BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

AUGUST, 1937.

Molecular asymmetry. H. HILLEMANN (Angew. Chem., 1937, **50**, 435—447).—A discussion of mol. asymmetry of allenes and spirans, steric asymmetry, racemisation, and the effect thereon of condensed ring systems, asymmetric synthesis and the Walden inversion, polyphenyl systems and combinations with heterocyclic rings, and open-chain compounds. H. W.

Mesomerism. I. How does the conception of mesomeric structure arise? II. Attempt to represent in a conventional way electronic linkings and unions between linkings. A. CORNILLOT (Bull. Soc. chim., 1937, [v], **4**, 1045—1052, 1053—1064).—I. A discussion of the mechanism of mesomeric change.

II. Theoretical. J. L. D.

Oxidation of organic compounds with atmospheric oxygen. A. RIECHE (Angew. Chem., 1937, **50**, 520—524).—Recent work on the oxidation of aldehydes, ketones, olefines, fatty acids, hydrocarbons, and ethers by atm. O_2 is summarised and the importance of the intermediate peroxide and per-acid formation is pointed out. The O frequently enters between C and H atoms, rather than attacking a double linking. J. W. S.

Combustion of paraffin hydrocarbons.—See A., I, 416.

Ethane pyrolysis in the presence of steam. D. S. CRYDER and D. J. PORTER (Ind. Eng. Chem., 1937, **29**, 667—673).—Various steam–C_2H_6 mixtures were passed through a SiO_2 tube at different temp. and, at each temp., data were obtained for the decomp. of the gaseous mixtures with the tube empty, with a SiO_2 gel catalyst, and with SiO_2 gel catalyst impregnated with Ni. Interaction of steam and C_2H_6 in the presence of Ni commenced at 430°, and practically complete decomp. of the C_2H_6 was obtained at 500°; the corresponding temp. in both the blank and SiO_2 gel runs were 600° and 800°, respectively. In the absence of Ni, C_2H_4 formation commenced at 500—600°, increased rapidly to a max. at 700°, and then gave place at higher temp. to CH_4 formation which reached a max. at 1000°. In the Ni runs, C_2H_4 was found only at 800° and then in small concn. which decreased with increasing steam concn. The production of H_2 increased with temp. and the steam : C_2H_6 ratio, in both the presence and absence of Ni. In the absence of Ni, CO_2 production, though small, increased steadily with temp. whereas in the Ni runs there was an indicated max. CO_2 production at 450° and then a steady decrease with temp. CO formation increased uniformly with temp. in all the experiments. These results indicate that CO is a primary and CO_2 a secondary product of the interaction of steam and C_2H_6. H. C. M.

Thermal decomposition of ethane, ethylene, acetaldehyde, etc.—See A., I, 366.

Thermal decomposition of propane–propylene–hydrogen equilibrium mixtures.—See A., I, 366.

Activation of specific linkings in complex molecules at catalytic surfaces. III. Carbon–hydrogen and carbon–carbon linkings in propane and ethylene.—See A., I, 418.

Synthesis of large molecules. H. MARK (Proc. Roy. Inst., 1937, **29**, 683—694).—A lecture.

Reaction between sulphur dioxide and olefines and acetylenes. VI. Ascaridole as a catalyst for the reaction. L. L. RYDEN, F. T. GLAVIS, and C. S. MARVEL (J. Amer. Chem. Soc., 1937, **59**, 1014—1015; cf. this vol., 226).—Ascaridole is a better catalyst than paraldehyde containing peroxides for the addition of SO_2 to acetylenes and Δ^{α}-ethylenes and causes addition to ethylenic CO_2H-, CN-, and CO_2Et-compounds, and to phenols. No known catalyst causes addition to tri- or tetra-substituted ethylenes or to acetylenes, CR:CR or $CHR_2{\cdot}C{:}CH$. Polymeric SO_2-additive *compounds* are reported from *o*-allyl-anisole, m.p. 150—106°, and -phenol, m.p. 120—160°, *p*-bromallylbenzene, m.p. 255°, allylacetic acid, m.p. 180—230°, allyl cyanide, m.p. 222°, undecenoic acid, m.p. 255—275°, Me undecenoate, *cyclo*hexylpropinene, m.p. 110—145°, and Δ^{α}-*pentadecinene* (I), m.p. 120—140°. $C_{12}H_{25}{\cdot}MgBr$ and $CH_2{:}CBr{\cdot}CH_2Br$ give *β-bromo-*Δ^{α}*-pentadecene*, b.p. 145—155°/3—4 mm., converted by $NaNH_2$ in liquid NH_3 into (I), b.p. 112—113° (Hg *derivative*, $C_{30}H_{56}Hg$, m.p. 93°). R. S. C.

(A) Hydro- and dehydro-polymerisation of ethylenic hydrocarbons. S. S. NAMETKIN, L. N. ABAKUMOVSKAJA, and M. G. RUDENKO. **(B) Transformations of unsaturated hydrocarbons under the influence of aluminium chloride.** S. S. NAMETKIN and M. G. RUDENKO (J. Gen. Chem. Russ., 1937, **7**, 759—762, 763—775).—(A) The reaction between H_2SO_4 and butenes is represented as $BuHSO_4 + C_4H_8 \rightarrow H_2SO_4 + C_8H_{16}$; $BuHSO_4 + C_8H_{16} \rightarrow C_3H_7{\cdot}HSO_4$ (I) $+ C_8H_{18}$; n(I) $\rightarrow n H_2SO_4 + (C_4H_6)_n$.

(B) Complex mixtures of polymerides, dehydro- and hydro-polymerides of amylene, octene, or *cyclo*hexene (II) are obtained by heating the hydrocarbons with $AlCl_3$ at 60—90°. In the case of (II) the pro-

ducts contain mono-, di-, and tri-*cyclo*hexyl*cyclo*hexane, a pentameride of (II), and *cyclo*hexyltetrahydrobenzene. It is concluded that the process of hydro-dehydro-polymerisation is of general application. R. T.

Equilibrium dehydrogenation of *n*-butylenes to butadiene.—See A., I, 411.

Thermal reactions of unsaturated hydrocarbons. II. Kinetics and mechanism of thermal reactions of Δ^{β}-butene. V. G. Moor, A. V. Frost, and L. V. Schilaeva. **III. Thermal transformation of propene.** V. G. Moor, N. V. Strigaleva, and A. V. Frost (J. Gen. Chem. Russ., 1937, **7**, 818—831, 860—868).—II. The products given by $(CHMe{:})_2$ at 575—600°/1 atm. are CH_4, C_3H_6, and C_8H_{14}; at 600—700° the yield of gaseous products (CH_4, H_2, C_2H_4, C_2H_6) and of $(CH_2{:}CH\cdot)_2$ rises. The reaction is not uni- or bi-mol. Possible intermediate reactions are discussed.

III. The reaction at 610—726°/1 atm. is represented as $3C_3H_6 \rightarrow CH_4 + C_2H_4 + C_6H_{10}$. The velocity of reaction cannot be represented by any simple equations. R. T.

Structure of the trimeride of *ψ*-butylene. S. M. Orlov (J. Gen. Chem. Russ., 1937, **7**, 923—927).—Ozonisation at −20° leads to production of a mixture of acids with 1, 2, 3, 4, 5, 7, and 9 C. It is concluded that the trimeride is a mixture of $(CHMeEt\cdot CMe{:})_2$ and $CHMe{:}CMe\cdot CHMe\cdot CHMe\cdot CHMeEt$. R. T.

Polymerisation of divinyl by sodium in presence of *iso*butylene. V. N. Lvov (J. Gen. Chem. Russ., 1937, **7**, 928—946).—A series of polymerides, $(C_4H_6)_{n-1},C_4H_8$, where n is the no. of C_4 groups and of double linkings in the mol., is obtained from $CMe_2{:}CH_2$ (I) and $(CH_2{:}CH\cdot)_2$ (II) in presence of Na at 25°. The yield of polymerides and their content of low b.p. fractions rise with the (II) content of the original mixture. The dimeride is shown by identification of the ozonation products to be β-methyl-$\Delta^{\alpha\epsilon}$-heptadiene. The η of C_6H_6 solutions of the higher polymerides varies with their mol. wt. in accordance with Staudinger's formula. The *isomerides* in which $n = 3$, b.p. 85—87°/19 mm., $n = 4$, b.p. 70—80°/0·15 mm., $n = 5$, b.p. 95—105°/0·15 mm., $n = 6$, b.p. 150—170°/0·15 mm., and $n = 14$ and 24 are described. R. T.

Polymerisation of C_nH_{2n-4} hydrocarbons with vicinal double and triple linkings. A. E. Favorski and A. I. Zacharova (J. Gen. Chem. Russ., 1937, **7**, 973—976).—$CH{:}C\cdot CMe{:}CHMe$ in MeOH at 120° (12 hr.) gives 1 : 2-*dimethyl*-4-*α*-*methyl*-Δ^{α}-*propenylbenzene*, b.p. 85—87°/10 mm., which yields 1 : 2 : 4-$C_6H_3(CO_2H)$, 1 : 2 : 4-$C_6H_3Me_2\cdot CO_2H$, and AcOH when oxidised ($KMnO_4$ in aq. KOH). R. T.

Configurative relationship of alkyl halides with α-halogeno-acids. P. A. Levene and A. Rothen [with M. Kuna] (J. Biol. Chem., 1937, **119**, 189—192).—(−)-γ-Chloro-Δ^{α}-heptene is reduced in MeOH–HCl (Adams; H_2 at 3 atm.) to (+)-γ-*chloroheptane*, b.p. 87—90°/113 mm., α_D^{25} +1·46°. This change of sign had already been observed when passing from (+)-γ-chloro-Δ^{α}-heptene to (−)-α-chloro-*n*-hexoic acid (A., 1929, 1272); the active acids of type $CHRCl\cdot CO_2H$ and the structurally related halides CHREtCl thus rotate in the same direction. This confirms previous formulations (Levene and Haller, A., 1929, *passim*). E. W. W.

Aliphatic chloro-derivatives. VI. Reactivity of polychlorides of the allyl type. D. V. Tischtschenko. **VII. Chlorination of *sec.*-butyl chloride. VIII. Chlorination of α-chlorobutane.** D. V. Tischtschenko and A. Tschurbakov. **IX. Inductive effect and order of substitution of hydrogen by chlorine atoms in saturated hydrocarbons and their chloro-derivatives.** D. V. Tischtschenko (J. Gen. Chem. Russ., 1937, **7**, 658—662, 663—666, 893—896, 897—900).—VI. The products of hydrolysis with an aq. suspension of $CaCO_3$ of $CMeCl{:}CH\cdot CH_2Cl$ (80°; 7 hr.) are chiefly $OH\cdot CH_2\cdot CH{:}CMeCl$, with $CH_2{:}CH\cdot COMe$, and of *cis*- and *trans*-$CHMe{:}CCl\cdot CH_2Cl$ (90°; 36 hr.) are β-*chloro*-Δ^{β}-*buten*-α-*ol*, b.p. 52—53°/19 mm. (*α-naphthylurethane*, m.p. 95—96°), and γ-*chloro*-Δ^{γ}-*buten*-β-*ol*, b.p. 67—68°/19 mm. (*α-naphthylurethane*, m.p. 92—92·5°), whilst $CH_2{:}CCl\cdot CHCl\cdot CH_2Cl$ is not hydrolysed under these conditions. It is concluded that the presence of α-Cl reduces the mobility of other Cl atoms, and that αα′-substitution abolishes reactivity completely.

VII. $CHMeEtCl$ and Cl_2 yield αβ- (I), αγ- (II), ββ- (III), and βγ-dichlorobutane (IV); Meyer's rule does not therefore apply to this case. (II), but not (I), is readily hydrolysed to butanediol by aq. K_2CO_3. (III) and (IV) yield $CMeCl{:}CHMe$ when similarly hydrolysed.

VIII. The mixture of dichlorides obtained from $Bu^{\alpha}Cl$ and Cl_2 contains αα- 3, αβ- 17, αγ- 50, and αδ-dichlorobutane 25%. Meyer's rule is not followed in this case.

IX. The readiness with which H atoms in primary, *sec.*-, and *tert.*-hydrocarbons are replaced by Cl varies according to the structure of the hydrocarbon, and the no. and position of Cl already present. The results are explained on the basis of the negative and positive induction effects of Cl and alkyl radicals respectively. R. T.

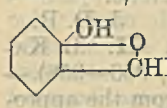
Photochemical chlorination of *cis*-dichloroethylene to tetrachloroethane and of trichloroethylene to pentachloroethane.—See A., I, 370.

Preparation of polymethylene dihalides with long chains. K. Ziegler and H. Weber (Ber., 1937, **70**, [*B*], 1275—1279).—The difficulty of converting long-chained ethers $OPh\cdot[CH_2]_n\cdot OPh$ into $Hal\cdot[CH_2]_n\cdot Hal$ can be overcome by introducing suitable substituents into the C_6H_6 nucleus. One-sided reaction between $Hal\cdot[CH_2]_n\cdot Hal$ and an equiv. amount of NaOAr is achieved by the use of a solvent in which the former dissolves much more freely than does $OAr\cdot[CH_2]_n\cdot Hal$., the alkali being introduced gradually into the mixture. Gradual addition of KOH–MeOH to a mixture of p-$OH\cdot C_6H_4\cdot OMe$ and a large excess of $Br\cdot[CH_2]_{10}\cdot Br$ at 100° gives p-*anisyl κ-bromodecyl ether*, b.p. 190°/0·05 mm., 61—62°, converted by NaI in boiling $COMe_2$ or MeOH into p-*anisyl κ-iododecyl ether* (I), m.p. 75°, more conveniently obtained by gradual addition of powdered

KOH to I·$[CH_2]_{10}$·I and *p*-OH·C_6H_4·OMe in $Bu^{\alpha}OH$ at 35° (yield 90%). (I) is transformed by Na in Et_2O into *αψ-di-p-anisyloxyeicosane*, m.p. 121°, transformed by boiling 56% HI into *αψ-di-iodoeicosane*, m.p. 71°. H. W.

Nitration of *n*-paraffins. II. T. Urbański and M. Słoń (Rocz. Chem., 1937, **17**, 161—164).—Mixtures of α-nitro- and αω-dinitro-paraffins are obtained on 30—80% yield from NO_2 and *n*-C_5H_{12}, -C_6H_{14}, -C_7H_{16}, -C_8H_{18}, or -C_9H_{20} at 200°. R. T.

Mechanism and applicability of the Guerbet reaction. C. Weizmann, E. Bergmann, and L. Haskelberg (Chem. and Ind., 1937, 587—591).—The following mechanism is suggested for Guerbet's condensation of alcohols at high temp. under the influence of Na: $2Pr^{\alpha}OH \rightarrow 2Pr^{\alpha}CHO + 2H_2 \rightarrow CHPr^{\alpha}{:}CEt{\cdot}CHO \rightarrow CH_2Pr^{\alpha}{\cdot}CHEt{\cdot}CH_2{\cdot}OH$. In the first stage of the change H_2 is set free as such, but the last stage does not require mol. H_2 since large amounts of $Bu^{\alpha}OH$ are converted into $Pr^{\alpha}CO_2H$. NaOEt mainly enhances the condensation of the aldehyde mols. and possibly accelerates the dehydrogenation of the alcohol, which is a purely thermolytic process. Na can therefore be replaced by other mild alkalis. The part played by catalytic influences is established by the increased yield of end products if Cu-bronze is added to the reaction mixture, $Bu^{\alpha}OH$, $NaOBu^{\alpha}$, and Cu-bronze at 210° give unchanged material, $Pr^{\alpha}CO_2H$ and substances of higher b.p., $Pr^{\alpha}CO_2Bu^{\alpha}$, *β-ethylhexyl butyrate*, b.p. 118—120°/25 mm., and *β-ethylhexanol* (I), b.p. 181°/760 mm., 90°/26 mm. (corresponding *phenylcarbamate*, b.p. 162°/4 mm., m.p. 33—34°). (I) is converted by $SOCl_2$ and $NPhMe_2$ into *β-ethylhexyl chloride*, b.p. 73°/18 mm. (corresponding *bromide*, b.p. 80°/18 mm.). *β-Ethylhexyl iodide*, b.p. 90°/18 mm., and NMe_3 in $PhNO_2$ at room temp. afford *trimethyl-β-ethylhexylammonium iodide*, m.p. 208°. *Benzyldimethyl-β-ethylhexylammonium iodide*, has m.p. 127°. *β-Ethylhexylaniline*, b.p. 166°/2 mm. (*Ac* derivative, b.p. 185°/20 mm.), and *β-ethylhexyl-2-naphthylamine*, b.p. 224°/18 mm., are described. *Et*$_2$ *β-ethylhexylmalonate*, b.p. 189°/20 mm., is very smoothly converted by $CH_2{:}CH{\cdot}CH_2Br$ and NaOEt in EtOH into *Et*$_2$ *allyl-β-ethylhexylmalonate*, b.p. 205°/18 mm. Catalytic dehydrogenation of (I) gives *α-ethylhexanal* (II), b.p. 160°/760 mm., 65°/25 mm. [*$NaHSO_3$* derivative; 2 : 4-*dinitrophenylhydrazone*, m.p. 120—121°; (?) *semicarbazone hydrochloride*, m.p. 144—145°]. Oxidation of (I) by CrO_3 or of (II) by Ag_2O yields *α-ethylhexoic acid*, b.p. 220—222°/754 mm. (*p-phenylphenacyl* ester, m.p. 49·5—50°; *amide*; *Me* ester, b.p. 82°/24 mm.). Condensation of $CH_2Ph{\cdot}OH$ with $Pr^{\alpha}OH$ in presence of Na and Cu-bronze at 260° affords β-benzylpropyl alcohol and BzOH. *α-Benzylpropionic acid*, b.p. 160°/12 mm. (*p-phenylphenacyl* ester, m.p. 73°), and *α-benzylpropaldehyde* (2 : 4-*dinitrophenylhydrazone*, m.p. 119°) are described. β-Benzylbutanol, obtained from $CH_2Ph{\cdot}OH$ and $Bu^{\alpha}OH$, is dehydrogenated to *α-benzylbutaldehyde*, b.p. 109°/20 mm. (*$NaHSO_3$* derivative; 2 : 4-*dinitrophenylhydrazone*, m.p. 115°). *α-Benzylbutyric acid*, b.p. 174°/13 mm., gives a *p-phenylphenacyl* ester, m.p. 92·5°. Condensation of *p*-OMe·C_6H_4·CH_2·OH with $Bu^{\alpha}OH$ affords unchanged materials and *β-p-methoxybenzylbutanol*, b.p. 138—140°/1·5 mm. $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ and $Bu^{\alpha}OH$ give *β-cinnamylbutanol*, b.p. 110°/0·8 mm., and *di-γ-phenylpropyl ether*, b.p. 147—150°/1·8 mm.; *cinnamyl* 3 : 5-*dinitrobenzoate* has m.p. 125°. *cyclo*Hexanol and $Bu^{\alpha}OH$ yield *o-butylcyclohexanol*, b.p. 116°/21 mm. (3 : 5-*dinitrobenzoate*, m.p. 73°; *acetate*, b.p. 129—130°/26 mm.; *butyrate*, b.p. 160°/27 mm.), and a *substance* (annexed formula), b.p. 155—160°/21 mm., m.p. 110·5°. *o-Butylcyclohexanone*, b.p. 86°/22 mm., gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 113—114°, and a semicarbazone, m.p. 143—144°. A *by-product*, $C_{16}H_{28}O_2$, b.p. 115°/1·5 mm., is obtained in the condensation of $Bu^{\alpha}OH$ with *cyclo*hexanone. *o-Propylcyclohexanol*, b.p. 195°/750 mm., 90°/18 mm., possibly a mixture of isomerides, gives a cryst. 3 : 5-*dinitrobenzoate*, m.p. 75° (*α-naphthylamine* derivative, m.p. 89°); *cyclohexyl H* 3-*nitrophthalate* has m.p. 134°. $CH_2Ph{\cdot}OH$ and *cyclo*hexanol afford *o-benzylcyclohexanol*, b.p. 165°/18 mm., m.p. 75° (3 : 5-*dinitrobenzoate*, m.p. 134·5°; *phenylurethane*, m.p. 109°; *acetate*, b.p. 177°/18 mm.), and 2 : 6-*dibenzylcyclohexanol* (III), b.p. 194°/18 mm., m.p. 124° (*acetate*, m.p. 101°). Hydrogenation (Pd–$BaSO_4$) of 2 : 6-dibenzylidene*cyclo*hexanone gives 2 : 6-*dibenzylcyclohexanone*, m.p. 114° (and its *peroxide*, m.p. 130—131°), reduced by Na in moist Et_2O to (III), stout prisms, m.p. 121—122°, or needles, m.p. 101°. Cetyl alcohol and *cyclo*hexanol give unchanged material, palmitic acid, and a non-homogeneous material, m.p. 85°. $CH_2Ph{\cdot}CH_2{\cdot}OH$ and *cyclo*hexanol give mainly polystyrene with Na but in presence of $CH_2Ph{\cdot}CO_2Na$ afford *o-β-phenylethylcyclohexanol*, b.p. 125°/0·4 mm. (*phenylurethane*, m.p. 143—144°). H. W.



Action of carbon dioxide in the vapour-phase oxidation of alcohol at metallic catalysts. A. M. Rubinschtein and A. J. Kronrod (J. Appl. Chem. Russ., 1937, **10**, 888—899).—The principal reaction taking place between *iso*-C_5H_{11}·OH (I), H_2O, and CO_2 in presence of Ag–asbestos at 375—425° is that of oxidation of $Bu^{\beta}CHO$ (II), with simultaneous reduction of CO_2 to HCO_2H, which decomposes to yield CO_2 and H_2. Dehydration of (I) to *iso*amylene, and oxidation of (II) to $Bu^{\beta}CO_2H$, take place to a limited extent. R. T.

Micro- and submicro-determination and identification of ethyl alcohol. M. Nicloux (Ann. Ferment., 1936, **1**, 449—467; Chem. Zentr., 1936, i, 3375).—The EtOH (0·1—4·6 mg.) is oxidised in a closed tube at 100° with a slight excess of standard $K_2Cr_2O_7$–H_2SO_4; the excess of reagent is reduced with excess of $FeSO_4$ and this latter titrated with $KMnO_4$. H. N. R.

Electrochemical oxidation of *n*-butyl alcohol. —See A., I, 419.

Catalytic dehydrogenation of alcohols to yield esters. VI. Mechanism of esterification of *iso*amyl alcohol. N. M. Abramov and B. N. Dolgov (J. Gen. Chem. Russ., 1937, **7**, 1009—1014).—The yields of *iso*amyl *iso*valerate (I) fall, and of *iso*valeric acid and aldehyde (II) rise, with increasing

[CO_2] or [N_2] of the reaction mixture, when the latter is passed over a CuO–U_3O_8 catalyst at 280°; the opposite effects are obtained by increasing the [H_2] of the mixture. (I) is obtained in good yield from (II) and H_2 under similar conditions. R. T.

Criegee and Grignard reactions. A. Gillet (Bull. Soc. chim. Belg., 1937, **46**, 171—172).—The Criegee reaction is considered to be the inverse of the addition of the Grignard reagent to a ketone. J. D. R.

Preparation of acetylenic glycols. II. L. Kazarjan (J. Gen. Chem. Russ., 1937, **7**, 956—958).—Glycols, $(OH\cdot CRR'\cdot C{:})_2$, are obtained from the appropriate ketones with CaC_2 and KOH in Et_2O, at room temp.: R = R′ = Me, from $COMe_2$; R = Me, R′ = Ph, from COPhMe; R = R′ = Ph, from $COPh_2$; RR′ = *cyclo*hexyl, from *cyclo*hexanone. R. T.

β-Triphenylmethyl derivatives of glycerol. P. E. Verkade, J. van der Lee, and (Frl.) W. Meerburg (Rec. trav. chim., 1937, **56**, 613—622).—The ready formation of compounds of this type affords further proof that CPh_3Cl is not sp. for primary OH. α-Monostearin is converted by CPh_3Cl in quinoline at 100° into *βγ-diphenylmethylglyceryl α-stearate*, m.p. 83·5—84°, also obtained analogously from γ-triphenylmethylglyceryl α-stearate. *αγ-Ditriphenylmethylglycerol* and stearyl chloride in $CHCl_3$–quinoline yield *αγ-ditriphenylmethylglyceryl β-stearate*, m.p. 83—84°, the formation of *modifications* of lower m.p. being indicated. Glycerol and CPh_3Cl in C_5H_5N at 100° during 3 hr. give *αγ-ditriphenylmethylglycerol*, m.p. 177—178° (occasionally m.p. 181—182°), transformed by CPh_3Cl in quinoline at 100° during 7 hr. into *αβγ-tri(triphenylmethyl)glycerol* (+0·5$CHCl_3$), m.p. 196—197° (also +1CCl_4 and +2C_6H_6). H. W.

Titration of nitric esters.—See A., I, 425.

Preparation of crystalline β-4-glucosidosorbitol and its monomethyl derivative. P. A. Levene and M. Kuna (Science, 1937, **85**, 550; cf. this vol., 83).—Reduction (Raney Ni) of cellobiose in H_2O at 75°/100 atm. yields cryst. platelets of *β-4-glucosidosorbitol*, m.p. 133°, $[\alpha]_D^{25}$ −8·7° in H_2O. One methylation with Me_2SO_4 by West and Holden's method gave the fully methylated *product*, b.p. 170°/0·2 mm., $[\alpha]_D^{25}$ −4·93° in abs. EtOH. L. S. T.

Thermal decomposition of dimethyl ether.—See A., I, 366.

Explosions attributed to interaction between ethyl peroxide and sulphur. H. F. Taylor (Mem. Manchester Phil. Soc., 1937, **81**, 15—18).—Conditions favourable for the explosion of Et_2O_2 are infrequent, but presence of S or other readily oxidisable material may cause explosion. J. W. S.

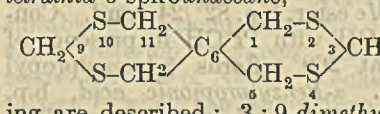
Molecular compounds of dioxan. V. Dioxanates of the halides of bivalent metals. H. Rheinboldt, A. Luyken, and H. Schmittmann (J. pr. Chem., 1937, [ii], **149**, 30—54).—The following *dioxanates* (R = $C_4H_8O_2$) are prepared by crystallisation of the halide from dioxan (I), by pptn. from EtOH by (I), or by displacement of Et_2O from the etherates. Power of addition and stability of the products increase generally from chloride to iodide and the dioxanates are more stable than the corresponding etherates. $CaCl_2,R$; $CaBr_2,R_2$; CaI_2,R_2; $SrBr_2,R_2$; SrI_2,R_2; BaI_2,R_2, readily decomposed by exposure to light; $MgCl_2,R_2$, very hygroscopic; $MgBr_2,R_2$; MgI_2,R_2, decomp. about 150°; $ZnCl_2,R_2$; $ZnBr_2,R_2$; ZnI_2,R_2, decomp. about 75—80° in a sealed capillary; $CdCl_2,R$; $CdBr_2,R$, decomp. about 200°; CdI_2,R, decomp. about 175—180°; $HgCl_2,R$, decomp. about 160—165°; $HgBr_2,R$; HgI_2,R; $Hg(CN)_2,R_2$, very unstable; $Hg(CNS)_2,R$; $CuCl_2,R$; $CuBr_2,R$; $SnCl_2,R$; $SnBr_2,R$; $MnCl_2,R$; $MnBr_2,R_2$; MnI_2,R_2; $FeCl_2,R_2$; $FeBr_2,R_2$; FeI_2,R_2; $CoCl_2,R$; $CoBr_2,R_2$; CoI_2,R_4; CoI_2,R_2; $NiCl_2,R_2$; $NiBr_2,R_2$; NiI_2,R_2. Dioxanates could not be obtained from $SrCl_2$, $BaCl_2$, and $BaBr_2$. H. W.

Hydrolysis of monoacid triglycerides under the influence of pancreatic extract.—See A., III, 268.

Preparation of hexose monophosphate from yeast extract.—See A., III, 271.

Monothioformals. F. W. Wenzel, jun., and E. E. Reid (J. Amer. Chem. Soc., 1937, **59**, 1090—1091).—RSH and $CH_2Cl\cdot OR$ in NaOH–EtOH at room temp. give Et_2, b.p. 135·8°, Pr^a_2, b.p. 179·2°, and Bu^a_2 *monothioformal*, b.p. 220°, $SR\cdot CH_2\cdot OR$. d_4^0, d_4^{25}, and n_D^{25} are recorded. The compounds are stable at the b.p. and react only slowly with Grignard reagents; the Et_2 compound with MgEtBr at 100° gives EtSH and EtOPr, showing that SR is replaced more readily than OR. HCl rapidly decomposes the compounds to the formal and dithioformal; unchanged $CH_2Cl\cdot OR$ must, therefore, be removed from the reaction products before storage. Oxidation proceeds readily, but does not yield a sulphone. R. S. C.

Tetrathiolmethylmethane (tetrathiopentaerythritol), a reagent for aldehydes and ketones. H. J. Backer and N. Evenhuis (Rec. trav. chim., 1937, **56**, 681—690).—Reduction of 2 : 3 : 7 : 8-tetrathia-5-*spirocyclo*nonane by Na in liquid NH_3 affords *tetrathiolmethylmethane* (I), m.p. 73—73·5° (*Tl*, *Ag*, *Hg*, *Cu*, and *Pb* salts), in 80% yield. It is oxidised by I in EtOH to the dimeric *thio-ether*, $\left[\cdot S\cdot CH_2>C<CH_2\cdot S\cdot\right]_2$, m.p. 147·5—148·5°, and by 30% H_2O_2 in AcOH to the tetrasulphonic acid $C(CH_2\cdot SO_3H)_4$, isolated as the Ba salt. (I) reacts with aldehydes and ketones and HCl, alone or in presence of EtOH, $CHCl_3$, or mixtures thereof, giving characteristic derivatives of 2 : 4 : 8 : 10-*tetrathia*-6-spiro*undecane*,



of which the following are described: 3 : 9-*dimethyl*-, m.p. 110°; 3 : 9-*diacetyl*-3 : 9-*dimethyl*-, m.p. 164—165·5°; 3 : 9-*difuryl*-, m.p. 132·5—133°; 3 : 3 : 9 : 9-*tetramethyl*- (II), m.p. 192—193°; 3 : 9-*dimethyl*-3 : 9-*diethyl*- (III), m.p. 143—143·5°; 3 : 3 : 9 : 9-*tetraethyl*-, m.p. 118—118·5°; 3 : 3-*dimethyl*-9 : 9-*di*tert.-*butyl*-, m.p. 165—167°; 3 : 9-*diethyl*-3 : 9-*di*tert.-*butyl*-, m.p. 177—178°; 3 : 9-*di*(*tetramethylene*)- (IV),

$CH_2{\cdot}CH_2{>}C{<}^{S{\cdot}CH_2}_{S{\cdot}CH_2}{>}C{<}^{CH_2{\cdot}S}_{CH_2{\cdot}S}{>}C{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}$, m.p. 212·5—213°; 3 : 9-*di*(*pentamethylene*)- (V), m.p. 206—207°; 3 : 9-*di*(*thiodiethylene*)-, m.p. 273°, from $S{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}{>}CO$; 3 : 9-*di*-(p-*carboxypentamethylene*)-; 3 : 9-*diphenyl*-, m.p. 233—234°; 3 : 9-*di*-p-*tolyl*-, m.p. 244—245°; 3 : 9-*di*-(4′-*hydroxy*-3′-*methoxyphenyl*)-; m.p. 269—271°; 3 : 9-*di*-(3′ : 4′-*methylenedioxyphenyl*)-, m.p. 265—267°; 3 : 9-*di*-(β-*phenylvinyl*)-, m.p. 225—226° (slight decomp.); 3 : 9-*diphenyl*-3 : 9-*dimethyl*-, m.p. 184—185°; 3 : 3 : 9 : 9-*tetraphenyl*-, m.p. 222—223°; 1-hydrindone and fluorenone afford *compounds* m.p. 258—259° and m.p. >300° (decomp.), respectively. The spirocyclic *tetrasulphones*, $RR'C{<}^{SO_2{\cdot}CH_2}_{SO_2{\cdot}CH_2}{>}C{<}^{CH_2{\cdot}SO_2}_{CH_2{\cdot}SO_2}{>}CRR'$, derived from (II), (III), (IV), and (V) become discoloured without melting at about 350°, 300°, 300°, and 300°, respectively. H. W.

Hydrates. II. Sodium acetate. W. Qvist (Acta Acad. Aboensis, 1935, 9, No. 2, 18 pp.; Chem. Zentr., 1936, i, 3259; Acta Acad. Aboensis, 1933, 7, 43 pp.).—$NaOAc,3H_2O$ (I) dehydrates directly to the anhyd. salt (II) which, when prepared at room temp., rehydrates with H_2O to (I). After heating at >80°, (II) dissolves directly without hydration, but if chilled from 200° to −80°, (II) hydrates to (I). The effects are due to the existence of allotropic modifications of (II) (cf. Vorländer and Nolte, A., 1913, i, 1300) with a transition temp. at 198°, a third form being postulated which hydrates directly to (I). J. S. A.

Heats of hydrogenation of unsaturated esters.—See A., I, 413. H. M. D.

Action of sodium on anhydrides of certain organic acids. I. F. Sukhevitsch and N. F. Levkin (J. Gen. Chem. Russ., 1937, 7, 857—859).—Boiling Ac_2O and Na yield Ac_2, $CH_2{:}CH{\cdot}OAc$ (I), $CHMe(OAc)_2$ (II), and H_2. (II) and Na at 140° yield (I). The sole product obtained from Bz_2O and Na (140°; 4 hr.) is Bz_2. Succinic anhydride and Na do not react at 140—180°. R. T.

Decomposition of methylene diacetate, dipropionate, and dibutyrate.—See A., I, 416.

Rate of alkaline hydrolysis of pentenoic esters.—See A., I, 416.

Esterification and hydrolysis from the viewpoint of the electronic theory of union. II. J. von Braun and P. Kurtz (Ber., 1937, 70, [*B*], 1224—1229; cf. A., 1933, 257).—The authors' views of the effect of the relationship of electric charges on the esterification of acids with a chain branched at $C_{(\beta)}$ and the hydrolysis of their esters are supported by the behaviour of compounds which are unbranched or branched in a more remote position. The effect of branching in alkyl halides on the readiness of the Fittig–Würtz synthesis could not be determined but the side reaction resulting in the production of paraffin and olefine, $2{>}CH{\cdot}CH_2Hal \rightarrow 2{>}CH^*{\cdot}CH_2{\cdot} \rightarrow {>}C{:}CH_2 + {>}CHMe$, appears to be favoured as the proton-like nature of H* increases. The prep. of *Et* δ-*methyl*-α-γ′-*methylbutylhexoate* (I), b.p. 122°/15 mm., and its hydrolysis are described. (I) is reduced by Na and EtOH to ε-*methyl*-β-γ′-*methylbutylhexan*-α-*ol*, b.p. 122—124°/12 mm., transformed by conc. HBr into the corresponding *bromide*, b.p. 122°/12 mm., which is converted by Na and Et_2O into βλ-*dimethyl*-δθ-*di*-γ′-*methylbutyldodecane*, b.p. 162°/0·1 mm., with a mixture of $CHMe(C_5H_{11})_2$ and $CH_2{:}C(C_5H_{11})_2$. *Et*$_2$ cyclo*pentyl*iso*amylmalonate*, b.p. 158—161°/14 mm., is obtained with difficulty from *Et*$_2$ *cyclo*pentylmalonate and *iso*amyl bromide but readily by interaction of *Et*$_2$ *iso*amylmalonate and Δ²-*cyclo*pentenyl chloride to *Et*$_2$ cyclo*pentenyl*iso*amylmalonate*, b.p. 164—166°/14 mm., which is hydrogenated (Ni). It is only partly hydrolysed by 50% alkali at 100° since after distillation, the products of the action are *Et* δ-*methyl*-α-cyclo*pentylhexoate* (II), b.p. 134°/15 mm., and δ-*methyl*-α-cyclo*pentylhexoic acid* (III), b.p. 170—172°/14 mm. Reduction (Na in EtOH) of (II) leads with some difficulty to ε-*methyl*-β-cyclo*pentylhexan*-α-*ol*, b.p. 134—136°/14 mm.; the corresponding *bromide* (IV), b.p. 130—132°/14 mm., is transformed by Na in Et_2O into the hydrocarbons $C_{12}H_{24}$ and $C_{12}H_{22}$ and εθ-*dicyclopentyl*-βλ-*dimethyldodecane*, b.p. 172°/0·2 mm. (IV) reacts very readily with Mg and the product is transformed by CO_2 into β-cyclo*pentyl*-ε-*methyl*-n-*heptoic acid*, b.p. 134—136°/0·05 mm., which is more readily esterified than (III); *Et* β-cyclo*pentyl*-ε-*methyl*-n-*heptoate*, b.p. 136—138°/12 mm., is more readily hydrolysed than (II). Interaction of BuBr with *Et*$_2$ *cyclo*hexylmalonate leads with great difficulty to *Et*$_2$ cyclo*hexylbutylmalonate*, b.p. 176—178°/4 mm., hydrolysis followed by distillation of which affords *Et* α-cyclo*hexylhexoate* (V), b.p. 136—138°/14 mm., and α-cyclo*hexylhexoic acid*, b.p. 172—176°/14 mm. (V) is transformed by Na in EtOH into β-cyclo*hexyl*-n-*hexyl alcohol*, b.p. 134°/14 mm.; the corresponding *bromide*, b.p. 138—140°/14 mm., is converted by Na into $C_{12}H_{24}$, $C_{12}H_{22}$, and εθ-*dicyclo*-*hexyldodecane*, b.p. 170°/0·2 mm. H. W.

Addition of hydrogen bromide to non-terminal double bonds. Effect of the alkyl groups. E. P. Abraham, E. L. R. Mowat, and J. C. Smith (J.C.S., 1937, 948—954).—Δ$^{\theta}$-Undecynoic acid with 85% H_2SO_4 at 0° yields ι- and θ-ketoundecoic acid (I), m.p. 58—59° (lit. 43·5°) (*semicarbazone*, m.p. 161°). The Me ester of (I) is reduced by $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ to Me θ-hydroxyundecoate (not isolated), hydrolysed to θ-*hydroxyundecoic acid*, m.p. 34—35°, converted by HBr into θ-*bromoundecoic acid*, m.p. 31°. The addition of HBr to *iso*undecoic acid in hexane, AcOH, and C_6H_6 both under "oxidant" and "anti-oxidant" conditions yields, in all cases, 50% each of θ- and ι-bromoundecoic acid, the binary system of these being used for analysis of the mixed additive products; the addition is fastest in C_6H_6. Addition of HBr to *iso*undecenoamide in C_6H_6 and to *iso*undecenol in hexane is much faster than with the acid, but has little effect on the proportions of the θ- and ι-Br-compounds formed, the products from the amide being analysed by conversion (HNO_2) of $CO{\cdot}NH_2$ into CO_2H, and from the alcohol by oxidation ($Na_2Cr_2O_7$–aq. H_2SO_4 or CrO_3–AcOH–$KHSO_4$), followed by analysis by m.p. of the mixed acids formed. In the

reaction $CH_3{\cdot}CH{:}CHR + HBr$, the reactivity of the unsaturated C atoms is independent of the length of the alkyl chain. J. D. R.

Long-chain carbon compounds. *n*-Tetratriacontanoic and *n*-hexatetracontanoic acids and their derivatives. F. Francis, A. M. King, and J. A. V. Willis (J.C.S., 1937, 999—1004).—Condensation of behenoyl chloride [from behenic acid and $(COCl)_2$ in C_6H_6] with Et sodio-α-acetylbrassylate (I) in Et_2O or C_6H_6 affords μ-*ketotetratriacontanoic acid* (II), m.p. 107·7° (*Et* ester, m.p. 80·9°), and λ-*acetyl-lauric acid*, m.p. 73·5°. (II) when reduced (Clemmensen) affords n-*tetratriacontanoic acid* (III), m.p. 98·2° [*Et* ester, m.p. 75·4°; *anilide*, m.p. 114°; *chloride* (IV), m.p. 73·1°], converted (Hell and Sadomsky) into α-*bromotetratriacontanoic acid*, dimorphic (β-form, m.p. 89·1°; α-form, m.p. 77·37°), hydrolysed (KOAc–AcOH) to α-*hydroxytetratriacontanoic acid*, m.p. 109—110°. Electrolysis of the K salt of (III) affords n-*hexahexacontane*, m.p. 103·6°. n-*Heptahexacontane*-34-*one* [from (III), by heating with Fe] is reduced (Clemmensen) to n-*heptahexacontane*, m.p. 104·1°. From (III) by reduction (Bouveault) of the Et ester followed by conversion into the iodide, condensation with $CHNa(CO_2Et)_2$, and subsequent hydrolysis is prepared n-*hexatriacontanoic acid*, m.p. 99·9°, [*Et* ester, m.p. 78·6°, reduced (Bouveault) to n-*hexatriacontan*-α-*ol* (V), m.p. 92·9°]. Similar stepwise synthesis from (V) affords n-*octatriacontanoic acid*, m.p. 101·6° (*Et* ester, m.p. 80·55°, reduced to n-*octatriacontan*-α-*ol*, m.p. 93·6°). (I) and (IV) in dry Et_2O in an atm. of N_2 afford impure *ethyl*-α-*acetyl*-α-*tetratriacontanoyl brassylate*, m.p. 68—90°, hydrolysed (EtOH–KOH) to μ-*ketohexatetracontanoic acid*, m.p. 115° (*Et* ester, m.p. 93·76°), reduced (Clemmensen) to *hexatetracontanoic acid*, m.p. 107·1° (*Et* ester, m.p. 90·5°). The crystal spacings of many of these acids and their derivatives are given, and the heat of crystallisation of Et tetratriacontanoate is recorded. J. D. R.

Liquid acids of sapucainha oil. H. Paget (J.C.S., 1937, 955—960).—The seeds of *Carpotroche brasiliensis*, Endl, yield to CCl_4 sapucainha oil, hydrolysed (KOH–EtOH) to chaulmoogric (I), hydnocarpic, and palmitic acids, and mixed liquid acids, the Cu salts of which are separated into sol. (*A*) and insol. (*B*) in $COMe_2$. Distillation of the Me esters of acids (*A*) yields (fraction of b.p. 185—210°/0·5 mm.) after hydrolysis *ketochaulmoogric acid*, $\begin{matrix}CO—CH\\ CH_2{\cdot}CH_2\end{matrix}\!>\!C{\cdot}[CH_2]_n{\cdot}CO_2H$ (II; $n = 12$), m.p. 116° [*semicarbazone*, m.p. 157° (decomp.)], and *ketohydnocarpic acid* (II; $n = 10$), m.p. 108° [*semicarbazone*, m.p. 156° (decomp.)]. Ketochaulmoogric acid with PtO–H_2 in EtOH affords dihydrochaulmoogric acid (III) (p-*bromoanilide*, m.p. 102°) and a *dihydroketo-acid*, $C_{18}H_{32}O_3$ (*semicarbazone*, m.p. 164°), which is oxidised ($KMnO_4$) to γ-keto-*n*-pentadecanedicarboxylic acid (IV). The non-volatile Me esters of acids (*A*) on hydrolysis yield liquid acids (*C*), hydrogenated (H_2–Pd–$BaSO_4$) to (III) and stearic acid. Oxidation ($KMnO_4$–KOH) of the acids affords dihydroxystearic acid and *tetrahydroxydihydrochaulmoogric acid*, m.p. 111—113°, $[\alpha]_D^{18}$ −17·9° in EtOH (*Me* ester, by CH_2N_2, m.p. 88°; *tetramethoxyacetyl* derivative of Me ester; *tetraphenylurethane*, m.p. 145°), further oxidised (H_2CrO_4) to adipic acid (V), a *ketone* (probably δ-*keto*-n-*decane*-αω-*dicarboxylic acid*; *semicarbazone*, m.p. 187°), and n-*nonane*-αγω-*tricarboxylic acid* (Me_3 ester, b.p. 200—217°/15 mm.; *trianilide*, m.p. 189°), which latter is further oxidised (H_2CrO_4) to $(\cdot CH_2{\cdot}CO_2H)_2$, (V), and suberic acid. The liquid acids (*C*) therefore must contain *dehydrochaulmoogric acid*, $\begin{matrix}CH{:}CH—\\ CH_2—CH_2\end{matrix}\!>\!CH{\cdot}[CH_2]_6{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO_2H$. Et chaulmoograte or sapucainha oil on long exposure to sunlight and air is oxidised to (II); this explains the occurrence of (IV) in the oxidation products of (I) observed by Barrowcliff and Power (J.C.S., 1907, **91**, 557), (II) being an intermediate stage in the oxidation. J. D. R.

Isomerisation of linoleic acid. II. G. V. Pigulevski and I. V. Rokitianski (J. Gen. Chem. Russ., 1937, **7**, 882—884).—Oxidation of poppy-seed oil with BzO_2H leads to production of the solid and liquid isomerides of the dioxide of linoleic acid (I), and of the oxide of oleic acid. The content of α-isomeride in natural is the same as in synthetic (I). R. T.

Hydnocarpic and chaulmoogric acids and ethyl esters. H. I. Cole and H. Cardoso (J. Amer. Chem. Soc., 1937, **59**, 963—965).—Details are given for the prep. of pure hydnocarpic (I), m.p. 60·5°, $[\alpha]_D^{25}$ +69·3° (Et ester, b.p. 184°/10 mm., $[\alpha]_D^{25}$ +61·94°), and chaulmoogric acid (II), m.p. 68·5°, $[\alpha]_D^{25}$ +60·3° (Et ester, b.p. 206°/10 mm., $[\alpha]_D^{25}$ +55·42°), best from *Hydnocarpus Wightiana* oil [which contains no palmitic acid (III)], the essential step being careful fractionation of the Et esters. The best criteria of purity are [α] and crystal form. Mixed m.p. curves for (I)–(II) and (I)–(III), and *d* and *n* for the Et esters at 20°, 25°, and 30° are given. R. S. C.

Odour and constitution. II. Lactones. J. von Braun [with E. Anton and W. May] (Ber., 1937, **70**, [*B*], 1251—1253; cf. A., 1930, 68).—In lactones $\begin{matrix}CHAlk{\cdot}CO\\ CH_2{\cdot}CHMe\end{matrix}\!>\!O$ the intensity of odour attains its max. when 11 C are present if in a straight chain. Branching of the chain causes increase in the intensity. The lactones described below are obtained by the introduction of C_3H_5 into monoalkylmalonic esters, followed by hydrolysis, decarboxylation, and heating with 70% H_2SO_4. The following are new: Et_2 n-*decylmalonate*, b.p. 193—195°/13 mm.; Et_2 *allyl*-n-*decylmalonate*, b.p. 210—212°/13 mm.; α-*allyldodecoic acid*, b.p. 170°/0·3 mm.; α-n-*decyl*-γ-*valerolactone*, b.p. 203—205°/16 mm., m.p. 46°; Et_2 γη-*dimethyloctylmalonate*, b.p. 183—187°/13 mm.; Et_2 *allyl*-γη-*dimethyloctylmalonate*, b.p. 200—203°/13 mm.; δθ-*dimethyl*-α-*allyldecoic acid*, b.p. 165°/0·1 mm.; α-γη′-*dimethyloctyl*-γ-*valerolactone*, b.p. 193°/13 mm.; Et_2 n-*octylmalonate*, b.p. 175—177°/17 mm.; Et_2 *allyl*-n-*octylmalonate*, b.p. 192°/16 mm.; α-*allyldecoic acid*, b.p. 155°/0·2 mm.; α-n-*octyl*-γ-*valerolactone*, b.p. 196°/16 mm., m.p. 40°; Et_2 n-*heptylmalonate*, b.p. 163°/17 mm.; Et_2 *allyl*-n-*heptylmalonate*, b.p. 175—180°/17 mm.; α-*allylnonoic acid*, b.p. 145°/0·5 mm., α-n-*heptyl*-γ-*valero*-

lactone, b.p. 170—172°/17 mm.; Et_2 n-*hexylmalonate*, b.p. 152°/17 mm.; Et_2 *allyl*-n-*hexylmalonate*, b.p. 167°/17 mm.; *allyl*-n-*hexylmalonic acid*, m.p. 91°; α-*allyloctoic acid*, b.p. 130°/0·1 mm.; α-n-*hexyl*-γ-*valerolactone*, b.p. 153°/14 mm.; Et_2 cyclo*hexylallylmalonate*, b.p. 168°/14 mm.; cyclo*hexyl-allylmalonic acid*, m.p. 127°; α-cyclo*hexyl*-Δ^{δ}-*pentenoic acid*, b.p. 152—155°/14 mm.; α-cyclo*hexyl*-γ-*valerolactone*, b.p. 150—152°/14 mm.; Et_2 *allylamylmalonate*, b.p. 140—143°/10 mm.; *allylamylmalonic acid*, m.p. 96—98°; α-*allylheptoic acid*, b.p. 132—135°/11 mm.; α-n-*amyl*-γ-*valerolactone*, b.p. 128°/10 mm. H. W.

Course of diene syntheses. K. Alder and G. Stein (Angew. Chem., 1937, **50**, 510—519).—A summary of recent work on diene polymerisation. J. W. S.

Biological oxidation of highly unsaturated fatty acids. Preparation of polyenedicarboxylic acids. R. Kuhn, F. Köhler, and L. Köhler (Z. physiol. Chem., 1937, **247**, 197—219).—Feeding of sorbic acid to rabbits is followed by excretion of 0·1—0·2% (calc. on amount fed) of *trans-trans*-muconic acid [isolated as Me_2 ester (A., 1936, 1093)]; feeding of Me and Et sorbate yields 0 and 0·5%, respectively, whilst that of the acid amide affords 32% of *muconamic acid*, m.p. 281—282° (corr., decomp.). Similarly, *sorbmethylamide*, m.p. 141° (corr.) (from the acid chloride and NH_2Me), gives 44% of *muconmethylamic acid*, m.p. 217° (corr., decomp.), sorbanilide yields 36% of *muconanilic acid*, m.p. 261—263° (corr., decomp.), and β-*methylsorbamic acid*, m.p. 136—141° [from the acid (A., 1932, 600)], gives 62% of β-*methylmuconamic acid*, m.p. 259—261° (corr.). Thus with aliphatic polyenecarboxylic acids, $Me\cdot[CH{:}CH]_n\cdot CO_2H$, β-oxidation in the organism is diminished by introduction of $CO\cdot NH_2$ and β-Me groups. Feeding of crotonanilide yields neither male- nor fumaranilide but 14% of N-*crotonyl*-p-*aminophenol*, m.p. 189—190° (corr.) [also from crotonyl chloride and p-$NH_2\cdot C_6H_4\cdot OH$; hydrogenated to N-*butyl*-p-*aminophenol*, m.p. 139—140° (corr.), afforded by BuCl and p-$NH_2\cdot C_6H_4\cdot OH$]. ββ-*Dimethylacrylamide*, m.p. 110—111° (corr.), yields mesacon-α-amic acid (Anschütz, A., 1907, i, 468) (*i.e.*, only the Me *trans* to the $CO\cdot NH_2$ is oxidised); β-methyl-β-ethylacrylic acid (prepared by condensation of $CH_2Br\cdot CO_2Me$ with COMeEt in presence of Zn to yield *Me* β-*hydroxy*-β-*methylvalerate*, b.p. 74—78°/12 mm., which is treated with $ZnCl_2$–Ac_2O and the resulting *Me* β-*methyl*-β-*ethylacrylate*, b.p. 151—153°, is hydrolysed) and its *amide*, m.p. 128—128·5° (corr.) (from the acid *chloride*, b.p. 48°/13 mm.), yield no urinary oxidation acid. The above biological oxidation phenomena also occur with furancarboxylic acids. Thus 5-methylfuran-2-carboxylamide yields 32% of 5-*carboxyfuran*-2 : 5-*carboxylamide*, m.p. 284° (corr.), whilst β-(5-*methyl*-2-*furyl*)*acrylamide*, m.p. 130—131° (corr.) (from the corresponding acid *chloride*, m.p. 37°, b.p. 124°/9 mm.), gives 83% of 2-(β-*acrylamido*)*furan*-5-*carboxylic acid*, m.p. 280° (corr., decomp.). The acyclic analogue, ζ-methyl-$\Delta^{\alpha\gamma\epsilon}$-hexatriene-α-carboxylic acid, yields no urinary dicarboxylic acid, but its *amide*, m.p. 208—209°, affords 42% of α-*carboxy*-$\Delta^{\alpha\gamma\epsilon}$-*hexatriene*-ζ-*carboxylamide*, decomp. 263° (corr.). Similarly θ-methyl-$\Delta^{\alpha\gamma\epsilon\eta}$-octatetraene-α-carboxylic acid gives no unchanged or dicarboxylic acid product whilst its *amide*, m.p. 227° (corr.), affords 20% of α-*carboxy*-$\Delta^{\alpha\gamma\epsilon\eta}$-*octatetraene*-θ-*carboxylamide*, m.p. approx. 258° (decomp.). The observed pharmacological effects following ingestion of the above compounds are described. F. O. H.

Synthesis of decrocetin [$\Delta^{\alpha\gamma\epsilon\eta\iota\lambda\nu}$-**tetradecaheptaene-αζ-dicarboxylic acid**]. R. Kuhn and C. Grundmann (Ber., 1937, **70**, [*B*], 1318—1333).—It is proposed to base the nomenclature of synthetic compounds resembling carotenoids on the trivial names of the latter whereby the prefix *apo* denotes the presence of one fewer Me and "de" implies that all side Me groups have been removed from the natural material. Crotonaldehyde (I) is condensed by AcOH and piperidine to *dodecapentaenal* (II), $Me\cdot[CH{:}CH]_5\cdot CHO$, m.p. 166°, and octatrienal from which (II) is readily obtained by similar condensation with (I). Condensation of (II) with $CH_2(CO_2H)_2$ takes place in poor yield in presence of C_5H_5N but readily if piperidine is added; similar enhanced yields are observed with all the higher polyene aldehydes but not with the simpler members which thereby suffer increased auto-condensation. *Dodecapentaenylidenemalonic acid*, $Me\cdot[CH{:}CH]_6\cdot CH{:}C(CO_2H)_2$, is very unsatisfactorily decarboxylated when heated alone or as pyridinium salt, readily in boiling AcOH–Ac_2O to $\Delta^{\alpha\gamma\epsilon\eta\iota\lambda}$-*tetradecahexaenoicacid* (III), $Me\cdot[CH{:}CH]_6\cdot CO_2H$, m.p. 265—266° (decomp.). Attempted esterification of (III) by treatment with various alcohols and HCl, H_2SO_4, $KHSO_4$, etc., by CH_2N_2, $CHMeN_2$, $CHPhN_2$ even with addition of H_2O or EtOH, or by treatment of the *Ag* salt with Me_2SO_4 or alkyl halide were unsuccessful but the *Me* ester, m.p. 220°, is obtained by the action of CH_2N_2 in presence of much 96% EtOH + Et_2O. Condensation of the ester with $Et_2C_2O_4$ is effected by KOEt or RbOEt in presence of C_5H_5N or quinoline but not of other *tert.* amines, thus giving Et_2 *oxalotetradecahexaenoate*, m.p. 190—191°. The corresponding *Ac* derivative, m.p. 167°, is converted by Al–Hg in C_6H_6–Et_2O–H_2O into *dedihydrocrocetin* Et_2 *ester*, m.p. 163—165°, transformed by NaOEt in C_5H_5N into *decrocetin* Et_2 *ester*, m.p. 217° (corresponding Me_2 ester, m.p. 236°), which is hydrolysed to *decrocetin*, $CO_2H\cdot[CH{:}CH]_7\cdot CO_2H$, decomp. >300°. The following new spectroscopic rules are advanced for symmetrical polyenes. CO_2H in conjugation is equiv. to one conjugated ethylenic linking. Conjugated Ph corresponds with 1·5 conjugated ethylenic linkings. Me attached to the polyene chain is equiv. to 0·25 double linking. A conjugated cyclic double linking is equiv. to 0·5 aliphatic ethylenic linking. H. W.

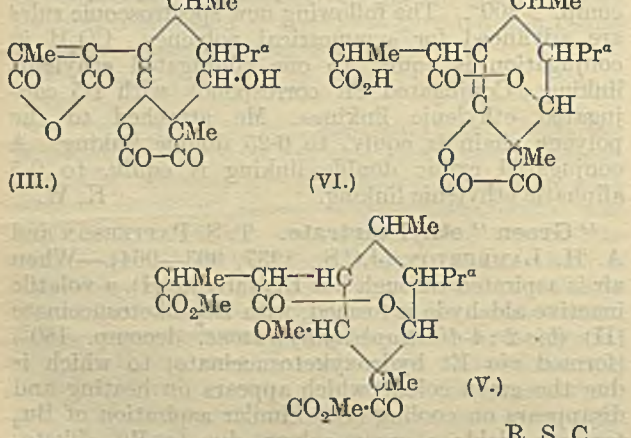
"Green" ethyl tartrate. T. S. Patterson and A. H. Lamberton (J.C.S., 1937, 963—964).—When air is aspirated through hot Et_2 tartrate (I), a volatile inactive aldehyde is formed, with Et_2 diketosuccinate (II) (*bis*-2 : 4-*dinitrophenylhydrazone*, decomp. 180°) (formed *via* Et hydroxyketosuccinate) to which is due the green colour which appears on heating and disappears on cooling (I). Similar aspiration of Bu_2 tartrate yields a green colour, due to Bu_2 diketo-

succinate. The colour change on heating and cooling may be due to hydration. J. D. R.

Calcium citrate complexes. C. ARTOM and G. SARZANA (Boll. Soc. ital. Biol. sperim., 1936, **11**, 1029—1031).—The dialysis of aq. $CaCl_2$ + Na citrate at p_H 6·7—7·6 and 0° with parchment membranes against H_2O or aq. KCl or $CaCl_2$ indicates the formation of semi-colloidal complexes of Ca citrate. F. O. H.

Salts of gluconic acid. S. V. NILKANTUM (J. Sci. Tech. India, 1936, **2**, 39—51).—Colour, shape, m.p., solubility in H_2O and EtOH, and $[\alpha]_D$ are recorded for the following salts: Mg, K, Na, Mn, Co, Cd, Cr, NH_4, Al, Cu, Ag, Pb, Ba, Zn, Bi, $Fe^{\cdots}$, $Fe^{\cdot\cdot}$, Ca, quinine, berberine, brucine, strychnine, ephedrine, NH_2Ph, and $CO(NH_2)_2$. F. R. G.

Constitution of glauconic acids. VI. K. KRAFT (Annalen, 1937, **530**, 20—33; cf. this vol., 109).—Glauconin (I) and HI–red P at 140—150° give by reduction and hydrolysis *dihydroglauconinic acid* (II), $C_{11}H_{12}O_7$, m.p. 199—200°, which titrates tetrabasic when heated; this is stable to O_3, but its Me ester with O_3–AcOH gives methyltricarballylic acid. This and known data prove the structures $CO<^{CMe}_{O\cdot CO}>C\cdot CH_2\cdot C<^{CMe}_{O\cdot CO}>CO$ (I) and $\underset{CO_2H}{CHMe\cdot CH\cdot CH_2}\underset{CO_2H}{}$ (II). Hydrogenation (PtO_2) of the Me_2 ester of (I) gives a product, hydrolysed by NaOH to an *acid*, $^{CO\cdot CMe}_{O\quad CO}>C\cdot CH_2\cdot CH(OMe)\cdot CHMe\cdot CO\cdot CO_2H$, m.p. 195°. (I), (II), and glauconic acid (III) give only a little CO with H_2SO_4. With hot NaOH–Me_2SO_4 (III) affords by hydrolysis of an anhydride ring the *Me*$_2$ ester (IV), $C_{20}H_{26}O_8$, m.p. 185°, which by hydrogenation and subsequent hydrolysis gives *tetrahydroglauconic acid*, $C_{18}H_{24}O_7$, m.p. 178—180°, which titrates as a tribasic acid when heated, but with hot Me_2SO_4–NaOH gives the *Me*$_3$ ester (V), $C_{21}H_{30}O_8$, m.p. 112°, with some *Me*$_1$ ester, m.p. 201°. (IV) gives a *Bz* derivative, m.p. 177°, which is stable to O_3, thus proving a difference in the position of the second ethylenic linking in (I) and (III). These and facts already reported support the following formulæ and that for dihydroglauconic acid (VI).



R. S. C.

Preparation and properties of alkyl thioacetates. F. W. WENZEL, jun., and E. E. REID (J. Amer. Chem. Soc., 1937, **59**, 1089—1090).—The following *n-alkyl thioacetates* (*alkyl acetylmercaptans*) are prepared from the alkyl mercaptans by (*a*) AcCl, (*b*) hot Ac_2O–NaOAc (best for the higher members), or (*c*) Ac_2O in conc. aq. NaOH (best for volatile mercaptans): Me, b.p. 98°, Et, b.p. 116·4°, Pr, b.p. 139·8°, Bu, b.p. 163·4°, amyl, b.p. 185·1°, hexyl, b.p. 205·8°, heptyl, b.p. 227·4°, and octyl, b.p. 247°. n_D^{25}, d_4^0, and d_4^{25} are recorded. R. S. C.

Thiolacetic acids and methyl sulphate. B. HOLMBERG (Arkiv Kemi, Min., Geol., 1937, **12**, A, No. 11, 27 pp.).—$SR\cdot CH_2\cdot CO_2H$ (1/40 mol.) in aq. NaOH (*a*/40 mol.) with Me_2SO_4 (2/40 mol.) give $OH\cdot SMeR\cdot CH_2\cdot CO_2H$ (identified through $HgCl_2$ additive compounds) in amounts varying with the [NaOH]; the % yields in parenthesis are for a = 3, 2, 1, and 0. R = Me [*compound*, $SMe_2Cl\cdot CH_2\cdot CO_2H,6HgCl_2$, m.p. 188—189° (decomp.)] (58, 100, 100, 100); Et (48, 87, 100, 90); Pr$^{\alpha}$ [*compound*, $SMePr^{\alpha}Cl\cdot CH_2\cdot CO_2H,6HgCl_2$, m.p. 137—138° (decomp.)] (56, 90, 99, 91); Pr$^{\beta}$ [*compound*, $SMePr^{\beta}Cl\cdot CH_2\cdot CO_2H,6HgCl_2$, m.p. 173° (decomp.)] (44, 84, 97, 81); Bu$^{\gamma}$ (30, 62, 100, 100); Ph [*compound*, $SMePhCl\cdot CH_2\cdot CO_2H,3HgCl_2$, m.p. 121—123° (decomp.)] (11, 63, 73, 33); CH_2Ph (I) (48, 89, 94, 67); CHPhMe (II), (36, 85, 90, 65); $CH_2\cdot CH_2Ph$ (60, 94, 100, 95), and $CH_2\cdot CH{:}CHPh$ (20, 84, 90, 60). The sulphonium compounds are decomposed in neutral, acid, or alkaline solution by rise of temp., yielding $SMe\cdot CH_2\cdot CO_2H$ and ROH. (I) in addition affords $CH_2Ph\cdot SMe$ and (?) $CH_2Ph\cdot S\cdot CH_2\cdot CO_2Me$ (or $SMe\cdot CH_2\cdot CO_2CH_2Ph$) whilst (II) yields $CHPhMe\cdot S\cdot CH_2\cdot CO_2Me$ and $SMe\cdot CH_2\cdot CO_2CHPhMe$ in neutral solution and styrene in alkaline solution. F. N. W.

Fission of disulphides by alkali. IV. Mode of reaction of tertiary mercaptans and their disulphides. A. SCHÖBERL (Ber., 1937, **70**, [*B*], 1186—1193; cf. A., 1936, 1232).—The determination of SH by 18-phosphotungstic acid is described. $SH\cdot CMe_2\cdot CO_2H$ does not react with I in acid solution and irregularities are observed with $SH\cdot CPh_2\cdot CO_2H$. In alkaline solution the acids are smoothly oxidised to αα′-dimethyl-αα′-dithiopropionic acid, m.p. 198°, which is stable towards alkali and tetraphenyldithiodiacetic acid (I), decomp. (indef.) 185—186°, respectively. (I) is transformed by NaOH into $SH\cdot CPh_2\cdot CO_2OH$ and $OH\cdot S\cdot CPh_2\cdot CO_2H$ which passes into $CSPh_2$, H_2O, and CO_2. H. W.

Separation of *dl*-α-methylthiolpropionic acid into its optical antipodes. A. MELLANDER (Arkiv Kemi, Min., Geol., 1937, **12**, **B**, No. 27, 8 pp.).—Resolution is effected through the *quinine* salt (+0·33H_2O), m.p. 153·4—154·6°, or *brucine* salt (+3H_2O), m.p. 159·4—160·4°, of the *l*-acid, $[\alpha]_D^{25}$ −81·2° in H_2O, and the *quinidine* salt, m.p. 83·4—84·8°, of the *d*-acid, $[\alpha]_D^{25}$ +81·1° in H_2O. F. N. W.

Active racemate from αα′-dithio- and αα′-diseleno-dipropionic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1937, **12**, **B**, No. 22, 8 pp.).—M.p. diagrams of diseleno- (I) and dithio-propionic acid (II) are given as follows: +(I) and −(II), +(I) and +(II), −(I) and +(I), +(II) and −(II), and +(I) −(II),

and +(II) — (II). +(I) —(II) and +(II) —(II) from a continuous series of mixed crystals whilst +(I) and —(II) form a 1 : 1 mol. compound. F. N. W.

Determination of sensitivity of certain colour reactions for aldehydes and ketones. V. M. Platkovskaja and S. F. Vatkina (J. Appl. Chem. Russ., 1937, **10**, 955—959).—The lowest concns. detectable with $(NH_4)_2MoO_4$ and 50% HCl are: PhCHO 0·0005, citral 0·005, citronellal 0·05, anisaldehyde, cinnamaldehyde, CH_2O, chloral hydrate, and $COMe_2$ 0·5, *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ 1, and COMeEt and COPhMe 5%. The colorations given with phosphomolybdic acid and aq. NH_3, or *m*-$C_6H_4(NO_2)_2$ and KOH, are less intense. R. T.

Spontaneous polymerisation of liquid propaldehyde. E. J. Buckler (J.C.S., 1937, 1036).—EtCHO spontaneously polymerises to a substance of no definite b.p. and with mol. wt. corresponding with 2·8 EtCHO units. The second stage of polymerisation yields a volatile portion, $(EtCHO)_x$, and a non-volatile liquid, corresponding with 2·7 methylethylacraldehyde units. The results suggest aldol condensation. No effective stabiliser of EtCHO is known. F. R. S.

Transposition of aldoximes under the influence of Raney's nickel. R. Paul (Bull. Soc. chim., 1937, [v], **4**, 1115—1121).—This reaction (cf. this vol., 152; also observed with $Me{\cdot}[CH_2]_5{\cdot}CH{:}N{\cdot}OH$) can be used for prep. of amides; it is ascribed to presence of Fe and Al with the Ni. E. W. W.

Raman spectra of deuterium compounds of the type $CD_3{\cdot}CO{\cdot}X$.—See A., I, 345.

Use of deutero-compounds as indicators for the presence of free radicals in organic decomposition reactions. E. W. R. Steacie and W. A. Alexander (J. Chem. Physics, 1937, **5**, 372).—Mixtures of $CO(CD_3)_2$ and Me_2O were heated at 590° for 5 min. and the H_2 was separated and analysed in an attempt to establish the course of decomp. of these substances. The general courses are $CO(CD_3)_2 = CD_4 + CD_2 + CO = CD_4 + CO + 0{\cdot}5C_2D_4$, and $Me_2O = CH_4 + CH_2O =$ either (i) $CH_4 + CO + H_2$ or (ii) $CH_4 + H + CHO$. Thus if (i) is correct the H_2 should be "light," whereas if (ii) is correct the probability of the H atom extracting another atom from the ether or from the ketone is equal and the resulting H should be approx. 25% "heavy." The mean D content is 3·3% and it is concluded that CH_2O does not decompose by a free radical mechanism. The mechanism suggested by Fletcher and Rollefson (A., 1937, I, 36) for the decomp. of CH_2O through sensitisation by Me radicals from the ether decomp. also involves H atoms and is therefore probably wrong. W. R. A.

Isomerism of αβ-ethylenic ketones. I. *iso*-Butylideneacetone. R. Heilmann (Bull. Soc. chim., 1937, [v], **4**, 1064—1071).—Interaction of *iso*butaldehyde with $COMe_2$ affords sometimes *cis*- and sometimes *trans*-β-methyl-Δ^{γ}-hexen-ε-one (I) (identified as their semicarbazones). Dehydration of β-methylhexan-δ-ol-ε-one (II) with $H_2C_2O_4$ leads to analogous conflicting results (cf. A., 1930, 893; J.C.S., 1920, **117**, 324; A., 1913, i, 1165). (I) with MgEtBr and $MgPr^{\beta}Br$ affords respectively 50—55 and 70—75% of enol (cf. A., 1930, 67) and after boiling with dil. H_2SO_4 which eliminates the enol form from (I), 25—35 and 60% of enol, respectively. (I) with N_2H_4,H_2O affords 5-*methyl*-3-iso*propylpyrazoline*, b.p. 76—78°/11 mm., [oxidised to (I)], and its azine, which when hydrolysed gives (I) and a little Me *iso*amyl ketone. The crude product obtained by interaction of (I) with N_2H_4,H_2O with H_2SO_4 affords β-methyl-Δ^{β}-hexen-ε-one, the semicarbazone of which on hydrolysis (conc. $H_2C_2O_4$) gives a ketone, b.p. 152—153°/745 mm. These reactions with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ are interpreted in the light of the isomerism of the double linking. J. L. D.

***iso*Amylideneacetone.** R. Heilmann (Compt. rend., 1937, **204**, 1345—1346).—$COMe_2$ with *iso*valeraldehyde affords Me δ-methyl-Δ^{α}-pentenyl ketone (I) which with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ gives a *semicarbazidosemicarbazone*, m.p. 205°, a *monosemicarbazone* (II), m.p. 113—114°, and a gum (III) which probably contains other stereoisomeric forms of (II). Hydrolysis of (II) affords (I), which yields the same products with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$. When (II) is heated it affords 2-carbamyl-5-methyl-3-*iso*butylpyrazoline (IV). (III) with boiling dil. acid affords (IV) and 5-*methyl*-3-iso*butylpyrazoline*, b.p. 91—92°/10 mm., which when oxidised and then hydrolysed gives Me *iso*hexyl ketone. J. L. D.

Isomerism of αβ-ethylenic ketones. II. *iso*-Amylideneacetone. R. Heilmann (Bull. Soc. chim., 1937, [v], **4**, 1072—1080; cf. preceding abstract).—$MgBu^{\beta}Br$ with $CH(OEt)_3$ affords δδ-diethoxy-β-methylbutane, hydrolysed (dil. H_2SO_4) to *iso*valeraldehyde (*semicarbazone*, m.p. 131—132°); this with $COMe_2$ followed by removal of H_2O gives pure β-methyl-Δ^{δ}-hepten-ζ-one (I), which with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ affords a semicarbazone (II), m.p. 113—114°, and another product, gradually converted by recrystallisation into (II) and a gum (III). Hydrolysis of (II) with $H_2C_2O_4$ gives a ketone which with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ reacts exactly as does (I) and indicates that Me β-*iso*butylidene-ethyl ketone is not an impurity in (I) which gives rise to (III). When (II) is heated to near its m.p., part of it is changed to a gum, hydrolysed to (I) and an unhydrolysable residue (a pyrazoline?) which is oxidised to a ketone [semicarbazone, m.p. 153—154° (IV)]. (III) probably contains 2-carbamyl-5-methyl-3-*iso*butylpyrazoline, a cyclised form of (I), for it is hydrolysed (HCl) to 5-methyl-3-*iso*butylpyrazoline, which is oxidised spontaneously to Me *iso*hexyl ketone [semicarbazone, m.p. 153—154°, identical with (IV)]. J. L. D.

(A) Alkylation of ketones by means of sodamide. Propylation of ketones. (B) Synthesis of *tert.*-alcohols of the general formulæ $OH{\cdot}CMe_2{\cdot}CHR_2$ and $OH{\cdot}CMe_2{\cdot}CR_3$, by the action of magnesium methyl bromide on highly branched ketones. I. N. Nazarov (J. Gen. Chem. Russ., 1937, **7**, 688—692, 693—701).—(A) Pinacolin in C_6H_6 is boiled with $NaNH_2$ until evolution of NH_3 ceases, when $Pr^{\alpha}I$ is added, to yield ββ-*dimethylheptan-γ-one*, b.p. 168—170°, which when similarly treated gives ββ-*dimethyl*-δ-*propylheptan-γ-one*, b.p. 211—213°.

ββγ-, b.p. 178—181°, and βδδ-*tri*-, b.p. 178—181°, and ββδδ-*tetra-methylheptan-γ-one*, b.p. 193—196°, δδζζ-*tetramethylnonan-ε-one*, b.p. 229—232°, ββδε-*tetra*-, b.p. 170—173°, and ββδδε-*penta-methylhexan-γ-one*, b.p. 195—197°, and γε-*dimethyl*-, b.p. 170—173°, and γε-*dimethyl-γ-ethyl-heptan-δ-one*, b.p. 204—207°, have been prepared analogously.

(B) The following alcohols have been prepared from the above (and similar ketones) by the Grignard reaction: ββγδ-, b.p. 190—193°, and βγδδ-*tetramethyl*-, b.p. 197—199°, ββγ-*trimethyl-δ-ethyl*-, b.p. 208—211°, ββγδε-, b.p. 207—210°, and ββγδδ-*pentamethyl*-, b.p. 237—240°, ββγ-*trimethyl-δδ-diethyl*-, b.p. 252—256°, and ββγδδε-*hexamethyl-hexan-γ-ol*, b.p. 235—238°, γδε-*trimethyl-γ-ethyl*-, b.p. 235—238°, and γγδεε-*penta-methyl-heptan-δ-ol*, b.p. 243—246°, ββγ-*trimethyl-δ-propyl*-, b.p. 234—237·5°, ββγδ-, b.p. 212—215°, and βγδδ-*tetramethyl*-, b.p. 215—217°, and ββγδδ-*penta-methyl-heptan-γ-ol*, b.p. 233—235°, and δδεζζ-*penta-methylnonan-ε-ol*, b.p. 266—269°. R. T.

(A) **Action of magnesium *tert.*-butyl chloride and magnesium butyl bromide on ethyl *iso*-valerate and butyrate.** A. D. Petrov and M. S. Malinovski. (B) **Action of magnesium *sec.*-propyl chloride, *sec.*-butyl bromide, and *sec.*-amyl chloride on ethyl octoate.** A. D. Petrov and D. N. Andreev (J. Gen. Chem. Russ., 1937, 7, 565—569, 570—575).—(A) $MgBu^{\gamma}Cl$ yields $COBu^{\beta}Bu^{\gamma}$ and $COBu^{\beta}_2$ with $Bu^{\beta}CO_2Et$ (I) in Et_2O, and $COPr^{\alpha}Bu^{\gamma}$ and $COPr^{\alpha}_2$ with $Pr^{\alpha}CO_2Et$ (II). $MgBu^{\alpha}Br$ (III) gives *di*-n-*butylisobutylcarbinol*, b.p. 140—145°/10 mm., with (I), and $CPr^{\alpha}Bu^{\alpha}_2{\cdot}OH$ with (II). It is concluded that anomalous formation of ketones in place of the expected *tert.*-alcohols is associated with presence of Bu^{γ} in the Grignard reagent.

(B) $n\text{-}C_7H_{15}{\cdot}CO_2Et$ (IV) and (III) in Et_2O yield *di*-n-*butyl*-n-*heptylcarbinol*, b.p. 131—135°/5 mm., which gave a mixture of ε-n-*butyl*-Δ^{ϵ}- and -Δ^{δ}-*dodecene*, b.p. 261—267°, when dehydrated by heating with $H_2C_2O_4$ or K xanthate. (IV) yields chiefly $CO(C_7H_{15})_2$ (V), together with *sec.*-amyl heptyl ketone, with *sec.*-$C_5H_{11}{\cdot}MgCl$, (V) and *sec.*-butyl heptyl ketone with $MgBu^{\beta}Br$, and (V) and Pr^{β} heptyl ketone with $MgPr^{\beta}Cl$. R. T.

Hydrogenation of certain oximes by the aid of Raney's nickel. R. Paul (Bull. Soc. chim., 1937, [v], 4, 1121—1125).—In the hydrogenation of ald-oximes at room temp. and normal pressure, Raney's Ni behaves normally, giving primary, *sec.*, and (?) *tert.* amines; with $CMe_2{:}N{\cdot}OH$, $CMeEt{:}N{\cdot}OH$, $CPhMe{:}N{\cdot}OH$, $CPh_2{:}N{\cdot}OH$, and *cyclo*hexanoneoxime, at 70—85°/50—60 atm., however, only primary amines are formed. E. W. W.

Dichromate method of determination of reducing sugars. S. M. Strepkov (Ukrain. Chem. J., 1937, **12**, 105—113).—10 ml. of solution are heated for 15 min. at 100° with 20 ml. of 0·02*N*-$K_3Fe(CN)_6$ in 4% Na_2CO_3, the solution is cooled, 15 ml. of 5% H_2SO_4 are added, and the solution is titrated with 0·05*N*-$K_2Cr_2O_7$ ($NHPh_2$ indicator). R. T.

Action of organic bases on sugars and their derivatives. H. Vogel (Ber., 1937, **70**, [*B*], 1193—1202).—When heated with a 10-fold excess of piperidine (I) glucose yields solutions with a powerful reducing action towards methylene-blue and dichlorophenol-indophenol which disappears when the solution is acidified. C_5H_5N does not behave analogously. The formation of 1-piperidylglucose is considered inadequate to account for the properties of the compound and the formation of 1 : 2-*dienolglucose*-1-*piperidide* is postulated. Protracted heating of the solution causes decomp. into strongly coloured materials. Similar reducing dienols are derived from fructose, mannose, galactose, lactose, and maltose whereas sucrose (II), raffinose, starch, inulin, cellulose, β-glucosan, α- and β-methylglucoside are indifferent. [The sparing solubility of (II) in boiling (I) can be used for its separation from other sugars, particularly from hexoses.] The free 1 : 2-dienols are obtained when the sugars are warmed with (I) in H_2O. Monocarboxylic acids and their esters derived from sugars do not give enols with (I). Analogously to the production of ascorbic acid from esters of α-keto-acids, glucosone hydrate tetra-acetate acquires when treated with (I) a greatly enhanced activity which persists for a time in acid solution but ultimately diminishes and almost disappears. Betaine and CNS-compounds have no enolising action whereas salts of guanidine closely resemble (I). Sugar acetates suffer partial loss of Ac and afford enols. Hexose anhydrides with bridge between $C_{(1)}$ and any other C are not enolised and *al*-glucose penta-acetate does not afford reducing substances in acid or alkaline medium. H. W.

Crystalline acetal derivatives of *d*-arabinose. (Miss) E. M. Montgomery, R. M. Hann, and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 1124—1129).—With 3 : 7 AcOH–Ac_2O containing 8% of $ZnCl_2$ β-methyl-*d*-arabinoside triacetate gives by slow acetylating rupture of the ring an approx. 1 : 1 mixture of two isomeric d-*arabinose Me semiacetal penta-acetates* (I) and (II), m.p. 76° and 68—70°, $[\alpha]_D^{20}$ +26·9° and +34·7° in $CHCl_3$, respectively; 0·16% of H_2SO_4 in the same solvent gives rapidly the same two penta-acetates with 8% of the cyclic β-*d*-arabinose tetra-acetate, $[\alpha]_D^{20}$ −147·2°; 4% of H_2SO_4 in the same solvent causes complete hydrolysis of OMe, giving 11% of the tetra-acetate and 56% of *aldehydo*-d-*arabinose hexa-acetate*, m.p. 89·5° (corr.), $[\alpha]_D^{20}$ +28·1° in $CHCl_3$. The same mixtures are obtained from pure (I) or (II) by the appropriate reagents. With $AlCl_3$ in $CHCl_3$ (I) and (II) yield isomeric 1-*chloro*-d-*arabinose Me semiacetal* 2 : 3 : 4 : 5-*tetra-acetates*, m.p. 70° and 73° (corr.), $[\alpha]_D^{20}$ +28·8° and +52·5° in $CHCl_3$, respectively, both converted by Ag_2O–MeOH into d-*arabinose* Me_2 *acetal tetra-acetate*, m.p. 80° (corr.), $[\alpha]_D^{20}$ +21·8° in $CHCl_3$, and thence by MeOH–$Ba(OMe)_2$ into d-*arabinose* Me_2 *acetal*, m.p. 122°, $[\alpha]_D^{20}$ −18·5° in H_2O, and finally (HCl) into *d*-arabinose and methyl-*d*-arabinosides. R. S. C.

Crystalline α-methyl-*d*-arabinofuranoside. (Miss) E. M. Montgomery and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 992—993).—When the reaction of *d*-arabinose with MeOH–HCl is stopped at the time of max. positive [α], there is obtained 9% of α-*methyl*-d-*arabinofuranoside*, m.p. 65—67°, $[\alpha]_D^{20}$ +123° in H_2O, the structure of which is proved

by its rapid hydrolysis by aq. acid and by HIO_4–Br degradation (see below). R. S. C.

Two new methyl-*l*-fucoside triacetates. J. Minsaas (Rec. trav. chim., 1937, **56**, 623—626).—α-Methyl-*l*-fucoside is converted by Ac_2O and C_5H_5N at 0° into *α-methyl-l-fucoside triacetate*, m.p. 74°, $[\alpha]_D^{20}$ −151° in $CHCl_3$. *β-Methyl-l-fucoside triacetate* has m.p. 99°, $[\alpha]_D^{20}$ +7·0° in $CHCl_3$. H. W.

Two forms of anhydrous *l*-rhamnose. Preparation of crystalline *l*-rhamnose β-tetra-acetate. E. L. Jackson and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 1076—1078).—Rhamnose monohydrate with hot BaO–$COMe_2$ or dry EtOH gives a form (I), m.p. 112·5—113·5° (corr.), $[\alpha]_D^{20}$ +14·6° → +8·9° in H_2O, which, when seeded in $COMe_2$, affords β-rhamnose (II), anhyd., m.p. 123·5—124·5° (corr.), $[\alpha]_D^{20}$ +38·4° in H_2O [tetra-acetate, m.p. 98·5—99°, $[\alpha]_D^{20}$ +13·4° in $CHCl_3$, prepared in 89% yield by Ac_2O–C_5H_5N at −12° to 0°, or in 43% yield from (I)]. (I) is an αβ mol. compound, 1 : 1 if the above [α] for (II) is correct, 3 : 2 if Minsaas' val., +44° (A., 1934, 1337), for (II) is correct. R. S. C.

Configuration of the pyranoses in relation to their properties and nomenclature. H. S. Isbell (J. Res. Nat. Bur. Stand., 1937, **18**, 505—534).—Methods of comparison of the optical rotation, mutarotation, and Br oxidation measurements originally employed with the hexoses (A., 1930, 581) have been extended to the heptoses, and reveal similarities in the properties of sugars classified in the following groups: α-*l*-arabinose, α-*l*-fructose, α-*d*-galactose, α-*d*-α-mannoheptose, and α-*l*-β-galoheptose; β-*l*-arabinose,$CaCl_2$,$4H_2O$, β-*d*-galactose and β-*d*-α-mannoheptose; β-*d*-glucose and β-*l*-β-galoheptose; α-*d*-lyxose, α-*d*-mannose, and α-*l*-α-galoheptose; β-*d*-gulose and β-*d*-α-glucoheptose; β-*d*-idose and β-*d*-β-glucoheptose. The evidence suggests that the pyranose ring is strainless and dissymmetric, and that the sugars in each group have similar ring conformations. The structural characteristics of the α- and β-sugars are discussed in relation to their reactions and nomenclature. α-, $[\alpha]_D^{20}$ +120°, and β-*d*-α-mannoheptose are described. F. N. W.

Molecular refraction of α-*d*-galactose. C. N. Riiber and N. A. Sörensen (Kgl. Norske Videns. Selsk. Skr., 1935, No. 22, 24 pp.; Chem. Zentr., 1936, i, 3513).—The difference in mol. refraction for α-methylgalactoside and α-galactose is 7·49, as with other sugars. H. N. R.

Determination of invert sugar (and other reducing sugars) without filtration of cuprous oxide. E. Roboz-Rosenblüh and G. Vavrinecz (Magyar chem. Fol., 1935, **41**, 192—195; Chem. Zentr., 1936, i, 3374).—An iodometric method is described. H. N. R.

Ketone sugar series. VII. Action of titanium tetrachloride on the methylfructoside acetates. E. Pacsu and F. B. Cramer (J. Amer. Chem. Soc., 1937, **59**, 1059—1062; cf. this vol., 230).—β-Methylfructoside tetra-acetate and $TiCl_4$ in $CHCl_3$ give a yellow halochromic salt, from which only the original β-tetra-acetate is recovered. The α-tetra-acetate gives β-acetochlorofructose (I) and some unchanged material, but no β-tetra-acetate. The "ortho-ester" form of methylfructoside tetra-acetate with $TiCl_4$ gives (I) and with HBr–AcOH–$CHCl_3$ gives β-acetobromofructose. The "ortho-ester" methylmaltoside hepta-acetate with $TiCl_4$ gives α-acetochloromaltose and with HBr gives α-acetobromomaltose. The acetohalogeno-derivatives of fructose and turanose probably have normal structure, but the structure of turanose is doubtful. R. S. C.

Preparation of penta-acetylketofructose. F. B. Cramer and E. Pacsu (J. Amer. Chem. Soc., 1937, **59**, 1148).—Prep. of ketofructose penta-acetate by $ZnCl_2$ and Ac_2O in 50% yield is described. For high yields conditions must be those facilitating preliminary formation of the β-tetra-acetate. R. S. C.

Reactions in concentrated sulphuric acid. II. Influence of gases.—See A., I, 417.

New disaccharide, labiose. S. M. Strepkov (Ber., 1937, **70**, [*B*], 1166—1167).—Extraction of the root nodules of *Eremostachys labiosa* with boiling 96% EtOH affords *labiose* (I), m.p. 156—157°, $[\alpha]_D^{18}$ +140·82° in H_2O (non-mutarotatory). (I) is not fermentable with yeast and reduces Fehling's solution only after hydrolysis with dil. HCl at about 68°. It is oxidised by HNO_3 (*d* 1·15) at 69—70° to mucic acid. It is derived from 1 mol. of galactose and 1 mol. of a ketose. H. W.

Cleavage of the carbon chain of glucosides by oxidation. Method for determining ring-structures and α- and β-configurations of glucosides. E. L. Jackson and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 994—1003).—The ring-structure of glucosides is determined by oxidation by HIO_4 to dialdehydes, which with aq. Br in the presence of metallic carbonates give salts of dicarboxylic acids retaining the ether linking originally present in the glucoside. If C is removed during the oxidation, this is disclosed by the amount of HIO_4 consumed. Structures assigned to the resultant acids are confirmed by hydrolysis. The ring-structures thus assigned are in harmony with the results of methylation. α-Methyl-*d*-aldohexopyranosides afford the same *Sr D'-methoxy*-D-*hydroxymethyldiglycollate* (I), $Sr\langle^{O\cdot CO\text{—}C^*H(OMe)}_{O\cdot CO\cdot CH(CH_2\cdot OH)}\rangle O$, $[\alpha]_D^{20}$ −53° in H_2O (corresponding *acid*, not isolated, $[\alpha]_D^{20}$ +25·5° in H_2O), examples investigated being α-methyl-*d*-manno- (II), -galacto-, -gluco-, and -gulopyranoside. The prefix *D'* (or *L'*) refers to the Fischer nomenclature of $C_{(1)}$ of the glucoside and the C marked * in (I); *D* (or *L*) refers to the other C to which the etheral O is attached. The syrupy dialdehyde, CHO·CH(OMe)·O·CH(CHO)·CH_2·OH, produced as intermediate product in the above cases has $[\alpha]_D^{20}$ about +120°. This limits the ring-structure of the above glucosides to the pyranoside or septanoside type; the former is indicated by formation of α-methyl-*d*-mannuronic acid [*brucine*, m.p. 232° (decomp.), $[\alpha]_D^{20}$ −2·5° in H_2O, and K salt, +0·5EtOH, $[\alpha]_{5780}^{20}$ +47·1° in H_2O] as a by-product in the $Ba(OBr)_2$-oxidation of (II) and by formation of (I) from methyl-*d*-arabinofuranoside, $[\alpha]_D^{20}$ +123°. β-Methyl-*d*-aldohexo-(-galacto- and -gluco-)pyranosides afford a dialdehyde, $[\alpha]_D^{20}$ −148° to −151°, and thence *Ba* L'-

methoxy-D-*hydroxymethyldiglycollate*, $+2H_2O$, $[\alpha]_D^{20}$ +35·9° (corresponding *acid*, $[\alpha]_D^{20}$ +45° in H_2O). α-Methyl-*d*-arabino- and -xylo-pyranoside give the same dialdehyde, $[\alpha]_D^{20}$ about +125° in H_2O, and thence *Sr* D′-*methoxydiglycollate*, $Sr<\begin{matrix}O\cdot CO\cdot CH(OMe)\\ O—CO—CH_2\end{matrix}>O$, $[\alpha]_D^{20}$ −55·5° in H_2O (corresponding *acid*, $[\alpha]_D^{20}$ about −125° in H_2O); β-methyl-*d*-arabino- and -xylo-pyranoside afford the optical antipodes thereof, characterised particularly as *Sr* L′-*methoxydiglycollate*, $[\alpha]_D^{20}$ +55·5°. α-Methyl-*l*-rhamnoside gives the *dialdehyde*, CHO·CHMe·O·CH(OMe)·CHO, m.p. 101—102°, $[\alpha]_D^{20}$ −143° in H_2O. R. S. C.

The alkaloid of *Solanum auriculatum*, Ait. A. R. Anderson and L. H. Briggs (J.C.S., 1937, 1036—1037).—"Solanine," the gluco-alkaloid of *S. auriculatum*, is probably identical with solanine-*s*, from *S. sodomeum* (Oddo, A., 1911, i, 670), since the aglucon prepared by hydrolysis (HCl–EtOH) yields derivatives identical with those obtained by Oddo. J. D. R.

Pigments of cotton flowers. IV. Constitution of herbacitrin and herbacetin. K. Neelakantam and T. R. Seshadri (Proc. Indian Acad. Sci., 1937, **5**, A, 357—364).—Herbacitrin (a flavonol glucoside from *Gossypium herbaceum*) (*octa-acetate*, m.p. 214—216°) on hydrolysis yields *herbacetin*, m.p. 280—283° (*penta-acetate*, m.p. 192—193°), and when oxidised by air in KOH yields *p*-OH·C_6H_4·CO_2H. Its colour reactions and recent synthesis show that it is the 7-glucoside of 3 : 5 : 7 : 8 : 4′-pentahydroxyflavone. A. Li.

Highly polymerised compounds. CLXI. Determination of the mol. wt. of polysaccharides by the terminal group method. H. Staudinger and E. Husemann (Ber., 1937, **70**, [*B*], 1451—1457).—Haworth's investigations in conjunction with viscosimetric and osmometric measurements indicate a thread-like form for the macromols. of cellulose whereas those of starch are extended but branched and those of glycogen are approx. spherical. The end-group method leads to a determination of mol. wt. only in the case of thread mols. Misleading results are obtained with greatly branched mols. The applicability of the method to cellulose is discussed. H. W.

Micro-modification of Pflüger's method of determining glycogen. T. von Brand (Skand. Arch. Physiol., 1936, **75**, 195—198).—The method is based on adsorption of the glycogen (I) from alkaline solution on $Zn(OH)_2$ prepared *in situ* by adding mixed aq. NaCl and $ZnSO_4$. ≮2—3 mg. of (I) can be determined. Nutr. Abs. (*m*)

Constitution of starch. I. Homogeneity of natural starch. W. S. Reich and A. F. Damansky (Bull. Soc. Chim. biol., 1937, **19**, 158—189; cf. A., 1933, 811, 1038).—Methods of esterifying starch are criticised on the grounds that modification in mol. structure occur. Potato starch on acetylation affords a mixture of Ac_2 (I) (82%) and Ac_3 derivative (II) (16%). Hydrolysis of (I) affords a substance similar to natural starch ("amylogen") and that of (II) a different substance ("amylon"; the "amylose" of most authors). Acetolysis of (I) yields (II). Comparative data for benzoylation and cinnamylation and also for maize starch are given. F. O. H.

Constitution of starch. II. Relationship between starch and the substances known as "amylopectin" and amylose, and the action of water on starch. W. S. Reich and A. F. Damansky (Bull. Soc. Chim. biol., 1937, **19**, 357—391).—The methods applied previously to potato starch are extended to the investigation of "amylopectin" and "amylose" (Ling and Nanji, J.C.S., 1923, **123**, 2666). The former consists of amylogen and amylon in varying proportions depending on the method of prep.; the latter is amylon formed by hydrolysis of the amylogen. A. L.

Starch. VIII. Trimethylstarch. K. Hess and K. H. Lung (Ber., 1937, **70**, [*B*], 1259—1262).—Potato starch is partly methylated with NaOH and Me_2SO_4 and the product is freed from salts by thorough washing with H_2O and then by cautious treatment with light petroleum (I) and MeOAc, after which it is pptd. from solution by an excess of (I). The substance is dissolved in anisole and treated with Na in liquid NH_3; after removal of NH_3, the solution is heated with MeI at 60—70°, thereby giving cryst. *trimethylstarch*, $[\alpha]_D^{20}$ +210° in $CHCl_3$, +187° in C_6H_6. H. W.

Highly polymerised compounds. CLV. Constitution of glycogen. H. Staudinger and E. Husemann (Annalen, 1937, **530**, 1—20; cf. this vol., 278).—Solutions of pure P-free glycogen (I), $[\alpha]_D$ +200° in HCO·NH_2, in H_2O, $CaCl_2$, and HCO·NH_2, obey van 't Hoff's law (osmosis) and thus (I) is not a micelle-colloid. In the three solvents the degree of polymerisation is about 1750. 2*N*-HCl at 100° (2 min.) degrades (I) to a substance (II), $[\alpha]_D$ +200° in HCO·NH_2, the degree of polymerisation of which is 407—420. Fractional addition of MeOH to a HCO·NH_2 solution of (I) gives a material (III), $[\alpha]_D$ +198° in HCO·NH_2, the degree of polymerisation of which is about 5000. C_5H_5N–Ac_2O gives triacetates, $[\alpha]_D$ +156°, +150°, and +160°, respectively, in $CHCl_3$, of (I), (II), and (III); these esters and the glycogens recovered therefrom by hydrolysis in absence of O_2 have unchanged degree of polymerisation. These facts prove that (I) is a polymeric-homologous series of substances, which reacts as an individual in the classical sense and that the macro-mol. is a spherical colloid. η of (I), (II), and (III) are identical and very low and independent of concn. up to 5%, which confirms the spherical nature of the mol., which is shown to be hydrated ($5H_2O$ for each C_6 unit). From the above and Haworth's data it is concluded that the mol. consists of a central chain of glucosidically bound glucose units, carrying glucosidically, on $C_{(2)}$, $C_{(3)}$, and $C_{(6)}$ of each unit, chains of 12—18 glucosidically bound glucose units. In (I) the central chain contains 30—40 glucose units, in (III) a larger and in (II) a smaller no. Starch is intermediate between (I), a spherical colloid giving only sols, and cellulose, a thread colloid giving only gels. The above conception also accounts for the powdery nature of (I), its inability to swell, its low η, and obedience to the Hagen–Poiseuille law. R. S. C.

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

Synthesis of spermidine and analogous triamines of the fatty series. J. VON BRAUN and W. PINKERNELLE (Ber., 1937, 70, [*B*], 1230—1240).—A profitable synthesis of spermidine has been realised along the lines $NHBz\cdot[CH_2]_4\cdot NHBz \rightarrow NHBz\cdot[CH_2]_4\cdot Cl \rightarrow NHBz\cdot[CH_2]_4\cdot NH_2 \rightarrow NHBz\cdot[CH_2]_4\cdot NH\cdot[CH_2]_3\cdot OPh \rightarrow NH_2\cdot[CH_2]_4\cdot NH\cdot[CH_2]_3\cdot Br \longrightarrow NH_2\cdot[CH_2]_4\cdot NH\cdot[CH_2]_3\cdot NH_2$. Simplification could not be effected by use of $NHBz\cdot[CH_2]_3\cdot Br$ or $o\text{-}C_6H_4(CO)_2N\cdot[CH_2]_3\cdot Br$ but the use of their higher homologous in the synthesis of analogous amines is very advantageous. $OPh\cdot[CH_2]_3\cdot Br$ and benzoylputrescine (I) at 100° yield *γ-phenoxypropyl-δ′-benzamidobutylamine*, b.p. 235°/0·4 mm. (*hydrobromide*, m.p. 167°; non-cryst. *picrate*; *hydrochloride*, m.p. 198°, best obtained from $OPh\cdot[CH_2]_3\cdot NH_2$ and $NHBz\cdot[CH_2]_4\cdot Cl$ in EtOH). The base and its salts are transformed by fuming HBr at 125° into γ-bromopropylputrescine dihydrobromide, m.p. 231° (corresponding *picrate*, m.p. 159°), converted by prolonged action of liquid NH_3 into *spermidine*, $NH_2\cdot[CH_2]_4\cdot NH\cdot[CH_2]_3\cdot NH_2$, b.p. 128—130°/14 mm. (picrate, m.p. 211°; aurichloride, m.p. 222°). Benzoylcadaverine and $OPh\cdot[CH_2]_3\cdot Br$ afford *γ-phenoxypropyl-ε′-benzamidoamylamine*, m.p. 67° (*hydrobromide*, m.p. 153°; non-cryst. *picrate*; *hydrochloride*, m.p. 180°), converted by conc. HCl at ≯100° into *γ-phenoxypropylcadaverine*, b.p. 155°/0·4 mm. (*dihydrochloride*, m.p. 265°), whence the unstable *γ-bromopropylcadaverine* (*dihydrobromide*, m.p. 203°; *picrate*) and *γ-aminopropyl-ε′-aminoamylamine* (as-*homospermidine*), b.p. 138°/14 mm. (*trihydrochloride*, m.p. 223—227°; *platinichloride*; *aurichloride*, m.p. 220°; *picrate*, $C_{26}H_{30}O_{21}N_{12}$, m.p. 182°). (I) and $NHBz\cdot[CH_2]_4\cdot Cl$ give *di-δ-benzamidobutylamine hydrochloride*, m.p. 230°, transformed by conc. HCl at 130° into *di-δ-aminobutylamine* (s-*homospermidine*), b.p. 146°/13 mm., m.p. 16—17° (*trihydrochloride*, m.p. 287°; *picrate*, m.p. 249°; aurichloride, m.p. 215°). *δ-Benzamidobutyl-ε′-benzamidoamylamine*, m.p. 136° (*hydrochloride*, m.p. 188°), from (I) and $NHBz\cdot[CH_2]_5\cdot Cl$, is converted by HCl at 130—140° into *δ-aminobutyl-ε′-aminoamylamine*, b.p. 165—166°/14 mm., m.p. 40° (*trihydrochloride*, m.p. 269°; *aurichloride*; *picrate*, m.p. 192°). Di-ε-benzamidoamylamine, b.p. 172°/14 mm., m.p. 25°, gives a *trihydrochloride*, decomp. 291—293°, *aurichloride*, decomp. 203°, and *picrate*, m.p. 186°. $OPh\cdot[CH_2]_2\cdot Br$ and EtOH–NH_3 yield $NH([CH_2]_3\cdot OPh)_2$, converted by conc. HBr at 130° into *di-γ-bromopropylamine hydrobromide*, m.p. 199°, which with liquid NH_3 affords *di-γ-aminopropylamine*, b.p. 115°/14 mm. (*trihydrochloride*, m.p. 254°; *aurichloride*, m.p. 203°; *picrate*, m.p. 230°). $OPh\cdot[CH_2]_4\cdot Br$ and $NHBz\cdot[CH_2]_5\cdot NH_2$ in EtOH give *β-phenoxyethyl-ε′-benzamidoamylamine hydrobromide*, m.p. 158°, in modest yield; the corresponding *hydrochloride* has m.p. 180°. When distilled the free base decomposes to $NHBz\cdot[CH_2]_5\cdot NH_2$ and $CH_2{:}CH\cdot OPh$. The salts are transformed by HBr at 120° into *β-bromoethyl-ε′-aminoamylamine dihydrobromide*, m.p. 180°, which with liquid NH_3 affords a mixture of di-ε-aminoamylpiperazine and *vinyl-ε-aminoamylamine*, b.p. 85°/12 mm., hydrogenated to *ethyl-ε-aminoamylamine* (*dihydrochloride*, m.p. 210°). $OPh\cdot[CH_2]_2\cdot Br$ and $NHBz\cdot[CH_2]_4\cdot NH_2$ yield *β-phenoxyethyl-δ′-benzamidobutylamine hydrobromide* (corresponding *hydrochloride*, m.p. 191°), which give *β-phenoxyethyl-δ′-benzamidobutylamine*, m.p. 58° (*picrate*, m.p. 112°), whence *β-bromoethyl-δ′-aminobutylamine dihydrobromide*, m.p. 197°, which with liquid NH_3 gives complex products and *vinyl-δ-aminobutylamine*, b.p. 73°/13 mm.

H. W.

Amino-alcohols derived from pentaerythritol. E. FOURNEAU, J. MATTI, and Y. DUNANT (Bull. Soc. chim., 1937, [v], **4**, 1155—1157).—Compounds, $OH\cdot CH_2\cdot C(CH_2\cdot NR_2)_3$ and $(OH\cdot CH_2)_2C(CH_2\cdot NR_2)_2$, are prepared from the amines and bromohydrins in C_6H_6 at 130—140°. The following are described. *ββ-Di(methylaminomethyl)propane-αγ-diol*, m.p. 40°, b.p. 185°/25 mm. (*dihydrobromide*, m.p. 214°; *dihydrochloride*, m.p. 198°); *ββ-bis(dimethylaminomethyl)propane-αγ-diol*, b.p. 160—162°/24 mm. (*dihydrochloride*, m.p. 208°, and its *Bz* derivative, m.p. 224°); *ββ-bis(dimethylaminomethyl)-αγ-propylene di-α′-acetoxyphenylacetate dihydrochloride*, m.p. 212°; *ββ-di(piperidinomethyl)propane-αγ-diol*, m.p. 84°, b.p. 198°/4·5 mm. (*dihydrochloride*, m.p. 251°). ββ-Di(bromoethyl)propane-αγ-diol with $NHEt_2$ in C_6H_6 at 118° gives *αγ-epoxy-β-hydroxymethyl-β-diethylaminomethylpropane*, $O<\begin{matrix}CH_2\\CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot OH\\CH_2\cdot NEt_2\end{matrix}$, b.p. 132°/14 mm. (*hydrochloride*, m.p. 135·5°, and its *Bz* derivative, m.p. 142°), with ββ-bis(diethylaminomethyl)propane-αγ-diol. $(CH_2Br)_3C\cdot CH_2\cdot OH$ and NH_2Me in C_6H_6 at 150° give the *hydrobromide* of *γγ′γ″-tri(methylamino)tert.-amyl alcohol*, b.p. 142°/15 mm. (*hydrochloride*, m.p. 229°, or, from MeOH, 155°). *Tri(dimethylamino)tert.-amyl alcohol*, b.p. 125°/13 mm. (*trihydrochloride*, m.p. 238°), is also prepared.

E. W. W.

Oxidation of hexosamines: *d*-glucosamine and *d*-glucosamic acid. R. M. HERBST (J. Biol. Chem., 1937, **119**, 85—91).—Either *d*-glucosamine or *d*-glucosamic acid in aq. NaOH is oxidised by chloramine-*T* at 37·5° to *d*-arabinose and *d*-erythrose, with traces of HCN. Acetyl-*d*-glucosamine is not oxidised under these conditions.

E. W. W.

Action of diazomethane on amino-acids. R. KUHN and W. BRYDOWNA (Ber., 1937, 70, [*B*], 1333—1341).—Methylation is effected in homogeneous system by passing gaseous CH_2N_2 into the NH_2-acid in H_2O. In anhyd. Et_2O most NH_2-acids are very sparingly sol. In moist Et_2O the products resemble those obtained in H_2O. NH_2-acids which according to measurements of dissociation and dielectric const. do not form zwitterions in H_2O give exclusively the corresponding Me esters. Conversely many NH_2-acids which are present almost exclusively as zwitterions in H_2O afford a mixture of betaine and Me ester. The presence of zwitterions is a necessary but not sufficing condition for betaine formation with CH_2N_2. The observations are generally explicable on the assumption that in the equilibrium, zwitterion $\rightleftharpoons$ NH_2-acid, the latter reacts with the greater rapidity with CH_2N_2. Frequently the difference is so great that the Me ester is formed as main product when according to physical measurements

>1% of the NH_2-acid exists as true carboxylic acid. The behaviour towards CH_2N_2 cannot be predicted from the physical consts. Thus glycine gives solely betaine whereas alanine (I) gives about equal amounts of betaine and Me ester. *l*-Leucine, *dl*-phenylalanine, *l*-proline, and *l*-hydroxyproline resemble (I). *o*-$NMe_2 \cdot C_6H_4 \cdot CO_2H$, which forms zwitterions in H_2O and can be titrated only with CH_2N_2, gives with gaseous CH_2N_2 in H_2O 18% of anthranilbetaine and 75% of *o*-$NMe_2 \cdot C_6H_4 \cdot CO_2Me$, whilst in anhyd. Et_2O the latter is formed in 97% yield. 5-Bromo-*o*-dimethylaminobenzoic acid gives 70% of the *Me* ester, b.p. 153°/6·5 mm., and 20% of *betaine*, m.p. 130°. 2 : 3-$NHMe \cdot C_6H_3(OMe) \cdot CO_2H$ in H_2O and Et_2O affords the corresponding Me ester. NH_2-acids which contain comparable amounts of ion and betaine give only the corresponding Me ester (pyridine-2- and -3-carboxylic acid; *o*-, *m*-, and *p*-$NH_2 \cdot C_6H_4 \cdot CO_2H$); these acids can be titrated sharply in H_2O. With aminosulphonic acids the presence of minute amounts of $NH_2 \cdot R \cdot SO_3H$ causes marked electrolytic conductivity, acid reaction and titratability in H_2O. Hence a sharply titrated acid $^+NH_3 \cdot SO_3^-$ gives exclusively $^+NMe_3 \cdot SO_3^-$. *p*-$NH_2 \cdot C_6H_4 \cdot SO_3H$ gives $^+NMe_3 \cdot C_6H_4 \cdot SO_3^-$ and (?) the Me ester. If SO_3H is paired with a strong aliphatic NH_2 as in taurine, titratability in H_2O is lost and a complete analogy with glycine is presented and *taurobetaine* $NMe_3 \cdot CH_2 \cdot CH_2 \cdot SO_3^-$ is almost quantitatively obtained. The simplest NH_2-phenols do not give zwitterions so that the production of *o*-Me ethers is observed with *o*- and *p*-$NH_2 \cdot C_6H_4 \cdot OH$, the yields being 40% and 70%, respectively; the remainder passes into brown condensation products. In anhyd. Et_2O reaction between CH_2N_2 and NH_2-phenols is not observed. H. W.

Action of mercuric oxide on glycine in an alkaline medium. R. Truhaut (Compt. rend., 1937, **204**, 1348—1349; cf. A., 1933, 292).—5% glycine reduces HgO (8 mols.) in boiling *N*-NaOH with the formation of NH_3, glycollic acid, and $H_2C_2O_4$. CO_2, HCN, HCO_2H, and glyoxylic acid (?) are also formed. J. L. D.

Nature of the compounds of tyrosine with polysaccharides. S. J. von Przyłecki and M. Kołaczkowska (Biochem. Z., 1937, **291**, 76—78; cf. A., 1935, 1390).—The solubility of tyrosine (I) in H_2O at const. p_H is increased by addition of glucose, sucrose, and other sugars. The *X*-ray diagrams (Debye–Scherrer) of the compounds of (I) with dextrin, amylose, and starch closely resemble each other and indicate that in the compounds the (I) crystals are regularly arranged in the protein micelle. W. McC.

Synthesis of α-amino-β-hydroxy-*n*-butyric acids. III. Simple method of preparing a mixture of the two forms. IV. Separation of mixtures of the two forms and preparation of *d*(−)- and *l*(+)-threonine. H. D. West and H. E. Carter (J. Biol. Chem., 1937, **119**, 103—108, 109—119).—III. In an attempt to prepare *dl*-threonine (I) [the racemic mixture of the α-amino-β-hydroxy-*n*-butyric acid from proteins (A., 1936, 1494) with its enantiomorph], crotonic acid was brominated in MeOH, but gave only α-bromo-β-hydroxy-*n*-butyric acid-*A* [the suffix *A* is used to indicate substances related to the aminohydroxybutyric acid prepared by Abderhalden's method, as distinct from precursors of (I)]. Crotonic acid and $Hg(OAc)_2$–MeOH, however, give a *product* (reduced by H_2S to β-methoxy-*n*-butyric acid; decomp. on heating to a *product*, decomp. 170—180°), which with Br in aq. KBr (sunlight), followed by HBr, forms mixed α-bromo-β-methoxy-*n*-butyric acids, converted into mixed α-amino-β-methoxy-*n*-butyric acids (II), and thence (HBr) into mixed α-amino-β-hydroxy-*n*-butyric acids, containing 30—40% of (I).

IV. This last mixture of (I) with dl-allo*threonine* (the name now given to the *dl*-α-amino-β-hydroxy-*n*-butyric acid which does not contain the natural form) is benzoylated to N-*benzoyl*-dl-allo*threonine* (III), m.p. 175—176°, and -dl-*threonine* (IV), m.p. 143—144°; this is not, however, a satisfactory method for isolating (I). Formylation or benzoylation of the mixture (II) gives, on the other hand, readily separable *formyl*-dl-O-*methyl-threonine* (V), m.p. 174—175°, and -allo*threonine*, m.p. 153—154°, and *benzoyl*-dl-O-*methyl-threonine*, m.p. 158—159°, and -allo-*threonine*, m.p. 129—130°. These compounds are hydrolysed (HBr or HCl) to dl-O-*methyl-threonine*, m.p. 215—218°, and -allo*threonine*, m.p. 230—233°. These are further hydrolysed (48% HBr) to dl-*threonine*, m.p. 227—229°, and dl-allo*threonine*, m.p. 237—239°, also obtained from (IV) and (III), respectively. Resolution of (V) gives *formyl*-d(−)-, m.p. 163—164°, $[\alpha]_D^{26}$ +11·8° (*brucine* salt, m.p. 186—188°, $[\alpha]_D^{26}$ −19·4°), and *formyl*-l(+)-O-*methyl-threonine*, m.p. 164—165°, $[\alpha]_D^{26}$ −11·9° (*brucine* salt, m.p. 139—141°, $[\alpha]_D^{26}$ −21·5°), hydrolysed to d(−)-, m.p. 214—216°, $[\alpha]_D^{26}$ −37·8°, and l(+)-O-*methyl-threonine*, m.p. 214—216°, $[\alpha]_D^{26}$ +38·2°, and thence to *d*(−)-threonine (Bz derivative; cf. A., 1936, 233), and l(+)-*threonine*, m.p. 251—252°, $[\alpha]_D^{26}$ +28·4° (*Bz* derivative, m.p. 147—148°, $[\alpha]_D^{26}$ −25·5°). E. W. W.

Fission of the disulphide linking with sodium sulphite and potassium cyanide and colorimetric determination of thiol compounds and disulphides. A. Schöberl and E. Ludwig (Ber., 1937, **70**, [*B*], 1422—1432).—Folin's colorimetric method with $(H_2O)_3P_2O_5(WO_3)_{18}$ gives accurate results with $SH \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, $SH \cdot CH_2 \cdot CO_2H$, $SH \cdot CMe_2 \cdot CO_2H$, $SH \cdot CPh_2 \cdot CO_2H$, $SH \cdot CHMe \cdot CO_2H$, $CO_2H \cdot CH(SH) \cdot CH_2 \cdot CO_2H$, and $CHPh:C(SH) \cdot CO_2H$. Rapid oxidation and constancy of colour intensity are best attained at p_H 5 but in practice it is necessary to await the development of max. colour in an acetate buffer. $SH \cdot CH_2 \cdot CH_2 \cdot CO_2H$ is a less powerful reducing agent under these conditions but behaves normally in presence of $NaHCO_3$. The presence of H_2SO_3 increases the intensity of the colour given by Folin's reaction which may become doubled in presence of much H_2SO_3. The changes are $2R \cdot SH + (H_2O)_3P_2O_5(WO_3)_{18} \rightleftharpoons SR \cdot SR + H_2O + (H_2O)_3P_2O_5(WO_3)_{17}WO_2$ and $SR \cdot SR + H_2SO_3 = R \cdot SH + R \cdot S \cdot SO_3H$, which are repeated until $R \cdot SH$ is completely converted into $R \cdot S \cdot SO_3H$. It is essential for the success of the method that oxidation of $R \cdot SH$ and disproportionation of $SR \cdot SR$ occur with sufficient

rapidity. In general determinations with SO_3'' which allow measurement of very small concns. of $SH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ are as accurate as those with CN′. Quant. doubling of colour intensity is not reached with $CHPh{:}C(SH){\cdot}CO_2H$, $SH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, or $SH{\cdot}CH_2{\cdot}CO_2H$, whilst the determination of $SH{\cdot}CMe_2{\cdot}CO_2H$ and $SH{\cdot}CPh_2{\cdot}CO_2H$ is not influenced by the presence of SO_3''. The ready fission of the S·S linking in cystine by SO_3'' gives a simple method for its determination by means of the Pulfrich photometer. It is necessary to use a very large excess of the reagent at p_H about 5. Attempts to apply Folin's reagent to the determination of disulphides other than cystine were not generally successful, union of ·S·S· to *sec.* and *tert.* C atoms usually causing non-reducibility. The most important source of error in the determination of SH by Na nitroprusside is the fugitive nature of the red colour. Measurements (in glycine buffer at p_H 10·4) must be made very rapidly. KCN stabilises the colour in a remarkable degree owing to its restriction of the oxidation of the SH-compound by O_2. The intensity of the colour is not the same for different substrates. In the main, disulphides show the same differences in their behaviour towards KCN as towards SO_3''. H. W.

Synthesis of cyanamide by the oxidation of glucose and ammonia. R. Fosse and R. de Larambergue (Compt. rend., 1937, **204**, 1285—1287).—Glucose in aq. NH_3 at 75° containing $KMnO_4$ affords $CN{\cdot}NH_2$, isolated as the Ag derivative. J. L. D.

Production of cyanamide by ammoniacal oxidation of fructose, arabinose, mannitol, and glycerol. R. de Larambergue (Compt. rend., 1937, **204**, 1431—1432).—Oxidation of these by ammoniacal $KMnO_4$ yields small quantities of $CN{\cdot}NH_2$, determined by pptn. of the Ag salt, hydrolysis to $CO(NH_2)_2$, and pptn. with xanthhydrol. A. Li.

Condensation of cyanoacetamide and formaldehyde. I. Condensation products under different conditions. T. Enkvist (J. pr. Chem., 1937, [ii], **149**, 58—64).—Equimol. amounts of $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ and CH_2O at room temp. in alkaline, aq., or dil. alcoholic solution rapidly form sol. products $CN{\cdot}CH(CH_2{\cdot}OH){\cdot}CO{\cdot}NH_2$ or $CN{\cdot}C(CH_2{\cdot}OH)_2{\cdot}CO{\cdot}NH_2$ and then slowly a yellow *ppt.* (I), probably a mixture of $C_7H_{10}O_3N_4$ and $C_7H_7O_3N_3$ (*Ag* salt), which does not give an enol or biuret reaction and is not apparently affected by PCl_5. (I) is hydrolysed by HCl to NH_4Cl, glutaric (II), and pentane-$\alpha\gamma\epsilon$-tricarboxylic acid. A scheme of reaction is suggested. Preservation of (I) under the mother-liquor causes its conversion into an orange-red resin (III) which becomes hard and brittle when dry; it appears to be produced by further condensation of (I) with the sol. compounds in the reaction solution. Hydrolysis of the mother-liquors from (I) gives considerable amounts of (II). During the condensation CH_2O becomes attached to N only in minor degree. The nature and amount of the products depend greatly on conditions. The condensation is accelerated by KOH and, preferably, by piperidine, which hinders the transformation of (I) into (III). H. W.

Reduction of nitroguanidine. VIII. Formation of aminoguanidine by reduction in liquid ammonia solutions. L. P. Fuller, E. Lieber, and G. B. L. Smith (J. Amer. Chem. Soc., 1937, **59**, 1150—1152; cf. this vol., 10).—Nitro- (I) and nitrosoguanidine are unchanged by dissolution in liquid NH_3 or $NaNH_2$–NH_3; the former gives colourless, the latter yellow, solutions. When Na is added to (I) in liquid NH_3, vigorous reaction occurs with colour changes, consumption of 3·7—4·5 Na, and formation of 10% of $CN{\cdot}NH_2$ (Ag_2 salt, m.p. 39·5°) and 27—30% of N_2 (probably by way of $NH_2{\cdot}NO_2$). However, addition of Na (6 atoms) to (I) and NH_4Cl (6 mols.) (or NaOAc) in liquid NH_3 gives 50—60% of aminoguanidine (CHPh: derivative, m.p. 178·5°), formed in 60—70% yield by addition of a Na–NH_4Cl mixture (6 equivs. of each) to (I) in liquid NH_3; this is due to NH_4^+ acting as ammoniated H^+, and the use of liquid NH_3 as a solvent for catalytic hydrogenations is suggested. R. S. C.

Synthesis of ureides of some monobasic acids and ketones. C. E. Miller and R. A. Cain (J. Amer. Pharm. Assoc., 1937, **26**, 418—420).—The following were prepared: *α-bromohexoyl ureide*, m.p. 175°, *α-bromoisohexoyl ureide*, m.p. 161°, and *compounds*, $C_7H_{12}O_2N_2Br_2$, m.p. 145°, and $C_9H_{16}O_2N_2Br_2$, m.p. 123°. F. O. H.

Synthesis of decamethylenebisguanidine (synthalin). K. S. Toptschiev and L. N. Pavlov (Chim. Farm. Prom., 1935, No. 1, 24—25).—Sebacic acid (I) is dissolved in the picoline fraction of C_5H_5N bases and treated with dry NH_3 and $POCl_3$. The dinitrile of (I) is extracted from the aq. solution with C_6H_6 and after removal of solvent is distilled in a vac. The nitrile with *iso*-$C_5H_{11}{\cdot}OH$ and Na yields decamethylenediamine, which is heated with guanidine thiocyanate at 135° to form decamethylenebisguanidine (II). The product is poured into 20% aq. KOH and the dried ground material is extracted with abs. EtOH and treated with HCl to form the hydrochloride of (II). Ch. Abs. (*p*)

Preparation and cracking of nitriles of high mol. wt. A. W. Ralston, H. J. Harwood, and W. O. Pool (J. Amer. Chem. Soc., 1937, **59**, 986—992).—Distillation of stear- and laur-amide at 1 atm. gives about equal amounts of acid and nitrile, formed by disproportionation of the amide to nitrile and NH_4 salt, which latter then dissociates to NH_3 and acid. Heating higher fatty acids (stearic or mixed acids from fats, oils, etc.) in a stream of NH_3 under reflux gives excellent yields of nitrile. The equilibrium, $RCO_2H + NH_3 \rightleftharpoons RCO_2NH_4$, is displaced by the excess of NH_3; the subsequent equilibria, $RCO_2NH_4 \rightleftharpoons H_2O + RCO{\cdot}NH_2 \rightleftharpoons RCN + 2H_2O$, are displaced by removal of the H_2O in the stream of NH_3. Higher fatty acid nitriles from fats and oils are cracked by passage at 450—600° over catalysts (glass, pumice, Al_2O_3 on C, Al_2O_3, or Cu or Fe on Al_2O_3), or, better, by heating alone or in N_2 at 420°, to mixed $<C_{13}$ fatty acid nitriles and saturated and unsaturated hydrocarbons; the nature of the products is investigated by hydrolysis of the nitrile, partial separation by solvents (alcohols, PhOH), and adsorption of the nitriles on to SiO_2 gel, from which they are removed

by hot H_2O. Hexo- to lauro-nitrile were identified in the products by hydrolysis to the acid and conversion into 2-alkylbenziminazoles. R. S. C.

Maleo- and fumaro-nitrile. J. JENNEN (Bull. Soc. chim. Belg., 1937, **46**, 199—210).—Reaction does not occur with *trans*-C_2I_2 and KCN–EtOH or $Hg(CN)_2$ whereas with CuCN at 135—200° *fumaronitrile* (I), b.p. 101°/46 mm., m.p. 96—96·4°, is obtained. Somewhat impure *cis*-C_2I_2 similarly gives (I) and *maleonitrile* (II), b.p. 99—99·5°/13 mm., m.p. 32·2—32·6°. Indications of the formation of (I) and (II) are not obtained when mixtures of C_2H_2 and C_2N_2 are irradiated or when C_2H_2 is passed into an irradiated solution of C_2N_2 in C_6H_6. (I) is transformed by conc. H_2SO_4 (*d* 1·84) into fumardiamide whereas (II) under like conditions yields maleamic acid. Ill-defined products are obtained by the action of NaOH on (I) or (II). H. W.

Maleo- and citracono-nitrile. P. BRUYLANTS and J. JENNEN (Bull. Soc. chim. Belg., 1937, **46**, 197—198).—The product (I) obtained by the action of P_2O_5 on maledіamide is not identical with maleonitrile (II) since it is hydrolysed by NaOH to maleic acid whereas HCN is withdrawn from (II) under these conditions. (I) and (II) are transformed by conc. H_2SO_4 into maleamic acid. Fresh analyses of (I) show it to be *maleimide*. Similarly *citraconimide* is derived from P_2O_5 and citracondiamide. H. W.

Photolysis of azomethane.—See A., I, 419.

Complex compounds of bivalent platinum with glycine. A. A. GRÜNBERG and L. M. VOLSCHTEIN (Bull. Acad. Sci. U.R.S.S., 1937, 3—24).—K_2PtCl_4 and glycine (HG) yield K_2PtG_4, from which H_2PtG_4 (I) [Ba, $(NH_4)_2$, and Ag_2 *salts*] is obtained with HCl or HNO_3. (I) has markedly amphoteric properties, the series (I) → $[PtG_3(HG)]'$ → $[PtG_2(HG)_2]$ → $[PtG(HG)_3]^{\cdot}$ → $[Pt(HG)_4]^{\cdot\cdot}$ being obtained by varying the p_H of the solutions. The *salts* $[Pt(HG)_4]X_2$ [$X_2 = (NO_3)_2$, $[PtCl_4]$, Cl_2, and SO_4] are prepared from (I) and the appropriate acids. (I) yields chiefly *cis*-PtG_2 with boiling H_2O, and chiefly *trans*-$PtCl_2G_2$ with 6*N*-HCl. The mechanism of the reactions is discussed. R. T.

Constitution, optical activity, and photochemical behaviour of platinous complexes. III.—See A., I, 423.

Characteristic contact-catalytic transformations of *cyclo*hexane hydrocarbons. N. I. SCHUJKIN (J. Gen. Chem. Russ., 1937, **7**, 1015—1021).—*cyclo*Hexane (I) yields CH_4, C_6H_6, and PhMe when passed over Ni–Al_2O_3 at 375°, in H_2; in presence of Pt the products are C_6H_6 and Ph_2. Methyl*cyclo*hexane (II) gives *p*-xylene, C_6H_6, and CH_4, and dimethyl*cyclo*hexane gives *p*-xylene, PhMe, (I), (II), and CH_4 with Ni–Al_2O_3, at 330—375°. The results are explained on the basis of methylation by CH_2 radicals, and of destructive hydrogenation by H_2. R. T.

Hydrogenation of homologues of benzene under pressure. M. K. DJAKOVA, A. V. LOZOVOI, and T. G. STEPANTZOVA (J. Gen. Chem. Russ., 1937, **7**, 722—728).—Hydrogenation to alkyl*cyclo*hexanes of PhPr, *o*-, *m*-, and *p*-xylene, 1 : 2 : 4 : 5-tetra-, penta-, and hexa-methylbenzene takes place at 200—240°/120—230 atm. (Ni catalyst) without elimination of side-chains. *Penta-*, b.p. 183—186°, and *hexamethyl*cyclo*hexane*, b.p. 214—216°, are described. R. T.

Products of condensation of benzene with *cyclo*hexene in presence of aluminium chloride. S. S. NAMETKIN and E. S. POKROVSKAJA (J. Gen. Chem. Russ., 1937, **7**, 962—972).—C_6H_6, *cyclo*hexene (I), and $AlCl_3$ at 0° yield mono-, *m*- and *p*-di- (III), 1 : 3 : 5-*tri*- (IV), m.p. 65—66°, and 1 : 2 : 4 : 5-*tetra*- (V), m.p. 60°, -cyclo*hexylbenzene*. The sole product obtained from (I) and (II) or (III) is (IV), and from (I) and (IV) is (V), showing that the process of condensation is accompanied by isomerisation. R. T.

Stable dibromide of $\Delta^{1:3}$-*cyclo*hexadiene. P. BEDOS and A. RUYER (Compt. rend., 1937, **204**, 1350—1352).—$\Delta^{1:3}$-*cyclo*Hexadiene (I) with dry HBr at −10° affords 1-*bromo*-Δ^2-cyclo*hexene*, b.p. 71·5°/26 mm., which with Br in dry CCl_4 at 15° gives substitution products. The Raman spectrum shows that the dibromide (II), m.p. 108°, of (I) contains a double linking, which is very inert chemically. With hot MeOH containing $NaHCO_3$, (II) affords 1 : 4-dimethoxy-Δ^2- and 1-bromo-2-methoxy-Δ^3-*cyclo*hexene. (II) with hot NaOH gives nearly pure *trans*-1 : 2-dihydroxy-Δ^3-*cyclo*hexene, m.p. 77°, whereas with hot H_2O, the cis-*compound*, an oil [p-*nitrobenzoate*, m.p. 117° and 137° (two forms)], is formed which with H_2–Pt gives *cyclo*hexane-1 : 2-diol. (II) with excess of aq. $NaHCO_3$ gives the above *cis*- and *trans*-compounds, and cis-1 : 4-*dihydroxy*-Δ^2-cyclo*hexene*, an oil, reduced (H_2–Pt) to *cis-cyclo*hexane-1 : 4-diol. This isomerisation leaves the structure of (II) undecided. J. L. D.

Action of nitrous anhydride on santene. A. S. ONISCHTSCHENKO (Bull. Acad. Sci. U.R.S.S., 1937, 209—223).—Santene in light petroleum and N_2O_3 yield 3-*nitro*-2-*nitroso*-2 : 3-*dimethyl*-1 : 4-*methylene*-cyclo*hexane* (I), m.p. 123—124°, converted by reduction (Sn and HCl) into 2-*amino*-3-*hydroxy*-2 : 3-*dimethyl*-1 : 4-*methylene*cyclo*hexane*, m.p. 280—282° [*platinochloride*, m.p. 228—230° (decomp.); *aurichloride*, m.p. 186—188°]. (I) yields NO and 1 : 3-*diacetyl*cyclo*pentane*, m.p. 123—127° (*semicarbazide*, m.p. 216—217°), when warmed with EtOH. A solution of (I) in Et_2O gradually deposits 2-*nitroso*-3-*hydroxy*-2 : 3-*dimethyl*-1 : 4-*methylene*cyclo*hexane*, m.p. 114°, on keeping. R. T.

Beryllium bromide as a reagent in syntheses. R. PAJEAU (Compt. rend., 1937, **204**, 1347).—Bu^{a}Br with boiling PhMe containing $BeBr_2$ affords some PhBu^a, but the catalytic action of $BeBr_2$ is not general. CH_2PhCl with excess of boiling C_6H_6 containing $BeBr_2$ affords CH_2Ph_2. PhMe, PhEt, and *m*-xylene react similarly. Acid chlorides do not react with C_6H_6 and $BeBr_2$. J. L. D.

Reversibility of the Friedel–Crafts reaction. N. N. ORLOV and P. G. VAISFELD (J. Appl. Chem. Russ., 1937, **10**, 861—868).—Products of low b.p. are not obtained from xylene and $AlCl_3$ at 200°, condensed rings being produced under these conditions. Addition of C_6H_6 does not favour demethylation

of xylene in presence of $AlCl_3$, at the b.p., whilst addition of $C_6H_3Me_3$ leads to increased production of products of high b.p. Demethylation of xylene is achieved by heating at the b.p. with moist $AlCl_3$. $FeCl_3$ and PCl_3 act similarly to $AlCl_3$ in the above reactions, but are less active. Xylene forms complexes with $AlCl_3$, the activity of which is comparable with that of $AlCl_3$ alone. R. T.

Identification of alkylbenzenes. I. Identification of monoalkylbenzenes by means of the acetamido-derivative. V. N. Ipatiev and L. Schmerling (J. Amer. Chem. Soc., 1937, **59**, 1056—1059).—Monoalkylbenzenes are readily identified by mono- (1 : 1 H_2SO_4–HNO_3) or di-nitration (2 : 1 H_2SO_4–HNO_3) at room temp. and conversion into the *p*-NHAc- or 2 : 4-$(NHAc)_2$-derivatives. $C_6H_4R{\cdot}NH_2$ form Et_2O-sol. salts, $2C_6H_4R{\cdot}NH_2,SnCl_2,2HCl$, readily separable from the insol. $(NH_2)_2$-derivatives. *p*-$C_6H_4Me{\cdot}NHAc$, m.p. 145°, *p*-ethyl-, m.p. 94°, -n-, m.p. 96°, and *-iso*-propyl-, m.p. 106°, -n-, m.p. 105°, -sec.-, m.p. 126°, and tert.-*butyl*-, m.p. 170°, -tert.-*amyl*-, m.p 142°, and *-cyclo*hexyl-acetanilide, m.p. 130—131°, 2 : 4-*diacetamido*-toluene, m.p. 221°, -ethyl-, m.p. 223°, -n-, m.p. 208°, and -iso-*propyl*-, m.p. 216°, -n-, m.p. 214°, -sec.-, m.p. 192°, and -tert.-*butyl*-, m.p. 210°, -tert.-*amyl*-, m.p. 181°, and -cyclo*hexyl-benzene*, m.p. 261—262°, and 2 : 4-*diamino*cyclo*hexylbenzene*, m.p. 105—106°, are described. Identification of $PhPr^{\alpha}$ and $PhPr^{\beta}$ in a mixture of the two is detailed. R. S. C.

Condensation of alcohols with aromatic hydrocarbons in presence of aluminium chloride. III. Condensation of primary alcohols with benzene and toluene. I. P. Tzukervanik and G. Vichrova. **IV. Condensation of aliphatic alcohols with naphthalene.** I. P. Tzukervanik and I. Terentieva. **V. Condensation of *cyclo*hexanol with benzene and toluene.** I. P. Tzukervanik and N. G. Sidorova (J. Gen. Chem. Russ., 1937, **7**, 632—636, 637—640, 641—645).—III. *n*-Alcohols condense with aromatic hydrocarbons at 120—124° in presence of $AlCl_3$ (2 mols. per mol. of alcohol), to yield alkylbenzenes. Thus C_6H_6 and EtOH (120—130°; 10 hr.) yield PhEt, *m*-$C_6H_4Et_2$, $C_6H_3Et_3$, $C_6H_2Et_4$, and $C_6H_4(C_6H_4Et)_2$, C_6H_6 and $Pr^{\alpha}OH$ (110°; 10 hr.) give $PhPr^{\alpha}$ and *m*-$C_6H_4Pr^{\alpha}_2$, PhMe and EtOH (140°; 8 hr.) yield *m*- and *p*-C_6H_4MeEt and $C_6H_3MeEt_2$, and PhMe and $Pr^{\alpha}OH$ (125°; 4 hr.) afford *m*- and *p*-$C_6H_4MePr^{\alpha}$ and $C_6H_3MePr^{\alpha}_2$.

IV. $C_{10}H_8$ is condensed with *n*-, *sec.*-, and *tert.*-alcohols, in presence of 2, 1, and 0·5 mols. of $AlCl_3$ per mol. of alcohol, respectively. $C_{10}H_8$ and $Pr^{\beta}OH$ in ligroin (24 hr. at room temp., and 4 hr. at 100°) give 2-$C_{10}H_7Pr^{\beta}$, oxidised by 20% HNO_3 (130°; 15 hr.) to 4-iso*propylphthalic acid*, m.p. 216° (decomp.), 2 : 7-*di*iso*propylnaphthalene*, b.p. 278—280° (*picrate*, m.p. 86°), and $C_{10}H_5Pr^{\beta}_3$, oxidised to di*iso*propylphthalic acid by 20% HNO_3. $C_{10}H_8$ and $CHMeEt{\cdot}OH$ in ligroin (100°; 5 hr.) give 1-$C_{10}H_7{\cdot}CHMeEt$ and $C_{10}H_6(CHMeEt)_2$. $C_{10}H_8$ and $Bu^{\gamma}OH$ (100°; 3 hr.) yield 1-, b.p. 287—289° (*picrate*, m.p. 93°), and 2-tert.-*butylnaphthalene*, b.p. 274—276° (*picrate*, m.p. 84—85°), and *di*tert.-*butylnaphthalene*, m.p. 132° (*picrate*, m.p. 99°). $C_{10}H_8$ and *tert.*-$C_5H_{11}{\cdot}OH$ (100°; 2 hr.) afford 1-, b.p. 301—303° (*picrate*, m.p. 110—113°), and 2-tert.-*amylnaphthalene*, b.p. 287—290° (*picrate*, m.p. 83°), and *di*tert.-*amylnaphthalene*, m.p. 154—155°. The side-chains of the above alkylnaphthalenes are oxidised by 5% HNO_3 (170°; 10 hr.) to yield naphthoic acids, whilst 20% HNO_3 oxidises the unsubstituted ring, to give substituted phthalic acids.

V. *cyclo*Hexanol (I) in presence of $AlCl_3$ (100°; 2 hr.) yields *cyclo*hexyl- (II), *m*- and *p*-di-, and 1 : 3 : 7-*tri*-cyclo*hexylbenzene*, m.p. 68°, with C_6H_6, and *m*- and *p-cyclo*hexyl-, and 3 : 5-*di*cyclo*hexyltoluene*, m.p. 93·5°, with PhMe. (I) alone gives *cyclo*hexane (III) and chloro*cyclo*hexane (IV) when heated with $AlCl_3$. The reaction is represented as: (I) + $AlCl_3$ → (III) + $AlCl_2{\cdot}OH$ + HCl; (III) + HCl → (IV); C_6H_6 + (III) → (II); C_6H_6 + (IV) → (II) + HCl. R. T.

Halogenation. XVIII. Halogenation of ethylbenzene. P. S. Varma, V. Sahay, and B. R. Subramonium (J. Indian Chem. Soc., 1937, **14**, 157—159).—*p*-C_6H_4EtCl is obtained in good yield by chlorinating PhEt in presence of I in the dark. Employing Br and I in a reaction medium containing $NO_2{\cdot}SO_3H$ there are obtained CHPhMeBr (II), *p*-C_6H_4BrEt, 2 : 4-$C_6H_3Br_2Et$, and *p*-C_6H_4IEt (III). Further halogenation of (I), (II), and (III) yields 3-*bromo*-4-*iodo*-, m.p. 88—89°, 4-*chloro*-3-*bromo*-, b.p. 143—144°/10 mm., and *p-chloro*-α-*bromo-ethylbenzene*, b.p. 120—121°/8 mm. D. J. B.

(A) Synthesis of *m*- and *p*-allyl- and *p*-propenyl-toluene. R. J. Levina. **(B) Catalytic isomerisation of unsaturated hydrocarbons with a double linking in the αβ-position.** R. J. Levina and D. A. Petrov (J. Gen. Chem. Russ., 1937, **7**, 684—687, 747—749).—(A) *p*-Allyl- (I) and m-*allyl*-, b.p. 60—60·5°/11 mm., and *p*-propenyl-toluene (II) have been prepared by the Grignard reaction.

(B) (I) is converted into (II) by passing over Pt at 300° in CO_2. Δ^{γ}-Butenylbenzene similarly yields Δ^{α}- and Δ^{β}-butenylbenzene. R. T.

Thermal polymerisation of styrene.—See A., I, 416.

Magnesium pentamethylphenyl halides. H. Clément and J. Savard (Compt. rend., 1937, **204**, 1742—1743; cf. A., 1936, 852).—$C_6Me_5{\cdot}MgBr$ (I) with EtI (or EtBr) and allyl iodide affords *ethyl*-, sublimes at 118°, and *allyl-pentamethylbenzene*, sublimes at 128°, respectively. MeBr reacts but no pure compound is isolated. (I) with $COMe_2$ affords *pentamethylphenyldimethylcarbinol*, m.p. 134° (decomp.), easily dehydrated to β-*pentamethylphenyl*-β-*methylethylene*, sublimes at 122°. $CH(OEt)_3$ reacts with (I) with difficulty to give $C_6Me_5{\cdot}CHO$. J. L. D.

[Constitution and reactivity. XIX.] K. Lauer and R. Oda (J. pr. Chem., 1937, [ii], **148**, 287—288; cf. A., 1936, 1239).—Theoretical explanations of the mode of nitration of $PhNO_2$ (A., 1936, 297) are revised. R. S. C.

Action of nitrogen peroxide on benzene, toluene, or chlorobenzene. III. Nitration by means of nitrogen peroxide in presence of aluminium

chloride, PCl_3, and mercuric nitrate. IV. Nitration by means of nitrogen peroxide of benzaldehyde and of nitro-derivatives of benzene, toluene, and chlorobenzene. A. I. Titov (J. Gen. Chem. Russ., 1937, **7**, 591—594, 667—672).—III. Nitration of C_6H_6 or PhCl by N_2O_4 at 0° in presence of anhyd. $AlCl_3$ proceeds: $RH + N_2O_4 + 2AlCl_3 \rightarrow RNO_2,AlCl_3$ (I) + $AlCl_2{\cdot}OH,NOCl$ (II) $\rightleftharpoons$ $RNO_2,AlCl_2{\cdot}OH + AlCl_3,NOCl$; (I) + N_2O_4 + RH $\rightarrow$ $AlCl_2{\cdot}OH,2RNO_2,NOCl$; (II) + N_2O_4 + RH $\rightarrow$ $AlCl(OH)_2,RNO_2,2NOCl$, or, summarily, $2AlCl_3 + 3RH + 3N_2O_4 \rightarrow 3RNO_2 + 3NOCl + Al_2Cl_3(OH)_3$. Impure products are obtained in low yield when $PhNO_2$, BzCl, or p-$C_6H_4Me{\cdot}NO_2$ is used in place of C_6H_6 or PhCl. $C_6H_4Cl{\cdot}NO_2$ is obtained in 50% yield when PCl_3 is substituted for $AlCl_3$ in the above reaction. The products obtained in presence of $HgNO_3$ at 0° explode when the temp. is raised to 20°.

IV. $C_6H_4(NO_2)_2$, $C_6H_3Me(NO_2)_2$, $C_6H_3Cl(NO_2)_2$, and $NO_2{\cdot}C_6H_4{\cdot}CHO$ are obtained in good yield by nitrating the $(NO_2)_1$-derivatives or PhCHO at 0—10° with N_2O_4 in oleum. Alternatively, 35% oleum containing 30% of N_2O_4 is added to $PhNO_2$ at 70°, followed by $K_2S_2O_8$; the reactions are: $RH + N_2O_4 + H_2SO_4 \rightarrow RNO_2 + NO{\cdot}HSO_4 + H_2O$; $RH + NO{\cdot}HSO_4 + K_2S_2O_8 \rightarrow RNO_2 + H_2SO_4 + SO_3 + K_2SO_4$.

R. T.

Bromination of 4-diphenylyl benzenesulphonate. S. E. Hazlet (J. Amer. Chem. Soc., 1937, **59**, 1087—1088).—Although p-$C_6H_4Ph{\cdot}OH$ gives 3-bromo-4-hydroxydiphenyl (*PhSO*$_2$ derivative, m.p. 102—103°), p-$C_6H_4Ph{\cdot}O{\cdot}SO_2Ph$ gives *4′-bromo-4-diphenylyl benzenesulphonate*, m.p. 79—81°, hydrolysed to and also prepared from 4-bromo-4′-hydroxydiphenyl.

R. S. C.

Sulphonation by means of sulphites. I. Mechanism of the Piria reaction. S. V. Bogdanov and S. A. Cheifetz (J. Gen. Chem. Russ., 1937, **7**, 911—916).—$PhNO_2$ or p-$C_6H_4Me{\cdot}NO_2$ and aq. $NaHSO_3$ or Na_2SO_3 yield mixtures of sulphimino-benzenesulphonic acid and sulphimino-benzene (or -toluene), the proportion of the former rising with increasing alkalinity of the solution. NO-compounds are supposed to be intermediate products in both cases.

R. T.

Halogenation. XVII. Bromination and iodination of diphenyl. P. S. Varma and M. Krishnamurti (J. Indian Chem. Soc., 1937, **14**, 156).—Bromination of Ph_2 in presence of CCl_4, $NaNO_2$, and oleum gives 2 : 2′- and 4 : 4′-$(C_6H_4Br)_2$. With I and $NO_2{\cdot}SO_3H$ 4 : 4-*di-iododiphenyl*, m.p. 202°, is obtained.

D. J. B.

Mesitylene derivatives. II. Derivatives of di-2 : 4 : 6-trimethylphenylmethane (dimesitylmethane). W. T. Nauta and P. J. Wuis (Rec. trav. chim., 1937, **56**, 535—540).—Passage of dry HCl into a boiling C_6H_6 solution of dimesitylcarbinol (I) (Kohler *et al.*, A., 1932, 1250) affords *dimesitylmethyl chloride* (II), m.p. 104—105°, converted by heating with *N*-KOH–EtOH into *dimesitylmethyl Me ether* (III), m.p. 61°, and by AgOAc into *dimesitylmethyl acetate* (IV), m.p. 98°. Boiling MeOH converts either (II) or (IV) into (III). The conductivity ($\Lambda_{19·1}$ 3·82; Λ_{199} 10·7) of (II) in liquid SO_2 at −10° is intermediate between that of $CHPh_2Cl$ ($\Lambda_{20·3}$ 0·005) and $(p$-$OMe{\cdot}C_6H_4)_2CHCl$ ($\Lambda_{26·79}$ 4·84) and CPh_3Cl ($\Lambda_{20·8}$ 7·70). (II) gives evidence of free radical formation when it is treated with Ag in C_6H_6 (O_2 exclusion). (III) and (IV) also give coloured solutions in liquid SO_2 and possess small conductivity but (I) gives a colourless, non-conducting solution.

J. W. B.

***cis–trans* Isomerisation by bromine atoms.** M. S. Kharasch, J. Y. Mansfield, and F. R. Mayo (J. Amer. Chem. Soc., 1937, **59**, 1155).—*iso*Stilbene in C_6H_6 is stable in the dark or in light in the presence of HBr and antioxidants, in the dark in the presence of HBr alone in air or vac., but is isomerised to stilbene by HBr in light (more rapidly in air) or in the presence of peroxides in the dark. Br–HBr in the dark and HCl under any conditions do not cause isomerisation, which is thus considered to be caused by Br atoms.

R. S. C.

Synthesis of optically-active molecules with the aid of circularly polarised light. G. Karagunis and G. Drikos (Praktika, **9**, 177—181; Chem. Zentr., 1936, i, 3298).—Irradiation of asymmetrical triarylmethyl radicals with circularly polarised light in the presence of Cl_2 or Br yields optically active products, right-polarised light giving *l*-materials and *vice versa*. No activity is observed with symmetrical radicals or with ordinary light; control experiments show that the reaction is an asymmetric synthesis, not an asymmetric decomp. It is concluded that triarylmethyl radicals have a tetrahedral configuration.

H. N. R.

Radical containing three triphenylmethyl groups. E. Connerade (Bull. Soc. chim. Belg., 1937, **46**, 179—193).—$CO(C_6H_4Bz$-$p)_2$ is converted by LiPh into *di*-4 : 4′-*hydroxybenzhydryltriphenylmethylcarbinol* (I), $OH{\cdot}CPh(C_6H_4{\cdot}CPh_2{\cdot}OH)_2$, m.p. 104—105° after becoming vitreous at 98°, decomp. 180—200°, less readily obtained by use of MgPhBr or from $CO(C_6H_4{\cdot}CO_2Me$-$p)_2$. (I) in $CHCl_3$ is transformed by HCl and ultimately by $SOCl_2$ into *di*-4 : 4′-*chlorobenzhydryltriphenylmethyl chloride*, m.p. 160—161° (slight decomp.) after becoming darker at 141°, the solution of which in boiling C_6H_6 is reduced by Ag powder to the *triradical* (II), $CPh_2{\cdot}C_6H_4{\cdot}CPh{\cdot}C_6H_4{\cdot}CPh_2$. Treatment of (II) in C_6H_6 with air cause colour change from red-violet to orange-red and addition of light petroleum ppts. the *triperoxide*, $\left(\begin{array}{c}CPh_2{\cdot}C_6H_4{\cdot}CPh{\cdot}C_6H_4{\cdot}CPh_2\\ \llcorner\!\!-\!\!O\!\!-\!\!\lrcorner \qquad\qquad O-\end{array}\right)_2$, m.p. 165°, and then a mixture of the dimeric monoperoxide diquinone and dimeric diperoxide monoquinone. (II) is rapidly transformed by Br into *di*-4 : 4′-*bromobenzhydryltriphenylmethyl bromide*.

H. W.

Cracking of decahydroanthracene in presence of anhydrous aluminium chloride. R. J. Levina, J. K. Juriev, and A. I. Loschkomoinikov (J. Gen. Chem. Russ., 1937, **7**, 1005—1008).—The products contain aromatic 16—24, naphthenic 64—76%, and traces of aliphatic hydrocarbons.

R. T.

Dissociable organic oxides. Action of oxidising agents on *meso*-diphenylanthracene: two stereoisomeric *meso*-dihydroxides. C. Dufraisse

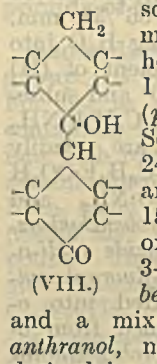
and J. Le Bras (Bull. Soc. chim., 1937, [v], 4, 1037—1045).—An improved prep. of 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracene (I) is described (cf. A., 1932, 507). Simultaneously an *isomeride* (II), m.p. 185° and after solidification 195—196°, is formed in small (0·25—0·5%) yield. Diphenylanthracene with $KMnO_4$ in C_6H_6–aq. H_2SO_4 below 8° affords (II) in 75% yield under carefully controlled conditions. With KI in AcOH, (II) and (I) afford *meso*-diphenylanthracene (III), which with CrO_3 in aq. AcOH at 20° affords mainly (I), but some (II). In the absence of H_2O, *o*-$C_6H_4Bz_2$ is formed, whereas 18% HNO_3 affords some (I) but mostly gums. Attempts to reduce (I) and (II) to the monoxide were unsuccessful (cf. A., 1931, 1052). An explanation is advanced in the light of Baeyer's strain theory. J. L. D.

Photo-sensitive nitro-compounds. III. *meso*-Nitroanthracenemonosulphonic acids. IV. Action of light on nitro-sulphonic acids in water, or on wool or paper. N. N. Voroschcov and V. V. Kozlov (J. Gen. Chem. Russ., 1937, 7, 729—738, 996—1004).—III. Anthracene-1-sulphonic acid in AcOH and HNO_3 (2—3 days at room temp.) yield 9-nitroanthracene-1-sulphonic acid (I) (Na, $+H_2O$; Ca, $+2H_2O$; Ba, $+3H_2O$; Cu^{II}, $+3H_2O$; Hg^{I}, $+2H_2O$; Hg^{II}, $+3H_2O$; Fe^{III}, $+2H_2O$; Pb, $+6H_2O$; Ag, $+2H_2O$ *salts*); sulphonation of 9-nitroanthracene was unsuccessful. (I) is reduced to the 9-NH_2-derivative (II) by Zn in H_2SO_4 at 95°, the product of diazotisation of which does not yield the expected sultone with boiling H_2O. The *sultone*, m.p. 156—159°, of (II) is obtained by heating (II) with $POCl_3$ (130°; 3 hr.), and yields 9-hydroxyanthracene-1-sulphonic acid when hydrolysed with 5% NaOH. An attempt at determining the position of the NO_2-group of *meso*-nitroanthracene-2-sulphonic acid (Cu^{II}, $+3H_2O$; Ba, $+H_2O$; Pb, $+\frac{1}{2}H_2O$; Fe^{II}, $+4H_2O$; Ag *salts*) was not successful. (I) exhibits considerable photo-sensitivity.

IV. The effect of light on the coloration of a no. of nitro-sulphonic acids and their salts has been studied. R. T.

10-Substituted 1 : 2-benzanthracene derivatives. L. F. Fieser and E. B. Hershberg (J. Amer. Chem. Soc., 1937, 59, 1028—1036).—10-Substituted derivatives of 1 : 2-benzanthracene and its 7-OMe-derivative are obtained in good yield (with, in some cases, by-products) from the benz-10-anthrones. The latter compounds must be pure, since they decompose readily if impure; satisfactory syntheses are described. The 1 : 2-benz-10-anthranol–anthrone equilibrium lies more to the anthranol side than in the unsubstituted anthrone series.

o-$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_{10}H_7$-α (I), m.p. 174—176°, obtained pure only with much loss by the Friedel–Crafts reaction in $C_2H_2Cl_4$, is best (75%) prepared from 1-$C_{10}H_7{\cdot}MgBr$ and *o*-$C_6H_4(CO)_2O$, and with Zn–NaOH gives a 20% or with H_2–Cu chromite at 175°/102—156 atm. (no reduction in EtOH) gives an 82% yield of *o*-α-naphthylmethylbenzoic acid (II), m.p. 148—148·5°; if prepared by the Friedel–Crafts reaction, (I) gives a mixture with the β-isomeride, which is difficulty separable; if prepared from crude 1-$C_{10}H_7Br$, (I) contains sufficient Br-acid (derived from $C_{10}H_6Br_2$) as impurity to inactivate the Cu chromite by reduction to the metal by HBr. With H_2SO_4–H_3PO_4 at 20—30° (II) gives 94% of crude 1 : 2-*benz*-10-*anthrone* (III), m.p. 130—135°, which decomposes when kept and is unsuitable for further work; H_2SO_4–AcOH at 50—60° gives crude 1 : 2-*benzanthryl* 10-*acetate* (IV), m.p. 152—154°, and some (III); 0·1 mol. of $ZnCl_2$ in boiling AcOH–Ac_2O (3 : 2) gives a 91% yield of pure (IV), m.p. 163—163·5° (softens at 161°), which with $MgBu^aBr$ gives 84% of yellow 1 : 2-*benz*-10-*anthranol* (V), m.p. 154·5—155·5° (fluorescent; colourless $COMe_2$ *compound*), obtained less well by hydrolysis by HCl–MeOH. Isomerisation of (V), best in $COMe_2$, is accompanied by decomp., but gives pure (III), m.p. 180—181° (decomp.) (not fluorescent; yellow). 10-*Methoxy*-1 : 2-*benzanthracene*, m.p. 110·5—111°, is best (55%) obtained by interaction of (IV) with $MgBu^aBr$ in Et_2O, heating with Me_2SO_4 in PhMe, and removing (V) and more oxygenated compounds by adsorption on Al_2O_3. By isomerising pure (V) in hot PhMe and adding MgRX to the equilibrium mixture are obtained 10-*ethyl*-, m.p. 113·5—114° (*picrate*, m.p. 141—141·5°), 10-n-*propyl*- (VI), m.p. 107—108° [*picrate*, m.p. 126·5—127·5°; with some 1 : 2-benzanthracene (VII)], 10-*allyl*-, m.p. 125·5—126·5° [*picrate*, m.p. 132—133°; hydrogenated to give (VI)], 10-n-*butyl*-, m.p. 96·8—97·5° (*picrate*, m.p. 115—115·5°), and 10-n-*amyl*-1 : 2-*benzanthracene*, m.p. 82·5—83·5° [*picrate*, m.p. 111—111·5°; with some of the compound (VIII), $C_{36}H_{24}O_2$, m.p. 265—267° (decomp.)]; $MgPr^{\beta}Cl$, however, gives 10-iso*propyltetrahydro*-1 : 2-*benzanthracene*, m.p. 72·5—73·5° (*picrate*, m.p. 134·5—135·5°), which with Se at 300—305° gives (VII), but at 240—245° gives 10-*iso*propyl-1 : 2-benzanthracene, m.p. 93—93·5° (*picrate*, m.p. 159—160°). Cyclisation of *o*-4′-methoxy-1′-naphthylmethylbenzoic acid at 3—5° gives 35% of pure 3-*methoxy*-1 : 2-*benz*-10-*anthrone* (IX), m.p. 183—184°, and a mixture thereof with the corresponding *anthranol*, m.p. 192—193°, the latter being also derived by the action of C_5H_5N on (IX) with some of the condensation *product*, $C_{38}H_{28}O_4$, m.p. 268—275° (decomp.), analogous to (VIII). Action of MgRX on (IX) gives good yields of 3-*methoxy*-10-*methyl*-, m.p. 183—183·5° (*dipicrate*, m.p. 149—150°), -*ethyl*-, m.p. 161—161·5° (*dipicrate*, m.p. 143·5—144°), and -n-*propyl*-1 : 2-*benzanthracene*, m.p. 136—136·5° (*dipicrate* m.p. 140—140·5°); the 10-Me compound with HBr–AcOH gives 3-*hydroxy*-10-*methyl*-1 : 2-*benzanthracene*, m.p. 193—194° (decomp.). M.p. are corr.


(VIII.)

R. S. C.

Catalytic oxidation of alicyclic amines with the side-chain $CH_2{\cdot}NH_2$. I, II. Z. I. Schujkina (J. Gen. Chem. Russ., 1937, 7, 983—988, 989—993).—I. Aq. aminomethyl*cyclo*propane, O_2, and Cu or OsO_4 give *cyclo*propanealdehyde (*oxime*, m.p. 86°; *phenylhydrazone*, m.p. 67°), which with dimedon yields cyclo*propyl*-2 : 6-*diketo*-4 : 4-*dimethyl*cyclo*hexyl*-2′-*hydroxy*-6′-*keto*-4′ : 4′-*dimethyl*-Δ^1-cyclo*hexenylmethane*, m.p. 168°, and with $MeNO_2$ and K_2CO_3 gives α-hydroxy-

β-nitroethyl*cyclo*propane, reduced by Sn and HCl to *α-hydroxy-β-aminoethylcyclopropane* (*platinichloride*).

II. $NH_2{\cdot}CH_2R$ (I) (R = *cyclo*butyl), Cu, and O_2 yield R·CHO (II), which condenses with (I) to a Schiff's *base*, $CHR{:}N{\cdot}CH_2R$, b.p. 88—90°/15 mm. This, when distilled from aq. $H_2C_2O_4$, regenerates (II), which undergoes a Cannizzaro reaction, giving $R{\cdot}CO_2CH_2R$. Cryst. products are not formed with NH_2OH or $NHPh{\cdot}NH_2$ and (II), which gives a *compound*, m.p. 154°, analogous to that with *cyclo*propanealdehyde. R. T.

Pterotactic derivatives of bivalent platinum with optically active, cyclic *trans*-1 : 2-diamines. —See A., I, 423.

Benzylation of aromatic amines. V. Reactions between *o*-, *m*-, and *p*-cyanobenzyl chlorides and aniline, ethylaniline, and dimethylaniline. D. H. Peacock, and P. Tha (J.C.S., 1937, 955).—Velocity coeffs. of the above reactions are tabulated; *m*- reacts faster than *p*-cyanobenzyl chloride, CN thus resembling NO_2. Introduction of CN lowers rate of reaction. *o*-Cyanobenzyl chloride reacts more slowly than CH_2PhCl; with NH_2Ph it is fastest, with $NPhMe_2$ slowest, of the three CN-compounds. E. W. W.

Aromatic compounds of fluorine. XXII. Question of an *ortho*-effect. G. Schiemann and H. G. Baumgarten (Ber., 1937, **70**, [*B*], 1416—1422).—Chlorination of o-C_6H_4MeF under defined conditions gives *o-fluorobenzotrichloride* (I), b.p. 94·6°/12 mm., *o-fluorobenzylidene chloride*, b.p. 71·6°/13 mm., or *o-fluorobenzyl chloride*, b.p. 86°/38 mm. (I) is transformed by $CaCO_3$ and boiling H_2O into o-$C_6H_4F{\cdot}CO_2H$ (II), m.p. 126°. Treatment of (II) in conc. H_2SO_4 with HN_3 in $CHCl_3$ at 0° and subsequently at 65—70° does not give o-$C_6H_4F{\cdot}NH_2$ whereas p-$C_6H_4F{\cdot}NH_2$ and NH_2Ph are readily obtained under similar conditions from p-$C_6H_4F{\cdot}CO_2H$ and BzOH, respectively. o-$C_6H_4F{\cdot}CO{\cdot}NH_2$ and N_2H_4,H_2O in boiling H_2O yield *o-fluorobenzhydrazide*, m.p. 70°, whence the non-cryst. *azide* (*s-di-o-fluorophenylcarbamide*, m.p. 226°) and *o-fluorophenylurethane* which could not be converted into o-$C_6H_4F{\cdot}NH_2$; this could not be obtained from o-$C_6H_4F{\cdot}CO{\cdot}NH_2$ and NaOBr. *o-Fluorobenzchloroamide*, m.p. 87—88°, is converted by $Ba(OH)_2$ and steam into o-$C_6H_4F{\cdot}NH_2$ in 89% yield. H. W.

Preparation of methylethylaniline. J. J. Makarov-Zemlianski (J. Appl. Chem. Russ., 1937, **10**, 660—670).—NPhMeEt is obtained in 90% yield from NHPhEt and Me_2SO_4, $MeHSO_4$ and MeOH, or MeOH and H_2SO_4, at 170—240°. R. T.

Homologues of *o*-nitrophenylhydroxylamine. R. Kuhn, H. Vetter, and P. Desnuelle (Ber., 1937, 70, [*B*], 1314—1318).—The homologues of *o*-nitrophenylhydroxylamine are much more stable than the parent substance and can be preserved unchanged for months in an evacuated desiccator. They give dark violet primary alkali salts and are converted by conc. NaOH into brown or yellowish-brown secondary salts which are readily hydrolysed by H_2O. 3-Nitro-2-amino-5 : 6 : 7 : 8-tetrahydronaphthalene is converted by $K_2S_2O_8$ in conc. H_2SO_4 into 3-*nitro*-2-*nitroso*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, decomp. 153°, oxidised to 2 : 3-*dinitro*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 107·5°, and reduced by ascorbic acid in EtOH–H_2O to 3-*nitro*-2-*hydroxylamino*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 125°. 6-*Nitro*-5-*nitrosohydrindene*, m.p. 155—156°, is oxidised to 5 : 6-*dinitrohydrindene*, m.p. 111—112°, and reduced to 6-*nitro*-5-*hydroxylaminohydrindene*, m.p. 117° (decomp.). 4-*Nitro*-5-*hydroxylamino*-*o*-*xylene* has m.p. 88° (decomp.). 4-Nitro-5-nitroso-*m*-xylene is reduced to 4-*nitro*-5-*hydroxylamino*-m-*xylene*, m.p. 87° (decomp.). H. W.

Tenacity of organic radicals. X. J. von Braun, R. Michaelis, and H. Spänig (Ber., 1937, 70, [*B*], 1241—1249; cf. A., 1933, 1285).—The firmness of union of $\cdot CH_2Ph$ to N is most appreciably increased by the introduction of $\cdot NO_2$, to a smaller extent by ·CN, and to a minor degree by ·NHAc, the effect of which is similar to that of halogen (except F). The three firmly attached $NO_2{\cdot}C_6H_4{\cdot}CH_2$ residues show little differences among themselves; the more mobile $CN{\cdot}C_6H_4{\cdot}CH_2$ groups are similar only in the two firmly attached groups (*o* and *m*), whereas among the labile $NHAc{\cdot}C_6H_4{\cdot}CH_2$ groups a distinct differentiation is observed according to the position of the substituent. The amines $CH_2R'{\cdot}NMe{\cdot}CH_2R''$ are obtained by warming $CH_2R'Cl$ or $CH_2R'Br$ (1 mol.) with a *sec.* base $NHMe{\cdot}CH_2R''$ (2 mols.) derived from $CH_2R''Cl(Br)$ with excess of NH_2Me in C_6H_6. Treatment with CNBr occurs at 0° and finally at 100°. The product is dissolved in Et_2O, shaken with dil. H_2SO_4 and the bromide and cyanamide are separated from one another by fractional distillation. The following substances are new : m-*nitrobenzylmethylamine*, b.p. 118°/0·3 mm. (*hydrochloride*, m.p. 191°; *picrate*, m.p. 160°); *di*-m-*nitrobenzylmethylamine*, b.p. 230°/0·3 mm., m.p. 80°; *benzyl*-p-*nitrobenzylmethylamine*, b.p. 221°/12 mm. (*hydrochloride*, m.p. 172°; *methiodide*, m.p. 173°); p-*nitrobenzylmethylcyanamide*, b.p. 190°/0·5 mm.; p-*chlorobenzyl*-p'-*nitrobenzylmethylamine*, b.p. 200°/0·3 mm. (*hydrochloride*; *picrate*, m.p. 166°); p-*chlorobenzyl bromide*, b.p. 119°/12 mm., m.p. 48°; m-*chlorobenzyl*-p'-*nitrobenzylmethylamine*, b.p. 224°/0·5 mm. (*hydrochloride*, m.p. 181°; *methiodide*, m.p. 179°); m-*chlorobenzyl chloride*, b.p. 120°/14 mm.; o-*chlorobenzyl*-p'-*nitrobenzylmethylamine*, b.p. 234°/0·5 mm.; p-*chlorobenzyl*-m'-*nitrobenzylmethylamine*, b.p. 220°/0·3 mm. (*hydrochloride*, m.p. 188°; *picrate*, decomp. 56°); m-*nitrobenzylmethylcyanamide*, b.p. 168—170°/0·5 mm.; o-*chlorobenzyl*-o'-*nitrobenzylmethylamine*, b.p. 178—180°/0·3 mm. (*hydrochloride*, m.p. 152°; *picrate*, decomp. 68°); o-*nitrobenzylmethylcyanamide*, b.p. 173—175°/0·3 mm.; m-*nitrobenzyl*-p'-*nitrobenzylmethylamine*, b.p. 232—234°/0·3 mm. (*hydrochloride*, m.p. 229°; *picrate*, m.p. 160°); o-*nitrobenzyl*-m'-*nitrobenzylmethylamine*, b.p. 220°/0·5 mm., m.p. 86° (hygroscopic *hydrochloride*; *picrate*, m.p. 161°; *methiodide*, m.p. 137°); o-*iodobenzyl*-o'-*nitrobenzylmethylamine*, b.p. 205°/0·5 mm., m.p. 40—42° (*hydrochloride*, m.p. 157°; *picrate*, m.p. 118°); p-*cyanobenzylmethylamine*, b.p. 148—151°/14 mm.; *di*-p-*cyanobenzylmethylamine*, b.p. 212—215°/14 mm.; m-*cyanobenzylmethylamine*, b.p. 144—145°/14 mm. (*hydrochloride*, m.p. 155°); *benzyl*-p-*cyanobenzylmethylamine*, b.p. 220—224°/11 mm. (non-cryst.

picrate; *methiodide*, m.p. 198°); p-*cyanobenzyl*-*methylcyanamide*, b.p. 145°/0·2 mm.; o-*iodobenzyl*-p-*cyanobenzylmethylamine*, b.p. 258—260°/14 mm. (non-cryst. *picrate*; *methiodide*, m.p. 220°); o-*iodobenzyl bromide*, b.p. 118—120°/0·5 mm., m.p. 56°; p-*cyanobenzylmethylcyanamide*, b.p. 150°/0·3 mm.; p-*nitrobenzyl*-p'-*cyanobenzylmethylamine*, b.p. 197—199°/12 mm. (*methiodide*, m.p. 210°); p-*cyanobenzyl bromide*, b.p. 141—143°/12 mm., m.p. 115°; p-*nitrobenzylmethylcyanamide*, b.p. 178—180°/12 mm.; m-*cyanobenzyl*-p'-*cyanobenzylmethylamine*, b.p. 252—254°/14 mm. (non-cryst. *picrate*; *methiodide*, m.p. 262°); o-*cyanobenzyl*-m'-*cyanobenzylmethylamine*, b.p. 216—218°/0·2 mm. (non-cryst. *picrate*; *methiodide*, m.p. 198°); *benzyl*-p-*aminobenzylmethylamine*, b.p. 164—167°/0·4 mm., m.p. 48°; *benzyl*-p-*acetamidobenzylmethylamine*, m.p. 104°; p-*acetamidobenzylmethylcyanamide*, m.p. 108°; p-*chlorobenzyl*-p'-*aminobenzylmethylamine*, b.p. 200°/0·4 mm. (*picrate*, m.p. 102°); p-*chlorobenzyl*-p'-*acetamidobenzylmethylamine* (not volatile without decomp.; non-cryst.) (*picrate*, m.p. 124°); o-*iodobenzyl*-p'-*nitrobenzylmethylamine*, m.p. 104° (*picrate*, m.p. 191°); *o-iodobenzyl*-p'-*aminobenzylmethylamine*, b.p. 210—212°/0·5 mm. (hygroscopic *hydrochloride*, m.p. 200°); non-cryst. o-*iodobenzyl*-p'-*acetamidobenzylmethylamine*; p-*acetamidobenzyl bromide*, b.p. 130—132°/0·2 mm.; o-*iodobenzylmethylcyanamide*, b.p. 205—208°/12 mm.; o-*nitrobenzyl*-p'-*nitrobenzylmethylamine*, b.p. 226—230°/0·3 mm. (*picrate*, m.p. 140°); o-*aminobenzyl*-p'-*aminobenzylmethylamine*, b.p. 186—188°/0·5 mm., m.p. 60° (*picrate*, m.p. 112°); o-*acetamidobenzyl*-p'-*acetamidobenzylmethylamine*, b.p. 226—228°/0·3 mm.; o-*aminobenzylmethylamine*, b.p. 133—137°/11 mm. [*hydrochloride*, m.p. 218°, also obtained by reduction of o-*nitrobenzylmethylamine*, b.p. 138—140°/12 mm. (*hydrochloride*, m.p. 175°)]; o-*aminobenzyl*-m'-*aminobenzylmethylamine*, b.p. 188—190°/0·3 mm., m.p. 58°; o-*acetamidobenzyl*-m'-*acetamidobenzylmethylamine*, b.p. 220—225°/0·2 mm. (*picrate*, m.p. 95°).

H. W.

Nitration and halogenation of αβ-dianilinoethane and its derivatives. I. A. E. SCHOUTEN (Rec. trav. chim., 1937, **56**, 541—561).—(·CH_2·NHPh)$_2$ (I) with HNO_3 (*d* 1·52) at −10° gives αβ-di-(2 : 4 : 6-trinitrophenylnitroamino)ethane, named "ditetryl," the structure of which is proved by its similar formation from αβ-di-*o*- and -*p*-nitro- (*Ac* derivative, m.p. 217°), -2 : 4-dinitro- (*Ac* derivative, m.p. 234°), and -2 : 4 : 6-trinitro- (*Ac* derivative, m.p. 242°) -anilinoethane, and by the formation of picric acid when hydrolysed by NaOH. Exactly similar series of reactions are carried out with various halogeno-derivatives of (I), the following data being new: *o*-C_6H_4Cl·NH_2 and (·CH_2Br)$_2$ with NaOAc at 150° afford αβ-*di*-o-*chloroanilinoethane*, m.p. 67° (*Ac* derivative, m.p. 118°), nitrated to give αβ-*di*-(2-*chloro*-4 : 6-*dinitrophenylnitroamino*)*ethane* (II), m.p. 238°. 1 : 2 : 4-$C_6H_3Cl_2$·NO_2 with (·CH_2·NH_2)$_2$,H_2O–EtOH at 150° gives αβ-*di*-2-*chloro*-4-*nitroanilinoethane*, m.p. 308° (*Ac* derivative, m.p. 232°); the corresponding 4 : 6-(NO_2)$_2$-compound, m.p. 172° (*Ac* derivative, 293°), is similarly prepared from 2-chloro-4 : 6-dinitroanisole, m.p. 36°, (lit. amorphous). Nitration of either gives (II). Similarly are obtained αβ-*di*-o-*bromoanilinoethane*, m.p. 76° (*Ac* derivative, m.p. 192°), and its 4-NO_2-, m.p. 318° (*Ac* derivative, m.p. 264°), and 4 : 6-(NO_2)$_2$-derivative, m.p. 156° (*Ac* derivative, m.p. 308°), whence αβ-*di*-(2-*bromo*-4 : 6-*dinitrophenylnitroamino*)*ethane*, m.p. 240°, is obtained: αβ-*di*-p-*chloroanilinoethane*, m.p. 99° (*Ac* derivative, m.p. 138°), its 2-NO_2-, m.p. 253° (*Ac* derivative, m.p. 265°), and 2 : 6-(NO_2)$_2$-derivative, m.p. 222° (*Ac* derivative, m.p. 248°), and αβ-*di*-(4-*chloro*-2 : 6-*dinitrophenylnitroamino*)*ethane*, m.p. 203°; αβ-*di*-p-*bromoanilinoethane*, m.p. 108° (*Ac* derivative, m.p. 158°), its 2-NO_2-, m.p. 247° (*Ac* derivative, m.p. 281°), and 2 : 6-(NO_2)$_2$-derivative, m.p. 199° (*Ac* derivative, m.p. 225°); αβ-*di*-(4-*bromo*-2 : 6-*dinitrophenylnitroamino*)*ethane*, m.p. 205°, and αβ-*di*-(2 : 6-*dinitro*-p-*tolylnitroamino*)*ethane*, m.p. 229°. The Ac_1, m.p. 235°, and Ac_2 derivative, m.p. 110°, of 2-bromo-4 : 6-dinitroaniline are described.

J. W. B.

Constitution of double salts. XX. Diammines with benzidine and tolidine. G. SPACU and C. G. MACAROVICI (Bul. Soc. Ştiinţe Cluj, 1935, **8**, 286—295; Chem. Zentr., 1936, i, 3446).—By the action of tolidine (Tld) and benzidine (Bzd) on the double salts $CdCl_2$,$2NiCl_2$,$12H_2O$, $CdCl_2$,$CuCl_2$,$4H_2O$, and $HgCl_2$,$CoCl_2$,$4H_2O$, the following *compounds* are obtained: $[CdCl_6][NiBzd_3]_2$; $[CdCl_6][MnBzd_2][CdBzd_2]$; $[CdCl_4][CuBzd_2]$; $[CdCl_4][CuTld_2]$; $[HgCl_4][CoTld_2]$. By the action of NH_3 on $[CdCl_4][Cu(C_5H_5N)_4]$, $[CdCl_4][Cu(NH_3)_4]$ is formed.

J. S. A.

Preparation of soluble aromatic amido-compounds of therapeutic value.—See B., 1937, 620.

Azo-indicators with a quaternary ammonium group. G. S. HARTLEY (J.C.S., 1937, 1026—1029).—For use as acidimetric indicators in aq. solutions containing long paraffin chain cations etc., colour-ions with resultant positive charge in both acid and alkaline form are prepared. *p*-NO_2·C_6H_4·CH_2Cl and NMe_3 yield p-*nitrobenzyltrimethylammonium chloride* (*iodide* also prepared), reduced to the p-NH_2-compound. This when diazotised couples with amines to give *azo-compounds*, viz., with $NHMe_2$ (*iodide*), α-$C_{10}H_7$·NH_2, α-$C_{10}H_7$·NMe_2, and β-$C_{10}H_7$·NH_2; these are indicators, changing from yellow (alkaline) to red at p_H 3·3, 4·5, 4·5, and 1·3, respectively. A compound with α-$C_{10}H_7$·OH, changing from red (alkaline) to orange-yellow at p_H 8·5, is also prepared.

E. W. W.

Reaction between *p*-hydroxyazobenzene and organo-magnesium compounds. A. TAURINS (J. pr. Chem., 1937, [ii], **149**, 1—29).—Gradual addition of a dil. solution of a suitable Grignard reagent to a dil. solution of *p*-OH·C_6H_4·N_2·Ph does not cause evolution of a hydrocarbon and results in the separation of additive *compounds* (I) $Mg(R\cdots OH\cdot C_6H_4\cdot N{:}NPh)_2$,$MgX_2$,$4Et_2O$. Such compounds have been obtained with MgEtBr, MgEtI, $MgPr^aBr$, $MgPr^sI$, and MgPhBr. Sol. compounds appear to arise with $MgPr^aCl$ and $MgBu^aCl$. If solutions of the Grignard reagent and *p*-OH·C_6H_4·N_2·Ph (1 : 1) are rapidly mixed, one-half of the expected vol. of hydrocarbon is evolved and additive *compounds* (II), $NPh{:}N\cdot C_6H_4\cdot O\cdot Mg\cdot R\cdots OH\cdot C_6H_4\cdot N{:}NPh$,$MgX_2$,$4Et_2O$, are pptd. These are observed with MgMeI, MgEtI,

$MgPr^{\alpha}I$, $CH_2Ph{\cdot}MgCl$, MgPhBr, and α-$C_{10}H_7{\cdot}MgBr$. (I) and (II) lose Et_2O when kept in open vessels whereby the red-brown colour of (I) passes into the red-violet of (II). Treatment of p-$OH{\cdot}C_6H_4{\cdot}N_2{\cdot}Ph$ with a large excess of MgMeI, MgEtCl, MgEtBr, MgEtI, $MgPr^{\alpha}Cl$, $MgPr^{\beta}Br$, $MgPr^{\alpha}I$, $MgBu^{\alpha}Cl$, $MgBu^{\alpha}Br$, $MgBu^{\alpha}I$, or MgPhBr causes reduction to NH_2Ph and p-$NH_2{\cdot}C_6H_4{\cdot}OH$ with evolution of saturated (III) and unsaturated (IV) hydrocarbons. The ratio of (III) to (IV) suggests the schemes $NPh{:}N{\cdot}C_6H_4{\cdot}OMgBr + 2MgEtBr \rightarrow MgBr{\cdot}NPh{\cdot}N(MgBr){\cdot}C_6H_4{\cdot}OMgBr$ (V) $+ 2C_2H_5$; (V) $+ 2MgEtBr \rightarrow NPh(MgBr)_2 + (MgBr)_2N{\cdot}C_6H_4{\cdot}OMgBr + 2C_2H_5$; $4C_2H_5 \rightarrow 2C_2H_4 + 2C_2H_6$ except in the case of MgMeI. $MgEt_2$, $MgPr^{\alpha}_2$, and $MgBu^{\alpha}_2$ react at approx. the same rate with p-$OH{\cdot}C_6H_4{\cdot}N_2{\cdot}Ph$ and give about the same amounts of reaction products. Their reaction appears similar to that of the Mg alkyl bromides with the same alkyl radical. H. W.

Action of bases on nitrophenylhydrazines. II. A. K. Macbeth and J. R. Price (J.C.S., 1937, 982—984).—In the reaction between NaOH, KOH, or $Ba(OH)_2$ with 2 : 4-dinitrophenylhydrazine, at 20°, or at 60°, to give m-$C_6H_4(NO_2)_2$ (I), *mm'*-dinitroazoxybenzene (II), and 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole (III) (cf. A., 1934, 1344), the amount of (III) is independent of the cation present, and is a min. for a certain concn. of alkali, with corresponding max. for (I) and (II). Among the products from 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ and N_2H_4, the supposed dinitroazonaphthalene (A., 1926, 163) is 4 : 4'-*dinitro*-2 : 2'-*azoxynaphthalene*, m.p. 305—306°. E. W. W.

Decomposition of fluorene- and fluorenone-2-diazonium chloride in acetic acid. H. V. Claborn and H. L. Haller (J. Amer. Chem. Soc., 1937, **59**, 1055—1056).—Fluorene-2-diazonium chloride in H_2O gives 2-hydroxyfluorene (I) [*Ac* derivative (II), m.p. 128°]; in glacial AcOH it gives 46·7% of (II), 11% of (I), and 10% of 2-chlorofluorene. Fluorenone-2-diazonium chloride in H_2O gives 55% and in dil. AcOH 80% of 2-hydroxyfluorenone and in glacial AcOH 60% of 2-*acetoxyfluorenone*, m.p. 157°. R. S. C.

Equimolar condensations of aldehydes with phenols. Preparation of primary saturated phenols. J. B. Niederl, Y. Niederl, S. Shapiro, and M. E. McGreal (J. Amer. Chem. Soc., 1937, **59**, 1113—1115).—1 mol. each of phenols and aldehydes in AcOH–HCl at —5° give polymeric alkylenephenols, which, when slowly pyrolysed, give alkylphenols. Thus are obtained p-$C_6H_4Et{\cdot}OH$, b.p. 210—212° (90°), 2-, b.p. 223—228° (125°), and 3-*methyl*-4-*ethyl*-, b.p. 230—235° (131°), 4-*methyl*-2-*ethyl*-*phenol*, b.p. 215—221° (133°), p-*n*-propyl-, b.p. 228—230° (86°), -*n*-, b.p. 238—242° (81°), and -*iso*-butyl-, b.p. 235—239° (124—125°), -*n*-amyl-, b.p. 248—253° (90°), and -*n*-heptyl-phenol, b.p. 271—278° (94°), the figures in parentheses being the m.p. of the corresponding *aryloxyacetic acids*. PhOH and CH_2O give a cresol in small yield. *n*, *d*, and PhOH coeff. of the alkylphenols are recorded. R. S. C.

Preparation of thymol from *m*-cresol. V. Action of phosphoric acid, zinc chloride, and the Niederl reagent on thymol *iso*propyl ether. K. Ono and M. Imoto (J. Soc. Chem. Ind. Japan, 1936, **39**, 483—484B; cf. this vol., 58).—Thymol Pr^{β} ether with H_3PO_4 or $ZnCl_2$ at 190—200° affords about equal amounts of 6-*iso*propyl-*m*-tolyl Pr^{β} ether and thymol and with $AcOH–H_2SO_4$ much (?) 4 : 6-di*iso*propyl-*m*-cresol and a little thymol. R. F. P.

Preparation of thymol from *m*-cresol. VI. Action of phosphoric acid and of zinc chloride on *m*-tolyl *iso*propyl ether in presence of *iso*propyl alcohol. VII. Decomposition of *iso*propyl ethers of *m*-cresol and its homologues by Grignard reagents. K. Ono and M. Imoto (J. Soc. Chem. Ind. Japan, 1937, **40**, 90B).—VI. Treatment of m-$C_6H_4Me{\cdot}OPr^{\beta}$ (I) with $Pr^{\beta}OH$ and H_3PO_4 at 160—170° affords (in low yield) a mixture of 1 : 4 : 3- (II) and 1 : 2 : 5-$C_6H_3MePr^{\beta}{\cdot}OPr^{\beta}$ (III); the major portion of (I) is recovered. (I) with $ZnCl_2$ under reflux affords a mixture of (II), (III), the corresponding phenols, and possibly 5-*methyl*-2 : 4-*di*-*isopropylphenyl* Pr^{β} *ether*, b.p. 265—270°.

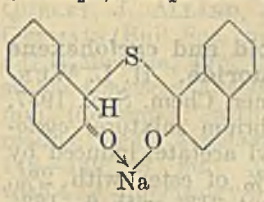
VII. It is stated (no experimental data) that m-$C_6H_4Me{\cdot}OPr^{\beta}$ and (II) are converted by Grignard reagents into *m*-cresol and thymol, respectively. P. G. C.

Migration reactions in polycyclic systems. II. Fries rearrangement of 4-acetoxydiphenyl. K. H. Cheetham and D. H. Hey (J.C.S., 1937, 770—772; cf. A., 1936, 991; this vol., 23).—With $AlCl_3$, 4-acetoxydiphenyl gives, with some 4-hydroxydiphenyl, 4-hydroxy-3-acetyldiphenyl (cf. A., 1936, 1374; 4-OMe-derivative). This is converted by $NaOAc–Ac_2O$ into 3-*acetyl*-6-*phenyl*-2-*methylchromone* (I), m.p. 143·5°, and by Na–EtOAc into the *Na* salt of 3-acetoacetyl-4-hydroxydiphenyl, which with AcOH–HCl yields 6-*phenyl*-2-*methylchromone* (II), m.p. 163·5°. With PhCHO, (II) forms 6-*phenyl*-2-*styrylchromone*, m.p. 202·5°. Both (I) and (II) are hydrolysed to 4-hydroxydiphenyl-3-carboxylic acid. E. W. W.

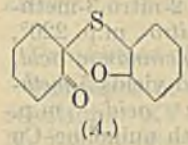
Derivatives of the hydroxydiphenyls. III. 4-Nitro-3-hydroxydiphenyl. J. C. Colbert, W. Meigs, and R. L. Jenkins (J. Amer. Chem. Soc., 1937, **59**, 1122—1124; cf. A., 1934, 1345).—m-$C_6H_4Ph{\cdot}OH$ and 1 mol. of HNO_3 in AcOH at 10—15° give amongst oily products 4-*nitro*-3-*hydroxydiphenyl*, m.p. 103·1—103·3° (x-*Br*-derivative, m.p. 109°), the structure of which is proved by its formation also from p-$C_6H_4Ph{\cdot}NO_2$ and KOH in C_6H_6 at 72—76°; excess of HNO_3 gives 2 : 4-*dinitro*-3-*hydroxydiphenyl*, m.p. 172·5—173° (also obtained from the 4-NO_2-compound), the structure assigned being based on lack of reactivity. Br gives only oils, unless <3 mols. are used, when (?) 2 : 4 : 6-*tribromo*-3-*hydroxydiphenyl*, m.p. 92°, is formed. 2 : 4-*Di*-, m.p. 100°, 2 : 4 : 6'-*tri*-, m.p. 131°, and 2 : 4 : 6-*trinitro*-3'-*phenyldiphenyl ether*, m.p. 143°, are described. R. S. C.

Covalent alkaline derivatives of di-2-hydroxy-1-naphthyl sulphide and of di-2-hydroxy-1-naphthylmethane. W. J. Evans and S. Smiles (J.C.S., 1937, 727—730).—Di-2-hydroxy-1-naphthyl sulphide (I) in 5% NaOH gives the *Na* derivative

(+4H_2O), m.p. 255°. This, being highly sol. in Et_2O, is regarded as having the annexed structure (without resonance). With MeI–MeOH it gives the Me ether of (I) (cf. A., 1931, 723), and with NaOMe–MeI–MeOH, the Me_2 ether (J.C.S., 1913, **103**, 345). The *Li* (+4H_2O and +2H_2O), no m.p., *K* (+2H_2O), m.p. 230°, and *Rb* (+2H_2O), m.p. 212°, compounds are obtained similarly. Di-3-bromo-2-hydroxy-1-naphthyl sulphide gives a *Na* derivative (+2H_2O), m.p. 300°. Di-2-hydroxy-1-naphthylmethane (II) gives *Na* (+4H_2O), m.p. 255° [converted by MeI or Me_2SO_4 into the *Me* ether of (II), m.p. 142° (*Ac* derivative, m.p. 131—133°, also obtained from di-2-methoxy-1-naphthylmethane and Ac_2O)], *Li* (+4H_2O), no m.p., and *K* (+2H_2O), m.p. 245°, derivatives, and the *compound* $C_{21}H_{15}O_2K,C_{21}H_{16}O_2,2H_2O$, m.p. 170°. E. W. W.



Rearrangement of *o*-hydroxy-sulphones. VI. C. S. McCLEMENT and S. SMILES (J.C.S., 1937, 1016—1021).—Certain substituted *o*-hydroxyphenyl-*o'*-nitrophenyl sulphones are converted by NaOH into *o*-*o'*-nitrophenoxysulphinic acids, characterised by conversion into sulphones and by elimination of the SO_2H. The sulphones are prepared by H_2O_2–AcOH oxidation of the corresponding sulphides, derived from 2-nitrophenylchlorothiol and the appropriate phenol. The following are described. 2'-*Nitro*-2-*hydroxy*-3 : 5 : 6-*trimethyldiphenyl sulphone* (I), m.p. 177°; 5-*chloro*-2'-*nitro*-2-*hydroxy*-3 : 6-*dimethyldiphenyl sulphide*, m.p. 191°, and *sulphone* (II), m.p. 164°; 3-*chloro*-2'-*nitro*-2-*hydroxy*-5 : 6-*dimethyldiphenyl sulphide*, m.p. 189°, and *sulphone* (III), m.p. 177°; 3-*chloro*-2'-*nitro*-2-*hydroxy*-4 : 6-*dimethyldiphenylsulphone* (IV), m.p. 164°; 5-*chloro*-2'-*nitro*-2-*hydroxy*-3-*methyldiphenyl sulphide*, m.p. 139°, and *sulphone* (V), m.p. 159°; 3-*chloro*-2'-*nitro*-2-*hydroxy*-5-*methyldiphenyl sulphide*, m.p. 142° (best from 2-nitrophenyl-4'-hydroxy-*m*-tolyl sulphide and SO_2Cl_2 in $CHCl_3$), and *sulphone* (VI), m.p. 198°; and 3-*chloro*-2'-*nitro*-2-*hydroxy*-4 : 5-*dimethyldiphenyl sulphide*, m.p. 152° (by action of SO_2Cl_2 on 2'-*nitro*-2-*hydroxy*-4 : 5-*dimethyldiphenyl sulphide*, m.p. 157°, from *o*-4-xylenol), and *sulphone* (VII), m.p. 155°. With 2*N*-NaOH, the following are obtained, at varying rates, and are degraded by $HgCl_2$ followed by EtOH–HCl to the ethers mentioned. From (I), 2'-*nitro*-6-*methylsulphonyl*-2 : 4 : 5-*trimethyldiphenyl ether*, m.p. 146° (giving 2'-*nitro*-2 : 4 : 5-*trimethyldiphenyl ether*, m.p. 80°); from (II), 5-*chloro*-2-*o*-*nitrophenoxy*-3 : 6-*dimethylbenzenesulphinic acid*, m.p. 125° (*methylsulphone*, m.p. 148°; 4-*chloro*-2'-*nitro*-2 : 5-*dimethyldiphenyl ether*, m.p. 70°); from (III), a *sulphinic acid* giving 2-*chloro*-2'-*nitro*-6-*methylsulphonyl*-3 : 5-*dimethyldiphenyl ether*, m.p. 71°; from (IV), 4-*chloro*-2'-*nitro*-6-*methylsulphonyl*-3 : 5-*dimethyldiphenyl ether*, m.p. 113° (*disulphide*, m.p. 142°; 4-*chloro*-2'-*nitro*-3 : 5-*dimethyldiphenyl ether*, m.p. 64°); from (V), 4-*chloro*-2'-*nitro*-2-*methyldiphenyl ether*, m.p. 39°; from (VI), 2-*chloro*-2'-*nitro*-4-*methyldiphenyl ether* m.p. 57°; and from (VII), 2-*chloro*-2'-*nitro*-3 : 4-*dimethyldiphenyl ether*, m.p. 115°. The above ethers are also synthesised directly (cf. A., 1927, 660). Substituted di-*o*-hydroxyphenyl sulphides are also prepared, and, by the action of $K_3Fe(CN)_6$, their dehydro-derivatives, in confirmation and extension of the work of Lesser and Gad (A., 1923, i, 561), whose formulæ for the latter are corr. to the basic structure (*A*).


(*A*.)

5-*Chloro*-*o*-*cresol* 3-*sulphide* has m.p. 145°. 5-Chloro-*p*-2-xylenol 3-sulphide forms a *dehydro-compound*, m.p. 165°, and a *Na* derivative (+4H_2O), m.p. 155°; ψ-cuminol sulphide a *dehydro-compound*, m.p. 97°, and a *Na* derivative (+4H_2O), m.p. 245°. The *Na* derivative of 2-chloro-*m*-5-xylenol 6-sulphide loses H_2O when heated, and passes into the electrovalent state (no m.p.). All sulphides which furnish dehydro-compounds are either derivatives of β-naphthol 2-sulphide, or, if derived from 2 : 2'-dihydroxydiphenyl sulphide, contain the 6-Me group, which is also necessary for the formation of a covalent Na derivative. The formation of both thus depends on the possibility of a hydroxy-ketonic structure being formed.

E. W. W.

Syntheses in the phenanthrene series. VII. 5 : 9-Dimethoxy- and 5-methoxy-1-methylphenanthrene. P. HILL, W. F. SHORT, and H. STROMBERG (J.C.S., 1937, 937—941).—1 : 5-$C_{10}H_6(OMe)_2$ (I) with succinic anhydride (II) and $AlCl_3$ in $PhNO_2$ or CS_2 gives β-(4 : 8-*dimethoxy*-1-*naphthoyl*)*propionic acid* (III), m.p. 173·5—174° (*Me* ester, m.p. 91—92°), also obtained from the Mg derivative of 4 : 1 : 5-$C_{10}H_5Br(OMe)_2$ and (II). In $C_2H_2Cl_4$, (I) and (II) with $AlCl_3$ give β-(4-*hydroxy*-8-*methoxy*-1-*naphthoyl*)-*propionic acid*, m.p. 184°, methylated to (III). Zn or Cu–Zn in aq. NaOH–NH_3 does not reduce (III), which with Zn–Hg in AcOH–HCl, followed by MeOH–HCl, yields the *Me* ester, m.p. 67—67·5°, of γ-(4 : 8-*dimethoxy*-1-*naphthyl*)*butyric acid* (IV), m.p. 154° (yield 20%), with (I). P_2O_5 in C_6H_6 converts (IV) into 1-*keto*-5 : 9-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 124° [2 : 4-*dinitrophenylhydrazone*, m.p. 295° (decomp.)], which with MeMgI gives 5 : 9-*dimethoxy*-1-*methyl*-3 : 4-*dihydrophenanthrene*, m.p. 111—111·5°, dehydrogenated (Pd–C) to 5 : 9-*dimethoxy*-1-*methylphenanthrene*, m.p. 139—140° (*picrate*, m.p. 200°), oxidation of which gives red amorphous products from which 5-methoxy-1-methylphenanthra-9 : 10-quinone could not be isolated. 1 : 5-OMe·$C_{10}H_6$·OH (V), CH_2:CH·CH_2Br, and K_2CO_3 in $COMe_2$ give 5-*methoxy*-α-*naphthyl allyl ether*, m.p. 103°, which at 240°/22 mm. yields 5-*methoxy*-2-*allyl*-α-*naphthol* (VI), m.p. 82—83°. This with Me_2SO_4 in Claisen's KOH gives 1 : 5-*dimethoxy*-2-*allylnaphthalene*, m.p. 24—25°, oxidised ($KMnO_4$) to 1 : 5-dimethoxy-2-naphthoic acid. With C_5H_5N,HCl at 220° (N_2), (VI) gives 5-*methoxy*-1-*methyl*-1 : 2-*dihydro*-α-*naphthafuran*, m.p. 116°. With $KHCO_3$ at 220°, (V) gives 1-*hydroxy*-5-*methoxy*-2-*naphthoic acid* (VII), m.p. 212·5—213° (*Me* ester, m.p. 118—119°), which with CH_2N_2 yields the *Me* ester, m.p. 80—81°, of 1 : 5-*dimethoxy*-2-*naphthoic acid*, m.p. 151—152°, hydrolysed to (VII). Alternatively (VII) is prepared by oxidation of 1 : 5-dimethoxy-2-naphthaldehyde. 4 : 1 : 5-$C_{10}H_5Br(OMe)_2$ yields (Grignard and CO_2) 4 : 8-*dimethoxy*-1-*naphthoic acid*, m.p. 222·5° (*Me* ester, m.p. 173—173·5°), also obtained by methylation of 4 : 8-dihydroxy-1-naphth-

aldehyde (VIII) to the Me_2 ether, m.p. 131—131·5°, oxidised to the acid. With KOH at 180—200° (VIII) gives 4 : 8-*dihydroxy*-1-*naphthoic acid*, m.p. 213°. *o*-Allyltoluene is oxidised to *o*-tolylacetic acid. A reproducible method of nitrating *m*-OMe·C_6H_4·CHO is described. K *o*-tolylacetate and 2-nitro-3-methoxybenzaldehyde, with Ac_2O, give 2-*nitro*-, m.p. 220°, reduced to 2-*amino*-3-*methoxy*-α-*o*-*tolylcinnamic acid*, m.p. 205—206°, which when diazotised yields 5-*methoxy*-1-*methylphenanthrene*-10-*carboxylic acid*, m.p. 224—225°. The last when heated with quinoline–Cu gives 5-*methoxy*-1-*methylphenanthrene*, m.p. 76—77° (*picrate*, m.p. 180—181°). E. W. W.

Manufacture of condensation products from hydroxy- and amino-derivatives of pyrene and chrysene.—See B., 1937, 527.

Manufacture of alkylphenols and related compounds.—See B., 1937, 528.

Manufacture of hydroarylated aromatic hydroxy-compounds.—See B., 1937, 358.

Oxidation of quinol in air in presence of *n*-butylammonium sulphite. (Mlle.) Y. Garreau (Compt. rend., 1937, **204**, 1570—1572; cf. this vol., 66, 251).—When quinol is stirred in aq. solution containing NH_2Bu^n (236 g.), SO_2 65 g., and $Cu(OH)_2$ 4·5 g. per litre, different products are obtained according to the concn. of quinol used. With 0·2 mol. of quinol per litre after 8 days, *butylammonium* α-2 : 5-*dibutylamino*-1 : 4-*benzoquinonemonosulphonate* (I), m.p. 150° (hydrolysed immediately by dil. HCl to 2 : 5-di-*n*-butylamino-1 : 4-benzoquinone), and *butylammonium* 2 : 5-*dibutylamino*-1 : 4-*benzoquinone*-3 : 6-*disulphonate* (II), m.p. 200—205°, are formed. With quinol (0·5 mol.), a β-*form*, m.p. 215° (+H_2O), of (I) (converted by dil. HCl into the corresponding acid) is formed together with *butylammonium* 2 : 5-*dihydroxy*-1 : 4-*benzoquinone*-3 : 6-*disulphonate*, m.p. 220—225°, which may result from the decomp. of (II). J. L. D.

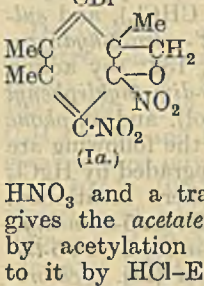
2 : 7 : 2′ : 7′-Tetrahydroxy-1 : 1′-dinaphthyl. K. Brass and R. Patzelt (Ber., 1937, 70, [*B*], 1341—1348).—2 : 7-$C_{10}H_6(OH)_2$ is oxidised by $FeCl_3$ under exactly defined conditions to 2 : 2′ : 7 : 7′-tetrahydroxy-1 : 1′-dinaphthyl (I), m.p. 214° (also +1H_2O, softens at 150—152°, and +2H_2O, m.p. 114°). All forms of (I) become discoloured when preserved in substance or in boiling H_2O but the change does not appear deep-seated. When heated at about 300° (I) gives 2 : 7-$C_{10}H_6(OH)_2$. (I) is converted by boiling AcOH–Ac_2O–NaOAc into a *tetra-acetate*, m.p. 184°, by BzCl and 25% KOH into a *tetrabenzoate*, m.p. 242·5°, and by Me_2SO_4–NaOH in boiling MeOH into a Me_4 *ether*, m.p. 150°. *p*-NO_2·C_6H_4·N_2Cl and (I) in alkaline solution give 8-*p*-*nitrobenzeneazo*-2 : 2′ : 7 : 7′-*tetrahydroxy*-1 : 1′-*dinaphthyl* or the *di*-*p*-*nitrobenzeneazo*-compound if a large excess of the reagent is used. Distillation of (I) with Zn dust affords $C_{10}H_8$ and perylene (II) but not dinaphthyl (III) which, moreover, is not an intermediate in the formation of $C_{10}H_8$ and (II). Under similar conditions 3 : 3′ : 4 : 4′-tetrahydroxydinaphthyl or its Ac_4 derivative gives $C_{10}H_8$ and (III) but not (II). H. W.

Preparation of alkyl*cyclo*hexanols.—See B., 1937, 529.

Condensation of acetic acid and *cyclo*hexene in the presence of boron fluoride. H. L. Wunderly and F. J. Sowa (J. Amer. Chem. Soc., 1937, **59**, 1010—1011).—The equilibrium mixture, *cyclo*hexene + AcOH ⇌ *cyclo*hexyl acetate, induced by BF_3 at 80° contains 8·1—8·8% of ester with 2%, 23·5—23·8% with 4%, and about 31% with 6—18% of BF_3; with <15% of BF_3 the % of ester decreases slowly with time. The ester dissolves 1 mol. of BF_3 and the low yield of ester with small amounts of catalyst is due to removal of the latter. The peculiar conditions of the above apparent equilibrium are due to the combined results of truly reversible esterification, irreversible polymerisation by higher concns. of BF_3, and reversible removal of BF_3. R. S. C.

Application of Curtius reaction to the synthesis of β-methoxy-β-phenylethylamine hydrochloride. P. P. T. Sah and C. Z. Tseu (J. Chinese Chem. Soc., 1937, **5**, 134—139).—Me cinnamate and $Hg(OAc)_2$ yield Me α-(acetatomercuri)-β-methoxy-β-phenylpropionate, m.p. 140°, decomposed by NH_3–H_2S to *Me* β-*methoxy*-β-*phenylpropionate*. This ester gives (N_2H_4) the *hydrazide*, m.p. 145—147° (*m*-NO_2·C_6H_4·CHO *derivative*, m.p. 192°), of β-methoxy-β-phenylpropionic acid, which through the azide forms the *urethane*, m.p. 68—69°, hydrolysed (HCl) to β-*methoxy*-β-*phenylethylamine hydrochloride*, m.p. 157—159°. F. R. S.

Polymethylbenzenes. XVIII. Action of nitric acid on bromodurene. L. I. Smith, F. L. Taylor, and (Miss) I. M. Webster (J. Amer. Chem. Soc., 1937, **59**, 1082—1086).—The compound (I), $C_{10}H_{11}O_5N_2Br$, obtained from bromodurene by fuming HNO_3 (cf. Smith *et al.*, A., 1935, 1114), is shown by the following reactions and those described previously to be probably 3-*bromo*-6-*nitro*-2 : 4 : 5-*trimethylbenzyl nitrate* or possibly (I*a*). CH_2O (guaiacol colour reaction only) is probably formed, as well as 2-bromo-5 : 6-dinitro-1 : 3 : 4-trimethylbenzene, by the action of conc. H_2SO_4 on (I). H_2SO_4 in aq. AcOH converts (I) into 3-*bromo*-6-*nitro*-2 : 4 : 5-*trimethylbenzyl alcohol* (II), m.p. 188°, with HNO_3 and a trace of HNO_2, and H_2SO_4 in Ac_2O gives the *acetate*, m.p. 86°, of (II), also obtained by acetylation of (II) and readily hydrolysed to it by HCl–EtOH. HNO_3 (*d* 1·5) and (II) at 0° give (I). HCl–EtOH converts (I) into the *chloride*, m.p. 112·5—113·5°, of (II), which, however, cannot be obtained directly from (II) and resists hydrolysis, but with NaI in $COMe_2$ gives the *iodide*, m.p. 113—115°, converted by $AgNO_3$ in hot dioxan into (I). NaOEt converts (I) into 3-*bromo*-6-*nitro*-2 : 4 : 5-*trimethylbenzaldehyde*, m.p. 193°, sensitive to light and KOH–H_2O–$COMe_2$. Oxidation of (I) is slow and gives indefinite material. Durylaldehyde with Br in H_2SO_4 gives (?) α : 2 : 5-*tribromoduryl* 2 : 5-*dibromodurylate*, m.p. 219—220°, and with KNO_3–H_2SO_4 at −8° gives a *substance*, m.p. 139—140°, which resists Br. R. S. C.



(I*a*.)

Synthesis of methoxybenzyl alcohols. R. Quelet, J. Allard, J. Ducasse, and (Mlle.) Y. Germain (Bull. Soc. chim., [v], 1937, 4, 1092—1101).—*o*-$C_6H_4Me{\cdot}OMe$, 40% CH_2O, and HCl yield very unstable 4-*methoxy*-3-*methylbenzyl chloride*, b.p. 119°/12 mm. (decomp.); with NaOAc the crude substance readily yields 4-*methoxy*-3-*methylbenzyl alcohol*, b.p. 148—149°/18 mm. (*phenylurethane*, m.p. 90·5°), with 4 : 4′-dimethoxy-3 : 3′-dimethyldiphenylmethane. Similarly *m*-$C_6H_4Me{\cdot}OMe$ gives, after treatment of the chloride, 4-*methoxy*-2-*methylbenzyl alcohol*, m.p. 143—147°/18 mm. (*phenylurethane*, m.p. 71°), with 4 : 4′ - dimethoxy - 2 : 2′ - dimethyldiphenylmethane. *p*-$C_6H_4Me{\cdot}OMe$ gives ($ZnCl_2$) 2-*methoxy*-5-*methylbenzyl chloride*, b.p. 124°/16 mm., which with NaOAc–AcOH gives the *acetate*, b.p. 146°/16 mm., of 2-*methoxy*-5-*methylbenzyl alcohol*, b.p. 140—141°/16 mm. (*phenylurethane*, m.p. 90°). 2 : 4 : 1-$OMe{\cdot}C_6H_3MePr^{\beta}$ gives 4-*methoxy*-2-*methyl*-5-iso*propyl-benzyl chloride*, b.p. 148°/16 mm., of which the crude product is converted into the -benzyl alcohol, new m.p. 35° (*phenylurethane*, m.p. 101°), with 4 : 4′-*dimethoxy*-2 : 2′-*dimethyl*-5 : 5′-*di*iso*propyl-diphenylmethane*, m.p. 73°, b.p. 225—230°/16 mm., oxidised to the corresponding *-benzophenone*, m.p. 139°. *o*-$NO_2{\cdot}C_6H_4{\cdot}OMe$ gives ($ZnCl_2$) 3-nitro-4-methoxybenzyl chloride, m.p. 85·5—86°, converted into the *acetate*, m.p. 37°, of 3-nitro-4-methoxybenzyl alcohol. The above benzyl alcohols are all oxidised ($KMnO_4$) to the corresponding benzoic acids. E. W. W.

Oxidation of ergosterol-B_3. Y. H. Chen (Ber., 1937, 70, [*B*], 1432—1437).—Ergosteryl-B_3 acetate, m.p. 132°, $[\alpha]_D^{20}$ — 183·5°, is oxidised by $Pb(OAc)_4$ in AcOH to *ergostadienetriol triacetate* (I), $C_{28}H_{43}O_3Ac_3$, m.p. 172—173°, $[\alpha]_D^{20\cdot3}$ +14·3° in $CHCl_3$, hydrolysed by KOH–EtOH to *ergostadienetriol*, m.p. 227°, converted by boiling Ac_2O partly into (I) but mainly into *acetylergostadienone* (II), $C_{30}H_{46}O_3$, m.p. 180—181°, $[\alpha]_D^{19\cdot2}$ +36·5° in $CHCl_3$, which does not afford a semicarbazone and is converted by NaOAc, Ac_2O, and Zn dust into a *substance*, $C_{32}H_{50}O_4$, m.p. 168°. Hydrogenation (Pt-sponge in AcOH) of (II) yields acetylergostanol, m.p. 144—145°. Ozonisation of (I) affords αβ-dimethylbutaldehyde. H. W.

Thermal decomposition of α-tocopherol. E. Fernholz (J. Amer. Chem. Soc., 1937, 59, 1154—1155).—α-Tocopherol is probably a mono-ether of duroquinol, since at 350° it decomposes to this quinol and an oil. R. S. C.

Constituents of senega root. I. α-Spinasterol. J. C. E. Simpson (J.C.S., 1937, 730—733; cf. A., 1932, 381; 1935, 210).—α-Spinasterol (I) (isolated from senega root as the benzoate), new $[\alpha]_D^{17}$ —3·7° (all rotations in $CHCl_3$), is oxidised (CrO_3–AcOH) to *α-spinastadienone* (II), m.p. 176—176·5°, $[\alpha]_D^{17}$ +19·5° (*oxime*, m.p. 253—255°). Its Ac derivative (III) gives with BzO_2H in $CHCl_3$ *α-spinasteryl acetate oxide*, m.p. 158·5—159°, $[\alpha]_D^{17}$ +1·4°, converted by MeOH—KOH into *α-spinasterol oxide*, m.p. 165°, also obtained from (I). (III) is oxidised (CrO_3–AcOH) to an *acetate*, $C_{30}H_{46}O_3$ or $C_{30}H_{48}O_3$, m.p. 211—213·5° (converted by NH_2OH into a *product*, m.p. 191—193°, and by EtOH–KOH into an *alcohol*, $C_{28}H_{44}O_2$ or $C_{28}H_{46}O_2$, m.p. 151—152°), with a *substance*, $C_{30}H_{46}O_4$ or $C_{30}H_{48}O_4$, m.p. 170—171°. (I) is unchanged by maleic anhydride, and thus lacks conjugated ethylenic linkings. It is regarded as a tetracyclic sterol, not containing a 5 : 6-double linking [since it has not high lævorotation, and since (II) shows only slight absorption at 2520 and 2440 A., and not at 2450 A.]. E. W. W.

Properties of calciferol.—See A., III, 327.

Influence of solvent on the course of chemical reactions. XV. Aromatic monocarboxylic acids. K. Lauer (Ber., 1937, 70, [*B*], 1288—1293).—The product of the dissociation const. of BzOH, 1- and 2-$C_{10}H_7{\cdot}CO_2H$, and anthracene-1-, -2-, and -9-carboxylic acid and the squares of the dipole moment of the corresponding Me esters is not const. as with phenols; the same holds for the product, dissociation const. × sp. exaltation of the Et esters. The divergence is shown particularly by carboxylic acids having a *peri* H atom; in these there is present a six-membered, subsidiary valency ring in which only one ion participates, thereby raising the electrolytic dissociation const. This view is in harmony with the observation that the α-hydroxyanthraquinones which contain a similar ring involving both ions have a remarkably small dissociation const. H. W.

Isomorphism of organic compounds. II. H. Lettré, H. Barnbeck, W. Fuhst, and F. Hardt (Ber., 1937, 70, [*B*], 1410—1416).—Isomorphism among *o*-, *m*-, and *p*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, -$C_6H_4Cl(Br){\cdot}CO_2H$, and -$C_6H_4Me{\cdot}CO_2H$ has been investigated. None of the twelve substituted acids gives mixed crystals with BzOH. Mixed crystals are formed by the similarly oriented chloro- and methyl-benzoic acids whereas the hydroxybenzoic acids do not form mixed crystals with the corresponding chloro- and methylbenzoic acids. The three bromobenzoic acids give mixed crystals with the similar chloro- and methylbenzoic acids but not with the OH-acids. Mixed crystals are never observed with combinations of position isomerides with the same substituents or, as far as observations have been made, with different substituents. Relationships in this series differ from those recorded for derivatives of $C_{10}H_8$. There is no known exception to the isomorphous replacability of Cl and Br but with other substituents this ability can be very greatly influenced by the complete structure of the mol. H. W.

Coupling of diazonium salts with derivatives of cyclic β-ketonic acids. R. P. Linstead and A. B. L. Wang (J.C.S., 1937, 807—814).—Et *cyclo*pentanone-2-carboxylate (I) condenses with diazotised NH_2Ph to the phenylhydrazone (cf. A., 1926, 1151) of Et H α-ketoadipate, with some cyclo*pentane*-1 : 2-*dionemonophenylhydrazone*, m.p. 201—203°, converted by $NHPh{\cdot}NH_2$ into the osazone. Using *o*- or *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, cyclo*pentane*-1 : 2-*dione-mono*-o- (II) (dimorphous, yellow and orange), m.p. 176—177°, and *-mono*-p-*nitrophenylhydrazone* (III), m.p. 242°, are obtained. By action of aq. EtOH–KOH, (II) undergoes ring fission to *ω-aldehydovaleric acid o-nitrophenylhydrazone*, m.p. 170—172°. With the diazonium salt from 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH_2$, (I) gives *Et* 2-(2′ : 4′-*dinitrobenzeneazo*)cyclo*pentanone*-2-*carboxylate*, m.p. 162—164°, which with aq. Na_2CO_3 undergoes

acid fission to *Et H α-ketoadipate* 2 : 4-*dinitrophenylhydrazone*, m.p. 168—170° (decomp.), hydrolysed to *α-ketoadipic acid* 2 : 4-*dinitrophenylhydrazone*, m.p. 238—240° (decomp.) (*Et*$_2$ ester, m.p. 48—50°). With NH_2Ph in C_5H_5N and xylene, (I) gives *cyclo*pentanone-2-carboxyanilide (IV), with its *anil*, m.p. 128—129°; with NH_2Ph and a trace of AcOH, (I) yields Et 1-anilino-Δ^1-*cyclo*pentene-2-carboxylate, m.p. 58·5° (cf. A., 1929, 1312). *Bis*cyclo*pentanone*-2-*carboxybenzidide* (V), no m.p. <250°, is also prepared. With *o*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$, (IV) gives 2-o-, m.p. 177°, and 2-p-*nitrobenzeneazo*cyclo*pentanone*-2-*carboxyanilide*, m.p. 242°, with (II) and (III), respectively. 2-(2′ : 4′-*Dinitrobenzeneazo*)cyclo*pentanone*-2-*carboxyanilide*, m.p. 206—207°, and, from (V), *bis*-2-o-, m.p. 265—268° (decomp.), and *bis*-2-p-*nitrobenzeneazo*cyclo*pentanone*-2-*carboxybenzidide*, m.p. 245—250° (decomp.), are also prepared.

The product from Et *cyclo*hexanone-2-carboxylate (VI) and NH_2Ph, Et H α-ketopimelate phenylhydrazone (A., 1931, 363), is hydrolysed by EtOH–KOH to *α-ketopimelic acid phenylhydrazone*, m.p. 153—154°, reduced to α-aminopimelic acid. *Et H α-ketopimelate* p-*nitrophenylhydrazone* (VII), m.p. 150°, and *α-ketopimelic acid* p-*nitrophenylhydrazone*, m.p. 174—175°, are also prepared. With *p*-nitrobenzenediazonium sulphate (VIII), (VI) yields *Et* 2-p-*nitrobenzeneazo*cyclo*hexanone*-2-*carboxylate*, m.p. 130—131°; this, which shows no tendency towards ring-fission, is converted by aq. Na_2CO_3 into (VII). Hydrolysed (VI), or pure *cyclo*hexanone-2-carboxylic acid, with diazotised NH_2Ph or *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, gives *cyclo*hexane-1 : 2-dione-phenylhydrazone (A., 1933, 835) and *-mono*-p-*nitrophenylhydrazone*, m.p. 245—246° (of which the *phenylhydrazone*, m.p. 243—244°, is prepared, in orange and blue dimorphic forms); the last is also the product when (VIII) is used, no azo-acid being formed. With *cyclo*hexanone-2-carboxyanilide, (VIII) gives 2-p-*nitrobenzeneazo*cyclo*hexanone*-2-*carboxyanilide*, m.p. 214°. 1-Phenyl-3 : 4-*cyclo*hexano-5-pyrazolone (IX) and (VIII) give a crude *azopyrazolone*, which with boiling EtOH yields (IX), MeCHO, $PhNO_2$, and N_2, and with $NPhMe_2$ gives *p*-nitrobenzeneazodimethylaniline.

E. W. W.

Derivatives of salicylic acid. XI. Bromosalicylic acids and their methyl ethers. N. W. Hirwe and B. V. Patil. **XII.** N. W. Hirwe and (Miss) K. D. Gavanker (Proc. Indian Acad. Sci., 1937, **5**, **A**, 321—325, 377—380).—XI. 3-Bromo- is prepared from 5-sulpho-salicylic acid by brominating and passing steam through its conc. aq. solution at 130°, and its *Me* ester, b.p. 277—278°, from the Ag salt and MeI. Other new derivatives described are those of 3-bromo- (*Et* ester, b.p. 270°; *amide*, m.p. 105—106°), 5-bromo- (*Et* ester, b.p. 295°; *amide*, m.p. 153—154°), and 3 : 5-dibromo- (*Et* ester, b.p. 295°; *amide*, m.p. 173—174°) -2-methoxybenzoic acid.

XII. The following are described: *Me* 3-, m.p. 60°, and *Et* 5-*nitro*-2-*methoxybenzoate*, m.p. 80—81°; 3-, m.p. 124°, and 5-*nitro*-, m.p. 213°, and 3 : 5-*dinitro*-2-*methoxybenzamide*, m.p. 166—167°; 3-*nitro*-5-*bromo*-, m.p. 221°, and 3 : 5-*dinitro*-, m.p. 181°, -2-*hydroxybenzamide*.

A. Li.

Preparation of *o*-phthalaldehydic acid. B. B. Dey and T. K. Srinivasan (Proc. Indian Acad. Sci., 1937, **5**, **A**, 329—335).—$C_{10}H_8$ is oxidised ($KMnO_4$) to phthalonic acid, the $NaHSO_3$ derivative of which (cf. Graebe and Trümpy, A., 1898, i, 318), after two evaporations with conc. HCl, yields diphthalide ether (I) (hydrolysed by NaOH to *o*-$CHO{\cdot}C_6H_4{\cdot}CO_2H$) and a *compound* (extracted with C_6H_6), $C_{16}H_{12}O_6$, m.p. 98°, clearing point 168°, probably $C_6H_4<\begin{matrix}CH(OH)-O-CO\\CO{\cdot}O{\cdot}C_6H_4(OH)\end{matrix}>C_6H_4$ (II), which gives with boiling H_2O or conc. HCl *o*-$CHO{\cdot}C_6H_4{\cdot}CO_2H$, and with boiling EtOH (I) and *ψ*-phthalaldehydic Et ester. Applying these observations, the yield of phthalaldehydic acid from the phthalonic acid by the method of Gardener and Naylor (Org. Syntheses, 1936, **16**, 68) can be made as high as 77% by working up the residue left after the C_6H_6 extraction. The *NO*$_2$-derivative of (II) ($KNO_3 + H_2SO_4$), m.p. 120—140°, is hydrolysed to 1 : 2 : 3-$NO_2{\cdot}C_6H_4(CHO){\cdot}CO_2H$.

A. Li.

Condensation of aldehydes with malonic acid in presence of organic bases. VIII. Condensation of *o*- and *m*-anisaldehyde. K. C. Pandya and T. A. Vahidy (Proc. Indian Acad. Sci., 1937, **5**, **A**, 437—441; cf. A., 1936, 1377).—The yields of *o*- (or *m*-)methoxycinnamic acid afforded by condensing of *o*- (or *m*-)anisaldehyde with $CH_2(CO_2H)_2$ in presence of five different bases are compared. C_5H_5N gives the best yield (100%) and cleanest product, but condensation also occurs (more slowly) without using a base.

F. N. W.

Friedel–Crafts condensation of substituted glutaric anhydrides with benzene and the formation of isomeric benzoylphenylpropionic acids in the reaction between phenylsuccinic anhydride and benzene. A. Ali, R. D. Desai, R. F. Hunter, and S. M. M. Muhammad (J.C.S., 1937, 1013—1016).—The anhydrides of glutaric acid and its ββ-Me_2 and β-methyl-β-ethyl derivatives react with C_6H_6 ($AlCl_3$) to give *γ-benzoyl*-n-*butyric acid*, m.p. 132° [*semicarbazone*, m.p. 213° (decomp.)], -ββ-*dimethyl*-n-*butyric acid*, b.p. 115°/35 mm. [*semicarbazone*, m.p. 178° (decomp.)], and -β-*methyl*-β-*ethyl*-n-*butyric acid*, m.p. 49° [*semicarbazone*, m.p. 164—165° (decomp.)]. These are reduced (Clemmensen) to $CH_2Ph{\cdot}[CH_2]_3{\cdot}CO_2H$, δ-*phenyl*-ββ-*dimethyl*-, b.p. 120—121°/15 mm., and δ-*phenyl*-β-*methyl*-β-*ethyl*-n-*valeric acid*, b.p. 138°/20 mm., but with H_2SO_4 none of these condenses to the expected benz*cyclo*heptane derivative, there being extensive sulphonation. β-Phenylglutaric anhydride does not condense with C_6H_6, but internally, giving ketohydrindene-3-acetic acid [semicarbazone, new m.p. 260° (decomp.)]. CPh:CHBz and $CHNa(CO_2Et)_2$ give a *substance*, m.p. 255°, and $CH_2Bz{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$. *cyclo*Pentane-1 : 1-diacetic anhydride with C_6H_6 and $AlCl_3$ gives 1-*phenacyl*cyclo*pentane*-1-*acetic acid*, m.p. 85° [*semicarbazone*, m.p. 196° (decomp.)], reduced to 1-β-*phenylethyl*-cyclo*pentane*-1-*acetic acid*, an oil, with 1-β-*hydroxy*-β-*phenylethyl*cyclo*pentane*-1-*acetic acid lactone* (?), m.p. 216°. 1-*Phenacyl*-3-*methyl*cyclo*pentane*-1-*acetic acid*, m.p. 65° [*semicarbazone*, m.p. 187° (decomp.)], is prepared. 1-*Phenacyl*cyclo*hexane*-1-*acetic acid*, m.p.

99° [*semicarbazone*, m.p. 189° (decomp.], is reduced to 1-β-*phenylethyl*cyclo*hexane*-1-*acetic acid*, an oil, with 1-β-*hydroxy*-β-*phenylethyl*cyclo*hexane*-1-*acetic acid lactone* (?), m.p. 265°. In the condensation of phenylsuccinic anhydride with C_6H_6 ($AlCl_3$), in addition to β-benzoyl-β-phenylpropionic acid (I) (reduced to βγ-diphenylbutyric acid), *β-benzoyl-α-phenylpropionic* acid (II), m.p. 154° (reduced to *αγ-diphenyl-n-butyric acid*, m.p. 110°), and *γ-hydroxy-αγγ*[or βγγ]-*triphenyl-n-butyric acid lactone* (?), m.p. 285° (decomp.), are formed. The compounds (I) and (II) are synthesised from CH_2PhBz, NaOEt, and $CH_2Br{\cdot}CO_2Et$ and from $CH_2Ph{\cdot}CN$ and CH_2BzBr, respectively. E. W. W.

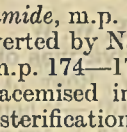
Bridged ring systems. Density, refraction, and hydrolysis of esters. H. Bode (Ber., 1937, 70, [*B*], 1167—1186).—Measurements of *d* and *n* are recorded for the isomeric Me 2 : 5-*endo*methylenehexahydrobenzoates, Me_2 3 : 6-*endo*methylenehexahydro-*o*-phthalates, and Me_2 3 : 6-*endo*methylene-Δ^4-tetrahydro-*o*-phthalates. The *endo*- and *endo-cis*-forms are the most compact; the *exo*- and *exo-cis*-isomerides have somewhat greater mol. vols. whilst the *trans*-isomerides have the largest vols. The differing mol. vols. are probably caused by difference in size of the individual mols. rather than by differences in the intermol. forces. The mol. refraction of isomeric esters is practically const. The abs. vals. of the mol. refraction agree well with those calc. according to Roth–Eisenlohr particularly in the cases of the saturated esters. This is attributed to compensation of the diminution of polarisability caused by the compact, spatial structure of the mol. by the strain in the mol. In a corresponding strainless mol. (Me_2 *cis*-3 : 6-*endo*ethylene-Δ^4-tetrahydro-*o*-phthalate and the corresponding H_6-compound; di*cyclo*hexadiene; tetrahydrodi*cyclo*hexadiene) a depression of the mol. refraction is observed. Examination of recorded rates of hydrolysis of esters of borneol and *iso*borneol and the corresponding *epi*-compounds shows that, for each corresponding pair, one form (*iso*-alcohols, α-esters) is characterised by higher *d* and *n* and smaller rate of hydrolysis and can be converted into the other isomeride. The mol. refractions of each isomeride are equal. In properties, therefore, the isomerides correspond completely with the *endo-exo*-compounds of the norcamphane series and, if the rules developed for the latter are applied, the *iso*borneol, *epi-iso*borneol, and α-acid derivatives are to be regarded as isomerides with *endo*-placed groups. H. W.

Identification of alcohols by 3-nitrophthalic anhydride. G. M. Dickinson, L. H. Crosson, and J. E. Copenhaver (J. Amer. Chem. Soc., 1937, 59, 1094—1095).—The following *alkyl H* 3-*nitrophthalates*, 3 : 1 : 2-$NO_2{\cdot}C_6H_3(CO_2H){\cdot}CO_2R$, are obtained, with a little of the 1-mono-ester, by heating the acid anhydride and alcohol at the b.p., at 100°, or in PhMe : Me, m.p. 152·9—153·4°, Et, m.p. 157·7—158·3°, Pr^{α}, m.p. 144·9—145·7°, Pr^{β}, m.p. 153·9—154·3°, Bu^{α}, m.p. 146·8—147°, Bu^{β}, m.p. 179·9—180·6°, sec.-*Bu*, m.p. 130·6—131·4°, n-*amyl*, m.p. 136·2—136·4°, *iso*amyl, m.p. 163·2—163·4°, n-*hexyl*, m.p. 123·9—124·4°, n-*heptyl*, m.p. 126·9—127·2°, n-*octyl*, m.p. 127·8—128·2°, n-*nonyl*, m.p. 124·8—125·2°, n-*decyl*, m.p. 122·7—122·8°, n-*undecyl*, m.p. 123·2—123·3°, n-*dodecyl*, m.p. 123·9—124°, n-*tridecyl*, m.p. 124—124·2°, n-*tetradecyl*, m.p. 123·2—123·5°, n-*pentadecyl*, m.p. 122·4—122·6°, n-*hexadecyl*, m.p. 121·4—122°, n-*heptadecyl*, m.p. 121—121·8°, and n-*octadecyl*, m.p. 118·3—119·2°. M.p. are corr. R. S. C.

Reaction between phthalic anhydride and ethylene glycol.—See A., I, 417.

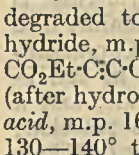
Optical resolution of 1 : 1′-dianthryl-2 : 2′-dicarboxylic acid. K. Lauer, R. Oda, and M. Miyawaki (J. pr. Chem., 1937, [ii], 148, 310—316).—Fractional crystallisation of the quinine salt of the *dl*-acid affords *quinine* d-1 : 1′-*dianthryl*-2 : 2′-*dicarboxylate* (I), m.p. 165—185° (decomp.), $[\alpha]_D^{20}$ +233·2° in $CHCl_3$, and *quinine* l-1 : 1′-*dianthryl*-2 : 2′-*dicarboxylate* (II), m.p. 160—185° (decomp.), $[\alpha]_D^{20}$ −245·0° in $CHCl_3$. (I) and HCl afford d-1 : 1′-*dianthryl*-2 : 2′-*dicarboxylic acid* (III), m.p. 187—198° (decomp.), $[\alpha]_D^{20}$ +352·0° in $COMe_2$ (*chloride*, $[\alpha]_D^{20}$ +256·0° in $CHCl_3$; *amide*, m.p. 171—175°, $[\alpha]_D^{20}$ +250·0° in $CHCl_3$). Similarly, (II) affords l-1 : 1′-*dianthryl*-2 : 2′-*dicarboxylic acid* (IV), m.p. 190—200° (decomp.), $[\alpha]_D^{20}$ −358·2° in $COMe_2$ (*chloride*, $[\alpha]_D^{20}$ −250·0° in $CHCl_3$; *amide*, m.p. 172—180°, $[\alpha]_D^{20}$ −251·5° in $CHCl_3$), converted by NaOBr into l-2 : 2′-*diamino*-1 : 1′-*dianthryl*, m.p. 174—175°, $[\alpha]_D^{20}$ −336·7° in $CHCl_3$. (IV) was not racemised in Ac_2O solution at 145° for 5 hr. The esterification rates, and $[\alpha]_D^{20}$ vals. in $CHCl_3$, AcOH, and 0·1*N*-KOH, of (III) and (IV) are given, as well as *X*-ray (powder) figures for (III). P. G. C.

Diene synthesis. II. Thermal decomposition of the additive products of acetylenedicarboxylic ester. K. Alder and H. F. Rickert (Ber., 1937, 70, [*B*], 1354—1363).—*cyclo*Heptadiene (I) and $CO_2Me{\cdot}C{:}C{\cdot}CO_2Me$ give the normal adduct, hydrogenated (colloidal Pd), hydrolysed, and dehydrated by AcCl to 3 : 6-endo*propylene*-Δ^1-*tetrahydrophthalic anhydride*, m.p. 137°. (I) therefore resembles *cyclo*pentadiene. Furan is heated with $CO_2Et{\cdot}C{:}C{\cdot}CO_2Et$ at 100° and the product is hydrogenated (Pd–$CaCO_3$) and then hydrolysed to 3 : 6-endo-*oxido*-Δ^1-*tetrahydrophthalic acid* (II), m.p. 167°, and furan-



(II.)

3 : 4-dicarboxylic acid, m.p. 212° (Me ester, m.p. 46°). When treated similarly, 2-methylfuran yields 2-*methylfuran*-3 : 4-*dicarboxylic acid*, m.p. 230—231° (non-cryst. Me_2 ester; *dianilide*, m.p. 211—212°), and 3 : 6-endo-*oxido*-3-*methyl*-Δ^1-*tetrahydrophthalic acid*, degraded to 3-methylphthalic acid, m.p. 154° (anhydride, m.p. 118°). When boiled with $CO_2Et{\cdot}C{:}C{\cdot}CO_2Et$. Et *iso*dehydracetate gives CO_2 and (after hydrolysis) 5-*carbethoxy*-4 : 6-*dimethyl*-*o*-*phthalic acid*, m.p. 164° (K_2 salt), oxidised by fuming HNO_3 at 130—140° to $C_6H(CO_2H)_5$. Analogously, trimellitic acid is derived from Et coumalate. 4-Methylpyronone reacts as enol giving a primary adduct (III), which becomes stabilised by loss of CO_2 and formation of an aromatic nucleus whereby 5-hydroxy-*m*-toluic acid is obtained in place of the expected 4-hydroxy-6-methyl-*o*-phthalic acid. H. W.



(III.)

Synthesis of conjugated bile acids. III. Sodium taurocholate and taurodeoxycholate. F. Cortese and J. T. Bashour (J. Biol. Chem., 1937, **119**, 177—183; cf. A., 1936, 724).—The chloride of triformylcholic acid (I) with conc. aq. taurine (II) and conc. aq. NaOH [amount required depending on purity of (I)] are shaken for 5 hr., and neutralised with HCl. $COMe_2$ is added, and recovered (II) removed. The filtrate is evaporated, and the boiling EtOH extract of the resulting oil or gum is pptd. with Et_2O, giving Na triformyltaurocholate. This is treated with NaOH, followed by HCl, and Na taurocholate (III) obtained in 50% yield, $[\alpha]_D^{20}$ +23·7° in H_2O, identical with the natural product. Decomp. points of normal (130—145°) and *para* (225—235°) forms of (III) are of little val. for characterisation. The amount of H_2O in (III) depends on atm. R.H. The chloride from diformyldeoxycholic acid (*loc. cit.*) with taurine similarly gives Na taurodeoxycholate (IV), $[\alpha]_D^{21}$ +35·4°, which at 117° gives a *para* form, decomp. 160—175°. Full details of prep. of (III) and (IV) are given. The work of Tanaka (A., 1933, 1162) is criticised: (III) does not isomerise in H_2O at 100°. The Bondi and Müller method (cf. A., 1919, i, 576) yields (IV) and not the free acid.

E. W. W.

Sulphur studies. XI. Sulphur derivatives of benzaldehyde. J. H. Wood and R. W. Bost (J. Amer. Chem. Soc., 1937, **59**, 1011—1013).—When $CHPhCl_2$ and Na_2S are kept in EtOH under N_2 for a week or heated for 6—8 hr., PhCHS is formed, but cannot be isolated; some gives the β-trimeride (I), some undergoes the Cannizzaro reaction to give $CH_2Ph{\cdot}SH$, $PhCS_2H$, and a little $PhCS_2{\cdot}CH_2Ph$ (II), whilst some of the $CH_2Ph{\cdot}SH$ formed reacts with PhCHS to give a little $CHPh(S{\cdot}CH_2Ph)_2$. PhCHS undergoes the Cannizzaro reaction by way of the ester (II); if it is brought about by Na_2S, the ester cannot be isolated owing to its immediate hydrolysis to $PhCS_2H$ and $CH_2Ph{\cdot}SH$, but if (I) is distilled at 3 mm. in the presence of a few drops of H_2SO_4, the distillate is mainly the monomeride [with a little $(CHPh)_2$, S, and tetraphenylthiophen], which partly reverts to (I) and partly polymerises to (II); the Cannizzaro reaction can then be completed by adding Na_2S. When (I) is distilled alone, tetraphenylthiophen is the main product. Passage of H_2S into PhCHO in EtOH saturated with HCl gives (I); in presence of less acid [HCl, H_2SO_4, $ZnCl_2$, AcOH, $Mg(ClO_4)_2$, P_2O_5], a pink gummy polymeride is formed, which decomposes when distilled, mainly into $(CHPh)_2$ and S, and does not undergo the Cannizzaro reaction. Passage of H_2S into PhCHO in KOH–EtOH gives mainly a pink oily polymeride, and a residue, which undergoes the Cannizzaro reaction; distillation of this polymeride gives mainly $(CHPh)_2$ and S, but also some (II), indicating partial depolymerisation. $PhCS_2Na$, CH_2PhCl, and NaOH in equiv. amounts in hot EtOH give *benzyl dithiobenzoate* (II), b.p. 179—180°/3 mm., identified by hydrolysis by Na_2S; contrary to Fromm *et al.* (A., 1913, i, 175), an excess of CH_2PhCl and NaOH leads to $(CH_2Ph)_2S$, m.p. 50°, obtained by hydrolysis of the (II) formed and interaction of the resulting $CH_2Ph{\cdot}SNa$ with CH_2PhCl. $(CHPh{:}NH,HCl)_2,SnCl_4$ and H_2S in EtOH give a plastic *substance*, m.p. 100—110°, and a pink gum.

R. S. C.

κ-Phenylundecapentaenal and φ-phenylpentadecaheptaenal. R. Kuhn and K. Wallenfels (Ber., 1937, **70**, [*B*], 1331—1333).—$CHPh{:}CH{\cdot}CHO$ is transformed by $CHMe{:}CH{\cdot}CHO$ in presence of piperidine–AcOH into *κ-phenylundecapentaenal* (I), m.p. 183° (vac.), the constitution of which is established by its conversion by $CH_2Ph{\cdot}MgCl$ into $Ph{\cdot}[CH{:}CH]_6{\cdot}Ph$. Condensation of (I) with $CH_2(CO_2H)_2$ in C_5H_5N containing piperidine affords *phenylundecapentaenylidenemalonic acid*, decarboxylated in boiling Ac_2O to *μ-phenyl-*$\Delta^{\alpha\gamma\epsilon\eta\lambda}$*-tridecahexaenoic acid*, m.p. 255°. (I) is reduced by $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ to *λ-phenyl-*$\Delta^{\beta\delta\zeta\iota\kappa}$*-undecapentaenol*, m.p. 203°. *φ-Phenylpentadecaheptaenal*, m.p. 234°, is obtained in minor amount during the prep. of (I).

H. W.

Studies in the synthesis of vitamin-*A*. III. J. W. Batty, A. Burawoy, I. M. Heilbron, W. E. Jones, and A. Lowe (J.C.S., 1937, 755—760).—Experiments directed towards the synthesis of ι-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-$\Delta^{\beta\delta\zeta\theta}$-nonatetraen-α-ol by way of β-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)acraldehyde are described. The view (A., 1931, 961) that "citrylidenemalonic acid" is not δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene-αα-dicarboxylic acid is confirmed by its lack of selective absorption, and its failure to give $COMe_2$ when treated with O_3. Its quant. conversion by Cu-bronze at 130—140°/10—15 mm. into *δθ-dimethyl-*$\Delta^{\alpha\gamma\eta}$*-nonatriene-α-carboxylic acid* (I), b.p. 132—134°/1 mm. (*Me* ester, b.p. 137—140°/15 mm.), is, however, difficult to reconcile with the dilactonic formula (*loc. cit.*). The *Ba* salt of (I) with $(HCO_2)_2Ba$ and sand at 150—160°/1 mm. gives α-aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene (II) (citrylideneacetaldehyde; cf. A., 1936, 316), which with aq. $CN{\cdot}CH_2{\cdot}CO_2Na$ yields *α-cyano-ζχ-dimethyl-*$\Delta^{\alpha\gamma\epsilon\iota}$*-undecatetraene-α-carboxylic acid*, m.p. 150°. (II) forms only one semicarbazone, m.p. 167° (cf. *loc. cit.*), but this is accompanied by a small quantity of a *semicarbazone* (III), m.p. 158° (see below). Citral condenses with $CHMe{:}CH{\cdot}CHO$ ($C_5H_{11}N$–AcOH) at 110° (CO_2) to a *product* separated into three fractions. Fraction *A* is an *oil*, b.p. 86—88°/0·03 mm. [*semicarbazone*, $C_{15}H_{23}ON_3$ (IV), m.p. 206°; *phenylhydrazone*, $C_{21}H_{27}ON_3$, m.p. 173°]. Fraction *B*, b.p. 115—118°/0·1 mm., gives (IV) and (III) (see above), m.p. 160°, identified as the *semicarbazone* of *α-aldehydo-ζχ-dimethyl-*$\Delta^{\alpha\gamma\epsilon\iota}$*-undecatetraene* (V), b.p. 114—118°/0·05 mm. (*phenylsemicarbazone*, m.p. 134°; 2 : 4-*dinitrophenylhydrazone*, m.p. 104—105°; *anil*, b.p. 178—182°/15 mm.), into which it is converted by $H_2C_2O_4$. With O_3, (V) gives $COMe_2$ and lævulaldehyde. Fraction *C* yields a *semicarbazone*, $C_{15}H_{23}ON_3$, m.p. 197°. Microhydrogenation of (III) shows 5 double linkings. $\lambda_{max.}$ and $\varepsilon_{max.}$ of the above compounds are tabulated.

E. W. W.

Polymethylbenzenes. XVII. Acetopentamethylbenzene. L. I. Smith, (Miss) I. M. Webster, and C. Guss (J. Amer. Chem. Soc., 1937, **59**, 1078—1082).—*Acetopentamethylbenzene* (I), prepared by Smith and Guss' method (this vol., 293), has b.p. 144—145°/8 mm., m.p. 84°, is completely enolised by MgEtBr, and the enolic OMgBr-compound with AcCl gives *pentamethylbenzoyldiacetylmethane* [*γ-penta-*

methylbenzoylpentane-βδ-dione] (II), m.p. 110—111° (*Cu* derivative), which with NH_2OH gives a *compound*, m.p. 176°, 4-*pentamethylbenzoyl*-3 : 5-*dimethyl*- or 4-*acetyl*-5-*pentamethylphenyl*-3-*methyl*-isooxazole. C_6Me_5·MgBr with AcCl by most procedures gives mainly C_6HMe_5 with some C_6Me_5Br and (?) $CMeEt_2$·OH; methods of separating (I) and (II) from such reaction products are devised, but only in one case was (I) (6% only) found. Clémont's compound, m.p. 110° (A., 1936, 852), was not (I) or (II).

[With J. H. Paden.] C_6HMe_5, $Zn(CN)_2$, HCl, and $AlCl_3$ give *pentamethylbenzaldehyde*, m.p. 142—147°, b.p. 144°/6 mm. (*oxime*, m.p. 187—188°; *semicarbazone*, m.p. 270—275°) (cf. Clémont, *loc. cit.*). R. S. C.

Benzoyl chloride. Aromatic ketones. J. B. Senderens (Compt. rend., 1937, **204**, 1296—1299).—When a mixture of BzCl and a fatty acid is passed over ThO_2 at 400—450°, the product contains the mixed fatty-aromatic ketone and the fatty ketone, with decomp. products of BzCl. Thus Pr^aCO_2H gives COPhPr^a and COPr$^a_2$ at 450°; AcOH at 300° gives only $COMe_2$ whilst COPhMe appears at 400°. BzCl alone over ThO_2 at 370° decomposes to a gas (60% H_2, 40% CO_2), HCl, H_2O, and C. A mixture of BzCl and glacial AcOH in a closed flask at room temp. slowly deposits crystals and evolves HCl; the crystals when distilled give AcOH and BzOH. AcOH from Ac_2O does not react thus but propionic, butyric, and valeric acids (commercial pure) give small amounts of BzOH. J. L. D.

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

Condensation of deoxybenzoin with aromatic aldehydes and ketones. II. Condensations using substituted deoxybenzoins and substituted acetophenones. H. J. Callow and D. W. Hill (J.C.S., 1937, 844—847; cf. A., 1936, 997).—COPhMe and deoxybenzoin in EtOH–KOH, exposed to air, give *phenacylidenedideoxybenzoin*, $CHBz(CHPhBz)_2$ (I), m.p. 199—200°, and iso*phenacylidenedideoxybenzoin*, m.p. 175°. These are shown to be stereoisomerides by their being both dehydrated by AcOH–HCl or by H_2SO_4 to the same *substance*, m.p. 118—119°, which is either 4-*benzoyl*-2 : 3 : 5-*tetraphenylpyran* or 4-α-*phenylphenacyl*-2 : 3 : 5-*triphenylfuran*. It is suggested that the above reaction proceeds through an intermediate oxide, OH·CPh$<^{\text{O·CHPh}}_{\text{CHPh·O}}>$CPh·OH, which either reacts with COPhMe to form (I), or oxidises further to CHPh·CPh·OH (O——O), and thence to BzOH, which is also obtained. Substituted deoxybenzoins give similarly *phenacylidene-di*-(4-*methyldeoxybenzoin*), m.p. 238—240° (and the iso-*compound*, m.p. 175—176°); -*di*-(4′-*methyldeoxybenzoin*), m.p. 255—256° (and the iso-*compound*, m.p. 240—241°); -*di*-(4-*methoxydeoxybenzoin*), m.p. 225° (and the iso-*compound*, m.p. 190°); -*di*-(4-*chlorodeoxybenzoin*), m.p. 255—256° (and the iso-*compound*, m.p. 211—212°), -*di*-(4′-*chlorodeoxybenzoin*), m.p. 248° (and the iso-*compound*, m.p. 234—235°), and -*di*-(4-*bromodeoxybenzoin*), m.p. 248° (from 4-*bromodeoxybenzoin*, m.p. 115°, prepared from *p*-bromobenzamide and $CH_2PhMgBr$). With the above compounds, the corresponding benzoic acid is also formed. Using deoxybenzoin and substituted acetophenones, p-*methyl*-, m.p. 217° (iso-*compound*, m.p. 196—197°), p-*methoxy*-, m.p. 209° (iso-*compound*, m.p. 190—191°), p-*bromo*-, m.p. 231° (iso-*compound*, m.p. 213—215°), and *p-amino-phenacylidenedideoxybenzoin*, m.p. 205°, are obtained. E. W. W.

Reactions of α-aminoketones. T. S. Stevens and B. A. Hems (J.C.S., 1937, 856—857).—That N in compounds of type Ph·CO·CH(NMe$_2$)·CH_2Ph (I) (cf. A., 1930, 1437) occupies the α- and not the β-position with respect to CO, is shown by conversion of (I) by MgPhBr into β-*dimethylamino*-α-*hydroxy*-αα*γ*-*triphenylpropane*, m.p. 75° (*picrate*, m.p. 188°), which is oxidised by persulphate to $COPh_2$ and CH_2Ph·CHO. Substituted benzylacetophenones (*loc. cit.*) similarly give β-*dimethylamino*-α-*hydroxy*-αα*γ*-*triphenylbutane*, not cryst. [*hydrochloride*, m.p. 226—231° (decomp.)], oxidised to $COPh_2$ and CHPhMe·CHO; β-*piperidino*-α-*hydroxy*-αα*γ*-*triphenylpropane*, m.p. 145—147°; and β-*dimethylamino*-α-*hydroxy*-αα*γγ*-*tetraphenylpropane*, m.p. 105° (*sulphate*), oxidised to $COPh_2$, without $CHPh_2$·CHO or $CHPh_2$·CO_2H. In EtOH–NaOEt, (I) is oxidised by air to *Ph* α-*dimethylaminostyryl ketone*, m.p. 62° (synthesised), with BzOH and CH_2Ph·CPh(OH)·CO_2H. BrCN in Et_2O converts (I), with loss of a Me group, into *Ph* α-*methylcyanoamido*-β-*phenylethyl ketone*, m.p. 110° (corresponding *carbamide*, m.p. 226°). ω-Piperidino-ω-benzylacetophenone similarly gives, by ring fission, *Ph* α-(ε-*bromoamylcyanoamido*)-β-*phenylethyl ketone*, m.p. 83°. E. W. W.

Detection and determination of aldehydes by halogen derivatives of dimedon. T. Voitila (Suomen Kem., 1937, **10**, B, 14).—Reduction of 2 : 4 : 6-tribromo-1 : 1-dimethyl*cyclo*hexane-3 : 5-dione with acid KI yields 2 : 6-*dibromo*-1 : 1-*dimethyl*-cyclo*hexane*-3 : 5-*dione* (I), m.p. 145—147° (decomp.). (I) (2 mols.) gives with CH_2O (1 mol.) a *compound*, m.p. 203—204°, and with MeCHO (1 mol.) a *compound*, m.p. 182° (decomp.). 4-Bromo-1 : 1-dimethyl*cyclo*hexane-3 : 5-dione reacts with CH_2O with loss of HBr, the *product* having m.p. 213—214°. M. H. M. A.

Pyrenium. XXVIII. Constitution of benzoylnaphthol. W. Dilthey and O. Dornheim (J. pr. Chem., 1937, [ii], **149**, 55—57).—The action of MgPhBr on 2 : 1-OH·$C_{10}H_6$·CHO gives *phenyl*-2-*hydroxy*-1-*naphthylcarbinol*, m.p. 118—119°, also obtained by reduction of 1 : 2-$C_{10}H_6$Bz·OH (I) in alkaline but not in acid medium. The constitution of (I) is thus established. H. W.

Synthesis of dicyclic α-ketones with an angular methyl group. G. A. R. Kon, R. P. Linstead, and C. Simons (J.C.S., 1937, 814—817).—8-Methyl-1-hydrindanone and 9-methyldecahydronaphthal-1-one are synthesised by new methods. With OEt·$[CH_2]_3$·MgBr, Et 2-methyl*cyclo*hexanone-2-carboxylate gives Et 2-methyl-2-γ-ethoxypropyl*cyclo*hexan-1-ol-2-carboxylate (cf. this vol., 197), b.p. 144°/4 mm., which when boiled with aq. $H_2C_2O_4$ gives *Et* 2-*methyl*-1-γ-*ethoxypropyl*-$\Delta^{6(1)}$-cyclo*hexene*-2-*carboxylate*, b.p. 122°/2 mm., reduced (Adams) to

Et 2-*methyl*-1-γ-*ethoxypropyl*-$\Delta^{6(7)}$-cyclo*hexane*-2-*carboxylate* (I), b.p. 123°/3 mm. (hydrolysed with difficulty to the *acid*). This with HI gives the *I-acid* (II), oxidised by CrO_3–AcOH to 2-*methyl*cyclo*hexane*-2-*carboxylic*-1-β-*propionic acid* (III), also obtained from (I) by oxidation through the *OEt-acid*. When distilled with $Ba(OH)_2$, (III) gives 8-methyl-1-hydrindanone, m.p. 33—34°, b.p. 84°/5 mm. (cf. A., 1936, 988) (semicarbazone, new m.p. 224·5°), which with conc. HNO_3 forms 2-methyl*cyclo*hexane-1-carboxylic-2-acetic acid. OEt·$[CH_2]_3$·OH gives rise to δ-*ethoxybutyl bromide*, b.p. 169°, which similarly furnishes *Et* 2-*methyl*-1-δ-*ethoxybutyl*cyclo*hexan*-1-*ol*-2-*carboxylate*, b.p. 165°/0·5 mm., *Et* 2-*methyl*-1-δ-*ethoxybutyl*-$\Delta^{6(7)}$-cyclo*hexene*-2-*carboxylate*, b.p. 135°/0·4 mm., and *Et* 2-*methyl*-1-δ-*ethoxybutyl*cyclo*hexane*-2-*carboxylate*, b.p. 149°/0·8 mm., hydrolysed to the acid. The *OEt-acid* with CrO_3–AcOH, followed by $Ba(OH)_2$ distillation, gives 9-methyldecahydronaphthal-1-one (cf. A., 1936, 988), also obtained by converting (II) by EtOH–H_2SO_4 into *Et* 2-*methyl*-1-γ-*iodopropyl*cyclo*hexane*-2-*carboxylate*, and treating this with KCN–EtOH. E. W. W.

Sterol group. XXXII. Bromination of 6-ketocholestanyl acetate. I. M. Heilbron, E. R. H. Jones, and F. S. Spring (J.C.S., 1937, 801—805).—Experiments directed towards the prep. of 7-dehydrocholesterol are described. 6-Ketocholestanyl acetate (I), with Br–AcOH at 0°, gives a 5-*Br*-derivative (II), m.p. 162° (decomp.), $[\alpha]_D^2$ −133° (all rotations in $CHCl_3$). At the b.p. the product is the 7-*Br*-derivative (III), m.p. 144—145° (stable), $[\alpha]_D^{22}$ +41°. With HBr–AcOH, at 100°, (II) yields (III); both are reduced by Al–Hg to (I). In C_5H_5N, (II) gives 6-*keto*-3-*acetoxy*-Δ^4-*cholestene* (IV), m.p. 110°, $[\alpha]_D^{22}$ −50·5°, absorption max. at 2360 and 3200 A., which is converted by MeOH–KOH at the b.p. into 3 : 6-diketocholestane (V), or, at room temp., into 3-*hydroxy*-6-*keto*-Δ^4-*cholestene*, m.p. 150—151°, $[\alpha]_D^{20}$ −13°, absorption max. at 2390 and 3190 A., which with hot EtOH–KOH yields (V). With $Al_2(OPr^\beta)_3$–$Pr^\beta OH$, followed by MeOH–KOH, (IV) gives 3 : 6-*dihydroxy*-Δ^4-*cholestene*, m.p. 178—179° [Ac_2 derivative, m.p. 154—155—157° (third temp. clearing point), $[\alpha]_D^{22}$ +24·8°; Bz_2 derivative, m.p. 198—199—208°, $[\alpha]_D^{22}$ +83·9°]. With EtOH–KOH, (II) gives 3 : 5-*dihydroxy*-6-*ketocholestane*, m.p. 138°, $[\alpha]_D^{22}$ +29·3° (*Bz* derivative, m.p. 170°, $[\alpha]_D^{20}$ +23·0°). Conversion of (III) into (IV) was not effected, but on prolonged heating of (III) with $AgNO_3$ in C_5H_5N, 6 : 7-*diketocholestanyl acetate*, m.p. 156—157°, $[\alpha]_D^{20}$ −108° (*quinoxaline* derivative, m.p. 186—187°), was obtained, and with EtOH–KOH, 3 : 7-*dihydroxy*-6-*ketocholestane*, m.p. 179°, sublimes at 220°/0·001 mm., $[\alpha]_D^{22}$ +31·4° (*Bz*$_2$ derivative, m.p. 169—170°, $[\alpha]_D^{20}$ +62·0°). E. W. W.

Replacement of the 3-hydroxyl in pregnenolone and androstendiol by chlorine. A. Butenandt and W. Grosse (Ber., 1937, **70**, [*B*], 1446—1450).—Δ^5-Pregnen-3-ol-20-one is converted by $C_6H_4Me·SO_2Cl$ in C_5H_5N at room temp. into the *p-toluenesulphonate*, m.p. 139—140°, $[\alpha]_D^{21}$ +9° in $CHCl_3$, converted by MeOH at 100° into *pregnenolone Me ether*, m.p. 123—124°, $[\alpha]_D^{18}$ +18° in $CHCl_3$, and by KOAc in boiling MeOH into iso*pregnenolone Me ether*, m.p. 124—125°, $[\alpha]_D^{20}$ +132° in $CHCl_3$; this with conc. HCl–AcOH at room temp. yields 3-*chloro*-Δ^5-*pregnen*-20-*one*, m.p. 146·5°, $[\alpha]_D^{21}$ +31·5° in $CHCl_3$ (*oxime*, m.p. 181°). *Androstene*-3 : 17-*diol di*-p-*toluenesulphonate*, m.p. 140—141°, $[\alpha]_D^{20}$ −59° in $CHCl_3$, gives iso*androstenediol Me ether* 17-p-*toluenesulphonate*, m.p. 124°, $[\alpha]_D^{20}$ +23·5° in $CHCl_3$, whence 3-*chloro*-Δ^5-*androstenol* 17-p-*toluenesulphonate*, m.p. 150°, $[\alpha]_D^{20}$ −60° in $CHCl_3$. H. W.

Manufacture of 17-hydroxy-3-keto-compounds of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1937, 620.

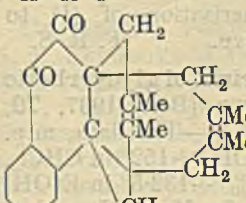
Constitution of shikonin. Syntheses of *iso*hexylnaphthapurpurin and related compounds. (Miss) C. Kuroda and M. Wada (Proc. Imp. Acad. Tokyo, 1937, **13**, 158—160).—In a similar manner to the prep. of naphthapurpurin from naphthazarin (A., 1927, 886), *iso*hexylnaphthazarin (this vol., 66) gives iso*hexylnaphthapurpurin* [3 : 5 : 8-*trihydroxy*-2-iso*hexylnaphthaquinone*] (I), m.p. 117°. 3 : 5 : 8-*Trihydroxy*-2-*ethylnaphthaquinone*, m.p. 195°, is obtained similarly, as is the 2-Me derivative [which on keeping changes its m.p. from 192° to 176° (subliming)]; the identity of the last with the known compound (A., 1935, 623) establishes the structure of (I). No details or analyses are given. E. W. W.

Salts of 1-aminoanthraquinone-2-carboxylic acid. J. V. Dubský, M. Hrdlička, and K. Štěpán (Publ. Fac. Sci. Univ. Masaryk, 1937, No, 232, 1—9).—Normal *salts* of Pb$^{··}$, Hg$^{··}$, Cu$^{··}$, Cd$^{··}$, Co$^{··}$, Ni$^{··}$, Mn$^{··}$, Fe$^{··}$, Fe$^{···}$, Al$^{···}$, Ba$^{··}$, Sr$^{··}$, and Mg$^{··}$ are pptd. by adding equiv. amounts of these cations in solution to a carefully neutralised solution of the K salt (I) of the acid. A slightly alkaline solution of (I) gives the basic *salts* of Pb$^{··}$, Cu$^{··}$, Cd$^{··}$, Co$^{··}$, Ni$^{··}$, Mn$^{··}$, Zn$^{··}$, Fe$^{··}$, Fe$^{···}$, Al$^{···}$, and Ca$^{··}$. All these salts are dark red in colour. Only the alkali and NH_4 salts are H_2O-sol. F. R.

Addition of dienes to halogenated and hydroxylated naphthaquinones. L. F. Fieser and J. T. Dunn (J. Amer. Chem. Soc., 1937, **59**, 1016—1021).—Hydroxy-1 : 2-naphthaquinones decompose rather than add dienes, and OH-substituents depress the rate of reaction of the 1 : 4-quinone; 3- and 4-halogeno-1 : 2-naphthaquinones, however, condense readily with dienes to give adducts which readily lose HCl to alkali and then oxidise in air to phenanthraquinones. Prep. of the following is described: 6- and 7-hydroxy-1 : 2-naphthaquinone [do not condense with $(CH_2{:}CMe·)_2$], juglone and its Ac derivative, m.p. 153—154°, 1 : 2 : 4 : 5-(or 1 : 2 : 4 : 8-)*tetra-acetoxynaphthalene*, m.p. 154°, 2 : 5-(or 2 : 8-)$C_{10}H_6(OH)_2$, decomp. about 220°, naphthazarin diacetate, m.p. 195—196°, 5 : 6 : 8-triacetoxy-1 : 4-naphthaquinone, m.p. 165—166°, 3-bromo- (I), m.p. 177—178°, 3 : 4-dichloro- (II), m.p. 183·5—184·5°, and 4-chloro-1 : 2-naphthaquinone (III) (from 1 : 1-dichloro-2-ketodihydronaphthalene by way of 1 : 4-dichloro-2-naphthol and -1-nitro-2-ketodihydronaphthalene), m.p. 132—136° (decomp.). 6-Bromo-1 : 2-naphthaquinone and $(CH_2{:}CMe)_2$ give a product, oxidised during

reaction to a *substance*, $C_{16}H_{13}OBr$, m.p. 237—238° (decomp.). $(CH_2{:}CMe)_2$ forms *adducts* with acetyljuglone (94% in 30 min.), m.p. 126—128°, juglone (I) (95% in 20 min.), m.p. 141—142° [with Ac_2O–NaOAc gives 5 : 9 : 10-*triacetoxy*-2 : 3-*dimethyl*-1 : 4-*dihydroanthracene*, m.p. 197—198°, converted by 10% KOH into 5-*hydroxy*-2 : 3-*dimethylanthraquinone*, m.p. 178·5—179·5°, also obtained similarly from (I)], naphthazarin (83% in 6 hr.), m.p. 195° (decomp.), diacetylnaphthazarin (92% in 3 hr.), m.p. 175° (decomp.), 5 : 6 : 8-trihydroxy- (33% in 60 hr.), m.p. 255° (decomp.), and 5 : 6 : 8-triacetoxy- (70% in 27 hr.), m.p. 186° (decomp.), and 2-methyl-8-hydroxy-1 : 4-dihydroanthracene (84% in 19 hr.), m.p. 78—79·5° (decomp.). Juglone and $(CH_2{:}CH)_2$ give an *adduct* (94% in 30 min.), m.p. 124—125°. 3-Chloro-1 : 2-naphthaquinone in pure $CHCl_3$ affords with $(CH_2{:}CMe)_2$ an *adduct*, m.p. 87—88°, which rapidly decomposes when kept or when warmed with NaOAc–EtOH, yielding 2 : 3-dimethylphenanthraquinone, m.p. 237—238°, 242—243° (corr.), also obtained from (III) by way of an impure Cl-compound and from (I) by way of a Br-compound which was oxidised by CrO_3. (II) gives an *adduct* with $(CH_2{:}CMe)_2$, m.p. 130·5—131·5°, which only slowly gives up Cl to hot 10% KOH–EtOH, yielding thereby an oil. R. S. C.

Further reaction product from 3-chloro-1 : 2-naphthaquinone and dimethylbutadiene. L. F. Fieser and J. T. Dunn (J. Amer. Chem. Soc., 1937, **59**, 1021—1024).—When 3-chloro-1 : 2-naphthaquinone and $(CH_2{:}CMe)_2$ are heated at 100° in $CHCl_3$, the initial red colour fades to yellow in about 45 min. owing to addition to form 11-chloro-2 : 3-dimethyl-1 : 4 : 11 : 12-tetrahydrophenanthraquinone; in 35—50 min., particularly in light, the red colour returns, probably due to loss of HCl and formation of 2 : 3-dimethyl-1 : 4-dihydrophenanthraquinone; in a further 2 hr. the colour has faded again to yellow (green fluorescence) and the solution yields a *substance*, $C_{22}H_{24}O_2$, colourless and yellow *forms*, m.p. 135° after sintering at 130°, believed to be (I). (I) absorbs 2 O_2 from BzO_2H and with H_2O_2 gives 4 : 5-*dimethyl*-2 : 2′-*diphenic acid*, m.p. 203—204°, also obtained from 2 : 3-dimethylphenanthraquinone (II); it resists hydrogenation and does not form a semicarbazone and quinoxaline derivative; above the m.p. it gives a substance oxidised by air to (II), obtained directly in 91% yield by CrO_3. The prep. of 3 : 7-dimethyl-1 : 2-naphthaquinone is improved, as also is its condensation with $(CH_2{:}CMe)_2$ to 2 : 3 : 7 : 11-tetramethyl-1 : 4 : 11 : 12-tetrahydrophenanthraquinone; this forms normally a *quinoxaline* derivative, m.p. 137—138°, adds 2 H to give the 1 : 2 : 3 : 4 : 11 : 12-H_6-derivative, m.p. 131°, and with H_2O_2 gives 2 : 4 : 5 : 4′-*tetramethyl*-1 : 2 : 3 : 6-*tetrahydro*-2 : 2′-*diphenic acid*, m.p. 248—249° (Me_2 ester, m.p. 88—89°; *anhydride*, m.p. 97—98°), converted at 330—333° by loss of CO_2 into 2 : 3 : 7 : 10-*tetramethyl*-1 : 4 : 10 : 11-*tetrahydrofluorenone* [*semicarbazone*, softens at 244°, m.p. 260° (decomp.)]. R. S. C.


(I.)

Application of the diene synthesis to halogenated 1 : 2- and 3 : 4-phenanthrenequinones. L. F. Fieser and J. T. Dunn (J. Amer. Chem. Soc., 1937, **59**, 1024—1028).—Chrysene- and 3 : 4-benzphenanthra-quinones are smoothly obtained by diene addition to halogenophenanthraquinones, followed by elimination of HCl and oxidation. Phenanthra-3 : 4-quinone and Br–AcOH give a dibromide, converted by hot H_2O into 2-*bromophenanthra*-3 : 4-*quinone* (I), m.p. 212—213° [corresponding *quinol*, m.p. 164—165·5° (*Me_2 ether*, m.p. 79—80°)], the structure of which is proved by conversion by Ac_2O–H_2SO_4 into 2-*bromo*-1 : 3 : 4-*triacetoxyphenanthrene*, m.p. 195—196°, which by hydrolysis and aërial oxidation gives 2-*bromo*-3-*hydroxyphenanthra*-1 : 4-*quinone*, m.p. 198—199°; this quinone is stable to boiling dil. alkali and is unchanged by hot MeOH–HCl, which respectively degrade and methylate the Br-free OH-quinone. $(CH_2{:}CMe)_2$ adds to (I) in $CHCl_3$ at 100° (2 hr.), giving a Br-compound, converted by CrO_3 into 8 : 9-*dimethylchrysene*-5 : 6-*quinone*, m.p. 250—251°. Phenanthra-1 : 2-quinone (II) similarly yields the 3-*Br-quinone* (III), m.p. 245—246°, 3-*bromo*-1 : 2-*dihydroxyphenanthrene*, m.p. 195—196° (*Me_2 ether*, m.p. 82—83°), and 3-*bromo*-1 : 2 : 4-*triacetoxyphenanthrene*, m.p. 188—189° [hydrolysed to an indefinite *substance*, m.p. 222° (decomp.)]. From (III) is obtained a 79% yield of 6 : 7-*dimethyl*-3 : 4-*benzphenanthra*-1 : 2-*quinone*, m.p. 194—195°, also obtained, but only in 29% yield, from (II). $(CH_2{:}CH)_2$ and (III) give 3 : 4-benzphenanthra-1 : 2-quinone, m.p. 190—191° (*quinol*, m.p. 194—195°), in 65% yield. 3-Phenanthrol and Cl_2 (excess) in AcOH at 13—17° give 1(or 2) : 4 : 4′ : 9 : 10-*pentachloro*-3-*keto*-3 : 4 : 9 : 10-*tetrahydrophenanthrene*, m.p. 175—180° (decomp.), converted by many reagents into indefinite products, but by $SnCl_2$–AcOH at room temp. into 1(or 2) : 4 : 9(or 10)-*trichloro*-3-*phenanthrol*, m.p. 130—131° (*acetate*, m.p. 164—165°), which with HNO_3–AcOH gives 1(or 2) : 9(or 10)-*dichlorophenanthra*-3 : 4-*quinone*, m.p. 239—240°, and with Ac_2O–H_2SO_4 yields 9(or 10)-*chloro*-1(or 2) : 3 : 4-*triacetoxyphenanthrene*, m.p. 230—231°. R. S. C.

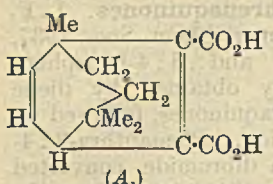
Two-step oxidation treated for the case of phenanthrenequinonesulphonate.—See A., I, 415.

Carbonyl constituents of eucalyptus oils. I. Occurrence of cryptal. P. A. Berry, A. K. Macbeth, and T. B. Swanson (J.C.S., 1937, 986—989).—*l*-4-*iso*Propyl-Δ^2-*cyclo*hexen-1-one (*oxime*, b.p. 160—161°/33 mm.) has been isolated from various eucalyptus oils, and on the evidence of oxidation, reduction, and identity of derivatives, is identical with "cryptal." It seems clear that the corresponding aldehyde (A., 1930, 602) has not been isolated from eucalyptus oils. F. R. S.

Supposed transformation of dihydroxydihydro-α-campholenic acid into pinonic acid. M. Delépine (Bull. Soc. chim., 1937, [v], **4**, 1145—1147).—The distillate from *d*-dihydroxydihydro-α-campholenic acid contains, not "pinonic acid," but d-α-*campholonic acid*, $[\alpha]_D$ +158° in H_2O (*semicarbazone*, $[\alpha]_D$ +129° in ammoniacal H_2O) (cf. this vol., 67). E. W. W.

Diene synthesis. III. Products obtained from α-terpineol by loss of water. K. Alder and

H. F. Rickert (Ber., 1937, 70, [*B*], 1364—1369).—The product obtained by the dehydration of α-terpineol is transformed by $CO_2Et{\cdot}C{:}C{\cdot}CO_2Et$ mainly into C_2H_4 and *Et*$_2$ 6-*methyl*-3-iso*propylphthalate* (I), b.p. 180—190°/15 mm., mixed with small amounts of a


(*A*.)

product (II), b.p. 196°/15 mm. Hydrolysis of (I) gives 6-*methyl*-3-iso*propylphthalic anhydride*, m.p. 102°, identified by oxidation to 3-*methyl*-6-*hydroxy*iso*propylphthalic acid*, m.p. 288°, and mellophanic acid. Probably (II) is a *cyclo*heptadiene derivative (*A*) hydrogenated to a *compound*, $C_{14}H_{20}O_4$, m.p. 202—203° (decomp.). H. W.

Structure and probable biogenesis of β-caryophyllene. K. Ganapathi (Current Sci., 1937, 5, 586).—The relationship of β-caryophyllene to orthodene by addition of an isoprene unit is discussed. F. R. S.

Constitution of α-cyperone. A. E. Bradfield, R. R. Pritchard, and J. L. Simonsen (J.C.S., 1937, 760—763).—The formula $CH_2{\cdot}CH_2{\cdot}CMe{-}CH{:}CH$ / $CH_2{:}CMe{\cdot}CH{-}CH_2{\cdot}CH{\cdot}CHMe{\cdot}CO$ (I) for α-cyperone (II) (A., 1936, 856) is abandoned in favour of $CH_2{\cdot}CH_2{\cdot}CMe{\cdot}CH_2{\cdot}CH_2$ / $CH_2{:}CMe{\cdot}CH{-}CH_2{\cdot}C{:}CMe{-}CO$ (III). The hydrocarbon $C_{15}H_{18}$ from hydroxymethylene-α-cyperone is now identified as 1 : 3 : 7-$C_{10}H_5Me_2Pr^{\beta}$ (IV), which is synthesised (see below). The hydrocarbon from tetrahydroeremophilone and MgMeI followed by Se, previously regarded as (IV), is now identified as 1 : 5 : 7-$C_{10}H_5Me_2Pr^{\beta}$; the non-identity of the two hydrocarbons is thus no longer an argument against formula (III). A third formula, $CH_2{\cdot}CH_2{\cdot}CMe{-}CH_2{-}CH_2$ / $CH_2{:}CMe{\cdot}CH{-}CH_2{\cdot}CH{\cdot}C(CH_2){\cdot}CO$ (V), is excluded, since on this the action of O_3 on the semicarbazone of (II) would give a product $C_{14}H_{21}O_3N_3$, whereas the product obtained (*loc. cit.*) is $C_{15}H_{23}O_4N_3$, and is now formulated as

$$CHAc{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{-}CO\end{matrix}{>}CMe{\cdot}[CH_2]_2{\cdot}CAc{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2.$$

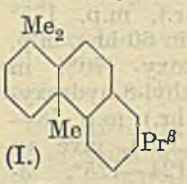
The acid from (II) and O_3, previously regarded (*loc. cit.*) as $C_{13}H_{20}O_5$, dibasic (VI), is now formulated as

$$CHAc{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{-}CO\end{matrix}{>}CMe{\cdot}[CH_2]_2{\cdot}CO_2H$$ (VII), and the

supposed Me_2 ester of (VI) becomes the *Me* ester of (VII). The product from (II) and H_2O_2–NaOH, regarded as 6-acetyl-1-methyl-4-*iso*propenyl*cyclo*hexane-1-carboxylic acid, is renamed 1-*methyl*-4-iso*propenyl*cyclo*hexan*-2-*one*-1-*propionic acid*, the formation of which is an additional argument against formula (V).

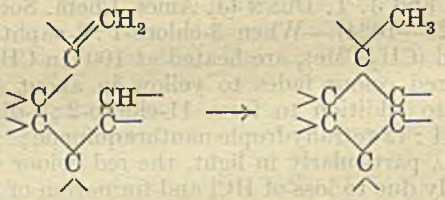
Cuminaldehyde and $CHMeBr{\cdot}CO_2Et$–NaOEt give *Et* αβ-*epoxy*-β-*cumyl*-α-*methylpropionate*, b.p. 180—181°/24 mm., which is converted by KOH–MeOH, and heating, into *cuminyl Me ketone* (VIII), b.p. 137°/22 mm. (*semicarbazone*, m.p. 142—143°; 2 : 4-*dinitrophenylhydrazone*, m.p. 137—138°), and αβ-*dihydroxy*-β-*cumyl*-α-*methylpropionic acid*, decomp. 170—171°. With $CH_2Br{\cdot}CO_2Et$–Zn–C_6H_6, (VIII) yields *Et* β-*cuminylbutyrate*, b.p. 170—174°/18 mm., which with H_2SO_4 gives 3-*methyl*-7-iso*propyl*-1 : 2 : 3 : 4-*tetrahydronaphthal*-1-*one*, b.p. 165—173°/17 mm. (*semicarbazone*, decomp. 180—182°; 2 : 4-*dinitrophenylhydrazone*, m.p. 235—236°), methylated (MgMeI) and dehydrogenated (Se) to 1 : 3-*dimethyl*-7-iso*propylnaphthalene* (see above), b.p. 165—167°/19 mm. [*picrate*, m.p. 102·5—104°; *s*-$C_6H_3(NO_2)_3$ *derivative*, m.p. 117—119—121°]. E. W. W.

Identity of α-dihydrophyllocladene with iosene. L. H. Briggs (J.C.S., 1937, 1035—1036).—Iosene (I) is identical with α-dihydrophyllocladene. The C skeleton suggested for (I) is compatible with the Se dehydrogenation (cf. Soltys, A., 1929, 1429).


(I.)

F. R. S.

Characterisation of basseol, a tetracyclic triterpene alcohol, and its isomerisation to β-amyrenol. J. H. Beynon, I. M. Heilbron, and F. S. Spring (J.C.S., 1937, 989—991).—The fat from the bark of *Alstonia scholaris* contains no basseol (I), but mainly the amyrenols (chiefly β-) and lupeol. From the shea cambium, lupeol, α-amyrenol, and (I) have been isolated, but the yield of (I) is < that from the nut oil. The determination of the equiv. of basseol acetate and its isomerisation by various reagents to β-amyrenyl acetate lead to the formula $C_{30}H_{50}O$ for (I) (cf. Heilbron *et al.*, A., 1934, 1330). The acetate is hydrogenated to *bassenyl acetate*, m.p.

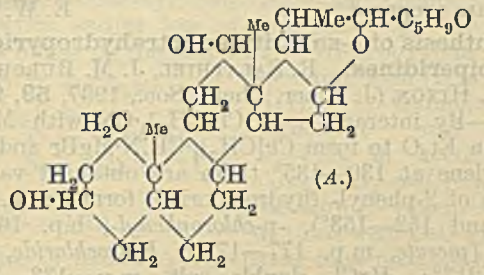


119—120°, $[\alpha]_D^{20}$ +32·5° in $CHCl_3$, hydrolysed to bassenol (*benzoate*, m.p. 156°, $[\alpha]_D^{19}$ +48·1° in $CHCl_3$), and gives CH_2O on ozonolysis. The ethylenic linkings of (I) are not conjugated and the reactive one is probably exocyclic. The isomerisation of (I) to β-amyrenol is formulated as above. F. R. S.

Glycyrrhizin. III. Isomerism of glycyrrhetic acid. W. Voss and G. Butter (Ber., 1937, 70, [*B*], 1212—1218; cf. this vol., 87).—The data, m.p. 253—255°, $[\alpha]_D^{21}$ + 159·1° in EtOH, +152° in $CHCl_3$, and m.p. 224·6—227° (corr.), $[\alpha]_D^{21}$ +132·5° in EtOH, +124·6° in $CHCl_3$, are recorded for Me β- (I) and α- (II) -glycyrrhetate, respectively, obtained from varied sources and by differing processes. (I) and (II) are regarded as isomerides, not polymorphous forms (cf. Ruzicka *et al.*, *ibid.*, 202), since they are distinguished from one another by m.p., cryst. form, solubility, and $[\alpha]_D$ and the differences persist after crystallisation or sublimation. Reasons are advanced for considering that this isomerism persists through the aglucon to the glucoside and that glycyrrhizic acid is a mixture. The C skeleton of glycyrrhetic acid is discussed. H. W.

Saponins and sapogenins. V. Oxidation products and structure of chlorogenin. C. R. Noller (J. Amer. Chem. Soc., 1937, 59, 1092—1094; cf. A., 1936, 1095).—Chlorogenin (I), m.p. 277—279°, and

$Na_2Cr_2O_7$–H_2SO_4 in AcOH give a *diketone* (II), $C_{27}H_{40}O_4$, m.p. 247—248° after sintering at 236°, $[\alpha]_D^{22}$ — 69·6° in dioxan [*dioxime*, m.p. 242—243°; with *o*-$C_6H_4(NH_2)_2$ gives a *substance*, $C_{33}H_{46}O_3N_2$, m.p. 265—267° (rapid heating), 255—261° (slow heating)], and a ketodibasic *acid*, $C_{27}H_{40}O_7$, m.p. 235—237° (decomp.) after sintering, $[\alpha]_D^{22}$ — 42·8° in dioxan (Me_2 ester, m.p. 158—159°, $[\alpha]_D^{20}$ — 39·1°, readily hydrolysed). Since the acid is probably not an α- or β-keto-acid, (I) is thus probably (*A*).



(*A*.)

Digitonin does not ppt. (I), but (II) is reduced by Na–EtOH to a small amount of a substance, which is so pptd.; the configuration of $C_{(3)}$ is thus opposite to that in cholesterol. R. S. C.

Toad poisons. VI. Constitution of Ch'an Su (Senso). M. Kotake and K. Kuwada (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, **32**, 1—3).—"Bufagin," previously described as obtained from senso (A., 1928, 1138), is shown by separation with $CHCl_3$ to be a mixture of cinobufagin (cf. Tschesche and Offe, A., 1936, 1516) and *cinobufotalin*, $C_{23}H_{32}O_6$, m.p. 248—249·5°, from which were prepared the Ac_2, m.p. 219—220°, α-, m.p. 222—224° and β-H_4-derivatives, m.p. 162—165°, and *cinobufotalone*, $C_{23}H_{28}O_6$, m.p. 246—248°. The H_4-derivatives of bufagin previously described are shown to be hexahydrocinobufagins. F. R. G.

Locoine.—See A., III, 309.

Constitution of cozymase.—See A., III, 313.

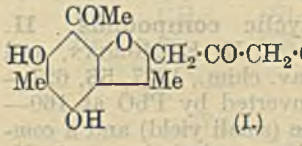
Cannizzaro reaction. V. M. Rodionov and A. M. Fedorova (J. Gen. Chem. Russ., 1937, **7**, 947—950).—Opianic acid, aq. CH_2O, and KOH or NaOH (55°; 12 hr.) give meconine in 93% yield. *o*-Hydroxymethylbenzoic acid or phthalide, and benzyl, anisyl, or furfuryl alcohols are prepared analogously from the appropriate aldehydes and CH_2O. R. T.

Constitution of the scoparoside (scoparin) of *Sarothamnus scoparius*, Koch. M. Mascré and R. Paris (Compt. rend., 1937, **204**, 1581—1583).—Scoparin with boiling 10% KOH affords acetylvanillin; fermentative hydrolysis (rhamnodiastase of *Rhamnus utilis*) affords rhamnose and a flavin, scoparol, probably a Me ether of quercitol (cf. A., 1918, i, 503). J. L. D.

Synthesis of 1 : 2-diphenylcoumarones. II. B. I. Arventi (Bull. Soc. chim., 1937, [v], **4**, 999—1007; cf. A., 1936, 732).—*o*-Benzylphenol with BzCl and NaOH affords *o-benzoyloxydiphenylmethane*, b.p. 249°/18 mm., which is not converted into 1 : 2-diphenylcoumarone at 280—300°. The lactone of phenyl-β-1-hydroxynaphthylacetic acid with BzCl in Na_2CO_3 affords a compound converted at 250—270°, with liberation of gaseous products, into 1 : 2-*diphenyl-α-naphthofuran* (I), m.p. 100°, which with CrO_3–AcOH at 60° gives 2 : 1-$C_{10}H_8Bz$·OBz, m.p. 163° (lit., 154°), hydrolysed (NaOH) to 2 : 1-C_1H_6Bz·OH. The lactone of phenyl-*o*-tolylacetic acid gives a Bz derivative which at 270—280° is converted into 1 : 2-*diphenyl*-6-*methylcoumarone*, m.p. 64—65°. 1 : 2-Diphenyl-4-methylcoumarone (cf. A., 1936, 732) with excess of CrO_3 gives a mixture of 2-benzoyloxy-5-methylbenzophenone and *m*-benzoyl-*p*-benzoyloxybenzoic acid; milder oxidation yields only the former (cf. A., 1936, 997). Prepared similarly to (I), 1 : 2-*diphenyl*-4 : 5- and -4 : 6-*dimethylcoumarone* have m.p. 143° and 128—129°, respectively. All these coumarones afford coloured solutions in conc. H_2SO_4. J. L. D.

Walder's "dinaphthyl," 1 : 1′-dinapthyl, and the ultra-violet absorption of β-dinaphthylene oxide. K. Brass and R. Patzelt (Ber., 1937, **70**, [*B*], 1349—1353).—The "1 : 1′-dinaphthyl" of Walder (A., 1883, 208), obtained by the distillation of β-dinaphthol (I) with Zn dust, is shown to be β-dinaphthylene oxide, identical with that obtained from (I) and P_2O_5. 1 : 1′-Dinaphthyl (II) cannot be obtained by distilling (I) with Zn dust and is best obtained from 1-$C_{10}H_7I$. (II) appears unable to add picric acid. H. W.

Usnic acid. V. F. H. Curd and A. Robertson (J.C.S., 1937, 894—901).—Usnic acid and 96% EtOH heated under pressure (cf. Widman, A., 1903, i, 96) give decarbousnic acid (I), m.p. 178—179° (*pyrazole* derivative, m.p. 237—238°, regarded by Widman as a hydrazone), and *deacetylcarbousnic acid* (II), m.p. 199—200° (Ac_2 derivative, m.p. 146—147°). Hydrolysis (KOH) of (I) affords AcOH, $COMe_2$, usnetic and pyrousnetic acids, and (II). The experimental evidence for formula (I) is discussed (cf. Asahina *et al.*, A., 1936, 1262). Alternative formulæ are suggested for usnic acid but the evidence available does not permit a decision. The formation of decarbousnol by dehydration of (I) with conc. H_2SO_4 and the isomerisation of usnic acid to usnolic acid (III) with H_2SO_4 have been confirmed. Decarboxylation of (III) yields decarbousnol and indicates that the C atom lost in degradation of usnic acid to (I) appears as the CO_2H of (III). F. R. S.

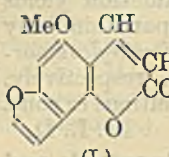


(I.)

Preparation of halogenated derivatives of dihydroxydiphenylene dioxide. J. Frejka, B. Sefranek, and J. Zika (Coll. Czech. Chem. Comm., 1937, **9**, 238—246).—Tetrachloropyrocatechol with $NaNO_2$ and AcOH affords 1 : 4 : 5 : 6 : 7 : 8-*hexachlorodiphenylene dioxide* 2 : 3-*quinone*, m.p. 288·5°, reduced (Sn–HCl or SO_2) to 1 : 4 : 5 : 6 : 7 : 8-*hexachloro*-2 : 3-*dihydroxydiphenylene dioxide*, m.p. 276° (decomp.) (*diacetate*, m.p. 300—301°). Similarly, 4 : 5-dichloropyrocatechol affords 6 : 7-*dichlorodiphenylene dioxide* 2 : 3-*quinone*, reduced (Sn–HCl) to 6 : 7-*dichloro*-2 : 3-*dihydroxydiphenylene dioxide* (*diacetate*, m.p. 218°), and from tetrabromopyrocatechol are prepared 1 : 4 : 5 : 6 : 7 : 8-*hexabromodiphenylene*

dioxide 2 : 3-*quinone* and 1 : 4 : 5 : 6 : 7 : 8-*hexabromo*-2 : 3-*dihydroxydiphenylene dioxide* [*diacetate*, m.p. > 300° (decomp.)]. 4-Chloropyrocatechol (improved prep.) with $NaNO_2$–AcOH affords 4′-(4-*chloro*-2-*hydroxy*-*phenoxy*)-1′ : 2′-*benzoquinone*, reduced (SO_2) to 4′-(4-*chloro*-2-*hydroxyphenoxy*)*pyrocatechol* (*triacetate*, m.p. 178°). J. D. R.

Natural coumarins. XXX. Synthesis of bergaptol and of *iso*bergapten. E. Späth and G. Kubiczek (Ber., 1937, **70**, [*B*], 1253—1255).—



(I.)

3 : 4 : 6-Triacetoxycoumaran is condensed with Et sodioformylacetate and the product, after acidification, is distilled, thus giving *allo*bergaptol and bergaptol, m.p. 276—278° (vac.). The latter substance is partly methylated and then distilled, thereby giving *iso*bergapten (I), m.p. 224° (vac.), identical with the natural product. H. W.

Natural coumarins. XXXI. Constitution of ammoresinol. E. Späth and F. Kesztler (Ber., 1937, **70**, [*B*], 1255—1258).—Mainly a reply to Raudnitz (this vol., 204). The substance obtained by oxidation of diacetylhexahydroammoresinol and decarboxylation of the product is identified as δθμ-trimethyl-*n*-tetradecoic acid by analyses and comparison of its *p*-xenylamide, m.p. 101—102°, with that of the synthetic acid derived from farnesol. γηλ-*Trimethyl*-n-*trideco*-p-*xenylamide* has m.p. 94·5—95·5°. H. W.

Principal optical and physical properties of the carbon tetrachloride solvate of rotenone. E. L. Gooden and C. M. Smith (J. Amer. Chem. Soc., 1937, **59**, 787—789).—Crystallo-optical data are recorded for the rotenone-CCl_4 compound. It has d^{30} 1·40. The dissociation pressure from 60° to 90° is given by $\log P_{mm.} = 9·308 - 2313/T$. R. S. C.

Synthesis of heterocyclic compounds. II. N. M. Cullinane, (Miss) N. M. E. Morgan, and C. A. J. Plummer (Rec. trav. chim., 1937, **56**, 627—631).—*o*-$C_6H_4Ph·OH$ is converted by PbO at 160—170° into diphenylene oxide (small yield) and a *compound*, m.p. 194°. Thianthren and Cu-bronze in H_2 afford diphenylene sulphide. Diphenylene selenide is obtained from diphenylene sulphone and Se and the diselenide similarly from the corresponding disulphone obtained by oxidising thianthren with CrO_3 in boiling AcOH. Production of a four-membered ring appears more difficult. Diphenylene is not obtained from *o*-$C_6H_4Ph·OH$ and P_2O_5, 50% or conc. H_2SO_4, whilst when 70% H_2SO_4 is used the product is the *sultone*, $C_6H_4<^{C_6H_4}_{SO_2}>O$, m.p. 110°. PhOBz is transformed by $AlCl_3$ into *o*-$C_6H_4Bz·OH$, m.p. 41°, which passes into xanthone, PhOH, and BzOH when heated at 280°. H. W.

Condensation of chlorohydrins with piperidine. C. Vassiliadès (Bull. Soc. chim., 1937, [v], **4**, 1131—1136).—Piperidine (I) (2 mols.) and $CH_2Cl·CH_2·OH$ (1 mol.) in $COMe_2$ give β-*piperidinoethyl alcohol* (II), b.p. 90°/12 mm., of which the *hydrochloride*, m.p. 64—65°, is obtained when only 1 mol. of (I) is used, in PhMe. With BzCl, (II) gives β-*piperidinoethyl benzoate hydrochloride*, m.p. 167—168°. Similarly obtained is β-*piperidinoethyl* p-*nitrobenzoate hydrochloride*, m.p. 175—176°, reduced ($NHPh·NH_2$) to the p-*aminobenzoate hydrochloride*, m.p. 88—90° (*dihydrochloride*, decomp. 208—235°). With $OH·CH(CH_2Cl)_2$, (I) (4 mols.) yields s-*dipiperidino*iso*propyl alcohol*, b.p. 172—173°/12 mm., of which the *dihydrochloride* (III), m.p. 209—210°, is obtained when only 2 mols. of (I) are used. The *benzoate*, m.p. 240°, and p-*nitrobenzoate*, m.p. 220—235°, of (III) are prepared. E. W. W.

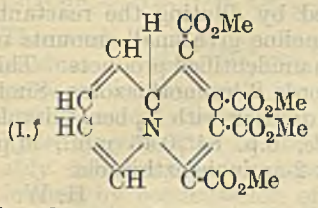
Synthesis of α-substituted tetrahydropyridines and piperidines. R. Salathiel, J. M. Burch, and R. M. Hixon (J. Amer. Chem. Soc., 1937, **59**, 984—986).—By interaction of $Cl·[CH_2]_4·CN$ with MgRX first in Et_2O to form $Cl·[CH_2]_4·CR{:}N·MgBr$ and then in xylene at 130—135° there are obtained varying yields of 2-phenyl- (hydrochloride, forms, m.p. 86—87° and 152—153°), -p-*chlorophenyl*-, b.p. 165°/13 mm. (*picrate*, m.p. 177—178°; *hydrochloride*, m.p. 215—217°; $HgCl_2$ double salt, m.p. 133—135°), -p-*tolyl*-, b.p. 145°/13 mm. (*platini*-, m.p. 186—187°, and *hydro-chloride*, $+H_2O$, m.p. 137—137·5°, and anhyd., m.p. 175—177°; $HgCl_2$ double salt, m.p. 119·5°; *picrate*, m.p. 178—179°), -cyclo*hexyl*-, b.p. 118—125°/17 mm. (*hydrochloride*, m.p. 222—224°), and -n-*butyl-tetrahydropyridine*, b.p. 195—200° (*hydrochloride*, unstable; *platinichloride*, m.p. 156°), reduced by Sn–HCl to 2-phenyl-, -p-*chlorophenyl*-, b.p. 145°/8 mm., m.p. 16° (*hydrochloride*, m.p. 259—260°), -p-*tolyl*-, b.p. 135°/8 mm. (*hydrochloride*, m.p. 209—210°), -cyclo*hexyl*-, b.p. 135°/35 mm. (*hydrochlorides*, m.p. 197—198° and 250°), and -n-butyl-*piperidine*, b.p. 185—192° (hydrochloride, m.p. 185—186°). R. S. C.

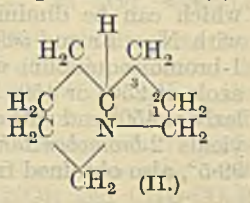
Action of hypoiodite on some pyridinium bases. P. Karrer, F. Schlenk, and H. von Euler (Arkiv Kemi, Min., Geol., 1937, **12**, B, No. 26, 5 pp.).—Cozymase, glucosido-1-pyridinium bromide, and nicotinamide methiodide absorb approx. 6·5, 8, and 7·5 atoms of I, respectively, from alkaline solution. F. N. W.

Neutral substances formed in Tschitschibabin's β-collidine synthesis. Reply to Huntenberg. A. E. Tschitschibabin (J. pr. Chem., 1937, [ii], **148**, 266).—Huntenburg's results (A., 1936, 612) are in line with those of Tschitschibabin. C_6H_6 is the only recognisable substance among the products obtained from PhCHO and Al_2O_3 at 400—450°. R. S. C.

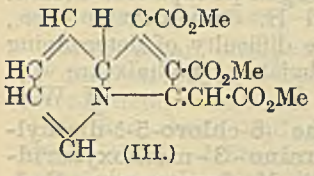
Syntheses in the hydroaromatic series. XXVII. Diene syntheses of hetero-rings containing nitrogen. XII. Decomposition of the "yellow substance" to an isomeride of norlupinane (1-methyloctahydroindolizine). O. Diels and H. Schrum. **XIII. α-Picoline and acetylenedicarboxylic ester.** O. Diels and H. Pistor (Annalen, 1937, **530**, 68—86, 87—98; cf. A., 1935, 1389).—XII. The stable "yellow substance," obtained from C_5H_5N and $(CO_2Me·C{:})_2$ (A., 1934, 782), is probably Me_4 quinolizine-1 : 2 : 3 : 4-tetracarboxylate (I). Its hydrolysis leads to partial loss of CO_2 and a multiplicity of products; all the bases obtained therefrom by decarboxylation and reduction are

related to octahydroindolizine (II); the acids are colourless and melt at lower temp. than does (I);


(I.)

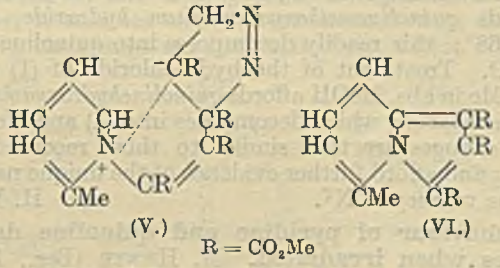

(II.)

therefore, probably, ring-crumpling occurs during hydrolysis and/or loss of CO_2 and, *e.g.*, the ester which might be the Me_3 1 : 2 : 4-tricarboxylate corresponding with (I) is really (III). (?) Quinolizinedicarboxylic acid and H_2–PtO_2 in AcOH give slowly a *H_4-acid*, m.p. 218° (decomp.), which, when distilled with CaO gives a mixture of bases, hydrogenated to a mixture of (II) and 1-methyloctahydroindolizine (IV), b.p. 168—169°/760 mm. (picrate, m.p. 193°; *aurichloride*, m.p. 145—146°; *methiodide*, m.p. 311—312°); identification of (IV) is effected by direct comparison with the synthetic base (cf. Ochiai *et al.*, A., 1934, 901) and by degradation. BrCN converts (IV) into 2-n-*butylpiperidine*, b.p. 188—190°/764 mm. (*hydrochloride*, m.p. 185°; impure picrolonate, m.p. 204°; *aurichloride*, an oil), which is obtained (*picrolonate*, m.p. 184—186°) also by reaction of Li α-picolinyl with Pr$^{\alpha}$Br and hydrogenation of the product; the difference in the m.p. of the picrolonates is believed to be due to the BrCN-fission having occurred to a small extent in the piperidine ring, leading to formation of some 2-methyl-6-*n*-butylpyrrolidine. Bases, which might have been formed by BrCN-fission of (IV), were synthesised for comparison. PhLi and 2-picoline give Li α-picolinyl, which with Pr$^{\beta}$Br gives a base, hydrogenated to 2-*iso*propylpiperidine (hydrochloride, m.p. 205—206°). 2-*tert.*-Butylpiperidine hydrochloride has m.p. 188—189°. PrCOCl, Et 2-methylpyrrole-3-carboxylate, and $AlCl_3$ give Et 2-methyl-5-butyrylpyrrole-3-carboxylate, hydrolysed to the corresponding *acid*, m.p. 242° (decomp.), which at 300—320° gives 2-*methyl*-5-*butyrylpyrrole*, m.p. 88—89, converted (N_2H_4–NaOEt) into 2-*methyl*-5-n-*butylpyrrole*, b.p. 100—102°/13 mm., and thence by NH_2OH into βε-*dioximinononane*, m.p. 119—120°, or by H_2–PtO_2 into 2-*methyl*-5-n-*butylpyrrolidine*, b.p. 177—179°/765 mm. (*picrolonate*, m.p. 215—217°; *aurichloride*, an oil; *hydrochloride*, m.p. about 98—103°). $NaNH_2$, $BuCO_2Et$, and COMeBu$^{\alpha}$ give *undecane-*εη*-dione*, b.p. 110—123°/14 mm., which with OH·N:CAc·CO_2Et and Zn–AcOH gives *Et* 3-*methyl*-5-*butyl*-4-*valerylpyrrole*-2-*carboxylate*, m.p. 75—76°, converted by H_2SO_4–H_2O (3 : 2) into 3-*methyl*-5-n-*butylpyrrole*. 2-Butyrylpyrrole (modified prep.) with N_2H_4–NaOEt at 160—170° gives 2-n-*butylpyrrole*, b.p. 80—81°/11—12 mm., which gives (Grignard; $ClCO_2Et$) *Et* 2-n-*butylpyrrole*-5-*carboxylate*, b.p. 150—160°/10—11 mm.; this gives (HCN–HCl–$CHCl_3$) the 3- (or 4-)*aldehyde*, m.p. 55—57°, reduced (N_2H_4–NaOEt) to 3- (or 4-)*methyl*-2-n-*butylpyrrole*, b.p. 91°/10—11 mm., hydrogenated to 3- (or 4-)*methyl*-2-n-*butylpyrrolidine*, b.p. 180° (*hydrochloride*, m.p. about 100°; *aurichloride*, m.p. 95—96°).


(III.)

XIII. (:C·CO_2Me)$_2$ condenses with 2-picoline only in the dimeric form; it reacts partly at the N to give the "unstable" *product* (I) and partly at the Me to give βγδε-*tetracarbomethoxy*-$\Delta^{\beta\delta}$-*pentadienylpyridine* (II); "stabilisation" of (I) occurs at the CH and not at the Me, the sole product from (I) being the "stable adduct," *Me_4* 1-*methylquinolizine*-5 : 6 : 7 : 8-*tetracarboxylate* (III). Structures are proved by the reactions described below. (II), m.p. 126°, does not react with CH_2N_2, is red, but gives colourless salts with acids, is hydrogenated (PtO_2) in EtOAc (not colloidal Pd in MeOH) to 2-βγδε-*tetracarbomethoxyamylpyridine*, m.p. 132°, gives a *Br_3*-derivative, m.p. 126°, and, when evaporated in MeOH, loses MeOH by ring-closure to 2-6′-*hydroxy*-2′ : 3′ : 4′-*tricarbomethoxyphenylpyridine* (IV), m.p. (anhyd.) 128°, (+H_2O) 95—105° (deep red $FeCl_3$ colour; *phenylurethane*, m.p. 148°; *Br*-derivative, m.p. 133°); when boiled with AcOH, (I) gives an *acid*, $C_{13}H_6O_3N(OMe)_2$·CO_2H, +0·5H_2O, m.p. 208° (decomp.), which gives a brownish-red $FeCl_3$ colour, gives an indigo-blue compound with Ac_2O, and with CH_2N_2 yields the *Me ether*, m.p. 136° (decomp.), of (IV). (I), m.p. 135°, yellow, with CH_2N_2 gives the yellow *adduct* (V), m.p. 125° (decomp.), gives a *dibromide*, m.p. 187° (decomp.), which does not react with CH_2N_2, and, when boiled for a long time in AcOH, gives (III), yellow, m.p. 234° (decomp.).

(I.)


(V.) (VI.)

R = CO_2Me

H_2O_2 converts (III) into 2-picoline-6-carboxylic acid *N*-oxide, m.p. 177° (synthesis from 2 : 6-dimethylpyridine described). $Na_2Cr_2O_7$–AcOH oxidises (III) with ring-crumpling to the colourless *indolizine* ester (VI), m.p. 116°, also obtained by the action of dil. Na_2CO_3 on the N-*tribromide*, m.p. 135° (decomp.), of (III). R. S. C.

Fission of tertiary amines by nitrous acid. II. Synthesis of β-*o*-carboxyphenylethylamines. R. Wegler and W. Frank (Ber., 1937, **70**, [*B*], 1279—1287; cf. A., 1936, 1373).—Treatment of 1-alkylpiperidines with HNO_2 results in elimination of the alkyl group and formation of 1-nitrosopiperidine. With the 1-octyl compound the action proceeds with difficulty but in no case is there any evidence of opening of the piperidine ring. *cyclo*Hexylamine (I), *o*-$C_6H_4(CH_2Br)_2$, and powdered NaOH in PhMe at 200° give 2-cyclo*hexyl*-1 : 3-*dihydroisoindole*, b.p. 112°/0·2 mm., m.p. 64°, converted by NO_2 + O_2 in AcOH at 80—90° into cyclo*hexylphthalimide*, m.p. 167°,

also obtained from (I) and *o*-$C_6H_4(CO)_2O$ at 170° and reduced by Sn and HCl in AcOH to cyclo*hexylphthalimidine*, m.p. 109—110°. 2-Benzoyltetrahydro*iso*quinoline and $NO_2 + O_2$ in AcOH at 70—90° give BzOH. 2-*iso*Amyltetrahydro*iso*quinoline, $NaNO_2$, and AcOH give a *substance*, $C_{14}H_{20}O_3N_2$, b.p. 192°/16 mm., indicating the fission of the ring. Oxidation of tetrahydro*iso*quinoline by NO_2 in AcOH at >70° affords the *lactone* (II), $C_6H_4<^{CH_2\cdot CH_2}_{CO-O}$, b.p. 165°/16 mm., transformed by very cautious treatment with NaOH followed by H_2SO_4 into o-β-*hydroxyethylbenzoic acid* (III), m.p. 87°. The course of the change is probably $C_6H_4<^{CH_2\cdot CH_2}_{CH_2\cdot NH}$ → $C_6H_4<^{CH_2\cdot CH_2}_{CO-NH}$ (or $C_6H_4<^{CH_2\cdot CH_2}_{CH_2\cdot N\cdot NO}$) → $C_6H_4<^{CH_2\cdot CH_2}_{CO-N\cdot NO}$ → $CO_2H\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH\cdot NO$ → (III) → (II). Addition of (III) to $SOCl_2$ at < −3° followed by heating of the mixture at 80° yields o-β-*chloroethylbenzoyl chloride*, b.p. 135°/15 mm., converted by $NHEt_2$ under differing conditions into o-β-*diethylaminoethylbenzdiethylamide*, b.p. 190°/16 mm. (*hydrochloride*, m.p. 168° after softening at 155°), or o-β-*chloroethylbenzdiethylamide*; the latter with NH_2Me affords o-β-*methylaminoethylbenzdiethylamide*, b.p. 182°/15 mm., and the *compound* $NMe(CH_2\cdot CH_2\cdot C_6H_4\cdot CO\cdot NEt_2)_2$, b.p. 230°/high vac. (*hydrochloride*). H. W.

Methiodide of quinoline 1-oxide. M. Henze (Ber., 1937, **70**, [*B*], 1270—1273).—Quinoline 1-oxide (I) is converted by MeI into the very hygroscopic *methiodide*, m.p. (indef.) 70—75°, which with NaOH affords *quinolinemethoxyammonium hydroxide*, m.p. 66—68°; this readily decomposes into quinoline and CH_2O. Treatment of the hydrochloride of (I) with NaOMe in abs. MeOH affords *quinolinehydroxyammonium methoxide*, which decomposes into (I) and MeOH. The changes are thus similar to those recorded for NMe_3 and afford further evidence of the unique nature of one valency of N^V. H. W.

Behaviour of pyridine and quinoline derivatives when irradiated. M. Henze (Ber., 1937, **70**, [*B*], 1273—1274).—Treatment of 2-methylquinoline with PhCHO and $ZnCl_2$ or Ac_2O gives benzylidenequinaldine (I) and benzylidenediquinaldine (*hydrochloride*, m.p. 150—155°; *platinichloride*, decomp. 260°). Exposure of (I) as solid or in C_6H_6 to sunlight leads to the *dimeride*, $C_9H_6N\cdot CH<^{CHPh\text{———}}_{CH(C_9H_6N)}>CHPh$, m.p. 198° after subliming at 180° (*picrate*, m.p. 228—230°). Attempts to dimerise the corresponding C_5H_5N derivative or to obtain compounds of the truxillic acid type by irradiation of pyridyl- or quinolylacrylic acids were unsuccessful. H. W.

Bromination of quinoline, *iso*quinoline, thiazole, and benzthiazole in the gaseous phase. H. E. Jansen and J. P. Wibaut (Rec. trav. chim., 1937, **56**, 699—708).—Bromination of quinoline at 300° gives 3-bromoquinoline in >25% yield whereas at 450—500° the main product is 5-bromoquinoline (yield 50—60%). The influence of temp. therefore, is similar to that observed with C_5H_5N. In both cases small amounts of unidentified dibromoquinolines are produced. Considerable carbonisation is observed, which can be diminished by diluting the reactants with N_2. Br and *iso*quinoline give small amounts of 1-bromo*iso*quinoline with unidentified products. Thiazole at 250° or 450° affords 2-bromothiazole. Similarly at 450° and without dilution with N_2 benzthiazole yields 2-*bromobenzthiazole*, b.p. 84°/0·45 mm., m.p. 39·5°, also obtained from 2-aminobenzthiazole. H. W.

Manufacture of acid amides substituted at the nitrogen atom [quinolines].—See B., 1937, 652.

Acridine salts of hydrogen phosphoric esters. T. Wagner-Jauregg and H. Griesshaber (Ber., 1937, **70**, [*B*], 1458).—The difficulty of determining C in these compounds is obviated by admixture with V_2O_5. H. W.

Synthesis of acriquine (8-chloro-5-δ-diethylamino-α-methylbutylamino-3-methoxyacridine). O. J. Magidson, A. M. Grigorovski, V. I. Maximov, and R. S. Margolina (Chim. Farm. Prom., 1935, No. 1, 26—34).—Two stages in the synthesis are described, viz., (i) *p*-$C_6H_4Me\cdot NO_2$ → 1 : 2 : 4-$C_6H_3MeCl\cdot NO_2$ → the amine → 1 : 2 : 4-$C_6H_3MeCl_2$ → 2 : 4-$C_6H_3Cl_2\cdot CO_2H$ + anisidine → *N*-*p*-anisyl-4-chloroanthranilic acid → 5 : 8-dichloro-3-methoxyacridine (I), and (ii) $NEt_2\cdot CH_2\cdot CH_2\cdot OH$ → $NEt_2\cdot CH_2\cdot CH_2Cl$ → $NEt_2\cdot[CH_2]_3\cdot Ac$ → the oxime → $NEt_2\cdot[CH_2]_3\cdot CHMe\cdot NH_2$ (II). Acriquine is formed by (acid or alkali) condensation of (I) and (II). Ch. Abs. (*p*)

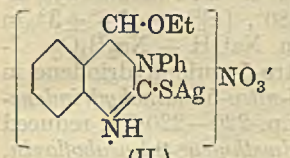
Reactions of 2-bromo- and 3-bromo-quinoline. H. E. Jansen and J. P. Wibaut (Rec. trav. chim., 1937, **56**, 709—713).—2-Bromoquinoline (I) is only slowly affected by warm liquid NH_3 but in presence of Cu powder at 70° 2-aminoquinoline, m.p. 129°, is obtained in 50% yield. KCN and (I) in EtOH–H_2O at 200° yield only carbostyril. When distilled with CuCN (I) gives 2-cyanoquinoline (II), m.p. 94° (yield 63%). Towards *o*-$NH_2\cdot C_6H_4\cdot CO_2H$ (I) behaves in the same manner as does 2-chloroquinoline. K pyrrole and (I) in C_6H_6 at 160° afford 2-2′-*pyrrylquinoline*, m.p. 129°, in 40% yield. 3-Bromoquinoline (III) and Cu powder in liquid NH_3 at 70° give 3-aminoquinoline, m.p. 83—84°, in 60% yield. 3-*Cyanoquinoline*, m.p. 107°, is obtained from (III) and CuCN. Hydrogenation (Pd in 80% EtOH containing HCl) of (II) yields 2-quinolylmethylamine (*dihydrochloride*, m.p. about 240°). K pyrrole, $CHNa(CO_2Et)_2$, or Mg did not react with (III). H. W.

Structure of benzamidine-glyoxal and of its compounds with aromatic aldehydes. J. B. Ekeley and A. R. Ronzio (J. Amer. Chem. Soc., 1937, **59**, 1118—1121).—Absorption spectra support the open-chain formula for the additive products of aromatic amidines with glyoxal and of $NH_2\cdot CPh{:}NH$ with Ac_2, and indicate that amidines, glyoxal, and aldehydes condense thus: $RCHO + (CHO)_2$ → $RCO\cdot CH(OH)\cdot CHO$; $+NH_2\cdot CR'{:}NH$ → $RCO\cdot CH<^{CH{:}N}_{N=CR'}$ (*A*) ⇌ $OH\cdot CR{:}C<^{CH{:}N}_{N=CR'}$ (*B*), (*A*) existing in acid or neutral and (*B*) in alkaline solution. The product from *p*-$NH_2\cdot C_6H_4\cdot CHO$ is coloured in acid solution and thus probably

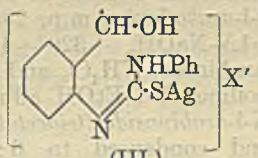
exists as (*B*) in alkaline, as (*A*) in neutral, but as $Cl\{NMe_2{\cdot}C_6H_4{\cdot}C(OH){\cdot}C\ll^{CH:N}_{NH\cdot CPh}$ in acid, solution. The acid, $C_{11}H_8O_3N_2$, m.p. 255°, obtained as by-product in the $NH_2{\cdot}CPh{:}NH$–$(CHO)_2$ reaction, is prepared in 75% yield by adding $CHO{\cdot}CO_2H$ to the main reaction product, and, since it resembles phenylhydroxypyrimidine in absorption spectrum, is probably *5-hydroxy-2-phenylpyrimidine-4-carboxylic acid*, formed by condensation of $(CHO)_2$ and $CHO{\cdot}CO_2H$ to $CO_2H{\cdot}CH(OH){\cdot}CO{\cdot}CHO$ before reaction with $NH_2{\cdot}CPh{:}NH$. R. S. C.

Manufacture of compounds of the anthracene series [pyrimidones].—See B., 1937, 653.

Heteropolar compounds. III. Argenti-salts of derivatives of 4-hydroxy-2-thion-1 : 2 : 3 : 4-tetrahydroquinazoline. (MLLE.) L. MANOLESCU (Bull. Soc. chim., 1937, [v], **4**, 1126—1131; cf. A., 1935, 1253).—4-Ethoxy-2-thion-3-phenyltetrahydroquinazoline (I) with $AgNO_3$ in EtOH gives *Ag 4-ethoxy-2-thiol-3-phenyl-3 : 4-dihydroquinazolinium nitrate* (II), m.p. 183°, which with acids in Et_2O or EtOH yields *salts* (III) of Ag 4-hydroxy-2-thiol-3-



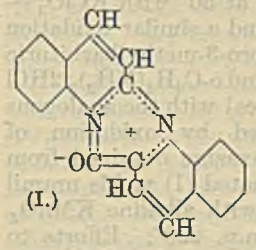
(II.)

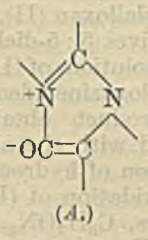


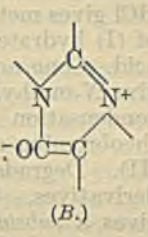
(III.)

phenyl-3 : 4-dihydroquinazoline; the *perchlorate*, m.p. 227°, *hydrochloride*, m.p. 175—177°, *hydrobromide*, m.p. 161—162°, and *hydroiodide*, m.p. 165—166°, are described, in coloured and colourless forms. 4-Ethoxy-2-thion-3-allyl- and -3-*o*- and -*p*-tolyl-tetrahydroquinazoline give only *Ag 4-ethoxy-2-thiol-3-allyl-*, m.p. 140°, -3-o-*tolyl-*, decomp. 173°, and -3-p-*tolyl-3 : 4-dihydroquinazoline*, decomp. 180—182°. The 6-Br-derivative of (I) gives *Ag 6-bromo-4-hydroxy-2-thiol-3-phenyl-3 : 4-dihydroquinazolinium nitrate*, decomp. 180°. E. W. W.

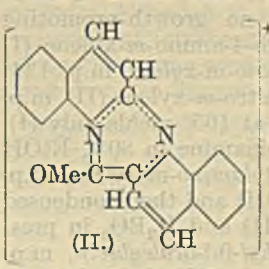
Dyes from quinaldic and *iso*quinaldic acid. F. KROLLPFEIFFER and K. SCHNEIDER (Annalen, 1937, **530**, 34—50).—Besthorn's dye (I), $C_{19}H_{12}ON_2$ (A., 1904, i, 527), is obtained without intermediate products from quinaldoyl chloride, quinoline, and NaCN, NaOH, or NaOAc in aq. $COMe_2$ or Et_2O, and by addition of BzCl to quinoline and quinaldic acid in hot C_6H_6. *Quinoline-2-carboxylic anhydride*, sinters at 100°, m.p. about 245—250°, is obtained by shaking the acid chloride in Et_2O with aq. C_5H_5N, NaOAc, $NaHCO_3$, or Na quinaldate; it yields the amide and *anilide*, m.p. 138—139°, normally, but gives (I) when heated. With hot H_2O or MeOH it is partly hydrolysed and partly converted into (I) by loss of CO_2; it is stable when pure, but, when impure, yields (I) if kept. Formulæ hitherto ascribed to (I) are incorrect. It is unimol. (cryoscopy in $PhNO_2$; ebullioscopy in Ac_2O and NH_2Ph); it is not a free radical, since it does not react with dry O_2 or N_2O and is diamagnetic ($\chi \times 10^6 = -0{\cdot}65$ at 20°, $-0{\cdot}9 \pm 0{\cdot}05$ at −183°); its absorption (detailed) in C_6H_6 and EtOH differs only in the position of the band; the annexed formula is, therefore, assigned; the formulation of the central ring is intended to denote mesomerism (Ingold) (or resonance) between (*A*) and (*B*). Hot Me_2SO_4 and (I) rapidly

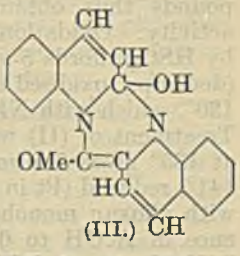

(I.)


(*A*.)

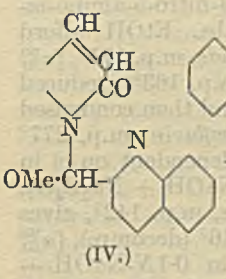

(*B*.)

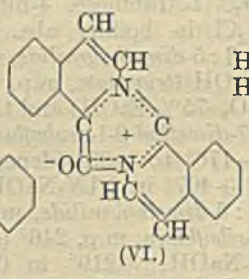
give the yellow *salt* (II), m.p. 179—180° (decomp. from 170°); with warm aq. NaOH this gives first a clear solution, then gives a red oil, which is sol. in dil. HCl and is thus the hydroxide corresponding with (II), and on longer heating partly regenerates (I) and partly gives a colourless *substance*, m.p. 213·5—214·5°, which contains labile OMe and with hot 48% HBr

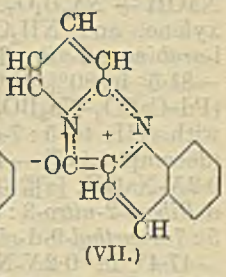

(II.)


(III.)

slowly gives carbostyril and quinoline-2-aldehyde and is thus (III) or, less probably, (IV). When *iso*quinaldic [*iso*quinoline-1-carboxylic] acid (V) (prep. modified to give a 60% yield) is boiled in Ac_2O, or when it and its chloride are treated with BzCl in C_6H_6, the orange-red *dye*, $C_{19}H_{12}ON_2$ (VI), m.p. about


(IV.)


(VI.)


(VII.)

280° (decomp. from 100°), is formed; this regenerates (V) and *iso*quinoline when boiled with 48% HBr, and gives with Me_2SO_4 an *ether salt*, m.p. 205—208° (decomp.), analogous to (II), which regenerates the dye with hot NaOH. C_5H_5N (2 mols.) and quinaldoyl chloride (1 mol.) in hot C_6H_6 give the brownish-red *dye*, $C_{15}H_{10}ON_2$ (VII), $+0{\cdot}5H_2O$, m.p. 238—240° (decomp.), converted by HBr into quinaldic acid and C_5H_5N, and by Me_2SO_4 into the *Me ether methosulphate*, m.p. 165—168° (decomp.; sinters at 150°), analogous to (II), which yields the corresponding *methiodide*, decomp. about 190° after sintering, and *methopicrate*, m.p. 193—194°, and with NaOH partly regenerates the dye. R. S. C.

Constitution of toxoflavin. A. G. VAN VEEN and J. K. BAARS (Proc. K. Akad. Wetensch. Amsterdam, 1937, **40**, 498—505; cf. A., 1934, 537).—

Toxoflavin (I), $C_6H_6O_2N_4$, is considered to be $\begin{matrix}NMe\cdot CO\cdot C{:}N\\ CO-NH\cdot C{:}N\end{matrix}>CH_2$, which is in agreement with all its reactions. Oxidation of (I) at 50° with $KClO_3$ + HCl gives methylalloxan (II), and a similar oxidation of (I) hydrate gives 5 : 5-dichloro-3-methylbarbituric acid. Conc. aq. solutions of (I) and *o*-$C_6H_4(NH_2)_2$,2HCl give *N*-methylalloxazine, identical with the analogous condensation product obtained by oxidation of theobromine and with the alloxazine obtained from (II). Degradation of hydrogenated (I) yields uramil derivatives. Oxidation of (I) with alkaline $KMnO_4$ gives a *substance*, $C_6H_7ON_5$, m.p. 220°. Efforts to isomerise (I) to *N*-methylxanthine failed. J. N. A.

Specificity of lactoflavin. Significance of the position of the methyl groups. R. KUHN, P. DESNUELLE, and F. WEYGAND (Ber., 1937, **70**, [*B*], 1293—1301).—Displacement of Me from the 6- to the 5- or from the 7- to the 8-position annihilates the co-enzyme action of lactoflavin and the compounds thus obtained have no growth-promoting activity. Oxidation of 5-nitro-4-amino-*m*-xylene (I) by HSO_4 affords 5-*nitro*-4-*nitroso*-m-*xylene*, m.p. 134° (decomp.), oxidised to 4 : 5-dinitro-*m*-xylene (II), m.p. 130°, which with NH_3–EtOH at 165° yields only (I). Treatment of (II) with *l*-arabinamine in 80% EtOH at 135° gives 5-*nitro*-4-l-*arabitylamino*-m-*xylene*, m.p. 141°, reduced (Pt in 80% EtOH) and then condensed with alloxan monohydrate (III) and H_3BO_3 in presence of AcOH to 6 : 8-*dimethyl*-9-l-*araboflavin*, m.p. 256° (decomp.), $[\alpha]_D^{21}$ −212° to −126° (dependent on *c*) in 0·2*N*-NaOH, $[\alpha]_D^{21}$ +165° in 0·1*N*-NaOH + $Na_2B_4O_7$. *d*-Ribamine similarly yields 5-*nitro*-4-d-*ribitylamino*-m-*xylene*, whence 6 : 8-*dimethyl*-9-d-*riboflavin*, m.p. 230° (decomp.), $[\alpha]_D^{20}$ −275° to −189° in 0·2*N*-NaOH (dependent on *c*), $[\alpha]_D^{20}$ +145° in 0·1*N*-NaOH + $Na_2B_4O_7$. *l*-Arabinose, 4-nitro-5-amino-*m*-xylene, and NH_4Cl in boiling abs. EtOH afford l-*arabinose*-2-*nitro*-3 : 5-*dimethylanilide*, m.p. 171°, $[\alpha]_D^{21}$ −81·5° in 80% EtOH (*triacetate*, m.p. 163°), reduced (Pd–$CaCO_3$–Na_3BO_3–75% EtOH) and then condensed with (III) to 5 : 7-*dimethyl*-9-l-*araboflavin*, m.p. 277° (decomp.), $[\alpha]_D^{20}$ −176° to −93° (dependent on *c*) in 0·2*N*-NaOH, $[\alpha]_D^{20}$ +407° in 0·1*N*-NaOH + $Na_2B_4O_7$. d-*Ribose*-2-*nitro*-3 : 5-*dimethylanilide*, m.p. 142°, gives 5 : 7-*dimethyl*-9-d-*riboflavin*, m.p. 246° (decomp.), $[\alpha]_D^{20}$ −47·4° in 0·2*N*-NaOH, +219° in 0·1*N*-NaOH + $Na_2B_4O_7$. p-*Methoxybenzylidene*-d-*ribamine*, m.p. 137—138°, p-*methoxybenzylidene*-l-*rhamnamine*, m.p. 141—142°, and l-*rhamnamine oxalate*, m.p. 167—168°, are incidentally described. H. W.

Specificity of lactoflavin. Replacement of the methyl groups by the tetramethylene and trimethylene ring. R. KUHN, H. VETTER, and H. W. RZEPPA (Ber., 1937, **70**, [*B*], 1302—1314).—The ability to form a catalytically active compound with proteins is retained when the $Me_{(6)}$ and $Me_{(7)}$ groups of flavins are replaced by the tri- or tetramethylene ring. 2-Nitro-3-amino-5 : 6 : 7 : 8-tetrahydronaphthalene (I) is converted by *p*-$C_6H_4Me\cdot SO_2Cl$ in C_5H_5N at 100° into 2-*nitro*-3-p-*toluenesulphonamido*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 145·5—146·5°, which with 50% KOH and Me_2SO_4 at 50° affords 2-*nitro*-3-p-*toluenesulphonmethylamido*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 198°, hydrolysed by AcOH–conc. H_2SO_4 at 100° to 2-*nitro*-3-*methylamino*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 115·5°. The last-named substance is reduced by $SnCl_2$ and conc. HCl to 2-*amino*-3-*methylamino*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 83°, the *dihydrochloride*, m.p. 184—186° (decomp.) when rapidly heated, of which is condensed with alloxan tetrahydrate to 6 : 7-*tetramethylene*-9-*methylisoalloxazine*, m.p. >360° after decomp. at 345°. Similarly (I) is reduced to 2 : 3-*diamino*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 134·5°; the *dihydrochloride*, m.p. 302° (decomp.) when rapidly heated, yields 6 : 7-*tetramethylenealloxazine*, m.p. >360°. *l*-Arabinose, (I), and NH_4Cl in boiling abs. EtOH afford 2-*nitro*-3-*amino*-5 : 6 : 7 : 8-*tetrahydronaphthalene*-N-l-*arabinoside* (*triacetate*, m.p. 217°, $[\alpha]_D^{21}$ +108·6°±1·5 in MeOAc), reduced (Pd–$NaBO_2$–H_2O–EtOH), condensed with alloxan and H_3BO_3, and then acetylated to 6 : 7-*tetramethylene*-9-l-*araboflavin tetra-acetate*, m.p. 243° (decomp.). *l*-Arabinamine and 2 : 3-dinitro-5 : 6 : 7 : 8-tetrahydronaphthalene in boiling C_5H_5N give 2-*nitro*-3-l-1′-*arabitylamino*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 208—209°, reduced (PtO_2 in 80% EtOH) and then condensed to 6 : 7-*tetramethylene*-9-l-*araboflavin*, m.p. 285—286°, $[\alpha]_D^{19}$ −45·8°±3° in 0·1*N*-NaOH, +320°±10° in NaOH + $Na_2B_4O_7$. *l*-Arabinose, NH_4Cl, and 6-nitro-5-aminohydrindene in boiling abs. EtOH afford 6-*nitro*-5-*aminohydrindene*-N-l-*arabinoside* (*triacetate*, m.p. 220—220·5°), reduced and condensed to 6 : 7-*trimethylene*-9-l-*araboflavin*, m.p. 300° (decomp.), $[\alpha]_D^{19}$ −61°±4° in 0·1*N*-NaOH, +326°±10° in NaOH + $Na_2B_4O_7$ [*tetra-acetate*, m.p. 200·5—201·5° (decomp.)]. 2-*Nitro*-3-d-1-*ribitylamino*-5 : 6 : 7 : 8-*tetrahydronaphthalene* has m.p. 138—139°. *d*-Ribose and 3-nitro-*p*-toluidine in boiling EtOH give 3-*nitro*-p-*toluidine*-N-d-*riboside*, reduced and condensed to 6-*methyl*-9-d-*riboflavin*, m.p. 276—277° (decomp.), $[\alpha]_D^{19}$ −62·5°±4° in 0·1*N*-NaOH, +275°±10° in NaOH + $Na_2B_4O_7$. 6-*Methyl*-9-l-*araboflavin*, obtained similarly, has m.p. 276° (decomp.) when rapidly heated, $[\alpha]_D^{19}$ −67·5°±4° in 0·1*N*-NaOH, +277°±10° in NaOH + $Na_2B_4O_7$. 6(7)-*Methylalloxazine*, decomp. 335°, is described. H. W.

Phthalocyanines. IX. Derivatives of thiophen, thionaphthen, pyridine, and pyrazine. Nomenclature. R. P. LINSTEAD, E. G. NOBLE, and J. M. WRIGHT. **X. Experiments in the pyrrole, *iso*oxazole, pyridazine, furan, and triazole series.** J. A. BILTON and R. P. LINSTEAD. **XI. Preparation of octaphenylporphyrazines from diphenylmaleinitrile.** A. H. COOK and R. P. LINSTEAD. **XII. Experiments on the preparation of tetrabenzporphyrins.** R. P. LINSTEAD and E. G. NOBLE (J.C.S., 1937, 911—921, 922—929, 929—933, 933—936).—IX. Theoretical considerations of the ease of formation of the porphyrazine structure in different heterocyclic systems are discussed. Coloured substances closely resembling phthalocyanines have been obtained in the thiophen (2 : 3), thionaphthen, C_5H_5N, and pyrazine series. Acetylation of 3-methylthiophen gives a mixture of ketones, oxidised to thiophen-2 : 3- and -2 : 4-dicarboxylic acids, which can be separated since the 2 : 3-acid forms an *anhydride*, m.p. 140°. The *diamide*, m.p.

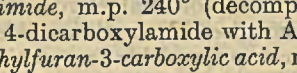
228°, from the 2 : 3-acid, is dehydrated to the *imide*, m.p. 204°, and to 2 : 3-*dicyanothiophen*, m.p. 140°, which with Cu_2Cl_2 affords *Cu tetra*-2 : 3-*thiophenoporphyrazine*. Thiophen-3 : 4-dicarboxylic acid could not be prepared. *Thionaphthen*-2 : 3-*dicarboxylamide*, m.p. 204—205°, prepared from the thionaphthenquinone, is dehydrated to the *-dicarboxylimide*, m.p. 240°, 2(or 3)-*cyanothionaphthen*-3(or 2)-*carboxylamide*, m.p. 192—194°, or 2 : 3-*dicyanothionaphthen*, m.p. 148°. The dinitrile and Cu_2Cl_2 afford a *Cu tetra*-2 : 3-*thionaphthenoporphyrazine*, containing one Cl. Quinolinamide and AcOH–Ac_2O yield 2(or 3)-*cyanopyridine*-3(or 2)-*carboxylamide* (I), m.p. 255—260°, and with Ac_2O alone, the *Ac* derivative of quinolinimide, m.p. 150°, is obtained. 2 : 3-*Dicyanopyridine*, m.p. 130°, is derived by catalytic treatment of the amide and NH_3. Mg and (I) form a metallic derivative which gives *tetra*-2 : 3-*pyridinoporphyrazine* (*dimethiodide*). Diaminomaleinitrile (II) condenses with glyoxal to 2 : 3-dicyanopyrazine, hydrolysed to pyrazinemonocarboxylic acid (cf. Grischkevitsch-Trochimovski, A., 1928, 745). Ac_2, benzil, and phenanthraquinone condense with (II) to give respectively 2 : 3-*dicyano*-5 : 6-*dimethyl*-, m.p. 166°, and *-diphenylpyrazine*, m.p. 245°, and 2 : 3-*dicyanophenanthra*-(9′ : 10′ : 5 : 6)*pyrazine*, m.p. 320°. 3 : 4-Dicyanopyrazine with Cu_2Cl_2 forms *Cu tetrapyrazinoporphyrazine tetra*-, *tri*-, and *mono-hydrate*, and with Mg yields *tetrapyrazinoporphyrazine tetrahydrate*.

X. No phthalocyanine-like pigment has been isolated in any of the five series investigated. A striking difference has been observed in the ease with which heterocyclic *o*-dicarboxylic esters could be converted into the corresponding amides : amides were readily formed from esters derived from C_5H_5N, pyrazine, pyridazine, and *iso*oxazole, but not from the corresponding derivatives of pyrrole and furan. 2 : 5-Dimethylpyrrole-3 : 4-dicarboxylic ester does not react with NH_3, nor does the 1 : 2-*diacetylsuccinate*, m.p. 113·5°. α-*Bromocyanoacetone*, b.p. 43°/12 mm., does not condense with $CN{\cdot}CH_2{\cdot}COMe$. Decarboxylation of 3-*cyano*-2 : 5-*dimethylpyrrole*-4-*carboxylic acid*, m.p. 288° (decomp.), prepared from the Et ester, gives 3-*cyano*-2 : 5-*dimethylpyrrole*, m.p. 89°. This is converted into 4-*formyl*-3-*cyano*-2 : 5-*dimethylpyrrole*, m.p. 207°, the *oxime*, m.p. 223°, of which with NaOAc–Ac_2O yields 3 : 4-*dicyano*-2 : 5-*dimethylpyrrole*, m.p. 239°. *Et* 5-*cyano*-2 : 3-*dimethylpyrrole*-4-*carboxylate*, m.p. 180°, prepared from 4-carbethoxy-2 : 3-dimethylpyrrole-5-aldoxime, is hydrolysed to the *acid*, m.p. 242°, which could not be converted into the corresponding $(CN)_2$-compound, nor could this substance be obtained from 5-*cyano*-2 : 3-*dimethylpyrrole*, m.p. 121·5°. 5-*Methyl*isoo*xazole*-3 : 4-*dicarboxyamide*, m.p. 216°, obtained from the Et ester, is dehydrated (P_2O_5) to 3 : 4-*dicyano*-5-*methyl*isoo*xazole*, m.p. 32°, which with HCl forms 4(or 3)-*cyano*-5-*methyl*isoo*xazole*-3(or 4)-*carboxylamide*, m.p. 225°. 3 : 6-*Dimethylpyridazine*-4 : 5-*dicarboxyl*-*amide*, m.p. 240°, from the Et ester, sublimes to the *-imide*, m.p. 240° (decomp.). 2 : 5-Dimethylfuran-3 : 4-dicarboxylamide with Ac_2O gives 4-*cyano*-2 : 5-*dimethylfuran*-3-*carboxylic acid*, m.p. 174°. *Me* 5-*cyano*-3-*methylfuran*-4-*carboxylate*, m.p. 49°, could not be converted into the amide.

XI. Diphenylmaleinitrile (III) and Mg give *Mg octaphenylporphyrazine*, which with HCO_2H yields *octaphenylporphyrazine diformate*, hydrolysed to *octaphenylporphyrazine*. The *Cu* compound is very stable; (III) and Cu_2Cl_2 afford *Cu monochloro-octaphenylporphyrazine*. *Mg octa*-p-*nitrophenylporphyrazine* is obtained from the corresponding nitrile.

XII. Reduction of 4-chloro-1-methylphthalazine with metal and acid gives only methyldihydro*iso*indole (IV) (*hydrochloride*, m.p. 170°) and not 1-methyl-ψ-*iso*indole (cf. Gabriel *et al.*, A., 1893, i, 348; Fenton and Ingold, A., 1929, 195). Oxidation of (IV) yields no isolable products and bromination affords 1-*methyldihydroisoindole hydrobromide*, m.p. 160°. *o*-Cyanocinnamic acid and Br give the *dibromide*, m.p. 184—186° (decomp.), debrominated (KOH) to 1-*bromo*-2-*o*-*cyanophenylacrylic acid*, m.p. 156—158°, and *o*-cyanophenylpropiolic acid, which is decarboxylated to *o*-*cyanophenylacetylene*, m.p. 76°. These compounds did not form stable pigments with numerous metallic reagents. *o*-*Cyanocinnamonitrile*, m.p. 108°, is described. Although it is not possible to exclude the formation of tetrabenzporphyrins with complete certainty, there is no pronounced tendency for their formation from the foregoing intermediates. F. R. S.

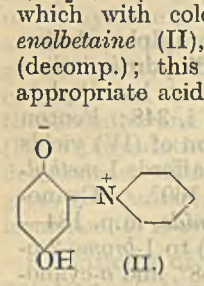
Synthesis of arylidene*iso*oxazolones. J. J. Donleavy and E. E. Gilbert (J. Amer. Chem. Soc., 1937, **59**, 1072—1076).—The following observations replace and amplify the erroneous conclusions of Minunni *et al.* (A., 1928, 1245; 1929, 555, 556). $CH_2Ac{\cdot}CO_2Et$ or $CH_2Bz{\cdot}CO_2Et$ and the appropriate aldoxime in strong acid, best 10% by wt. of 85% H_3PO_4, give 4-benzylidene-3-methyl- (I), m.p. 146—147° (also obtained from PhCHO and $OH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ in AcOH), 3-phenyl-4-benzylidene- (II), m.p. 193—194° [also obtained from phenyl*iso*oxazolone (III) and PhCHO], 3-phenyl-4-anisylidene- (IV), m.p. 164—165° [also obtained from (III) and $OMe{\cdot}C_6H_4{\cdot}CHO$], 3-methyl-4-*iso*propylidene-, m.p. 120—121° (also obtained from $OH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO_2Et$ and $COMe_2$), and 4-*anisylidene*-3-*methyl*-isoo*xazol*-5-*one*, m.p. 180—181°. Reaction occurs by hydrolysis of the oxime, condensation of the liberated aldehyde with the acylacetic ester, oximation of the product, and finally ring-closure. Aliphatic aldoximes give only resins, doubtless formed by polymerisation of the liberated aldehyde by the acid condensing medium. Na_2CO_3 at 70° decomposes (I) into PhCHO (0·5 mol.) and (?) 4 : 4′-benzylidenebis-3-methyl*iso*oxazol-5-one (V), m.p. 150—151° (*Et*$_2$ derivative, m.p. 159—161°, obtained by Et_2SO_4–Na_2CO_3), also prepared from (I) by $OH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ in AcOH at room temp. Na_2CO_3 merely hydrolyses (II) to PhCHO and (III), and it does not affect (IV). $NHPh{\cdot}NH_2$ in warm MeOH hydrolyses (II) and (IV), yielding the *NHPh*·*NH*$_2$ salt, m.p. 153—154°, of (III); with (I) it gives $CHPh{:}N{\cdot}NHPh$ and (V). The so-called 3-methyl*iso*oxazol-5-one, m.p. 168—169°, obtained from $CH_2Ac{\cdot}CO_2Et$ and NH_2OH, is 3-*methyl*-5-4′-3′-*methyl*isoo*xazolidene*isoo*xazole*,



M.p. are corr. R. S. C.

Polymerisation processes caused by pyridine. I. O. Diels and R. Kassebart (Annalen, 1937,

530, 51—67).—C_5H_5N, benzoquinone (I), and the appropriate acid give C_5H_5N 2 : 5-*dihydroxyphenoformate*, m.p. 187—188° (decomp.), *-acetate*, m.p. 215° (decomp.), -chloride, m.p. 225° (*Ac*$_2$ derivative, $+H_2O$, m.p. 122°), and *-maleate*, m.p. 189° (decomp.), which with cold, saturated, aq. Na_2CO_3 give the *enolbetaine* (II), $+2H_2O$ and anhyd., m.p. 240° (decomp.); this regenerates the above salts with the appropriate acid and with $(CH\cdot CO_2H)_2$ in MeCN gives the *salt*, $C_{15}H_{11}O_6N$, which at the m.p., 141—142°, gives CO_2 and the *propiolate*, m.p. 165° (decomp.). C_5H_5N dissolves (I) with absorption of heat, giving a solution from which (II) can be isolated; addition of a few drops of HCO_2H or H_2O causes evolution of heat and formation of a red oily *product* (also obtained as yellow crystals), which is considered to be $OH\cdot C_6H_3<O—C\cdot CO\cdot C\cdot NPh / NPhC\cdot CO\cdot C—O>C_6H_3\cdot OH$ (III), formed by addition of 2 mols. of (II) to 1 mol. of (I). With hot or cold MeOH (III) gives 2 : 5-dimethoxybenzoquinone, new m.p. 303° (decomp.), the structure of which is proved by (*a*) conversion by HNO_3–H_2SO_4 into 3 : 6-*dinitro*-2 : 5-*dimethoxybenzoquinone* (*nitroanilic acid*), $+6H_2O$, m.p. 86—88° with loss of H_2O, resolidifies, explodes mildly at about 170°, (*b*) hydrolysis (KOH) to 2 : 5-dihydroxybenzoquinone, m.p. 215—220° (decomp.) (Ac$_2$ derivative, m.p. 152—153°), and (*c*) bromination in hot $CHCl_3$ to the 3 : 6-*Br*$_2$-derivative, m.p. 158°, which with HBr–AcOH is partly reduced to 3 : 6-*dibromo*-2 : 5-*dimethoxyquinol*, m.p. 208—211° (*Ac*$_2$ derivative, m.p. 191°), and partly hydrolysed to 3 : 6-dibromo-2 : 5-dihydroxybenzoquinone, m.p. about 285° (decomp.) (Ac$_2$ derivative, m.p. 203—205°). H_2O converts (III) into 2 : 5-*di*-p-*hydroxyphenylbenzoquinone*, m.p. 260—261° (decomp.), $+PhNO_2$, HCO_2H, or AcOH [*Ac*$_2$ derivative, m.p. 221—222°; (*NO*$_2$)$_2$-derivative, m.p. about 295° (decomp.) (*Ac*$_2$ derivative, m.p. 242°); *oxime*, m.p. 255° (decomp.)], the structure of which is proved by formation of the corresponding substituted *quinol*, m.p. 234° (*Ac*$_4$ derivative, m.p. 165—168°), and by converson by Me_2SO_4–KOH into *p*-$C_6H_4(OMe)_2$ and 2 : 5-dihydroxybenzoquinone. R. S. C.



(II.)

Substituted phenyl- and benzyl-thiazolium salts. Karimullah (J.C.S., 1937, 961—962).—Thioformylmonoacetyl-*o*-phenylenediamine and $CH_2Cl\cdot COMe$ give N-o-*acetamidophenyl*-4-*methylthiazolium chloride*, m.p. 222°, which with NaOH forms the *hydrochloride*, m.p. 188°, of the *tert.* base; N-o-*tolyl*-4-*methylthiazolium iodide*, m.p. 230° (decomp.), is similarly prepared. Condensation of 4-methylthiazole with CH_2PhCl, *o*-$NO_2\cdot C_6H_4\cdot CH_2Cl$, and *o*-$C_6H_4Cl\cdot CH_2Cl$ yields respectively N-*benzyl*-, m.p. 188°, N-o-*nitrobenzyl*-, m.p. 200°, and N-o-*chlorobenzyl*-4-*methylthiazolium chloride*, m.p. 190° (decomp.), whilst *o*-$C_6H_4Cl\cdot CH_2Cl$ with 2-amino-4-methylthiazole and 2-aminothiazole affords 2-o-*chlorobenzylamino*-4-*methylthiazole hydrochloride*, m.p. 260° (decomp.), and *-thiazole hydrochloride*, m.p. 245°. Reduction (HI–P) of the NO_2-compound gives N-o-*aminobenzyl*-4-*methylthiazolium chloride hydrochloride*, m.p. 213° (decomp.), which is obtained through the *iodide*, m.p. 237° (decomp.), and with $K_3Fe(CN)_6$ did not give a cryst. substance like thiochrome. F. R. S.

Oryzanin, "antineuritic vitamin-*B*." VI. Constitution of oryzanin. S. Ohdake and T. Yamagishi (J. Agric. Chem. Soc. Japan, 1937, **13**, 1—3; cf. A., 1935, 1175, 1428).—The constitution of oryzanin (I) as 3-(6′-amino-2′-methyl-5′-pyrimidylmethyl)-4-methyl-5-β-hydroxyethylthiazole is confirmed. The dihydrochloride with Na_2SO_3 gives 6-*amino*-2-*methyl*-5-*pyrimidylmethylsulphonic acid* (II), m.p. >360°, and 4-*methyl*-5-*hydroxyethylthiazole* (III) (*hydrochloride*, m.p. 95—96°; *picrate*, m.p. 164°; *picrolonate*, m.p. 185°; *platinichloride*, m.p. 173°; *aurichloride*, m.p. 138°). With conc. HCl at 150° (I) gives 3-(6′-*hydroxy*-2′-*methyl*-5′-*pyrimidylmethyl*)-4-*methyl*-5-β-*chloroethylthiazolium chloride* (*hydrochloride*, m.p. 130°; *picrolonate*, m.p. 118°), whilst (II) and (III) with the same reagent give 6-*hydroxy*-2-*methyl*-5-*pyrimidylmethylsulphonic acid* m.p. >360°, and 4-methyl-5-β-chloroethylthiazole (*hydrochloride*; *picrate*, m.p. 139°), respectively. $KMnO_4$ oxidation of (I) yields 6-*amino*-2-*methyl*-5-*aminoethylpyrimidine* (*hydrochloride*, m.p. 263°; *picrate*, m.p. 225°; *picrolonate*, m.p. 250°; *platinichloride*, m.p. >290°). J. N. A.

Crystalline vitamin-B_1. XVII. Synthesis of vitamin-B_1. J. K. Cline, R. R. Williams, and J. Finkelstein (J. Amer. Chem. Soc., 1937, **59**, 1052—1054; cf. A., 1937, III, 153).—$OEt\cdot C_5H_4\cdot CO_2Et$, HCO_2Et, and Na give Et sodioformyl-β-ethoxypropionate, which with $NH{:}CMe\cdot NH_2,HCl$ and NaOEt gives 6-*hydroxy*-2-*methyl*-5-*ethoxymethylpyrimidine*, m.p. 175—176° (3·5% yield), and thence by $POCl_3$ at 78° the 6-*chloro*-, b.p. 72—73°/0·5 mm., and by NH_3–EtOH at 140° the substituted 6-*amino*-*pyrimidine*, m.p. 89·5—90·5°, the *hydrobromide*, m.p. 192—193°, of which with 4-methyl-5-β-hydroxyethylthiazole in BuOH at 120° gives 45% of vitamin-B_1 bromide hydrobromide, forms, m.p. 232—234° and 248—250°. The vitamin salts under crossed Nicols appear to undergo change at 190° and the m.p. are not sharp or characteristic. The forms do not differ crystallographically, spectrometrically, electrometrically, or pharmacologically. R. S. C.

Azacyanines. (Miss) N. I. Fisher and (Miss) F. M. Hamer (J.C.S., 1937, 907—911).—2-Iodoquinoline ethiodide and 2-aminopyridine give 2-2′-*pyridylaminoquinoline ethiodide*, m.p. 216° (*methiodide*, m.p. 206°), which, after removal of HI, with EtI affords 1 : 1′-*diethyl*-2-*pyrido*-2′-*azacyanine iodide* or (1-*ethyl*-2-*pyridine*)(1-*ethyl*-2-*quinoline*)*azamethincyanine iodide*, m.p. 240°. Similarly prepared are 1-*methyl*-1′-*ethyl*-, m.p. 232°, and 1 : 1′-*dimethyl*-2-*pyrido*-2′-*azacyanine iodide*, m.p. 258°, 1 : 2′-*diethyl*-2-*pyrido*-1′-*azacyanine iodide*, m.p. 213°, and 3 : 1′-*diethylthiazolo*-2′-*azacyanine iodide*, m.p. 239°. Condensation of 2-ethylbenzthiazolonehydrazone with the *p*-dimethylaminoanil of quinaldehyde ethobromide, of benzthiazole-1-aldehyde ethochloride, and of *benzselenazole*-1-*aldehyde ethobromide* [+0·5MeOH, m.p. 225° (decomp.)] yields respectively 2 : 1′-*diethyl*-αβ-*diazathia*-2′-*carbocyanine bromide* or (1-*ethyl*-2-*quinoline*)(2-*ethyl*-1-*benzthiazole*)-αβ-*diazatrimethincyanine bromide*, m.p. 221° (decomp.), 2 : 2′-*diethyl*-αβ-

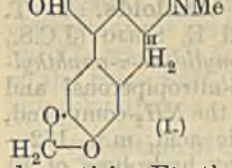
diazathiacarbocyanine bromide or *bis*-(2-*ethyl*-1-*benzthiazole*)-αβ-*diazatrimethincyanine bromide*, m.p. 219° (decomp.), and 2 : 2′-*diethyl*-β*γ*-*diazaselenathiacarbocyanine bromide* or (2-*ethyl*-1-*benzthiazole*)(2-*ethyl*-1-*benzselenazole*)-αβ-*diazatrimethincyanine bromide*, m.p. 259° (decomp.). 1-Methylbenzthiazole ethiodide, NaOAc, Ac_2O, and 1-β-acetanilidovinylbenz-thiazole and -selenazole give respectively 2 : 1′-diethylthia-2′-carbocyanine iodide, m.p. 248° (decomp.) (Ogata, A., 1934, 1370), and 2 : 2′-*diethylselenathiacarbocyanine iodide* or (2-*ethyl*-1-*benzthiazole*)(2-*ethyl*-1-*benzselenazole*)*trimethincyanine iodide*, m.p. 257° (decomp.). 2-Aminoquinoline ethiodide, Et orthoformate, and C_5H_5N form 1 : 1′-*diethyl*-α*γ*-*diaza*-2 : 2′-*carbocyanine iodide* or *bis*-(1-*ethyl*-2-*quinoline*)-α*γ*-*diazatrimethincyanine iodide*, m.p. 209° (1 : 1′-*dimethyl* compound, m.p. 193°). Absorption and sensitising data are recorded. F. R. S.

Constitution of nymphæine. E. Burès and F. Plzák, jun. (Časopis českoslov. Lék., 1935, **15**, 223—226, 242—247; Chem. Zentr., 1936, i, 3340).—An improved method of isolation from roots of *Nymphæa alba* is described. The crude alkaloid is amorphous, m.p. 76—77°, but forms a cryst. *hydrochloride*, m.p. 230°, and *sulphate*; the regenerated nymphæine has m.p. 71—72°, is a *sec.* base, $C_{14}H_{23}O_2N$, and has a pyrrole nucleus and 1 OH. H. N. R.

Properties of the ecgonines and their esters. III. αβ-Position of the double linking in ecgonidine; the structural formulæ and autoracemisation of the ecgonines. A. W. K. de Jong (Rec. trav. chim., 1937, **56**, 678—680).—The presence of a double linking at αβ in ecgonidine has already been established by Willstätter, Gadamer, and von Auwers. *l*-Ecgonine is partly racemised when heated with H_2O. H. W.

Lupin alkaloids. XII. Synthesis of *dl*-lupinine and *dl-iso*lupinine. G. R. Clemo, W. McG. Morgan, and R. Raper (J.C.S., 1937, 965—969).—Several methods of approach for a satisfactory lupinine synthesis have been investigated, one of which has given *dl*- and *dl-iso*-lupinine in amounts too small for resolution. Me 1-keto-octahydropyridocoline-9-carboxylate and N_2H_4 give in small yield 3-*ketodecahydroperipyridazopyridocoline*, m.p. 137°. Bromination of 2-acetylpyridine affords ω-*bromoacetylpyridine*, b.p. 88°/1 mm., in which the Br could not be replaced by OMe or OPh. Et 2-pyridylacetate (I), HCO_2Et, and K form *Et hydroxymethylene*-2-*pyridylacetate* (II), m.p. 97°, which could not be readily reduced, and which with $Al(OPr^{\beta})_3$ and $Pr^{\beta}OH$ gives *Pr*$^{\beta}$ *hydroxymethylene*-2-*pyridylacetate*, m.p. 78° (*picrolonate* of Pr^{β} 2-pyridylacetate, m.p. 187°). Catalytic hydrogenation of (II) yields a mixture of *picrolonates*: of Et pyridyl-α-propionate (?), m.p. 124°, *C*, m.p. 209°, and *D*, m.p. 185°. Condensation of the base from *C* with $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ gives *Et piperidyl*-1-β-*propionate*-2-α-*propionate* E, b.p. 136—138°/1 mm. (*picrolonate*, m.p. 115°), and similarly the base from *D* affords an isomeric *ester F*, b.p. 145°/1 mm. (*picrolonate*, m.p. 136°). Reduction (K–PhMe) of *E* and *F* leads to 2-keto-1-methyloctahydropyridocoline, b.p. 78—80°/1 mm. (*picrate*, m.p. 202°; *picrolonate*, m.p. 209°). Condensation of (I) and $CH_2Cl{\cdot}CO_2Et$ gives *Et pyridylsuccinate*, b.p. 143—147°/1 mm. (*picrolonate*, m.p. 95°), which is reduced (PtO_2–H_2) to Et 2-piperidylsuccinate (?) (*picrolonate*, m.p. 166°), further cyclised to *Et* 3-*keto-octahydropyrrocoline*-1-*carboxylate*, b.p. 148—150°/1 mm. γ-Phenoxy-*n*-propyl bromide and (I) condense to *Et* δ-*phenoxy*-α-2-*pyridyl*-n-*valerate*, b.p. 205—207°/1 mm., reduced catalytically to the *-piperidyl* ester, b.p. 190—192°/1 mm., which is further reduced (Na–EtOH) to ε-*phenoxy*-β-2-*piperidyl*-n-*amyl alcohol*, b.p. 195—200°/1 mm. The carbinol with HBr followed by PBr_5 gives a mixture of dl-*bromolupinane L*, b.p. 107°/1 mm. (*picrolonate*, m.p. 202°; *methiodide*, m.p. 216°; *picrate*, m.p. 135°), and *M*, b.p. 107°/1 mm. (*picrolonate*, m.p. 169°; *picrate*, m.p. 144°). Hydrolysis (NaOAc) of *L* affords 1-*octahydropyridocolylcarbinol N*, b.p. 107°/1 mm., m.p. 59° [*methiodide*, m.p. 303° (decomp.); *picrolonate*, m.p. 203°; *picrate*, m.p. 127°], and of *M* yields the *carbinol O*, b.p. 122°/1 mm., m.p. 81° (*picrate*, m.p. 139°; *picrolonate*, m.p. 225°; *methiodide*, m.p. 248°). The compounds *N* and *O* should be either *dl*- or *dl-iso*-lupinine. F. R. S.

Constitution of domesticine. Z. Kitasato and H. Shishido (Acta phytochim., 1937, **9**, 265—266).—6-Methoxy-7-ethoxy-1-6′-aminopiperonyl-2-methyltetrahydro*iso*-quinoline is converted into 6′-methoxy-5-ethoxy-2 : 3-methylenedioxy-*N*-methylaporphine, the *d*-form of which, m.p. 131°, $[\alpha]_D$ +110°, is identical with domesticine Et ether. Domesticine is therefore (I).



(I.)

H. W.

Strychnine and brucine. XXXVI. Preliminary synthetical experiments. H. I. Openshaw and R. Robinson (J.C.S., 1937, 941—946).—*cyclo*Hexanone-2-β-propionic acid condenses with $NHPh{\cdot}NH_2$ to give the *lactam* of *tetrahydrocarbazole*-1-β-*propionic acid*, m.p. 126°, and *tetrahydrocarbazolenine*-11-β-*propionic acid* (I), m.p. 226°. The lactam is reduced electrolytically to 1 : 9-*trimethylenehexahydrocarbazole*, m.p. 81—82°, dehydrogenated to 1 : 9-*trimethylene*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m.p. 86—87°. (I) is reduced (Sn–HCl) and acetylated to N-*acetylhexahydrocarbazole*-11-β-*propionic acid*, m.p. 202°. Et 2-carbethoxy*cyclo*hexanone-2-β-propionate and NaOEt give *Et* 6-*carbethoxy*cyclo*hexanone*-2-β-*propionate*, b.p. 189—190°/11 mm., which with $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ in C_6H_6 affords the -2 : 6-ββ′-*dipropionate* (II), b.p. 182—183°/0·2 mm., and in EtOH yields some *Et heptane*-1 : 3 : 7-*tricarboxylate*, b.p. 147—148°/0·15 mm. (II) is hydrolysed (HCl) to cyclo*hexanone*-2 : 6-ββ′-*dipropionic acid*, m.p. 145°. The phenylhydrazone of the Et ester, m.p. 60—61°, of this acid, with EtOH–HCl, followed by reduction gives the *lactam*, m.p. 271°, of *hexahydrocarbazole*-1 : 11-ββ′-*dipropionic acid*. A reply is made to the criticisms of Kotake (cf. A., 1936, 1003). F. R. S.

Veratrine alkaloids. I. Degradation of cevine. W. A. Jacobs and L. C. Craig (J. Biol. Chem., 1937, **119**, 141—153).—Cevine heated in H_2 with soda-lime gives, first H_2O, then an unsaturated oily distillate catalytically reduced to a complex mixture,

giving first a neutral fraction (I), then a fraction (II), b.p. 60—70°/8 mm., and a fraction, b.p. 100—140°/8 mm. The distillate also contains [*l*?]-coniine (cf. J.C.S., 1922, **121**, 1571); *d*-coniine forms a 2 : 4-*dinitrobenzoyl* derivative, m.p. 108°. From (II), a picrate (III), m.p. 148—150°, and an unsaturated picrate, m.p. 118—120°, hydrogenated to (III), are obtained. After decomp. by HCl, (III) gives a mixed methiodide, m.p. 200—230°, which with Ag_2O–MeOH, followed by distillation and catalytic reduction, gives a *base*, $C_{11}H_{23}N$ (*picrate*, m.p. 138—140°), of which the *methiodide*, m.p. 248—250°, is converted by Ag_2O etc. into a *base*, $C_{12}H_{27}N$ [*hydrochloride*, m.p. 185—193° (subliming); *platinichloride*, m.p. 118—120°], resembling, but not identical with, dimethyl-*n*-decylamine. Fractionation of (I) gives an *oil*, $C_7H_{12}O$ (*semicarbazone*, m.p. 217—219°), an oil, b.p. 150—160°/25 mm., a hydrocarbon, b.p. 120—130°/0·2 mm., and an *oil*, $C_{11}H_{18}O$ (*semicarbazone*, m.p. 160—170°). Covine heated in H_2 with Zn dust gives a product catalytically hydrogenated to *bases*, $C_7H_{15}N$, apparently active *N*-methyl-β-pipecoline (picrate, m.p. 178—180°), $C_8H_{11}N$ (picrate, m.p. 128—133°), and $C_9H_{13}N$ (picrate, m.p. 131—142°). E. W. W.

Synthetical experiments in the chelidonine–sanguinarine group of the alkaloids. I. T. Richardson, R. Robinson, and E. Seijo (J.C.S., 1937, 835—841).—6-*Nitropiperonylidene-α-naphthylamine*, m.p. 151—153°, from 6-nitropiperonal and α-$C_{10}H_7$·NH_2, is reduced (Na_2S) to the NH_2-compound, m.p. 150—151°. Veratrylsuccinic acid, m.p. 172—174° (+H_2O, m.p. 126—128°), by hydrolysis of Et α-cyano-β-veratrylacrylate, gives the Me ester, m.p. 64—66°, which with piperonal affords the *anhydride*, m.p. 127—129°, of piperonylideneveratrylsuccinic acid. These substances could not be used as starting points of the desired reactions. Veratraldehyde and acetoveratrone form 3 : 4 : 3′ : 4′-*tetramethoxychalkone* (I), m.p. 116—118°, which with NH_2OH leads to a *substance*, m.p. 152—154°, with NHPh·NH_2,HCl yields the *phenylhydrazone* or *pyrazoline*, m.p. 159—160°, and is reduced to α-*keto-αγ-diveratrylpropane*, m.p. 88—90°. (I) and NaCN in MeOH give γ-*keto-α-cyano-αγ-diveratrylpropane*, m.p. 143—144°, hydrolysed to β-*veratroyl-α-veratrylpropionamide*, m.p. 160—162°, which affords the *-propionic acid*, m.p. 193—194° [*phenylhydrazone anhydride* (?), m.p. 149—151°]. This acid is reduced (Zn–Hg) to *αγ-diveratrylbutyric acid*, m.p. 118—120° [$(NO_2)_2$-derivative, m.p. 186—188°], which is cyclised ($POCl_3$) to 1-*keto*-6 : 7-*dimethoxy*-2-*veratryl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 147—149°, from the *oxime*, m.p. 200—202°, of which the 1-NH_2-compound, m.p. 119—121°, is obtained by reduction (Na). This amine gives a *formamido*-derivative, m.p. 202—203°, which is dehydrated ($POCl_3$) to 6 : 7 : 4′ : 5′-*tetramethoxy*-3 : 4 : 11 : 12-*tetrahydro*-1 : 2-*benzphenanthridine*, m.p. 230—231°.

Veratraldehyde and acetopiperone condense to *veratrylideneacetopiperone*, m.p. 133—135°, which with HCN forms γ-*keto*-α-*cyano*-α-*veratryl*-γ-*piperonylpropane*, m.p. 144—146°, converted into α-*veratryl*-β-*piperonylpropionamide*, m.p. 178—180°. Piperonylacetonitrile and Na yield 6-*amino*-5-*piperonyl*-2 : 4-*dihomopiperonylpyrimidine*, m.p. 170—171°, and chiefly β-*imino*-α-*cyano*-αγ-*dipiperonylpropane*, m.p. 113—114°, converted into the β-*keto*-compound, m.p. 122—123° (*oxime*, m.p. 150—151°). The imino-compound and keto-nitrile could not be converted into $C_{10}H_8$ derivatives by the action of HCl–AcOH. Veratrylacetonitrile (II) and Na give β-*imino*-α-*cyano*-αγ-*diveratrylpropane*, m.p. 132—133°, and a trimeride, m.p. 168—168·5. 6-*Bromoveratrylacetonitrile*, m.p. 90—92°, from (II) and Br, could not be dimerised. F. R. S.

Sterin alkaloids. H. Rochelmeyer (Arch. Pharm., 1937, **275**, 336—342).—Glucosido-alkaloids containing the methyl*cyclo*pentenophenanthrene (I) nucleus are termed sterin alkaloids. Solanine-*t* and -*s* are renamed solatunine and solasonine (II) and their aglucones solatubine (III) and solasodine (IV). (IV) [hyriodide, m.p. 228—229° (uncorr.)] contains 23—27 C, crystallises with 0·5H_2O or 1 mol. of dioxan, gives 1·16 mols. of AcOH, gives a 1 : 2 *digitonide*, and with Se affords (I) and a pyrrole derivative (crude picrate, m.p. 140—142°). With NaOH–MeOH (III) gives *solanosodine*, $C_{27}H_{41}ON$ or $C_{29}H_{45}ON$, +0·5H_2O, m.p. 176—177°, which gives no digitonide. The absorption spectra of (II), solatubenone, and (III) are detailed and formulæ are discussed. R. S. C.

Organo-arsenic compounds. III. Arsination of phenol and derivatives of hydroxyphenylarsinic acids. P. S. Yang and T. Y. Wang (J. Chinese Chem. Soc., 1937, **5**, 89—95).—Arsination of phenol (A., 1923, i, 1149) yields *p*- and *o*-hydroxyphenyl-, *pp′*- and *op′*-dihydroxydiphenyl-, and *oo′*-*dihydroxydiphenyl-arsinic acids*, the last m.p. 209—210°. The *Sb*, *Bi*, and *Hg* salts of *p*- and *o*-hydroxyphenylarsinic acids were prepared. A. Li.

Arsenicals containing the dibenzfuran nucleus. B. F. Skiles and C. S. Hamilton (J. Amer. Chem. Soc., 1937, **59**, 1006—1008).—Arsination of dibenzfuran is shown to occur at position 3. H_3AsO_4 at 175—220° gives *dibenzfuran-3-arsinic acid*, m.p. >250°, converted by PCl_3 in AcOH into the 3-*dichloroarsine*, an oil, hydrolysed to the 3-*arsine oxide*, m.p. >250°; with $Hg(OAc)_2$ etc. this yields the 2-mercurichloride, m.p. 235°. 2-Aminodibenzfuran affords (Bart) *dibenzfuran-2-arsinic acid* (I), m.p. >275°, and thence the 2-*dichloroarsine*, m.p. 130°, and 2-*arsine oxide*, m.p. >250°. 6-*Nitrodibenzfuran-2-arsinic acid* (II), m.p. >280°, is obtained from 6-nitro-2-aminodibenzfuran by the Bart reaction and by nitration (HNO_3, *d* 1·48) at 5° of (I), and gives the *dichloroarsine*, m.p. 152° [which with $Hg(OAc)_2$ at 350° gives 3-nitrodibenzfuran], and *arsine oxide*, m.p. >250°. With H_2–Raney Ni (II) gives 6-*amino-dibenzfuran-2-arsinic acid*, m.p. >250°. H_2SO_4 and (I) at 100° yield the (? 8)-*sulphonic acid*, m.p. >300°, and thence (? 8)-*sulphodibenzfuryl-2-arsine oxide*, m.p. >275°. R. S. C.

Salts of tetrahydro-*N*-methylnicotinic acid methyl ester with amino-substituted arsinic acids.—See B., 1937, 730.

Derivatives of *o*-hydroxyphenylmercury chloride. H. P. Anderson and M. C. Hart (J. Amer. Chem. Soc., 1937, **59**, 1115—1116).—Bacteriostatic

data are recorded for o-*hydroxyphenylmercuri-acetate*, m.p. 150—151°, *-nonoate*, m.p. 135°, *-oleate*, m.p. 95—96°, *-laurate*, m.p. 135·5—136·5°, *-myristate*, m.p. 135—136°, *-palmitate*, m.p. 129—131°, and *-stearate*, m.p. 135—137°, and o-*hydroxyphenylmercuri-succinimide* (I), m.p. 232—235°, *-saccharin*, m.p. 242—243°, *-phthalimide*, m.p. 223—224°, *-piperidine* (*hydrochloride*, m.p. 126°), *-theobromine*, $+H_2O$, m.p. 145—165°, and *-barbituric acid*. Bactericidally (I) is as effective as o-$OH{\cdot}C_6H_4{\cdot}HgCl$. Compounds could not be obtained from pyrrole, auramine, or carbazole. R. S. C.

Mercuration of *O*-trimethylgallaldehyde and related substances. I. M. SHARP (J.C.S., 1937, 852—853).—Mercuration of *O*-trimethylgallaldehyde gives 2-*acetoxymercuri*-3 : 4 : 5-*trimethoxybenzaldehyde*, m.p. 145—146°, which is sol. in oils. The following compounds are not oil-sol.: 2-*bromomercuri*-3 : 4 : 5-*trimethoxybenzoic acid*, m.p. 194° (*basic salt*, m.p. 190°, and *chloromercuri*-compound, m.p. 212°) (from *O*-trimethylgallic acid); 2-*bromomercuri*-4-*hydroxy*-3 : 5-*dimethoxybenzaldehyde*, m.p. 260—265° (from syringaldehyde); and 2-*chloromercuri*-4-*hydroxy*-3 : 5-*dimethoxybenzoic acid*, m.p. 230° (decomp.) (from syringic acid). F. R. S.

Mercuration of "acetone anil." P. KALNIN (Latvij. Univ. Raksti, 1936, **3**, 315—320).—The condensation product of $COMe_2$ and NH_2Ph yields a *Hg* derivative containing 63·47% Hg, probably $C_{12}H_{12}NHg_4(OAc)_5$ (one OAc group being in a special position). This is reduced by H_3PO_3 to a base with an odour of quinoline. A. LI.

Mercuration of nitrotoluidines. A. E. GODDARD (J.C.S., 1937, 984—986).—Mercuration (Hg acetate) of the nitrotoluidine gives the acetoxymercuri-derivative (in the 5-position), which with EtOH–AcOH forms a quinoneimide: 4-*nitro*-5-, m.p. 212° (*quinoneimide*, m.p. about 250°), and 5-*nitro*-3-*acetoxymercuri*-o-*toluidine*, m.p. 223° (*quinoneimide*, m.p. >300°); 6-*nitro*-4(?)-*acetoxymercuri*-m-*toluidine*, m.p. >300°; and 2-*nitro*-5- (*quinoneimide*), and 3-*nitro*-5(?)-*acetoxymercuri*-p-*toluidine*. F. R. S.

Monoacetoxymercurialkylphenolsulphonic acids.—See B., 1937, 730.

Manufacture of water-soluble heterocyclic mercury compounds [pyridines].—See B., 1937, 730.

Interaction of selenium tetrachloride and benzene in presence of anhydrous aluminium chloride. W. E. BRADT and J. F. GREEN (J. Org. Chem., 1937, **1**, 540—543).—$SeCl_4$ (50) and $AlCl_3$ (30) in C_6H_6 (136·5 g.) give PhCl (1), Ph_2Se (20), b.p. 301—303°/700 mm. (identified by conversion into $SePh_2Cl_2$, m.p. 183°), Ph_2Se_2 (I) (5), m.p. 63° [$2HgCl_2$-additive compound, m.p. 187—188° (corr.)], and $SePh_3Cl$, isolated as $SePh_3Cl,ZnCl_2$ (20 g.), m.p. 274°. The reaction is formulated: $SeCl_4 + 3C_6H_6 \rightarrow SePh_2Cl + 3HCl$; $SePh_3Cl \rightarrow Ph_2Se + PhCl$; $Ph_2Se + Se \rightarrow Ph_2Se_2$. (I) with Br gives $SePh_2Br_2$, converted by heat into $(p\text{-}C_6H_4Br)_2Se$, m.p. 115°. R. S. C.

1 : 2-Diselena*cyclo*pentanes. H. J. BACKER and H. J. WINTER (Rec. trav. chim., 1937, **56**, 691—698).—Interaction of $CPhMe(CH_2Br)_2$ with K_2Se affords the hydrocarbon $C_{10}H_{12}$, b.p. 176°/750 mm. (also obtained by the action of Zn), and 4-*phenyl*-4-*methyl*-1 : 2-*diselena*cyclo*pentane* (I), $\begin{matrix}Se{\cdot}CH_2\\ Se{\cdot}CH_2\end{matrix}>CPhMe$, m.p. 114—114·5°, better obtained by use of K_2Se_2. (I) is oxidised by HNO_3 to β-*phenyl*-β-*methylpropane*-αγ-*diseleninic acid*, m.p. 113° (decomp.) (*dinitrate*, decomp. about 70°). $CMe_2(CH_2Br)_2$ and KCNSe in EtOH at 140° yield αγ-*diselenocyano*-ββ-*dimethylpropane* (II), m.p. 69·5°, converted by NaOEt in EtOH into 4 : 4-*dimethyl*-1 : 2-*diselena*cyclo*pentane*, m.p. 34°, which is oxidised by HNO_3 to ββ-*dimethylpropane*-αγ-*diseleninic acid*, m.p. 115° (decomp.), the *dinitrate*, m.p. 125—126° (decomp.), of which is also produced by the oxidation of (II). According to conditions (II) and Br afford αγ-*bromoselenol*-ββ-*dimethylpropane*, m.p. 127—128°, or α-*bromoselenol*-γ-*tribromoselenol*-ββ-*dimethylpropane* $SeBr{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2SeBr_3$, m.p. 114—115° (decomp.), which are inter-convertible. H. W.

Complex formation and halochromy in organic tin compounds. K. A. KOTSCHESCHKOV (Sci. Rep. Moscow State Univ., 1934, No. 3, 297—303).—$SnRCl_3$ in Et_2O and C_5H_5N in Et_2O at 0° yield double salts of the type $SnRCl_3,2C_5H_5N$ (R = Ph, *o*- and *p*-C_6H_4Me). Coloured complexes of CPh_3Cl with chlorostannans are formed only with those of the type $SnRCl_3$, where R is aryl, but not alkyl; compounds of the types SnR_2Cl_2, SnR_3Cl, or SnR_4 do not give any coloration. R. T.

Preparation of tin triaryl halides. R. POHLAND (Ber., 1937, **70**, [*B*], 1458).—The prep. of $SnAr_3Hal$ from $SnAr_4$ and $SnCl_4$ at high temp. has been developed in principle by Grüttner (A., 1915, i, 335). H. W.

Nature of the linkings in proteins. D. M. WRINCH (Nature, 1937, **139**, 718).—A discussion and a reply to criticism. L. S. T.

Intramolecular folding of proteins by keto-enol interchange. W. T. ASTBURY and D. M. WRINCH (Nature, 1937, **139**, 798).—A keto–enol interchange can be used as an alternative mechanism to the lactam–lactim interchange recently proposed for the intramol. folding of protein mols. L. S. T.

Formation of ammonia by boiling certain proteins with alkali. G. LAUDE (Compt. rend., 1937, **204**, 1428—1431).—The variation with time of the rate of evolution of NH_3 on boiling casein, gelatin, and fibrin with KOH is recorded. A. LI.

Constituents of hydrochloric acid hydrolysates of elastin. R. ENGELAND and W. BIEHLER (Bull. Soc. Chim. biol., 1937, **19**, 100—108; cf. A., 1936, 352).—The leucine fraction of the hydrolysate yields two diamino-dicarboxylic *acids*, $C_{13}H_{22(24)}O_4N_2$ ("hammatine"), m.p. 255—258° (decomp.), $[\alpha]_D$ approx. −6°, and $C_{14}H_{20}O_4N_2$ (isolated as *Cu* salt). F. O. H.

Ultracentrifugal studies of compounds of proteins with polysaccharides.—See A., III, 252.

Sulphites as protein precipitants.—See A., III, 296.

Crystallisation of melts ("freezing-out") and centrifuging as a preparative method in organic chemistry. L. Ramberg (Svensk Kem. Tidskr., 1937, **49**, 134—138).—A variable-temp. centrifuge for separation of semi-solid melts is described. M. H. M. A.

Application of nitric acid to ashing. B. S. Dmitriev (J. Appl. Chem. Russ., 1937, **10**, 917—919).—The ash obtained from incineration of org. substances with addition of HNO_3 contains >0·01% of nitrite. R. T.

Modification of the Friedrich absorption apparatus for micro-carbon–hydrogen determination. E. Abrahamczik (Mikrochem., 1937, **22**, 227—232).—A modified form of absorption tube is described. J. S. A.

Manometer for carbon and hydrogen pressure regulation. W. H. Hamill (Ind. Eng. Chem. [Anal.], 1937, **9**, 355). E. S. H.

Detection of elements in organic substances. L. Rosenthaler (Z. anal. Chem., 1937, **109**, 31—35; cf. this vol., 128).—C may be detected as CO_2 by wet oxidation with $K_2Cr_2O_7$ + syrupy H_3PO_4 at 250° and H, as H_2S, by heating with Na_2SO_3 (cf. A., 1930, 1460). $Na_2S_2O_3$ is not desirable as S is thereby liberated. P may be converted into PH_3, detected by its green flame coloration, by heating the material with Mg powder in a closed Fe crucible, and subsequently treating the product with H_2O. As and Sb may be detected by application of the Marsh–Gutzeit test to the undestroyed material. J. S. A.

Electrically-heated, thermostatically-controlled, constant-temperature device for Pregl carbon and hydrogen determination. F. Schneider and H. L. van Mater (Ind. Eng. Chem. [Anal.], 1937, **9**, 295). E. C. S.

Volumetric determination of oxygen in organic compounds. J. Lindner and W. Wirth (Ber., 1937, **70**, [*B*], 1025—1038).—The substance (about 4 mg.) is volatilised in H_2, degraded by a glowing Ni spiral, and the products are passed over heated CaO if halogen is present. This is followed by hydrogenation over finely-divided Ni, passage over CaO, and again over Ni. The moist gas stream passes over naphthylphosphoryl chloride. The liberated HCl is collected in H_2O and titrated with 0·1*N*-$Ba(OH)_2$. The apparatus is figured. H. W.

Micro-analytical determination of oxygen in organic compounds. J. Unterzaucher and K. Bürger (Ber., 1937, **70**, [*B*], 1392).—The method depends on the catalytic hydrogenation of O to H_2O in presence of Ni–ThO_2 on an inert carrier. The substance is degraded by SiO_2 at 1000° and hydrogenation is effected at 300°. H. W.

Direct determination of oxygen in organic compounds by hydrogenation. P. Goodloe and J. C. W. Frazer (Ind. Eng. Chem. [Anal.], 1937, **9**, 223—225).—Use of an active Ni chromite catalyst at 400° makes the ter Meulen method suitable for determination of O in org. compounds containing C, H, O, N, and S. Low results are obtained with tartaric acid and sucrose. F. N. W.

Determination of nitrogen in refractory organic substances by a modified Dumas micromethod. J. R. Spies and T. H. Harris (Ind. Eng. Chem. [Anal.], 1937, **9**, 304—306).—After the first, incomplete, combustion of the refractory substance, the current of CO_2 is stopped and the reduced CuO reoxidised by O_2 generated by heating $KClO_3$ contained in a separate boat. This process is repeated until combustion is complete. E. C. S.

Modified micro-Dumas nitrogen determination with readily available air-free carbon dioxide. F. Breuer (Ind. Eng. Chem. [Anal.], 1937, **9**, 354—355).—Apparatus and technique are described. E. S. H.

Kjeldahl digestion apparatus. W. M. Clark (Ind. Eng. Chem. [Anal.], 1937, **9**, 338—339). E. S. H.

Determination of nitrogen by modified Kjeldahl methods. W. R. Campbell and M. I. Hanna (J. Biol. Chem., 1937, **119**, 1—7).—Addition of Se to a 3 : 1 mixture of H_2SO_4 and H_3PO_4 containing Cu produces a rapid and effective reagent for digesting nitrogenous material. J. N. A.

Detection of sulphur in organic compounds. Preparation of the necessary reagent. H. Freytag (Z. anal. Chem., 1937, **109**, 93—95; cf. A., 1934, 1321).—The advantages are outlined of detecting SO_2, formed by oxidation, by means of irradiated 2-benzoylpyridine (obtained by irradiation of a 0·2% solution of the base in 50% aq. EtOH with light of λ >3000 A.). The solution so prepared may be used to impregnate test-papers. J. S. A.

Micro-determination of sulphur in organic substances. P. Piutti and D. Dinelli (Gazzetta, 1937, **67**, 133—136).—The substance, in fuming HNO_3, is electrolysed in a cylindrical vessel with the anode at the bottom, and the resulting H_2SO_4 determined as $BaSO_4$. The method is successful with $CS(NHPh)_2$, sulphides, sulphonic acids, etc., but gives low vals. for S in sulphonal, sulphobenzide, and dinitrothiophen. E. W. W.

Micro-, semimicro-, and macro-determination of halogens in organic compounds. W. H. Rauscher (Ind. Eng. Chem. [Anal.], 1937, **9**, 296—299).—$NH_2{\cdot}[CH_2]_2{\cdot}OH$ is substituted for EtOH in Stepanov's method; it readily converts aliphatic halogen into the ionic form, but is without action on aromatic halogen except of the activated type. Two procedures are described, for the determination of total and aliphatic (or reactive) halogen, respectively, and a qual. test for distinguishing the two types is developed. E. C. S.

[Determination of] arsenic [in organic matter]. C. C. Cassil (J. Assoc. Off. Agric. Chem., 1937, **20**, 171—178).—Although excellent catalysts for the breakdown of refractory org. matter, $CuSO_4$, HgO, and Se interfere in the subsequent Gutzeit test. $HClO_4$ has no such objection and a procedure is outlined employing this agent. Dry ashing with $Ce(NO_3)_3$ and $Mg(NO_3)_2$ gave 14—17% and 100% recoveries of As, respectively, from shrimp and tobacco. The most satisfactory stains were produced by 20-mesh spherical granular Zn. A method of impregnating strips with $HgBr_2$

is described which produces curves of standard slope and curvature. E. C. S.

Micro-elementary analysis of organic boron compounds. H. Roth (Angew. Chem., 1937, **50**, 593—595).—For C and H combustions, org. B compounds are mixed with V_2O_5 as an oxidation catalyst, to prevent the formation of B carbides. V_2O_5 has advantages over $K_2Cr_2O_7$ for other combustions also. B is determined volumetrically by titration of H_3BO_3 in presence of mannitol. The compound is first fused with Na_2CO_3, or, where possible, B is distilled off as $B(OMe)_3$ by heating with H_2SO_4 + MeOH; a suitable form of apparatus is described. Metals are determined as sulphates by evaporating the compounds down with H_2SO_4 + MeOH. J. S. A.

Determination of organic phosphorus by the Parr bomb method. C. L. Tseng and F. Wei (Sci. Rep. Nat. Univ. Peking, 1937, **2**, 15—16).—The sample is fused with Na_2O_2 in a Parr S bomb, the product dissolved in H_2O, a slight excess of 6*N*-HNO_3 added, and the solution evaporated to <100 c.c. After filtration the vol. is adjusted to about 100 c.c., and a mixture of 6*N*-HNO_3 (30 c.c.), H_2O (20 c.c.), and Noyes' NH_4 molybdate solution (50 c.c.) is added. After warming at 60—65° for 1 hr. the yellow ppt. is filtered on a Gooch crucible, washed with 5% aq. NH_4NO_3 containing 1% HNO_3 until the washings are free from Mo, dried at 160°, and weighed. J. W. S.

Application of chromous salts to reductometric determination of organic substances. A. P. Terentiev and G. S. Goriatscheva (Sci. Rep. Moscow State Univ., 1934, No. 3, 277—282).—The prep. of standard $CrCl_2$ solutions, and their use for titration of quinones and azo- and NO_2-compounds, are described. R. T.

Micro-analysis for exchangeable hydrogen. W. H. Hamill (J. Amer. Chem. Soc., 1937, **59**, 1152—1153).—A technique, depending on the decrease in *d* of D_2O, is described for determining exchangable H with 2—5 mg. of a H_2O-sol., non-volatile substance. The following nos. of exchangable H are found, the second val. (if given) being due to slow exchange: $CO(NH_2)_2$ 4, glycine 3·13, hystidine hydrochloride 6·07, 6·36, natural and synthetic vitamin-B_1 hydrochloride 3·6—3·94, 4·5—4·83, quinol 1·95, HCO_2Na 0, succinic acid 2·14, $CH_2(CO_2H)_2$ 2, 3·99. R. S. C.

Determination of unsaturated hydrocarbons in mixtures. Thiocyanogen iodide in volumetric analysis. H. P. Kaufmann and H. Grosse-Oetringhaus (Ber., 1937, **70**, [*B*], 911—915).—A mixture of pure C_6H_6, Ac_2O, and AcOH is kept for at least 8 days, after which $Pb(CNS)_2$ and Br are added and the mixture is shaken in diffused light until decolorisation is complete. After addition of I the mixture is filtered; the filtrate retains a const. titre for months in the dark. A weighed quantity of mineral oil is kept with excess of this CNSI solution for 24 hr. in the dark, after which aq. KI is added and the liberated I is immediately titrated with $Na_2S_2O_3$. A blank experiment is advisable. Only in exceptional cases is the harmony of CNS and CNSI vals. satisfactory. The former are generally the higher and do not show a pronounced termination either owing to continued addition of CNS or, more important, to ready reaction with other components of the technical materials examined. A well-marked termination of the addition of CNSI is observed. CNS appears better adapted to the examination of oils and fatty acids than is CNSI since addition of the latter is not sufficiently selective, and although pauses in the addition to substances with several unsaturated linkings exist, they are easily passed. H. W.

Semimicro qualitative test for the nitro-group in organic compounds. W. M. Hearon and R. G. Gustavson (Ind. Eng. Chem. [Anal.], 1937, **9**, 352—353).—45 NO_2-compounds examined give a reddish-brown ppt. of $Fe(OH)_3$ in <0·5 min. when a 10-mg. sample is mixed with 7 c.c. of a solution of 25 g. of $FeSO_4,(NH_4)_2SO_4,6H_2O$ in 500 c.c. of H_2O + 2 c.c. of conc. H_2SO_4, followed by the addition of 5 c.c. of 15% EtOH–KOH after removal of air by a stream of inert gas. 75 compounds not containing NO_2 gave negative results; exceptions are NO-compounds, aliphatic nitrates and nitrites, quinones, and NH_2OH. F. N. W.

Simultaneous determination of methoxyl and ethoxyl in organic substances. M. Phillips and M. J. Goss (J. Assoc. Off. Agric. Chem., 1937, **20**, 292—297).—MeI and EtI produced as in Zeisel's method are converted with NMe_2I and NMe_3EtI, which are separated by the Willstätter–Utzinger method (cf. A., 1911, *i*, 659). E. C. S.

Relative reactivities of organo-metallic compounds. XVI. Detection of the SH group. H. Gilman and J. F. Nelson (J. Amer. Chem. Soc., 1937, **59**, 935—937; cf. this vol., 221).—$BiEt_3$ and $PbEt_4$ are diagnostic of SH, since they react, though not quantitatively, therewith, but not appreciably with OH, NH, C:CH, $CH_2Ac{\cdot}COMe$, Ph_2N_2, $PhNO_2$, $C_6H_4(NO_2)_2$, $C_6H_3(NO_2)_3$, or Et_2S_2. Acids also react (with $BiEt_3$ < with $PbEt_4$), the amount of reaction with strong acids, *e.g.*, $CCl_3{\cdot}CO_2H$, approaching that with SH. Both reagents indicate SH in MeCS·OH and 1-thiolbenzthiazole; the thiazole, however, does not react with $BiPr^{\alpha}_3$. Some SH is indicated in $CS(NHPh)_2$, but not in $CS(NH_2)_2$. $BiEt_3$ reacts with traces of O_2 and may be a reagent for O_2. R. S. C.

Manometric micro-titration with ferricyanide. E. Haas (Biochem. Z., 1937, **291**, 79—80).—When H in an org. compound (*e.g.*, glutathione, dihydropyridine nucleotide) in neutral solution containing HCO_3' is oxidised by $K_3Fe(CN)_6$, 1 mol. of CO_2 is produced for each H atom oxidised. Hence such compounds are determined in the Warburg apparatus in an atm. of CO_2 (10 vols.) and A (90 vols.) with accuracy > that of other methods. W. McC.

Determination of alcohol by Widmark's method. E. Flotow (Pharm. Zentr., 1937, **78**, 389; cf. A., 1936, 1359).—Improvements in the acid–dichromate method are described. E. H. S.

Micro-determination of *tert.*-butyl alcohol. A. Lindenberg (Compt. rend. Soc. Biol., 1937, **125**, 135—138).—The complex obtained by heating in a sealed tube with Deniges' reagent is decomposed with HCl and excess titrated. H. G. R.

Azides. VIII. β-Naphthazide as a reagent for identification of primary and secondary amines. P. P. T. Sah (J. Chinese Chem. Soc., 1937, **5**, 100—106).—β-Naphthazide, prepared by condensing Et β-naphthoate with N_2H_4 hydrate and diazotising in AcOH, readily reacts in hot C_6H_6 with alcohols, phenols, amines, amides, and aldoximes. The following derivatives β-$C_{10}H_7$·NH·CO·NHR were prepared, with the m.p. (corr.) given: from NH_2·R: phenyl-, 236—238°, o-*tolyl*-, 232—233°, m-*tolyl*-, 222—223°, p-*tolyl*-, 266—267°, p-*xylyl*-, 245—247°, p-*diphenylyl*-, 259—260°, α-*naphthyl*-, 249—250°, β-naphthyl-, 310—312°, o-*nitrophenyl*-, 203—205°, m-*nitrophenyl*-, 222—223°, p-*nitrophenyl*-, 275—276°, p-*bromophenyl*-, 286—288°, *p*-chlorophenyl-, 280—281°, m-*bromo*-p-*tolyl*-, 230—232°, m-*nitro*-p-*tolyl*-, 220—221°, o-*nitro*-p-*tolyl*-, 217—218°, o-*hydroxyphenyl*-, 191—193°, p-*hydroxyphenyl*-, 255—256°, o-*carboxyphenyl*-, 213—214°, m-*carboxyphenyl*-, 277—278°, p-*carboxyphenyl*-, 291—292°, benzoyl-, 223—224°, acetyl-, 305—306°, p-*aminophenyl*- (>320°), p-*amino*-p-*diphenylyl*- (>320°), n-*octyl*-, 98—99°, and o-*carbethoxyphenyl*-, 165—167°; from NHRR′: *diphenyl*-, 157—158°, *acetylphenyl*-, 311—312°, and *phenylmethyl*-, 153—155°. A. Li.

Identification of the amino-acids: *p*-toluenesulphonyl chloride as a reagent. E. W. McChesney and W. K. Swann, jun. (J. Amer. Chem. Soc., 1937, **59**, 1116—1118).—*p*-C_6H_4Me·SO_2 derivatives of the following are described: *dl*-, m.p. 138—139°, and *d*-alanine, m.p. 132—133°, *l*-cystine (disubstituted), m.p. 201—203° (decomp.), glycine, m.p. 147°, l-*histidine*, m.p. 202—204°, l-*hydroxyproline*, m.p. 153°, *dl*-, m.p. 139—140°, and d-iso*leucine*, m.p. 130—132°, *l*-leucine, m.p. 121—122°, dl-*methionine*, m.p. 104—105°, dl-*norleucine*, m.p. 124°, *dl*-, m.p. 134—135°, and *l*-phenylalanine, m.p. 161°, dl-*serine*, m.p. 212—213° (decomp.), *l*-tyrosine (disubstituted), m.p. 113—114°, and *d*-valine, m.p. 147°. The *l*-aspartic and *d*-glutamic acid *derivatives* are oils, but give Bu_2 esters, m.p. 61—62° and 64—65°, respectively. The *dl*-lysine and *l*-proline *derivatives* are oils, but give *Bu* esters, m.p. 111—113° and 53—55°, respectively. The oily *derivative* of *d*-arginine gives an oily *Bu* ester. R. S. C.

Physical aspects of colorimetric determination [of cholesterol] by the Liebermann–Burchard reaction. R. Latarjet and A. Husson (Compt. rend. Soc. Biol., 1937, **125**, 683—686).—Spectrophotometric observations indicate the correct proportion of reagents and that the colour is stable for 30—45 min. H. G. R.

Identification of allylbarbiturates. M. Pesez (J. Pharm. Chim., 1937, **59**, 508—514).—20—30 mg. of diallylbarbituric acid are shaken with 2 c.c. of conc. H_2SO_4, treated with 2 drops of a solution of KBr (2 g.) and $KBrO_3$ (0·5 g.) in H_2O (20 c.c.), warmed for 5 min. at 100°, and cooled. Addition of 2 drops of a solution of *o*-OH·C_6H_4·CO_2Me, cresopyrin, or guaiacol gives a reddish-violet (becoming intense rose in a few sec. at 100° and then reddish-brown), rose, or deep violet (becoming wine-red) colour, respectively. *iso*-Propyl- and -butyl-allylbarbituric acid give with these phenols violet, sky-blue (becoming dark blue when heated), and pale blue colours, respectively, and with thymol a red, with codeine a violet-blue, with β-$C_{10}H_7$·OH an emerald-green, and with resorcinol a blood-red (green fluorescence) colour. 0·1 mg. gives the test. Substances normally present in drugs and extracted by Et_2O, including other barbiturates, do not interfere. The reaction depends on the changes: CH_2:CH·CH_2· → CH_2Br·CHBr·CH_2· → OH·CH_2·CH(OH)·CH_2· → CHO·CO·CH_2·, and condensation of the glyoxal with the phenol. R. S. C.

Colorimetric determination of uric acid. A. Kern and E. Stransky (Biochem. Z., 1937, **290**, 419—427).—Various methods for colorimetric determination of uric acid (I) are critically investigated. The uranyl acetate method is preferred for deproteinisation, and isolation of (I) is found to be unnecessary with serum. Glucose in amounts >6 mg. per c.c. interferes with the determinations but glutathione up to 1 mg. per c.c. has no effect. By use of a new reagent consisting of a 10% solution of Na_2SiO_3 + glycerol, the colour max. can be maintained for 1 hr. without turbidity appearing. P. W. C.

Colour reaction of morphine and alkaloidal derivatives [thereof]. M. Pesez (J. Pharm. Chem., 1937, [viii], **25**, 504—508).—When 0·1 c.c. of 10% aq. KBr is added to 10—20 mg. of morphine (I) in 2 c.c. of conc. H_2SO_4 and the solution is warmed at 100° for 3 min., a yellowish-brown to -green colour develops; the solution is cooled and 20 c.c. of distilled H_2O are cautiously added, giving a pale to emerald-green colour. The reaction is positive with a few tenths of a mg. of (I). Large amounts give an amorphous green ppt., sol. to green or blue solutions in MeOH, EtOH, $COMe_2$, and $CHCl_3$, sparingly sol. in Et_2O, C_6H_6, and EtOAc; the colour is removed from the aq. solution by these solvents. Saturated Br–H_2O, but not KCl, KI, KIO_3, or KOCl, may be used. Codeine, dionin, heroin, and peronin give the same colour; thebaine gives a green with a bluer shade; narcotine, narceine, *apo*morphine, papaverine, colchicine, hydrastine, and other alkaloids and glucosides give no or different colours. Sugars interfere, but are removed by treating the mixture with NH_3 and extracting the (I) with $CHCl_3$. R. S. C.

Mannich's method for determination of morphine. J. R. Nicholls (Analyst, 1937, **62**, 440—443; cf. A., 1935, 507).—30% aq. EtOH is substituted for aq. MeOH, and aq. NH_3 is substituted for NaOH in the original method. The method, in either form, does not give accurate results with opium since other phenolic alkaloids interfere. E. C. S.

Principal chemical tests for morphine. C. C. Fulton (Amer. J. Pharm., 1937, **109**, 219—240).—A review. J. D. R.

Quantitative, spectrographic determination of quinine and cinchonine in mixtures of the two. L. Fuchs and A. Kampitsch (Sci. pharmaceutica, 1935, **6**, 125—132; Chem. Zentr., 1936, i, 3365).—Solutions in 0·1*N*-H_2SO_4 obey the Lambert–Beer law and absorption spectra may be used for this determination. Curves, diagrams, and tables are given. H. N. R.