Et H (IV), m.p. 219°, and Et_2, m.p. 149°, oxindolylidenemalonate. Dissolution of (IV) in alkali and acidification gives 2-hydroxyquinoline-3 : 4-dicarboxylic acid, m.p. 304—305° [3-Et_1 ester, m.p. >305°, obtained by reduction (Al–Hg, alkali) of (III) and treatment of the product with EtOH–conc. H_2SO_4]. Reduction ($SnCl_2$,AcOH) of (III) affords β-amino-α-oxindolylpropionic acid, m.p. 94°. CH. ABS. (*b*)

Hypaphorine : racemisation of its ester and properties of other derivatives. W. M. CAHILL and R. W. JACKSON (J. Biol. Chem., 1938, **126**, 627—631; cf. J.C.S., 1911, **99**, 2068).—Hypaphorine Me ester iodide (I) is completely racemised when heated with MeOH–MeI–NaOH for 8 hr., and is hydrolysed by aq. NaOH to a partly racemised betaine. *dl*-Hypaphorine melts at 248—249° (decomp.). Hypaphorine gives with HNO_3 the nitrate, $[\alpha]_D^{25}$ +91·2° in aq. NH_3, and with HI the *iodide*, m.p. 220—221° (decomp.), $[\alpha]_D^{25}$ +75·2° in aq. NH_3 [produced together with the nitrate by hydrolysing (I) and adding HNO_3]. All m.p. are corr. A. LI.

Direct introduction of the amino-group into the aromatic and heterocyclic nucleus. IV. Action of the alkali and alkaline-earth amides on some substituted quinolines. F. W. BERGSTROM (J. Org. Chem., 1938, **3**, 233—242; cf. A., 1938, II, 245).—Introduction of NH_2 by $Ba(NH_2)_2$, or sometimes KNH_2 or KNH_2–$Ba(CNS)_2$, in liquid NH_3 gives (? 2-)*amino*-8-, m.p. 86—86·3° (*picrate*, m.p. 242—243·5°), and -6-*methyl*-, m.p. 145·7—146·7°, -6-, m.p. 178·7—179·4°, and -8-*ethoxy*-, m.p. 211—212°, -6-*dimethylamino*-, m.p. 168·5—169·5°, -*quinoline*, 4-*aminoquinoline*-2-, (?) $+0{\cdot}25H_2O$, m.p. 280·5—281° (decomp.), and 2-*aminoquinoline*-4-*sulphonic acid* (I), m.p. (crude) 350—352° (*Et* ester, m.p. 191—192°), (? 2-)*aminoquinoline*-6-*carboxylic acid*, $+0{\cdot}5H_2O$, m.p. 323—324°, and *aminoquinoline*-6-*sulphonic acid*, $+H_2O$, m.p. >354°. No NH_2-derivative could be obtained from 7-methyl-, 2-methoxy- [gives 2-aminoquinoline (II)], 8- or 2-hydroxy-quinoline, (II), or quinoline-2-sulphonic acid (III). KNH_2 usually gives tars; with 6-methoxyquinoline it gives products (? the 2- and 4-NH_2-compounds), m.p. 119—121·5° and 160—175°, and with (III) gives (II) and a *product*, $C_{18}H_{19}O_2N_3$, m.p. 209—210° [or, in presence of KNO_3, (II)]. With KNH_2–$Ba(CNS)_2$ quinoline-4-carboxylic acid gives a poor yield of (I) or a *substance*, $C_{10}H_9ON_3$, m.p. 211·4—212·4°. CO_2H at $C_{(2)}$ or $C_{(4)}$ increases the yield of NH_2-derivative. R. S. C.

Aminoquinolines.—See B., 1939, 18.

Application of the Bischler–Napieralski reaction to δ-ketoazelaodi-β-veratrylethylamide. F. E. KING and R. ROBINSON (J.C.S., 1938, 2119—2120; cf. Child and Pyman, A., 1929, 1314).—Me δ-ketoazelate (I), new m.p. 34°, boiled with dil. HCl for 5 min. and the solution evaporated at 60°/vac., gives δ-ketoazelaic acid, m.p. 108—109°. (I) and 2 equivs. of β-veratrylethylamine at 170—180° afford *δ-ketoazelaodi-β-veratrylethylamide*, m.p. 147° (2 : 4-*dinitrophenylhydrazone*, m.p. 135—136°), converted by $POCl_3$–PhMe at 110° into γγ′-bis-(6 : 7-dimethoxy-3 : 4-dihydro*iso*quinolyl)dipropyl ketone [*monopicrate*, m.p. 181—182°, accompanied by a little of a *picrate*, m.p. 112—113° (decomp.)]. A. T. P.

Formation of *iso*cyanine dyes by intermolecular condensation of 4-chloroquinaldines. A. MEYER and H. DRUTEL (Compt. rend., 1938, **207**, 923—925).—When 4-chloro-2 : 6-dimethylquinoline (I) (cf. A., 1937, II, 431) containing a little impurity or H_2O is heated, an *iso*cyanine dye (II) is formed. (I) forms a quaternary NH_4 chloride which loses HCl to give 4-keto-2 : 6-dimethyl-1 : 4-dihydroquinoline, two mols. of which condense to give (II). A dry C_6H_6 solution of the product left when (II) is washed with NaOH ppts., with Et_2O, a rose-coloured dye (III), $C_{22}H_{18}ON_2$, which with dry HCl (gas) in C_6H_6 forms a *hydrochloride*, $C_{22}H_{19}ON_2Cl$, m.p. >300°, of *iso*cyanine-blue, which with NaOH becomes Cl-free. 4-

Chloro-2 : 8-dimethylquinoline does not give an *iso*-cyanine. J. L. D.

Carbazole ketones.—See B., 1939, 18.

Phthaloyl- and dibenz-carbazoles.—See B., 1939, 21.

2 : 8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-groups on the 5-carbon atom. XVII. Synthesis of 5-*o*-aminoanilino-2 : 8-dialkoxy-10-alkylacridinium derivatives and 5 : 5′-*o*-phenylenebis(amino-2 : 8-dimethoxy-10-methylacridium hydroxide). XVIII. Synthesis of the hydrochlorides of 5-*m*-aminoanilino-2 : 8-dialkoxy-10-alkylacridinium chlorides and 5 : 5′-phenylenediamino-compounds combined with various kinds of acridinium derivatives. XIX. Relation between 2 : 8-dialkoxy-*N*-alkylacridones and solvents. K. Ishihara (J. Chem. Soc. Japan, 1936, **57**, 12—25, 136—165, 326—345; cf. A., 1937, II, 468).—XVII. 5-Chloro- (or iodo-)2 : 8-dialkoxy-10-alkylacridinium chlorides (or iodides) and *o*-$C_6H_4(NH_2)_2$ give the 5-*o*-aminoanilino-derivatives solely. 5-*o*-Aminoanilino-2 : 8-dimethoxy-10-methyl-, m.p. 250° (decomp.), and -ethyl-, m.p. 231°, -acridinium iodide, and the -2 : 8-diethoxy-10-methyl chloride, m.p. 248° (decomp.), and iodide, m.p. 238°, and -10-ethyl chloride, m.p. 245° (decomp.), and iodide, m.p. 245°, are prepared. 5-*o*-Aminoanilino-2 : 8-dimethoxy-10-methylacridinium hydroxide is converted by 70% MeOH or C_6H_6–H_2O at 100°/10—15 hr. (sealed tube) into 2 : 8-dimethoxy-*N*-methylacridone (28%) and 5 : 5′-*o*-phenylenebis(amino-2 : 8-dimethoxy-10-methylacridinium hydroxide) (24—28%).

XVIII. 5-*m*-Aminoanilino-2 : 8-dialkoxy-10-alkylacridinium hydroxides and $\leq$2 mols. of HCl in aq. AcOH give the *acridinium chloride hydrochlorides* (contain 0·9HCl); the 2 : 8-*dimethoxy*-10-*methyl* ($+1\frac{1}{3}H_2O$, $\frac{1}{4}$AcOH), m.p. 215° (decomp.), and -*ethyl* ($+1\frac{1}{3}H_2O$, $\frac{1}{4}$AcOH), m.p. 206° (decomp.), and 2 : 8-*diethoxy*-10-*methyl* ($+1H_2O$), m.p. 248° (decomp.), and -*ethyl* ($+1\frac{1}{3}H_2O$), m.p. 240° (decomp.), derivatives are prepared. When these (singly or mixtures of two) are heated at 75°/2 hr. and the products treated with boiling aq. AcOH–KI, the basic *iodides*, AI_2,xAI(OH),$y$$H_2O$,$z$AcOH, are obtained; these with aq. KOH give the *hydroxides*, $A(OH)_2$. The respective m.p. of the iodides and hydroxides (for R, R′, R″, R‴ in the order quoted) are: Me, Me, Me, Me, 284°,

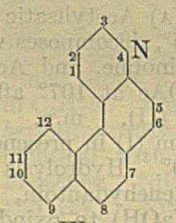
$$\cdot NR\lessgtr\begin{matrix}C_6H_3(OR')\\C_6H_3(OR')\end{matrix}\gtrless C\cdot NH\cdot C_6H_4\cdot$$

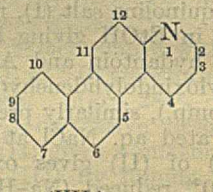
$$NH\cdot C\lessgtr\begin{matrix}C_6H_3(OR'')\\C_6H_3(OR'')\end{matrix}\gtrless NR'''. \quad (A.)$$

—; Et, Me, Me, Me, 277°, 228°; Me, Et, Me, Me, 245°, 235°; Et, Et, Me, Me, 266°, 218°; Et, Me, Me, Et, 270°, —; Me, Et, Me, Et, 249°, 196°; Et, Et, Me. Et, 255°, 182°; Me, Et, Et, Me, 268°, 198°; Et, Et, Et, Me, 281°, 180—183°; Et, Et, Et, Et, 285°, 194°.

XIX. Solubilities of 2 : 8-dialkoxy-*N*-alkylacridones in H_2O, MeOH, EtOH, AcOH, and C_6H_6 are determined. Ch. Abs. (*b*)

Phenanthrene series. XIX. Naphthoquinolines synthesised from aminophenanthrenes. E. Mosettig and J. W. Krueger (J. Org. Chem., 1938, **3**, 317—339).—Naphthoquinolines are prepared from 3- (I) and 2-*aminophenanthrene* and 2-amino-9 : 10-dihydrophenanthrene (II). Structures of the products are proved mainly by degradation. The direction of ring-closure is compared with that in similar cases. (I) (prep. from the oxime of the Ac derivative by Ac_2O–AcOH–HCl), m.p. 140—142°, gives only naphtho[1 : 2-*f*]quinoline (IV) (45% yield) (cf. A., 1936, 1125). Reduction of (IV) by Sn–HCl or Na–EtOH or electrolytically is unsatisfactory. With H_2–PtO_2 in AcOH (IV) gives very slowly a mixture of the 1 : 2 : 3 : 4-H_4- (V) and 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12- or 1 : 2 : 3 : 4 : 5 : 6 : 1*a* : 4*a*-H_8-derivatives (VI); hydrogenation of (V) to (VI) is much more rapid. At 170° H_2–Cu–Cr_2O_3 gives only 45% of (IV) (cf. *loc. cit.*). (V) gives the *methiodide*, m.p. 185—187° (decomp.), of the 4-Me derivative, which with AgCl gives the *methochloride*, m.p. 174—176° (decomp.), pyrolysis of which gives a mixture containing mostly the 4-*Me* derivative, m.p. 77—78·5° (corr.) [*hydrochloride*, m.p. 215—217° (decomp.)]; the above-mentioned quaternary salts are reduced by Na–Hg in H_2O to 4-*γ*-*dimethylamino*-n-*propylphenanthrene*, an oil [*hydrochloride*, m.p. (anhyd.) 159—160° or (+EtOH) 125—127°; *methiodide*, m.p. 208—208·5° (corr.)]. Emde degradation of the *methiodide*, m.p. 275—280° (decomp.), of (VI) is slow and produces decomp. With glycerol and $FeSO_4$ in $PhNO_2$ (II)


(IV.)


(VII.)

gives *naphtho*[2 : 1-f]*quinoline* [*naphtho*-2′ : 1′-5 : 6-*quinoline*] (VII), m.p. 226—227° (corr.) [*hydrochloride*, m.p. 296—300° (vac.)], hydrogenated in presence of PtO_2 in AcOH or Cu–Cr_2O_3 in EtOH at 130—136°/162 atm. to the 1 : 2 : 3 : 4-H_4-derivative (VIII), m.p. 157—159° (corr.) [*hydrochloride*, m.p. 310—313° (decomp.); *methochloride*, m.p. 188—190°], but with the latter catalyst at 230°/217 atm. to the 1 : 2 : 3 : 4 : 5 : 6-H_6-derivative (IX), m.p. 115—116° [*hydrochloride*, m.p. 274—285° (corr.; vac.)], also obtained impure from (VIII) by H_2–PtO_2 in AcOH. (VIII) gives the *methiodide*, m.p. 204—205° (decomp.), of the Me derivative; this, when distilled in vac., gives the 1-*Me* derivative, m.p. 170—171° (corr.) [*hydrochloride*, m.p. 240—260° (decomp.)], of (VIII), and, when reduced by Na–Hg, gives a product (*hydrochloride*, m.p. 206—207°). Emde degradation of the corresponding methochloride gives 1-*γ*-*dimethylamino*-n-*propylphenanthrene*, an oil [*hydrochloride*, m.p. 195—200°; *picrate*, m.p. 164·5—166·5° (corr.)]. (IX) yields similarly the 1-*Me* derivative, m.p. 129—131° (*methiodide*, m.p. 193—195°, unstable in hot H_2O), and 1-*γ*-*dimethylamino*-n-*propyl*-9 : 10-*dihydrophenanthrene* [*hydrochloride*, m.p. 207—209°; *picrate*, m.p. 145·5—146·5° (corr.)]. By the Skraup synthesis (III)

gives 5 : 6-*dihydronaphtho*[1 : 2-g]*quinoline* [3′ : 4′-*dihydronaphtho*-1′ : 2′-6 : 7-*quinoline*] (X), m.p. 72—74° (corr.) [*hydrochloride*, m.p. 258—262° (corr.; vac.)], which with H_2–PtO_2 in AcOH (less well, H_2–Cu–Cr_2O_3 in EtOH) gives the 5 : 6 : 8 : 9 : 10 : 11-H_6-derivative, m.p. 72—73°, which yields the *methiodide*, m.p. 196—200° (decomp.), of its Me derivative and thence 3-γ-*dimethylamino*-n-*propyl*-9 : 10-*dihydrophenanthrene* (XI) [*hydrochloride*, m.p. 150—151° (corr.); *picrate*, m.p. 101·5—103° (corr.)]. With Pd-black in N_2 at 300—360° (X) gives *naphtho*-[1 : 2-g]*quinoline*, m.p. 159—160° [*hydrochloride*, m.p. 280—295° (vac.)], hydrogenated (PtO_2; AcOH) to the 8 : 9 : 10 : 11-H_4-derivative, an oil, which yields the *methiodide*, m.p. 203—205° (decomp.), of its 8-Me derivative, and thence 3-γ-*dimethylamino*-n-*propylphenanthrene* (XII) [*hydrochloride*, m.p. 160—162° (corr.); *picrate*, m.p. 150·5—151·5° (corr.); *methiodide*, m.p. 173—174° (163—164°); *perchlorate*, m.p. 84·5—89° (corr.)], also obtained in one experiment from (XI) by Pd in N_2 at 190—200°. 3-γ-Dimethylamino-α-hydroxy-*n*-propylphenanthrene hydrochloride and PCl_5 in $CHCl_3$ give 3-α-*chloro*-γ-*dimethylaminopropylphenanthrene hydrochloride*, double m.p. 150—155° and 238—240°, which with H_2–$Pd(OH)_2$–$CaCO_3$ gives (XII). 2-γ-Dimethylamino-*n*-propylphenanthrene is unchanged by Na–Hg and Na–EtOH gives a mixture. 2-Acetyl-9 : 10-dihydrophenanthrene, $(CH_2O)_3$, and $NHMe_2$,HCl in hot *iso*-C_5H_{11}·OH give 2-β-*dimethylaminopropionyl*-9 : 10-*dihydrophenanthrene*, m.p. 70—71° (corr.) [*hydrochloride*, m.p. 162—163° (corr.)], hydrogenated (PtO_2; 60% EtOH) to 2-γ-*dimethylamino*-α-*hydroxy*-n-*propyl*-9 : 10-*dihydrophenanthrene*, m.p. 72—74° (corr.), the *hydrochloride*, m.p. 159—161° (corr.), of which with PCl_5 in $CHCl_3$ yields 2-α-*chloro*-γ-*dimethylamino*-n-*propyl*-9 : 10-*dihydrophenanthrene hydrochloride*, m.p. 214—216°, and thence 2-γ-*dimethylamino*-n-*propyl*-9 : 10-*dihydrophenanthrene hydrochloride*, m.p. 204—206° (corr.). R. S. C.

Polynuclear, condensed systems with heterocyclic rings. III. W. Borsche and O. Vorbach (Annalen, 1938, **537**, 22—38; cf. A., 1937, II, 518, 519).—2 : 3-Diphenylquinoline-4-carboxyl chloride is cyclised by $AlCl_3$ in $PhNO_2$ at 60° to 9-keto-4-phenyl-1 : 2-benzo-3-azafluorene (I), m.p. 263° (*oxime*, m.p. 254°; 2 : 4-*dinitrophenylhydrazone*, m.p. 320°), which does not appear to give a picrate. It is reduced by N_2H_4,H_2O at 200° in 20 hr. to 4-*phenyl*-1 : 2-*benzo*-3-*azafluorene*, m.p. 184° (*picrate*, m.p. 200°), also obtained by Sn powder with boiling AcOH–4N-HCl. Isatic acid and CH_2PhAc give 3-*phenyl*-2-*methyl*- (II), decomp. 312°, and 2-*benzyl*-, m.p. 220° (decomp.), -*quinoline*-4-*carboxylic acid*. The chloride of (II) is transformed by $AlCl_3$ in $PhNO_2$ into 9-*keto*-4-*methyl*-1 : 2-*benzo*-3-*azafluorene* (III), m.p. 198° (*oxime*, m.p. 292°; 2 : 4-*dinitrophenylhydrazone*, m.p. 317°; *picrate*, m.p. 235°), also obtained from (II) and conc. H_2SO_4 at 100°. Condensation of (III) with the requisite aldehyde affords 4-*styryl*-, m.p. 185°, 4-p-*methoxystyryl*-, m.p. 199°, and 4-o-*nitrostyryl*-, m.p. 224°, -1 : 2-*benzoazafluorene*. (III) is reduced by N_2H_4,H_2O at 200° to 4-*methyl*-1 : 2-*benzo*-3-*azafluorene*, m.p. 133° (*hydrochloride*, decomp. 285°; *picrate*, m.p. 180°). CH_2Ph·COEt, obtained with β-*hydroxy*-αγ-*diphenyl*-β-*ethylglutaric acid*, m.p. 181° (decomp.), by the action of EtCOCl on $CHPh(MgCl)\cdot CO_2Na$, isatin, and KOH in EtOH at 100° yield 3-*phenyl*-2-*ethyl*- (IV), m.p. 302—303° (decomp.), and 2-*benzyl*-3-*methyl*- (V), m.p. 235—237°, -*quinoline*-4-*carboxylic acid*. Distillation of (IV) with Cu-bronze yields 3-*phenyl*-2-*ethylquinoline*, b.p. 200—203°/17 mm. (*picrate*, m.p. 177°), whilst (V) affords 2-*benzyl*-3-*methylquinoline*, b.p. 187—192°/15 mm. (*picrate*, m.p. 184°). The chloride of (IV) is cyclised to 4-*ethyl*-1 : 2-*benzo*-3-*azafluorenone*, m.p. 157—158° [*sulphate*, m.p. 255° (decomp.)], also obtained from (IV) and conc. H_2SO_4. 4-*Ethyl*-1 : 2-*benzo*-3-*azafluorene* has m.p. 101°. 3-Phenyl-2-benzylquinoline-4-carboxylic acid (*Me* ester, m.p. 101°) [whence 3-*phenyl*-2-*benzylquinoline*, m.p. 60°, b.p. 260—265°/2 mm. (*picrate*, m.p. 190°)] is converted by PCl_5 in $POCl_3$ at 100° into 9-*keto*-4-*benzyl*-1 : 2-*benzo*-3-*azafluorene*, m.p. 220° (2 : 4-*dinitrophenylhydrazone*, m.p. 308°); the acid and conc. H_2SO_4 at 80° yield 9-*keto*-4-*benzyl*-1 : 2-*benzo*-3-*azafluorene*-?-*sulphonic acid*, m.p. 322°. 3-Phenyl-3-benzylquinoline-4-carboxyl chloride, $AlCl_3$, and C_6H_6 at 60° give 4-*phenyl*-1 : 2-*benzo*-3-*aza*-*anthran*-9-*ol*, m.p. 265° (*picrate*, m.p. 234°; *Ac* derivative, m.p. 197°), which does not react with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2; the corresponding free acid and conc. H_2SO_4 at 80° appear to give a *sulphonic acid*, $C_{23}H_{15}O_4NS$, m.p. >360°. Isatin, KOH, and $CO(CH_2\cdot CH_2Ph)_2$ give 3-*benzyl*-2-β-*phenylethylquinoline*-4-*carboxylic acid*, m.p. (anhyd.) 175°, (hydrated) 120° [whence 3-*benzyl*-2-β-*phenylethylquinoline*, m.p. 98° (*picrate*, m.p. 198°; *methiodide*, m.p. 193°)], transformed by PCl_5–$POCl_3$ into (?)-*chloro*-4-β-*phenylethyl*-1 : 2-*benzo*-3-*aza*-*anthranol*, m.p. 265° after softening at 255° (*picrate*, m.p. 244°), which does not react with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2. 2-β-*Phenylethylquinoline*-4-*carboxylic acid* has m.p. 221°. Decarboxylation of (II) by Cu-bronze gives 3-*phenyl*-2-*methylquinoline* (VI), b.p. 207—209°/12 mm. (*picrate*, m.p. 170°; *methiodide*, m.p. 196°), which with the appropriate aldehyde and Ac_2O at 140° affords 3-*phenyl*-2-*styryl*-, m.p. 103°, -2-p-*methoxystyryl*-, m.p. 120°, and -2-o-*nitrostyryl*-, m.p. 120°, -*quinoline*. 2-β-*Phenylethylquinoline* (*picrate*, m.p. 130°; *methiodide*, m.p. 189°) has b.p. 216—218°/13 mm., m.p. 29—30°. $Et_2C_2O_4$ and (VI) condense to *Et* 3-*phenylquinolyl*-2-*pyruvate*, m.p. 160° (*K* derivative; *picrate*, m.p. 145°; 2 : 4-*dinitrophenylhydrazone hydrochloride*, decomp. 197°), from which the following are obtained: *Et* α-*benzoyloxy*-3-*phenylquinolyl*-2-*acrylate*, m.p. 117°; *Et* α-*oximino*-β-3-*phenylquinolyl*-2-*propionate*, m.p. 173°, and the corresponding *acid* (+$1H_2O$), m.p. 141°; the *anhydride* of the acetyloximino-acid, $C_{20}H_{14}O_3N_2$, m.p. 147°, and the corresponding *Bz* derivative, m.p. 188°; 3-*phenylquinolyl*-2-*acetonitrile*, m.p. 93°. 2-*Benzylquinoline*, b.p. 212—213°/12 mm. (*picrate*, m.p. 155°; *methiodide*, m.p. 208°), gives an anisylidene derivative, isolated as its *picrate*, m.p. 225°. It is converted into *Et phenyl*-2-*quinolylpyruvate*, m.p. about 172° (*K* derivative), which does

not appear to form a picrate or a 2 : 4-dinitrophenylhydrazone. *Et α-oximino-β-phenyl-β-quinolyl-2-propionate*, m.p. 191°, and the corresponding *acid*, decomp. 164°, are described. H. W.

Formation of uramil from dialuric acid. D. DAVIDSON and H. SOLOWAY (J. Org. Chem., 1938, **3**, 365—371).—Formation of uramil from alloxantin by the action of NH_4Cl involves formation of the imine and interaction thereof with dialuric acid to give uramil and alloxan, since formation of uramil from dialuric acid and NH_4Cl is catalysed by O_2 or alloxan. Uramil probably exists as the enol. R. S. C.

New azo-compounds and iodo-derivatives of histidine and histamine. W. DIEMAIR and H. FOX (Ber., 1938, **71**, [*B*], 2493—2499).—N^{α}-Benzoylhistidine Me ester (I) and PhN_2Cl in 10% Na_2CO_3 yield *di(benzeneazo)-*N^{α}*-benzoylhistidine* (II), $NH{\cdot}C(N{:}NPh)\rangle C{\cdot}CH_2{\cdot}CH(NHBz){\cdot}CO_2H$, converted by CH_2N_2 in MeOH–Et_2O into the *Me* ester, m.p. 217°. Benzoylhistamine under similar conditions gives *benzeneazo-*N^{α}*-benzoylhistamine* (III), m.p. 186·5°. *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ gives *p-nitrobenzeneazoglyoxaline*, m.p. 248°, with glyoxaline and *di-p-nitrobenzeneazo-*N^{α}*-benzoylhistidine*, m.p. 160—161° (*Me* ester, m.p. 208°). Reduction of (II) with $SnCl_2$ and HCl gives a red aminohistidine hydrochloride, very sensitive to air, and much less stable than the simple aminoglyoxaline. Al–Hg is unsuitable as a reducing agent since it does not decolorise (II) completely. Reduction with catalytically excited H_2 confirms the constitution of (II) by the amount of gas absorbed. Rapid experiment in the absence of air leads to a red NH_2-compound of N^{α}-benzoylhistidine which decomposes to red, oily smears when its purification or union with compounds which stabilise the NH_2 group is attempted. Reduction of (III) with $SnCl_2$ and HCl gives colourless crystals which decompose rapidly on exposure to air and do not yield a Bz compound. (I), 0·1N-NaOH–MeOH, and I afford *monoiodo-*N^{α}*-benzoylhistidine Me ester* (IV), m.p. 190°; *monoiodo-*N^{α}*-benzoylhistidine* has m.p. 208°. Both compounds are stable towards conc. alkalis and moist Ag_2O. (IV) couples with PhN_2Cl to (II), I being immediately eliminated. H. W.

Nickel catalyst in hydrogenation of 4-amino-5-cyano-2-methylpyrimidine. M. DELÉPINE (Bull. Soc. chim., 1938, [v], **5**, 1539—1550; cf. A., 1938, II, 247).—4-Amino-2-methylpyrimidine-5-aldehyde (I), m.p. 192° [*hydrochloride* (+H_2O, lost at 100°), m.p. 280—281° (decomp.); *platinichloride* (+$2H_2O$, lost at 100° for 3 hr.); *chromate*; *picrate*, m.p. 220°; *oxime*; *semicarbazone*, m.p. 335—336° (decomp.); *hydrazone*, m.p. 296—297° (volatilises); *compound* with $NHPh{\cdot}NH_2$, m.p. 215°; internal *salt*, +H_2SO_3 (+H_2O) (formula)], affords *complexes*, $\left[C_5H_4N_2\langle{}^{CH:CH}_{NH}\rangle\right]_2M$, with Ni (+$7H_2O$; 6 mols. lost at 100°), Co (+$7H_2O$), and Cu (+$6H_2O$); mechanism of formation, though the 5-$CH_2{\cdot}OH$ compound, is discussed. With $AgNO_3$, a *compound* of 2 mols. of (I) and 1 mol. of $AgNO_3$, is obtained. 4-Amino-2-methyl-5-aminomethylpyrimidine gives a *hydrochloride*, +H_2O, m.p. 304—305° (decomp.). A. T. P.

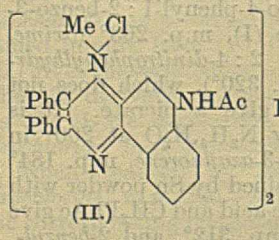
Anomalous decomposition of the tetrazo-derivative of 2 : 2′-diamino-1 : 1′-dinaphthyl. IV. Reaction of *o*-(4 : 5-1′ : 2′-naphth-3-pyrazolyl)cinnamic acid with thionyl chloride. A. CORBELLINI, C. BOTRUGNO, and F. CAPUCCI (R. Ist. lombardo Sci Lett., Rend., 1936, [ii], **69**, 477—484; Chem. Zentr., 1937, i, 1420).—*cis-o*-(4 : 5-1′ : 2′-Naphth-3-pyrazolyl)cinnamic acid (I) and boiling $SOCl_2$ give a *chloride*, $C_{20}H_{11}ON_2Cl$, m.p. ~250° (decomp.; darkens ~200°), hydrolysed (5% NaOH) to an *acid*, $C_{20}H_{12}O_2N_2$, m.p. 273·5° (*Me*, m.p. 238°, *Et*, m.p. 234°, and iso*amyl* esters; *amide*, m.p. 274°), which contains 2 H less than (I) and affords o-(4 : 5-1′ : 2′-*naphth-3-pyrazolyl)benzoic acid*, m.p. 266—268·5° (decomp.), when fused with KOH. Reduction (Zn dust, AcOH) of the acid (and esters) gives (I) (and esters). H. B.

Structure and properties of Pinacryptol-green. I. N. GORBATSCHEVA and I. I. LEVKOEV (Photo.-Kino Chem. Ind. U.S.S.R., 1936, **1**, 59—63).—Reduction ($SnCl_2$) of the product from *o*-$NH_2{\cdot}C_6H_4{\cdot}NHPh$ and (?) picryl chloride gives (?)1 : 3-diamino-5-phenylphenazonium chloride (Pinacryptol-green). CH. ABS. (*b*)

Derivatives of 3-carboline. R. H. FREAK and R. ROBINSON (J.C.S., 1938, 2013—2015).—Decomp. of 1-2′-pyridyl-1 : 2 : 3-benztriazole in H_3PO_4 gives 3-carboline, which forms a *methosulphate*, m.p. 204—205°, and a *methiodide*, m.p. 208°. The methosulphate and NaOH yield 3-*methyl*-3-iso*carboline*, m.p. 138—139°, which behaves as a resonance hybrid, and with EtI affords 3-*methyl*-1-*ethylcarbolinium iodide*, m.p. 195°. 3-*Carboline ethosulphate*, m.p. 114—115°, similarly gives 3-*ethyl*-3-iso*carboline*, m.p. 102°, which with NaI yields 3-*carboline ethiodide*, m.p. 199—200°. 3-Ethyl-3-carboline on methylation affords 1-*methyl*-3-*ethylcarbolinium iodide*, m.p. 209·5°. Reduction of 3-carboline with Na–BuOH gives 3-*γ*-aminopropylindole. 1 : 2-Naphthylenediamine and 2-chloropyridine yield 3-2′-*pyridyl*-β-*naphthaisotriazole*, m.p. 159°, which with H_3PO_4 forms 9 : 10-*benzo*-3-*carboline*, m.p. 256° (*picrate*, decomp. 300°). F. R. S.

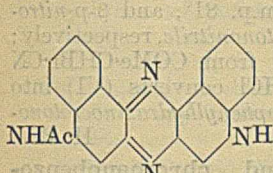
1 : 3-Diaza-anthraquinones.—See B., 1939, 18.

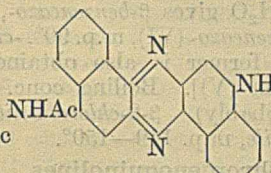
Azine dyes derived from naphthalene. S. MILHAÉLOV (Bull. Soc. chim., 1938, [v], **5**, 1655—1664).—4-Acetamidonaphthylene-1 : 2-diamine (I) and phenanthra-9 : 10-quinone give the cryst. acetamido-azine, hydrolysed by aq. H_2SO_4 to the azine, m.p. 309—313°. $(COPh)_2$ gives the *acetamido-azine*, m.p. 244·2—245°, hydrolysed to the *azine*, $C_{24}H_{17}N_3$, m.p. 235°, which gives the *salt* (II). Atm. oxidation of (I) or condensation of (I) with 4-acetamidonaphtha-1 : 2-quinone gives much of the *azine* (III) with some of the *azine* (IV), which are readily hydrolysed to the Ac-free *azines*, sensitive to NH_3. 3-Acetamidonaphtha-1 : 2-quinone and (I) give a similar mixture of isomeric *diacetamidoazines*. 4 : 5-Dihydroxy-*o*-benzoquinone and (I) give an *acetamidoazine* and thence the



(II.)

free *azine*. 4-Hydroxynaphtha-1 : 2-quinone and (I) give two *products*; the mixture is hydrolysed


(III.)

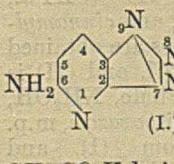

(IV.)

and the free azines are isolated as *dihydrochlorides*, $C_{20}H_{13}ON_3,2HCl$. R. S. C.

γ-Triazines. XXXVII. Liebig and Wöhler's so-called trigenic acid : 2 : 4-diketo-6-methyltriazidine or *cyclo*ethylidenebiuret. A. Ostrogovich and G. Ostrogovich (Gazzetta, 1938, **68**, 688—698).—Repeating the Liebig–Wöhler prep. (Annalen, 1846, **59**, 296), cyanuric acid (I) is heated with MeCHO; the resulting "trigenic acid" is 2 : 6-*diketo*-6-*methyltriazidine* (*cyclo*ethylidenebiuret) (II) (cf. A., 1936, 616), m.p. 272—273°, mixed with unchanged (I), which is now removed as the Ba salt, and the sol. Ba derivative of (II) decomposed by CO_2. Salts prepared from (II) are identical with those from the reduction product of dihydroxymethyltriazine (*loc. cit.*); the basic *Hg* salt, $C_4H_5O_2N_3(Hg{\cdot}OH)_2$, decomp. 250—252° (*Ac*$_2$ derivative), is also described. The Ac_2 derivative of (II) has new m.p. 175—176°. E. W. W.

Heterocyclically substituted pyruvic esters. III. Quinoxalyl-2-pyruvic esters and 3-methylquinoxalyl-2-pyruvic esters. W. Borsche and W. Doeller (Annalen, 1938, **537**, 39—52; cf. A., 1937, II, 32).—Addition of 2-methylquinoxaline to a solution of K and $Et_2C_2O_4$ in Et$_2$O–EtOH at 0° gives *Et quinoxalyl-2-pyruvate* (I), m.p. 161—162° [*K* derivative, *picrate*, m.p. 134°; *methiodide*, decomp. 176°; O-*Bz* derivative, m.p. 94—98°; *oxime* (II), m.p. 146—148; 2 : 4-*dinitrophenylhydrazone*, m.p. 136—137°; *hydrazone hydrazide*, $C_{11}H_{12}ON_6$, decomp. 225°]. It could not be smoothly hydrolysed to the corresponding acid and does not give characteristic condensation products with aromatic aldehydes. With *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ it readily gives *Et* 3-2′-*quinoxalylquinoline*-2-*carboxylate*, m.p. 153—154°; the corresponding *acid*, decomp. about 181° (*Na* salt; *Me* ester, m.p. 172—173°), passes at 200—205° into 3-2′-*quinoxalylquinoline*, m.p. 214—215° (*picrate*, m.p. 238—239°; *methiodide*, decomp. 268—269°). *o*-$C_6H_4(NH_2)_2$ and (I) at 100° give 3′-*hydroxy*-2 : 2′-*diquinoxalylmethane*, m.p. 307—309°. Diazotised NH_2Ph and (I) yield *Et* αβ-*diketo*-β-*quinoxalyl*-2-*propionate* β-*phenylhydrazone*, m.p. 158—160°, which gives only amorphous products when hydrolysed; the corresponding p-*tolylhydrazone*, m.p. 149—150°, is transformed by 5% KOH into an unidentified *compound*, in $C_{17}H_{12}O_2N_2$, decomp. 244—245°. Gradual addition of SeO_2 to 2-methylquinoxaline in xylene at 130° gives *quinoxaline*-2-*aldehyde*, m.p. 110° (*phenylhydrazone*, m.p. 229—230°; *oxime*, m.p. 197—198°). PhCHO, *p*-$C_6H_4Me{\cdot}NH_2$, and (I) in boiling EtOH slowly give 4 : 5-*diketo*-2-*phenyl*-1-p-*tolyl*-3-*quinoxalyl*-2-*pyrrolidine*, m.p. 283—285°; the corresponding β-*naphthyl* derivative decomposes at 290—292°. (II) is readily hydrolysed by alkali but the resulting acid is purified with difficulty and is therefore converted directly by Ac_2O at 45° into *quinoxalyl*-2-*acetonitrile* (II), m.p. 116—117° (boiling Ac_2O gives α-*cyano*-α-2-*quinoxalylacetone*, m.p. 228—229°). *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and (II) in boiling MeOH afford the p-*dimethylaminoanil* of *quinoxalyl*-2-*glyoxylonitrile*, m.p. 251°. With the requisite N_2-compound (II) gives *quinoxalyl*-2-*glyoxylonitrile* p-*tolylhydrazone*, m.p. 187—188°, and p-*anisylhydrazone*, m.p. 188—190°. With PhCHO in EtOH containing a little piperidine (II) yields α-2-*quinoxalylcinnamonitrile*, m.p. 146—147°; 4-*methoxy*-α-2-*quinoxalylcinnamonitrile*, m.p. 162—163°, and αβ-di-2-*quinoxalylacrylonitrile*, m.p. 245°, are obtained similarly. *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ and isatin give respectively 3-2-*quinoxalylcoumarin*, m.p. 196—197°, and 2-*keto*-3-2′-*quinoxalylcyanomethene*-2 : 3-*dihydroindole*, m.p. 306—308°. 2 : 3-Dimethylquinoxaline, $Et_2C_2O_4$, and KOEt yield Et 3-methylquinoxalyl-2-pyruvate (III), m.p. 129—130° (*picrate*, m.p. 140—141°; O-*Bz* derivative, m.p. 119—122°; *oxime*, m.p. 181—182°; 2 : 4-*dinitrophenylhydrazone*, m.p. 179—180°), hydrolysed to 3-*methyl*-2-*quinoxalylpyruvic acid*, decomp. 223—225° (*K* salt). (III) is unaffected by aromatic aldehydes (including *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$) and aromatic N_2-compounds under the usual conditions. With *o*-$C_6H_4(NH_2)_2$ it gives 3′-*hydroxy*-3-*methyl*-2 : 2′-*diquinoxalylmethane*, decomp. 355°. 3-*Methyl*-2-*quinoxalylacetonitrile*, m.p. 131—133°, is converted into 3-*methyl*-2-*quinoxalylglyoxylonitrile* p-*dimethylaminoanil*, m.p. 183—184°, p-*tolylhydrazone*, m.p. 223—224°, and p-*anisylhydrazone*, m.p. 204°. α-3-*Methyl*-2-*quinoxalylcinnamonitrile*, m.p. 138°, and α-3-*methyl*-2-p-*methoxyquinoxalylcinnamonitrile*, m.p. 143°, are described. H. W.

Dehydrogenation of pyridium and of neotropine : 8-substituted 6-amino-2 : 3-pyridino-7 : 8 : 9-triazoles. G. Charrier and M. Jorio (Gazzetta, 1938, **68**, 640—651).—"Pyridium" (3-benzeneazo-2 : 6-diaminopyridine hydrochloride) in EtOH with aq. $CuSO_4$ and NH_3 is dehydrogenated to


(I.)

6-*amino*-8-*phenyl*-2 : 3-*pyridino*-7 : 8 : 9-*triazole* (I) [6′-*amino*-2-*phenylpyrido*-2′ : 3′-4 : 5-*triazole*] (cf. A., 1935, 226), m.p. 215° [*hydrochloride*; *platinichloride*; *Ac* derivative, m.p. 241—242°; $(SO_3H)_2$ derivative; $CH_2{\cdot}CO_2H$ derivative, m.p. 242—243°]. With 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$, (I) gives the 6-(2′ : 3′-*dinitroanilino*)-derivative, m.p. 265—270°; and with CH_2O and $NaHSO_3$ forms a *product*, m.p. 275—280°. "Neotropine" (2 : 6-diamino-2′-*n*-butoxy-3 : 3′-azopyridine) in EtOH with aq. $CuSO_4$ and NH_3 yields 6-*amino*-8-(2′-n-*butoxy*-5′-*pyridyl*)-2 : 3-*pyridino*-7 : 8 : 9-*triazole*, m.p. 212°. E. W. W.

Tetrabenztriazaporphins.—See B., 1939, 18.

Constitution of some naturally occurring, sensitising dyes. A. Treibs (Strahlenther., 1938, **61**, 658—663).—A discussion of the constitution of porphyrins. H. W.

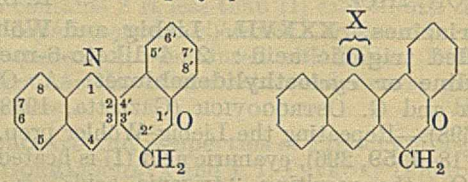
Preparation of adenosine.—See A., 1939, III, 197.

***iso*Oxazole series. VI. Amino-derivatives of aliphatic type.** A. QUILICO and L. PANIZZI (Gazzetta, 1938, **68**, 625—640).—3-*Methyl*isooxazole-5-*carboxyl chloride*, m.p. 39°, b.p. 89°/20 mm. (from the Na salt of the acid), yields, via the amide, 5-*cyano*-3-*methyl*-isooxazole (I), b.p. 174°, and, via the anilide, the -5-*anilide iminochloride* (II), m.p. 70—71°. 5-Methyl-*iso*oxazole-3-carboxyl chloride similarly gives 3-*cyano*-5-*methyl*isooxazole (III), m.p. 182—184°, and the -3-*anilide iminochloride* (IV), m.p. 70—73°. Anhyd. $SnCl_2$–HCl in Et_2O, followed by 15—20% aq. NaOH, reduces (II) to (3-*methyl*-5-isooxazolylmethyl)-*aniline*, m.p. 51—52° [*Bz* derivative, m.p. 86—87°; *NO* derivative, m.p. 74—75° (decomp.)]; similarly (IV) gives (5-*methyl*-3-isooxazolylmethyl)*aniline* [*Bz* derivative, m.p. 110°; *NO*-derivative, m.p. 67—68° (decomp.)]. In the same way, (I) and (III) are reduced to (3-*methyl*-5-isooxazolylmethyl)*amine*, b.p. 84—85°/5—8 mm. (*hydrochloride*, decomp. 221—222°; *platinichloride*, decomp. 211—216°; *picrate*, decomp. 179—181°; *Bz* derivative, m.p. 108°), and (5-*methyl*-3-isooxazolylmethyl)*amine*, b.p. 83°/5—8 mm. (*hydrochloride*, decomp. 202—203°; *platinichloride*, decomp. 203°; *picrate*, decomp. 179—181°; *Bz* derivative, m.p. 108·5—109·5°). 3-Phenyl-5-methyl-*iso*oxazole-4-carboxylamide (A., 1938, II, 462) heated with P_2O_5 gives the corresponding -4-*cyano*-compound, m.p. 83·5—84·5°. E. W. W.

***iso*Oxazole series. I.** A. QUILICO and R. FUSCO. **II. Halogen derivatives.** A. QUILICO and R. JUSTONI (R. Ist. lombardo Sci. Lett., Rend., 1936, [ii], **69**, 439—457, 587—601; Chem. Zentr., 1937, i, 1424—1425).—I. *iso*Oxazoles are synthesised from, *e.g.*, CPhCl:N·OH (I) and COR·CH_2X (X = COR, CHO, CO_2Et, CN, etc.); other methods are reviewed. Thus (I) and CN·CH_2·CO_2Et in cold EtOH–NaOEt give *Et* 5-*amino*-3-*phenyl*isooxazole-4-*carboxylate*, m.p. 124°, hydrolysed by aq. $Ba(OH)_2$ to the free *acid* (II), decomp. 181° [*Ag* salt; *amide*, m.p. 170—171°, from (I) and CN·CH_2·CO·NH_2], and by dil. KOH to 5-*amino*-3-*phenyl*isooxazole, m.p. 110—111° (*CHPh:*, m.p. 135—136°, *anisylidene*, m.p. 148°, and *cinnamylidene*, m.p. 161°, derivatives). *Azo*-dyes are obtained from (II) and PhN_2Cl or *p*-C_6H_4Cl·N_2Cl, and (II) is degraded by dil. HCl at 130° to COPhMe, NH_2OH, NH_3, and CO_2. 4-*Cyano*-3 : 5-*diphenyl*isooxazole, m.p. 130—131°, similarly obtained from (I) and COPh·CH_2·CN or from $CHBz_2$·CN and NH_2OH, is stable towards heat, alkalis, dil. acids, oxidising agents, and NHPh·NH_2; short treatment with conc. H_2SO_4 at 150° gives small amounts of (probably) 3 : 5-*diphenyl*isooxazole-4-*carboxylamide*, m.p. 210° (two modifications; cf. Betti *et al.*, A., 1922, i, 52).

II. 3 : 5-Dimethyl- and 3- and 5-methyl- (III) -*iso*oxazoles with Cl_2 and Br form additive compounds, which when heated or exposed to sunlight lose HHal to give the 4-halogeno-derivatives [those of (III) are converted by EtOH–NaOEt into COMe·CHHal·CN]. The following are described: 4-*chloro*- (IV), b.p. 135—135·5°, and 4-*bromo*- (V), b.p. 147—148°, -5-*methyl*-, 4-*bromo*-3-*methyl*-, b.p. 142·5—144·5°, and 4-*chloro*-, b.p. 150—150·5°, and 4-*bromo*-, b.p. 169°, -3 : 5-*dimethyl*-isooxazole. COMe·CHCl·CN [*Na* salt from (IV) and EtOH–NaOEt] with NHPh·NH_2 and *p*-NO_2·C_6H_4·NH·NH_2 in H_2O gives β-*benzeneazo*-, m.p. 81°, and β-p-*nitrobenzeneazo*- (VI), m.p. 90°, -*crotononitrile*, respectively; the former is also obtained from COMe·CHBr·CN [from (V)]. Boiling conc. HCl converts (VI) into (probably) β-2-*chloro*-4-*nitrophenylhydrazinocrotononitrile*, m.p. 149—150°. H. B.

Chromenoquinolines and chromenobenzopyrylium salts. P. PFEIFFER and G. VON BANK (J. pr. Chem., 1938, [ii], **151**, 312—318).—Chromanone (I) and *o*-NH_2·C_6H_4·CHO are condensed by



(II.) (III.)

2N-NaOH in cold MeOH to *chromenoquinoline* (II), m.p. 121·5°, which dissolves in conc. H_2SO_4 to a yellow solution with green fluorescence. It gives a well-cryst. *perchlorate*, m.p. 280—281° after darkening at about 260°, *H sulphate* without definite m.p., and *chloride*, m.p. 237° (decomp.). It is oxidised by H_2O_2 and boiling 2N-HCl to a *compound*, $C_{16}H_{16}O_4N$, m.p. 259°. Analogously, 7-methoxychromanone affords 7′-*methoxychromenoquinoline*, m.p. 118—119°, which dissolves in conc. H_2SO_4 to a yellow solution with a green to blue fluorescence [*perchlorate*, softens and commences to decompose at 270°; *nitrate*, m.p. 173° (decomp.); *chloride*, m.p. 232° (decomp.)]. 7-Hydroxychromanone gives 7′-*hydroxychromenoquinoline*, m.p. 160° (slight decomp.) after softening at 145° [*perchlorate*, m.p. 295° (decomp.) after softening and darkening at 290°]. *o*-OH·C_6H_4·CHO and (I) in MeOH are transformed by HCl at 0° followed by $HClO_4$ into *chromenobenzopyrylium perchlorate* (cf. III) (corresponding *platinichloride*, decomp. about 220°). 7′-*Methoxychromonobenzopyrylium perchlorate*, m.p. 232° (decomp.) after softening at 210°, and *platinichloride*, blackens at 220°, are described. H. W.

Dialkylthiazolidinediones. W. J. DORAN and H. A. SHONLE (J. Org. Chem., 1938, **3**, 193—197).—$CS(NH_2)_2$ with CRR′Br·COCl or with CRR′Br·CO_2H and NaOH in EtOH gives 2-*imino*-4-*keto*-5 : 5-diethyl-, new m.p. 237—238°, -5-*ethyl*-5-n-*propyl*-, m.p. 220—222°, -5-*ethyl*-5-iso*butyl*-, m.p. 225—227°, -5-*ethyl*-5-sec.-*butyl*-, m.p. 215—216°, and -5-*ethyl*-5-α-*methyl*-n-*butyl*-*thiazolidine*, m.p. 229—231°, hydrolysed by dil. HCl to the corresponding 2 : 4-*diketo*-5 : 5-*dialkylthiazolidines*, m.p. 78—78·5°, an oil, m.p. 70—72°, and 105—107°, respectively, which have short sedative and anæsthetic action, but cause tremors or convulsions. α-*Bromo*-γ-*methyl*-α-*ethyl*-n-*valeric*, b.p. 121—125°/2·5 mm., and α-*bromo*-β-*methyl*-α-*ethyl*-n-*hexoic acid*, b.p. 120—125°/1 mm., are prepared. R. S. C.

Indigoid vat dyes of the isatin series. III. 3-Indole-2′-(4′-methyl)thionaphtheneindigos. S. K. GUHA (J. Indian Chem. Soc., 1938, **15**, 501—508; cf. A., 1937, II, 393).—3-Hydroxy-4-methylthionaphthen and isatin in AcOH–HCl afford 3-

indole-2′-(4′-methyl)thionaphthenindigo [3-*keto*-2-*oxindolidene*-4-*methyldihydrothionaphthen*] (I). The respective substituted isatins give similarly the 5-*chloro*-, 5-*bromo*-, 5 : 7-*dibromo*-, 5-*bromo*-7-*nitro*-, and 5 : 7-*dinitroindole* derivatives of (I). 3-Hydroxythionaphthen and 5 : 7-dinitroisatin give 3-(5 : 7-*dinitro*)*indole*-2′-*thionaphthenindigo*. The dyeings on cotton and wool, and absorption spectra, are compared with those of the isomeric 5′- and 6′-Me compounds; change in shade is produced in the same way as observed in other series (cf. A., 1938, II, 243, 455). A. T. P.

Ox- and thi-azole derivatives [polarising substances].—See B., 1939, 106.

Thiazole derivatives.—See B., 1939, 106.

Heterocyclically substituted pyruvic esters. IV. Pyruvic esters from 1-methylbenzoxazole, 1-methylbenzthiazole, and 1-substituted 2-methylbenziminazoles. W. Borsche and W. Doeller (Annalen, 1937, **537**, 53—66).—1-Methylbenzoxazole (I), $Et_2C_2O_4$, and KOEt in EtOH–Et_2O afford *Et* 1-*benzoxazolylpyruvate* (II), $C_6H_4<^{N}_{O}>C\cdot CH_2\cdot CO\cdot CO_2Et$, m.p. 69° (*oxime*, m.p. 127—128°; 2 : 4-*dinitrophenylhydrazone*, m.p. 194°), which does not give a picrate or a methiodide. It is hydrolysed to 1-*benzoxazolylpyruvic acid*, decomp. 154° (*K* salt), converted by NH_2OH into the *compound*, $C_9H_8O_2N_2$, m.p. 199°, and oxidised by NaOH–H_2O_2 to 1-*benzoxazolylacetic acid*, decomp. 116°, which gives (I) when distilled. (II) and the requisite N_2-compound yield *Et* αβ-*diketo*-β-1-*benzoxazolylpropionate* β-*phenylhydrazone*, m.p. 131—132°, and β-p-*tolylhydrazone*, m.p. 165°. With PhCHO and *p*-$C_6H_4Me\cdot NH_2$ in boiling EtOH (II) affords 4 : 5-*diketo*-2-*phenyl*-1-p-*tolyl*-3-1′-*benzoxazolylpyrrolidine*, m.p. 288—290°; the corresponding 1-β-*naphthyl* derivative has m.p. 302—305°. When heated with *o*-$C_6H_4(NH_2)_2$ (II) affords 3-*hydroxy*-2-*quinoxalyl*-1′-*benzoxazolylmethane*, m.p. about 330°. (II) is converted by *o*-$NH_2\cdot C_6H_4\cdot CHO$ at 100° into *Et* 3-1′-*benzoxazolylquinoline*-2-*carboxylate*, m.p. 144—145°; the corresponding *acid*, decomp. 174°, is decarboxylated to 3-1′-*benzoxazolylquinoline*, m.p. 178—179° (*picrate*, m.p. 203°). 1-Methylbenzthiazole (III) and $Et_2C_2O_4$ give *Et* 1-*benzthiazolylpyruvate* (IV), m.p. 166° (*picrate*, m.p. 155—156°; 2 : 4-*dinitrophenylhydrazone*, m.p. 194—195°, and its *hydrochloride*; *oxime*, m.p. 147°). (IV) is hydrolysed to 1-*benzthiazolylpyruvic acid*, m.p. 173° (*K* salt), oxidised (H_2O_2 in alkaline solution) to the unstable 1-*benzthiazolylacetic acid*, characterised by decarboxylation to (III). With the appropriate N_2-compound (IV) yields *Et* αβ-*diketo*-β-1-*benzthiazolylpropionate* β-*phenylhydrazone*, m.p. 146—147° [hydrolysed to the corresponding *acid*, m.p. 243° (decomp.)], and p-*tolylhydrazone*, m.p. 143—144° [corresponding *acid*, m.p. 207° (decomp.)]. SeO_2 oxidises (III) to *benzthiazole*-1-*aldehyde*, m.p. 65° (*oxime*, m.p. 186—187°; *phenylhydrazone*, m.p. 204—205°). 4 : 5-*Diketo*-2-*phenyl*-1-p-*tolyl*-, decomp. 270—272°, and 4 : 5-*diketo*-2-*phenyl*-1-β-*naphthyl*-, decomp. 286—288°, -3-1′-*benzthiazolylpyrrolidine* are described. With *o*-$C_6H_4(NH_2)_2$ at 100° (IV) yields 3-*hydroxy*-2-*quinoxalyl*-1-*benzthiazolylmethane*, m.p. 318—320°. *Et* 3 : 1′-*benzthiazolylquinoline*-2-*carboxylate*, m.p. 158—159°, from (IV) and *o*-$NH_2\cdot C_6H_4\cdot CHO$ at 100°, is hydrolysed and decarboxylated to 3 : 1′-*benzthiazolylquinoline*, m.p. 198—199° (*picrate*, m.p. 223—224°; *methiodide*, decomp. 152—155°). The *oxime*, decomp. about 200°, of 1-benzthiazolylpyruvic acid is transformed by warm Ac_2O into 1-*benzthiazolylacetonitrile* (V), m.p. 98—100°, and converted by boiling Ac_2O into α-*cyano*-α-1-*benzthiazolylacetone*, m.p. 229°. *p*-$NO\cdot C_6H_4\cdot NMe_2$ and (V) in MeOH afford 1-*benzthiazolylglyoxylonitrile* p-*dimethylaminoanil*, m.p. 251—254°. With the appropriate N_2-compound in AcOH (V) yields 1-*benzthiazolylglyoxylonitrile* p-*tolylhydrazone*, m.p. 193—195°, and p-*anisylhydrazone*, m.p. 169—170°. With aromatic aldehydes or isatin in EtOH containing piperidine (V) gives α-1-*benzthiazolylcinnamonitrile*, m.p. 121—122°, p-*methoxy*-α-1-*benzthiazolylcinnamonitrile*, m.p. 145°, αβ-*di*-1-*benzthiazolylacrylonitrile*, m.p. 211—213° and 2-*keto*-3-*cyano*-1′-*benzthiazolylmethene*-2 : 3-*dihydroindole*, m.p. about 240°. Attempts to esterify (V) with boiling HCl–MeOH led to (III). 1 : 2-Dimethylbenziminazole and $Et_2C_2O_4$ slowly give *Et* 1-*methyl*-2-*benziminazolylpyruvate*, m.p. 154—156° (*K* compound), in very modest yield. With some uncertainty 1-phenyl-2-methylbenziminazole (VI) and $Et_2C_2O_4$ afford Et 1-*phenyl*-2-*methylbenziminazolylpyruvate*, m.p. 151—152° (*picrate*, decomp. 185—186°), which gives a green colour with $FeCl_3$. *o*-$C_6H_4(CO)_2O$ and (VI) at 200° yield 1-*phenyl*-2-*phthalidenemethenylbenziminazole*, $C_6H_4<^{N}_{NPh}>C\cdot CH{:}C<^{C_6H_4}_{O}>CO$, m.p. 280—281°. H. W.

New heterocyclic syntheses. IV. [Five-membered rings containing 2 N and S or Se.] R. Fusco and C. Musante (Gazzetta, 1938, **68**, 665—681; cf. A., 1938, II, 340).—NHPh·N:CPhCl (I), 2 : 4 : 1-$C_6H_3Br_2\cdot NH\cdot N{:}CPhBr$ (II), and *p*-$NO_2\cdot C_6H_4\cdot NH\cdot N{:}CBr\cdot CO_2Et$ (III) heated with NaS·CS·OEt (IV) in EtOH give respectively 2-*thion*-3 : 5-*diphenyl*-, m.p. 151—152°, -5-*phenyl*-3-(2′ : 4′-*dibromophenyl*)-, m.p. 129°, and -5-*carbethoxy*-3-(p-*nitrophenyl*)-1 : 3 : 4-*thiodiazoline*, m.p. 151°. With KS·CO_2Et (V), (I), (II), and (III) give respectively 2-keto-3 : 5-diphenyl-, 2-keto-5-phenyl-3-(2′ : 4′-dibromophenyl)- (cf. *loc. cit.*), and 2-*keto*-5-*carbethoxy*-3-(p-*nitrophenyl*)-1 : 3 : 4-*thiodiazoline* (VI), m.p. 91°. With KCNSe, (I), (II), and (III) give respectively 2-*imino*-3 : 5-*diphenyl*-, m.p. 111—113° [*hydrochloride*, m.p. 250° (decomp.)], -5-*phenyl*-3-(2′ : 4′-*dibromophenyl*)-, m.p. 70° (*hydrobromide*, m.p. 265°), and -5-*carbethoxy*-3-(p-*nitrophenyl*)-1 : 3 : 4-*selenodiazoline*, m.p. 178—179° [*hydrochloride*, m.p. 216° (decomp.)]. The *NO*-derivative, m.p. 124° (decomp.), of the last, when heated in xylene, gives 2-*keto*-5-*carbethoxy*-3-(4′-*nitrophenyl*)-1 : 3 : 4-*selenodiazoline*, m.p. 97—98°, which with dil. H_2SO_4 liberates Se. With KCNS, (III) gives 2-*imino*-5-*carbethoxy*-3-p-*nitrophenyl*-1 : 3 : 4-*thiodiazoline*, m.p. 175° [*hydrochloride*, m.p. 213° (decomp.)], of which the *NO*-derivative, m.p. 110° (decomp.), in boiling xylene gives 3-*carbethoxy*-1-p-*nitrophenyl*-1 : 2 : 4-*triazol*-5-*one*, m.p. 235°, hydrolysed (boiling aq. KOH) to the 5-*carboxy*-compound, m.p. 300° (decomp.) (softening at 260°). With CPhCl:N·OH, (IV) and (V) give only PhNCS,

whilst KCNSe gives a product, m.p. 188°, and NPh:C(SH)NH_2 gives PhNCS and PhNCO.

E. W. W.

Transformations of quinidine and quinine. E. Léger (J. Pharm. Chim., 1939, [viii], **29**, 12—32).—A review.

Salts of alkaloids. U. P. Basu and (in part) M. Roy (J. Indian Chem. Soc., 1938, **15**, 513—515).—Attempts are made to obtain less toxic salts of alkaloids for therapeutic use. *Emetine* d-*camphor*-β-*sulphonate*, m.p. 203—204°, is less toxic than the hydrochloride. *Ephedrine camphorsulphonate* has m.p. 173—174°. Quinine affords a *camphorsulphonate*, m.p. 218—219°, mandelate, m.p. 189—190°, 2-*hydroxy*-3-*naphthoate*, m.p. 149—150°, and 1 : 1′-*methylene*-2 : 2′-*dinaphthyl*-3 : 3′-*dicarboxylate*, m.p. 199—200°.

A. T. P.

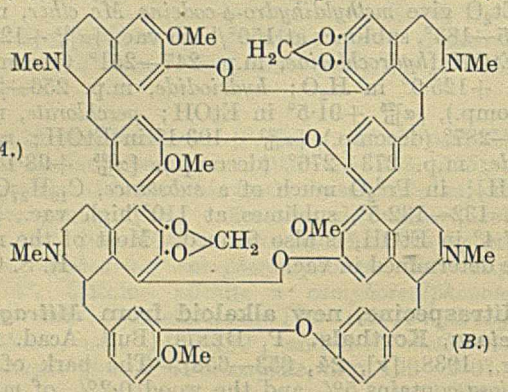
Addition of organomagnesium halides to ψ-codeine types. IV. Nuclear-substituted morphine derivatives. L. Small, S. G. Turnbull, and H. M. Fitch (J. Org. Chem., 1938, **3**, 204—232; cf. A., 1936, 1277).—Compounds of ψ-codeine type, *e.g.*, enol esters of 6-CO-derivatives and dihydrothebaine, react with MgAlkHal with opening of the oxide ring and introduction of an alkyl group. Sometimes isomerides are formed; this isomerism may be due to stereoisomerism of CHAlk at $C_{(5)}$ or to substitution at $C_{(5)}$ and $C_{(7)}$, but it cannot be due to stereoisomerism of CHAlk at $C_{(7)}$, since, *e.g.*, methyldihydrocodeinone enol acetate (I) also reacts with MgRX, showing that the grouping O·CH·C(OAcyl):CAlk· is present and thus that Alk is at $C_{(7)}$. Reaction of dihydrocodeine enol acetate (prep. described), m.p. 152—153·5°, with MgMeI is improved. iso*Methyldihydrothebainone hydriodide*, m.p. 259—260° (decomp.), $[\alpha]_D^{21}$ −28° in H_2O, *methiodide*, $+H_2O$ and anhyd., m.p. 194—196° (decomp.), $[\alpha]_D^{21}$ −18·6° in H_2O, *hydrochloride*, $+1{\cdot}5H_2O$ and anhyd., sinters at 182°, m.p. 191—193° (decomp.), $[\alpha]_D^{21}$ −122·1° in H_2O, and *hydriodide*, $+H_2O$, sinters at 205°, m.p. 209—210° (decomp.), $[\alpha]_D^{21}$ −102·1° in H_2O, are described. *iso*Methyldihydrothebainone (II) with <2 mols. of Br gives its 1-*Br*-derivative, m.p. 237—239°, $[\alpha]_D^{21}$ −66·2° in abs. EtOH [reduced catalytically to (II)], as well as 1-bromo*iso*methyldihydrocodeinone, and with 2·5 mols. of Br, followed by alkali and hydrogenation, gives (?) 7-*keto*iso*methyldihydrothebainone*, m.p. 172°, $[\alpha]_D^{21}$ −67·3° in EtOH, or, after sublimation, m.p. 258—259°, $[\alpha]_D^{21}$ −97·4° in EtOH. *iso*Methyldihydrocodeinone is hydrogenated (PtO_2) in EtOH to iso*methyldihydrocodeine*, $+0{\cdot}25H_2O$, m.p. 103—104°, $[\alpha]_D^{21}$ −126·9° in EtOH [*salicylate*, m.p. 235—237° (decomp.), $[\alpha]_D^{21}$ −87·3° in EtOH; *methiodide*, m.p. 252—254° (decomp.), $[\alpha]_D^{21}$ −56·8° in H_2O]. Dihydrothebaine and MgEtI (freed from EtI by NMe_3) in C_6H_6 give *ethyl*- (III), m.p. 190·5—191·5°, $[\alpha]_D^{25}$ +10·9° in EtOH [*hydrochloride*, m.p. 280—282° (decomp.), $[\alpha]_D^{21}$ +17·8° in H_2O; *hydriodide*, m.p. 253—255° (decomp.), $[\alpha]_D^{23}$ +14·0° in H_2O], and iso*ethyl-dihydrothebainone*, m.p. 188—189°, $[\alpha]_D^{22}$ −36·2° in EtOH, cryptophenolic (*hydriodide*, $+H_2O$, m.p. 191—193°, $[\alpha]_D^{23}$ −4·1° in H_2O; *methiodide*, $+0{\cdot}5H_2O$, sinters at 218°, m.p. 237—240°, $[\alpha]_D^{23}$ −5·8° in H_2O). With Br–AcOH, followed by treatment with NaOH, (III) gives 1-*bromoethyldihydrothebainone*, m.p. 201·5—202·5°, $[\alpha]_D^{23}$ −6·8° in EtOH [reduced catalytically to (III)], and oily 1-bromoethyldihydrocodeinone, which is hydrogenated to *ethyldihydrocodeinone* (IV), m.p. 163—164°, $[\alpha]_D^{23}$ −100·9° in EtOH [*methiodide*, $+0{\cdot}5H_2O$, m.p. 255—257° (decomp.), $[\alpha]_D^{21}$ −48·8° in H_2O; enol *acetate*, m.p. 129—130°, $[\alpha]_D^{25}$ −124·1°], and thence to *ethyldihydrocodeine*, an oil, $[\alpha]_D^{22}$ −84·8° in EtOH (*perchlorate*, m.p. 275—276°, $[\alpha]_D^{22}$ −60·5° in abs. EtOH; *hydriodide*, m.p. 274—275°, $[\alpha]_D^{22}$ −50·6° in H_2O). Hydrolysis of (IV) by 48% HBr gives *ethyldihydromorphinone*, m.p. 213—214°, $[\alpha]_D^{25}$ −103·5° in abs. EtOH [*hydriodide*, m.p. 285—286° (decomp.), $[\alpha]_D^{22}$ −49·1° in H_2O; *methiodide*, $+0{\cdot}5H_2O$ and anhyd., m.p. 263—265° (decomp.), $[\alpha]_D^{22}$ −42·2° in H_2O]. Dihydrothebaine and MgRBr in C_6H_6 give iso*propyldihydrothebainone* (V), m.p. 217·5—219·5°, $[\alpha]_D^{23}$ −31° in $CHCl_3$ [*hydrochloride*, m.p. 273—275°, $[\alpha]_D^{25}$ −18·3° in H_2O; *hydrobromide*, m.p. 277—277·5°, $[\alpha]_D^{24}$ −12·6° in H_2O; *salicylate*, m.p. 165—185°, $[\alpha]_D^{25}$ −8·9° in $COMe_2$; *perchlorate*, m.p. 236—238°, $[\alpha]_D^{25}$ −16·0° in $COMe_2$; *fumarate*; *succinate*; *hydriodide*; *picrate*; *oxime*, $+2H_2O$, double m.p. 130—137° (partly) and 199—201°, $[\alpha]_D^{25}$ +13·5° in EtOAc (*hydrochloride*, m.p. 213—215°, decomp. 228°, $[\alpha]_D^{26}$ +43·8° in H_2O); 1 : 5-Br_2-derivative *hydrobromide*, $+2H_2O$ and anhyd., m.p. 230—232°, $[\alpha]_D^{24}$ −2·7° in EtOH], n-*amyldihydrothebainone* (VI), m.p. 153—155°, sublimes at 150°/high vac., $[\alpha]_D^{26}$ −12·8° in EtOH (*hydrochloride*, $+H_2O$, m.p. 203—205°, $[\alpha]_D^{24}$ +2·8° in EtOH; *hydrobromide*, m.p. 223—224·5°, $[\alpha]_D^{25}$ +1·5° in EtOH; *hydriodide*, m.p. 238—239°, $[\alpha]_D^{25}$ −1·4° in EtOH; *perchlorate*, $+0{\cdot}5H_2O$, m.p. 235—236°, $[\alpha]_D^{25}$ −2·13° in EtOH; *sulphate*, $+2{\cdot}5H_2O$, m.p. 95—105°, $[\alpha]_D^{24}$ 0 in EtOH; *oxime*, $+1{\cdot}5H_2O$, m.p. 113—115°, $[\alpha]_D^{25}$ +18·6° in EtOH), *benzyldihydrothebainone* (VII), m.p. 227—229°, $[\alpha]_D^{25}$ −51·6° in $CHCl_3$ [*hydrochloride*, m.p. 243—244° (decomp.), $[\alpha]_D^{25}$ −29° in H_2O; *oxime*, m.p. 135—142°, $[\alpha]_D^{25}$ +5·5° in $CHCl_3$], *phenyldihydrothebainone* (VIII), m.p. 230—232°, $[\alpha]_D^{24}$ −165·9° in $CHCl_3$ [*perchlorate*, m.p. 201° (decomp.), $[\alpha]_D^{25}$ −97·6° in $COMe_2$; *methiodide*, m.p. 245—248° (decomp.), $[\alpha]_D^{25}$ −96·5° in EtOH; *oxime*, m.p. 198—200°, $[\alpha]_D^{24}$ −106·7° in EtOH], and iso*phenyldihydrothebainone* (IX), m.p. 213—215°, $[\alpha]_D^{24}$ +34·8° in $CHCl_3$ (*methiodide*, m.p. 214—215°, $[\alpha]_D^{24}$ 0 in EtOH; *oxime*, m.p. 230—232°, $[\alpha]_D^{24}$ −157° in EtOH). With Br, followed by 10N-NaOH, (V) gives 1-*bromo*iso*propyldihydrocodeinone*, m.p. 164—167°, $[\alpha]_D^{24}$ −79·4° in $COMe_2$, hydrogenated (colloidal Pd) in AcOH–KOAc to iso*propylcodeinone*, m.p. 175—177°, sublimes at 155°/high vac., $[\alpha]_D^{26}$ −110·5° in EtOH [*hydrobromide*, m.p. 202—203°, $[\alpha]_D^{25}$ −58·3° in H_2O; *hydriodide*, $+H_2O$, m.p. 196—198°, $[\alpha]_D^{25}$ −67·2° in EtOH; *methiodide*, m.p. 274—275° (decomp.), $[\alpha]_D^{25}$ −66·0° in $COMe_2$; *oxime*, m.p. 224—226°, $[\alpha]_D^{23}$ −25·0° in EtOH]; this is not reduced catalytically, by $Na_2S_2O_4$, or $SnCl_2$, but with Zn–Hg–HCl gives (V), and with 48% HBr gives iso*propyldihydromorphinone*, m.p. 236—238°, sublimes at 180°/high vac., $[\alpha]_D^{26}$ −107·5° in EtOH [*hydrochloride*, $+H_2O$, m.p. 340—341° (decomp.), $[\alpha]_D^{25}$ −64·2° in H_2O; *hydrobromide*, m.p. 215—220°, $[\alpha]_D^{23}$ −56·4° in H_2O; *hydriodide*, $+H_2O$, m.p. 199—201°, $[\alpha]_D^{25}$ −61·5° in $COMe_2$; *perchlorate*, $+$(?)$1{\cdot}25H_2O$, m.p. 168—170°, $[\alpha]_D^{25}$ −69·9° in EtOH],

unaffected by H_2–Pd or –PtO_2, reduced by Zn–Hg–HCl to a (?) bimol. *product*, decomp. 277—280°, $[\alpha]_D^{25}$ —117·6° in EtOH. With Br, followed by 10N-NaOH, (VI) gives 1-*bromoamyldihydro-thebainone*, m.p. 241—242°, $[\alpha]_D^{25}$ —30·6° in EtOH, and -*codeinone*, m.p. 143—145°, $[\alpha]_D^{24}$ —76·7° in EtOH [*oxime*, +0·25H_2O, double m.p. 121—123° (partly) and 170—174°, $[\alpha]_D^{24}$ —29·7° in EtOH], and thence *amyldihydrocodeinone*, m.p. 153—155°, $[\alpha]_D^{26}$ —9·3° in EtOH [*picrate*, m.p. 174—177° (sinters at 130°), $[\alpha]_D^{24}$ —52·8° in $COMe_2$; *styphnate*, +0·75H_2O, m.p. 142—145° (decomp.), $[\alpha]_D^{25}$ —45·4° in $COMe_2$; *salicylate*], and *amyldihydromorphinone*, +0·5H_2O, m.p. 113—116° (decomp.), $[\alpha]_D^{25}$ —97·3° in EtOH [*hydrochloride*, m.p. 322—325° (decomp.), $[\alpha]_D^{25}$ —63·9° in H_2O; *hydrobromide*, +H_2O, m.p. 189—190°, $[\alpha]_D^{25}$ —66·0° in EtOH; *hydriodide*, +H_2O, m.p. 182—184°, $[\alpha]_D^{25}$ —59·8° in EtOH], not hydrogenated catalytically and giving amorphous products by Clemmensen's method. Similarly (VII) gives 1-*bromo*-x-*benzyldihydro-thebainone*, m.p. 230—232°, $[\alpha]_D^{23}$ —59·4° in EtOH, and -*codeinone*, m.p. 167—168°, $[\alpha]_D^{23}$ —101·4° in EtOH (*salicylate*; *fumarate*; *perchlorate*; *sulphate*), *benzyldihydro-codeinone* (X), an oil, b.p. 160°/high vac., $[\alpha]_D^{25}$ —114·3° in $CHCl_3$, and -*morphinone* (*hydrochloride*, +H_2O, m.p. 241—242°, $[\alpha]_D^{24}$ —100·6° in H_2O), and an *isomeride* of (X), m.p. 166—167·5°, $[\alpha]_D^{24}$ —439° in $CHCl_3$. When similarly treated, (VIII) gives oily Br-compounds and thence *phenyldihydro-codeinone*, m.p. 149—151°, $[\alpha]_D^{24}$ —166·2° in EtOH, and -*morphinone*, m.p. 278—280° (decomp.), $[\alpha]_D^{24}$ —164·5° in $COMe_2$ [*hydrochloride*, m.p. 334—337° (decomp.), $[\alpha]_D^{24}$ —126·9° in H_2O; *hydrobromide*, +1·25H_2O, m.p. 281—284°, $[\alpha]_D^{25}$ —97·4° in $COMe_2$; *hydriodide*, +H_2O, m.p. 273—276°, $[\alpha]_D^{25}$ —95·1° in $COMe_2$]. With MeI–NaOMe–MeOH (IX) gives *iso*phenyldihydrothebainone *Me ether methiodide*, m.p. 264—265°, $[\alpha]_D^{24}$ +49·3° in EtOH, converted by AgCl into the unstable *methochloride*, m.p. 239—243°, which at 200—205°/high vac. yields 6-*keto*-3 : 4-*dimethoxy*-5- or -7-*phenyl*-5 : 6 : 7 : 8-*tetrahydrophenanthrene*, m.p. 227—230°, $[\alpha]_D^{22}$ —130° in C_6H_6. By way of oily intermediates (IX) gives oily *iso*phenyldihydrocodeinone, which is not demethylated by HBr, but gives instead a rearrangement *product*, $C_{24}H_{25}O_3N$, m.p. 189—190°, $[\alpha]_D^{24}$ —127·5° in EtOH. Prep. of (V) gives also by demethylation some *dihydromorphinone enol acetate*, m.p. 233—235°, $[\alpha]_D^{24}$ —206·5° in EtOH [*hydrochloride*, m.p. 309—310° (decomp.), $[\alpha]_D^{25}$ —180·6° in H_2O; *hydriodide*, m.p. 274—275° (decomp.), $[\alpha]_D^{25}$ —140·5° in H_2O; *benzoate*, m.p. 229—230°, $[\alpha]_D^{25}$ —150·7° in EtOH; *salicylate*, +0·25H_2O (retained at 130°), m.p. 268—270°, $[\alpha]_D^{25}$ —130·8° in $COMe_2$; *methiodide*, +H_2O, m.p. 259—261°, $[\alpha]_D^{25}$ —123·6° in $COMe_2$], hydrolysed by cold, conc. HCl to dihydromorphinone, methylated (CH_2N_2) to dihydrothebaine, and obtained in poor yield also from dihydrothebaine by NaOMe–MeOH at 125—140°. With MgMeI in C_6H_6 (I) or its *iso*-isomeride gives *dimethyldihydrothebainone* (XI), m.p. 199—202°, $[\alpha]_D^{26}$ +3·52° in EtOH (*hydrochloride*; *oxime*, m.p. about 70—90°), and a *compound* X (*fumarate*). With Br in AcOH (XI) gives a (?) perbromide and thence a Br-compound (not isolated), converted by NaOH into impure *bromodimethyldihydrothebainone*, m.p. 218—221°, cryptophenolic [reduced to (XI)]. *ψ*-Codeine Me ether (prep. from α-chlorocodide by MeOH, which also causes much rearrangement to β-chlorocodide) and MgMeI in Et_2O give *methyldihydro-ψ-codeine Me ether*, m.p. 182·5—183°, sublimes at 150°/high vac., $[\alpha]_D^{23}$ +121·0° in EtOH [*hydrochloride*, m.p. 247—251° (decomp.), $[\alpha]_D^{25}$ +125·9° in H_2O; *hydriodide*, m.p. 256—257° (decomp.), $[\alpha]_D^{25}$ +91·5° in EtOH; *perchlorate*, m.p. 285—287° (decomp.), $[\alpha]_D^{23}$ +103·1° in EtOH; *methiodide*, m.p. 273—276° (decomp.), $[\alpha]_D^{25}$ +98·1° in EtOH]; in Pr^{β}_2O much of a *substance*, $C_{19}H_{27}O_3N$, m.p. 132—132·5°, sublimes at 110°/high vac., $[\alpha]_D^{25}$ —57·4° in EtOH, is also formed. Most of the m.p. were determined in vac. R. S. C.

Mitraspecine, new alkaloid from *Mitragyna speciosa*, Korthals. P. Denis (Bull. Acad. roy. Belg., 1938, [v], **24**, 653—658).—The bark of *M. speciosa* contains 5%, and the wood 0·2%, of *mitraspecine*, $C_{25}H_{27}O_2N_2(OMe)_3$, m.p. 244—245°, $[\alpha]_D^{23}$ —59·15° in $CHCl_3$ (*picrate*, m.p. 136°). The extraction and pptn. and colour reactions are described. A. Li.

***Sinomenium* and *Cocculus* alkaloids. XLVIII. Constitution of cepharanthine.** H. Kondo and I. Keimatsu (Ber., 1938, **71**, [*B*], 2553—2560).—Purest cepharanthine (I) with C_6H_6 of crystallisation is $C_{37}H_{38}O_6N_2$,1·25C_6H_6, m.p. 103° (decomp.). The solvent-free alkaloid is a yellow, amorphous powder, m.p. 145—155°, $[\alpha]_D^{20}$ +277° in $CHCl_3$. It contains 2 OMe, CH_2O_2, and 2 NMe; OH, CO, and CO·O· are absent. The first stage of the Hofmann degradation of (I) gives mainly the optically inactive *cepharanthine-α-methine* (I), $C_{39}H_{42}O_6N_2$,3H_2O, m.p. 98—100°, with some optically active *cepharanthine-β-methine*, $C_{39}H_{42}O_6N_2H_2O$, m.p. 183—184°, $[\alpha]_D^{27}$ +58° in $CHCl_3$. (I) gives a *methiodide*, m.p. 305—306° (decomp.), which in the second stage of the degradation affords NMe_3 and *de*-N-*cepharanthine*, $C_{35}H_{30}O_7$,0·5MeOH, m.p. about 210° (decomp.). Oxidation of (I) with $KMnO_4$ gives 6-methoxy-3 : 4′-dicarboxydiphenyl ether, m.p. 305°. Ozonisation of (I) in 25% AcOH at 0° and reduction of the product in presence of Pt-black yields 6-methoxy-3 : 4′-dialdehydodiphenyl ether, m.p. 77—78°, and 2-methoxy-2′ : 3′-methylenedioxy-5 : 6-dialdehydo-4 : 5-di-β-dimethylaminoethyldiphenyl ether, the *methiodide*, m.p. 217—220° (decomp.), of which is degraded (Hofmann) to 2-*methoxy*-2′ : 3′-*methylenedioxy*-5 : 6-*dialdehydo*-4 : 5′-*divinyldiphenyl ether* (II), m.p. 166—168° [*dioxime*, m.p. 181—182° (decomp.)]. The same products are obtained from the methohydroxide of (I). Hydrogenation (Pt-black in EtOH–$COMe_2$) leads to 2-*methoxy*-2′ : 3′-*methylenedioxy*-5 : 6′-*dialdehydo*-4 : 5′-*diethyldiphenyl ether*, m.p. 160—161° (*disemicarbazone*, m.p. 218°). This is reduced (Clemmensen) to 2-*methoxy*-2′ : 3′-*methylenedioxy*-5 : 6′-*dimethyl*-4 : 5′-*diethyldiphenyl ether* (III), m.p. 88—89°. 5-Hydroxy-4-methoxy-2-ethyltoluene (IV), b.p. 111—112°/7 mm., m.p. 57·5°, is converted into 6-*bromo*-5-*hydroxy*-4-*methoxy*-2-*ethyltoluene*, b.p. 165—170°/11 mm., m.p. 48·5—49°. This is transformed into its *acetate*, m.p. 67—68°, which with Ac_2O–HBr (*d* 1·78) at 115—120° gives 6-*bromo*-4 : 5-*diacetoxy*-2-*ethyltoluene*, m.p. 150—151° after softening at 120°, whence (CH_2SO_4 and NaOH in $COMe_2$–H_2O)

6-*bromo*-4 : 5-*methylenedioxy*-2-*ethyltoluene*, m.p. 55—58° (V). When heated with Cu powder and $Cu(OAc)_2$



at 165—200°, (IV) and (V) give (III). (I) is therefore *A* or *B*. H. W.

Organo-arsenic compounds. VIII. Synthesis of arsindole derivatives from phenylacetylene. IX. Synthesis of succinylphenylarsine. H. N. Das-Gupta (J. Indian Chem. Soc., 1938, **15**, 495—497; 498—500).—VIII. CPh:CH and $AsPhCl_2$ at 140—150° for 7 hr. (probably through the adduct, CPhCl·CH·AsPhCl) afford 3-*chloro*-1-*phenylarsindole*, b.p. 165—175°/10 mm. (*picrate*, m.p. 115—116°; *mercurichloride*, m.p. 232—233°; *methiodide*, m.p. 152—153°; *ethiodide*, m.p. 161°), oxidised (H_2O_2) to *o*-carboxydiphenylarsinic acid, m.p. 166°.

IX. $(\cdot CH_2 \cdot COCl)_2$ and $AsPhCl_2$–Na–C_6H_6–EtOAc afford *succinylphenylarsine*, b.p. 119—120°/10 mm. (*picrate*, m.p. 117°; *mercurichloride*, m.p. 245°; *methiodide*, m.p. 176°; *ethiodide*, m.p. 165—167°), reduced by Na–PhMe–EtOH to phenyl*cyclo*tetramethylenearsine, b.p. 125—130°/15 mm. A. T. P.

Hydrolysis of some arsphenamines. S. Orlić (Arh. Hemiju, 1938, **12**, 153—172).—Max. hydrolysis of *p*-arsanilic acid takes place in 0·08N-NaOH, at 160°, and of *o*-arsanilic acid in 0·4N-NaOH, at 130—160°; *m*-arsanilic acid is resistant to hydrolysis at p_H 2—10 (90 min. at 200°). 4 : 4′-Diaminodiphenylarsinic acid is hydrolysed at 100° and 130° in acid solution (max. hydrolysis in 0·6N-HCl. Arsenobenzenes decompose as follows: $3AsR{:}AsR + 3H_2O \rightarrow 4As + As_2O_3 + 6RH$ (R = *p*-$C_6H_4 \cdot NH_2$, 4 : 3-$OH \cdot C_6H_3 \cdot NH_2$); $3AsR_2 \cdot AsR_2 + 6H_2O \rightarrow 2As + 2As_2O_3 + 12RH$ (R = *p*-$C_6H_4 \cdot NH_2$). These compounds are more resistant to hydrolysis in neutral and alkaline than in acid media, at 140—180°. R. T.

Decomposition of unsymmetrical organomercuric compounds. Method of establishing the relative degree of electronegativity of organic radicals. III. M. S. Kharasch, H. Pines, and (Miss) J. H. Levine (J. Org. Chem., 1938, **3**, 347—354; cf. A., 1932, 409).—Cleavage of HgPhEt by HCl–EtOH, HBr–EtOH, HBr–AcOH, HBr–C_6H_6, HI–AcOH, or HI–C_6H_6 gives in all cases only HgEtHal. Cleavage of HgRR′ by HCl proves the following orders of relative electronegativity: *p*-C_6H_4F > Ph > *p*-C_6H_4Cl, *o*-, *m*-, or *p*-C_6H_4Br, *m*-C_6H_4F; Ph, *m*-C_6H_4Cl > *m*-$C_6H_4 \cdot CF_3$; CH_2Ph > *o*-, *m*-, or *p*-$C_6H_4Cl \cdot CH_2$; *o*- = *m*-$C_6H_4Cl \cdot CH_2$. The following are described: m-, m.p. 243°, and p-*fluoro*-, m.p. 291°, p-*chloro*-, m.p. 238°, and m-*trifluoromethyl-phenylmercuric chloride*, m.p. 151°; o-, m.p. 115°, and m-*chlorobenzylmercurichloride*, m.p. 141°; *di*-o-*chlorobenzylmercury*, m.p. 100°; *phenyl*-m-, m.p. 107—111°, and -p-*fluoro*-, m.p. 115—118°, -p-*chloro*-, m.p. 172—200°, -o-, m.p. 73—75°, -m-, an oil, and -p-*bromo*-, m.p. 151—175°, and -m-*trifluoromethylphenylmercury*, m.p. 100—103°; m-*chlorophenyl*-m-*trifluoromethylphenylmercury*, m.p. 130—143°; *benzyl*-o-, an oil, -m-, an oil, and -p-*chlorobenzylmercury*, m.p. 80—82°; o-*chlorobenzyl*-m-, an oil, and -p-*chlorobenzylmercury*, m.p. 98—129°. R. S. C.

Acetylation of proteins by keten. I. Method. Results with antidiphtheritic serum. G. Sandor and H. Goldie (Bull. Soc. Chim. biol., 1938, **20**, 1130—1146).—A convenient apparatus for the production of keten is described. Acetylation is effected at ~p_H in the presence of octyl alcohol, and the serum is buffered with NaOAc, aq. NaOH being added at intervals to avoid acidification. It is advisable to introduce the serum gradually to avoid the formation of a clot. OH groups are not affected until at least 90% of the NH_2-groups are acetylated. Characteristic modifications of the physico-chemical properties of the proteins occur. The flocculating power of antidiphtheritic serum towards the toxin disappears when 17—19% of the NH_2-groups are acetylated, the antitoxic power and original specificity when 70—80% are acetylated, and the anaphylactogenic power when ~20% are acetylated. P. G. M.

Ashing of organic matter with bromine + nitric acid. H. Waelsch and A. Dimter (Mikrochim. Acta, 1938, **3**, 201—203).—Org. material is repeatedly evaporated (~160°) to dryness in a quartz vessel with fuming HNO_3 saturated with Br. 0·5 c.c. of serum, or 0·5 g. of brain, or 0·1 g. of filter-paper can be ashed in 60—90 min., and the method is quicker than that using $HNO_3 + H_2O_2$. In determining K*, the last traces of NH_3 can be removed by treatment of the residue from the ashing with aq. NaOH + Br. L. S. T.

Determination of halogens in organic substances by the method of ter Meulen. W. Theilacker and E. Gessner (Angew. Chem., 1938, **51**, 892—893).—Minor modifications of the apparatus and method of ter Meulen (A., 1928, 724) are described. With substances which char readily, the low vals. obtained may be improved by mixing with $(HCO_2)_2Ni$. J. D. R.

Micro-determination of halogens in organic substances using filter beakers. E. Abrahamczik and F. Blümel (Mikrochim. Acta, 1938, **3**, 185—189).—The Pregl tube with its layer of asbestos is replaced by the Schwarz–Bergkamf beaker, which is more const. in wt. (~4 μg.) than the filter-tube. Also, the time required for a determination is shortened. L. S. T.

Catalyst for the determination of nitrogen by the Kjeldahl method.—See A., 1939, I, 96.

Preparation of hydriodic acid suitable for alkoxyl and Friedrich–Kjeldahl nitrogen determinations.—See A., 1939, I, 92.