BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1941.

I.—ALIPHATIC.

Synthesis of paraffins. III. Synthesis of paraffins by means of activated adsorption. S. Matsumura, K. Tarama, and S. Kodama (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 181—184B).—The reactions in the synthesis of paraffins from H_2 and CO in presence of Co or Fe are: Co_2C or Fe_2C + adsorbed at. H → $CH_2<$, which polymerises to $C_nH_{2n}<$; reduction of this gives C_nH_{2n+2}, which is adsorbed and liberated by evaporation. The high temp. of initiation of the syntheses are due to low adsorption of H_2 on Co below 160° and the low adsorption of CO on Fe below 190°. W. A. R.

Nitric oxide-inhibited decomposition of ethane.—See A., 1941, I, 51.

Determination of second virial coefficients for seven unsaturated aliphatic hydrocarbons.—See A., 1941, I, 35.

Macropolymerisation; mechanism of activation.—See A., 1941, I, 50.

Catalytic addition of hydrogen chloride to ethylene.—See A., 1941, I, 52.

Allene series. I. Preparation of allene hydrocarbons. J. I. Ginzburg (*J. Appl. Chem. Russ.*, 1940, **10**, 513—516).—$CHCl{:}C{:}CMe_2$ or $CMe_2Cl{\cdot}C{:}CH$ is converted by Zn and Cu in boiling EtOH or BuOH into $CMe_2{:}C{:}CH_2$ (62—85% yield). R. T.

Hydrogenation of acetylenic compounds. XXXII. Catalytic hydrogenation of alcohols with double and triple linkings. J. S. Salkind and N. D. Chudekova (*J. Gen. Chem. Russ.*, 1940, **10**, 521—526).—Hydrogenation of $OH{\cdot}CMeEt{\cdot}C{:}C{\cdot}CH{:}CH_2$ takes place in three stages (Pd or Pt catalyst), the first product being $OH{\cdot}CMeEt{\cdot}CH{:}CH{\cdot}CH{:}CH_2$. This then yields $OH{\cdot}CMeEt{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, $OH{\cdot}CMeEt{\cdot}CH{:}CHEt$, and $OH{\cdot}CMeEt{\cdot}CH_2{\cdot}CH{:}CHMe$, in approx. equal amounts. The last two atoms of H combine very slowly with these compounds, as compared with the first four H atoms. R. T.

Stabilisation of alkali alcoholates and alcoholic solutions of alcoholates and hydroxides.—See B., 1940, 843.

Decomposition of methyl alcohol at high pressures. A. Apin, O. Leipunski, and N. Reinov (*J. Gen. Chem. Russ.*, 1940, **10**, 863—865).—At 350°/600—8000 atm. the chief reactions are: $2MeOH \rightarrow Me_2O + H_2O$; $Me_2O \rightarrow CH_4 + H_2 + CO$; $MeOH + CO \rightarrow CH_4 + CO_2$; $MeOH + H_2 \rightarrow CH_4 + H_2O$. The velocity of all these reactions rises with increasing pressure. R. T.

Catalytic preparation of ethyl alcohol by the hydration of ethylene. A. Balandin and M. Nesvishski (*Utschen. Zapiski*, 1934, **2**, 233—235; *Chem. Zentr.*, 1935, ii, 1528; cf. A., 1932, 1232).—2% of EtOH is obtained on passing C_2H_4 and H_2O with air over activated C impregnated with 70% H_2SO_4 and Ag_2SO_4 at 150°. The catalyst is readily fatigued. Ch. Abs. (*c*)

Free radicals in the process of pyrolysis and in the electrical discharge. A. Balandin and A. Lieberman (*Utschen. Zapiski*, 1934, **2**, 209—211; *Chem. Zentr.*, 1935, ii, 1525).—The disappearance of a Ag mirror in presence of products of pyrolysing *iso*-$C_5H_{11}{\cdot}OH$ in a quartz tube at 700—800° (modified Paneth–Rice apparatus) indicates the formation of free radicals but at 1100—1200° the mirror is unattacked and a resin is deposited, as also when C_2H_6 is led through a glow discharge. Limitations of this method of detecting free radicals are suggested. Ch. Abs. (*c*)

Isomeric transformations of unsaturated halogen compounds of the aliphatic series. III. Action of hydrochloric acid on methylethylacetylenylcarbinol in presence of ammonium chloride and cuprous chloride. T. A. Favorskaja and A. I. Zacharova. **IV. Action of hydrochloric acid on diethylacetylenylcarbinol in presence of ammonium chloride and cuprous or cupric chloride.** T. A. Favorskaja and I. A. Favorskaja. **V. Reaction of dimethylacetylenylcarbinol with hydrobromic or hydriodic acid.** T. A. Favorskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 446—450, 451—460, 461—467).—III. $OH{\cdot}CMeEt{\cdot}C{:}CH$ and conc. HCl containing CuCl and NH_4Cl (4 hr. at room temp.) yield *γ-chloro-γ-methyl-Δ$^{\alpha}$-pentine*, b.p. 48—50°/100 mm., with *α-chloro-γ-methyl-Δ$^{\alpha\beta}$-pentadiene*, b.p. 68—70°/100 mm., converted by prolonged contact (8 months) with CuCl and NH_4Cl in HCl into *α-chloro-γ-methyl-Δ$^{\alpha\gamma}$-pentadiene*, b.p. 62—63°/100 mm.

IV. $OH{\cdot}CEt_2{\cdot}C{:}CH$ and HCl in presence of $CuCl_2$ and NH_4Cl (2 hr. at room temp., then 3 hr. at 50°), yield *α-chloro-γ-ethyl-Δ$^{\alpha}$-pentine* (I), b.p. 73—76°/100 mm. When CuCl is used in place of $CuCl_2$, the products are (I), *γ-ethyl-Δ$^{\alpha}$-pentin-Δ$^{\gamma}$-ene* (II), b.p. 41—43°/100 mm., and *α-chloro-γ-ethyl-Δ$^{\alpha\beta}$-pentadiene* (III), b.p. 85—88°/100 mm. (II) is also obtained similarly from (I). (II) in dil. HCl, in presence of $HgCl_2$, yields $CHMe{:}CEtAc$, which with p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ affords 2-p-*nitrophenyl*-3 : 5-*dimethyl*-4-*ethylpyrazoline*, m.p. 165—166°.

V. $OH{\cdot}CMe_2{\cdot}C{:}CH$ and $CuCl_2$ or CuCl in conc. HBr containing NH_4Cl yield *α-bromo-γ-methyl-Δ$^{\alpha\gamma}$-butadiene*, b.p. 48°/42 mm. With HI the product is a mixture of $CMe_2{:}C{:}CHI$ and $CH_2{:}CMe{\cdot}CH{:}CHI$, decomp. spontaneously at room temp. or during distillation. R. T.

Electrolytic hydrogenation of dimethylvinylacetylenylcarbinol. A. P. Golovtschanskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 435—445).—$CH{:}C{\cdot}CH{:}CH_2$ in Et_2O–$COMe_2$ and KOH (4 hr. at 0°) give $OH{\cdot}CMe_2{\cdot}C{:}C{\cdot}CH{:}CH_2$ (I), in 80% yield. $COMe_2$ is eliminated from (I) by boiling with aq. KOH. Electrolytic hydrogenation of (I) [Cu cathode, Ni anode; anolyte, saturated aq. NaOH; catholyte, a solution of (I) in 3 : 7 EtOH–1% $NaHCO_3$] affords a mixture of $OH{\cdot}CMe_2{\cdot}C{:}CEt$, $OH{\cdot}CMe_2{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, and $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}C{:}CMe$. R. T.

Tertiary acetylenecarbinols with the acetylenic hydrogen substituted by halogen. T. D. Nagibina (*J. Gen. Chem. Russ.*, 1940, **10**, 427—434).—$OH{\cdot}CMeBu^{\gamma}{\cdot}C{:}CH$ in light petroleum and aq. KOCl yield *α-chloro-δδ-dimethyl-Δ$^{\alpha}$-pentin-γ-ol* (I), b.p. 62—63°/10 mm. (+0·5H_2O, m.p. 38—39°), converted by heating at 100° with 85% HCO_2H into *α-chloro-γ*-tert.-*butyl-Δ$^{\alpha}$-butin-Δ$^{\gamma}$-ene*, b.p. 23—27°/4 mm.; the corresponding *α-Br*-compound, b.p. 51—52°/6 mm., is prepared analogously. (I) and $CuCl_2$ in NH_4Cl–HCl (4 hr. at room temp.) afford *αγ-dichloro-γδδ-trimethyl-Δ$^{\alpha}$-pentine*, b.p. 61—62°/8 mm., m.p. 19—20°. (I) and CuCl in NH_4Cl–HCl (36 hr. at room temp.) yield *αα-dichloro-γδδ-trimethyl-Δ$^{\alpha\beta}$-pentadiene*, b.p. 57—58°/11 mm., with some *αα-dichloro-γδδ-trimethyl-Δ$^{\alpha}$-pentene*, b.p. 96—97°/13 mm. R. T.

Action of hypochlorous acid on βε-dimethyl-Δ$^{\gamma}$-hexine-βε-diol. V. N. Krestinski and N. I. Summ (*J. Gen. Chem. Russ.*, 1940, **10**, 927—934).—$(OH{\cdot}CMe_2{\cdot}C{:})_2$ and $NH_2{\cdot}CO{\cdot}NHCl$ (30 hr. at room temp.) yield *γ-chloro-* (I), m.p. 85° (*semicarbazone*, m.p. 233°), and *γγ-dichloro-δ-keto-βε-dimethylhexane-βε-diol* (II), m.p. 103—104°, and *di-(β-chloro-γ-keto-ααδ-trimethyl-Δ$^{\delta}$-pentenyl) ether* (III), m.p. 122—123°. (III) is also obtained from (I) and (II). (II) and NH_2OH yield *γδ-dioximino-βε-dimethylhexane-βε-diol*, m.p. 145—146°. R. T.

Synthesis of asymmetric γ-acetylene glycols. A. T. Babajan (*J. Gen. Chem. Russ.*, 1940, **10**, 480—482).—The reactions $CORR' + KOH + C_2H_2 \rightarrow OK{\cdot}CRR'{\cdot}C{:}CH$ (I); (I) + $COR''R''' + KOH \rightarrow OK{\cdot}CR''R'''{\cdot}C{:}C{\cdot}CRR'{\cdot}OK$ are of

general applicability. C_2H_2 is passed into a suspension of KOH in $COMe_2$–Et_2O (4 hr. at 0°), COMeEt is added, and the mixture is kept for 48 hr. at room temp., and then hydrolysed to a mixture of $(OH{\cdot}CMe_2{\cdot}C:)_2$ and *aε-dimethyl-Δγ-heptine-aε-diol*, b.p. 213—216°. The product obtained similarly with $COMePr^a$ in place of COMeEt is *aε-dimethyl-Δγ-octine-aε-diol*, b.p. 222—227°/680 mm., whilst with *cyclo*hexanone it is *α-1-hydroxycyclohexyl-γ-methyl-Δα-butin-γ-ol*, m.p. 94—95°. (**II**) is in all cases a by-product. R. T.

Thioacetals and related substances. I. Polar effect of sulphur in thioacetals. II. Reaction between α-bromopropaldehyde diethyl acetal and ethylthiol. III. Comparison of the polar effect of sulphur with that of oxygen and nitrogen. E. Rothstein (*J.C.S.*, 1940, 1550—1553, 1553—1558, 1558—1560).—I. $CH_2Cl{\cdot}CH_2{\cdot}CH(SEt)_2$, EtSH, AcOH (66%), and HCl give *γ-chloro-aα-di(ethylthiol)propane* (**I**), b.p. 115—117°/11 mm., which with KOH–EtOH affords a mixture of *aα-di(ethylthiol)-Δα-propene* (**II**), b.p. 83°/9 mm. [oxidised (H_2O_2–AcOH) to *aα-di(ethylsulphonyl)-Δα-propene* (**III**), m.p. 95·3°], and *γ-ethoxy-aα-di(ethylthiol)propane*, b.p. 115°/9 mm. [oxidised to *γ-ethoxy-aα-di(ethylsulphonyl)propane*, m.p. 35—37°]. With KOBu, (**I**) yields mainly (**II**), in 77% yield, with some *γ-hydroxy-aα-di(ethylthiol)propane*, b.p. 143—145°/10 mm., oxidised to the (*ethylsulphonyl*) compound, m.p. 105—107°; the formation of (**II**) is due to "pinacolic electron displacement" and is enabled to proceed because of the resonance contribution to the transition state of valency structures which can be set up only if the expansion of the S octet is taken into consideration. $HgCl_2$ and (**II**) in MeOH lead to $EtCO_2H$ and an aldehyde forming a 2 : 4-*dinitrophenylhydrazone*, m.p. 149°. BzO_2H and (**II**) in $CHCl_3$ give *αβ-epoxy-aα-di(ethylsulphonyl)propane*, m.p. 75—77°, which with HCl yields a *sulphone*, m.p. 109—110°. $CH_2Br{\cdot}CHBr{\cdot}CHO$ and EtSH in C_6H_6 with HCl afford $CH_2Br{\cdot}CHBr{\cdot}CH(SEt)_2$, which with Zn gives *aα-di(ethylthiol)-Δβ-propene*, b.p. 73°/0·5 mm., also prepared, as well as *γ-chloro-α-ethylthiol-Δβ-propene*, b.p. 60—61°/12 mm., from $CH_2{:}CH{\cdot}CHCl_2$ and NaSEt.

II. From consideration of the hypothesis advanced, it follows that an atom or group which forms a stable anion should be easily eliminated from a mol. in which it was in a β-position to ·SAlk. When $CHMeBr{\cdot}CH(OEt)_2$ (**IV**) is condensed with EtSH, AcOH, and HBr at 0°, followed by distillation, HBr is eliminated and *αβ-di(ethylthiol)-Δα-propene* (**V**), b.p. 88—97°/9 mm., is formed, which is oxidised to the *-(ethylsulphonyl)* compound (**VI**), m.p. 73—74°. Boiling a xylene solution of the mixture gives *aαβ-tri(ethylthiol)propane*, b.p. 100°/0·3 mm., oxidised to the *sulphone*, m.p. 114—115°, (**III**), and (**VI**), and by treatment with aq. $HgCl_2$ forming *α-ethylthiolpropaldehyde*, b.p. 34—37°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 95—96°), and AcCHO [the 2 : 4-dinitrophenylosazone is not identical with *malonaldehydebis-2 : 4-dinitrophenylhydrazone*, m.p. 284° (decomp.)]. A $CHCl_3$ solution of (**V**) is ozonised to a *sulphide*, b.p. 115—118°/9 mm. *β-Ethylthiolpropaldehyde Et₂ acetal*, b.p. 94—97°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 107°), prepared from the corresponding Cl-compound, with EtSH and AcOH–HCl gives *aαγ-tri(ethylthiol)propane*, b.p. 87°/0·2 mm., oxidised to the *-sulphonyl* compound, m.p. 105—106°. *α-Ethylthiolpropaldehyde Et₂ acetal*, b.p. 78—80°/9 mm., is obtained in small yield from the corresponding α-Br-compound. *α-n-Butylthiolpropaldehyde*, b.p. 71·5—72·5°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 107—109°), prepared from BuSH, NaOEt, and $CHMeBr{\cdot}CHO$, with EtSH and AcOH–HCl affords *aα-di-(ethylthiol)-β-n-butylthiolpropane*, b.p. 114—116°/0·3 mm., oxidised to (**III**) and *α-ethylsulphonyl-β-n-butylsulphonyl-Δα-propene*, m.p. 52°, and yielding on treatment with $KOBu^{\gamma}$ Bu^aSH, identified as *Hg dibutylthiol*. *aαγ*-Tri(ethylthiol)-propane is stable under conditions whereby an SEt group is removed from the *aαβ*-derivative.

III. $OH{\cdot}[CH_2]_3{\cdot}NMe_3Cl$ (*picrate*, m.p. 158—159°) with $SOCl_2$ gives the γ-Cl-compound (*picrate*, m.p. 132—134°), which with NaOEt is converted into the allyl compound (*picrate*, m.p. 214—215°); the Δ^{α}-unsaturated compound is not formed, in accordance with the theory put forward. Similarly the action of $KOBu^{\gamma}$ on $CH_2Cl{\cdot}CH_2{\cdot}CH(OEt)_2$ yields acraldehyde acetal and an acetal forming a 2 : 4-*dinitrophenylhydrazone*, m.p. 78—79°, and not methylketen acetal. These results are to be expected since N and O cannot expand the outer valency shell. F. R. S.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system. VI. Unbalanced systems. E. Rothstein (*J.C.S.*, 1940, 1560—1565).—$CHMeCl{\cdot}CH_2{\cdot}NMe_3Cl$ (*picrate*, m.p. 161—162°) with KOH–EtOH gives the *-Δα-propenyl picrate*, m.p. 170—172°, when kept for some hr. at room temp., and when boiled for 20 min. yields a *NNNN'N'N'*-hexamethylenediammonium salt (*picrate*, m.p. 315—316°). The Δ^{α}-isomeride showed no tendency to be converted into the allyl compound, mobility of the system depending on similarity of constitution of the two isomerides. Ozonolysis of $CHMe{:}CH_2{\cdot}NMe_3Cl$ affords MeCHO and a substance forming a *picrate*, m.p. 189°. Acraldehyde, EtSH, and $ZnCl_2$ in CCl_4 yield a mixture of *β-ethylthiolpropaldehyde*, b.p. 60°/10 mm., *aαγ*-tri(ethylthiol)propane, and an unidentified fraction, b.p. 160—170° (decomp.)/0·5 mm. The action of alkali on *γ-chloro-*, m.p. 96—97°, or *γ-iodo-aα-di(ethylsulphonyl)propane*, m.p. 95° (prepared from the *γ-OEt*-compound, m.p. 35—37°), gives 1 : 1-*di(ethylsulphonyl)*cyclo*propane* (**I**), m.p. 131—132°. Oxidation (30% H_2O_2) of the product from dibromopropaldehyde and EtSH affords a small amount of *γ-bromo-aα-di(ethylsulphonyl)-Δβ-propene* (?), m.p. 102°. *αβ-Dimethoxypropaldehyde Et₂ acetal*, b.p. 83—85°/10 mm., with EtSH gives *βγ-dimethoxy-aα-di(ethylthiol)propane*, b.p. 129—130°/8 mm., oxidised to *γ-hydroxy-β-methoxy-aα-di(ethylsulphonyl)propane*, m.p. 108°. Distillation of trimethyl-γγ-di(ethylsulphonyl)propylammonium hydroxide with EtSH followed by treatment with picric acid leads to the *-(ethylthiol) picrate*, m.p. 94°, which is oxidised to (**I**). The foregoing methods were attempts to prepare aα-di(ethylsulphonyl)-Δβ-derivatives.

aα-Di(ethylsulphonyl)-Δα-propene is stable to heat and can be distilled without change; with Br it forms a *dibromide*, with NaOMe it gives a *sulphone*, $C_9H_{16}O_4S_2$, but with NaOMe–MeI, a *sulphone*, $C_{15}H_{30}O_8S_4$, m.p. 162°, is obtained and this is oxidised (O_3) to a *di(ethylsulphonyl)-propionic acid*, m.p. 131°. F. R. S.

Organic selenium compounds. Their decomposition in alkaline solutions and their properties related to the behaviour of selenium compounds in cereals. E. P. Painter, K. W. Franke, and R. A. Gortner (*J. Org. Chem.*, 1940, **5**, 579—589).—The prep. of $(Se{\cdot}CH_2{\cdot}CO_2H)_2$ (**I**), m.p. 100°, $(Se{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H)_2$ (**II**), m.p. 134·5—135·5°, and $Pr^a{}_2S_2$ (**III**) is reported. K_2S_2 and CH_2PhCl in aq. EtOH at 100° afford *dibenzyl diselenide*, m.p. 92—93°. $Br{\cdot}[CH_2]_2{\cdot}CO_2K$ and K_2S give *β-selenodipropionic acid* (**IV**), m.p. 147—148°. *Dibenzyl selenide* has m.p. 45°. Addition of 30% H_2O_2 to (**I**) in Et_2O gives a 90% yield of *seleninoacetic acid*, $CO_2H{\cdot}CH_2{\cdot}SeO_2H$, m.p. 101°. *β-Seleninopropionic acid*, m.p. ~106° (decomp.), is obtained similarly in $COMe_2$. *n-Propylseleninic acid*, obtained by oxidising (**III**) with conc. HNO_3, gives a *compound*, $PrSeO_2H,HNO_3$, m.p. 98°. The corresponding substance, $CH_2Ph{\cdot}SeO_2H,HNO_3$, could not be obtained pure. Se compounds appear less stable in air and in neutral solutions than the corresponding S compounds. Most are stable in neutral org. solvents. The diselenides of org. acids decompose slowly giving metallic Se after they have aged for several days or weeks. (**II**) decomposes much more rapidly than (**I**). Se ethers appear stable, no decomp. being noticeable after several months. The acids decompose rapidly in H_2O and in air, giving metallic Se and diselenide. Diselenides, like disulphides, decompose in alkaline solution giving inorg. selenide and selenite. Se ethers, like S ethers, are stable but (**IV**) is decomposed in alkaline plumbite to give nearly all the Se as PbSe. Se from seleninic acids of org. acids appears to be quantitatively cleaved whilst the seleninic acids of hydrocarbons are partly cleaved, selenide and PbSe being formed. The mechanism of decomp. of these compounds is probably identical with that of the corresponding S compounds.

The relationship of Se compounds in plants and synthesised compounds in regard to their stability in different solutions and on storage is discussed. H. W.

Thermal decomposition of nickel formate.—See A., 1941, I, 51.

Inhibiting action of some asymmetric organic acids on asymmetric oxidation.—See A., 1941, I, 52.

***iso*Propyl and *iso*butyl acrylates.** A. V. Ipatov (*J. Gen. Chem. Russ.*, 1940, **10**, 866—868).—*Prβ*, b.p. 108—112°, and *Buβ acrylate*, b.p. 130—134°, were prepared by the reactions $CH_2Br{\cdot}CHBr{\cdot}CO_2R + Zn \rightarrow CH_2{:}CH{\cdot}CO_2R + ZnBr_2$ or $OH{\cdot}[CH_2]_2{\cdot}CN + ROH + H_2SO_4 \rightarrow CH_2{:}CH{\cdot}CO_2R + NH_4HSO_4$. R. T.

Kinetics of the olefine–bromine reaction.—See A., 1941, I, 51.

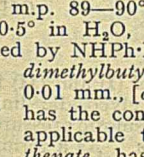
Hydrogenation and exchange reactions of methyl oleate. J. H. Baxendale and E. Warhurst (*Trans. Faraday Soc.*, 1940, **36**, 1181—1188).—Me oleate is treated with D_2 in presence of Pt-black at 170°, and the products of the incomplete reaction, as well as their oxidation ($COMe_2$–$KMnO_4$) products, are examined quantitatively. Exchange of D with H on saturated C atoms is inappreciable. "Heavy" products (oleic, elaidic, and *cis*- and *trans*-esters with the double linking shifted to the Δ^7 or Δ^1 positions) are formed in small quantities only, the main product being "light" *trans*-esters. These results cannot be accounted for by any dissociative mechanism, nor do they provide positive evidence for the associative mechanism discussed by Greenhalgh and Polanyi (A., 1939, I, 322). A mechanism which would lead to the production of "light" *trans*-products, and is at the same time reconcilable with the association hypothesis, is proposed.

F. L. U.

Formation of carbonic and carboxylic esters. E. Baur and M. Namek (*Helv. Chim. Acta*, 1940, **23**, 1101—1110).—Photodynamic pigments which contain CO_2Alk give CH_2O under definite conditions in light. Probably CH_2O is derived from CO_2H of the pigment resulting from decarboxylation and consequent liberation of the alcohol. The re-formation of the pigment requires the reactions, $ROH + CO_2 = OR{\cdot}CO_2H$ (**I**) and $R'H + (I) = R'{\cdot}CO_2R + H_2O$. These reactions can be observed separately. The absorption of CO_2 by H_2O, Bu_2O, or octane is complete within 10 min. and thereafter there is no further change during many days. With alcohols there is a rapid initial physical absorption followed by a much slower chemical absorption which is attributed to the formation of alkyl carbonates. Physical and chemical absorption are not parallel phenomena. Much physical and little chemical absorption is observed with EtOH; the reverse is the case with glycerol (**II**). The chemical absorption varies between 1 mol. per thousand and 2 mol.-%. Max. vals. are observed with (**II**), phytol, and cetyl alcohol. As expected, CO_2 expedites hydrolysis of glycerides and waxes; cottonseed oil, lecithin, and cetyl palmitate are placed in order of increasing action. The absorption of CO_2 in (**II**), EtOH, or BuOH is increased by the presence of phloroglucinol but the phloroglucinolcarboxylic ester could not be isolated. A similar effect is caused by rosolic acid in (**II**) or BuOH and the product is fluorescent in H_2O, doubtless owing to carboxylation.

H. W.

Crystalline quinine salts of (+)- and (−)-pantothenic acid and the biological activity of ethyl *d*(+)-pantothenate. A. Grüssner, M. Gätzi-Fichter, and T. Reichstein (*Helv. Chim. Acta*, 1940, **23**, 1276—1286).—*dl*-α-Hydroxy-ββ-dimethylbutyrolactone is boiled with $Ba(OH)_2$ in MeOH and the solution is treated successively with CO_2 and quinine sulphate whereby quinine salts of the crude (+) and (−) acids are obtained. These are re-converted into the Ba salts, which are purified from H_2O–$COMe_2$. Thus are obtained *Ba* (+)-, m.p. 198—200° (decomp.), $[\alpha]_D^{19}$ +5·5°±1° in H_2O, *Ba* dl-, m.p. 220° (corr.; decomp.), and *Ba* (−)-, m.p. 198—200° (corr.; decomp.), $[\alpha]_D^{20}$ −6·5±1·5° in H_2O, -salts. The requisite salts are transformed by HCl–EtOH into the (−)-, m.p. 89—90°, $[\alpha]_D^{17}$ −17·4°±0·5° in $COMe_2$, $[\alpha]_D^{17.5}$ −49°±0·5° in H_2O, and the (+)-, m.p. 89—90°, $[\alpha]_D^{18}$ +14·5°±0·5° in $COMe_2$, $[\alpha]_D^{17}$ +51·5°±0·5° in H_2O, -lactone. The former compound is transformed by $NHPh{\cdot}NH_2$ at 100° into d-α*γ*-*dihydroxy*-ββ-*dimethylbutyrphenylhydrazide*, b.p. 155° (bath)/0·01 mm., $[\alpha]_D^{18}$ +33·2°±1° in EtOH, so that it has the configuration (*A*) if Hudson's rules are applicable to this compound. *Et* d(+)-*pantothenate* has b.p. 135—140°/0·01 mm., $[\alpha]_D^{18}$ +36·8°±0·5° in abs. EtOH, whereas $[\alpha]_D^{19}$ −37·3°±1° in abs. EtOH is recorded for the l(−)-*ester*. *Quinine* d(+)-*pantothenate* (*monohydrate*, m.p. 136—137°, $[\alpha]_D^{19}$ −95°±2° in H_2O), and l(−)-*pantothenate*, m.p. 183—183·5°, $[\alpha]_D^{18}$ −121°±2° in H_2O, are characteristic.

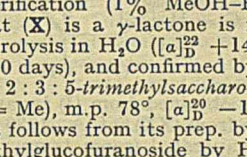

(*A.*)

[With H. Pfaltz.] The biological action of the acids is described, particularly in regard to growth-promoting properties; the *d*(+)-acid esters are much more active in this respect than those of the *l*(−)-acid, which, indeed, are in many cases almost inactive.

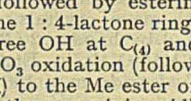
H. W.

Constitution of arabic acid. V. Methylated arabic acid. F. Smith (*J.C.S.*, 1940, 1035—1051).—Gum arabic or arabic acid (**I**) is treated with Me_2SO_4–NaOH, followed by remethylation of the resulting Na salt, with addition of $COMe_2$. After 6—10 methylations, *methylated arabic acid* (**II**), $[\alpha]_D^{18}$ −47° in $CHCl_3$, is obtained, apparently essentially homogeneous. This with CH_2N_2 in Et_2O, followed by Purdie methylation, gives its *Me* ester (**III**), $[\alpha]_D^{24}$ −48° in $CHCl_3$. Attempted hydrolysis of (**II**) by dil. HCl causes decomp., with formation of CO_2 and reductinic acid. With boiling 4% MeOH–HCl, (**III**) undergoes hydrolysis and glycoside formation, the seven glycosides (**VIII**), (**IX**), (**XIII**)—(**XVI**), and (**XIX**) (see below) being formed. The mixture with 0·3N-$Ba(OH)_2$ at 60° gives an Et_2O-insol. Ba salt (**IV**), and a mixture of methylated glucosides sol. (**V**) and insol. (**VI**) in light petroleum.

H_2SO_4–$PbCO_3$–H_2S converts (**IV**) into 2 : 3-*dimethylmethylglucuronoside* (**VII**) (*A*; R = R′ = H), $[\alpha]_D^{18}$ +68° in H_2O {which when distilled gives no lactone, but an acid [identical with (**VI**) (?)], b.p. 186° (bath)/0·03 mm., $[\alpha]_D^{18}$ +65° in H_2O}, which with boiling MeOH–HCl forms its *Me* ester (**VIII**) (*A*; R = H, R′ = Me), b.p. 145° (bath)/0·04 mm., $[\alpha]_D^{18}$ +76° in H_2O (p-*nitrobenzoate*, m.p. 157°), and the Me ester (**IX**) (*A*; R = R′ = Me), b.p. 125° (bath)/0·03 mm., $[\alpha]_D^{18}$ +85° in H_2O, of 2 : 3 : 4-trimethylmethylglucuronoside. With $NHPh{\cdot}NH_2$ at 110°, (**VIII**) gives the *phenylhydrazide*, m.p. 225—227°, of (**VII**). As the glucuronic acid residues of degraded (**I**) have pyranose structures, so must the corresponding uronic acid residues which furnish (**VII**) and (**VIII**). Thus neither Me can be in the 5-position, and (**VII**) and (**VIII**) have 2 : 3-, 2 : 4-, or 3 : 4-Me_2. (**VIII**) is hydrolysed [$Ba(OH)_2$, H_2SO_4] to (**VII**), and this (dil. H_2SO_4 at 100°; $BaCO_3$) to the Ba salt of 2 : 3-dimethylglucuronic acid (*B*). This salt is oxidised (Br–H_2O, followed by Ag_2O and H_2S) to the acid Ba salt of 2 : 3-dimethylsaccharic acid, which with 4% MeOH–HCl at the b.p. gives 2 : 3-*dimethylsaccharo*-*γ*-*lactone Me ester* (**X**) (*C*; R = H), m.p. 190° (bath)/0·03 mm., $[\alpha]_D^{18}$ +12·0° in H_2O (see also below). This is also obtained [with (**XII**), below] by


(*B.*)

(*C.*)

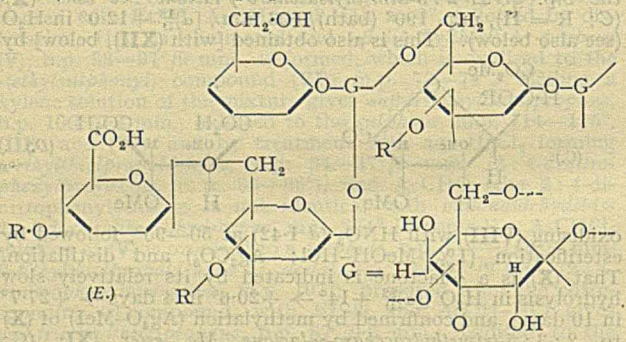

(*D.*)

oxidising (**VIII**) with HNO_3 (*d* 1·42) at 50—95°, followed by esterification (1% MeOH–HCl; Ag_2CO_3) and distillation. That (**X**) is a *γ*-lactone is indicated by its relatively slow hydrolysis in H_2O ($[\alpha]_D^{22}$ +14° → +20·6° in 4 days → +27·7° in 10 days), and confirmed by methylation (Ag_2O–MeI) of (**X**) to 2 : 3 : 5-*trimethylsaccharo*-*γ*-*lactone Me ester* (**XI**) (*C*; R = Me), m.p. 78°, $[\alpha]_D^{20}$ −10° in H_2O. The constitution of this follows from its prep. by oxidation of 2 : 3 : 5-trimethylmethylglucofuranoside by HNO_3, followed by esterification and distillation. The presence of the 1 : 4-lactone ring in (**X**) and (**XI**) shows that (**VIII**) has free OH at $C_{(4)}$ and thus 2 : 3-Me_2. This is confirmed by HNO_3 oxidation (followed by esterification) of both (**VIII**) and (**X**) to the Me ester of *l*(+)-threodimethoxysuccinic acid (*d*-dimethoxysuccinic acid) (**XII**) (*D*), identified as the *diamide*, m.p. 293° (decomp.), $[\alpha]_D^{18}$ +90° in H_2O. Further, synthetically, 4 : 6-benzylidene-α-methylglucoside gives (Purdie) its 2 : 3-Me_2 derivative, which in N-H_2SO_4, followed by $BaCO_3$, yields 2 : 3-dimethylglucose, and (1% MeOH–HCl) 2 : 3-dimethylmethylglucoside, which in HNO_3, followed by esterification, gives (**X**) and the ester of (**XII**). Attempted prep. of (**X**) from 2 : 3 : 6-trimethylglucono-δ-lactone by HNO_3 oxidation gives (**XII**). Purdie methylation of (**VIII**) gives (**IX**), identified by conversion (MeOH–NH_3) into 2 : 3 : 4-trimethyl-*d*-methylglucuronoside (cf. A., 1940, II, 5); the 2 : 3 : 4-Me_3 structure of (**IX**) is also shown by its hydrolysis by dil. H_2SO_4 to 2 : 3 : 4-trimethylglucuronic acid, oxidised by Br to the corresponding saccharic acid, identified as 2 : 3 : 4-trimethylsaccharo-δ-lactone Me ester.

The mixture (**V**) contains 2 : 3 : 5-trimethylmethylarabino-

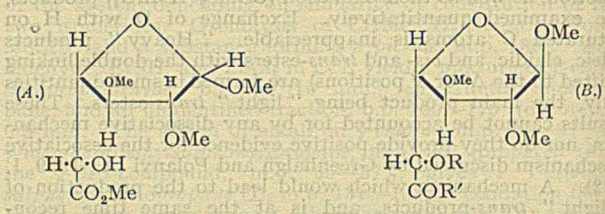
(furano)side (**XIII**), 2 : 3 : 4-trimethylmethylrhamno(pyrano)-side (**XIV**), 2 : 3 : 4 : 6-tetramethylmethylgalactoside (**XV**), and 2 : 5-dimethylmethylarabinoside (**XVI**). Separation of (**V**) into its constituents cannot be effected by fractional distillation, since (**XIII**) and (**XIV**) form a mixture of const. b.p., as do (**XV**) and (**XVI**). 0·1N-H_2SO_4 hydrolyses both (**XIII**) and (**XIV**) and effects no separation; the presence of 2 : 3 : 4-trimethylrhamnose in the hydrolysate is confirmed by the prep. of its anilide. The hydrolysate is oxidised by Br to a mixture of lactones containing 2 : 3 : 4-trimethylrhamnonic acid (phenylhydrazide) and 2 : 3 : 5-trimethylarabonic acid (amide). Hydrolysis of (**XV**) + (**XVI**) by 0·1N-H_2SO_4 gives unchanged (**XV**) [hydrolysed (N-H_2SO_4) to 2 : 3 : 4 : 6-tetramethylgalactose (**XVII**), which gives its anilide (**XVIII**)], and a const.-boiling mixture of 2 : 5-dimethylarabinose and (**XVII**). This mixture with EtOH–NH_2Ph gives (**XVIII**). Oxidation (Br) gives 2 : 3 : 4 : 6-tetramethylgalactonic acid (phenylhydrazide) and 2 : 5-dimethylarabonic acid (phenylhydrazide; amide). Hydrolysis of heptamethyl-3-galactosido-*l*-arabofuranose with boiling MeOH–HCl gives a mixture of the methylated glycosides, and this (N-H_2SO_4) a mixture of sugars, with similar properties to the above mixture. The presence of (**XVI**) is also shown by completely hydrolysing (**V**) (N-H_2SO_4, 10 hr.; $BaCO_3$) to a reducing methylated sugar, which after extraction by light petroleum, and treatment with 1% MeOH–HCl to const. [α], neutralisation, distillation, hydrolysis, and oxidation (Br) gives 2 : 5-dimethylarabono-γ-lactone. The residue (**VI**) consists of α- and β-forms of 2 : 4-dimethylmethylgalactoside (**XIX**) (cf. *loc. cit.*), both hydrolysed (N-H_2SO_4) to the same 2 : 4-dimethylgalactose, oxidised to 2 : 4-dimethylgalactono-δ-lactone.

The identification of the products from (**III**) shows the branched structure of (**I**), and shows that *l*-arabinose (**XX**), *l*-rhamnose, and 3-galactopyranosido-*l*-arabinose, liberated in the autohydrolysis of (**I**), are joined to the nucleus of degraded (**I**) in the form of *l*-arabofuranose (**XXI**), *l*-rhamnopyranose (**XXII**), and 3-galactopyranosido-*l*-arabofuranose (**XXIII**). In addition to the 1 : 3- and 1 : 6-linkings in (**I**), isolation of (**VIII**) shows the presence of a 1 : 4-linking. The repeating structure (*E*), in which the residues R consist of (**XXI**), (**XXII**), and (**XXIII**), is proposed for (**I**).

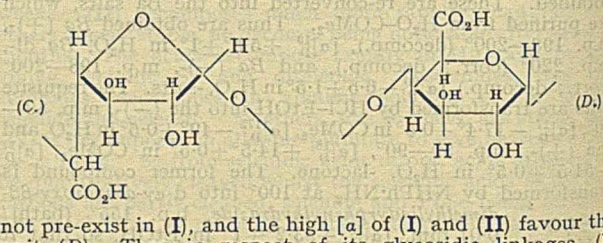


The mixture of reducing sugars obtained from (**I**) by autohydrolysis freed as far as possible from (**XX**) (cf. A., 1939, II, 298), dissolved in MeOH, and evaporated (room temp.; 18 months) gives crystals of *l*-rhamnose hydrate, which are separated by hand. 2 : 3 : 5-Trimethyl-*l*-rhamnono-γ-lactone with NHPh·NH_2 in Et_2O gives 2 : 3 : 5-*trimethyl-l-rhamnon-phenylhydrazide*, m.p. 160°. E. W. W.

Constitution of pectic acid. I. Methylation of pectic acid, and isolation of the methyl ester of 2 : 3-dimethylmethyl-galacturonoside. II. Synthesis of the methyl ester of 2 : 3 : 5-trimethyl-β-methylgalacturonoside. (Miss) S. Luckett and F. Smith (*J.C.S.*, 1940, 1106—1114, 1114—1118).—I. Pectic acid (**I**) from citrus pectin, corresponding with Ehrlich's "tetragalacturonic acid" (A., 1933, 491), when boiled in H_2O hydrolyses to give ultimately galacturonic acid. The partly degraded product is converted by MeOH–HCl at room temp., followed by Purdie methylation, into the Me ester of 2 : 3 : 4-trimethyl-α-methylgalacturonoside. When repeatedly treated with Me_2SO_4–NaOH, (**I**) gives a partly methylated product, purified by addition of H_2SO_4 and dialysis. After renewed methylation, and treatment of the Th (or Ag) salt with MeI–MeOH, the product is methylated (Purdie), and after fractional pptn. in $COMe_2$ by Et_2O gives the *Me* ester (**II**), $[\alpha]_D^{20}$ +223·5° in H_2O, of *methylated pectic acid*. 1% MeOH–HCl at the b.p. causes only slight hydrolysis of (**II**), but at 120° gives the *Me* ester (**III**), b.p. 120—125° (bath)/0·04 mm., $[\alpha]_D^{15}$ −64° in H_2O, of 2 : 3-*dimethylmethylgalactofururonoside* (**IV**), with a methylmethylgalacturonoside (cf. A., 1939, II, 242). Formula (*A*) is assigned to (**III**), which with MeOH–NH_3 gives the *amide* (*B*; R = H, R′ = NH_2), m.p. 124°, $[\alpha]_D^{17}$ −151° in H_2O, of 2 : 3-dimethyl-β-methylgalactofururonoside.



Purdie methylation of (**III**) gives the *Me* ester (**V**) (*B*; R = Me, R′ = OMe) (for synthesis, see below), m.p. 42°, $[\alpha]_D^{12}$ −123° in MeOH, of 2 : 3 : 5-*trimethyl-β-methylgalactofururon-oside* (**VI**), converted by MeOH–NH_3 (−5°; 2 days) into the *amide* (*B*; R = Me, R′ = NH_2), m.p. 106°, $[\alpha]_D^{14}$ −151·5° in H_2O. In HNO_3 (*d* 1·42) at 50—80°, (**V**) gives the *γ-lactone Me ester* (**VII**), m.p. 62°, b.p. 160° (bath)/0·01 mm., $[\alpha]_D^{20}$ −83° in H_2O, of βγε-trimethylmucic acid (**VIII**). In MeOH–NH_3 (room temp.; 2 days), (**VII**) gives the *diamide* (**IX**), m.p. 255° (decomp.), of (**VIII**). Hydrolysis of (**III**) by 0·244N-$Ba(OH)_2$ gives the Ba salt, which with N-H_2SO_4 at 100° yields, fairly slowly ($[\alpha]_D$ −41° → +80° in 24 hr.) [suggesting that a furanoside ring is present in (**IV**) and therefore in (**III**)] a dimethylgalacturonic acid. This is oxidised by Br to an acid which is esterified to the *γ-lactone Me ester* (**X**), m.p. 92°, b.p. 160—165° (bath)/0·02 mm., $[\alpha]_D^{17}$ −55·8° → −4° in H_2O, of βγ-dimethylmucic acid (**XI**). That (**X**) contains a 1 : 4-γ-lactone ring is shown by Purdie methylation to (**VII**) (with Me βγδε-tetramethylmucate), which is synthesised (below). (**X**) is also obtained by oxidising (**III**) by HNO_3 (*d* 1·42) and esterifying the resulting (**XI**). (**VII**) and (**IX**) are enantiomorphs of the 3 : 6-γ-lactone Me ester of βδε-trimethylmucic acid and its diamide (cf. A., 1940, II, 5): $C_{(4)}$ in (**III**) thus does not carry OMe. In MeOH–NH_3, (**X**) forms the *diamide* (**XII**), m.p. 228° (decomp.), of (**XI**), and in MeOH–NH_2Me the corresponding *bismethylamide* (**XIII**), m.p. 184°, $[\alpha]_D^{17}$ −7·5° in H_2O. With NaOCl, (**XII**) undergoes a Weerman degradation with formation of NaNCO; there must thus be free OH at $C_{(2)}$ or $C_{(5)}$. The 2 : 3-position of Me_2 is confirmed synthetically. 2 : 3-Dimethylgalactose (Robertson *et al.*, A., 1934, 1206) in HNO_3 (*d* 1·42; 55—75°), followed by boiling 1% MeOH–HCl, Ag_2CO_3, and distillation, gives (**X**), from which (**XII**) and (**XIII**) are prepared as before. It is thus shown that (**I**) is composed of galacturonic acid residues joined by linkings not involving positions (2) and (3). The alternative repeating units (*C*) and (*D*) are possible. Although (**III**) has a furanose structure, this may



not pre-exist in (**I**), and the high [α] of (**I**) and (**II**) favour the unit (*D*). Thus in respect of its glycosidic linkages, (**I**) resembles starch and not cellulose. Osmotic pressure indicates that (**II**) has a mol. size of ~13 units. As a terminal group (the Me ester of a trimethylmethylgalacturonoside) is not detected in cleavage products, (**II**) may consist of galacturonic acid residues arranged loop-wise. Aq. *dl*-γ-lactone Me ester of trimethylmucic acid, with Me_2SO_4–NaOH, gives a product esterified (1% MeOH–HCl) to *Me βγδε-tetramethylmucate*, m.p. 109°, [α] 0°.

II. Methylgalactofuranoside (cf. Haworth *et al.*, A., 1925, i, 117) in C_5H_5N gives its 6-*CPh*$_3$ *ether*, $[\alpha]_D^{18}$ −33° in $COMe_2$, which on repeated methylation by Me_2SO_4–NaOH in $COMe_2$ gives the 6-*CPh*$_3$ *ether*, $[\alpha]_D^{15}$ −19° in $CHCl_3$, of 2 : 3 : 5-*tri-methylmethylgalactofuranoside* (**XIV**), b.p. 150° (bath)/0·05 mm., $[\alpha]_D^{18}$ −55° in H_2O (isolated by use of Et_2O–HCl and $PbCO_3$). The last with 0·1N-H_2SO_4 at 100° (bath) gives

2 : 3 : 5-*trimethylgalactose*, $[\alpha]_D^{15}$ −5° in H_2O, oxidised by Br–H_2O, followed by Ag_2O and H_2S, to 2 : 3 : 5-*trimethylgalactono-γ-lactone*, m.p. 90°, $[\alpha]_D^{18}$ −37° → −32° (5 days, incomplete) in H_2O, which with MeOH–NH_3 at −5° forms the *amide*, m.p. 152°, $[\alpha]_D^{16}$ +3° in H_2O, and with NHPh·NH_2 the *phenylhydrazide*, m.p. 144°, $[\alpha]_D^{14}$ +18° in EtOH, of βγε-trimethylgalactonic acid. With $KMnO_4$–KOH, followed by H_2SO_4 and evaporation, (**XIV**) gives a residue from which $CHCl_3$ extracts (**VI**), of which the Ba salt with 1% MeOH–HCl (8 hr.) yields (**V**) (which gives the amide as before), as a mixture of the α- with the cryst. *β-form* (**XV**). In HNO_3 (*d* 1·42; 50—80°), (**XIV**) or (**XV**) gives (**VII**). With MeOH–NH_3 (−5°; 3 days) (**VII**) yields (**IX**) as before; intermediately the *amide*, m.p. 173°, of the Me_1 ester of (**VII**) is obtained. In MeOH–NH_2Me (room temp.; 3 days), (**VII**) forms the *bismethylamide*, m.p. 232°, $[\alpha]_D^{17}$ −22° in H_2O, of (**VIII**). The furanoside structure of (**XIV**) and (**XV**) is confirmed by the fact that (**IX**) gives a negative Weerman test for α-hydroxyamide.

E. W. W.

Constitution of pectic acid. III. Hydrolysis of the methyl ester of methylated pectic acid and isolation of the methyl ester of 2 : 3-dimethyl-β-methylgalactopyruronoside. (Miss) S. Luckett and F. Smith (*J.C.S.*, 1940, 1506—1511; cf. preceding abstract).—Prolonged boiling of the Me ester of methylated pectic acid with 2% MeOH–HCl yields the *Me* ester (**I**), m.p. 111°, $[\alpha]_D^{17}$ −11° in H_2O, of 2 : 3-dimethyl-β-methylgalactopyruronoside. Hydrolysis (1% HNO_3), oxidation (HNO_3, *d* 1·42), esterification (CH_2N_2), and distillation of (**I**) yields the γ-lactone of Me βγ-dimethylmucate. Methylation (MeI–Ag_2O) of (**I**) yields the *Me* ester of 2 : 3 : 4-trimethyl-β- (**II**), m.p. 102°, $[\alpha]_D^{18}$ −20° in MeOH, converted by 2% MeOH–HCl at 100° under pressure into 2 : 3 : 4-trimethyl-α-methylgalactopyruronoside Me ester. The latter (prepared by methylation of α-methylgalactopyruronoside) on hydrolysis (dil. H_2SO_4) and methylation (Me_2SO_4) yields (**II**). Methylation (Me_2SO_4) of 6-triphenylmethyl-β-methylgalactoside yields *6-triphenylmethyl-2 : 3 : 4-trimethyl-β-methylgalactopyranoside*, $[\alpha]_D^{17}$ −23° in $CHCl_3$, hydrolysed (Et_2O–HCl) to 2 : 3 : 4-*trimethyl-β-methylgalactopyranoside* (**III**), m.p. 70—72°, $[\alpha]_D^{18}$ +11° in H_2O, methylated (MeI–Ag_2O) to the 2 : 3 : 4 : 6-tetramethylgalactoside, and converted by hydrolysis (N-H_2SO_4) and treatment with NH_2Ph into 2 : 3 : 4-trimethylgalactose anilide. Oxidation (KOH–$KMnO_4$) and esterification (CH_2N_2) of (**III**) yields (**II**).

A. Li.

Manufacture of formaldehyde.—See B., 1940, 843.

Composition of the Ponndorff–Meerwein reduction product of mesityl oxide. J. Kenyon and D. P. Young (*J.C.S.*, 1940, 1547—1550).—Reduction of mesityl oxide (**I**) with $Al(OPr^{\alpha})_3$ gives *αγγ*-trimethylallyl alcohol (**II**) (p-*xenylurethane*, m.p. 94°, identical with that prepared from an authentic specimen) and some δ-methyl-Δ^{δ}-penten-β-ol, recognised by the formation of its H phthalate. This is held to confirm the conclusion of Dupont and Menut (A., 1939, II, 402) that (**I**) contains a significant amount of CH_2:CMe·CH_2·COMe. Catalytic dehydration (small quantity of I) affords the abnormal product, CHMe:CH·CHMe:CH_2, the course of the reaction apparently being dependent on the experimental conditions.

F. R. S.

Di-imides of enolisable diketones and dialdehydes. G. Schwarzenbach and K. Lutz (*Helv. Chim. Acta*, 1940, **23**, 1139—1146).—The great stability of the imides of enolisable diketones and dialdehydes is related to mesomerism. The di-imides of glutacondialdehyde have a chain of three conjugated double linkings and yield salts the cation of which can be expressed by two limiting formulæ of the mesomeric particle. Since these are identical, the cation is a so-called symmetrical resonance system resembling C_6H_6. Symmetrical resonance systems are invariably remarkably stable since they have a high resonance energy which stabilises the otherwise unstable imide. Only the salts are stable whereas the bases are unsymmetrical and readily hydrolysed. 2′ : 4′-Dinitrophenylpyridinium chloride is converted by NH_2Et at room temp. into glatacondiethylimide (isolated as the *perchlorate*, decomp. 99°) and 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH_2. *Glutacondiisobutylimide perchlorate* is described. CH_2Ac_2 is transformed by anhyd. NH_2Et into the monoethylimide, b.p. 91°/15 mm., converted by anhyd. NH_2Et and AcOH at 100° into acetylacetonediethylimide, isolated as the *perchlorate*, m.p. 167·5°. CH_2Ac_2 and $(CH_2$·$NH_2)_2$ give the amphoteric compound $(CH_2$·NH·CMe:CHAc$)_2$, m.p. 111·5°, but if AcOH is gradually added to these reactants heated at 120° the product is the stable 2 : 7-*dimethyl*-3 : 6-*diaza*-$\Delta^{1:6}$-cyclo*heptadiene* (*perchlorate*, m.p. 140°). Dihydroresorcinol is transformed by NH_2Ph and AcOH at ~180° followed by $NaClO_4$ into dihydroresorcinoldianil perchlorate, m.p. 218·5°. Dimedon and NH_2Et in EtOH give the monoethylimide, m.p. 118°, transformed by 33% NH_2Et and AcOH at 180° into *dimedondiethylimide perchlorate*, m.p. 75·5°. Similar processes lead to *dimedondidimethylaminoanil hydrochloride*, m.p. >280°, and *dimedondi-p-hydroxyanil hydrochloride*, m.p. >280°.

H. W.

2-Aldopolyhydroxyalkylbenziminazoles [in characterisation of carbohydrates].—See A., 1941, II, 53.

Isomerisation of hydroxyaldehydes. VII. Re-grouping of galactose, and galactodesonic acid. VIII. Conversion of *l*-arabinose into *l*-arabosaccharic acid. A. M. Gachokidze (*J. Gen. Chem. Russ.*, 1940, **10**, 497—506, 507—512).—VII. Galactal triacetate (**I**) and Cl_2 or Br in $CHCl_3$ yield 1 : 2-*dichloro-*, m.p. 105°, $[\alpha]_D$ +188·7° (all $[\alpha]_D$ refer to $CHCl_3$ solutions), or 1 : 2-*dibromo-galactose triacetate*, decomp. at the b.p., $[\alpha]_D$ +17·8°. These react with moist Ag_2CO_3 in $CHCl_3$ to yield 2-*chloro-* (**II**), $[\alpha]_D$ +76·4°, or 2-*bromo-galactose triacetate*, uncrystallisable syrups. (**II**) when heated with aq. PbO (30 hr. at 100°) yields *galactodesonic acid* (**III**), m.p. 155—158°, $[\alpha]_D$ +6·8° [*Ba* and *Ca* salts; *lactone*; *phenylhydrazide*, m.p. 170—173°; *tetra-acetate*, m.p. 125—128° (*phenylhydrazide*, m.p. 150°)]. With MeI and Ag_2O (40 hr. at 35—40°) (**III**) yields *Me tetramethylgalactodesonate*, m.p. 83—85°, $[\alpha]_D$ +69·8°. Galactal is methylated similarly to 3 : 4 : 6-*trimethylgalactal*, a syrup, $[\alpha]_D$ −35·45°, from which the following substances are prepared [as from (**I**)]: 1 : 2-*dichloro-*, $[\alpha]_D$ +110·2°, and 2-*chloro*-3 : 4 : 6-*trimethylgalactose*, and 3 : 4 : 6-*trimethylgalactodesonic acid* (*Ba* salt; *phenylhydrazide*, m.p. 130—135°).

VIII. *l*-Arabinal diacetate in $CHCl_3$ and Cl_2 afford 1 : 2-*dichloro-l-arabinose diacetate*, m.p. 100—101°, $[\alpha]_D$ +166°, which with moist Ag_2CO_3 gives 2-*chloro-l-arabinose diacetate*, a syrup, $[\alpha]_D$ +150·5°. This when heated with PbO in H_2O (120 hr. at 100°) yields *l*-arabodesonic acid (*Ba* salt; *lactone*, m.p. 155°; *phenylhydrazide*, m.p. 175—180°), from which *Me trimethyl-l-arabodesonate*, m.p. 102—105°, is obtained by the action of Me_2SO_4.

R. T.

Determination of the relationship between refractive index and specific rotation in mixtures of 2 : 3 : 4 : 6-tetramethyl-α- and -β-methyl-*d*-galactosides. D. J. Bell (*J.C.S.*, 1940, 1543—1545).—The graphical relationship between *n* and $[\alpha]$ of mixtures of α- and β-forms of 2 : 3 : 4 : 6-tetramethylmethyl-*d*-galactoside has been found to be a straight line.

F. R. S.

Carbohydrate sulphuric esters. I. Glucose and galactose sulphates. E. G. V. Percival and T. H. Soutar (*J.C.S.*, 1940, 1475—1479).—Galactose in C_5H_5N with $ClSO_3H$ in $CHCl_3$ at −10°, followed by PbO and $BaCO_3$, yields a crude salt from which *brucine galactose sulphate*, $[\alpha]_D^{17}$ −5° (5 min. in H_2O), −11° (24 hr.), and the *Ba* salt (**I**), $[\alpha]_D^{18}$ +46° in H_2O, are obtained. Di*iso*propylidenegalactose similarly yields *Ba diisopropylidenegalactose 6-sulphate* (**II**), $[\alpha]_D^{14}$ −35·7° in H_2O, and, by hydrolysis (1% AcOH), *brucine*, $[\alpha]_D^{18}$ +5° (30 min. in H_2O), +1° (24 hr.) [*dihydrate*, $[\alpha]_D^{18}$ +5° (30 min. in H_2O), +1° (24 hr.)], and *Ba galactose 6-sulphate* [different from (**I**)], $[\alpha]_D^{18}$ +56° in H_2O, converted into (**I**) by $COMe_2$ and a trace of H_2SO_4, followed by $BaCO_3$. Ba α-methylglucoside and *galactoside sulphate*, $[\alpha]_D^{17}$ +142° in H_2O (from α-methylgalactoside as above), with aq. $Ba(OH)_2$ at 100° yields *anhydromethylhexosides*, m.p. 105—106°, $[\alpha]_D^{18}$ +52° and +50·2° in H_2O respectively. The rates of hydrolysis of these Ba salts and Ba glucose sulphate (**III**) by 0·1N-HCl have been determined, but are not suitable for distinguishing the salts. At 100°, (**I**) and (**III**) are immediately hydrolysed, with decomp., by 0·1N-NaOH, whilst (**II**) is unaffected by 2N-NaOH.

A. Li.

Fructosephenylmethylhydrazone. W. J. Heddle and E. G. V. Percival (*J.C.S.*, 1940, 1511—1512; cf. A., 1937, II, 400).—Ofner's prep. of fructosephenylmethylhydrazone (A., 1905, i, 937) has been repeated, giving a product, m.p. 118—119°, $[\alpha]_D^{18}$ ±0° in C_5H_5N–EtOH (4 : 6), which on acetylation gave only a syrup, $[\alpha]_D^{17}$ −75° in $CHCl_3$.

A. Li.

Action of sulphuric acid of a certain concentration on sucrose. M. Fukui (*J. Chem. Soc. Japan*, 1936, **57**, 424).—A condensation product of sucrose (**I**) is obtained as a hydrophilic colloid containing no SO_4 by the action of 75% H_2SO_4 on (**I**) at 0—5°.

Ch. Abs. (*e*)

Cellobiosazone, galactosazone, and other sugar osazones. J. R. Muir and E. G. V. Percival (*J.C.S.*, 1940, 1479—1481; cf. A., 1937, II, 400).—*Cellobiosazone hepta-acetate* (Ac_2O in C_5H_5N), m.p. 90°, $[\alpha]_D^{18}$ −37° in $CHCl_3$, on hydrolysis (H_2O–$COMe_2$–NaOH) yields *anhydrocellobiosazone hydrate* (**I**), m.p. 218°, $[\alpha]_D^{18}$ −142° in MeOH, identical with that obtained by Diels' method (A., 1936, 1364). Acetylation of (**I**) yields a *penta-acetate*, m.p. 193°, $[\alpha]_D^{18}$ −142° in $COMe_2$, deacetylated to (**I**). No cryst. deacetylation products could be obtained from the *hepta-acetates* of *melibiosazone*, m.p. 105°, $[\alpha]_D^{17}$ +32° in $CHCl_3$, or *gentiobiosazone*, m.p. 98°, $[\alpha]_D^{17}$ −46° in $CHCl_3$. Methylation (Me_2SO_4) of galactosazone (**II**) yields *trimethylgalactose methylphenylphenylosazone* (**III**), m.p. 160°, $[\alpha]_D^{18}$ +86·5° (5 min. in $CHCl_3$), +32·4° (48 hr.). (**II**) does not react with CPh_3Cl in C_5H_5N. It is concluded that (**II**) contains a tagatopyranose ring. (**II**) with p-NO_2·C_6H_4·CHO gives a 30% yield of galactosone, but no osone could be so obtained from (**III**). A. Li.

Seed mucilages. I. Mucilaginous polysaccharide of the seed of *Pluntago lanceolata*. J. Mullan, E. G. V. Percival, and [in part] R. Burnett (*J.C.S.*, 1940, 1501—1506).—Pptn. of the aq. extract of the seeds with EtOH yields an acid polysaccharide (**I**), $[\alpha]_D^{16}$ −60° in H_2O, equiv. wt. 1100, uronic anhydride 15·2%, pentosan 72%, and methylpentosan 11%. Hydrolysis ($H_2C_2O_4$) of (**I**) and treatment with $CaCO_3$ gives *α-d*-xylose and (30%) the Ca salt, $(C_{12}H_{21}O_{11})_2Ca$, $[\alpha]_D^{17}$ +89° in H_2O, of an aldobionic acid having a methylpentosan residue. Hydrolysis (15% H_2SO_4) of (**I**) gives an acid (? galacturonic) (Ba salt, $[\alpha]_D^{16}$ +22° in H_2O) which suffers a reversal of rotation in presence of 1% MeOH–HCl, and is oxidised (aq. Br or HNO_3) to mucic acid. Acetylation (Ac_2O in C_5H_5N) of (**I**) yields fractions (*A*) (40%), Ac 41·0%, $[\alpha]_D^{17}$ −72° in $COMe_2$ (methylated product, OMe 35%, $[\alpha]_D^{18}$ −104° in $CHCl_3$), and (*B*), Ac 36%, unaffected by further acetylation, methylated to a product, OMe 34%, $[\alpha]_D^{18}$ −99° in $CHCl_3$, having a mol. size (η in *m*-cresol) double the corresponding val. for (*A*). Methylation of acetylated (**I**), hydrolysis (MeOH–HCl), and fractionation yields trimethylmethylxylopyranosides (30%), 3 : 4-dimethylmethylxylopyranosides (**II**) (28%), a mixture of (**II**) with 2 : 4 : 6-trimethylmethylgalactosides (**III**) (isolated as the tri- and tetra-methylgalactose anilides) and glycosides of lower OMe content (22%), and a mixture of (**III**) with a partly methylated methyluronoside (Ba salt of hydrolysis product, OMe 17·7%, $[\alpha]_D^{18}$ +43° in H_2O) and other glycosides (17%). Methylation and hydrolysis (2% HNO_3) of (**II**) yields trimethylxylopyranose. Hydrolysis of (**II**) gives dimethylxylose (**IV**), oxidised (aq. Br) to 3 : 4-*dimethylxylonolactone*, m.p. 67°, $[\alpha]_D^{18}$ +41° (5 min. in H_2O), +31° (4 hr., const. val.), converted by MeOH–NH_3 into the *amide*, $[\alpha]_D^{14}$ +54° in H_2O, which with NaOCl followed by NH_2·NH·CO·NH_2 gives a hydrazodicarbonamide, m.p. 257° (decomp.). Oxidation (HNO_3) and esterification of (**II**) yields *Me dimethoxyglutarate*, b.p. 130—150° (bath temp.)/0·05 mm., $[\alpha]_D^{15}$ +41° in MeOH [the amide from which gives a hydrazodicarbonamide, m.p. 254° (decomp.)], methylated (MeI–Ag_2O) to Me *i*-xylotrimethoxyglutarate. More vigorous oxidation (HNO_3) of (**II**), esterification, and amide formation gives some *l*-dimethoxysuccinamide. (**IV**) gives no cryst. anilide. A. Li.

Fractionation of potato starch by electrophoresis. R. H. Hopkins, E. G. Stopher, and D. E. Dolby (*J. Inst. Brew.*, 1940, **46**, 426—432).—Electrophoresis of starch, alternating with redispersion (*e.g.*, at 120°) of the amylopectin fraction, yields up to 80% of amyloamylose (**I**), which is more completely though less rapidly degraded by barley diastase than is the original starch. On keeping, (**I**) reverts to a form more closely resembling starch in its susceptibility to attack by this enzyme. I. A. P.

Theory of nitration of cellulose.—See A., 1941, I, 44.

Manufacture of aliphatic amines.—See B., 1940, 843.

Chemical war materials. XIX. Chemical and spectroscopic properties of ββ′β″-trichlorotriethylamine (skin poison) and its hydrochloride. H. Mohler and W. Hämmerle (*Helv. Chim. Acta*, 1940, **23**, 1211—1216).—$N([CH_2]_2$·$Cl)_3$,HCl (**I**), m.p. 131° (corr.), is detected by the formation of oily drops which become brown when warmed and the development of an odour of amines and geranium on addition of alkali to its solutions, by the production of a yellow turbidity in the cold and a brown ppt. on warming with Nessler's reagent (sensitiveness 1 in 5000), by the production of a picrate, m.p. 135° (corr.) (sensitiveness 1 in 1000), and by the formation of a picrolonate, m.p. 135° (corr.). The spectra of (**I**) in EtOH and of the base in hexane and EtOH resemble those of substances with a hetero-atom in the ring [furan, thiophen, pyrrole, yperite (**II**) and its derivatives]. It appears unlikely that (**I**) will replace (**II**) in warfare. H. W.

Complex sodium bismuth salts of triethanolamine and tri-*iso*propanolamine. W. T. Miller (*J. Amer. Chem. Soc.*, 1940, **62**, 2707—2709).—The prep. and properties of *Na bismuthyltriisopropanolamine*, *Na bismuthyltriethanolamine*, and *Bi triethanolamine* are given. These compounds represent new types of complex Bi salts. W. R. A.

Separation of amino-acids from acid hydrolysates of proteins.—See B., 1940, 843.

Resolution of synthetic alanine. E. Pascu and J. W. Mullen (*J. Biol. Chem.*, 1940, **136**, 335—342; cf. Fischer, A., 1899, i, 888).—Crystallisation of strychnine benzoyl-*dl*-alanine followed by removal of the alkaloid gives benzoyl-*l*(+)-alanine (73% yield); benzoyl-*d*(−)-alanine is obtained from the mother-liquors through the brucine salt. Hydrolysis (20% HCl) gives *l*(+)- and *d*(−)-alanine in 90% yields, without racemisation. Some racemisation occurs during benzoylation. A. Li.

Preparation of *dl*-asparagine and *dl*-aspartic acid. W. Cocker (*J.C.S.*, 1940, 1489—1491).—Reduction (Al–Hg) of CO_2Et·C(N·OH)·CH_2·CO_2Et yields Et_2 aspartate (*phenylcarbamido-*, m.p. 104°, and *Ac* derivative, b.p. 143—145°/4—5 mm.), which gives with H_2O at 140—150° under pressure, aspartic acid (*phenylhydantoin*, m.p. 225—225·5°; SO_2Ph derivative, m.p. 181—182°), and with aq. NH_3 at 100° under pressure, asparagine. A. Li.

Interaction of *n*-butyl alcohol and the chlorides and oxychlorides of phosphorus in absence and in presence of pyridine. W. Gerrard (*J.C.S.*, 1940, 1464—1469; cf. A., 1940, II, 127).—BuOH with PCl_3 at −10°, agitated by CO_2, yields PCl_2·OBu, *P di-n-butoxy chloride*, b.p. (impure) 90—110°/13 mm., and OH·$P(OBu)_2$, in proportions varying with the amounts of reagents and mode of addition. BuOH (3 mols.) with PCl_3 (1 mol.) and HCl gives BuCl, OH·$P(OBu)_2$, and (?) $(OH)_2$P·OBu. $P(OBu)_3$ with PCl_3 at room temp. gives PCl_2·OBu and $PCl(OBu)_2$. BuOH with $POCl_3$ at −5°, agitated by CO_2, yields n-*butoxyphosphoryl dichloride*, b.p. 90°/17 mm. $PO(OBu)_3$ with $POCl_3$ at 100° gives $POCl_2$·OBu or *di-n-butoxyphosphoryl chloride*, b.p. 132—133°/15 mm. (also obtained, with BuCl, from $P(OBu)_3$ and Cl_2 at −10°), according to proportions. $PO(OBu)_3$ with HCl gas at room temp. gives BuCl. PCl_3 and $POCl_3$ with BuOH and C_5H_5N in Et_2O at −10° give 90% yields of $P(OBu)_3$ and $PO(OBu)_3$ respectively. $POCl_2$·OBu with EtOH and C_5H_5N in Et_2O at −10° yields *Et$_2$ Bu phosphate*, b.p. 123°/15 mm. PCl_2·OBu with C_5H_5N or C_5H_5N,HCl at 100° yields $P(OBu)_3$, but no BuCl. $PCl(OBu)_2$ with C_5H_5N gives no BuCl. $POCl_2$·OBu with C_5H_5N at 0° or C_5H_5N,HCl at 100° yields BuCl and C_5H_5N–P compounds. $POCl(OBu)_2$ with C_5H_5N or C_5H_5N,HCl at 100° yields BuCl and a gum, C_5H_5N,$P_2O_4(OBu)_2$. With EtOH and C_5H_5N in Et_2O, $POCl(OBu)_2$ gives a mixture of $PO(OBu)_2$·OEt and $PO(OBu)(OEt)_2$, whilst $POCl_2$·OBu gives $PO(OBu)(OEt)_2$ and $PO(OEt)_3$. Thermal decomp. of PCl_2·OBu and $POCl_2$·OBu gives no BuCl. BuOH with PCl_3 and C_5H_5N in boiling Et_2O yields some BuCl and $PO(OBu)_3$. It is concluded that BuCl is produced by the action of HCl on Bu phosphorous or phosphoric esters (a reaction inhibited by C_5H_5N), not by decomp. of Bu chloro-phosphites or -phosphates. A. Li.

Silico-organic compounds. III. Preparation and reactions of silicon analogues of certain aliphatic orthoesters. H. W. Post and C. H. Hofrichter, jun. (*J. Org. Chem.*, 1940, **5**, 572—578; cf. A., 1938, II, 535).—The exchange of alkoxy-groups between the homologous alcohols and ethane- or propane-orthosiliconates takes place thus: $SiEt(OEt)_3 + ROH \rightleftharpoons SiEt(OEt)_2$·OR + EtOH. The co-ordination of alcoholic H results in the creation of a net positive charge on the Si atom of the mol. which can then exert an attractive force on the surrounding O atoms. The moving in of any particular O atom aids the elimination of the other alcohol and results in an exchange. The mechanism makes it possible for heavier compounds to form when the groups are larger. Thus, $2SiPr(OEt)_3 + BuOH \rightleftharpoons [(OEt)_2SiPr]_2O + Et_2O +$ BuOH. The formation of 1 : 3 compounds during alkoxy-

interchange between homologous alkyl orthosilicates has been established. Gradual addition of the product of the action of Mg–Cu and MeI in Et_2O to $Si(OEt)_4$ affords $SiMe(OEt)_3$, b.p. 150—151°/760 mm., *diethoxydimethylsilicane*, b.p. 110—111°/760 mm., and impure *Et methanesiliconate*, $Me{\cdot}SiO_2Et$, b.p. 73°/760 mm. $Si(OBu)_4$, b.p. 142—144°/3 mm., is prepared by dropwise addition of BuOH to $SiCl_4$. Dropwise addition of MgBuBr to $Si(OEt)_4$ affords *Et butaneorthosiliconate*, b.p. 190—193°/740 mm., in 27% yield whereas *tetrabutylsilicane*, b.p. 231°/760 mm., is derived by the addition of $Si(OEt)_4$ (0·825 mol.) to MgBuBr (4 mols.). *Et_3 Bu orthosilicate*, b.p. 82·5°/15 mm., and *Et_2 Bu_2 orthosilicate*, b.p. 100°/15 mm., are obtained in 22% and 30·4% yield by protracted boiling of a mixture of $Si(OEt)_4$ and $Si(OBu)_4$. An attempt to prepare Bu propaneorthosiliconate from $SiPr(OEt)_3$ and BuOH was unsuccessful. H. W.

II.—HOMOCYCLIC.

Introduction of an ethylenic linking into the trimethylene cycle. I. Attempted preparation of methylene*cyclo*propane by the action of zinc dust on γ-chloro-β-chloromethylpropene in alcoholic solution. II. Action of phosphorus pentachloride on acetyl*cyclo*propane. I. A. Djakonov (*J. Gen. Chem. Russ.*, 1940, **10**, 402—413, 414—426).—I. $OH{\cdot}CMe(CH_2Cl)_2$ does not eliminate H_2O when heated with I, *o*-$C_6H_4(CO)_2O$, $H_2C_2O_4$, Ac_2O, $KHSO_4$, $NaHSO_4$, or $MgSO_4$ (230—300°). With P_2O_5 at 110° the product is *αγ-dichloro-β-methylpropene* (**I**), b.p. 131—132°. An inseparable mixture of (**I**) with $CH_2{:}C(CH_2Cl)_2$ (**II**) is obtained by chlorination of $CH_2{:}CMe_2$, and this mixture when heated at 70—75° with Zn dust in 75% EtOH, in the hope of obtaining methylene*cyclo*propene from (**II**), gives only $CH_2{:}CMe_2$.

II. *cyclo*Propyl Me ketone and PCl_5 at ≯20° yield *βε-dichloro-Δ$^{\beta}$-pentene*, b.p. 40—41°/8 mm., but not the expected α-chloroethenyl*cyclo*propane. The trimethylene ring cannot exist in conjugation with a double linking, and partakes of the nature of an unsaturated group. R. T.

Chlorination of benzene.—See B., 1940, 844.

Synthesis and properties of mono-*n*-alkylbenzenes. II. Preparation and properties of the intermediate ketones and hydrocarbons. T. Y. Ju, G. Shen, and C. E. Wood (*J. Inst. Petroleum*, 1940, **26**, 514—531; cf. A., 1940, II, 369).—C_6H_6–RCOCl (R = $[CH_2]_x{\cdot}$Me) (Friedel–Crafts) in CS_2 afford COPhR (**I**), reduced (Clemmensen or better by H_2–Pd–C in EtOH) to CH_2PhR. Yields of (**I**) decrease as the val. of *x* increases from 4 to 13. Optimum conditions for reactions are discussed. Many physical consts. are recorded. Effects of increase in the val. of *x* on physical properties are discussed; the Ph group has the main influence even when *x* is large. Ph *n*-butyl, m.p. −9°, b.p. 116°/10 mm. (oxime, new m.p. 55°; 2 : 4-*dinitrophenylhydrazone*, m.p. 163·5°), *n*-amyl, b.p. 111·5°/4 mm. (*oxime*, m.p. 52·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 166°), *n*-hexyl, b.p. 141°/9 mm. (2 : 4-dinitrophenylhydrazone, new m.p. 135°), *n*-octyl, new m.p. 14°, b.p. 166°/9 mm. (semicarbazone, new m.p. 133·5°; *oxime*, m.p. 53·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 119·5°), *n*-undecyl, new m.p. 44—45°, b.p. 193—194°/9 mm. (*semicarbazone*, m.p. 98°; *oxime*, m.p. 64·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 101—102°), and *n*-tridecyl ketone, new m.p. 52—53°, b.p. 194—196°/4 mm. (semicarbazone, new m.p. 101°; *oxime*, m.p. 69·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 98—98·5°), afford *n*-amyl-, b.p. 204—205°/760 mm., *n*-hexyl-, b.p. 226—227°/760 mm., *n*-heptyl-, b.p. 240—241°/760 mm., *n*-nonyl-, b.p. 280—281°/760 mm., *n*-dodecyl-, new m.p. −3°, b.p. 172—173°/9 mm., and *n*-tetradecyl-benzene, m.p. 8·6°, b.p. 195—196°/9 mm., respectively. With the ketones, change in val. of d_4^{θ} and η is linear with respect to temp.; increase in *x* decreases the val. of *d* and *n*. In the case of the hydrocarbons, increase in *x* decreases density for temp. <50°; at 70°, they have a similar density. Increase in *x* causes a decrease in *n* and an increase in η. A. T. P.

Isomerisation of unsaturated hydrocarbons in presence of oxides of metals. IV. Isomerisation of *p*-diallylbenzene and 1-allylnaphthalene in presence of aluminium oxide. R. J. Levina, L. E. Karelova, and I. A. Eliaschberg (*J. Gen. Chem. Russ.*, 1940, **10**, 913—916).—*p*-$C_4H_6(CH_2{\cdot}CH{:}CH_2)_2$ yields a mixture of $CH_2{:}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH{:}CHMe$ and *p*-$C_6H_4(CH{:}CHMe)_2$ when passed over Al_2O_3 at 300°. 1-$C_{10}H_7{\cdot}CH_2{\cdot}CH{:}CH_2$ [*dibromide*, b.p. 212—213°/10 mm. (decomp.)], similarly yields 1-$C_{10}H_7{\cdot}CH{:}CHMe$. R. T.

Complex formation between polynitro-compounds and aromatic hydrocarbons and bases. IX. Influence of solvents on the temperature coefficients of colour densities. D. L. Hammick and (Miss) R. B. M. Yule (*J.C.S.*, 1940, 1539—1542).—The effect of temp. change in various solvents has been studied for the following colour-producing interactions: $C(NO_2)_4$ with $C_{10}H_8$ and 1- or 2-$C_{10}H_7Me$; $NHPh_2$ with *o*-$C_6H_4Cl{\cdot}NO_2$ and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$. In *n*-C_6H_{14}, CCl_4, $C_2H_4Cl_2$, and $C_2H_2Cl_4$, the colour-producing interactions are exothermic, colour density decreasing with rise in temp. In COPhMe, *cyclo*hexanone, $COMe_2$ Pr$^{\alpha}$OH, EtOH, and MeOH, the $C(NO_2)_4$ interactions are endothermic, colour increasing with rise of temp. No endothermic reactions have been observed in the polar chloronitrobenzene–$NHPr_2$ systems. The facts are discussed in the light of the work of Gibson and Loeffler (A., 1940, I, 344). F. R. S.

Production of styrene and related compounds. Simultaneous production of vinylaromatic compounds and arylacetylenes.—See B., 1940, 844.

Addition of bromine and chlorine to βγ-diphenylbutadiene. J. S. Salkind and P. Mosunov (*J. Gen. Chem. Russ.*, 1940, **10**, 517—520).—$(CH_2{:}CPh)_2$ and Br or Cl_2 in CCl_4 at 0° yield *αδ-dibromo-* or *αδ-dichloro-βγ-diphenylbutane*, m.p. 143—144°. R. T.

Orientation of chrysene. M. S. Newman and J. A. Cathcart (*J. Org. Chem.*, 1940, **5**, 618—622).—The sole product of the action of HNO_3 (*d* 1·42) and conc. H_2SO_4 on chrysene (**I**) suspended in glacial AcOH is 8-nitrochrysene (**II**), m.p. 214·0—214·6°, oxidised by CrO_3 or $Na_2Cr_2O_7$ in glacial AcOH to 8-nitrochrysenequinone, which could not be obtained pure and is characterised by condensation with *o*-$C_6H_4(NH_2)_2$ to *7-nitrochrysophenazine*, m.p. 277·6—279·6°. Under more drastic conditions of nitration (**I**) gives 2 : 8-*dinitrochrysene*, m.p. 380·5—382·5°. The structure of (**II**) is established by its reduction [red P and HI (*d* 1·5) in boiling AcOH] to 8-*aminochrysene* (**III**), m.p. 210·0—211·0°, converted by 10% H_2SO_4 at 220—225° into 8-chrysenol, m.p. 248—250° (acetate, m.p. 158·6—159·2°; Me ether, m.p. 127·2—127·8°). (**III**) dissolved in EtOAc and AcOH is transformed by short treatment with boiling Ac_2O containing fused NaOAc into 8-*acetamido-*, m.p. 299·5—301·0°, and by more protracted treatment with boiling Ac_2O into 8-*diacetylamino-*, m.p. 221·8—223·0° after softening at 218°, *-chrysene*. Dropwise addition of $ClSO_3H$ to a well-stirred suspension of I in *s*-$C_2H_2Cl_4$ affords *chrysene-8-sulphonic acid*, m.p. 193—194° when heated at the rate of 4° per min. [*Na* and p-$C_6H_4Me{\cdot}NH_2$ salt, m.p. 273—274·5° (decomp.) when heated at rate of 5° per min.], oriented by fusion with KOH at 220° and acetylation of the product to 8-chrysenyl acetate, m.p. 158·0—158·6°. H. W.

Catalytic reduction of *p*-chloronitrobenzene. A. Balandin and A. Titova (*Utschen. Zapiski*, 1934, **2**, 229—231).—In the hydrogenation of *p*-$C_6H_4Cl{\cdot}NO_2$ using Ni at 238°, *p*-$C_6H_4Cl{\cdot}NH_2$ was first formed, and no $PhNO_2$. Ch. Abs. (*e*)

Catalytic action of Japanese acid clays on mixtures of aniline and methyl alcohol vapours. K. Kobayashi and M. Mizushina (*Mem. Fac. Sci. Eng. Waseda Univ.*, 1937, No. 12, 50—51; *Chem. Zentr.*, 1938, ii, 3527).—The yields of *p*-$C_6H_4Me{\cdot}NH_2$ and NHPhMe (max. 85% at 400° and 28·2% at 250°, respectively) obtained by passing the vapours over the clay at 220—400° have been determined. The catalytic action of the clay is attributed to strong adsorption of the NH_2-group, which facilitates reaction between the *p*-H and the OH. A. J. E. W.

Hydration of substituted amides of stearic acid. B. A. Toms (*Nature*, 1940, **146**, 560; cf. A., 1940, I, 410; II, 125).—Percentages of bound H_2O in stearanilide and 15 derivatives are tabulated. Substitution in the nucleus has little effect on H_2O-binding capacity, but an *o-* or *p*-CO_2H reduces the amount of H_2O bound. Replacement of the H of the NHAr prevents hydration. An explanation of these effects is advanced. L. S. T.

Alleged reduction of the phenylurethane of trichlorolactic ester and nitrile by dilute aqueous alkali. H. Irving and H. Marston (*J.C.S.*, 1940, 1512—1513).—The compounds formed from $NHPh{\cdot}CO_2{\cdot}CHR{\cdot}CCl_3$ (**I**) (R = CN or CO_2Et) and 10% aq. NaOH, formulated as $NHPh{\cdot}CO{\cdot}O{\cdot}CHR{\cdot}CHCl_2$ by

Lambling (cf. A., 1899, i, 52), are now shown to be *ββ-dichloro-α-cyano-* or *-α-carbethoxy-vinyl phenylcarbamates*, $NHPh{\cdot}CO_2{\cdot}CR{:}CCl_2$ (**II**). (**I**) (R = CN) undergoes quant. elimination of HCl with cold Et_2O–NEt_3 to give (**II**) (R = CN). (**I**) (R = CN) and boiling aq. Na_2CO_3 yield $CHCl_2{\cdot}CO{\cdot}NHPh$ (mechanism of formation given) and $CCl_2{:}C<^{O-CO}_{CO\cdot NPh}$ [not $CHCl_2{\cdot}CH<^{O-CO}_{CO\cdot NPh}$ as formulated by Lambling], formed by independent reactions. A. T. P.

Preparation of derivatives of sulphanilamide. W. Cocker (*J.C.S.*, 1940, 1574—1576).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and $CN{\cdot}CH_2{\cdot}NH_2,H_2SO_4$ with aq. NaOH afford N^4-*acetylsulphanilamido-acetonitrile* (**I**), m.p. 194—195°, and thence (H_2SO_4 at 45—85°) the *-acetamide*, m.p. 224—225°. Hydrolysis of (**I**) with conc. HCl at 100° (bath), evaporation to dryness, and extraction with EtOH gives the *hydrochloride*, m.p. 175°, of *Et sulphanilamidoacetate*, m.p. 92° (*Ac* derivative, m.p. 128°), similarly converted (conc. HCl; evaporation; MeOH) into the *Me* ester, m.p. 88·5—89°. (**I**) and MeOH–NaOMe–MeI or EtOH–NaOEt–EtI give N^4-*acetyl*-N^1-*methyl*- (**II**), m.p. 158—159°, or -N^1-*ethyl-sulphanilamido-acetonitrile* (**III**), m.p. 128—128·5°, and thence (H_2SO_4) the corresponding *-acetamides*, m.p. 185—186°, or 167—168°, respectively. (**II**) or (**III**) affords *Et* N^1-*methyl*-, m.p. 115° (corresponding *Me* ester, m.p. 105—106°), or *Et* N^1-*ethyl-sulphanilamidoacetate*, m.p. 88—89° (*Me* ester, m.p. 85), respectively. The substances have little therapeutic val. A. T. P.

Phosphoric acid derivatives of sulphanilamides.—See B., 1941, III, 21.

Naphthalene series. IX. Rearrangement of 1-naphthylamine-4-sulphonates to 1-naphthylamine-2-sulphonates. N. N. Voroshcov, V. V. Kozlov, B. V. Aristov, A. I. Barischev, and M. F. Fedulov (*J. Gen. Chem. Russ.*, 1940, **10**, 894—906).—Conversion of 1 : 4- (**I**) into 1 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3M$ (**II**) (M = Na, K, NH_4, 0·5Mg, 0·5Ba) involves the intermediate formation of 1-$C_{10}H_7{\cdot}NH{\cdot}SO_3M$ (**III**), isolated in small amount from the reaction product. The velocity of the reaction (**III**) → (**II**) is considerably > that of (**I**) → (**III**). R. T.

Reduction of aromatic nitro-compounds by hydrogen and Raney nickel at atmospheric temperature and pressure. A. Albert and B. Ritchie (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 74—81).—H_2 and Raney Ni in EtOH during ¼—4 hr. reduce *m*-$C_6H_4(NO_2)_2$ to *m*-$C_6H_4(NH_2)_2$ (88% yield), 1 : 2 : 6-$C_6H_3Me(NO_2)_2$ to 1 : 2 : 6-$C_6H_3Me(NH_2)_2$ (90), 1 : 2 : 4-$C_6H_3Me(NO_2)_2$, 4 : 1 : 2-$NO_2{\cdot}C_6H_3Me{\cdot}NH_2$, and 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}CHO$ to 1 : 2 : 4-$C_6H_3Me(NH_2)_2$ (96, 93, and 75, respectively), 3 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}CO_2H$ to 3 : 5 : 1-$(NH_2)_2C_6H_3{\cdot}CO_2H$ (91), *o*- and *m*-$NO_2{\cdot}C_6H_4{\cdot}OH$ to *o*- and *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$ (98 and 81, respectively), *m*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CHO$ to *m*-$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CHO$ (93), (*m*-$NO_2{\cdot}C_6H_4)_2N{\cdot}CHO$ to (*m*-$NH_2{\cdot}C_6H_4)_2N{\cdot}CHO$ (92), 5 : 5′-dinitro- to 5 : 5′-diamino-diphenylamine-2-carboxylic acid (77), m.p. 71° (decomp.), and 5-nitro- to 5-*amino-diphenylamine*-2-*carboxylic acid* (90), m.p. 140°. The amounts of H_2 absorbed show that the method might be suitable for determining NO_2-groups in a substance known not to contain other easily reducible systems. Reduction follows the normal course since a good yield of benzaldoxime *N*-Ph ether is obtained by partial reduction of $PhNO_2$ in presence of PhCHO. Preliminary results with compounds of the acridine series are summarised. A. Lt.

Manufacture of benzidine.—See B., 1941, II, 5.

Reductive ammonolysis of anthraquinone. N. N. Voroshcov and V. P. Schkitin (*J. Gen. Chem. Russ.*, 1940, **10**, 883—893).—Anthraquinone does not react with aq. NH_3 in presence or absence of $CuSO_4$ or $KClO_3$ at 200—220°. In presence of $(NH_4)_2SO_3$ and $Na_2S_2O_4$ the chief product is 9 : 10-*diaminoanthracene* (**I**), m.p. 142° (decomp.) [NN′-*Ac*$_2$, NN′-*Bz*$_2$, NN′-*dichlorocarbonyl*, m.p. 280° (decomp.), and NN′-*dibenzylidene*-derivative, m.p. 255°]. Air passed through a C_6H_6 solution of (**I**) (45 min. at 60°) yields 9 : 9′-*diamino*-10 : 10′-*dianthrylamine*, m.p. 141—142°, and 9 : 10-*dihydroxylaminoanthracene*, m.p. 155—156°. R. T.

New chemical reaction with the nitroxyl radical NOH. O. Baudisch (*Science*, 1940, **92**, 336—337; cf. A., 1940, II, 41). Freshly-prepared CuOH (0·5 g.) suspended in H_2O (200 c.c.) containing KNO_2 (0·5 g.), stirred with C_6H_6, dil. HCl (to p_H 2·5), and Merck's "superoxol" (**I**) (1 c.c.) yields Cu" *o*-nitrosophenoxide (**II**). $Cu(NO_3)_2$ (1 g.) and KNO_2 (0·5 g.) in H_2O (200 c.c.), C_6H_6, (**I**) (1 c.c.), and *iso*ascorbic acid (or vitamin-*C*) (0·5 g.) also yield (**II**). Freshly-prepared CuOH (0·5 g.) suspended in H_2O (200 c.c.) containing benzenesulphohydroxamic acid (**III**) (0·5 g.), stirred (1 hr.) with C_6H_6, dil. HCl (to p_H 2·9), and (**I**) (1 c.c.) gives (after acidification) *o*-$NO{\cdot}C_6H_4{\cdot}OH$ and the H_2O-sol. Cu *o*-nitrosophenolsulphinate. CuOH (0·5 g.) in H_2O (200 c.c.) containing (**III**) (0·5 g.), HCl (to p_H 2·9), (**I**) (1 c.c.) on acidification (HCl) and extraction with Et_2O gives *o*-nitrosophenolsulphinic acid, which gives characteristically coloured Cu^{II}, Fe^{II}, Co, Ni, and Hg salts. These reactions are discussed. L. S. T.

2 : 4-Dinitro-6-*cyclo*hexylphenol.—See B., 1941, II, 6.

Condensation of $SiCl_4$ with dihydric phenols. J. N. Volnov and B. N. Dolgov (*J. Gen. Chem. Russ.*, 1940, **10**, 550—556).—*o*-$C_6H_4(OH)_2$ and $SiCl_4$ in light petroleum–Et_2O yield the *substance*, *o*-$C_6H_4<^{O}_{O}>SiCl_2$, in a polymerised form, probably of the type [*o*-$C_6H_4(O{\cdot})SiCl_2{\cdot}]_n$. This with EtOH gives *o*-$C_6H_4(OH)_2$, $Si(OEt)_4$, and HCl. *m*- and *p*-$C_6H_4(OH)_2$ similarly afford the *substances*, *m*-, b.p. 261°, and *p*-$C_6H_4(O{\cdot}SiCl_3)_2$, b.p. 267°, which with MeOH yield the respective *esters*, *m*- and *p*-$C_6H_4[O{\cdot}Si(OMe)_3]_2$. R. T.

Conversion of eugenol and its ethers into the corresponding propenyl compounds. T. F. West (*J.C.S.I.*, 1940, **59**, 275—276).—K eugenoxide (**I**) dissolved in a mixture of diethylene glycol and $N(CH_2{\cdot}CH_2{\cdot}OH)_3$ (**II**) is isomerised endothermally at ~160° to K *iso*eugenoxide. Eugenol Et ether heated at 190° with KOH in diethylene glycol Et_1 ether and (**II**) is converted into a mixture of *trans-* (70%) and *cis-iso*eugenol Et ether. With the appropriate RBr in hot H_2O, (**I**) gives eugenol Pr^α, b.p. 122—124°/2 mm., Pr^β, b.p. 114—115°/1 mm., and n-*amyl*, b.p. 150—153°/1 mm., *ether*. T. F. W.

Substituted indenes. I. V. M. Trikojus and D. E. White (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 82—87).—5(or 6)-Methoxyindene (Ingold *et al.*, *J.C.S.*, 1923, **123**, 1469) with Br in CS_2 yields (cf. *loc. cit.*) a *dibromide*, m.p. 65—66°, decomp. >120° (blue liquid), a light petroleum solution of which with H_2O at 0° yields the *bromohydrin*, $C_{10}H_{11}O_2Br$, m.p. 117°. 4 : 5-*Dimethoxy*-1-*hydrindoneoxime*, m.p. 168°, is reduced (Na–Hg in hot 66% AcOH) to 4 : 5-dimethoxy-1-hydrindamine (*Ac* derivative, m.p. 176°), the *hydrochloride*, decomp. 209—210°, of which at 215—225°/22 mm. gives 4 : 5(or 6 : 7)-*dimethoxyindene*, m.p. 32°. The following were prepared by similar methods: 5 : 6-*dimethoxy*-1-*hydrindoneoxime*, m.p. 196°, *-hydrindamine hydrochloride*, decomp. 249—250°, and (by heating at 270°/atm. pressure) *-indene*, m.p. 71°; 5 : 6-*methylenedioxy*-1-*hydrindamine hydrochloride*, decomp. 254—255°, and *-indene*, m.p. 87—88°; 5-*methoxy*-6-*ethoxy*-1-*hydrindone*, m.p. 138—139° (from 3 : 4 : 1-$OMe{\cdot}C_6H_3(OEt){\cdot}[CH_2]_2{\cdot}CO_2H$ and P_2O_5 in boiling C_6H_6) (*oxime*, m.p. 188—189°), and *-hydrindamine hydrochloride*, m.p. 268—270° (decomp.), and 5(or 6)-*methoxy*-6(or 5)-*ethoxyindene*, m.p. 65—66°. A. Lt.

Nitro-derivatives of diphenyl ether-4-sulphonic acid. N. N. Voroschcov, jun. (*J. Gen. Chem. Russ.*, 1940, **10**, 935—941).—4-Sulphodiphenyl ether when nitrated yields 2 : 4′-*dinitro*- (**I**) (*Na* salt, +3H_2O; *Ba* salt; *chloride*, m.p. 134—136·5°) and 2 : 2′ : 4′-*trinitro*-4-*sulphodiphenyl ether* (**II**) (*Na* salt, +H_2O; *chloride*, m.p. 157—159°; *amide*, m.p. 188—190°), further nitration of which gives 2 : 4 : 2′ : 4′-tetranitrodiphenyl ether (**III**). (**I**) and boiling aq. NaOH afford 2 : 1 : 4-$NO_2{\cdot}C_6H_3(OH){\cdot}SO_3H$ (**IV**) and *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$ (**V**); (**II**) similarly yields (**IV**) and 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OH$ (**VI**). Aq. NH_3 and (**I**) at 100° afford (**V**) and 2 : 1 : 4-$NO_2{\cdot}C_6H_3(NH_2){\cdot}SO_3H$ (**VII**); (**II**) gives 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH_2$ (**VIII**) and (**IV**). The chloride of (**I**) with aq. NH_3 gives (**V**) and the amide of (**VII**); that of (**II**) gives (**VIII**) and the amide of (**IV**). (**III**) and aq. NH_3 or NH_2Ph afford (**VI**) and (**VIII**) or 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NHPh$, respectively. R. T.

Synthesis of local anæsthetics. IV. K. N. Gaind, J. N. Ray, and J. N. Yajnik (*J. Indian Chem. Soc.*, 1940, **17**, 400—404).—*o*-$OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$ and piperidine in boiling C_6H_6 give *piperidinoacet-o-phenetidide*, m.p. 98° (*hydrochloride*, m.p. 158°). Diethylaminoacet-, an oil (*hydrochloride*, m.p. 118°), *β-chloropropion-*, m.p. 77°, and *β*-piperidinopropion-, an oil (*hydrochloride*, m.p. 102°), *-o*-phenetidide are obtained analogously. The following are described. *Hydrochlorides* of *β-diethylaminopropion-o-phenetidide*, m.p.

126°, *piperidinoacet*-m-*phenetidide* (I), m.p. 159°, and *diethylaminoacet*-m-*phenetidide*, m.p. 180°. *β-Chloropropion*-m-*phenetidide*, m.p. 80—81°, and *β-piperidinopropion*-m-*phenetidide hydrochloride*, m.p. 244° (the β-diethylamino-derivative hydrochloride is an undistillable liquid); *piperidinoacet*-p-*phenetidide*, (II), m.p. 67°; *diethylaminoacet*-p-*phenetidide hydrochloride*, m.p. 154°; *β-chloropropion*-p-*phenetidide*, m.p. 123°; *β-piperidinopropion*-p-*phenetidide*, m.p. 96° (*hydrochloride*, m.p. 199°). *Hydrochlorides* of *β-diethylaminopropion*-p-*phenetidide*, m.p. 119°, *piperidinoacet*-o-*anisidide*, m.p. 104°, *diethylaminoacet*-o-*anisidide*, m.p. 171°, *β-piperidinopropion*-o-*anisidide*, m.p. 184°, *piperidinoacet*-m-*anisidide*, m.p. 154°, *diethylaminoacet*-m-*anisidide*, m.p. 144°, *β-piperidinopropion*-m-*anisidide*, m.p. 194°, *β-diethylaminopropion*-m-*anisidide*, m.p. 128°, *piperidinoacet*-p-*anisidide*, m.p. 160°, and *diethylaminoacet*-p-*anisidide*, m.p. 190°. *β-Diethylaminopropion*-o-*anisidide picrate*, m.p. 173°, *β-chloropropion*-m-*anisidide*, m.p. 92°, *β-chloropropion*-p-*anisidide*, m.p. 124°, *β-piperidinopropion*-p-*anisidide*, m.p. 104°, and *β-diethylaminopropion*-p-*anisidide picrate*, m.p. 123°. Substances in the *m*-series have pronounced local anæsthetic action reaching its max. in (I). In the *p*-phenetidine series appreciable activity is displayed by (II). In both compounds the side-chain has the piperidinoacetyl residue. H. W.

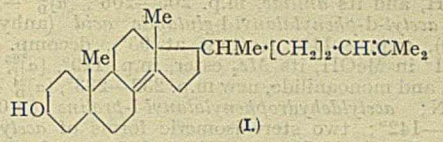
Reactions of 2 : 6-dichloro- and 2 : 4 : 6-trihalogeno-nitrobenzenes with a mercaptide reagent. J. D. Loudon (*J.C.S.*, 1940, 1525—1528).—Equimol. amounts of 2 : 6 : 1-$C_6H_3Cl_2{\cdot}NO_2$ (I) and *p*-$C_6H_4Me{\cdot}SH$ (II) in aq.-NaOH–EtOH at room temp. (3 weeks) afford unchanged (I), (*p*-$C_6H_4Me{\cdot}S)_2$, 2-*chloro*-6-p-*tolylthiol*-, m.p. 82—83° (H_2O_2–AcOH at 100° give the *sulphone*, m.p. 151°), and 2 : 6-*di*-p-*tolylthiol-nitrobenzene*, m.p. 168—169° (best prepared in EtOH) (*disulphone*, m.p. 196°). 2 : 4 : 6 : 1-$C_6H_2Cl_3{\cdot}NO_2$ (III) (1 mol.) [from *s*-$C_6H_3Cl_3$ and HNO_3 (*d* 1·5 + *d* 1·42) at 100°] and (II) (3 mols.) in NaOH–EtOH, heated for 10 min., afford 2 : 4 : 6-*tri*-p-*tolylthiol*- (IV), m.p. 142° [similarly obtained from (VI) (below)] [the *trisulphone*, m.p. 230°, and piperidine give 1-*piperidino*-2 : 4 : 6-*tri*-p-*toluenesulphonylbenzene*, m.p. 188°], and 4-*chloro*-2 : 6-*di*-p-*tolylthiol-nitrobenzene* (V), m.p. 206—207° (softens at 200°) (*disulphone*, m.p. 211°); (V) is best prepared from (III) (1 mol.) and (II) (2 mols.) in cold aq. EtOH–NaOH–dioxan, and with excess of piperidine yields 4-*piperidino*-2 : 6-*di*-p-*tolylthiolnitrobenzene*, m.p. 205°. Equimol. quantities of (III) and (II) in EtOH–NaOH afford (V) and 2 : 4-*dichloro*-6-p-*tolylthiolnitrobenzene*, m.p. 97° (*sulphone*, m.p. 171°). Similarly prepared from 2 : 4 : 6 : 1-$C_6H_2Br_3{\cdot}NO_2$ (VI) are 4-*bromo*-2 : 6-*di*-, m.p. 210°, and 2 : 4-*dibromo*-6-p-*tolylthiolnitrobenzene*, m.p. 132°, and 4-*bromo*-2 : 6-*di*-, m.p. 223°, and 2 : 4-*dibromo*-6-p-*toluenesulphonylnitrobenzene*, m.p. 182°. 4 : 3 : 5 : 1-$NO_2{\cdot}C_6H_2Cl_2{\cdot}NHAc$ and (II)–NaOH–EtOH (refluxed) yield 4-*nitro*-3 : 5-*di*-p-*tolylthiol-acetanilide*, m.p. 261°; the corresponding *-aniline*, m.p. 270° affords (V) by the diazo-reaction. Equimol. amounts of 2 : 3 : 5 : 1-$NO_2{\cdot}C_6H_2Cl_2{\cdot}NHAc$ and (II) in NaOH–EtOH at room temp. afford 5-*chloro*-2-*nitro*-3-p-*tolylthiol-acetanilide*, m.p. 166—167°, and thence the *-aniline*, m.p. 110—111°; in hot aq. EtOH 2 mols. of (II) give 2-*nitro*-3 : 5-*di*-p-*tolylthiol-acetanilide*, m.p. 188°, and thence the corresponding *-aniline*, m.p. 117°, which affords 2-*chloro*-4 : 6-*di*-p-*tolylthiolnitrobenzene*, m.p. 104° [*disulphone*, m.p. 174°; 2-*piperidino*-4 : 6-*di*-p-*tolylthiolnitrobenzene*, m.p. 135°; with (II) yields (IV)]. (I) or (VI), refluxed with excess of piperidine, gives 2-*chloro*-, m.p. 63°, or 2 : 4-*dibromo*-6-*piperidinonitrobenzene*, m.p. 167°, respectively. The corresponding derivative from (III) could not be crystallised. Theoretical considerations are discussed. (II) in piperidine–dioxan give a stable *piperidine* salt.

A. T. P.

Significance of oxidation of adrenaline to benzoquinone.—See A., 1940, III, 895.

Activation of cholesterol.—See B., 1941, III, 21.

Sterol group. XLII. Constitution of zymosterol. B. Heath-Brown, I. M. Heilbron, and E. R. H. Jones (*J.C.S.*, 1940, 1482—1489).—Zymosterol dibromide, m.p. 157°, $[\alpha]_D^{20}$ +7·4° (A., 1929, 1443), is converted by Zn dust–95% AcOH at room temp. or Zn dust (activated with NH_4Cl) in boiling EtOH into zymosterol (I), m.p. 107—109°, $[\alpha]_D^{20}$ +50° (acetate, m.p. 107—108°, $[\alpha]_D^{20}$ +35°), also obtained by fractional crystallisation of the benzoate and hydrolysis with 3% KOH–EtOH (method: Wieland *et al.*, A., 1929, 1200). (I) is a $\Delta^{8:14\text{-}24:25}$-cholestadienol and is the first example of a natural sterol devoid of the 5 : 6-ethenoid linking. With BzO_2H–$CHCl_3$ at 0° (I) absorbs 2·1 O per mol. in 24 hr.; no evidence



(I.)

of the formation of an αβ-unsaturated ketone is obtained on oxidation by the Oppenauer method (A., 1937, II, 250). Reduction (H_2, PtO_2, AcOH–Et_2O) at atm. pressure of (I) affords α-zymostenol (II), m.p. 119—120°, $[\alpha]_D^{20}$ +20·8° [acetate, m.p. 77—78°, $[\alpha]_D^{20}$ +7·6°; *benzoate* (III), m.p. 109—111°, $[\alpha]_D^{20}$ +6·4°], which absorbs 1·9 O per mol. in 24 hr., and is almost certainly identical with α-cholestenol; it is isomerised by dry HCl–$CHCl_3$ at 20° to an α- + β-zymostenol complex, m.p. 98—99°, $[\alpha]_D^{20}$ +26·9° (absorbs 1·1 O per mol. in 24 hr.) (acetate, m.p. 70—71°, $[\alpha]_D^{20}$ +11·0°). (III) and HCl–$CHCl_3$ at 0° give *β-zymostenyl benzoate*, m.p. 165—166°, $[\alpha]_D^{20}$ +31·9°, and thence (3% KOH–EtOH) *β-zymostenol* (IV), m.p. 128°, $[\alpha]_D^{20}$ +30·5° (*acetate*, m.p. 76—77°), probably identical with β-cholestenol (cf. acetate, m.p. 91—92°). Reduction (H_2, PtO_2, AcOH) of (IV) affords crude (V), which when treated with Ac_2O–CCl_4–H_2SO_4 followed by 3% KOH–EtOH gives pure zymostanol (V), m.p. 140—141°, $[\alpha]_D^{20}$ +24·8°, identical with cholestanol. Zymostanyl acetate, new m.p. 114—116°, $[\alpha]_D^{20}$ +10·9° (also obtained from β-zymostenyl acetate containing some α-isomeride by hydrogenation and treating the product with Ac_2O–H_2SO_4), *benzoate*, m.p. 131—133°, $[\alpha]_D^{20}$ +17·8°, and *phenylurethane*, m.p. 155—156°, $[\alpha]_D^{20}$ +11·3°, are identical with cholestanyl acetate, benzoate, and *phenylurethane*, m.p. 151° (mixed m.p. 151—153°), respectively. (V) and CrO_3–AcOH at 20° give *zymostanone* (VI), m.p. 125—126°, $[\alpha]_D^{20}$ +40°, identical with cholestanone, which with Br–AcOH + a little HBr–AcOH yields *bromozymostanone*, m.p. 166—167°, identical with 2-bromocholestanone, m.p. 167—168°. (V) and CrO_3–90% AcOH at 60° give *zymostane*-C_3||C_3-*dicarboxylic acid*, m.p. 196—197°, $[\alpha]_D^{20}$ +33·4° (*Me*$_2$ ester, m.p. 50°, $[\alpha]_D^{20}$ +23·7°), identical with the acid, m.p. 195—196° (Me$_2$ ester, m.p. 58—60°), prepared similarly from cholestanol. (VI) and Zn–Hg in AcOH–HCl afford *zymostane*, m.p. 74—76°, $[\alpha]_D^{20}$ +20·9°, identical with cholestane, m.p. 79—80°. Ozonolysis of (I) in AcOH gives a little CH_2O and 52% of $COMe_2$; (II) similarly affords no $COMe_2$. (II) and SeO_2 in aq. EtOH afford *dehydro-α-zymostenol*, m.p. 98—99°, $[\alpha]_D^{20}$ −9·1°, which gives no colour with $SbCl_3$–$CHCl_3$ [dehydro-α-ergostenol (VII) gives a faint pink colour]. It exhibits light absorption (max. at 2475 A.) similar to that of (VII). All [α] are in $CHCl_3$.

A. T. P.

Action of phosphorus halides and thionyl chloride on benzilic acid. S. A. Setlur and V. V. Nadkarny (*Proc. Indian Acad. Sci.*, 1940, **12**, **A**, 266—269).—PCl_5 appears first to attack the alcoholic OH of $OH{\cdot}CPh_2{\cdot}CO_2H$ (I) since in mol. proportions in C_6H_6 the reactants afford $POCl_3$ and $CPh_2Cl{\cdot}CO_2H$ (II), m.p. 120° (decomp.). With 5 mols. of PCl_5 followed by $(NH_4)_2CO_3$ (I) affords $OH{\cdot}CPh_2{\cdot}CO{\cdot}NH_2$, m.p. 153°, with intermediate formation of $CPh_2Cl{\cdot}COCl$. PCl_3 and (I) afford (II) (also obtained with $SOCl_2$ at room temp.).

H. W.

Oxygen inhibition in photobromination of cinnamic acid.—See A., 1941, I, 54.

Resolution of *dl*-phenylalanine by asymmetric enzymic synthesis. O. K. Behrens, D. G. Doherty, and M. Bergmann (*J. Biol. Chem.*, 1940, **136**, 61—68).—In presence of cysteine–papain, *acetyl*-d-*phenylalanylglycine*, m.p. 159—161°, $[\alpha]_D^{26}$ −1·90° in MeOH, with NH_2Ph forms the *anilide*, m.p. 208—209°, $[\alpha]_D^{25}$ −21·0°; reaction is very much slower than with the *l*-form (cf. A., 1938, II, 364). Details are given for the prep. of *d*- and *l*-phenylalanine starting from acetyl-*dl*-phenylalanylglycine and NH_2Ph, with subsequent hydrolysis (aq. HCl) of the anilides. The following (prep. by standard methods) are described: *carbobenzyloxy*-l-*phenylalanylglycine*, m.p. 151—152°, $[\alpha]_D^{26}$ −9·6° in AcOH, and its *anilide*, m.p. 180°, $[\alpha]_D^{26}$ +9·3° in AcOH; *carbobenzyloxy*-d-*phenylalanylglycine*, m.p. 150—151°, $[\alpha]_D^{25}$ +9·7° in AcOH, its *Et* ester, m.p. 109—111°, and *anilide*, m.p. 179°, $[\alpha]_D^{27}$ −9·4° in AcOH; *acetyldehydrophenylalanyl*-l-*leucine*, m.p. 218—219° (decomp.), and its *anilide*, m.p. 205—206, $[\alpha]_D^{25}$ −5·6° in AcOH; *acetyl*-l-*phenylalanyl*-l-*leucine*, m.p. 191—193°, $[\alpha]_D^{29}$ −5·4° in abs.

EtOH, and its *anilide*, m.p. 234—235°, $[\alpha]_D^{25}$ −41·7° in AcOH; *acetyl*-d-*phenylalanyl*-l-*leucine*, m.p. 183—184°, $[\alpha]_D^{29}$ −8·3° in abs. EtOH, and its *anilide*, m.p. 205—206°, $[\alpha]_D^{25}$ −24·8° in AcOH; *acetyl*-d-*phenylalanyl*-l-*glutamic acid* (anhyd. and +0·5H_2O), m.p. ~115° (softens at 95°), decomp. >240°, $[\alpha]_D^{25}$ −9·1° in MeOH, its *Me*$_2$ ester, m.p. 129°, $[\alpha]_D^{25}$ −20·7° in MeOH, and monoanilide, new m.p. 232—233°, $[\alpha]_D^{24}$ −118·1° in C_5H_5N; *acetyldehydrophenylalanyl*-l-*proline* (+0·5H_2O), m.p. 140—142°; two stereoisomeric forms of *acetylphenylalanyl*-l-*proline* (+H_2O), m.p. 174—175°, or (+0·5EtOH) m.p. 142°, and 186—187°, $[\alpha]_D^{25}$ −35·3° and −72·7° in MeOH, respectively. The *l*-phenylalanyl compounds form the anilides more rapidly than the *d*, except the proline derivatives which do not form anilides under the conditions described.

E. M. W.

***dl*-Deuterophenylalanine (benzoyl derivative, m.p. 185—186·5°) and deuterophenylacetic acid, m.p. 76·5—77°.**—See A., 1940, III, 917.

Thermal decomposition of benzoyl peroxide.—See A., 1941, I, 54.

Acetylsalicyl azide, m.p. 56—58° (decomp.), and benzylurethane, m.p. 74—76°. Salicylglycine Et ester, m.p. 98—99°. Acetylsalicylglycine, m.p. 147—149°.—See A., 1941, III, 56.

Reactivity of ·CHCl·CCl$_3$ group attached to an aromatic nucleus. H. V. Dharwarkar and R. L. Alimchandani (*J. Indian Chem. Soc.*, 1940, **17**, 416—421).—CCl_3·CH(OH)$_2$ and *o*-OH·C_6H_4·CO_2H in conc. H_2SO_4 containing NaCl in a closed flask yield 2-*hydroxy*-5-*αβββ-tetrachloroethylbenzoic acid* (**I**), m.p. 182—183° (*Ac* derivative, m.p. 146—147°; *anilide*, m.p. 201—202°; p-*toluidide*, m.p. 178—179°), also obtained by saturating a solution of 5 : 2 : 1-CCl_3·CH(OH)·C_6H_3(OH)·CO_2H in conc. H_2SO_4 with dry HCl. (**I**) and aq. NH_3 in 96% EtOH at room temp. afford 2-*hydroxy*-5-*βββ-trichloro*-α-*aminoethylbenzoic acid*, m.p. 212° after charring at 183—184°; the -α-*anilino-acid* has m.p. 182° (decomp.). Gradual addition of Zn dust to a hot solution of (**I**) in AcOH yields 2-*hydroxy*-5-*ββ-dichlorovinylbenzoic acid*, m.p. 170—171°, which does not absorb Br in AcOH or $CHCl_3$, decolorises $KMnO_4$, and gives a blue colour with $FeCl_3$; it is also obtained by use of KI in boiling $COMe_2$. KCN and (**I**) in boiling aq. EtOH give 2-*hydroxy*-5-*ββ-dichloro*-α-*cyanovinylbenzoic acid*, m.p. 224—225° (*Ac* derivative, m.p. 175—176°; *dibromide*, m.p. 210°), hydrolysed by KOH–EtOH to 4-*hydroxy*-3-*carboxyphenylacetic acid*, m.p. 207°, and oxidised (H_2O_2–5% NaOH) to 4 : 1 : 3-OH·C_6H_3(CO_2H)$_2$, m.p. 303°. 2-Methoxy-5-*αβββ*-tetrachloroethylbenzoic acid, m.p. 138° (*Me* ester, m.p. 105°), is converted by boiling 15% KOH–EtOH into 2-*methoxy*-5-*αββ-trichlorovinylbenzoic acid*, m.p. 151—152° [*Ca* salt (+5·5H_2O); *Me* ester, m.p. 85°], which does not absorb Br in AcOH, $CHCl_3$, or CCl_4 or decolorise cold $KMnO_4$. *p*-OH·C_6H_4·CO_2H and CCl_3·CH(OH)$_2$ afford 4-*hydroxy*-3-*αβββ-tetrachloroethylbenzoic acid*, m.p. 142° (decomp.) (*Ac* derivative, m.p. 189—190°), converted by KI in boiling 96% EtOH into 4-*hydroxy*-3-*ββ-dichlorovinylbenzoic acid*, m.p. 171°. 4-Methoxy-3-*αβββ*-tetrachloroethylbenzoic acid, m.p. 248—249° (*Me* ester, m.p. 110—111°), is converted by boiling 20% KOH–EtOH into 4-*methoxy*-3-*αββ-trichlorovinylbenzoic acid*, m.p. 212—213°. The inactivity of α-Cl of the OMe-derivatives is ascribed to OMe which causes a large diminution in the ionising tendency of α-Cl by a supply of electrons and as a result the halogen atom becomes resistant towards anionic attack by NH_3, NH_2Ph, KI, and KCN.

H. W.

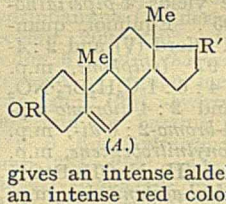
Mobility of groups in benzonitriles. C. W. N. Holmes and J. D. Loudon (*J.C.S.*, 1940, 1521—1525).—Careful addition of 10% aq. NaOH to 1 : 4 : 2-CN·C_6H_3Cl·NO_2 (**I**) and *p*-C_6H_4Me·SH (**II**) in EtOH at 70° affords 4-*chloro*-2-p-*tolylthiolbenzonitrile* (**III**), m.p. 117°; only a little Cl in (**I**) is replaced. (**III**) and H_2O_2–AcOH at 100° give 4-*chloro*-2-p-*toluenesulphonyl-benzonitrile* (**IV**), m.p. 187° [70% H_2SO_4 gives the corresponding -*benzoic acid* (**V**), m.p. 155°], and 4-*chloro*-2-p-*toluenesulphonylbenzamide*, m.p. 196° [30% H_2SO_4–aq. $NaNO_2$ or P_2O_5 at 200° yield (**V**) or (**IV**), respectively]. 1 : 2 : 4-CN·C_6H_3(NO_2)$_2$ and (**II**) as above give (mainly) 4-*nitro*-2-(**VI**), m.p. 156°, and 2-*nitro*-4-p-*tolylthiolbenzonitrile*, m.p. 115°, and thence 4-*nitro*-2- (**VII**), m.p. 176°, and 2-*nitro*-4-p-*toluenesulphonylbenzonitrile* (**VIII**), m.p. 201°, respectively. 1 : 2 : 4-CN·C_6H_3Cl·NO_2 (**IX**) [from 1 : 2 : 4-NH_2·C_6H_3Cl·NO_2 (modified prep.)] and (**II**) (as above or in NaOEt–EtOH) yield a mixture, m.p. 221—223°, of azoxy-, $C_{14}H_6ON_4Cl_2$, and azo-compound, $C_{14}H_6N_4Cl_2$. (**IX**) and excess of (**II**) in EtOH at 40°, treated slowly with 10% aq. NaOH, afford (**VI**) and 2-*chloro*-4-p-*tolylthiolbenzonitrile*, m.p. 95° [2-*chloro*-4-p-*toluenesulphonylbenzonitrile* (**X**), m.p. 175°]. (**VII**) or (**IV**) and (**II**) in boiling EtOH–dioxan–10% aq. NaOH yield 2-p-*toluenesulphonyl*-4-p-*tolylthiolbenzonitrile*, m.p. 132° (136° after some weeks). (**VIII**) or (**X**) similarly yields 4-p-*toluenesulphonyl*-2-p-*tolylthiolbenzonitrile*, m.p. 170°. In the above reactions, Cl or NO_2, but not CN, is replaced. (**I**) and piperidine afford 4-*chloro*-2-, m.p. 77°, and 2-*nitro*-4-*piperidinobenzonitrile*, m.p. 143°; the latter is also obtained similarly from 1 : 2 : 4-CN·C_6H_3(NO_2)$_2$. (**IX**) yields 4-*nitro*-2-*piperidinobenzonitrile*, m.p. 107°. (**IV**) or (**VII**) refluxed with piperidine for 3 or 30 min., respectively, gives 4-*piperidino*-2-, m.p. 198°, and (**VIII**) or (**X**) gives 2-*piperidino*-4-p-*toluenesulphonylbenzonitrile*, m.p. 150°. p-*Toluenesulphon*-2-*chloro*-4 : 6-*dinitroanilide*, m.p. 141°, is hydrolysed by 80% H_2SO_4 to 1 : 2 : 4 : 6-NH_2·C_6H_2Cl(NO_2)$_2$.

A. T. P.

Naphthalene derivatives from substituted γ-phenylcrotonic esters. L. Marion and J. A. McRae (*Canad. J. Res.*, 1940, **18**, B, 265—271).—Et α-carbethoxy-γ-phenyl-β-methyl-Δ^{α}-butenoate, one of the condensation products from CH_2Ph·COMe and CH_2(CO_2Et)$_2$ (method: Kon *et al.*, A., 1926, 1246; cf. A., 1930, 773), is hydrolysed to 1-*hydroxy*-3-*methyl*-β-*naphthoic acid* (**I**), m.p. 195° (decomp.). Decarboxylation (quinoline, Cu powder) of (**I**) gives 3 : 1-$C_{10}H_6$Me·OH (**II**), which by Kolbe synthesis affords (**I**). Et α-cyano-γ-phenyl-β-methyl-Δ^{α}-butenoate (*loc. cit.*), which does not undergo ring-closure on distillation, in glycerol at 240—250° (3 hr.) gives (probably) 1-*hydroxy*-3-*methyl*-β-*naphthonitrile*, m.p. 202°. (**II**) is synthesised by a method similar to that used by Veselý *et al.* (A., 1925, i, 804). M.p. are corr.

E. W. W.

Steroids. XXVII. Homologues of the testicular hormone. III. 20-Norpregnenolone. K. Miescher, F. Hunziker, and A. Wettstein [with, in part, C. Meystre] (*Helv. Chim. Acta*, 1940, **23**, 1367—1371; cf. A., 1940, II, 180).—Δ^5-Pregnene-3*t* : 20 : 21-triol 20 : 21-CMe_2 ether, m.p. 157—163° (Steiger *et al.*, A., 1938, II, 192), is hydrolysed to a mixture of Δ^5-pregnene-3*t* : 20 : 21-triols, m.p. 223—228°.



(*A.*)

This is transformed by aq. HIO_4 in dioxan and CO_2 at room temp. into Δ^5-*androsten*-3t-*ol*-17-*al* (20-*norpregnenolone*) (**I**) (*A*, R = H; R′ = CHO), a cryst. powder, m.p. 148—153° after transformation into rounded crystal forms at 130°, $[\alpha]_D^{21}$ −14·5°±4° in $CHCl_3$, which rapidly gives an intense aldehyde reaction with aq. NH_3–Ag_2O and an intense red coloration with 1 : 4-$C_{10}H_6$(OH)$_2$. If the HIO_4 fission is effected in MeOH instead of dioxan, the product is Δ^5-*androsten*-3t-*ol*-17-*al* *Me*$_2$ *acetal* [*A*, R = H; R′ = CH(OMe_2)], m.p. 185—189°, also obtained by the protracted action of 5% HCl–MeOH on (**I**) at room temp. (**I**) is converted by Ac_2O in C_5H_5N at room temp. into its *acetate*, m.p. 169—171°, $[\alpha]_D^{23}$ −13·5°±4° in $CHCl_3$, and is characterised by a *semicarbazone*, m.p. 226—228°, and a 2 : 4-*dinitrophenylhydrazone*, decomp. 207—209°. In 10—20-mg. doses 20-norprogesterone is now found to have slight progesterone activity. In the homologous series it is placed between androstenedione and progesterone; it shows the properties of both compounds in a slight degree. M.p. are corr. (vac.).

H. W.

Isomeric transformations of α-keto-alcohols. II. Acetylphenyl- and benzoylmethyl-carbinol. T. I. Temnikova (*J. Gen. Chem. Russ.*, 1940, **10**, 468—479).—MgPhBr and OH·CHMe·CN in Et_2O yield CHMeBz·OH (**I**), converted by heating with dil. HBr in MeOH (20 hr. at the b.p.), or with aq. $BaCO_3$ (20 hr. at 100°), into CHPhAc·OH (**II**). (**II**) is also obtained by reduction (Zn in 20% H_2SO_4) of Ph Me diketone. (**I**) and MgMeBr yield OH·CPhMe·CHMe·OH, also obtained, together with OH·CHPh·CMe_2·OH, from (**II**) and MgMeBr. (**I**) and MgPhBr afford chiefly OH·CPh_2·CHMe·OH, with some OH·CHPh·CPhMe·OH, which is the sole product obtained from (**II**). With BzCl, (**I**) gives CHMeBz·OBz, also obtained, together with some CHPhAc·OBz, from (**II**). The results point to the ready interconvertibility of (**I**) and (**II**), under the conditions of the various reactions, but do not afford evidence of tautomerism of the type (**I**) ⇌ (**II**).

R. T.

Effect of radicals on isomeric transformations of *tert.*-α-keto-alcohols. III. Effect of the α-naphthyl radical. A. M. Chaletzki (*J. Gen. Chem. Russ.*, 1940, **10**, 483—496).—1-$C_{10}H_7$·MgBr and COMe·CH_2Cl in Et_2O yield *α-chloro-β-1-naphthylpropan-β-ol*, an oil, decomp. at the b.p. COMeBu$^\gamma$ and $NaNH_2$ in Et_2O followed by 1-$C_{10}H_7$Br give *αβ*-dinaphthyl, but not the expected 1-$C_{10}H_7$·CH_2·COBu$^\gamma$. 1-$C_{10}H_7$·CH:CH_2 did not react with HBr in C_6H_6. 1-$C_{10}H_7$Ac is obtained in 75% yield by oxidation of 1-$C_{10}H_7$·CHMe·OH with CrO_3 in AcOH. 1-$C_{10}H_7$Ac with HCN in Et_2O at 0° yields *α-cyano-α-1-naphthylethyl alcohol*, decomp. 45°, which with MgBu$^\gamma$Cl in Et_2O gives *α-hydroxy-α-1-naphthylethyl Bu$^\gamma$ ketone*, b.p. 210—213°/3 mm., m.p. 168—169° (*semicarbazone*, m.p. 276—278°). This with dil. H_2SO_4–EtOH (8 hr. at 120°) gives *β-1-naphthyl-δδ-dimethyl-Δ$^\alpha$-penten-γ-one*, b.p. 198—199°/2 mm. (*semicarbazone*, m.p. 246—247°), which with MgMeBr gives *β-1-naphthyl-γδδ-trimethyl-Δ$^\alpha$-penten-γ-ol*, m.p. 139—140°. R. T.

Photochemical transformation of *trans*- into *cis*-di-*p*-toluoylethylene.—See A., 1941, I, 54.

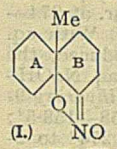
Nitration of the 3-halogeno-7-benzanthrones. F. H. Day (*J.C.S.*, 1940, 1474—1475).—3-Chloro- or -bromo-7-benzanthrone and 98% HNO_3 in $PhNO_2$ at 90—100° (bath) or 50°, respectively, afford 3-chloro-9-nitro- (I), m.p. 286°, or 3-bromo-9-nitro-7-benzanthrone, m.p. 298°, respectively; both are oxidised by CrO_3–aq. AcOH to 6-nitroanthraquinone-1-carboxylic acid, m.p. 277—278°. (I) and NH_2Ph,HCl–NH_2Ph–Zn dust at 120—140° yield the 9-NH_2-compound, m.p. 280—281°, converted (diazo-reaction) into 3 : 9-dichlorobenzanthrone, m.p. 267—268°, oxidised by CrO_3–aq. AcOH to 6-chloroanthraquinone-1-carboxylic acid, m.p. 305—306°. Relevant patent literature is reviewed. A. T. P.

Δ$^{5:7:9}$-Œstratrien-3-ol-17-one, m.p. 138—139·5°, [α]$_D$ +59° (acetate, m.p. 158° ; oxime, m.p. 195—197°), from urine of pregnant mares.—See A., 1940, III, 903.

Corticosterone and its esters. M. H. Kuizenga and G. F. Cartland (*Endocrinol.*, 1940, **27**, 647—651).—The following esters (cf. Reichstein, A., 1937, II, 506) of corticosterone are prepared using the acid anhydride or chloride in C_5H_5N : acetate, m.p. 148—152°, *propionate*, m.p. 180—182°, butyrate, m.p. 168—169°, *hexoate*, m.p. 130—132°, *α-ethylbutyrate* (I), m.p. 179—180°, *heptoate*, m.p. 139—141°, palmitate, m.p. 82—84°, H succinate, m.p. 195—197°, and benzoate, m.p. 199—201°; (I) has the greatest biological activity (see A., 1940, III, 897). H. B.

Steroids. XXVIII. Homologues of the testicular hormone. IV. Higher homologues of pregnenolone and progesterone. A. Wettstein (*Helv. Chim. Acta*, 1940, **23**, 1371—1379).—The reaction between Δ^5-3*t*-acetoxyætiocholenyl chloride (I) and $CHNa(CO_2Et)_2$ in C_6H_6 followed by hydrolysis and decarboxylation gives Δ^5-pregnen-3*t*-ol-20-one, m.p. 192—194°, $[\alpha]_D^{18}$ +30°±2° in EtOH (acetate, m.p. 149—150°, $[\alpha]_D^{20}$ +22°±2° in EtOH). Similar condensation of (I) with $CRNa(CO_2Et)_2$ (R = Me, Et, *iso*amyl) affords respectively Δ^5-21-*methyl*- (II), m.p. 170—171° (*acetate*, m.p. 175·5—176·5°), Δ^5-21-*ethyl*- (III), m.p. 125—127° (*acetate*, m.p. 114—115°), and Δ^5-21-iso*amyl*-, m.p. 136—138° (*acetate*, m.p. 142—143°), *-pregnen*-3t-*ol*-20-*one*. (II) is also prepared from (I) and $Mg[CMe(CO_2Et)_2]_2$ but a large proportion of (I) (isolable as Me Δ^5-3*t*-hydroxyætiocholenate) is unchanged. The prep. of (II) or (III) from (I) and $ZnEt_2$ or $ZnPr^\alpha I$ respectively is described. (II) and (III) are transformed by $Al(OPr^\beta)_3$ in PhMe–*cyclo*hexanone into 21-*methyl*-, m.p. 151—152°, and 21-*ethyl*-, m.p. 118—120°, *-progesterone*. Within the homologous series the pharmacological action diminishes more or less rapidly on both sides of progesterone. The next higher homologue is considerably more active than the next lower member and may be numbered with the small series of compounds with pronounced corpus luteum hormone action. M.p. are corr. H. W.

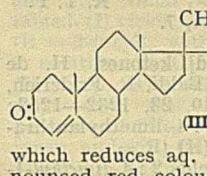
Sugar-cane wax. VI. 6-Nitro-derivatives of sterols. VII. Oxidation of sugar-cane sitosterol. II. T. Mitui (*J. Agric. Chem. Soc. Japan*, 1940, **16**, 910—916, 917—924; cf. A., 1939, II, 504).—VI. Reduction of 6-nitrocholesteryl acetate with Zn dust and Et_2O–AcOH (1 : 1) gives *6-ketocholestanyl acetate oxime*, m.p. 200°, which with Zn dust and AcOH gives 6-ketocholestanyl acetate. The *oximes* of 6-keto-sitostanyl and 6-ketostigmastanyl acetate have m.p. 136° and 172°, respectively, and are similarly prepared from the NO_2-compounds. 6-Nitrocholestene with 5% MeOH–KOH or –NaOMe yields an isomeric *substance* (I), $C_{27}H_{45}O_2N$, m.p. 113°, similarly obtained from 3-chloro-6-nitrocholestene. An analogous *substance*, m.p. 152° (*acetate*, m.p. 96·5°; *benzoate*, m.p. 175°; 3 : 5-*dinitrobenzoate*, m.p. 158°), is prepared by alkali treatment of 6-nitrocholesteryl acetate or propionate, whilst 6-nitrostigmasteryl acetate yields a *substance*, m.p. 91—93°.



(I.)

VII. The hydroxy-ketone, m.p. 114°, obtained by oxidation (cf. A., 1938, II, 232) of sugar-cane sitosteryl acetate dibromide is 3-*hydroxynorcholesten*-24-*one* (II) (*acetate*, m.p. 167—168°), which is prepared from MgEtI and 3-*acetoxycholenamide*, m.p. 210—212°. Clemmensen reduction of (II) or 3-hydroxynorcholesten-25-one yields 3-*hydroxynorcholestene*, m.p. 132° (*acetate*, m.p. 120°). Me 3-acetoxycholenate with MgEtI yields the corresponding 3-*hydroxydiethylcarbinol*, m.p. 160—163° [3-*acetate* (III), m.p. 129·5°; *dichloride*, m.p. 116°, which with NaOPr gives *norsitostene*, m.p. 66—67°]. (III) with Ac_2O at 100° yields 3-*acetoxy*-Δ$^{5:6\text{-}23:24}$-*norsitostadiene*, m.p. 117°, whilst with $SOCl_2$ it gives the *carbinyl chloride*, m.p. 130·5°, converted by NaOPr into 3-*hydroxynorsitostene*, m.p. 134·5° (*acetate*, m.p. 137°), reduction (PtO_2, H_2) of which yields 3-*hydroxynorsitostane*, m.p. 131—132° (*acetate*, m.p. 131°). J. N. A.

Constituents of the adrenal cortex and related substances. XLI. Δ^4-Pregnene-17 : 20-diol-21-al-3-one 20-monoacetate. J. von Euw and T. Reichstein (*Helv. Chim. Acta*, 1940, **23**, 1114—1125; cf. A., 1940, II, 350).—Hydroxylation of the triene obtained from allyltestosterone gives (cf. Butenandt *et al.*, A., 1939, II, 76) 17-*αβγ*-trihydroxypropyltestosterone (I), m.p. 239—244°, and a (?) *diol*, m.p. 142—143°. (I), $COMe_2$, and anhyd. $CuSO_4$ at room temp. give 17-*α-hydroxy-βγ-isopropylidenedioxypropyltestosterone*, m.p. 235—236·5°, $[\alpha]_D^{18}$ +66·7°±2° in dioxan, which is transformed (Ac_2O in C_5H_5N at 60°) into the 20-*acetate*, m.p. 221—223°, $[\alpha]_D^{17}$ +107·4°±2° in $COMe_2$. This is hydrolysed by dil. AcOH to 17-*αβγ-trihydroxypropyltestosterone* 20-*monoacetate* (II), m.p. 210—211·5°, $[\alpha]_D^{18}$ +100·2°±2° in dioxan, also obtained by a similar sequence of changes from the product of the interaction of (I) and *cyclo*hexanone. HIO_4 in dioxan oxidises



(III.)

(II) to Δ^4-*pregnene*-17 : 20-*diol*-21-*al*-3-*one* 20-*acetate* (III), m.p. 206—208° (slight decomp.), $[\alpha]_D^{18}$ +119·1°±±3° in dioxan (*semicarbazone*, darkens and decomp. 190° without melting), which reduces aq. NH_3–Ag_2O at room temp., gives a pronounced red colour with 1 : 4-$C_{10}H_6(OH)_2$, and affords a brown-orange solution with a bright green fluorescence in conc. H_2SO_4. The conversion of *t*-dehydroandrosterone acetate into 17*α*-allylandrostenediol and its oxidation to 17*α*-allyltestosterone are fully described. The last compound is best dehydrated by $POCl_3$ in boiling C_5H_5N. It is hydroxylated (OsO_4) to 17-*βγ*-dihydroxypropyltestosterone-*a*, m.p. 226—231°, and -*b*, m.p. 190—195°, which when treated with anhyd. $CuSO_4$ and $COMe_2$ at room temp. yield 17-iso*propylidenedioxypropyltestosterone*-a, m.p. 135—136°, $[\alpha]_D^{15}$ +37·7°±2°, $[\alpha]_{5461}^{15}$ +45·2°±2° in $COMe_2$, and -*b*, m.p. 107—107·5°, $[\alpha]_D^{16}$ +61·0°±2°, $[\alpha]_{5461}^{16}$ +71·3°±2° in $COMe_2$ (also +0·5H_2O). From these compounds the pure triols (*b* has m.p. 207—207·5°) are obtained and are converted into their *dibenzoates*, m.p. 169—170° and 161—162°, respectively, but the corresponding acetates are non-cryst. Attempts to withdraw H_2O from these substances were unsuccessful. M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. XLII. Partial synthesis of substance *S*. T. Reichstein and J. von Euw (*Helv. Chim. Acta*, 1940, **23**, 1258—1260).—Δ^4-Pregnene-17 : 20-diol-21-al-3-one 20-acetate is hydrolysed ($KHCO_3$ in aq. MeOH) to the non-cryst. aldehyde (I), which is extensively isomerised in boiling C_5H_5N to Δ^4-pregnene-17-21-diol-3 : 20-dione, m.p. 200—205° (corr. ; decomp.). This is identical with substance *S* (II). It is further characterised by its acetate, m.p. 236—238° (corr.) after becoming opaque at 130°, $[\alpha]_D^{19}$ +116·33°±4° in $COMe_2$. Since (II) has the *β*-configuration at $C_{(17)}$ this must also be true for (I). H. W.

Alkaline fusion. II. Reaction between anthraquinone and alkali. N. N. Voroshcov and A. P. Alexandrov (*J. Gen.*

Chem. Russ., 1940, **10**, 869—882).—Anthraquinone (**I**) does not react with aq. NaOH at room temp. (490 days). The products obtained from (**I**) and anhyd. NaOH (2 hr. at 274—276°) are BzOH, anthraquinol, and oxanthrone. With aq. NaOH at 275°, alizarin (**II**) and BzOH are produced, the yield of (**II**) rising with increasing $[H_2O]$. (**I**) and aq. NaOH–Na_2SO_3 (5·5 hr. at 210°) afford (**II**) and 2 : 10-*dihydroxy*-9-*keto*-2 : 9-*dihydroanthracene* (**III**) (*acetate*, m.p. 158—158·5°; *benzoate*, m.p. 192—193°), which decomposes at 274° to 2-hydroxyanthraquinone (**IV**) and dianthrone. (**III**) yields the same products when treated with C_6H_6 at the b.p., or with PbO_2 in xylene, and affords 2-methoxyanthraquinone with Me_2SO_4 or CH_2N_2. With aq. NaOH, (**III**) gives (**II**) and (**IV**). (**I**) and aq. NaOH–Na_2SO_3 at 235° yield (**II**), (**III**), and benzoylanthrone. R. T.

Organic cationoid reagents. R. Oda and U. Ueda (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1940, **38**, 44—49).—1-Nitroanthraquinone (**I**) in presence of conc. H_2SO_4 acts as a strong oxidising reagent (cationoid) with many org. compounds, whereby it is converted into 1-aminoanthraquinone (**II**) and 1-amino-4-hydroxyanthraquinone (**III**) (formed by rearrangement of the hydroxylamino-compound by H_2SO_4). Org. compounds readily oxidised at room temp. are α- and β-$C_{10}H_7$·OH, α-$C_{10}H_7$·NH_2, anthracene, acenaphthene, and carbazole; less readily oxidised are cresol, *p*-$C_6H_4(OH)_2$, 1-$C_{10}H_7$Me, tetrahydronaphthalene, anthrone, and unsaturated fatty oils; more difficultly oxidised are PhMe, PhOH, C_6H_4Me·NH_2, *m*-$C_6H_4(OH)_2$, $C_{10}H_8$, OH·$C_{10}H_6$·SO_3H, stilbene, and phenanthrene, whilst C_6H_6, PhCl, $PhNO_2$, BzOH, $COPh_2$, and PhCHO are not oxidised. Details are recorded for the interaction of (**I**), anthracene, and AcOH–H_2SO_4, to give (**II**), (**III**), and an impure, black oxidation–condensation product; a similar product is obtained using 1-nitroanthraquinone-sulphonic acid in place of (**I**), whereby the SO_3H-derivatives of (**II**) and (**III**) are formed. *o*-C_6H_4Bz·CO_2H (**IV**) also acts as a cationoid reagent in H_2SO_4 (ring-closure does not occur at room temp.); colour changes with various compounds are given. C_6H_6 and (**IV**) in conc. H_2SO_4 at 80° afford phthalophenone and anthraquinone; PhCl, BzOH, $PhSO_3H$, $PhNO_2$, and $C_{10}H_7$·SO_3H react with much difficulty or not at all. A. T. P.

Aminoanthraquinones.—See B., 1941, II, 7.

ω-Amino-derivatives of [quinones and] ketones. H. de Diesbach [with P. Lachat, M. Poggi, B. Baldi, R. Friderich, and H. Walker] (*Helv. Chim. Acta*, 1940, **23**, 1232—1252; cf. A., 1930, 607).—Condensation of 2 : 4-dimethylanthraquinone with the appropriate CH_2R·OH (*A*) (R = NH·CO·CCl_3 etc.) in conc. H_2SO_4 at 0° yields 2 : 4-*dimethyl*-1-*trichloroacetamidomethyl*- (**I**), m.p. 185°, and -1-*phthalimidomethyl*- (**II**), m.p. 199—200°, -*anthraquinone*. Reaction does not occur with NHBz·CH_2·OH. (**I**) is converted by boiling 30% KOH into NH_3, $CHCl_3$, and a mixture of aldehyde and alcohol oxidised by CrO_3 to pure 2 : 4-*dimethylanthraquinone*-1-*aldehyde* (**III**), m.p. 159°, which does not condense with NH_2OH or NHPh·NH_2 and does not give a violet colour with NH_2Ph in AcOH; it is oxidised by HNO_3 (*d* 1·15) at 220° to anthraquinone-1 : 2 : 4-tricarboxylic acid. Short treatment of (**I**) with boiling 10% NaOH–EtOH gives (**III**) accompanied by the very unstable 2 : 4-dimethyl-1-aminomethylanthraquinone (isolated as the *Bz* derivative, m.p. 160°) and αβ-2 : 2′ : 4 : 4′-*tetramethyl*-1 : 1′-*dianthraquinonylethylenediamine*; if the crude product is crystallised from quinoline instead of $PhNO_2$ *tetramethyldiisopyrroleanthrone* is isolated. NH_2·CH_2 is more stable in the hydroxyaminomethyl- than in the aminomethyl-anthraquinones. Condensation of phenanthraquinone and its derivatives in conc. H_2SO_4 at 0° with (*A*) occurs at $C_{(2)}$ and then at $C_{(7)}$. If a substituent is attached to $C_{(2)}$ reaction occurs at $C_{(7)}$. If OH is present at $C_{(2)}$ a second attack can occur at $C_{(3)}$. Thus are obtained 2-*chloroacetamidomethyl*-, m.p. 234°, 2-*trichloroacetamidomethyl*-, m.p. 203°, and 2-*phthalimidomethyl*-, m.p. 255°, 2 : 7-*di*(*trichloroacetamidomethyl*)- (**IV**), m.p. 238°, 2 : 7-*di*(*phthalimidomethyl*)-, m.p. >345°, 2-*nitro*-7-*trichloroacetamidomethyl*-, m.p. 215°, 2-*acetamido*-7-*phthalimidomethyl*-, m.p. >330°, 2-*hydroxy*-7-*benzamidomethyl*-, m.p. >290°, -7-*trichloroacetamidomethyl*-, m.p. ~200°, and -7-*phthalimidomethyl*-, m.p. 227°, 2-*hydroxy*-3 : 7-*di*(*trichloroacetamidomethyl*)-, decomp. ~190°, and -3 : 7-*di*(*phthalimidomethyl*)-, m.p. ~260° (decomp.), -*phenanthraquinone*. Hydrolysis (KOH) of these compounds gives NH_3 and probably compounds of high mol. wt.; thus (**IV**) affords a *substance*, $C_{32}H_{18}O_4N_2$. Condensation with benzanthrone occurs first at $C_{(3)}$ and then at $C_{(9)}$ but generally the disubstituted compound is obtained even when a deficiency of (*A*) is employed. NHBz·CH_2·OH is exceptional and enters only at $C_{(3)}$; if this position is occupied condensation does not occur. For other (*A*) entry is effected at $C_{(9)}$ if $C_{(3)}$ is substituted. Condensation is effected by cold, conc. H_2SO_4. The following are described: 3-*benzamidomethyl*-, m.p. 180°, oxidised by CrO_3 to anthraquinone; 3 : 9-*di*(*chloroacetamidomethyl*)-, m.p. 235°; 3 : 9-*di*(*phthalimidomethyl*)- (**V**), m.p. 285°; 3 : 9-*di*-(*trichloroacetamidomethyl*)-, m.p. ~235°, 3-*bromo*-, m.p. 247°, and 3-*nitro*-, m.p. 250°, -9-*trichloroacetamidomethyl*-; 3-*bromo*-9-*phthalimidomethyl*-, m.p. 257°, -*benzanthrone*. The position of the substituents is proved by the oxidation of (**V**) to 1-*phthalimidoacetyl*-6-*phthalimidomethylanthraquinone*, m.p. 260—265° (decomp.). Acenaphthenequinone and OH·CH_2·NH·CO·CCl_3 in conc. H_2SO_4 give 2-*trichloroacetamidomethylacenaphthenequinone*, m.p. 208°, oxidised by dil. HNO_3 to 1 : 2 : 3 : 5-$C_6H_2(CO_2H)_4$ (Me_4 ester, m.p. 108—109°). Fluorenone condenses immediately to 2 : 7-di-derivatives; if $C_{(2)}$ is occupied, entry occurs solely at $C_{(7)}$. The following are reported: 2 : 7-*di*(*benzamidomethyl*)-, m.p. 266°; 2 : 7-*di*(*chloroacetamidomethyl*)-, m.p. 259°; 2 : 7-*di*(*phthalimidomethyl*)-, m.p. >310°; 2 : 7-*di*(*trichloroacetamidomethyl*)- (**VI**), m.p. 248°, oxidised by HNO_3 (*d* 1·15) to fluorenone-2 : 7-dicarboxylic acid, m.p. 407° (Me_2 ester, m.p. 218°); 2-*nitro*-7-*mono*-, m.p. 211°, and -*tri*-*chloroacetamidomethyl*-, m.p. 190°; 2-*hydroxy*-, m.p. ~165°, and 2-*acetamido*-7-*trichloroacetamidomethyl*- (**VII**), m.p. 265°, -*fluorenone*. Xanthone condenses readily; thus by cautious working it is possible to obtain 2-*trichloroacetamidomethyl*-, whilst, by further substitution, (?) 2 : 4 : 5 : 7-*tetra*(*trichloroacetamidomethyl*)-, m.p. ~200° (decomp.), -*xanthone* is produced. Alkaline hydrolysis of acenaphthenequinone derivatives causes fission between the two CO whereas derivatives of fluorenone and xanthone yield NH_3 and polymerised products. Thus (**VI**) gives a *substance*, $C_{30}H_{22}O_4N_2$, m.p. >400°, and a *compound*, $C_{28}H_{21}O_3N_3$, m.p. >400°, is derived from (**VII**).

$COPh_2$ does not react with (*A*) but the presence of Me permits action, the position of Me governing that of the entering substituent. Thus *o*-C_6H_4Me·COPh affords 2-*methyl*-3 : 5-*di*(*phthalimidomethyl*)*benzophenone*, m.p. 198—200°, whilst *p*-C_6H_4Me·COPh yields 4-*methyl*-3-*phthalimidomethylbenzophenone*, m.p. 146·5°, and 2 : 4 : 1-$C_6H_3Me_2$·COPh affords 2 : 4-*dimethyl*-5-*trichloroacetamidomethyl*-, m.p. 163°, -5-*phthalimidomethyl*-, m.p. 147·5°, and -3 : 5-*di*(*phthalimidomethyl*)-, m.p. 233—235°, -*benzophenone*. If each C_6H_6 nucleus of $COPh_2$ contains one or more Me condensation takes place in both nuclei. Hydroxybenzophenones react readily giving diderivatives even in presence of a deficiency of (*A*); 2- (**VIII**), m.p. 116°, and 4-, m.p. 196°, -*hydroxy*-3 : 5-*di*(*trichloroacetamidomethyl*)*benzophenone* are described. Alkaline hydrolysis of these compounds gives NH_3 and polymerised products; thus (**VIII**) affords a *substance*, $C_{45}H_{42}O_8N_4$. The reactions established for anthraquinone are therefore repeated to a certain extent for other ketones and the changes must be ascribed to the CO groups.

o-C_6H_4Me·CO_2H gives 4-*benzamido*-, m.p. 191°, -*phthalimido*-, m.p. 226°, -*chloroacetamido*-, m.p. 152°, and -*trichloroacetamido*-, m.p. 244°, -*methyl*-*o*-*toluic acid*; these compounds are hydrolysed by conc. HCl to 4-*aminomethyl*-*o*-*toluic acid hydrochloride*, m.p. 244—245°. *p*-C_6H_4Me·CO_2H yields 2-*benzamido*-, m.p. 206°, -*phthalimido*-, m.p. 181°, -*chloroacetamido*-, m.p. 227·5°, and -*trichloroacetamido*-, m.p. 244°, -*methyl*-*p*-*toluic acid*. Hydrolysis (conc. HCl at ~180°) of these products affords 2-*aminomethyl*-*p*-*toluic acid hydrochloride*, m.p. 279—280°, converted by HNO_2 into 2-*hydroxymethyl*-*p*-*toluic acid*, m.p. 165°, which is oxidised by $KMnO_4$ to 1 : 2 : 4-C_6H_3Me$(CO_2H)_2$, m.p. 319—320°, and reduced by HI to 3 : 4 : 1-$C_6H_3Me_2$·CO_2H. *m*-C_6H_4Me·CO_2H gives 4-*phthalimidomethyl*-*m*-*toluic acid*, m.p. 261°, hydrolysed (conc. HCl) to 4-*aminomethyl*-*m*-*toluic acid hydrochloride*, m.p. 238°, transformed by the successive action of HNO_2 and $KMnO_4$ into 4 : 1 : 2-C_6H_3Me$(CO_2H)_2$. *m*-C_6H_4Me·CO_2H and OH·CH_2·NHBz in cold, conc. H_2SO_4 give 4-*methylphthalimidine*, m.p. 205° (*NO*-derivative, m.p. 225°). 2 : 4 : 1-$C_6H_3Me_2$·CO_2H affords 2 : 4-*dimethyl*-5-*trichloroacetamidomethylbenzoic acid*, m.p. 245°, hydrolysed to 2 : 4-*dimethyl*-5-*aminomethylbenzoic acid hydrochloride*, m.p. 284°, which gives 2 : 4-*dimethyl*-5-*hydroxymethylbenzoic acid*, m.p. 145°, oxidised to 4 : 6 : 1 : 3-$C_6H_2Me_2(CO_2H)_2$ (dichloride, m.p. 82—83°; diamide, m.p. 265—267°). H. W.

Composition and constitution of Turkey-red. H. E. Fierz-David and M. Rutishauser (*Helv. Chim. Acta*, 1940, **23**, 1298—1311).—Turkey-red (**I**) is a complex containing alizarin (**II**), Al, and Ca in the ratio 4 : 2 : 3; other substances do not appear to be present. It is readily prepared by prolonged heating of the three components (the metals in ionised form) in H_2O. This and similar lakes (*e.g.*, Fe^{III}, Cr) can be readily crystallised from H_2O–C_5H_5N, whereby a C_5H_5N complex is obtained. If this is heated at 130°/high vac. C_5H_5N and all H_2O excepting 2 mols. escape; these are so stably united that they are not expelled at 600°. The resulting complexes are black and on exposure to air absorb exactly 3 mols. of H_2O giving the colour lake, which probably has this composition on the fibre. Fatty substances used in dyeing with (**I**) probably serve to fix the metallic oxides as soaps on the fibre and then to bring the lake into the finest dispersion. Subsequently they separate from the complex which consists of (**II**), Al_2O_3, and CaO (4 : 2 : 3) with H_2O. In these lakes Ca can be replaced by other bivalent metals without marked alteration of the colour. The shade depends on the tervalent metal (Al, Fe, Cr). Treatment of (**I**) with $SnCl_2$ causes partial replacement of Ca but not of Al by SnO. Structures are suggested. H. W.

Biochemistry of the lower fungi. IV. Pigment of *Penicillium roseo-purpureum*, Dierckx. T. Posternak (*Helv. Chim. Acta*, 1940, **23**, 1046—1053; cf. A., 1940, II, 182).—The fungus is cultivated in the Czapek–Dox medium. The liquid is acidified with HCl and extracted with Bu$^{\beta}$OH after addition of NaCl; the mycelium is macerated with Bu$^{\beta}$OH. The combined extracts are heated with NaOH and the alkaline solution is acidified. BzOH is removed from the ppt., which, after purification through the acetate, gives *roseopurpurin* (**I**), $C_{16}H_{12}O_6$, m.p. 278—280° (decomp.; slowly heated), 285° (block). It gives a reddish-brown colour with $FeCl_3$; its variation in colour with p_H of its solutions is similar to that of 1 : 3-dihydroxyanthraquinone. The C_5H_5N salt forms orange needles. When distilled with Zn dust, (**I**) affords 2-methylanthracene. The presence of 3 OH in (**I**) is established by the isolation of a *triacetate*, m.p. 210°. The Me_3 derivative, m.p. 187°, of (**I**) is identical with tetramethylcitreorosein (*loc. cit.*). Oxidation of (**I**) by $KMnO_4$ first in alkaline and then in acid solutions leads to *anisole-2 : 3 : 5-tricarboxylic acid* (**II**), m.p. 251° (gas evolution) and 250° after re-solidification (*anhydride*, m.p. 252°). 1 : 3 : 4 : 5-$C_6H_2Me_2Ac{\cdot}OMe$ is oxidised by aq. $KMnO_4$ to *3-methoxy-5-carboxyphthalonic acid*, m.p. ~240° (decomp.), further oxidised in acid solution to (**II**). (**I**) is therefore 5 : 7-*dihydroxy-4-methoxy-2-hydroxymethylanthraquinone*. H. W.

Biochemistry of micro-organisms. LXVIII. Synthesis of cynodontin (1 : 4 : 5 : 8-tetrahydroxy-2-methylanthraquinone), a metabolic product of species of *Helminthosporium*. W. K. Anslow and H. Raistrick (*Biochem. J.*, 1940, **34**, 1546—1548).—The benzoylbenzoic acid obtained from 3 : 6 : 4 : 1 : 2-$(OMe)_2C_6HMe(CO)_2O$, *p*-$C_6H_4(OMe)_2$, and $AlCl_3$ in CS_2, is cyclised and demethylated by conc. H_2SO_4 at 150° (bath) to 1 : 4 : 5 : 8-*tetrahydroxy-2-methylanthraquinone*, m.p. 260—261° (when purified through the *tetra-acetate*, m.p. 224—226°), identical with cynodontin (A., 1933, 1082). P. G. M.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Biochemistry of micro-organisms. LXVI. Penicilliopsin, the colouring matter of *Penicilliopsis clavariæformis*, Solms-Laubach. A. E. Oxford and H. Raistrick (*Biochem. J.*, 1940, **34**, 790—803).—The fungus, when grown in the dark at 24° (best on an orange-extract medium), produces a cryst. colouring matter *penicilliopsin* (**I**), $C_{30}H_{24}O_8$, orange-red, m.p. 330° (decomp.) [*bisphenylcarbamate*, yellow, m.p. 238—240° (decomp.); *diacetate*, orange-yellow, decomp. above 280°]. With CH_2N_2 (**I**) gives a *compound*, $C_{34}H_{32}O_8$ (*i.e.*, $C_{30}H_{24}O_8 + 4CH_2$), orange-yellow, m.p. 340—360° (decomp.), OMe nil by Zeisel. $CHMeN_2$ affords the *isomeride* ($C_{30}H_{24}O_8 + 2C_2H_4$), yellow, m.p. ~310°, OEt nil by Zeisel. When heated alone or with Zn dust (**I**) gives *Frangula*-emodin anthranol. Distillation with Zn dust in H_2 affords 2-methylanthracene. Oxidation of (**I**) with HNO_3 yields tetranitro-*Frangula*-emodin, nitrococcusic acid, and $H_2C_2O_4$. (**I**) is oxidised in air in org. solvents in presence of org. bases to *oxypenicelliopsin* (**II**), $C_{30}H_{20}O_9$, purple-black, m.p. above 360° [*tetra*(?)-*acetate*, orange-red, m.p. 308—310° (decomp.)]. Solutions of (**II**) when exposed to light are converted into an *isomeride* (**III**), chocolate-brown, m.p. above 370°, giving intensely fluorescent solutions. (**III**) is closely related to hypericin derived from *Hypericum perforatum*. The absorption and fluorescence spectra of the two substances are indistinguishable (Dhéré and Castelli, A., 1939, III, 1007) but chemical reactions prove their non-identity. The substance "mycoporphyrin" obtained from naturally occurring *P. clavariæformis* was probably a mixture of (**I**), (**II**), and (**III**). (**I**) may be a polyhydroxy-derivative of a reduced *meso*dimethyldianthrone. J. H. B.

Sterols. CVII. Steroidal sapogenins of *Alestris*, *Asparagus*, and *Lilium*. R. E. Marker, D. L. Turner, A. C. Shabica, E. M. Jones, J. Krueger, and J. D. Surmatis (*J. Amer. Chem. Soc.*, 1940, **62**, 2620—2621).—*Alestris farinosa*, L., yields diosgenin. *Asparagus officinalis*, L., yields sarsasapogenin. *Lilium rubrum magnificum* yields *liligenin*, $C_{27}H_{44}O_4$, m.p. 245—246° (digitonide; *diacetate*, m.p. 158°), which with CrO_3–AcOH at 25° gives only acids and is thus a 2 : 3- or 3 : 4-diol. R. S. C.

Isomerides of bixin and methylbixin. Synthesis of dihydrobixin from dihydromethylbixin. T. Takahashi (*J. Pharm. Soc. Japan*, 1936, **56**, 352—355).—Bixin (**I**) and 3% HCl in MeOH give methylbixin. Labile (**I**) is apparently converted into the stable form by oxidising with BzO_2H and reducing the resulting compound, m.p. 216—217°. Dihydrobixin, m.p. 207—208° (cf. A., 1929, 1075), and dihydromethylbixin, m.p. 178°, are also described. Ch. Abs. (*c*)

Ultra-violet absorption spectra of lignin and related compounds.—See A., 1941, I, 27.

V.—HETEROCYCLIC.

Secondary and tertiary arylamines containing the furfuryl group. I. Furfurylaniline and furfurylethylamine. A. I. Umnova (*J. Gen. Chem. Russ.*, 1940, **10**, 569—576).—Furfurylideneaniline is reduced (Zn in aq. NaOH; 8 hr. at 75°) to *furfurylaniline* (**I**), b.p. 147—148°/10 mm. (*hydrochloride*; *oxalate*), from which *furfurylphenylnitrosoamine*, m.p. 28°, is obtained. (**I**) yields an azo-dye, $CH_2R{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3Na$ (R = 2-furyl), with *p*-$SO_3Na{\cdot}C_6H_4{\cdot}N_2Cl$ (**II**). $NaNH_2$ and a solution of (**I**) in Et_2O–EtBr yield *furfurylethylaniline* (**III**), b.p. 147—147·5°/11 mm. This gives p-*nitrosofurfurylethylaniline*, m.p. 75—76°, with HNO_2. With PhCHO in presence of 30% HCl (**III**) yields an analogue of malachite-green, and with (**II**) gives an analogue of helianthin. R. T.

Further homologue of α-tocopherol. P. Karrer and O. Hoffmann (*Helv. Chim. Acta*, 1940, **23**, 1126—1131).—3 : 5 : 1-$C_6H_3MeEt{\cdot}OH$ is transformed by boiling C_6H_6–AcCl into the acetate, b.p. 126—128°/15 mm., which is converted by $AlCl_3$ at 160—170° into a mixture of 2-*hydroxy*-4(6)-*methyl*-6(4)-*ethylacetophenones*, m.p. 93°, and b.p. 144°/12 mm., m.p. 18—19°, separated from one another through the *semicarbazones*, m.p. 228° and 193°. They are reduced (Zn–Hg and HCl) to the corresponding *methyldiethylphenols*, m.p. 121—123°/13 mm., and (**I**), b.p. 121—123°/12 mm. (**I**) in EtOH–conc. HCl with $NaNO_2$ at 0° gives 4-*nitroso*-3(? 5)-*methyl*-2 : 5(? 2 : 3)-*diethylphenol*, m.p. 150° (decomp.), converted by $NaNO_2$ and 7·5% HCl into 5(? 3)-*methyl*-2 : 3(? 2 : 5)-*diethyl*-1 : 4-*benzoquinone*, b.p. 94—99°/0·4—0·6 mm., which is reduced to the *quinol*, m.p. 141—142°. This is condensed ($ZnCl_2$ in boiling C_6H_6) with phytyl bromide to dl-7(? 5)-*methyl*-5 : 8(? 7 : 8)-*diethyltocol*, a pale yellow viscous liquid with marked reducing power (*allophanate*, m.p. 166°) which has full vitamin-*E* activity in 10-mg. doses. H. W.

Unsaturated derivative of the tocopherol series (? *dl*-Δ^3-dehydro-α-tocopherol). P. Karrer, R. G. Legler, and G. Schwab (*Helv. Chim. Acta*, 1940, **23**, 1132—1137).—γηλο-Tetramethyl-Δ$^{\alpha}$-hexadecinen-γ-ol (**I**) is transformed by PBr_3 in light petroleum at −15° into a mixture of bromides (very predominatingly γ-bromo-γηλο-tetramethyl-Δ$^{\alpha}$-hexadecinene) which condenses with trimethylquinol (**II**) in C_6H_6 or light petroleum containing $ZnCl_2$ to (?) *dl*-Δ^3-dehydro-α-tocopherol (**III**) (*allophanate*, m.p. 163°) in very poor yield. (**III**) is reduced (Pt in EtOH) to a substance (allophanate, m.p. 172°) very similar to or identical with *dl*-α-tocopherol. Attempts to improve the yield of (**III**) by purification through the acetate, b.p. 170°/0·01 mm., were unsuccessful. (**III**) is also

obtained in small yield by condensing (I) with (II) in presence of $ZnCl_2$ at 175°. H. W.

dl-α-**Tocopherolphosphoric ester.** P. Karrer and G. Bussmann (*Helv. Chim. Acta*, 1940, **23**, 1137—1138).—*dl*-α-Tocopherol (I) is readily converted by $POCl_3$ in anhyd. C_5H_5N at 0° into the H_2 phosphate, isolated as the Na_2 salt. This is remarkably resistant to hydrolysis but its vitamin-*E* activity is equal or superior to that of (I). It is not hydrolysed by kidney-, serum-, or yeast-phosphatase. H. W.

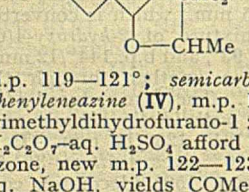
α-**Tocopheryl 3-bromocamphorsulphonate.**—See B., 1941, III, 21.

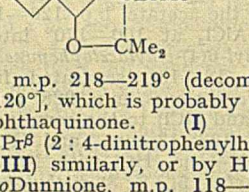
Catalytic hydrogenation of coumarone. N. I. Schujkin, I. I. Dmitriev, and T. P. Dobrinina (*J. Gen. Chem. Russ.*, 1940, **10**, 967—972).—The chief product of hydrogenation of coumarone with Pd catalyst at 175° is octahydrocoumarone, with 2-ethyl*cyclo*hexanol (I) and β-*cyclo*hexylethanol as by-products. With Ni catalyst the chief product is (I). The same products are obtained with Pt catalyst in EtOH at 50°. R. T.

Benzopyrylium salts. II. Ozonisation. R. L. Shriner and R. B. Moffett (*J. Amer. Chem. Soc.*, 1940, **62**, 2711—2714; cf. A., 1939, II, 385).—4′-Bromo-3-methoxyflavylium chloride and O_3 in AcOH give *o*-OH·C_6H_4·CHO (I), *p*-C_6H_4Br·CO_2H (II), and *Me* o-p′-*bromobenzoyloxyphenyl acetate*, m.p. 87—88° [hydrolysed by 25% KOH to (II) and *o*-OH·C_6H_4·CH_2·CO_2H]. 4′-Bromo-3-phenylflavylium chloride (III) [prep. from (I) and *p*-C_6H_4Br·CO·CH_2Ph and HCl in dioxan; corresponding *ferrichloride* (IV), m.p. 162—163·5°] and O_3 in AcOH give (I), 4-bromobenzil (V), and (II). Boiling KOH–EtOH converts (IV) into 2-*ethoxy*-3-*phenyl*-2-p-*bromophenyl*-1 : 2-*benzpyran*, m.p. 101—102·5°, obtained also from (III) by EtOH at 0°, and converted by O_3 in CCl_4 into (V), (I), (II), and EtOH. Pyrylium salts thus undergo cleavage at positions 2 : 3 and 3 : 4 and are best considered as $C_{(2)}$ and $C_{(4)}$ carbenium salts. R. S. C.

Benz-furans and -pyrans.—See B., 1941, III, 21.

Dunnione. II. J. R. Price and (Sir) R. Robinson (*J.C.S.*, 1940, 1493—1499; cf. A., 1939, II, 557).—Dunnione (I) (phenyleneazine, $[\alpha]_D^{16}$ +237° in $CHCl_3$) (improved method of isolation) is αα*β*-trimethyldihydrofurano-1 : 2-naphthaquinone (*loc. cit.*). α-Dunnione (II), $[\alpha]_D^{19}$ +104° in $CHCl_3$ (*dihydrodiacetate*, m.p. 119—121°, $[\alpha]_D^{18}$ +80·4° in $CHCl_3$), is the isomeric 1 : 4-naphthaquinone. (I) or (II) (Kuhn–Roth oxidation) affords 1·3 or 1·04 mols. of AcOH, respectively. (I) and H_2SO_4 at room temp. for 72 hr., then at 100° for 2 hr., give <5% of β-*iso*dunnione (III), m.p. 129—131° [*dihydrodiacetate*,





m.p. 119—121°; *semicarbazone*, m.p. 218—219° (decomp.); *phenyleneazine* (IV), m.p. 118—120°], which is probably αββ-trimethyldihydrofurano-1 : 2-naphthaquinone. (I) and $K_2C_2O_7$–aq. H_2SO_4 afford COMePr$^\beta$ (2 : 4-dinitrophenylhydrazone, new m.p. 122—123°). (III) similarly, or by H_2O_2–aq. NaOH, yields $COMe_2$. α-*iso*Dunnione, m.p. 118—119° (*dihydrodiacetate*, m.p. 135—136°; *semicarbazone*, m.p. 222—223°), and conc. H_2SO_4 at room temp. afford (III). The *iso*dunniones resemble the lapachones more closely than they do (I) or (II). A solution of (III) in 1—5% aq. NaOH, made faintly acid and kept at 0° for 2—3 hr., yields *hydroxyhydro*-iso*dunniol* (V), m.p. 112—113° (*dihydrotetra-acetate*, m.p. 183—184°). With *o*-$C_6H_4(NH_2)_2$ in AcOH, (V) affords (III) + (IV), but in EtOH + a little AcOH, it gives a *product*, $C_{21}H_{20}O_2N_2$, m.p. 193—194°, converted by H_2SO_4 into (IV). (V) and alkaline $KMnO_4$ give (III) only. The corresponding hydroxyhydrodunniol could not be obtained from (I) or (II) owing to its sensitivity to alkalis [which afford (VII)] and to acids (effect ring-closure). (III) and Br–$CHCl_3$ at room temp. (4—6 days) give *bromo*-β-iso*dunnione* (VI), m.p. 141—143° (α-bromo-αββ-trimethyldihydrofurano-1 : 2-naphthaquinone), whereas (I) does not react with Br–$CHCl_3$ at 55°. (VI) in Zn–aq. NaOH (2 hr.), and air drawn through for 2 hr., afford *iso*dunniol, m.p. 118—119° [H_2SO_4 gives (III)], which is possibly 3-trimethylvinyl-2-hydroxy-1 : 4-naphthaquinone. The structure of *allo*dunnione (VII) is not clear. (VII) is oxidised by CrO_3 to $COMe_2$ and reduced by Sn–HCl or Zn–AcOH to a H_2-compound, m.p. 141—142° (Ac_2O–NaOAc give the *diacetate*, m.p. 191—193°), or by Zn–10% aq. NaOH to *dihydrohydroxyhydro*allo*dunnione*, m.p. 160—161° (presumably due to opening of a lactone, coumaran, or chroman ring). (VII) and conc. H_2SO_4 at 100° give a *sulphonic acid*, $C_{15}H_{14}O_6S$. A. T. P.

Reactions of organic α-oxides with alcohols and compounds containing the carbonyl group, in presence of boron fluoride. A. A. Petrov (*J. Gen. Chem. Russ.*, 1940, **10**, 981—996).—Alcohols with oxides in presence of BF_3 yield ethers : $(CH_2)_2O$ + MeOH → OH·$[CH_2]_2$·OMe. Aldehydes react similarly with oxides, giving dioxolans; thus $(CH_2)_2O$ + CORR′ → $\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}$>CRR′ (R = Me, R′ = Me, *Et*, b.p. 118—118·5°, Pr$^\alpha$, b.p. 140—140·5°). OH·CH_2·CH(OH)·CH_2Cl and $COMe_2$, COMeEt, or COMePr yield similarly 4-chloromethyl-2 : 2-dimethyl-, -2-*methyl*-2-*ethyl*-, b.p. 174—177°, or -2-*methyl*-2-*propyl*-*dioxolan*, b.p. 192—196°. Me *βγ*-oxidopropyl ether reacts similarly with these ketones, affording 4-*methoxymethyl*-2 : 2-*dimethyl*, b.p. 154—155·5°, -2-*methyl*-2-*ethyl*-, b.p. 171·5—173°, and -2-*methyl*-2-*propyl*-*dioxolan*, b.p. 188—191°. $(CHMe)_2O$ and PrCHO yield 4 : 5-*dimethyl*-2-*propyldioxolan*, b.p. 155—157°, and with $COMe_2$, COMeEt, or COMePr the products are 2 : 2 : 4 : 5-tetramethyl-, 2 : 4 : 5-trimethyl-2-ethyl-, and 2 : 4 : 5-*trimethyl*-2-*propyl*-*dioxolan*, b.p. 161—163°. *iso*Butylene oxide and $COMe_2$ yield 2 : 2 : 4 : 4-*tetramethyldioxolan*, b.p. 109—110°. Hexene oxide and $COMe_2$, COMeEt, or COMePr similarly afford 2 : 2-dimethyl-, 2-*methyl*-2-*ethyl*-, b.p. 96—98°/25 mm., or 2-*methyl*-2-*propyl*-*benzdioxolan*, b.p. 111·5—113·5°/25 mm. R. T.

Splitting of pyrrolidine derivatives by cyanogen bromide. E. Ochiai and K. Tsuda (*J. Pharm. Soc. Japan*, 1936, **56**, 357—359).—*N*-Amylpyrrolidine and BrCN in C_6H_6 at 100° form *N*-*amylpyrrolidine bromocyanide*, b.p. 135°/0·016 mm., the non-basic reduction product of which (H_2–Pd–$CaCO_3$ in KOH–MeOH) when treated with 30% H_2SO_4 yields the *hydrochloride*, $C_9H_{22}NCl$, m.p. 285° (*Pt* salt, m.p. 179°; *Au* salt, m.p. 172°), of *N*-butylamylamine. Similarly, *N*-*iso*amylpyrrolidine gave *N*-butyl*iso*amylamine. Ch. Abs. (*c*)

Action of organometallic compounds on dimethylmaleic anhydride. D. S. Tarbell and C. Weaver (*J. Amer. Chem. Soc.*, 1940, **62**, 2747—2750).—(·CMe·CO)$_2$O and MgPhBr (2 mols.) in PhMe give *β-benzoyl-α-phenyl-α-methyl*-n-*butyric acid*, *forms*, (I) m.p. 185°, and (II) m.p. 113° (cf. A., 1938, II, 102). Either form with $SOCl_2$, followed by $NaNH_2$, gives 2-*keto*-3 : 5-*diphenyl*-3 : 4-*dimethyl*-2 : 3-*dihydropyrrole*, m.p. 67—69°, and, when distilled at 245—250°, gives 2-*keto*-3 : 5-*diphenyl*-3 : 4-*dimethyl*-2 : 3-*dihydrofuran* (III), m.p. 67—68°. Dissolution of (III) in NaOH and then acidification gives (I). Ozonisation of (III) gives 83% of BzOH. 78% of BzOH is obtained from (I) by boiling $K_2Cr_2O_7$–H_2SO_4–AcOH. Martin–Clemmensen reduction of (I) gives *αγ-diphenyl-α-methyl*iso*valeric acid*, m.p. 177—178°. COPh·CMe:CMe·CO_2H (IV) and MgPhBr (>2 mols.) in Et_2O give (I) and (II) (total 85·5%). (·CMe·CO)$_2$O is converted by ZnPhCl in boiling C_6H_6 into (IV) (83%) and by LiPh (2 mols.) in Et_2O into 2-*keto*-5 : 5-*diphenyl*-3 : 4-*dimethyl*-2 : 5-*dihydrofuran* (67·5%), m.p. 89—90° (with CrO_3 gives 72% of $COPh_2$), also obtained from (IV) by LiPh (2 mols.). R. S. C.

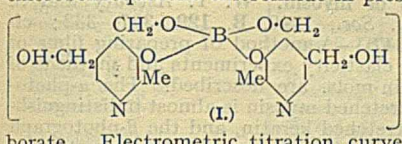
N-**Cyanomethylpyrrole and its Hoesch reaction.** E. Ochiai and S. Ikuma (*J. Pharm. Soc. Japan*, 1936, **56**, 379—381).—K pyrrole and CH_2Cl·CN in C_6H_6 give *N-cyanomethylpyrrole*, b.p. 84—87°/4 mm., which is hydrolysed to the amide (Clemo, A., 1931, 365) by H_2O at 120—130° and with HCl in Et_2O gives a *ketone*, C_6H_5ON or $C_{12}H_{10}O_2N_2$, m.p. 307—308° (semicarbazone, m.p. 273°) (structures suggested). Ch. Abs. (*c*)

Derivatives of pyrrolidine and piperidine. K. Tsuda (*J. Pharm. Soc. Japan*, 1936, **56**, 359—360).—2 : 6-Lutidine methiodide is converted into the methochloride with AgCl and then reduced (Pt–H_2 in AcOH at 2 atm.) to 1 : 2 : 6-*trimethylpiperidine*, b.p. 65—70°/55 mm. (*picrate*, m.p. 228°; *Au* salt, m.p. 162°). K 2-methylpyrrole and BuBr give 2-*methyl*-1-*butylpyrrole*, b.p. 110—115°/28 mm., which when reduced as above affords 2-*methyl*-1-*butylpyrrolidine*, b.p. 85—88°/57 mm. (*hydrochloride*, m.p. 168°; *methiodide*, m.p. 207°; *picrate*, m.p. 122°). Ch. Abs. (*c*)

Pyrimidines related to vitamin-B_1. I. New synthesis of 6-amino-2-methylpyrimidine-5-aldehyde. D. Price, (Miss)

E. L. May, and F. D. Pickel (*J. Amer. Chem. Soc.*, 1940, **62**, 2818—2820).—Addition of MeOH–H_2SO_4 to 6-*amino*-2-*methylpyrimidine*-5-*carboxylic acid* (prep. from the 5-CN-derivative by 10% KOH), m.p. 270—270·5° (decomp.) (*hydrochloride*, m.p. 238—239°), in conc. H_2SO_4 (no other method) gives the *Me* ester, m.p. 184—184·5° (*hydrochloride*, m.p. 181°), which with N_2H_4,H_2O in boiling aq. EtOH gives the *hydrazide*, m.p. 220—221° (decomp.). The *PhSO*$_2$ derivative, m.p. 228·5—229° (decomp.), thereof with Na_2CO_3 in $(CH_2{\cdot}OH)_2$ at 157—160° gives 6-amino-2-methylpyrimidine-5-aldehyde, m.p. 195—196° (lit. 192°) (p-$C_6H_4Me{\cdot}N$: derivative, m.p. 196—197°), hydrogenated (PtO_2; EtOH) to the alcohol (70%). 6-*Hydroxy*-2-*methylpyrimidine*-, m.p. 238°, and 4-*methylthiazole*-, m.p. 122°, -5-*acethydrazide* give no aldehyde. R. S. C.

Formation of vitamin-B_6–borate complex. J. V. Scudi, W. A. Bastedo, and T. J. Webb (*J. Biol. Chem.*, 1940, **136**, 399—406; cf. A., 1940, III, 514).—3-Hydroxy-2-methyl-5-hydroxymethyl-4-ethoxymethylpyridine and 3-hydroxy-2-methyl-4 : 5-oxidodimethylpyridine condense with 2 : 6-dichlorobenzoquinone chloroimide in presence of borate buffer.



(I.)

The shift in the absorption spectrum of vitamin-B_6 on passing from p_H 3 to 7·5 is eliminated by addition of borate. Electrometric titration curves of -B_6 and H_3BO_3 separately and together show that the complex contains 2 mols. of -B_6 to 1 of H_3BO_3. Formula (**I**) is proposed for the complex, which is as physiologically active as the vitamin, and is thermostable in neutral solution. A. Li.

Reduction of 1-acetyl-2-methylindolidine. E. Ochiai and E. Kobayashi (*J. Pharm. Soc. Japan*, 1936, **56**, 376—378).—Reduction of 1-acetyl-2-methylindolidine (H_2 at 2·3 atm., PtO_2 in AcOH) affords 2-methyl-1-ethylindolizidine, and a *compound*, $C_{11}H_{21}ON$, b.p. 102—103°/6 mm., probably 2-methyl-1-α-hydroxyethylindolizidine (*phenylurethane*, m.p. 137°; *acetate*, b.p. 110—111°/6 mm.). Ch. Abs. (*c*)

Preparation of 2-aldopolyhydroxyalkylbenziminazoles. S. Moore and K. P. Link (*J. Org. Chem.*, 1940, **5**, 637—643).—Direct oxidative condensation of aldo-monosaccharides with *o*-$C_6H_4(NH_2)_2$ gives low yields of benziminazole derivatives but if $Cu(OAc)_2$ is added the yield of galactobenziminazole increases to 40% whereas the results with glucose are poor. By effecting the reaction in dil. AcOH at 50° for 12 hr. the yield of glucobenziminazole (**I**) is raised to 25% but side reactions remain prominent. Concn. of the solution of an aldonic acid and a slight excess of *o*-$C_6H_4(NH_2)_2$ to a syrup in presence of HCl and H_3PO_4 at 135° gives 60—80% yields of aldobenziminazoles from arabonic, galactonic, gluconic, lyxonic, mannonic, and rhamnonic acid. Under these conditions xylonic acid does not give a benziminazole derivative with production of the *compound*, $C_{11}H_{16}O_5N_2$, m.p. 140—141° (*picrate*, m.p. 187—189°), but one equiv. of *o*-$C_6H_4(NH_2)_2$ reacts; at 180° in the presence of an acid catalyst (best $ZnCl_2$ and HCl) xylobenziminazole, m.p. 224°, is produced. The 2-aldopolyhydroxyalkylbenziminazoles are amphoteric compounds. H attached to *sec.* N is weakly acidic and aldobenziminazoles dissolve in excess of a strong base such as NaOH but not in aq. NH_3. They may be pptd. by CO_2 from solution in NaOH. Ammoniacal Ag, Cu, and Zn solutions cause the formation of insol. complex salts. In the absence of excess of aq. NH_3 the pptn. of aldobenziminazoles as Cu salts is quant. The *sec.* N can be alkylated. CH_2PhBr and (**I**) in aq. EtOH at 100° afford 1-*benzyl*-2-d-*glucopentahydroxyamylbenziminazole*, m.p. 188°, $[\alpha]_D^{25}$ +37·0°. The use of these compounds in the characterisation of carbohydrates is suggested. H. W.

Nucleic acid of rye ergot. II. M. Gatty-Kostyal and J. Tesarz (*Wiadom. Farm.*, 1936, **63**, 213—216, 229—233, 245—249; cf. A., 1934, 709).—Nucleic acid (**I**) from rye ergot contains P 8·30—8·46, N 14·63—15·47% (P : N = 1·75—1·84) and after twofold hydrolysis with H_2SO_4 and pptn. with Ag_2O, 10·87% of purine-N (10·12 N : 4 P). The isolation of adenine (*picrate*, m.p. 294° with decomp.), guanine (the sulphate gives the xanthine but not the Kossel test), cytosine [*picrate*, m.p. 265—266° (decomp.)], and uracil is described but xanthine and hypoxanthine could not be isolated in quantity. Of sugars only *d*-ribose and *d*-2-deoxyribose are present so that the constitutions of ergot-(**I**) and yeast-(**I**) are similar. Ch. Abs. (*c*)

Variation of the magnetic susceptibility of hæmin in various solvents.—See A., 1941, I, 33.

Morpholinomethyl ketones. J. P. Mason and S. D. Ross (*J. Amer. Chem. Soc.*, 1940, **62**, 2882—2883).—Morpholine (2 mols.) and the appropriate chloroketone (1 mol.) in Et_2O at room temp. give *morpholinoacetone*, b.p. 101—101·5°/14 mm. (*hydrochloride*, m.p. 183°; *picrate*, m.p. 145·5°), and α-*morpholinobutan*-β-*one*, b.p. 97—100°/9 mm. (*hydrochloride*, m.p. 171—172·5°; *picrate*, m.p. 127—129°). ω-*Morpholinoacetophenone*, m.p. 50—52° [hydrochloride, m.p. 212—214° (lit. 222—223°); *picrate*, m.p. 156—157°], and -p-*phenylacetophenone*, m.p. 113—114° (*hydrochloride*, m.p. 233—235°; *hydrobromide*, m.p. 233—234°; *picrate*, m.p. 160—162°), and p-*bromo*-ω-*morpholinoacetophenone*, m.p. 88·5—89° [*hydrochloride*, m.p. 218° (decomp.); *picrate*, m.p. 145—146°], are prepared by the method of Rubin *et al.* (A., 1940, II, 143). R. S. C.

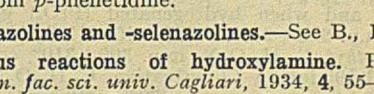
Tautomeric compounds. I. *iso*Oxazolone and oxazolone derivatives. A. E. Porai-Koschitz and N. V. Chromov (*J. Gen. Chem. Russ.*, 1940, **10**, 557—568).—OH·N:CMe·$CH_2{\cdot}CO_2Et$ (**I**) and Na at 80° give 3-methyl*iso*oxazolone (**II**), in 50% yield. In C_6H_6 or EtOH solution (**II**) exists only in the anhydride form, as 5′-hydroxy-3 : 3′-dimethyl-4′ : 5-di*iso*oxazolyl. Attempted condensation of (**II**) with aldehydes was unsuccessful. (**I**) and *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ (**III**) afford 4-p-*dimethylaminobenzylidene*-3-*methylisooxazolone* (**IV**), m.p. 203—204°, which in alkali gives p-*dimethylaminophenyldi*-(3-*methylisooxazolonyl*)*methane* (**V**) and (**III**); this reaction is reversed by acidifying. In acid solutions (**V**) yields (**IV**) and (**II**). A solution in Ac_2O of (**III**), hippuric acid, and NaOAc heated for 30 min. at 100° yields 2-p-*dimethylaminobenzylidene*-4-*phenyloxazolone*, m.p. 216·5—217°. R. T.

Metallation of phenoxthionine. H. Gilman, (Miss) M. W. van Ess, H. B. Willis, and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1940, **62**, 2606—2611).—Phenoxthionine (**I**) and LiBu^a in Et_2O give the 4-Li derivative, which with CO_2 gives *phenoxthionine*-4-*carboxylic acid* (**II**) (61%), m.p. 168—169° [10-*dioxide*, m.p. 183—184°; *Me* ester, m.p. 124°; *amide* (**III**), m.p. 185—186°; with Cu-bronze in quinoline at 200° gives (**I**)]. 4-*Aminophenoxthionine hydrochloride* [prep. from (**III**) by Br–NaOH etc. or from the Li derivative by NH_2OMe], m.p. 223—225° (decomp.), gives 4-chlorophenoxthionine 10-dioxide, proving the structure of (**II**). 2-Bromophenoxthionine and LiBu^a, followed by CO_2, give 52·3—63·7% (77—89·3% crude) of phenoxthionine-2-carboxylic acid, m.p. 260—265°. 4-Methylphenoxthionine 10-dioxide is stable to boiling, aq. $KMnO_4$–KOH. Dibenzfuran is metallated more readily than is dibenzthiophen by LiBu^a; the Li derivative of the latter metallates the former, but the reverse reaction does not occur. No ring-closure occurs with *o*-OPh·$C_6H_4{\cdot}CO_2H$, S, and $AlCl_3$. 3 : 2 : 1-$NH_2{\cdot}C_6H_3(OPh){\cdot}CO_2H$ (prep. from PhOK and 3 : 2 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}CO_2H$, followed by $SnCl_2$) does not give the sulphinic acid. Attempts to convert (**I**) into dibenzfuran by heating with catalysts failed. CaPhI converts (**I**) into a derivative, which with CO_2 gives phenoxthionine-*x*-carboxylic acid, m.p. 260—262°. R. S. C.

Preparation of substituted phenylenethiazthionium compounds. M. K. Bezzubetz and V. A. Ignatiuk-Maistrenko (*Prom. Org. Chim.*, 1940, **7**, 377—378).—A 2 : 3 *o*-$C_6H_4Me{\cdot}NH_2,HCl$–S_2Cl_2 mixture, heated at 55°, gives 6-chloro-4-methylphenylenethiazthionium chloride, in 65% yield. 6-Ethoxyphenylenethiazthionium chloride is prepared similarly from *p*-phenetidine. R. T.

Arylo-thiazolines and -selenazolines.—See B., 1941, II, 6.

Anomalous reactions of hydroxylamine. P. Dreyfuss (*Rend. semin. fac. sci. univ. Cagliari*, 1934, **4**, 55—58; *Chem. Zentr.*, 1935, ii, 46).—Formulæ, *e.g.*, *A*, are advanced for the



(*A.*)

products of interaction of NH_2OH with dibenzylidene*cyclo*hexanone (A., 1934, 773) and 4 : 5 : 4′ : 5′-tetramethoxy-2 : 2′-dibenzoylbenzophenone (Vorländer and Gärtner, A., 1899, i, 259). Ch. Abs. (*c*)

Cyanine dyes.—See B., 1941, II, 7, 8, and 27.

Δ^{α}-Norlupinene. K. Tsuda and J. Yokoyama (*J. Pharm. Soc. Japan*, 1936, **56**, 355—356).—The importance in alkaloid chemistry (*e.g.*, δ-coniceine, matrinidine) of reactions such as the ring-opening of Δ^{α}-picoline and its derivatives and further hydration and acetylation is emphasised. The reaction of α-norlupinine with MeMgI (A., 1936, 212) is paralleled by that of norlupenine. p-*Nitrobenzoyl*-Δ^{α}-1 : 3-*dimethylnorlupinene*, m.p. 95° (prep. described), is a δ-aminoketone (*semicarbazone*, m.p. 173°). Ch. Abs. (*c*)

Aconite alkaloids. III. Oxidation of aconitine and derivatives with nitric acid and chromic acid. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1940, **136**, 323—334; cf. A., 1939, II, 350).—Oxidation (HNO_3, *d* 1·42 or 1·2, at 100°) of aconitine (**I**), oxonitine (**II**), ketoaconitine (**III**), or aconitoline (**IV**) yields the neutral nitronitroso-derivative (**V**), $C_{28}H_{26}O_{10}N_3(OMe)_3$ (Suginome, A., 1938, II, 74; Lawson, A., 1936, 351). (**II**) and (**III**) with HNO_3 (*d* 1·42) at 25° give intermediate NO_2-derivatives, respectively $C_{32}H_{36}O_{13}N_2$ (or possibly $C_{33}H_{38}O_{13}N_2$), m.p. 288—289° (decomp. with previous darkening and sintering), converted by HNO_3 at 80° into (**V**), and $C_{33}H_{38}O_{13}N_2$, m.p. 180—190° to a resin, neither of which gives the Liebermann reaction. (**V**) is not affected by 4% MeOH–HCl at 100°, but with MeOH saturated at 0° with HCl, at 25°, yields a sec. *base*, $C_{31}H_{36}O_{12}N_2$, m.p. 252—253° (softening >245°) (cf. Lawson, *loc. cit.*), which reverts to (**V**) with HNO_2. (**I**) with HNO_2 gives a *NO*-derivative, $C_{34}H_{44}O_{13}N_2$, m.p. 281° (cf. Lawson, *loc. cit.*), which with HNO_3 (*d* 1·42) at 25° yields (**V**). (**IV**), proposed formula $C_{33}H_{41}O_{10}N$, which does not react with MeI, is hydrolysed (aq. EtOH–NaOEt) to a base, $C_{24}H_{35}O_8N$ (methiodide, m.p. 222—225°), identical with that obtained by oxidising aconine (Schulze, A., 1908, i, 560). A. Li.

Delphinine. III. Action of hydrochloric, nitric, and nitrous acids on delphinine and its derivatives. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1940, **136**, 303—321).—Delphinine (**I**) is not affected by 3·3% MeOH–HCl at 100° or by MeOH saturated at 0° with HCl, at room temp., but with MeOH at 100° loses AcOH giving *methylbenzoyldelphonine*, m.p. 173°, $[\alpha]_D^{25}$ +27° in 95% EtOH, oxidised ($KMnO_4$ in $COMe_2$) to methylbenzoyl-α-ketodelphonine (**II**), m.p. 221—223°, resolidifying and remelting at 236—237°, $[\alpha]_D^{25}$ −41·5° in MeOH. α-Ketodelphinine with HNO_3 (*d* 1·42) at 20—25° yields a *substance*, $C_{32}H_{41}O_{10}N$, m.p. 271—273° (decomp.), is not affected by MeOH at 130—140°, but with hot 3% MeOH–HCl (cf. A., 1939, II, 190, 350) yields (**II**) and an amorphous neutral *NO*-derivative, $C_{32}H_{42}O_{10}N_2$, m.p. 228—230°, and with MeOH saturated at 0° with HCl, at 25°, gives first a *Cl*-, $C_{32}H_{40}O_9NCl$, m.p. 242—243° (efferv.), $[\alpha]_D^{25}$ −60° in $CHCl_3$, and finally a Cl_2-derivative, $C_{32}H_{39}O_8NCl_2$ (?), m.p. 225—227° (efferv., previous sintering). The former yields with H_2–PtO_2 at 3 atm. pressure a *hexahydrobenzoyl* derivative, $C_{32}H_{46}O_9NCl$, m.p. 229° (efferv.), and with MeOH at 100°, a mixture containing a neutral substance, $C_{32}H_{39}O_9N$ (?), m.p. 282—284° (decomp.), and a base, $C_{32}H_{39}O_9N$, m.p. 218—220° (previous sintering) [NO-derivative, m.p. 236—238° (previous sintering)]. β-Ketodelphinine is not affected by HNO_3 (*d* 1·42) at 25°, or by MeOH saturated at 0° with HCl, at room temp., but with 4% MeOH–HCl at 100° yields *methylbenzoyl-β-ketodelphonine*, m.p. 182—185° (not sharp), $[\alpha]_D^{30}$ +27° in MeOH, unaffected by saturated MeOH–HCl at room temp. Pyro-α-ketodelphinine (**III**) yields, with aq. HCl (*d* 1·19), a *chloro*-, $C_{30}H_{36}O_7NCl$ (**IV**), m.p. 318—320° (previous darkening), and with MeOH saturated at 0° with HCl, at 20—25°, a Cl_2-derivative, $C_{29}H_{33}O_6NCl_2$ (discolours at >240°, sinters at 260—265°), which when boiled with MeOH yields the substance, $C_{31}H_{39}O_8N$, obtained (*loc. cit.*) by heating (**III**) with MeOH–HCl, and when hydrogenated (PtO_2) gives a H_6-derivative, m.p. 216—218°. (**III**) with HNO_3 (*d* 1·42) at 20° yields a *demethyl*, $C_{36}H_{37}O_8N$, m.p. 309—310°, converted by aq. HCl (*d* 1·19) into a *Cl*-derivative, $C_{30}H_{36}O_7NCl$ (sinters >242°, loses transparency >272°), different from (**IV**). (**III**) with HNO_3 (*d* 1·42) at 50° loses another OMe giving a *product*, $C_{28}H_{33}O_8N$ (?), m.p. 235—240° (sintering >200°). (**I**) with HNO_2 at 100° yields a *NO*-derivative, $C_{33}H_{44}O_{10}N_2$ [(N)Me 0·55%], m.p. 240—241° (decomp., previous sintering), and (chiefly) *hydroxydelphinine*, m.p. 180—182° (efferv.) (occasionally 193—195°), $[\alpha]_D^{20}$ +7° in EtOH, oxidised ($KMnO_4$ in $COMe_2$) to *γ-ketodelphinine*, m.p. 226—229°, $[\alpha]_D^{20}$ +40° in AcOH, which with 4·3% MeOH–HCl at 100° yields *methylbenzoyl-γ-ketodelphonine*, m.p. 184—188° (sinters at >140°), $[\alpha]_D^{30}$ +5° in MeOH. Both *benzoyldelphinine* (BzCl in C_5H_5N), m.p. 171—173°, and its oxidation product ($KMnO_4$ in $COMe_2$), *benzoylketodelphinine*, m.p. 185—187°, lose AcOH on heating. The significance of these results is discussed. A. Li.

Aminoanabasines. V. Aminomethylanabasines and their acyl derivatives. M. I. Kabatschnik and A. I. Zitzer (*J. Gen. Chem. Russ.*, 1940, **10**, 1007—1012).—*N*-Methylanabasine and $NaNH_2$ in $NPhMe_2$ (18 hr. at 120—150°) yield a mixture of 2-[2-N-*Ac*, m.p. 72—73°, and -Ac_2 derivative, b.p. 160—162°/4 mm. (+H_2O, m.p. 60·5—62·5°)], and 5-amino-3-(2′-*N*-methylpiperidyl)pyridine, m.p. 91·5—92·3° [*picrate*, m.p. 227·5—228° (decomp.); 5-N-*Ac*, m.p. 122—122·5°; 5-N-*propionyl*, m.p. 97—98°; 5-N-*Bz*, m.p. 104—106°; 5-N-Bz_2 derivative, m.p. 142—143°]. The toxicity and pharmacodynamic activity of the acylamino- is < that of aminomethylanabasines. R. T.

VII.—PROTEINS.

Molecular structure of myosin. W. T. Astbury and S. Dickinson (*Proc. Roy. Soc.*, 1940, **B**, **129**, 307—332; cf. Woods, A., 1938, I, 347).—A method of preparing films of myosin for *X*-ray and elasticity experiments and methods of orienting myosin chain-mols. are described. The α-photograph of oriented unstretched myosin is almost indistinguishable from that of unstretched keratin, and the β-photograph of stretched myosin is almost indistinguishable from that of stretched keratin, long-range elasticity in both substances depending on reversible intramol. transformation, and the fully extended β-form of the mol. being approx. twice as long as the folded α-form. The resemblance is not between myosin and normal keratin but between myosin and the labile supercontracting form of keratin in which cross-linkings (including S·S bridges) of the polypeptide grid are broken, and the selective orientation produced in moist myosin at room temp. is analogous to that produced in keratin only at higher temp. Similarly, myosin supercontracts in hot H_2O or cold dil. alkali without the preliminary stretching required by keratin. Supercontraction in myosin is due to disorientation of long thin units and, in addition, to folding of the polypeptide chain. An interpretation of the denaturation of myosin is given and it is suggested that the contraction of muscle depends on the supercontraction of its myosin. W. McC.

VIII.—ANALYSIS.

Apparatus for semi-microdetermination of carbon and hydrogen. C. Niemann and V. Danford (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 563—566).—The construction and operation of a furnace for the determination of C and H on 15—30-mg. samples are described in great detail. The normal Pregl combustion train is employed. J. D. R.

Micro-technique of organic qualitative analysis. Group tests for compounds of carbon, hydrogen, and oxygen. D. G. Foulke and F. Schneider (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 554—556).—Methods and procedure are outlined for carrying out the following tests: Fehling's test, osazone formation, the AcCl and $ZnCl_2$–HCl tests for alcohols, Br addition test for phenols, the phthalein fusion test for phenols (all carried out in capillary tubes), the $NaHSO_3$ test for ketones, the CHI_3 test, and the $AlCl_3$ test. Methods for determining *d* and solubility are indicated and detailed procedure is given for oxidation of side-chains and determination of sap. vals. on small quantities of material. J. D. R.

Determination of hydroxyl groups with Grignard reagent. W. Fuchs, N. H. Ishler, and A. G. Sandhoff (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 507—509).—A special apparatus designed for the determination of active H by the Zerevitinov method is described. It is specially suitable for occasional determinations and is simpler in design and operation than that of Kohler. The Grignard reagent is prepared in Bu^{α}_2O. J. D. R.

Effect of carbonyl derivatives as impurities in alcohols. B. J. Fontana and T. D. Stewart (*J. Amer. Chem. Soc.*, 1940, **62**, 2878—2879).—Dissociation of OH·CMe_2·CN in nine different alcohols has been studied. A method for estimating carbonyl impurities by calculation from their effects on the dissociation is outlined. W. R. A.

INDEX OF AUTHORS' NAMES, A., II.

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