BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

OCTOBER, 1938.

Chemical homology. J. K. Senior (J. Org. Chem., 1938, **3**, 1—10).—A discussion. Previous definitions of homology are unsatisfactory because of the attempt to limit the term only to useful and instructive cases. A general definition is proposed together with modifications which enable types of homology to be classified and any particular type to be designated. Suitable nomenclature is suggested. Illustrations of the system are given. H. G. M.

Large molecules in synthetic organic chemistry. G. O. Curme (J. Franklin Inst., 1938, **226**, 187—202).—A general account. K. W. P.

Detection of radicals in the chemical decomposition of alkyl iodides. R. van Tassel (Natuurwetensch. Tijds., 1938, **20**, 83—85).—C_2H_4 polymerises at 300° in presence of EtI and Hg vapour. The rate of polymerisation $\propto$ the concns. of C_2H_4 and EtI. S. C.

Reaction of oxygen atoms with methane. E. W. R. Steacie and N. A. D. Parlee (Canad. J. Res., 1938, **16**, **B**, 203—209).—O atoms (produced by a discharge-tube method) and CH_4 at 37—330° give CO and a smaller amount of CO_2, but no C_2H_6 or higher hydrocarbons. The activation energy is 8 kg.-cal. The reaction is thus: $O + CH_4 \rightarrow H_2O + CH_2$; $CH_2 + O \rightarrow CH_2O$; $CH_2 + 2O \rightarrow HCO_2H$; $CH_2O + O \rightarrow CO + H_2O$; $HCO_2H + O \rightarrow CO_2 + H_2O$. Formation of CH_2 must be slower than the oxidation of CH_2O and HCO_2H, as these products were not isolated. The reaction, $CH_2 + CH_4 \rightarrow C_2H_6$, must have an activation energy >11—12 kg.-cal. R. S. C.

Optically active aliphatic hydrocarbons. D. Duveen and J. Kenyon (Bull. Soc. chim., 1938, [v], **5**, 1120—1126).—*dl-n*-Propyl*sec.*-butylcarbinol, b.p. 70°/15 mm., obtained in 62% yield from $MgBu^{\beta}Cl$ and $Pr^{\alpha}CHO$, is transformed by *o*-$C_6H_4(CO)_2O$ in C_5H_5N at 60—70° into dl-n-*propyl*sec.-*butyl H phthalate*, m.p. 52°. This is resolved by brucine in $COMe_2$ into (+)-n-*propyl*sec.-*butylcarbinyl H phthalate*, m.p. 55°, $[\alpha]_{5461}$ +17·13° in C_5H_5N, +15·8° in $CHCl_3$, +19·9° in CS_2 (other vals. recorded) [*brucine* salt (I), m.p. 159° (decomp.)], hydrolysed (KOH) to (+)-n-*propyl*sec.-*butylcarbinol*, b.p. 70°/16 mm., $[\alpha]_{5461}$ +10·60°. Treatment of the alcohol with I and red P followed by Zn–Cu in Et_2O yields (+)-γ-methylheptane, b.p. 118°, $[\alpha]^{20}_{5461}$ +0·72°, which thus has been very extensively racemised during the final changes. Treatment of the mother-liquors from (I) by strychnine leads to (−)-n-*propyl*sec.-*butylcarbinyl H phthalate*, m.p. 51—52°, $[\alpha]_{5461}$ −17·2° in $CHCl_3$ (*strychnine* salt), whence (−)-n-*propyl*sec.-*butylcarbinol*, b.p. 70°/16 mm., $[\alpha]_{5461}$ −5·23°. *dl*-Ethyl*sec.*-butylcarbinol, b.p. 58—60°/15 mm., obtained in 65% yield from $MgBu^{\beta}Cl$ and EtCHO, yields isomeric *ethyl*sec.-*butylcarbinyl H phthalates*, m.p. 94—96° and 81—82°, respectively. The latter gives cryst. salts with brucine, strychnine, and quinidine by means of which it could not be resolved. The former is resolved by brucine in $COMe_2$ into (+)-*ethyl*sec.-*butylcarbinyl H phthalate*, m.p. 91—92°, $[\alpha]_{5461}$ −3·30° in CS_2 (*brucine* salt, m.p. 161—162°), and (−)-*ethyl*sec.-*butylcarbinyl H phthalate*, m.p. 91—93°, $[\alpha]_{5461}$ −3·6°. Resolution is effected more slowly through the quinidine salt. (−)-*Ethyl*sec.-*butylcarbinol*, b.p. 51°/14 mm., $[\alpha]^{20}_{5461}$ −0·67°, is transformed by $SOCl_2$ in light petroleum into *δ-chloro-γ-methylhexane*, b.p. 37°/15 mm., $[\alpha]^{20}_{5893}$ −1·19°. H. W.

Addition of hydrogen fluoride to the double linking. A. V. Grosse and C. B. Linn (J. Org. Chem., 1938, **3**, 26—32).—C_2H_4 when autoclaved with anhyd. HF at temp. between 0° and 90° and pressures between 10 and 20—25 atm. (depending on the temp.) gives EtF. The yield, based on the C_2H_4 reacting, increases at higher temp., and is >80% at 90° and 0% at −60°. By similar methods $CHMe{:}CH_2$ gives $Pr^{\beta}F$, in accord with Markovnikov's rule, and *cyclo*hexene gives *cyclo*hexyl fluoride, the yields diminishing with increasing temp. and prolongation of reaction time. The reaction is not catalytic and takes place as readily in paraffin as in metal vessels. Addition of 0·004—0·03 mol. of BF_3 per mol. of HF has no beneficial effect. In all cases polymerisation products were formed. *cyclo*Propane at 25° gives $Pr^{\alpha}F$ and a little $Pr^{\beta}F$. No reaction takes place between $CHMe{:}CH_2$ and 50% aq. HF at 25° during 18 hr. H. G. M.

Peroxide effect in the addition of reagents to unsaturated compounds. XIX. Addition of hydrogen bromide to trichloroethylene. M. S. Kharasch, J. A. Norton, and F. R. Mayo (J. Org. Chem., 1938, **3**, 48—54).—In presence of small amounts of $AlCl_3$ and of $FeCl_3$, HBr adds to $CHCl{:}CCl_2$ (I) giving *ααβ-trichloro-α-bromoethane*, b.p. 152°/760 mm., from which (I) is recovered by means of Zn in hot EtOH, or NaOPh–EtOH. No addition occurs in presence of antioxidants even after prolonged illumination. No addition of HI to (I) took place in an equimol. mixture in the dark or when illuminated, some $CHCl_2{\cdot}CH_2Cl$ and I being formed in the latter case. In presence of air and peroxides HBr adds to (I) giving $CHCl_2{\cdot}CHClBr$, the reaction being accelerated by light. H. G. M.

(A) Laboratory furnace and experimental equipment for, and (B) performance of the catalyst used in, the preparation of divinyl from

alcohol. (C) **Alcohols of the series C_5 and C_6,** (D) **aldehydes and ketones, and** (E) **piperylene and amylene in the products of catalytic decomposition of alcohols by the S. V. Lebedev method.** (F) **Utilisation of ψ-butylene obtained in divinyl synthesis from alcohol.** S. V. LEBEDEV [with N. Z. ANDREEV, J. A. GORIN, I. K. GORN, S. G. KIBIRKSHTIS, G. G. KOBLJANSKI, A. M. KOGAN, A. V. KOZLOVSKAJA, V. P. KRAUSE, M. A. KRUPUISHEV, I. A. LIVSCHITZ, O. M. NEIMARK, G. N. SIBIRJAKOVA, J. M. SLOBODIN, and I. A. VOLSHINSKI] (Trud. Gosud. Op. Zav. Sintet. Kautschuka, 1934, **B**, III, 7—16, 16—40, 41—44, 44—45, 50—68, 68—85).—(A) Laboratory and micro- (capacity 5 c.c. of EtOH) -furnaces and a furnace with reaction chambers of 1 m. length are described. EtOH is preheated to 400—525°, passed over the catalyst, the products are cooled, and uncondensed gases absorbed (*e.g.*, in turpentine). $(CH_2{:}CH)_2$ and ψ-C_4H_8 are recovered by fractionating the solution and removing MeCHO by passing through 50% aq. NaOH.

(B) The catalyst (composition not given), which is preferably of worm-like shape (diameter 1—3 mm.) and not compressed, consists of a dehydrogenating and a dehydrating substance (cf. B., 1930, 939). The furnace is of Cu or enamelled or Al-plated Fe; chambers of length 1 m. and 3 m. are compared. The unfavourable effect of Et_2O and H_2O, and the slightly favourable effect of 5—7% of MeCHO, are noted. Spent catalyst, which causes increase in the H_2, MeCHO, and BuOH yields, is regenerated by admitting air into the catalyst chamber.

(C) Normal primary saturated alcohols (C_{5-6}) are obtained.

(D) $COMe_2$, MeCHO, but-, croton-, valer-, hex-, and oct-aldehydes are obtained.

(E) The condensate from the prep. and the residues from the rectification of $(CH_2{:}CH)_2$ are rectified, the fractions of b.p. 30—45° isolated and united, and fractions of b.p. 35—37° and 37—40° collected. The diene and olefine (in each fraction) are brominated, the bromides separated, and piperylene and amylene regenerated. Condensation reactions are also described.

(F) ψ-C_4H_8 obtained as a by-product in the prep. of synthetic rubber from $(CH_2{:}CH)_2$ is treated in the liquid phase with 72—75% H_2SO_4 to yield 83% of $Bu^{\beta}OH$ and thence (with Ac_2O and fused NaOAc) $Bu^{\beta}OAc$. $(CH_2{:}CH)_2$ in ψ-C_4H_8 could be removed by Na but not by H_2SO_4. The use of Cu or Pb apparatus is recommended. CH. ABS. (*c*)

Acetylene and sulphuric acid. J. MILBAUER (Arh. Hemiju, 1938, **12**, 73—83).—Pure C_2H_2 reacts with conc. H_2SO_4, which is thereby coloured brown. The reaction is catalysed by $HgSO_4$, SeO_2, V_2O_5, Ag_2SO_4, and MoO_3, but not $CuSO_4$, and is retarded by $(NH_4)_2SO_4$. R. T.

Alkylacetylenes and their addition products. XXVI. Halogenation of Δ^{α}-hexinene in methanol. J. J. VERBANC and G. F. HENNION. **XXVII. Reactions of dialkoxyalkanes with alkinenylmagnesium bromides.** A. L. KRANZFELDER and R. R. VOGT. **XXVIII. Reactions of dialkylacetylenes.** E. A. BRIED and G. F. HENNION (J. Amer. Chem. Soc., 1938, **60**, 1711—1713, 1714—1716, 1717—1719; cf. A., 1938, II, 167).—XXVI. Cl_2 with $CH{:}CBu^{\alpha}$ in MeOH leads to addition of Cl_2 and MeOH. At 0—5° 20% of *αβ-dichloro-Δ^{α}-hexene* (I), b.p. 60—61°/34 mm., and 24% of *αα-dichloro-ββ-dimethoxyhexane* (II), b.p. 76—78°/2 mm., are formed by way of *α-chloro-β-methoxy-Δ^{α}-hexene* (III). At 25—30° 18% of (I), 35% of (II), and 37% of *αα-dichlorohexan-β-one* (IV), b.p. 64—66°/10 mm., are obtained. The (IV) arises by addition of Cl_2 to (III) and subsequent loss of MeCl (identified); its structure is proved by conversion by $Ca(OCl)_2$ into $CHCl_3$ and $Bu^{\alpha}CO_2H$. In CCl_4 only (I) (25% yield) and a polymeride are obtained. Br in MeOH gives 92·5% of *αβ-dibromo-Δ^{α}-hexene*, b.p. 89—91°/30 mm. $CCl{:}CBu^{\alpha}$ and Cl_2 in MeOH give 83% of *α-chloro-ββ-dimethoxyhexane*, b.p. 77—80°/14 mm., converted by p-$C_6H_4Me{\cdot}SO_3H$ into (III) (92·5% yield), b.p. 90—91°/65 mm., which with Cl_2 in MeOH at 25—30° gives 60% of (II) and with p-$C_6H_4Me{\cdot}SO_3H$ in aq. MeOH gives 82% of *α-chlorohexan-β-one*, b.p. 73—74°/20 mm. MeOCl is not concerned in these reactions, for which an electronic mechanism is suggested.

XXVII. $CHR(OR')_2$ with $CBu^{\alpha}{:}C{\cdot}MgBr$ gives, by elimination of $MgBr{\cdot}OR'$, *α-ethoxy-*, b.p. 90°/24 mm., and *α-propoxy-Δ^{β}-heptinene*, b.p. 61°/4 mm., *γ-ethoxy-Δ^{δ}-noninene* (V), b.p. 105°/25 mm., and *α-ethoxy-α-phenyl-Δ^{β}-heptinene* (VI), b.p. 115°/4 mm. $C_5H_{11}{\cdot}C{:}C{\cdot}MgBr$ and $CHMe(OEt)_2$ give *β-methoxy-Δ^{γ}-noninene*, b.p. 108°/40 mm. Similarly, $CBu^{\alpha}{:}C{\cdot}CHEt{\cdot}OEt$ and $CBu^{\alpha}{:}C{\cdot}MgBr$ give *η-ethoxy-$\Delta^{\epsilon 0}$-tridecadi-inene*, b.p. 121°/4 mm., whereas $CBu^{\alpha}{:}C{\cdot}CH(OMe)_2$ gives *η-methoxy-η-methyl-Δ^{ϵ}-undecinene*, b.p. 83°/4 mm. $CHMe(OEt)_2$ with $CH{:}C{\cdot}MgBr$ and $(:C{\cdot}MgBr)_2$ gives $CH{:}C{\cdot}CHMe{\cdot}OEt$ and $(:C{\cdot}CHMe{\cdot}OEt)_2$, respectively. $CHPh(OEt)_2$ and $CH{:}C{\cdot}MgBr$ give $CH{:}C{\cdot}CHPh{\cdot}OEt$. $CH_2(OPr)_2$ and $(:C{\cdot}MgBr)_2$ give $(:C{\cdot}CH_2{\cdot}OPr)_2$. The yields vary greatly according to the acetal used. The prep. of $CHEt(OEt)_2$, b.p. 122—123°, and $CHMe(OEt)_2$ is modified. Addition of EtOH to $CH{:}CBu^{\alpha}$ and HgO–BF_3 gives *αα-diethoxy-Δ^{β}-heptinene*, b.p. 97—98°/10 mm. $C_5H_{11}{\cdot}C{:}CNa$ (prep. by $NaNH_2$ in liquid NH_3) and $CHMe(OEt)_2$ give β-ethoxy-Δ^{γ}-noninene, b.p. 108°/40 mm. $CBu^{\alpha}{:}C{\cdot}CH(OEt)_2$ with MgEtBr and MgPhBr gives (V) and (VI), respectively, which proves the structure of the products.

XXVIII. Good yields of dialkylacetylenes are obtained from $CH{:}CNa$, $NaNH_2$, and RCl in liquid NH_3 only if R has a moderate mol. wt. The yield of *Δ^{ι}-octadecinene*, b.p. 163—164°/7 mm., is increased from 15 to 27% by 8 atm. pressure. *Δ^{η}-Tetradecinene*, b.p. 124°/15 mm., is prepared in 38% yield. $C_{10}H_{21}Br$ gives $CH{:}C{\cdot}C_{10}H_{21}$ and $C_{10}H_{21}{\cdot}NH_2$. $(:CBu^{\alpha})_2$ with H_2–Raney Ni at 3·7—1·3 atm. gives n-$C_{10}H_{22}$, with Br–$CHCl_3$ gives *dibromide* fractions, b.p. 123—124°/17 mm. and 127—128°/17 mm., with $Pr^{\beta}OH$ (Hg catalyst) at 80° gives *decan-ε-one*, b.p. 106—108°/27 mm., with MeOH–HgO–BF_3–$CCl_3{\cdot}CO_2H$ gives impure *εε-dimethoxydecane*, b.p. 98—99°/10 mm., with AcOH (Hg catalyst) gives *ε-acetoxy-Δ^{ϵ}-decene*, b.p. 95—97°/10 mm., and with $(CH_2{\cdot}OH)_2$ (Hg catalyst) gives *2-butyl-2-n-amyl-1 : 3-dioxacyclopentane* [*-dioxolane*], b.p. 103—105°/10 mm. $(CNS)_2$ in C_6H_6 with $(:CPh)_2$ gives a cryst., m.p. 192—

193°, and with $(:C\cdot C_8H_{17})_2$ an amorphous product, but $(:CBu^{\alpha})_2$ does not react. R. S. C.

Pinacols of pinacolin. H. J. Backer (Rec. trav. chim., 1938, **57**, 967—988; cf. Delacre, A., 1907, i, 579).—$(Bu^{\gamma}CO)_2$ with MgMeI in Et_2O, followed by hydrolysis, gives only *ββγεε-pentamethylhexan-γ-ol-δ-one*, m.p. 60°, but with excess of MgMeI in PhMe yields a *pinacol* (I) of pinacolin, m.p. 69°. Reduction of pinacolin with Na + H_2O in Et_2O yields a solid, m.p. 73·5—74·5°, which with HCl gives an isomeric *pinacol* (II), m.p. 88°. Measurements of the rates of oxidation (to pinacolin) by $Pb(OAc)_4$ in AcOH, and by $(EtCO_2)_4Pb$ in PrOH, and of the m.p. of mixtures of (I) and (II) show that the solid, m.p. 74·5°, is a mixture of (I) and (II) in the ratio 2 : 3. (II) is more stable to HCl than (I), but both (I) and (II) with dil. H_2SO_4 give pinacolin, $CMe_2{:}CMe_2$, and *βγ-di-tert.*-butylbutadiene [also obtained by the action of PCl_3 on (I) or (II)] (identified as the dibromide). With p-$NO_2\cdot C_6H_4\cdot CHO$ and HCl, (I) gives an *acetal*, m.p. 139—140°, but (II) does not react. It is concluded that (I) is the *dl*- and (II) the *meso*-form, the difference in properties being due to the large Bu^{γ} groups. A by-product in the reduction of pinacolin is $CMeBu^{\gamma}{:}CH\cdot COBu^{\gamma}$, identified by reduction [$Al(OPr^{\beta})_3$], dehydration, and treatment with SO_2 in Et_2O, giving the sulphone of $CHBu^{\gamma}{:}CH\cdot CBu^{\gamma}{:}CH_2$. A. Li.

Determination of the degree of unsaturation of the higher alcohols. V. G. Schaposchnikov and N. A. Kalinitscheva (Trud. Gosud. Op. Zav. Sintet. Kautschuka, 1934, **B**, III, 110—117).—Analyses were carried out by hydrogenation, with Pt and Ni catalysts, and by the Rosenmund Br titrimetric method (cf. A., 1923, ii, 886; B., 1924, 23). Ch. Abs. (*e*)

Isolation of the intermediate product in the catalytic isomerisation of dipropenyl glycol. L. Martineau and J. Wiemann (Compt. rend., 1938, **207**, 243—245).—Dipropenyl glycol at 130° in presence of Cu deposited on Th affords dibutyryl (I) (50% yield), b.p. 65°/17 mm. At 110°, besides (I), *ε-hydroxy-δ-keto-Δ$^{\alpha\zeta}$-octadiene* (II), b.p. 91°/13 mm. (30—40% yield), is formed. The Raman spectrum of (II) shows lines due to two double linkings, one propenyl, the other terminal. J. L. D.

Fission of βε-dimethyl-Δ$^{\gamma}$-hexine-βε-diol. A. T. Babajan (J. Gen. Chem. Russ., 1938, **8**, 578—580).—$(OH\cdot CMe_2\cdot C{:})_2$ yields $OH\cdot CMe_2\cdot C{:}CH$ and $COMe_2$ when distilled from CaC_2, C_2H_2 and $COMe_2$ when distilled from K, and $COMe_2$ and H_2O when heated with $CaCO_3$. R. T.

Condensation products of glycerol and halogeno- and hydroxy-ketones. V. V. Evlampiev and V. M. Zoroastrova (Utschen. Zap. Univ. Kazan, 1937, **97**, No. 8, 71—82).—By shaking glycerol with $COMe\cdot CH_2X$ in presence of HCl and Na_2SO_4 or $ZnCl_2$ the following cyclo*acetals*, $OH\cdot CH_2\cdot CH(-O-CH_2\cdot O>)CMe\cdot CH_2X$, were prepared: X = Cl, b.p. 127—129°/14—15 mm.; X = Br, b.p. 134—135°/14—15 mm.; X = I, b.p. 139—141°/13 mm. (decomp.); X = OAc, b.p. 148—149°/11 mm.; with aq. $Ca(OH)_2$ it forms the *compound* X = OH, b.p. 153—154°/13 mm. J. J. B.

Compounds of bivalent carbon. H. Scheibler (Congr. int. Quim. pura apl., 1934, **9**, IV, 250—254; Chem. Zentr., 1936, ii, 2695).—Compounds (*e.g.*, Na hydroxyethoxymethylene; cf. A., 1934, 390) and $C^{II}(OR)_2$ (*e.g.*, the acetals of CO; cf. A., 1936, 312; 67; 1933, 491) must contain C^{II}. A. H. C.

Rearrangement of vinyl allyl ethers. C. D. Hurd and M. A. Pollack (J. Amer. Chem. Soc., 1938, **60**, 1905—1911).—The change, $CH_2{:}CR\cdot O\cdot CH_2\cdot CH{:}CH_2 \rightarrow CH_2{:}CH\cdot[CH_2]_2\cdot CRO$, by pyrolysis, analogous to the arrangement of Ph allyl ethers, is realised. *Vinyl allyl ether* (I), b.p. 65—65·2°/733 mm., is best (51%) obtained from *β-bromoethyl allyl ether* (II), b.p. 68·5—69°/36 mm., and powdered KOH at 110—174°; a 12—19% yield is obtained from *αα-diallyloxyethane* (III), b.p. 148—149°/753 mm., and P_2O_5 in $NPhMe_2$ or quinoline, and a trace by p-$C_6H_4Me\cdot SO_3H$; a trace is obtained by the action of Zn dust (not Na) at 148° on *ββ-diallyloxyethyl bromide*, b.p. 102—104°/23 mm. [prep. in 26·4% yield from $CH_2Br\cdot CHO$, $CH_2{:}CH\cdot CH_2\cdot OH$ (IV), and a little H_2SO_4]. 62—68% of (III) is obtained from MeCHO, (IV), and $CaCl_2$ at 0°. $OH\cdot[CH_2]_2\cdot ONa$ and $CH_2{:}CH\cdot CH_2Br$ at 100° give 77—81% of *β-hydroxyethyl allyl ether*, b.p. 63—64°/18—19 mm., which with PBr_3 in EtOH–C_5H_5N gives 45% of (II). $CH(OEt)_3$, $COMe_2$, and a little p-$C_6H_4Me\cdot SO_3H$ in hot, abs. EtOH give 75% of *ββ-diethoxypropane*, b.p. 113—115°, which with (IV) and a little p-$C_6H_4Me\cdot SO_3H$ gives 38% of *ββ-diallyloxy-* (V), b.p. 61°/26 mm., and 12% of *β-ethoxy-β-allyl-propane* (VI), b.p. 43—45°/26 mm. When heated with a little p-$C_6H_4Me\cdot SO_3H$, (V) gives *allyl isopropenyl ether* (VII), b.p. 87·5—88°/745 mm., also obtained similarly in poor yield from (VI). $CH_2Br\cdot CHO$, $(CH_2Br\cdot CHO)_3$, (IV), and HCl at 0° give 62% of α-chloro-β-bromoethyl allyl ether, which with MgPhBr in Et_2O at 0° gives *β-bromo-α-phenylethyl allyl ether*, b.p. 129—130°/12 mm. (with some Ph_2), converted by distillation with powdered KOH into *α-phenylvinyl allyl ether* [*α-allyloxystyrene*] (VIII) (25% yield), b.p. 104—105°/12 mm. With HCl–EtOH (I), (VII), and (VIII) give readily MeCHO, $COMe_2$, and COPhMe, respectively. In boiling Ph_2O (252—255°; not at 215—218°) (I) gives 50% of Δ$^{\gamma}$-*pentenal*, b.p. 103—104°/749 mm. (dimedone *compound*, m.p. 98°), identified by conversion by O_3–Ag_2O into HCO_2H and $CO_2H\cdot[CH_2]_2\cdot CO_2H$. (VII) gives $CH_2{:}CH\cdot[CH_2]_2\cdot COMe$ quantitatively at 255°, and some change occurs at 200°. (VIII) gives $CH_2{:}CH\cdot[CH_2]_2\cdot COPh$ readily at the b.p./760 mm., and some change occurs at 175°. The effect of α-substituents in the vinyl group is thus marked. R. S. C.

Conjugated systems. VII. Synthesis and properties of βγ-halide ethers from butadiene. A. A. Petrov (J. Gen. Chem. Russ., 1938, **8**, 487—497).—$(CH_2{:}CH)_2$ in a no. of alcohols and $PhSO_2\cdot NBr_2$ were shaken at −12°; the resulting ethers extracted with Et_2O and treated with Cl_2 or Br in $CHCl_3$ yielded the ethers $CH_2Br\cdot CH(OR)\cdot CHCl\cdot CH_2Cl$ (R = *Me*, b.p. 97—97·5°/10 mm.; R = *Et*, b.p. 104—104·5°/10 mm.; R = Bu^{α}, b.p. 130°/10 mm.; R = CH_2Bu^{β}, b.p.

134—135°/10 mm.) or $CH_2Br{\cdot}CH(OR){\cdot}CHBr{\cdot}CH_2Br$ (R = *H*, b.p. 141—141·5°/10 mm.; R = *Me*, b.p. 120·5°/10 mm.; R = *Et*, b.p. 127°/10 mm.; R = *Pr*$^{\alpha}$, b.p. 137°/10 mm.; R = *Bu*$^{\alpha}$, b.p. 146—146·5°/10 mm.; R = *Bu*$^{\beta}$, b.p. 143·5—145°/10 mm.; R = CH_2Bu^{β}, b.p. 154·5°/10 mm.). The ethers were boiled with KOH in EtOH in presence of quinol, to yield the *ethers* $CH_2{:}C(OR){\cdot}CX{:}CH_2$ (R = Me, X = Cl, b.p. 64—67°/103 mm., X = Br, b.p. 48·5—49·5°/24 mm.; R = Et, X = Cl, b.p. 75—77°/86 mm., X = Br, b.p. 63·5—64°/24 mm.; R = Bu$^{\alpha}$, X = Cl, b.p. 66·5—67°/12 mm.; R = Bu$^{\beta}$, X = Br, b.p. 65·5—66°/10 mm.; R = CH_2Bu^{β}, X = Cl, b.p. 76·5—77°, X = Br, b.p. 87·5°/12 mm.). These ethers readily polymerise, to yield resinous and rubber-like products, and are converted by dil. aq. H_2SO_4 into *γ-chloro-*, b.p. 38·5°/30 mm., or *γ-bromo-*Δ^{γ}*-buten-*β*-one*, b.p. 38·5—39°/12 mm. R. T.

Benzyl*iso*thiocarbamide and its application to the identification of organic acids. S. Veibel and H. Lillelund (Bull. Soc. chim., 1938, [v], **5**, 1153—1158).—Benzyl*iso*thiocarbamide hydrochloride, (I), obtained in 92% yield from $CS(NH_2)_2$ and CH_2PhCl in boiling EtOH–H_2O, exists in two polymorphous modifications, m.p. 150—151° and 175—176°, respectively. Identical salts are obtained from each variety. For identification the acid is dissolved in 10 c.c. or the requisite amount of H_2O and the solution is neutralised to methyl-red with NaOH and then made slightly acid with HCl. The solution of (I) in H_2O is added and the mixture is kept at 0° until crystallisation is complete. It is crystallised from EtOH or EtOH–H_2O. The following normal salts of benzyl*iso*thiocarbamide are described: *formate*, m.p. 150—151°; *acetate* (+1H_2O), m.p. 135—136°; *propionate*, m.p. 151—152°; *glycollate*, m.p. 146—147°; *oxalate*, decomp. 195—196° when slowly heated, 203° when placed in bath preheated at 198°; *ethylmalonate* (+2H_2O), m.p. 120—121°; *fumarate* (+1H_2O), decomp. 182—183°; *benzene*-o-*disulphonate*, decomp. 205—206°. The following *H salts* are described: *malonate*, decomp. 145—146°; *maleate*, decomp. 173—174°; *benzoate*, m.p. 166·5—167·5°; *cinnamate*, m.p. 178—179°; o-*bromobenzoate*, m.p. 170—171°; *salicylate*, m.p. 147—148°; *anisate*, m.p. 184—185°; *anthranilate*, m.p. 142—143°; *amygdalate*, m.p. 164—165°; *benzenesulphonate*, m.p. 148—149°; o-, m.p. 170—171°, and p-, m.p. 182—183°, *-toluenesulphonate*; *sulphosalicylate* (1 : 2 : 3), m.p. 203—204°; *sulphanilate*, m.p. 187—188°; *benzene*-m-*disulphonate*, m.p. 163—164°. H. W.

Kinetics of the reaction between benzyl chloride and formic acid.—See A., 1938, I, 463.

Stability of formic acid dimer. E. A. Moelwyn-Hughes (J.C.S., 1938, 1243).—Calculation of the contribution of the dipole–dipole interaction to the energy of formation of the H bonds in HCO_2H dimer gives vals. sufficiently close to the observed val. (cf. A., 1928, 1084) to show the importance of electrostatic effects for the stability of this intermol. complex. H. G. M.

Free acetyl. G. Semerano (Gazzetta, 1938, **68**, 343—352).—Electrolytic reduction of Ac_2 at the dropping Hg cathode is normal in strongly acid systems; the current–potential graph is consistent with the mechanism $Ac_2 + H \rightarrow COMe{\cdot}CMe{\cdot}OH$ ($\rightarrow$ the pinacol). In neutral or feebly acid systems, however, two diffusion waves are shown, in which the second corresponds with reduction of MeCHO, presumably formed by the mechanism $Ac_2 + H \rightarrow MeCHO + Ac$ ($\rightarrow Ac_2$). It is suggested that free Ac is formed at the Hg surface (by dissociation of Ac_2), and then reduced. E. W. W.

Preparation of anhydrous acetates. M. R. Adams and A. W. Davidson (Trans. Kansas Acad. Sci., 1935, **38**, 129—130).—Anhyd. acetates (*e.g.*, of Al, Zn, Cu, Fe) are prepared by electrolysing a solution of an alkali or alkaline-earth acetate in AcOH (*e.g.*, 10% NaOAc in AcOH) with an anode of the appropriate (activated) metal. Ch. Abs. (*c*)

General method of testing ethyl acetate. A. Bohanes (Chem. Obzor, 1936, **11**, 71—73; Chem. Zentr., 1936, ii, 2761).—20 g. of ester are hydrolysed by 2N aq. KOH overnight or with warming and excess of KOH is titrated. EtOH is determined in the distillate. A. H. C.

(A) Synthesis and (B) relative velocities of hydrogenation of esters of oleic and elaidic acids. A. K. Plisov and U. P. Golendeev (Rep. U.S.S.R. Fat and Margarine Inst., 1935, No. 2, 3—11, 12—21).—(A) The following esters are described: *Pr*, b.p. 216—220°/14 mm., *Pr*$^{\beta}$, b.p. 215—217°/14—15 mm., *Bu*, b.p. 223—227°/14—15 m., *Bu*$^{\beta}$, b.p. 220—224°/12—13 mm., and *allyl*, b.p. 218—221°/12—13 mm., *oleate*; *Bu*, b.p. 224—227°/14 mm., *Bu*$^{\beta}$, b.p. 222—226°/12—13 mm., and *allyl*, b.p. 215—220°/13—15 mm., *elaidate*. Oxides of N (but not H_2SO_4) effect the oleic–elaidic change.

(B) Oleic esters are slightly more readily reduced (Pd) and are therefore presumed to have the *cis* configuration. Ch. Abs. (*c*)

Catalytic hydrogenation under reduced pressure. I. Hydrogenation under reduced pressure of arachis oil and of *p*-toluquinoline. R. Escourrou (Bull. Soc. chim., 1938, [v], **5**, 1184—1200).—Hydrogenation (Raney Ni on pumice) at 350°/55 mm. of arachis oil gives white fumes and a product which solidifies when cooled and contains stearic and oleic acid. At 300°/55 mm. decomp. is also observed. At about 220°/50 mm. there is no marked change but the condensible products have a strong fluorescence. Treatment at 180—190°/35 mm. results in improved odour, diminution of the I val., and constancy of the CNS val. showing thus the transformation of linoleic acid or its isomeride into oleic acid. It is therefore possible to remove those components of the oil which are least digestible and tend most strongly to become rancid without affecting the essential characteristics. Hydrogenation (Rancy Ni on pumice) of 6-methylquinoline at 260°/atm. pressure is accompanied by some fission with production of NH_3 and gives mainly 6-methyl-tetra- (I) with some -deca- (II) -hydroquinoline. At 250°/40 mm. there is no trace of fission and very little (II) is formed whilst at 200°/15 mm. the sole product is (I). Ag–pumice is a much less active catalyst and (II) is never produced in its presence. There is scarcely

any fixation of H_2 in a vac. or at atm. pressure. At 400° traces of indole derivatives are formed. In presence of Pt–pumice (I) is formed exclusively; (II) is not formed at 200°/atm. pressure. H. W.

Reaction between ethyl acetoacetate and diazomethane. F. ARNDT, L. LOEWE, T. SEVERGE, and I. TÜREGÜN (Ber., 1938, **71**, [*B*], 1640—1644).—In the complete absence of OH-compounds reaction between $CH_2Ac{\cdot}CO_2Et$ and CH_2N_2 occurs very slowly. In presence of MeOH a product is obtained the % composition of which accords with that of $OMe{\cdot}CMe{:}CH{\cdot}CO_2Et$ but it has a low OMe content. The isomeric impurity cannot be $CHMeAc{\cdot}CO_2Et$ since the product gives no reaction with $FeCl_3$ and gives solely $COMe_2$ when hydrolysed. It is identified as the oxide $\begin{matrix}O\text{—}\\CH_2\end{matrix}\!>\!CMe{\cdot}CH_2{\cdot}CO_2Et$, since treatment of the crude product with HCl and subsequent fractionation gives the *chlorohydrin*, $C_8H_{15}O_3Cl$, b.p. 75°/1 mm. H. W.

Photochemical decomposition of *l*-ascorbic acid. A. E. KELLIE and S. S. ZILVA (Biochem. J., 1938, **32**, 1561—1565).—Light from a Hg-vapour lamp causes the anaërobic decomp. of *l*-ascorbic acid (I) but not that of dehydroascorbic acid (III) in phosphate buffer solution in quartz-distilled H_2O at p_H 7. In the presence of O_2, (I) decomposed more rapidly with ultra-violet than with visible light, particularly when a sensitiser such as methylene-blue or lactoflavin was added, formation of (II) coinciding with the disappearance of (I). In the anaërobic decomp. of (II), formation of (II) or stimulation of photochemical change by sensitisers could not be detected. Acidity retards both aërobic and anaërobic decomp. of (I) by ultra-violet light. T. F. D.

Ketol condensation of β-keto-esters with acyclic aldehydes. H. GAULT (Congr. int. Quim. pura apl., 1934, **9**, IV, 352—359; Chem. Zentr., 1936, ii, 3295).—Reactions of $CH_2Ac{\cdot}CO_2Et$ with acyclic aldehydes are reviewed (cf. A., 1934, 1332). Following Gault and Wendling (A., 1935, 65; 1936, 706; cf. A., 1936, 590), 30% aq. MeCHO and $CHMeAc{\cdot}CO_2Et$ yield after shaking for 8 hr. with K_2CO_3 Et methyl-α-hydroxyethylacetoacetate, b.p. 118—120°/14 mm. A. H. C.

Chloral derivatives of lævulic acid. H. W. COLES (J. Amer. Pharm. Assoc., 1938, **27**, 477—480).—Lævulic acid (1 mol.) and chloral (1 mol.) in presence of NaOAc (1 mol.) at 100° for 4 hr. yield *β-chloral-lævulic acid* [*γ-keto-β-β′β′β′-trichloroethylidene-n-valeric acid*], m.p. 113·5° (*p-nitrophenylhydrazone*, m.p. 182°; *semicarbazone*, m.p. 205·5—206°; *p-bromophenylhydrazone*, m.p. 161°; *β-naphthylhydrazone*, m.p. 188—189°; *phenylhydrazone*, m.p. 174·5°; *oxime*, m.p. 103—104°; *thiosemicarbazone*, m.p. 177—177·5°), having no toxic or hypnotic action in rats. All m.p. are corr. F. O. H.

Oxidation of drying oils and cognate substances. IV. Properties of the ketol grouping. R. S. MORRELL and E. O. PHILLIPS (J.S.C.I., 1938, **57**, 245—247).—The equilibrium mixture of θ-hydroxy-ι-ketostearic acid (I) and ι-hydroxy-θ-ketostearic acid (II) in KOH–EtOH (cf. King, A., 1937, II, 48) with O_2 gives nonoic and azelaic acids quantitatively. Oxidation is less complete in 40% aq. KOH. 40% methylation of the ·CH(OH)· in (I), but practically none in the case of (II), occurs with HCl in MeOH. Me_2SO_4 followed by CH_2N_2 produces >50% methylation of the ketol group in (I) owing to tautomeric change. The methylation products of (I) and (II) are relatively stable to O_2 (25% oxidation in KOH–EtOH. Etherification with $(CH_2{\cdot}OH)_2$ gives similar results. *θι-Diketostearic acid semicarbazone*, m.p. 216° (decomp.), and *p-bromophenacyl nonoate*, m.p. 64·5°, are recorded.

Thermal decomposition of oxalates. I. Formation of peroxides by the thermal decomposition of oxalates in a vacuum. P. L. GÜNTHER and H. REHAAG (Ber., 1938, **71**, [*B*], 1771—1777).—It is shown in the instance of $Nd_2(C_2O_4)_3$ that the thermal decomp. of oxalates in a vac. can lead to true peroxides which can be formally represented by the elimination of two mols. of CO from one C_2O_4 group per mol. $Nd_2(C_2O_4)_3$ thus affords Nd peroxydioxalate in 100% yield. The formation of peroxides from the oxalates of Na, Ca, Ba, and Th is established qualitatively. The production of CO_2 during thermal decomp. is due to the secondary reaction, $2CO \rightarrow CO_2 + C$. The C gives a colloidal solution when the residue from the decomp. is treated with a suitable medium. The properties of such solutions are discussed. H. W.

Maleic acid production: vapour-phase oxidation of five-carbon olefinic acids. W. L. FAITH and M. F. YANTZI (J. Amer. Chem. Soc., 1938, **60**, 1988—1989).—Passage of $CHEt{:}CH{\cdot}CO_2H$ or $CHMe{:}CH{\cdot}CO_2Et$ with air over V_2O_5 on Al at 71·1° gives up to 38·8 and 42·2%, respectively, of maleic acid (I) and CO_2; other acids and aldehydes are also formed. Tiglic acid at 80·3° gives no (I). R. S. C.

Racemisation during esterification by diazomethane. E. BERGMANN and Y. SPRINZAK (J. Amer. Chem. Soc., 1938, **60**, 1998—1999).—(−)-$CO_2H{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H$ and CH_2N_2 in Et_2O give the *dl*-ester. The acid is not racemised by Et_2O–MeOH, nor the (−)-ester by CH_2N_2. R. S. C.

Mechanism of the cleavage of ethyl αα′-dibromoadipate by diethylamine. R. C. FUSON and W. E. LUNDQUIST (J. Amer. Chem. Soc., 1938, **60**, 1889—1893).—Cleavage of *meso*-$(CH_2{\cdot}CHBr{\cdot}CO_2Et)_2$ (I) by *sec.* bases is best explained as occurring by way of αδ-diradicals; its occurrence depends greatly on the solvent used. Et_2 Δ^1-*cyclo*butene-1 : 2-dicarboxylate and $NHEt_2$ in abs. EtOH at 100° gives *Et*$_2$ 1-*diethylamino*cyclo*butane*-1 : 2-*dicarboxylate*, b.p. 100—101°/2 mm. (*picrate*, m.p. 125—130·5°), which is too stable to be an intermediate in the cleavage referred to. NH_2Et and (I) in C_6H_6 at 100° give *Et*$_2$ 1-*ethylpyrrolidine*-2 : 5-*dicarboxylate* (II), b.p. 108—109°/2 mm. (*platinichloride*, m.p. 132·5—135·5°). In EtOH (I) and $NHEt_2$ give 27% of (II), no cleavage occurring; in $COMe_2$ some, and in C_6H_6 mainly, cleavage occurs. $NHMe_2$ and (I) give 35% of $NMe\!<\!\begin{matrix}CH(CO_2Et){\cdot}CH_2\\CH(CO_2Et){\cdot}CH_2\end{matrix}\!>$, b.p. 114—115°/4 mm. R. S. C.

Catalytic decarboxylation of β-keto-acids. S. KANEKO (J. Biochem. Japan, 1938, **28**, 1—18).—Spontaneous decarboxylation (at 37°) of hydroxyfumaric acid (I) at p_H 4·2 is > that at p_H 1·7. Decarboxylation of (I) and hydroxymaleic acid (II) at 0° is catalysed by NH_2Ph, the optimum p_H being approx. 5·0 and 4·2, respectively. Data for the catalytic action of various org. bases on the decarboxylation of (I) and (II) at 0° and p_H 4·2—4·3 are tabulated. With (I), 4-aminoantipyrine (which also catalyses decarboxylation of $CH_2Ac{\cdot}CO_2H$) has the greatest catalytic action (optimum p_H 3·6—5·0), the catalysis being partly inhibitied by $AcCO_2H$. F. O. H.

Typical examples of applications of polarimetry in chemistry. M. PARISELLE (Congr. int. Quim. pura apl., 1934, **9**, II, 415—427; Chem. Zentr., 1936, ii, 2328).—The formation of *ferritartaric acid* (I), $C_4H_3O_6Fe$, from tartaric acid and $Fe(NO_3)_3$ is indicated by [α], which is max. for equimol. mixtures. The reaction is reversible but (I) is obtained on neutralising free HNO_3 as an ochre-yellow ppt. yielding a Na_1 salt. *Salts* $(C_4H_4O_6Na_3)Fe$ and $(C_4H_3O_6Na_2)_3Fe$ are also formed. Narcotine and hydrastine are lævorotatory in neutral, dextro- in acid or alkaline, solution. A. H. C.

Rare-earth tartrates with antimonyl and potassium chloride.—See A., 1938, I, 501.

Synthesis of *dl*-xylomethylonic acid. O. WICHTERLE (Coll. Czech. Chem. Comm., 1938, 253—258).—Oxidation ($KMnO_4$ at 0°) of *dl*-Ca α-hydroxy-Δ^{β}-pentenoate and acidification yields *dl*-xylomethylonic acid (*brucine* salt, m.p. 183—184°, $[\alpha]_D^{20}$ −25·8° in H_2O) which readily lactonises on evaporation, and is oxidised (HNO_3) to *dl*-tartaric acid; it could not be epimerised by C_5H_5N to the acid obtained by oxidising β-angelicalactone (Thiele *et al.*, A., 1902, i, 156). A. LI.

Derivatives of glycuronic acid. IX. Synthesis of aldobionides and the relationship between the molecular rotation of derivatives of acetylated aldoses and uronic acids. W. F. GOEBEL and R. E. REEVES (J. Biol. Chem., 1938, **124**, 207—220).—Me α-hepta-acetylcellobiuronate (A., 1935, 1168) in $CHCl_3$ and AcOH–HBr give, after removal of solvent and HBr in vac., *Me α-bromohexa-acetylcellobiuronate* [designated α on Hudson's nomenclature], m.p. 200° (decomp.), $[\alpha]_D^{24}$ +99·4° (all rotations in $CHCl_3$), which with Ag_2O in MeOH–$CHCl_3$ gives *Me hexa-acetylcellobiuronate* β-*methylglucoside*, m.p. 200°, $[\alpha]_D^{23}$ −27·2°, or with *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ the corresponding β-p-*nitrobenzylglucoside*, m.p. 199—200°, $[\alpha]_D^{22}$ −41·7°. The aldobiuronic acid of gum acacia (A., 1930, 66), 6-β-glycuronosidogalactose, is now named *acaciabiuronic acid*. Me acaciabiuronate (I) with Ac_2O–C_5H_5N gives the first hepta-acetate (II) (cf. A., 1938, II, 45) [converted in Ac_2O–$ZnCl_2$ into a *second hepta-acetate* (III), m.p. 195—197°, $[\alpha]_D^{22}$ +46·5°], and a *third hepta-acetate* (IV), $[\alpha]_D^{22}$ +15·7°. Probably (II) and (III) are an α and β isomeric pair; (IV) may be a mixture. *Me bromohexa-acetylacaciabiuronate*, m.p. 201—202°, $[\alpha]_D^{22}$ +194·7° [from (II)], with AgOAc in $CHCl_3$ gives a *fourth hepta-acetate* of (I), m.p. 110—112°, $[\alpha]_D^{23}$ +92·1°, and with Ag_2O in $CHCl_3$–MeOH a *first methylglucoside* (V), m.p. 134·5°, $[\alpha]_D^{24}$ +86·4°, of Me hexa-acetylacaciabiuronate (probably α), of which a *second methylglucoside* (VI), m.p. 140°, $[\alpha]_D^{23}$ −58·8°, is also obtained from acaciabiuronic acid and MeOH–HCl, followed by acetylation. These are presumably not an α–β pair, but are of different ring structures. The velocity coeffs. of their hydrolysis suggest that the galactose portion of the acaciabiuronic acid mol. has in (V) a pyranose and in (VI) a furanose structure. Relations between $M[\alpha]$ of saccharides and of uronic acids are tabulated; their is an approx. const. change on the conversion of terminal $CH_2{\cdot}OAc$ into CO_2Me. E. W. W.

Excretion of menthoglycol glycuronate by rabbits after consumption of citronellal. R. KUHN and I. LÖW (Z. physiol. Chem., 1938, **254**, 139—143; cf. A., 1937, II, 321; Barbier and Leser, A., 1897, i, 537).—The urine of rabbits given an aq. emulsion of citronellal or menthane-3 : 8-diol by stomach tube contains the d-*glycuronate*, $C_{16}H_{28}O_8 + H_2O$, m.p. 192° (decomp.), $[\alpha]_D^{25}$ −15·2° in EtOH of the diol (*Me* ester, m.p. 193—194°, $+\frac{1}{3}$MeOH, m.p. 196°, $[\alpha]_D^{20}$ −10° in EtOH, and its *triacetate*, m.p. 171—172°, $[\alpha]_D^{20}$ −20° in $CHCl_3$ [Ac groups in the glycuronic acid residue]; p-*bromophenacyl* ester, $C_{24}H_{31}O_9Br + H_2O$, m.p. 189°), the acid being united to the diol through its *sec.* OH. The diol is obtained from citronellal by shaking for 48 hr. at 37° with 0·5% HCl. W. McC.

Preparation of *d*-galacturonic acid from *d*-galactose. H. M. SELL and K. P. LINK (J. Amer. Chem. Soc., 1938, **60**, 1813—1814).—Prep. of di*iso*propylidene-*d*-galactose (when pure, has b.p. 130—140°/0·01—0·001 mm., $[\alpha]_D^{20}$ −54·7° in $CHCl_3$) from α-*d*-galactose, and of K di*iso*propylidene-*d*-galacturonate, m.p. 200—205° (decomp.), $[\alpha]_D^{20}$ −61·1° in H_2O, the free acid, m.p. 157°, $[\alpha]_D^{20}$ −84°, and *d*-galacturonic acid, decomp. 159—160° (sinters at 110—111°), $[\alpha]_D^{20}$ +98° → 50·9° in H_2O, therefrom is improved to give 76—92, 49—65, 78—88, and 65—81% yield, respectively. R. S. C.

Constitution of thio-acids.—See A., 1938, I, 434.

Polymerisation and condensation of formaldehyde in heavy water. W. D. WALTERS (Z. physikal. Chem., 1938, **182**, 275—277).—Polymerisation of CH_2O in D_2O in presence of H_2SO_4 or KOH leads to inclusion of no D in the α-polyoxymethylene. Condensation of CH_2O in aq. MeOH in presence of CaO yields sugars which contain about 8·2% of D which cannot be removed by washing. Replacement of MeOH by MeOD increases this amount to 16·7%. The exchange of D for H is supposed to occur during enolisation of the intermediate aldehydes and ketones. J. W. S.

Reduction of acetaldehyde at the dropping mercury cathode.—See A., 1938, I, 465.

Structure of the aldol of acetaldehyde. M. BACKÈS (Compt. rend., 1938, **207**, 74—76; cf. A., 1935, 962).—Spectroscopic observations show that the aldol probably does not exist in an epoxy-form. In C_6H_6 it shows a band at 9674 A., characteristic of a *tert.*-OH. The polymeride does not exhibit this band, which indicates that polymerisation occurs through the *tert.*-C. The Raman spectra of

the monomeride and freshly formed dimeride in the absence of a solvent are the same, but on keeping at a temp. > its m.p., the latter shows additional weak lines. The spectra show lines characteristic of the linkings C·C, C·H, and C·OH, a line at 1150 cm.$^{-1}$ probably due to the CHO and C·OH arrangements at one C, and a line at 1206 cm.$^{-1}$ due to CO classified as carbonyl XII which differs from a "normal" and an "active" CO. J. L. D.

Polycondensation of acraldehyde. E. E. Gilbert and J. J. Donleavy (J. Amer. Chem. Soc., 1938, **60**, 1911—1914).—In presence of dil. aq. NaOH acraldehyde (I) gives an amorphous "*pentameride*" (II), OH·[CH_2·CH(CHO)]$_4$·CH_2·CH_2·CHO (*tetra*-2 : 4-*dinitrophenylhydrazone*, decomp. about 120°), by hydration followed by Michael addition of (I). Oxidation of (II) gives a *polyacrylic acid*, sinters at about 70°. (I) and (II) are in equilibrium, since the rate of formation of (II) depends on the concn. of NaOH, but the amount formed depends on the temp., a lower temp. favouring formation of (II). (I) polymerises more readily than does CH_2:CMe·CHO (cf. following abstract) since the latter gives mainly the trimeride. R. S. C.

Polycondensation of α-methylacraldehyde. E. E. Gilbert and J. J. Donleavy (J. Amer. Chem. Soc., 1938, **60**, 1737—1738).—In presence of NaOH in aq. EtOH CH_2:CMe·CHO (I) condenses by addition of H_2O to give OH·CH_2·CHMe·CHO, Michael addition of (I) thereto at the active CH to give OH·CH_2·CMe(CHO)·CH_2·CHMe·CHO, and further similar addition to give, as the product isolated, the *trimeride*, OH·CH_2[CMe(CHO)·CH_2]$_2$·CHMe·CHO, b.p. 113—118°/12 mm. (*tris*-2 : 4-*dinitrophenylhydrazone*, m.p. 173—174°). Reaction proceeds similarly further, yielding also small amounts of the *tetrameride*, b.p. 159—164°/12 mm., and *pentameride*, b.p. 175—180°/9 mm. (*tris*-2 : 4-*dinitrophenylhydrazones*, decomp. about 100°). R. S. C.

Condensation of *n*-butaldehyde with butan-β-one. II. S. G. Powell and D. A. Ballard (J. Amer. Chem. Soc., 1938, **60**, 1914—1916; cf. A., 1925, i, 7).—Condensation of Pr^{a}CHO and COMeEt by 2·5% NaOH gives CHPr^a:CMe·COMe and CHBu^a:CEt·CHO (I), which are separable only with difficulty. Similarly, Eccott and Linstead's substance (semicarbazone, m.p. 152°) (A., 1930, 893) obtained from Pr^{a}CHO and $COMe_2$ is (I). *γ-Methyl-*Δ$^\gamma$*-hepten-*β*-one*-2 : 4-*dinitrophenylhydrazone*, m.p. 137°, β*-ethyl-*Δ$^\beta$*-hexen-*α*-al*-2 : 4-*dinitrophenylhydrazone*, m.p. 124—125°, and α*-methyl-*Δ$^\alpha$*-hexeno-*p*-toluidide*, m.p. 85—88°, are described. R. S. C.

Aldehydes and hydroxyaldehydes of the polymethylene series. VII. By-products of synthesis of ethyl tetramethylenedicarboxylate by Kishner's method. E. D. Venus-Danilova (J. Gen. Chem. Russ., 1938, **8**, 477—483).—In the prep. of Et *cyclo*butanedicarboxylate from $CHNa(CO_2Et)_2$ and CH_2Cl·CH_2·CH_2Br *Et$_2$ di-γ-chloropropylmalonate* (I), m.p. 52—53°, is obtained as a by-product. (I) and NaOEt in EtOH (2 hr. at the b.p.) yield the *di-γ-lactone* of *di-γ-hydroxypropylmalonic acid* (II), m.p. 49—51°, hydrolysed by boiling aq. $Ba(OH)_2$ to the *Ba* salt of the corresponding mono-γ-lactone (III). (I) and (III) are also isolated from the acid fraction of the reaction product obtained by Kishner's method. A further by-product is EtOAc, formed by decarboxylation of $CH_2(CO_2Et)_2$. R. T.

Preparation of *l*-glyceraldehyde. E. Baer and H. O. L. Fischer (Science, 1938, **88**, 108).—*l*-Glyceraldehyde has been prepared in the following way: *l*-arabinose → *l*-mannonolactone → *l*-mannitol → 1 : 2-5 : 6-di*iso*propylidene-*l*-mannitol → *iso*propylidene-*l*-glyceraldehyde → *l*-glyceraldehyde (2 : 4-dinitrophenylhydrazone, m.p. 148°; dimedon compound, m.p. 198—200°, $[\alpha]_D^{21}$ −198° in EtOH). The optical rotations of *l*- and *d*-glyceraldehyde decrease in aq. solution on keeping from −14° to −7° and from +14° to +7°, respectively. The ·CHO content of the solution remains unchanged, and the higher-rotating forms of both aldehydes can be regained by evaporation. L. S. T.

Relations of *cis-trans* isomerism to asymmetric oxidation of sugars. M. R. Everett and F. Sheppard (J. Amer. Chem. Soc., 1938, **60**, 1792—1796).—The relative behaviour of sugars to Sumner's dinitrosalicylate and the Folin–Wu Cu reagent containing *d*-, *l*-, or *meso*-tartaric acid depends on the nature and stereochemistry of the ring. *cis–trans* Relations often have a predominating effect, but no completely comprehensive rules are found. R. S. C.

Nomenclature of higher monosaccharides. E. Votoček (Coll. Czech. Chem. Comm., 1938, 264—272).—A new system is proposed. A. Li.

2 : 4 : 6-Trimethylgalactose and its α- and β-methylgalactosides. D. J. Bell and S. Williamson (J.C.S., 1938, 1196—1200).—2 : 4 : 6-Trimethylgalactose (I), m.p. 102—105°, $[\alpha]_D^{23}$ (initial) +124°, (at equilibrium) +90·4°, has been synthesised by two methods and is identical with that isolated by Percival *et al.* (A., 1937, II, 445) from agar. 2-Methyl-β-methylgalactoside (simplified prep. described, based on the facile formation of 3 : 4-*iso*propylidene-β-methylgalactoside from the galactoside and $COMe_2$–H_2SO_4) with PhCHO and anhyd. $ZnCl_2$ gives 4 : 6-benzylidene-2-methyl-β-methylgalactoside, m.p. 160°, $[\alpha]_D^{20}$ −32·8° (cf. A., 1938, II, 127), the 3-p-*toluenesulphonyl* derivative, m.p. 126°, $[\alpha]_D^{20°}$ +38·4°, of which when hydrolysed with HCl–$COMe_2$–H_2O and then methylated with Purdie's reagents gives 2 : 4 : 6-*trimethyl*-β-*methylgalactoside* 3-p-*toluenesulphonate*, m.p. 130°, $[\alpha]_D^{22}$ +20·4°. This with NaOMe–MeOH (90°; 14 hr.) gives 2 : 4 : 6-*trimethyl*-β-*methylgalactoside*, m.p. 111—112°, $[\alpha]_D^{23}$ −40·9°, converted by 0·33N-HCl at the b.p. into (I). α-Methylgalactoside 6-*p*-toluenesulphonate when condensed with $COMe_2$ and then methylated by Purdie's method gives 2-*methyl*-3 : 4-iso*propylidene*-α-*methylgalactoside* 6-p-*toluenesulphonate*, m.p. 90°, $[\alpha]_D^{20}$ +90·9°, which when boiled with NaOH–H_2O–EtOH (36 hr.) gives 2-*methyl*-3 : 4-iso*propylidene*-α-*methylgalactoside* (II), m.p. 77—78°, $[\alpha]_D^{20}$ +157·4°, which when methylated by Purdie's reagents gives 2 : 6-*dimethyl*-3 : 4-iso*propylidene*-α-*methylgalactoside*, b.p. 120/0·1 mm., $[\alpha]_D^{20}$ +155° in H_2O, n_D^{20} 1·4550. This is hydrolysed

by 5% HCl to 2 : 6-dimethyl-β-galactose and converted by fuming HNO_3 in dry $CHCl_3$ into 2 : 6-*dimethyl-α-methylgalactoside* 3 : 4-*dinitrate*, m.p. 50—51°, $[\alpha]_D^{20}$ +160·7°. When boiled with 10% aq. AcOH, (II) gives 2-*methyl-α-methylgalactoside*, $[\alpha]_D^{18}$ +180° in MeOH, which did not crystallise, hydrolysed to 2-methyl-β-galactose, and with PhCHO and anhyd. $ZnCl_2$ gave 4 : 6-*benzylidene*-2-*methyl-α-methylgalactoside*, m.p. 152°, $[\alpha]_D^{20}$ +131·6°. This was converted into its 3-p-*toluenesulphonyl* derivative, m.p. 145°, $[\alpha]_D^{20}$ +158·4°, which when hydrolysed with HCl–$COMe_2$–H_2O and then methylated with Purdie's reagents gives 2 : 4 : 6-*trimethyl-α-methylgalactoside* 3-p-*toluenesulphonate*, m.p. 112°, $[\alpha]_D^{20}$ +150·0°, with some strongly reducing material. The former with NaOMe–MeOH (90°; 72 hr.) gives 2 : 4 : 6-*trimethyl-α-methylgalactoside*, m.p. 73—74°, $[\alpha]_D^{20}$ +163·9° in H_2O, which is very hygroscopic and is hydrolysed by dil. HCl to (I). Except where otherwise stated, all [α] were measured in $CHCl_3$. Hydrolysis of the *p*-$C_6H_4Me{\cdot}SO_2$ groups took place in accord with previous conclusions (A., 1935, 963), that Walden inversion does not occur when the formation of an anhydro-ring is inhibited by suitable substitution of the remaining OH groups in the sugar. In the present examples such inhibition greatly reduced the ease of hydrolysis. H. G. M.

β-Fucohexose and β-fucohexitol. E. Votoček (Coll. Czech. Chem. Comm., 1938, 273—277; cf. A., 1938, II, 127).—β-Fucohexonolactone is reduced (Na–Hg) to β-*fucohexose*, $[\alpha]_D$ (after 30 hr.) +59·7° in H_2O [*phenylhydrazone*, m.p. 163°; *phenylosazone*, m.p. 202° (decomp.); *phenylbenzylhydrazone*, m.p. 168° (decomp.)], further reduced to β-*fucohexitol*, m.p. 150°, [α] 0° in H_2O (*tribenzylidene* derivative, m.p. 186—187°). A. Li.

Colouring matter of Indian tulip (*Thespasia populnea*) flowers: populnin and populnetin. K. Neelakantam and T. R. Seshadri (Current Sci., 1938, **7**, 16—17).—The petals of this flower, collected in Coimbatore in October, contained *populnetin* (I), $C_{14}H_8O_6$, m.p. 270—275° (*Ac*$_4$ derivative, m.p. 127—129°), a smaller amount of *populnin* (II), m.p. 228—230° (decomp.) [the glucoside of (I)], and a trace of a substance (*Ac* derivative, m.p. 182—185°). Collected in Trichinopoly in the summer, the petals contained only (II). Colour reactions indicate that (I) is a tetrahydroxyanthraquinone. R. S. C.

***N*-Glucosides. I. Toluidino- and xylidino-*N*-glucoside.** K. Hanaoka (J. Biochem. Japan, 1938, **28**, 109—118).—The following were prepared by Kuhn and Dansi's method (A., 1936, 1095): *o*-, m.p. 101° (−99·0, −51·0; −103·0, −22·0) and *p*-toluidino-, m.p. 115° (−106·0, −50·0; −87·0, −35·0), m-*toluidino*-, m.p. 117° (−102·9, −50·3; −102·0, −32·0), and 1 : 2 : 3-, m.p. 154—155° (−104·0, −46·0; −88·0, −30·0), p-, m.p. 95—97° (−102·5, −45·0; −103·5, −25·0), as.-o-, m.p. 110—111° (−92·5, −41·5; −79, −29·5), s-m-, m.p. 145° (−102·5, −44·0; −96·0, −30·0), and as.-m-*xylidino-glucoside*, m.p. 105—106° (−101·0, −45·0; −95·0, −25·0). Vals. in parenthesis are for $[\alpha]_D^{20}$ in degrees, initially and after mutarotation, in MeOH and EtOH, respectively. Data for the rate of hydrolysis in dil. H_2SO_4 at 23° indicate that the greater is the proximity of NH_2 and Me groups of the aglucone, the greater is the tendency of the corresponding glucoside to resist acid hydrolysis. F. O. H.

Nitrogenous glucosides. IV. Attempts to synthesise pyrimidine glucosides. T. B. Johnson and W. Bergmann (J. Amer. Chem. Soc., 1938, **60**, 1916—1918; cf. A., 1935, 69).—Attempts to utilise carbamido-derivatives of sugars for the synthesis of pyrimidine glucosides failed. Bromotriacetoarabinose and AgNCO in boiling xylene give a product, deacetylated by conc., aq. NH_3 to *l*-arabinosylcarbamide, m.p. 192°, $[\alpha]_D^{25}$ +51·9° in H_2O. Bromotriacetoxylose gives similarly *s*-dixylosylcarbamide, decomp. 230—250°, $[\alpha]_D^{25}$ −20·5° in H_2O. Bromohepta-acetyl-lactose and AgNCS in boiling xylene give *hepta-acetyl-lactosylthiocarbimide*, m.p. 169—170°, converted by EtOH into *Et hepta-acetyl-lactosyl-thiourethane*, +$x$$H_2O$, m.p. 119°, and by $CO_2Et{\cdot}CH_2{\cdot}NH_2$,HCl and a little C_5H_5N in $CHCl_3$ into *Et hepta-acetyl-lactosylureidoacetate*, m.p. 100°. Tetra-acetylglucosylcarbamide (I), $CN{\cdot}CH_2{\cdot}CO_2H$, and Ac_2O at 100° give *N-tetra-acetylglucosyl-N′-cyanoacetylcarbamide*, m.p. 135° (*oximino*-derivative, m.p. 179—180°), hydrolysed by NH_3 to glucosylcarbamide. (I), $CH_2(CO_2H)_2$, and Ac_2O at 100° give *malonylbistetra-acetylglucosylcarbamide*, m.p. 206—207°. R. S. C.

Constitution of damson gum. I. Composition of damson gum and structure of an aldobionic acid (glycuronosido-2-mannose) derived from it. E. L. Hirst and J. K. N. Jones (J.C.S., 1938, 1174—1180).—The crude gum (neutral salt of metallic radicals) is purified and obtained ash-free as an acidic *polysaccharide* (I), $[\alpha]_D^{20}$ −26° (as Na salt in H_2O) (Tl salt and insol. Tl complex), of equiv. wt. about 1100. Analysis gives 16·4% of uronic anhydride and 36·2% of araban. Autohydrolysis of (I) occurs when it is heated with H_2O (90—95°; 24 hr.), and gives *l*-arabinose, *d*-galactose (II) (trace), and a *polysaccharide* (A) (III), insol. in EtOH, and containing a repeating unit of *d*-glycuronic acid (IV) (1 mol.), *d*-mannose (1 mol.), *d*-galactose (2 mols.). The repeated unit of (I) contains in addition *l*-arabinose (3 mols.). When boiled with 2N-H_2SO_4 for 6·5 hr. (III) gives (II) and an aldobionic acid, shown to be β-d-*glycuronosido*-2-d-*mannose*, and obtained as the impure Ba salt (V), $[\alpha]_D^{20}$ −16° in H_2O, mixed with a little (IV). With boiling 2N-H_2SO_4 (22 hr.) (V) is split, giving equal proportions of *d*-glycuronic acid and *d*-mannose. Methylation of (V) with Me_2SO_4–NaOH, followed by esterification with MeI and Ag_2O, gives the *Me* ester of *heptamethyl*-β-d-*glycuronosido*-2-d-*mannopyranose*, b.p. 175°/0·002 mm., n_D^{20} 1·4675, $[\alpha]_D^{20}$ −16° in H_2O, together with a little Me tetramethyl-*d*-glycuronate. Hydrolysis of the former with 7% HCl (90—95°; 6·5 hr.) gives an equimol. mixture of 2 : 3 : 6-trimethyl-*d*-glycuronic acid (VI) and 3 : 4 : 6-trimethyl-*d*-mannose (A., 1930, 1024), oxidised by Br–H_2O to 3 : 4 : 6-trimethylmannolactone (cf. *loc. cit.*), which with liquid NH_3 gives 3 : 4 : 6-*trimethyl*-d-*mannonamide*, m.p. 141°, $[\alpha]_D^{21}$ +25°. This gave a strong positive Weerman reaction (cf. A., 1917, i, 546) with NaOCl, indicating the presence of ·OH in $C_{(2)}$. Oxidation of (VI) with Br–H_2O (60°; 8 hr.) gives 2 : 3 : 4-trimethyl-

saccharic acid, identified as the Me ester of 2 : 3 : 4-trimethylsaccharolactone (A., 1932, 45). After simultaneous esterification and glycoside formation (VI) gives the *Me* ester, b.p. 140°/0·001 mm., $[\alpha]_D$ +31° in H_2O, of 2 : 3 : 4-trimethyl-*d*-glycuronoside, converted by MeOH–NH_3 into the corresponding *amide*, m.p. 158°, $[\alpha]_D^{20}$ +60° in H_2O, which is a mixture of α- and β-forms not separable by crystallisation. Hydrolysis of the methylated derivative of (III) gives a little 2 : 3 : 4-trimethylxylose. H. G. M.

Hydrolysis of starch by sweet potato amylase. K. V. Giri (J. Indian Chem. Soc., 1938, **15**, 249—262).—Sweet potato amylase resembles the β-amylase of barley in giving the same saccharification limit to Zulkowsky's sol. starch hydrolysis and the residual material resembles the erythrogranulose fraction of starch after hydrolysis by α- and β-amylases. The course of the hydrolysis of amyloamylose by sweet potato amylase also follows the same course as that found by Samec (A., 1935, 1415) for β-amylase. Van Klinkenberg's views on the composition of starch (cf. A., 1932, 1062; 1933, 92) are considered untenable. F. R. G.

Schardinger dextrins from starch. K. Freudenberg and M. Meyer-Delius (Ber., 1938, **71**, [*B*], 1596—1600).—The prep. of *methyl*-α- (I), m.p. 208—210°, $[\alpha]_D$ +162° in $CHCl_3$, and -β- (II), m.p. 156—158°, $[\alpha]_D$ +157° in $CHCl_3$, -*dextrin* is described. (I), (II), and α-dextrin (III) in H_2O give an intense red-brown colour whilst free β-dextrin (IV) gives a brown ppt. During hydrolysis of (I) and (II) by 34% HCl, α_D which is positive throughout increases to a max. and diminishes ultimately to the val. shown by 2 : 3 : 6-trimethylglucose in 34% HCl. Similar observations are made in 51% H_2SO_4. Hydrolysis and subsequent glucosidation of (I) and (II) gives 2 : 3 : 6-trimethylmethylglucoside in about 95% yield. The formation of tetramethylmethylglucoside could not be detected so that trimethylglucose is the sole product. The optical behaviour shows that the majority of the linkings are similar to those in maltose. The possibility of β-linkings resembling those of cellobiose is excluded since the initial increase in α_D takes place more rapidly than the fission of the remaining linkings. The possibility of a gentiobiose linking is excluded since if present the hydrolytic product would contain 2 : 3 : 4-trimethylglucose, the 6-*p*-toluenesulphonate of which would react with NaI in warm $COMe_2$ giving the 6-iodohydrin with separation of *p*-$C_6H_4Me{\cdot}SO_3Na$; this does not occur. The sole possibility therefore is that (III) and (IV) are composed of 5 or 6 glucose units united in rings and connected with each other exclusively by linkings of the maltose type. It is concluded that during the hydrolysis of (I), (II), (III), and (IV) the initial increase in α_D is due to ring-opening the rate of which greatly exceeds that of the decomp. of the open chains; after initial rise the graph therefore resembles the falling curve of the hydrolysis of starch or methylstarch. During acetolysis, ring-opening again causes an initial increase of α_D but the rate of change does not differ markedly from that of the acetolysis of open chains so that during the whole course of acetolysis of the dextrin acetates an increase in α_D is observed. Röntgen data of (III) are in harmony with a ring structure. H. W.

Effect of acetylation on the molecular chain-length of starch. R. S. Higginbotham and W. A. Richardson (J.S.C.I., 1938, **57**, 234—200).—Acetates have been prepared from potato starch (Cu-reducing power, R_{Cu}, 3·0 mg. per g.) by two methods, the catalysts used being either a mixture of SO_2 and Cl_2 (acetates I) or C_5H_5N (acetates II). Acetates from starches modified by treatment with cold aq. HCl for various periods, and ranging in R_{Cu} from 4·5 to 259 (acetates III), have been prepared in presence of C_5H_5N. After deacetylation the R_{Cu} of (II) and (III) were almost unchanged, whereas those of (I) were increased by 20—50 mg. per g. The viscosities of (I) were much lower in $C_2H_2Cl_4$ than those of (II) and were within the range covered by those of (III). (I) were degraded during prep., (II) were not. Since the methylated starches used to determine chain-length (A., 1932, 1116; 1935, 1226) were obtained from acetates prepared similarly to (I), the chain-length of 24—30 glucose units calc. from the yield of tetramethylglucose does not represent that of the original starch. The average chain-length calc. from R_{Cu} ranges from 17 to 1370 units and is almost a linear function of η, but the factor of proportionality differs according to the type of distribution of chain-lengths within the single samples of starch. W. A. R.

Composition of sugar humin. A. Schweizer (Rec. trav. chim., 1938, **57**, 886—890; cf. A., 1938, II, 220).—Sugar humin gives good analyses for $(C_{12}H_8O_4)_n$ after drying in N_2 at 100—105°. A. Li.

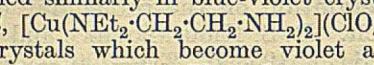
Optical properties of cellulose dispersed in cuprammonium hydroxide solution.—See A., 1938, I, 513.

Action of dilute acids on cellulose nitrates. Steric hindrance. J. Desmaroux (Compt. rend., 1938, **206**, 1483—1484).—Equiv. concns. of HNO_3, HCl, and H_2SO_4 at 50—60° hydrolyse cellulose nitrate to different extents, HNO_3 most and H_2SO_4 least easily. The different degrees of hydrolysis depend on the stereochemical configuration of the anions of the acids. J. L. D.

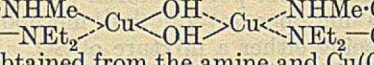
Structure from the solubility of denitrated cellulose nitrates. M. Mathieu and (Mlle.) T. Petitpas (Compt. rend., 1938, **206**, 1485—1486).—Cellulose trinitrate (I) containing 13·8—14·0% of N with 4·66N-HNO_3 at 50° loses N as the hydrolysis continues. Simultaneously, there is no large increase in the Et_2O–EtOH-sol. $(NO_2)_2$-fraction. (I) and its hydrolytic products containing down to 11·94% of N show the *X*-ray diagram of (I), which explains the relative insolubility of partly hydrolysed (I). J. L. D.

Complex salts of copper with *N*-alkylated ethylenediamines. P. Pfeiffer and H. Glaser (J. pr. Chem., 1938, [ii], **151**, 134—144).—The tendency of *N*-alkylated ethylenediamines to form complex salts is much less pronounced than that of $(CH_2{\cdot}NH_2)_2$. $CuSO_4$, $(CH_2{\cdot}NH_2)_2,H_2O$, and $NaClO_4$ give the blue-violet *salt*, $[Cu\ en_2](ClO_4)_2$. The blue-violet *compound*, $[Cu(NHMe{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2](ClO_4)_2$,

is obtained from the amine and $Cu(ClO_4)_2$ in MeOH; the *substance*, $[Cu(NHEt{\cdot}CH_2{\cdot}CH_2{\cdot}NHEt)_2](ClO_4)_2$, is obtained similarly in blue-violet crystals. The *compound*, $[Cu(NEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2](ClO_4)_2$ forms ruby-red crystals which become violet at 43—45° and almost black at 45°. The *salt*



best obtained from the amine and $Cu(ClO_4)_2$ in MeOH, forms dark blue, almost black crystals. The *compound*



is a blue-violet, cryst. powder which becomes red in liquid air; the transition temp. is −100° to −120°. Attempts to obtain a complex Cu salt from $NHPh{\cdot}[CH_2]_2{\cdot}NEt_2$ were fruitless, the greenish ppts. becoming brown and ultimately resinous. The praseo-salt [Co en$_2$Cl$_2$]Cl is converted by $(CH_2{\cdot}NH_2)_2$ into the *compound*, [Co en$_3$]Cl$_3$,3H$_2$O, also obtained by use of $NHEt{\cdot}[CH_2]_2{\cdot}NHEt$ or from chloropentamminecobaltic chloride and $(CH_2{\cdot}NH_2)_2$,H$_2$O; when heated with $NHMe{\cdot}[CH_2]_2{\cdot}NH_2$ or $NEt_2{\cdot}[CH_2]_2{\cdot}NH_2$ the purpureo-chloride evolves NH_3 but does not appear to give a complex salt. Trichlorotripyridinechromium and $(CH_2{\cdot}NH_2)_2$,H$_2$O give the *compound*, [Cr en$_3$]Cl$_3$,*n*H$_2$O; complex salts could not be obtained with $NEt_2{\cdot}[CH_2]_2{\cdot}NH_2$, $NHEt{\cdot}[CH_2]_2{\cdot}NHEt$, or $NHMe{\cdot}[CH_2]_2{\cdot}NEt_2$. H. W.

Hexamethylenetetramine mandelate. Preparation and toxicity. H. G. Kolloff and J. W. Nelson (J. Amer. Pharm. Assoc., 1938, **27**, 603—605).—$(CH_2)_6N_4$ with $OH{\cdot}CHPh{\cdot}CO_2H$ in H$_2$O affords *hexamethylenetetramine mandelate*, m.p. 130—132°; the salt is well tolerated in doses of 2—5 g. per kg. by rats. F. O. H.

New type of isomerisation and its application to the preparation of esters of amino-alcohols. H. Horenstein and H. Phälicke (Ber., 1938, **71**, [*B*], 1644—1657).—Treatment of the Ag salt of an org. acid with $Br{\cdot}[CH_2]_2{\cdot}NMe_2Br$ gives the corresponding trimethyl-β-bromoethylammonium salt, which is isomerised when heated to the methobromide of the β-dimethylaminoethyl ester. The reaction can be extended to the Cl-derivatives of other *tert.*-amines and the isolation of the intermediate salts is not invariably necessary. Partial esterification of polybasic acids is possible. With inorg. acids the change appears to follow a more complex course. *β-Dimethylaminoethyl lactate methobromide* is obtained (79% yield) in colourless, hygroscopic crystals when aq. solutions of $Br{\cdot}[CH_2]_2{\cdot}NMe_2Br$ and Ag lactate are mixed, AgBr and solvent are removed and the residue is heated for 6 hr. at about 90°. Corresponding *salts*, m.p. 152—154°, —, 210—212°, 232—234° (decomp.), and 236—238° (decomp.), respectively are obtained from mandelic, pyruvic, phenylquinolinecarboxylic, deoxycholic, and cholic acid.

$CH_2Br{\cdot}CH_2{\cdot}NMe_3Br$ and AgCNS yield *trimethyl-β-thiocyanoethylammonium bromide*. *Diethyl-β-thiocyanoethylammonium chloride* is obtained when $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$ is neutralised with HCNS in EtOH and the product is heated at 90—95°. In boiling $Pr^{\beta}OH$ $OH{\cdot}CPh_2{\cdot}CO_2H$ and $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$ afford *diethylaminoethyl benzilate hydrochloride*, m.p. 173—174·5° (corresponding *base*, m.p. 50—51°), also obtained from $OH{\cdot}CPh_2{\cdot}CO_2Na$ and $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$,HCl at 140°. *β-Piperidinoethyl benzoate hydrochloride*, m.p. 176°, *diethylaminoethyl salicylate hydrochloride*, m.p. 144—145°, and *γ-diethylaminopropyl cinnamate hydrochloride*, m.p. 131—133°, are described. *Diethylaminoethyl mandelate* and its *hydrochloride* are non-cryst. *γ-Diethylamino-ββ-dimethylpropyl* dl-*tropate* has m.p. 138—140°. Na$_2$ adipate and $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$,HCl at 110° afford *β-diethylaminoethyl H adipate hydrochloride*, which is an acidic resin. *β-Diethylaminoethyl H phthalate hydrochloride* is described. Partial isomerisation of the product from $p\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2H$ and $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$ yields *diethylaminoethyl* p-*nitrobenzoate* p-*nitrobenzoate*, decomp. 125—129°. H. W.

Esters of choline. A. Contardi and A. Ercoli (Congr. int. Quim. pura apl., 1934, **9**, V, 163—173; Chem. Zentr., 1936, ii, 3903).—The following esters were made by esterifying the appropriate acid with $CH_2Cl{\cdot}CH_2{\cdot}OH$ and heating the ester with NMe_3: *formylcholine chloride* (*β-chloroethyl formate*, b.p. 132°/764 mm.); *propionylcholine chloride* [*aurichloride*, m.p. 131—132°; *platinichloride*, m.p. 241·5° (decomp.)] (*β-chloroethyl propionate*, b.p. 162—164°/763 mm.); *oxalylcholine chloride* (*aurichloride*, m.p. 256·5°) (*β-chloroethyl oxalate*, m.p. 45°); *acetylcarbamylcholine chloride* (*β-chloroethyl acetamidoformate*, m.p. 73—74°); *methylenedicarbamylcholine dichloride* (*platinichloride*, m.p. 230°) (*β-chlorethyl NN′-methylenebisaminoformate*, m.p. 148°); *methylenecarbamylcholine chloride* (*β-chloroethyl methyleneaminoformate*); *phenylmethylcarbamylcholine chloride* (*platinichloride*, m.p. 222°; *aurichloride*, m.p. 190°) (*β-chloroethyl methylphenylaminoformate*, b.p. 165°/8 mm.); *chlorotrimethylcarbamylcholine chloride* (*aurichloride*, m.p. 273°) (*β-chloroethyl trimethylaminoformate*, m.p. <300°); *iminodicarboxydicholine dichloride* [*aurichloride*, m.p. 240° (decomp.); *platinichloride*, m.p. 248° (decomp.)] [*di*(*chloroethyl*) *iminodicarboxylate*, m.p. 202°]. A. H. C.

Onium compounds. XIX. Thio-esters of choline and β-methylcholine and their physiological activity. R. R. Renshaw, P. F. Dreisbach, M. Ziff, D. Green, and (in part) J. H. Williams (J. Amer. Chem. Soc., 1938, **60**, 1765—1770; cf. A., 1938, II, 224).—The additive *compound*, m.p. 201—202°, of $CHMeCl{\cdot}CH_2{\cdot}NMe_2$,HCl and $CS(NH_2)_2$ with aq. KOH gives *dimethyl-β-thiolpropylamine* (I), b.p. 153—154°/762 mm. [*picrate*, m.p. 159—166° (decomp.) after softening; *HgCNS* salt, decomp. from 125°]. With a slight excess of KOH, however, it gives mainly *di*-(*β-dimethylaminoisopropyl*) *disulphide*, b.p. 151—154°/14 mm. [*dimethiodide*, m.p. 207—208° (decomp.)]. With MeI in Et$_2$O, C$_6$H$_6$, or PhMe at room temp. (I) gives a *salt*, $C_7H_{18}NSI$, decomp. 197—200°, not identical with that of Mylius (A., 1916, i, 633). With the acyl chloride in Et$_2$O (I) gives *dimethyl-β-acet-*, m.p. 91—92°, *-β-benz-*, m.p. 122·5°, and *-β-p-nitrobenz-*, m.p. 199—200°, *-thiolpropylammonium chloride*, converted by way of the free bases (which are very readily hydrolysed) into *trimethyl-β-acet-* (II), m.p. 144—145°, *-β-benz-*, m.p. 185—186°, and *-β-p-nitrobenz-thiolpropylammonium iodide*, m.p. 190—191°. *Dimethyl-β-p-nitrobenzthiol-*

propylamine has m.p. 85°. The additive *compound*, m.p. 181—182°, of $Cl\cdot[CH_2]_2\cdot NMe_2,HCl$ and $CS(NH_2)_2$ similarly leads to $SH\cdot[CH_2]_2\cdot NMe_2$, $(S\cdot[CH_2]_2\cdot NMe_3I)_2$, *dimethyl-β-acet-*, m.p. 95°, *-benz-*, m.p. 164·5—165°, and *p-nitrobenz-thiolethylammonium chloride*, m.p. 187° (decomp.), *trimethyl-β-acet-* (III), m.p. 203—204°, *-benz-*, decomp. about 257°, and *-p-nitrobenz-thiolethylammonium iodide*, m.p. 212—216° (decomp. from 195°). (II), (III), and $SMe\cdot[CH_2]_2\cdot NMeI$ have pharmacological effects similar to those of choline, but weaker; the relatively large effect of (II) is contrary to experience in the S-free series. R. S. C.

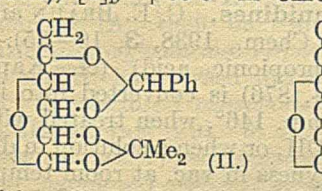
Synthesis of proteinogenic alcamines and their *NN*-dialkyl derivatives. C. C. Christman and P. A. Levene (J. Biol. Chem., 1938, **124**, 453—458; cf. A., 1924, i, 168).—The Me ester of *dl*-leucine is directly reduced in MeOH by H_2 (175°; 3600 lb./in.²; Cu chromite) to *NN*-dimethyl-*dl*-leucinol (*hydrochloride*, m.p. 103—104°; *picrate*, m.p. 105—106°; *methiodide*). The reduction is also effected in dioxan. *N*-Acetyl-*l*-norleucine Et ester is similarly reduced in MeOH to *NN-dimethyl*-dl-*norleucinol*, b.p. 115° (bath)/15 mm. (*picrate*, m.p. 89—90°), also obtained from *l*-norleucine Et ester. E. W. W.

Mechanism of *trans*-amination of amino-acids. F. Knoop and C. Martius (Z. physiol. Chem., 1938, **254**, I—II; cf. Braunstein and Kritzmann, A., 1937, II, 448).—$AcCO_2H$, shaken with arginine in H_2 in presence of a catalyst, gives octopine. The mechanism of the reaction is probably the same as in the interaction of glutamic acid and $AcCO_2H$.

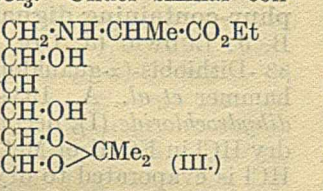
W. McC.

Action of acetylating agents on amino-acids. A. Neuberger (Biochem. J., 1938, **32**, 1452—1456).—*dl*-Phenylalanine can be acetylated (Ac_2O in C_5H_5N at 2°) without any ketone formation. Acetylation of *l*-histidine in the same way yields a compound (80%), m.p. 155° (indef.), which is partly racemised. Treatment of *l*-proline with keten yields 80% of *N*-acetyl-*l*-proline, whilst *l*-cysteine hydrochloride similarly yields NS-*diacetylcysteine* (50%), m.p. 111—112°, Et *dl*-β-hydroxyglutamate hydrochloride the corresponding N-*Ac* compound (53%), m.p. 46°, and α-thiolpropionic acid an S-*Ac* compound, b.p. 133°/1 mm. P. G. M.

New compounds from sugars and amino-acids. B. Helferich and R. Mittag (Ber., 1938, **71**, [*B*], 1585—1590).—Benzylidene*iso*propylidene-glucose 6-methanesulphonate (I) is transformed by anhyd. NaI in boiling $COMe_2$ into 3 : 5-*benzylidene*-1 : 2-iso*propylideneglucose* 6-*iodohydrin*, m.p. 140° (corr.), $[\alpha]_D^{21}$ +20·9° in $CHCl_3$, which is slowly converted by liquid NH_3 at room temp. into 3 : 5-*benzylidene*-1 : 2-iso*propylidene*-Δ⁵-*glucofuranose-ene* (II), m.p. 126° (corr.), $[\alpha]_D^{21}$ +66·6° in $CHCl_3$. Under similar con-



(II.)



(III.)

dition (I) is slowly transformed into 6-*amino*-3 : 5-*benzylidene*-1 : 2-iso*propylideneglucose*, m.p. 127° (corr.), $[\alpha]_D^{21}$ +25·4° in $CHCl_3$. Gradual addition of 1 : 2-*iso*propylidene-5 : 6-anhydroglucofuranose to alanine Et ester gives the non-cryst. *Et* α-1 : 2-iso*propylidene*-6-*glucofuranosylaminopropionate* (III), hydrolysed by aq. $Ba(OH)_2$ at room temp. to 6-N-dl(?)-*alanino*-1 : 2-iso*propylideneglucofuranose* (III), decomp. about 230°, $[\alpha]_D^{21}$ −13·8° in H_2O, which is acid towards litmus, dissolves $BaCO_3$ when heated, and reduces Fehling's solution only after hydrolysis. 6-N-l(+)-*Alanino*-1 : 2-iso*propylidene-glucofuranose*, decomp. about 210—220°, $[\alpha]_D^{21}$ −20·8° in H_2O, is obtained similarly. Hydrolysis of (IV) with 35% AcOH affords 6-N-dl(?)-*alaninoglucose*, m.p. indef. about 130—135° (decomp.), $[\alpha]_D^{20}$ +48·3° in H_2O, which reduces hot Fehling's solution and gives a *phenylosazone*, m.p .240° (block.; decomp.) after becoming discoloured at about 225°. 6-N-l-*Alaninoglucose*, $[\alpha]_D^{19}$ +57·2° in H_2O, and its *phenylosazone*, m.p. 252° (decomp.) after becoming discoloured at about 240°, are described. H. W.

Carbamic esters from carbamide. R. A. Jacobson (J. Amer. Chem. Soc., 1938, **60**, 1742—1744).—At the b.p. or 175—190° (whichever is the lower) $CO(NH_2)_2$ and ROH give *n*-dodecyl, new m.p. 81—82°, *n*-octyl, m.p. 67°, b.p. 136°/4 mm., and Bu^β carbamate, b.p. 117°/25 mm., m.p. 65—66°, formed also with Bu^β allophanate, new m.p. 174°, from $CO(NH_2)_2$, $Bu^\beta OH$, $o\text{-}C_6H_4(OBu^\beta)_2$, and glycerol at 123—170°. $(CH_2\cdot OH)_2$ and sorbitol give syrups. $CH_2(CH_2\cdot OH)_2$ gives a mixture, including a little of the *diurethane*, m.p. 108°. The reaction, $CO(NH_2)_2 + 2ROH \rightarrow R_2CO_3 + 2NH_3$, could not be realised; in the presence of H_2SO_4, $C_{10}H_{21}\cdot OH$ gives quantitatively $(C_{10}H_{21})_2O$. R. S. C.

Condensation of α-keto-acids and acetamide. D. Shemin and R. M. Herbst (J. Amer. Chem. Soc., 1938, **60**, 1954—1957).—$CO_2H\cdot[CH_2]_2\cdot CO\cdot CO_2H$ (I) and NH_2Ac at 70—75°/10—15 mm. give the *lactone* (II), m.p. 196°, of *α-acetamido-α-hydroxyglutaric acid*, converted by N-HCl into (I) and by EtOH into an unsaturated ester, which, when hydrogenated (Pt) and hydrolysed, gives glutamic acid. At 110°±5°/10—15 mm. (I) and NH_2Ac give by double condensation and loss of CO_2 *γγ-diacetamidobutyric acid*, m.p. 197°, obtained similarly from (I). At 110—115°/10—15 mm. $CH_2{:}C(NHAc)\cdot CO_2H$ and NH_2Ac give $(NHAc)_2CH\cdot CH_2\cdot CO_2H$. $CHPh{:}C(NHAc)\cdot CO_2H$ (III) does not react with NH_2Ac, and $CH_2Ph\cdot CO\cdot CO_2H$ gives only (III). $BzCO_2H$ gives *αα-diacetamido-phenylacetic acid*, $+H_2O$, m.p. 201—202° (decomp.) (uncorr.), with small amounts of $NHBz\cdot CHPh\cdot CO_2H$ (IV) and *αα-diacetamidotoluene*, m.p. 250° (decomp.; uncorr.). $NHAc\cdot CR(OH)\cdot CO_2H$ is a possible intermediate. The mechanism of the formation of (IV) is discussed. R. S. C.

Synthesis of dipeptides from α-keto-acids. D. Shemin and R. M. Herbst (J. Amer. Chem. Soc., 1938, **60**, 1951—1954).—Oximes of pyruvamido-acids or -esters are hydrogenated (PtO_2) in EtOH or aq. EtOH (for some esters addition of a little HCl is advantageous) at 2—3 atm. to yield dipeptides. *Pyruvylglycineoxime*, m.p. 202° (decomp.), and the *Et* ester thereof, m.p. 127°, carbethoxyalanylglycine Et ester, new m.p. 72·5—73·5°,

α′α′-diacetamidopropionylalanine, m.p. 175—176° (decomp.), *pyruvylalanine*, m.p. 143·5° [*oxime*, m.p. 186°; *Et* ester, an oil (*oxime*, an oil)], and *carbethoxyalanylalanine Et* ester, m.p. 71—72°, are described. *Pyruvylphenylalanineoxime*, m.p. 187—188°, gives anomalously *alanyl*cyclo*hexylalanine*, hydrolysed to *cyclo*hexylalanine (*Bz* derivative, m.p. 186—187°). The lactone of α-acetamido-α-hydroxyglutaric acid with Ac_2O gives the oily azlactone lactone, converted by glycine and NaOH into the *lactone*, m.p. 210° (decomp.), of *α′-acetamido-α′-hydroxyglutarylglycine*, $\left.\begin{matrix}CO——O\\CH_2\cdot CH_2\end{matrix}\right\rangle C(NHAc)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$. R. S. C.

Glutamic acid. E. Bartow (Congr. int. Quim. pura apl., 1934, **9**, V, 181—185; Chem. Zentr., 1936, ii, 2446).—The prep. of glutamic acid from cereal gluten or from molasses residues of beet sugar manufacture (yield, 0—8·8% of dry wt.) is improved by heating with 2N-HCl in a special autoclave. A. H. C.

Preparation of *d*- and *l*-alanyl-*l*-histidine; their effect on the blood pressure in comparison with *l*-carnosine. M. Hunt and V. du Vigneaud (J. Biol. Chem., 1938, **124**, 699—707).—Carbobenzyloxy-*l*(+)-alanine is treated with PCl_5 and anhyd. Et_2O at 0° and, after removal of part of the solvent, with histidine Me ester in well-cooled $CHCl_3$, thus giving *carbobenzyloxy*-l(+)-*alanyl*-l(−)-*histidine* (+2H_2O), m.p. 131° (corr.), transformed (H_2–Pd-black in 4N-H_2SO_4) into l(+)-*alanyl*-l(−)-*histidine* (I), m.p. 157° (corr.), $[\alpha]_D^{27}$ +27·0° in H_2O, which could not be freed completely from EtOH and H_2O without decomp.; the *sulphate*, m.p. 183° (corr.), $[\alpha]_D^{25}$ +14·1° in H_2O, and the *salt*, $C_9H_{14}O_3N_4,CuO$, are described. Non-cryst. *carbobenzyloxy*-d(−)-*alanyl*-l(−)-*histidine* is transformed into d(−)-*alanyl*-l(−)-*histidine* (II), m.p. 163° (corr.), $[\alpha]_D^{25}$ +7·0° in H_2O (*sulphate*, m.p. 215°, $[\alpha]_D^{24}$ −2·5°±0·5° in H_2O; *Cu* salt). The prep. of the dipeptides from carbobenzyloxy-*dl*-alanine is described. (II) is obtained also from d(−)-alanine cyclic carboxylic anhydride. Neither (I) nor (II) in 20 times the dose of *l*-carnosine showed any lowering of the blood pressure of cats under amytal anæsthesia. H. W.

Determination of reduced glutathione. A. B. Corkill and J. F. Nelson (Austral. J. Exp. Biol., 1938, **16**, 133—135).—Mason's method (A., 1930, 803) was followed, but a Zeiss Pulfrich photometer was used. D. M. N.

Synthesis of cyanamide by the action of silver oxide on formaldehyde and ammonia. R. Fosse, R. de Larambergue, and J. Gaiddon (Compt. rend., 1938, **207**, 12—13; cf. A., 1936, 597; 1937, II, 329).—A mixture of equal vols. of 0·1N-CH_2O, N-NH_3, 2N-$AgNO_3$, and 2N-KOH at 0—5° affords $CN\cdot NH_2$, isolated as the Ag derivative, in 1·01—3·75% yield. J. L. D.

Preparation of fully acetylated amides of aldonic acids. G. B. Robbins and F. W. Upson (J. Amer. Chem. Soc., 1938, **60**, 1788—1789).—Aldonolactones are converted by liquid NH_3 into the amides, which with Ac_2O–$ZnCl_2$ give Ac_5 and with Ac_2O–H_2SO_4 at 0° give Ac_6 derivatives. Thus are obtained penta-, m.p. 184—185°, $[\alpha]_D^{25}$ +23·6°, and *hexa-acetyl*-d-*gluconamide*, m.p. 110°, $[\alpha]_D^{25}$ +25·8°, penta-, m.p. 165—166°, $[\alpha]_D^{25}$ +26·7°, and *hexa-acetyl*-d-*galactonamide*, m.p. 149·5—150°, $[\alpha]_D^{25}$ +19°, *penta-acetyl*-d-*mannonamide*, m.p. 110°, $[\alpha]_D^{25}$ +38·7°, and -d-*gulonamide*, m.p. 162—164°, $[\alpha]_D^{25}$ +22·7°. [α] are in $CHCl_3$. R. S. C.

Condensation products of carbamide with different aldehydes. F. Vass (Brit. Plast., 1938, **10**, 115—118).—$CO(NH_2)_2$ (I) (2 mols.) and 40% CH_2O (1 mol.) in presence of 1% AcOH give methylenebiscarbamide, sol. in EtOH, and methylenecarbamide, insol. in EtOH. (I) (2 mols.) and CH_2O (3 mols.) with HCO_2H or $CH_2Cl\cdot CO_2H$ (3 min.) or AcOH (10—20 min.) or when heated alone, give methylenebis(methylenecarbamide), $CH_2(NH\cdot CO\cdot N{:}CH_2)_2$. More dil. solutions give similar products, no intermediates being obtained. The products are colourless and polymerise when kept. Hydrolysis by $CH_2Cl\cdot CO_2H$ or H_2SO_4 gives indefinite products (14·48—33·85% of N). (I) (2 mols.) and MeCHO (3 mols.; as 40% solution) alone or with 1% of AcOH give *ethylidenecarbamide*, colourless; 1% NH_3 gives only an aldehyde resin. The 2 : 1 vanillin–(I), 1 : 1 piperonal–(I), and 1 : 1 furfuraldehyde–(I) products are obtained as nearly colourless powders; products with other ratios of reactants could not be isolated. R. S. C.

Molecular compounds of carbamide and its derivatives with pharmaceutical compounds. F. Adamanis (Kron. farmac., 1936, **35**, 93—97, 110—114, 129—135, 154—155, 169—172; Chem. Zentr., 1936, ii, 2405).—The following mol. compounds were obtained: Veronal (I) : carbamide (II) (1 : 1), transition point 145·5°; (I) : $NH_2\cdot CO\cdot NHPh$ (III) (1 : 2), m.p. 231°; (I) and $NH_2\cdot CO\cdot NMe_2$ (IV) form no compound. (I) and $CO(NHMe)_2$ (V) form no compound. (I) : NH_2Ac (VI) (1 : 2). $NH_2\cdot CO\cdot CO_2Et$ (VII) and (III), (VII) and (IV), and (VII) and (VI) give only eutectics. $NHPh\cdot CO\cdot CO_2Et$ (VIII) and (II), (VIII) and (IV), (VIII) and (V), and (VIII) and (I) do not give compounds. Resorcinol (IX) : (III) (1 : 1), m.p. 109·2°. (IX) : (IV) (1 : 1), m.p. 68·0°. (IX) : (V) (1 : 1), m.p. 68·2°. Pyrogallol (X) : (II) (3 : 2), m.p. 68·2°. (IX) : (I) (1 : 1), transition point, 99·7°. *o*-, *m*-, and *p*-$C_6H_4(OH)_2$ do not give compounds with (I). Compounds are not formed from (XIII) and (IV), *o*-$OH\cdot C_6H_4\cdot CO_2H$ or (XIII) and (I). It is concluded that both NH_2 groups of (II) are active and that (I) forms additive compounds with (*a*) basic compounds through the H of the NH groups, (*b*) acidic compounds through the N atoms. Deviations from Kordes' results (A., 1927, 1132; 1931, 310) are noted and the probable non-existence of ternary compounds is discussed. A. H. C.

Guanidine structure and hypoglycæmia: sulphur-containing diguanidines. C. E. Braun and B. J. Ludwig (J. Org. Chem., 1938, **3**, 16—25).—ββ′-Dithiobis-(α-guanidopropionic acid) (cf. Kapfhammer *et al.*, A., 1934, 876) is converted into its *dihydrochloride* (I), decomp. 146°, when treated with dry HCl in EtOH or MeOH, or when a solution in dil. HCl is evaporated to dryness in vac. at room temp., the dihydrochloride (II) (A., 1935, 850) of 5 : 5′-(dithiodimethylene)diglycocyamidine (III) being also

formed. When treated with 3N-NH_3–H_2O, (I), like (II), gives (III). The guanidine groups of (I) and (II) in H_2O liberate N_2 with HNO_2, and the results of the determination of NH_2-N by Van Slyke's method on freshly prepared solutions of (I) and (II) accord with the view that these are in equilibrium in aq. solution. 4 : 4′-Dithioaniline dihydrochloride when refluxed (steam-bath, 18 hr.) with $CN{\cdot}NH_2$ in EtOH and then treated with cold 10% NaOH gives 4 : 4′-*diguanidodiphenyl disulphide* (IV), m.p. 178° (*picrate*, m.p. 199°; *sulphate*, m.p. 257—258°, turning into a yellow form of the same m.p. on storage). Similarly $(p\text{-}NH_2{\cdot}C_6H_4)_2S$ yields 4 : 4′-*diguanidodiphenyl sulphide* (V), m.p. 203—204° (decomp.) (*sulphate*, m.p. >290°, which did not turn yellow on storage; *picrate*, m.p. 168°). No hypoglycæmia followed administration of (I), (IV), or (V) in doses up to 100 mg. per kg. of body-wt. and there was no evidence of acute toxicity. The mere presence of $\cdot S_2\cdot$ and guanidine residues in a mol. does not give rise to hypoglycæmic activity. H. G. M.

Aliphatic azoxy-compounds. III. β-Azoxy-βε-dimethylhexane. J. G. Aston and D. E. Ailman. **IV. Preparation of α-azoxy-ketones. Molecular refractions and parachors of aliphatic azoxy-compounds.** D. E. Ailman (J. Amer. Chem. Soc., 1938, **60**, 1930—1933, 1933—1935; cf. A., 1934, 868).—III. β-Nitroso-βε-dimethyl-*n*-hexane (I) with $SnCl_2$–HCl or HCl alone at room temp. gives only the decomp. products of (I), viz., N_2, a little N_2O, *iso*-$C_5H_{11}{\cdot}CMe_2{\cdot}OH$ (II), *iso*-$C_5H_{11}{\cdot}CMe_2Cl$ (III), and octanes; with $SnCl_2$–HCl at 57—60° β-amino-βε-dimethylhexane, b.p. 94°/150 mm. (*hydrochloride*, m.p. 171°), is obtained. As (I) dissociates at 55° into the unimol. form, it is only this form which is reduced to the amine, and the bimol. form contains a N·N linking. *iso*-$C_5H_{11}{\cdot}CMe_2{\cdot}NH{\cdot}OH$, (I), and K_2CO_3–KOH at 50° give 75% of β-*azoxy*-βε-*dimethylhexane* (IV), b.p. 111°/5 mm., obtained also in 9·5% yield from the amine and NO_2-compound. $SnCl_2$–HCl merely hydrolyses (IV) to N_2, octenes, (II), and (III); $SnCl_2$ alone, but not HCl or $SnCl_4$, gives the same products. (IV) reacts very slowly with MgMeI, which is evidence against an open-chain structure for aliphatic azoxy-compounds.

IV. The parachor and [*n*] of (IV), *Et* α-*azoxy*-iso*propyl*, b.p. 126—126·5°/6 mm., and -iso*butyl ketone*, m.p. 30—31° (prep. from the NO-compounds by $SnCl_2$–HCl), give const. vals. for the N_2O group, but afford no evidence in favour of an open-chain structure. R. S. C.

Synthetic mannose- and galactose-1-phosphoric acid. S. P. Colowick (J. Biol. Chem., 1938, **124**, 557—558; cf. A., 1938, II, 39).—Acetobromogalactose (A., 1929, 682) and Ag_3PO_4 in C_6H_6 give *tris*(*tetra-acetylgalactose*-1)-*phosphoric acid*, $[\alpha]_D^{25}$ +118° in MeOH, hydrolysed (0·2N-HCl in 96% MeOH at 25°) to *galactose*-1-*phosphoric acid*, $[\alpha]_D^{25}$ +143° [*Ba* salt (+3H_2O), $[\alpha]_D^{25}$ +91° in H_2O]. Similarly *tris*(*tetra-acetylmannose*-1)-*phosphoric acid*, $[\alpha]_D^{27}$ +31·8° in MeOH, and *mannose*-1-*phosphoric acid*, $[\alpha]_D^{25}$ +58° [*Ba* salt (+3H_2O), $[\alpha]_D^{25}$ +36° in H_2O], are prepared. E. W. W.

Phosphorylation of glycogen *in vitro*. W. Z. Hassid and I. L. Chaikoff (Science, 1938, **88**, 15—16).—Details of the prep. of the *Ca* salt of the phosphoric ester of glycogen from glycogen, $CaCO_3$, and $POCl_3$ are given. The final H_2O-sol. product, $[\alpha]_D$ +174°, contained P 1·73 and Ca 2·66%, but gave no test for PO_4''' until it had been treated with H_2O_2 and conc. HNO_3 containing a trace of $Fe(NO_3)_3$. L. S. T.

"Phosphatatic" action of hydrogels. I. Fission of esters of phosphoric acid in the presence of lanthanum hydroxide. E. Bamann and M. Meisenheimer (Ber., 1937, **71**, [*B*], 1711—1720).—Solutions of Na β-glycerophosphate (I) are mixed with NH_4Cl–NH_3 at 37° and $LaCl_3$ is added; after definite intervals the H_3PO_4 liberated is determined colorimetrically. Hydrolysis occurs best at p_H 7·5—8·0. Generally, the process does not long continue in accordance with the initial rate; at p_H 9·5 the graph is linear until the change is about 30% complete but in less strongly alkaline solution the rate declines considerably sooner. Reaction is similar in presence of a veronal–NaOAc buffer but its extent is greater. The rate of hydrolysis increases with the concn. of the ester solution. Gels formed in the reaction mixture containing the substrate do not suffer appreciable loss of activity when rendered compact by being centrifuged or when washed with buffer solution. The substrate appears to protect the active parts of the surface, probably by the formation of a $La(OH)_3$–phosphate compound. Gels pptd. in the buffer mixture in the absence of substrate suffer considerable loss of activity when washed with a suitable medium; their initial low activity becomes improved as the experiment progresses. During the course of the hydrolysis the gel sometimes passes into an unstable sol from which a new gel is derived; the phenomenon depends on the p_H of the medium and the concn. of the substrate. The behaviour of phenyl- and diphenyl-phosphoric acid is similar to that of (I) whereas hexosediphosphoric acid (Ca or K salt) and inositolhexaphosphoric acid (Ca–Mg compound or Na salt) are less readily hydrolysed. H. W.

Alkyl- and aryl-substituted esters of orthosilicic acid. I. Preparation of magnesium organic compounds without the use of ethyl ether, in presence of ethyl silicate. II. Synthesis of alkyl-substituted ethyl esters of silicic acid. K. Andrianov and O. Gribanova (J. Gen. Chem. Russ., 1938, **8**, 552—557, 558—562).—I. The reaction $RX + Mg \rightarrow MgRX$ (R = Et, Bu^{β}, *iso*amyl, $CHMeBu^{\alpha}$, *sec.*-octyl, Ph; X = Cl, Br) takes place in presence of $Si(OEt)_4$, with or without solvent.

II. The reactions $RMgX + Si(OEt)_4 \rightarrow RSi(OEt)_3 + MgX{\cdot}OEt \leftarrow Mg + RX + Si(OEt)_4$ are described (X = Cl, Br). The compounds $SiR(OEt)_3$ (R = Et, R = Pr^{β}, R = Bu^{β}, b.p. 180—195°, R = *iso*amyl, R = *hexyl*, b.p. 200—220°) are described. R. T.

Decomposition of mercury dimethyl.—See A., 1938, I, 466.

Mercury derivatives of symmetrical dichloroethylene. M. FitzGibbon (J.C.S., 1938, 1218—1222).—*cis*-CHCl:CHCl with $Hg(CN)_2$–NaOH–H_2O gives Hg bischloroacetylide, $[(CCl{:}C)_2Hg]$ (I), which

explodes at 174—175° (cf. Hofmann *et al.*, A., 1910, i, 16) and with conc. HCl gives spontaneously inflammable CH:CCl. When this CH:CCl oxidises slowly, considerable quantities of O_3 are formed; the formation of an unstable ozonide may account for the explosive nature of crude (I). When pure, (I) is stable, but it slowly decomposes when kept under EtOH. *trans*-CHCl:CHCl with $Hg(CN)_2$–NaOH–H_2O gives *Hg bisdichloroethylenide*, [$(CHCl{:}CCl)_2Hg$] (II), m.p. 50·3°, together with more complex derivatives, m.p. < 185°, considered to be chain compounds, CHCl:CCl·[Hg·CCl:CCl]$_n$·H; *n* is probably 2 and 3, respectively, for the product less sol. than (II) in Et_2O, and the insol. residue. When heated with $HgCl_2$ in EtOH and the product steam-distilled, (II) gives *chloromercury dichloroethylenide* (III), m.p. 80·6°, which with KI gives the corresponding iodide, CHCl:CCl·HgI, m.p. 115° (decomp. 125°), which cannot be recrystallised owing to decomp. into I and HgI_2. With conc. HCl both (II) and (III) give $C_2H_2Cl_2$ and $HgCl_2$, and with hot Na_2S–H_2O, HgS is formed. Strong bases convert (III) into an insol. white amorphous substance. Better yields of (II) and of Hg bistrichloroethylenide (from C_2HCl_3) are obtained when the NaOH–H_2O is replaced by NaOEt–EtOH. H. G. M.

Lead organic complexes. M. Lesbre (Compt. rend., 1938, **206**, 1481—1483).—$PbMeCl_3$ (cf. A., 1937, II, 372) with excess of quinoline hydrochloride in presence of HCl affords $PbMeCl_5,2C_9H_8N$, hydrolysed to methylplumbonic acid (A., 1935, 611). The tribromide gives easily decomposable complexes. $PbEtI_3$ with C_5H_5N similarly affords $PbEtI_3,2C_5H_5N$ which decomposes at room temp. with liberation of I. No acids of the type $(PbRX_5)H_2$ or their alkali salts are isolable (cf. A., 1935, 966). Boiling aq. $PbCl_2$ with *o*-OH·C_6H_4·CO_2H in EtOH affords a complex (Pb^{IV}) which partly sublimes above 80° and dissociates strongly in concns. < 0·02N. 0·001N solutions form a basic Pb salicylate. No complex oxalate of the type described by Reis (A., 1881, 843) can be isolated. J. L. D.

Stereoisomeric forms of 1 : 2-diphenyl*cyclo*pentane. H. A. Weidlich (Ber., 1938, **71**, [*B*], 1601—1603; cf. Bernhauer and Hoffmann, A., 1937, II, 498).—Treatment of Me_2 *meso*-βγ-diphenyladipate with finely-divided Na in boiling C_6H_6 gives *cis*-3 : 4-diphenyl*cyclo*pentanone, b.p. 115°/0·02 mm., m.p. 107°, reduced (Clemmensen) to *cis*-1 : 2-diphenyl*cyclo*pentane (I), m.p. 47°. Analogously, Me *r*-βγ-diphenyladipate gives *trans*-3 : 4-diphenyl*cyclo*pentanone (II), b.p. 180°/0·02 mm., m.p. 177°, whence *trans*-1 : 2-diphenyl*cyclo*pentane, m.p. 65°. Von Liebig's observation (A., 1914, i, 845) of the reduction of (II) to (I) appears erroneous. H. W.

Monohalogeno-derivatives of methyl*cyclo*hexane. M. Mousseron and R. Granger (Compt. rend., 1938, **206**, 1486—1488).—1-Methyl*cyclo*hexanol (I) with HCl at 100° or PCl_5 in C_6H_6 at 0° affords only 1-chloro-1-methyl*cyclo*hexane (II), the Mg derivative of which is oxidised to (I) or converted into 1-*methyl*-cyclo*hexane*-1-*carboxylic acid*, m.p. 39° (*amide*, m.p. 68°). *trans*-2-Methyl*cyclo*hexanol with HCl affords (II), *trans*- and *cis*-1-chloro-2-methyl*cyclo*hexane, converted as above into the *cis*-1-carboxylic acid (*anilide*, m.p. 106°) and the *cis*-1-OH-compound (*Ph carbamate*, m.p. 94°) which with PCl_5 affords a mixture of isomeric Cl-compounds, the *trans*-isomeride predominating (corresponding *anilide* and *Ph carbamate*, m.p. 152° and 105°, respectively). *dl-trans*-3-Methyl*cyclo*hexanol with HCl affords 1-methyl-Δ^3-*cyclo*hexene (III) and a mixture of Cl-compounds containing 60% of cis-1-*chloro*-3-*methyl*cyclo*hexane* (IV), b.p. 40°/10 mm., converted as above into the 1-hydroxy- (*Ph carbamate*, m.p. 90°) and 1-carboxy- (V) (*anilide*, m.p. 102—103°) -compounds. (IV) with PCl_5 affords some (III) but mainly the trans-*isomeride*, b.p. 39°/10 mm., of (IV) (*Ph carbamate* and *anilide* corresponding with those from the *cis*-form have m.p. 93° and 110—111°, respectively). The Me esters of (V) and its *trans*-analogue when fractionally distilled are separated into *d*- and *l*-forms. *trans*-4-Methyl*cyclo*hexanol with HCl affords (III) (20%), *cis*- and *trans*-1-chloro-4-methyl-*cyclo*hexane. As above, the former is converted into a 1-carboxylic acid (*anilide*, m.p. 149—150°) and a 1-OH-compound (*Ph carbamate*, m.p. 118—119°) which with PCl_5 affords the *trans*-isomeride (corresponding *anilide* and *Ph carbamate* have m.p. 108—109° and 124—125°, respectively). *cis*- or *trans*-3-Methyl*cyclo*hexanol (VI) with HBr affords (III) and cis-1-*bromo*-3-*methyl*cyclo*hexane*, b.p. 59°/10 mm., converted into *cis*-(VI) (p-*nitrobenzoate*, m.p. 78—79°). *cis*- or *trans*-(VI) with PBr_5 affords trans-1-*bromo*-3-*methyl*cyclo*hexane*, b.p. 58°/10 mm., which rapidly loses HBr. *trans*-(VI) with HI affords cis-1-*iodo*-3-*methyl*cyclo*hexane*, b.p. 72°/10 mm. J. L. D.

Reduction of potassium permanganate by cyclic hydrocarbons.—See A., 1938, I, 463.

Free radicals containing a *cyclo*hexane ring. I. Diphenyl-*p*-*cyclo*hexylphenylmethyl. I. Zugravescu and S. Zugravescu (Bul. Soc. Chim. România, 1937, **19**, 85—92).—Me *p*-*cyclo*hexylbenzoate with MgPhBr (2 mols.) in Et_2O gives *diphenyl*-p-cyclo*hexylphenylcarbinol*, b.p. 100°/2 mm., converted by AcCl in C_6H_6 into *diphenyl*-p-cyclo*hexyl-phenylmethyl chloride* (I), m.p. 123°, which in dry C_6H_6 with Cu powder (CO_2 atm.) gives a red colour, due to *diphenyl*cyclo*hexylphenylmethyl*, and yields s-*tetraphenyldi*cyclo*hexylphenylethane* (an oil). Oxidation of (I) by air in C_6H_6 with Cu powder yields the *peroxide*, m.p. 164°. J. D. R.

Isomerisation of carotenoids. L. Zechmeister and P. Tuzson [with, in part, I. Berger] (Biochem. Z., 1938, **32**, 1305—1311).—Solutions of chromatographically pure lycopene, β-carotene, or cryptoxanthin undergo, when kept at room temp., a partial isomerisation which manifests itself in the decrease of the colorimetric val. and in the displacement of the absorption max. towards shorter λ. The rate of this spontaneous isomerisation, which tends towards an equilibrium, increases on heating. The interconversion is reversible. Partly isomerised solutions always give two distinct layers in the Tswett column; the phenomenon is not caused by the adsorption experiment itself but is already present in the solution. H. W.

Raman effect in diagnosis of the constituents of a mixture of isomeric dihalogenated benzene derivatives. R. PAJEAU (Compt. rend., 1938, **207**, 344—345).—On bromination in presence of $BeBr_2$, C_6H_6 gives small quantities of *o*- and *p*-$C_6H_4Br_2$, and PhCl gives *o*- and *p*-C_6H_4ClBr. In presence of $AlCl_3$ PhCl gives all three isomerides. A. J. E. W.

By-products in aromatic nitration. G. M. BENNETT and P. V. YOULE (Nature, 1938, **142**, 356).—OH by-products are formed in considerable amounts in the nitration of aromatic compounds with *m*-directive groups; *e.g.*, nitration of $PhNO_2$ gives 0·5—6·5% of styphnic acid. The mechanism of the process is discussed. L. S. T.

Reaction of double decomposition. G. K. HAÜSER (Mem. Inst. Chem. Tech. Ukrain. Acad. Sci., 1938, No. 7, 121—127).—When Na_2CO_3 containing $NaHCO_3$ is added to aq. *m*-$C_6H_4(SO_3)_2Ca$ CO_2 is not immediately evolved, owing to the formation of $Ca(HCO_3)_2$. R. T.

Separation of sulphuric acid from nitric, alkyl- and aryl-sulphonic, and alkyl sulphuric acids by means of liquid ammonia. J. H. BILLMAN and L. F. AUDRIETH (J. Amer. Chem. Soc., 1938, **60**, 1945—1946).—Since $(NH_4)_2SO_4$ is insol. in liquid NH_3, H_2SO_4 can be separated from HNO_3, RSO_3H, $ArSO_3H$, or $RHSO_4$ (R = alkyl) by dissolution in liquid NH_3 and filtration. By evaporating the filtrate *NH_4 sulphanilate*, +0·5H_2O, *benzene-*, o-*aminobenzene*,- +0·5H_2O, p-*toluene-*, 2-*aminotoluene*-5-, d-*camphor*,- o-, m-, and p-*nitrobenzene-*, and 2-*naphthalene-sulphonate*, *naphthionate*, *lauryl sulphate*, and *Et sulphate* are obtained. $PhSO_3Na$ and $Bu^{\alpha}SO_3Na$ are insol., and $Na(n\text{-}C_{12}H_{25})SO_4$ and $Na(CH_2Ph)SO_4$ slightly sol., in liquid NH_3. R. S. C.

Sulphonation of cold aromatic hydrocarbons. I. TANASESCU and M. MACAROVICI (Bull. Soc. chim., 1938, [v], **5**, 1126—1129).—C_6H_6 is transformed by H_2SO_4 (*d* 1·84) at 22° during 24 hr. into $PhSO_3H$, m.p. 52—53°, the bulk of which remains in the acid layer. The yield depends on the quality of C_6H_6 and H_2SO_4. Less satisfactory yields are obtained from pure C_6H_6, free from thiophen, and H_2SO_4 with 7% of added SO_3. Under the same conditions, PhCl gives exclusively *p*-$C_6H_4Cl{\cdot}SO_3H$, m.p. 92—93° (lit. m.p. 68°), PhBr gives *p*-$C_6H_4Br{\cdot}SO_3H$, m.p. 88—90°, and PhMe yields solely *p*-$C_6H_4Me{\cdot}SO_3H$, m.p. 103—104°, free from sulphone. H. W.

Catalytic effects in the bromination of toluene. M. S. KHARASH, P. C. WHITE, and F. R. MAYO (J. Org. Chem., 1938, **3**, 33—47).—The mechanism proposed for the formation of CH_2PhBr in the bromination of PhMe consists in a chain reaction initiated by Br atoms, and is in accord with previous work which is reviewed. Nuclear substitution, probably a bimol. reaction, increases in rate with increasing [Br], but does not involve Br atoms. The *ortho–para* ratio is unaffected by the presence of peroxides, but the yield of CH_2PhBr is greatly increased by addition of org. peroxides (Bz_2O_2, ascaridole, triacetone peroxide) to dil., but not conc., solutions of Br in PhMe in reactions in the dark in presence of air. In photobromination, the rate of reaction and the yield of CH_2PhBr are reduced, and the yield of C_6H_4MeBr is increased, by exclusion of O_2, presence of which, it is suggested, may be essential to this reaction. Side-chain substitution in photobromination and in the peroxide-catalysed reaction is completely inhibited by small amounts of NO-compounds. AcOH and $PhNO_2$, as solvents, inhibit the latter reaction, but increase the rate of nuclear substitution. CCl_4 acts as an inert diluent. Side-chain bromination of PhEt is greatly increased, in the dark, by addition of peroxides. These results support the proposed mechanism, and accord with the view that Br atoms may also be liberated from HBr by light in presence of O_2 and peroxides (cf. A., 1937, II, 373). H. G. M.

Catalysed polymerisation of styrene. II.—See A., 1938, I, 464.

Isomerisation of *iso*stilbene to stilbene by hydrogen bromide in presence of oxygen and of ferromagnetic metals. Y. URUSHIBARA and O. SIMAMURA (Bull. Chem. Soc. Japan, 1938, **13**, 566—569; cf. A., 1938, II, 48; Kharasch *et al.*, A., 1937, II, 332).—The change *iso*stilbene → stilbene in presence of HBr in the dark is accelerated by O_2 in C_6H_6, by reduced Ni or Fe (no solvent), much less by Pt-black, Pd-black, or Cu, and not at all by Ni in C_6H_6. *o*-$C_6H_4(OH)_2$ inhibits the action of HBr in sunlight, and of HBr and Ni, HBr and O_2, or HBr at 100°, in the dark. $NHPh_2$ inhibits slightly the action of HBr and O_2 in the dark, but has no effect on the others. A. LI.

Synthesis of disubstituted acetylenes. J. R. JOHNSON, A. M. SCHWARTZ, and T. L. JACOBS (J. Amer. Chem. Soc., 1938, **60**, 1882—1884).—Disubstituted acetylenes are readily prepared from *p*-$C_6H_4Me{\cdot}SO_3R$ and CR′:CNa or CR′:C·MgBr. Thus CPh:CNa in Bu^{α}_2O or PhMe gives 77% of CPh:CEt, b.p. 82°/5 mm. (hydrated to $COPhPr^{\alpha}$), in Bu^{α}_2O 75% of *α-phenyl-β-γ′-chloropropylacetylene*, b.p. 125—127°/4 mm. (converted by way of the nitrile into the acid, which with $KMnO_4$ yields BzOH and $CO_2H{\cdot}[CH_2]_3{\cdot}CO_2H$), and in PhMe 65—70% of $CPh{:}CBu^{\alpha}$, b.p. 109—110°/12 mm. (hydrated to $COPh{\cdot}C_5H_{11}$-*n*). *n*-$C_8H_{17}{\cdot}C{:}CNa$ in Bu^{α}_2O gives 63% of *Δ$^{\gamma}$-dodecinene*, b.p. 95°/12 mm. (oxidised to $EtCO_2H$ and $C_8H_{17}{\cdot}CO_2H$), and 65% of *α-chloro-Δ$^{\delta}$-tridecinene*, b.p. 123—124°/3 mm. (converted by way of the nitrile into the acid, which with $KMnO_4$ gives $CO_2H{\cdot}[CH_2]_3{\cdot}CO_2H$ and $C_8H_{17}{\cdot}CO_2H$). CPh:C·MgBr (not CPh:CNa) gives CPh:C·CH_2Ph and 46% of *δ-chloro-Δ$^{\alpha}$-butinenylbenzene*, b.p. 95°/3 mm. R. S. C.

Raman spectra of hydrocarbons containing tertiary C–D linkings. W. G. BROWN, C. J. MIGHTON, and M. SENKUS (J. Org. Chem., 1938, **3**, 62—75).—The Raman lines for $CHPh_3$ (freed from fluorescent material by distillation in vac.), $CHPh_2Me$, $CHPhMe_2$ (cf. A., 1937, I, 113), and $CHMe_2{\cdot}CH_2Ph$, and the corresponding *tert.*-deutero-compounds, *triphenyldeuteromethane*, m.p. 91—92° (prepared from $NaCPh_3$ and AcOD: reduction of CPh_3Cl with Zn–AcOD is accompanied by substitution of D in the C_6H_6 rings), *diphenylmethyldeuteromethane*, b.p. 136—137°/12 mm. (prepared from AcOD and $KCPh_2Me$, obtained from $CPh_2Me{\cdot}OMe$ and Na–K), *phenyldimethyldeuteromethane*, b.p. 150·0° (similarly pre-

pared), and *benzyldimethyldeuteromethane*, b.p. 170·5—171·5° (prepared from $CH_2Ph{\cdot}CMe_2{\cdot}MgCl$ and AcOD). The C–D lines for the last four compounds have frequencies of 2132, 2122, 2152, and 2147±5 cm.$^{-1}$, respectively. It is concluded that the binding force for the *tert.* C–H linking is essentially const. in this series of compounds and comparable with that of the corresponding linking in $CHMe_3$, and that the factors responsible for the differences in chemical behaviour exert a negligible influence on the normal states of the mols. The increase in the binding force of the C–H linking in halogen-substituted methanes is attributed primarily to electrostatic attraction between halogen and H. H. G. M.

Reaction between dichlorodiphenylmethane and salts of organic acids as a method of preparation of anhydrides of organic acids. V. V. Evlampiev and N. P. Gurianov (Utschen. Zap. Univ. Kazan, 1937, **97**, No. 8, 55—69).—CPh_2Cl_2 on warming with AgOAc without solvent to 100° or on mixing with AgOAc in light petroleum at room temp. gives $COPh_2$ and Ac_2O, presumably through the unstable ester $CPh_2(OAc)_2$. The yield is high. Analogous reactions are also possible with NaOAc, $Pr^{\alpha}CO_2Na$, NaOBz, $(CH_2{\cdot}CO_2Na)_2$, and Na palmitate. CPh_2Cl_2 and HCO_2Na give $COPh_2$, HCO_2H, HCl, etc. J. J. B.

Propinene–allene tautomerism. αγ-Diphenylpropinene (phenylbenzylacetylene) and related compounds. J. R. Johnson, T. L. Jacobs, and A. M. Schwartz (J. Amer. Chem. Soc., 1938, **60**, 1885—1889).—The prototropic change, $CAr{:}C{\cdot}CH_2Ar \rightleftharpoons CHAr{:}C{:}CHAr$, is similar to the changes, $CH_2R{\cdot}CN \rightleftharpoons CHR{:}C{:}NH$, and $CPh{:}C{\cdot}NH_2$ (produced by Hofmann degradation of $CPh{:}C{\cdot}CO{\cdot}NH_2$) $\longrightarrow CHPh{:}C{:}NH \rightleftharpoons CH_2Ph{\cdot}CN$, and analogous to the anionotropic changes, $CR_2Br{\cdot}C{:}CR \longrightarrow CR_2{:}C{:}CRBr$ and $OH{\cdot}CR_2{\cdot}C{:}CR \longrightarrow CR_2{:}CH{\cdot}COR$. It does not, however, occur when Ar = Ph or p-C_6H_4Br, since *αγ-diphenyl-* (I), *γ-phenyl-α-*p*-bromophenyl-* (II), and *α-phenyl-γ-*p*-bromophenyl-*Δ^{α}*-propinene* (III) exist and react only as such. C:CPh has thus less activating effect on CH_2 than has CN or C:CH, a result in line with electronic considerations. $CPh{:}C{\cdot}MgBr$ and p-$C_6H_4Me{\cdot}SO_3CH_2Ph$ (IV) in Et_2O give 72% of (I), b.p. 128—129°/1—2 mm., obtained also in 27% yield from MgPhBr and $CPh{:}C{\cdot}CH_2Br$. With $KMnO_4$ (I) gives BzOH (48%) and $CH_2Ph{\cdot}CO_2H$ (15%), with HgO–H_2SO_4–EtOH gives 50% of $CH_2Ph{\cdot}CH_2{\cdot}COPh$, and in CCl_4 yields *αβ-dibromo-αγ-diphenyl-*Δ^{α}*-propene*, m.p. 60°, and an oily I_2-compound. p-$C_6H_4Br{\cdot}C{:}CH$, b.p. 71—72°/3 mm., m.p. 62—63°, with MgEtBr gives a Grignard reagent, converted by (IV) into (II) (26% yield), m.p. 87°, which with HgO–H_2SO_4–EtOH gives p-*bromo-γ-phenylpropiophenone*, m.p. 98—99° (*semicarbazone*, m.p. 164—165°; *oxime*, m.p. 115—125°), also obtained from p-$C_6H_4Br{\cdot}CN$ and $CH_2Ph{\cdot}CH_2{\cdot}MgBr$. p-*Bromobenzyl* p-*toluenesulphonate*, m.p. 74—75°, and $CPh{:}C{\cdot}MgBr$ give 50% of (III), b.p. 166—169°/1—2 mm., m.p. 42—44°, which yields *αβ-dibromo-α-phenyl-γ-bromophenyl-*Δ^{α}*-propinene*, m.p. 108—108·5, and *γ-*p*′-bromophenylpropiophenone*, m.p. 68·5—69° (*semicarbazone*, m.p. 161—162°; 2 : 4-*dinitrophenylhydrazone*, m.p. 67—67·5°), also obtained from $CH_2Ph{\cdot}CH_2{\cdot}COCl$ and $ZnPh_2$. R. S. C.

Structure of distyrenes. L. Marion (Canad. J. Res., 1938, **16**, B, 213—217).—$CH_2Ph{\cdot}CH_2{\cdot}CHPh{\cdot}CO_2H$ (modified prep. from $CH_2Bz{\cdot}CHPh{\cdot}CO_2H$), m.p. 75°, yields (Na–EtOH reduction of the ester) $CH_2Ph{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}OH$ (I), b.p. 174—180°/1 mm., dehydrated by $KHSO_4$ to $CH_2Ph{\cdot}CH_2{\cdot}CPh{:}CH_2$ (II), b.p. 140°/2—3 mm., which is oxidised by $KMnO_4$ to $CH_2Ph{\cdot}CH_2{\cdot}COPh$ (III), isomerises when kept to (? trans-)*αγ-diphenyl-*Δ^{α}*-butene*, m.p. 47—47·5°, b.p. 130—140°/1 mm. [*dibromide* (IV), m.p. 86·5°; with O_3 gives PhCHO and $CHPhMe{\cdot}CHO$]. Dehydration of (I) by hot 20% H_2SO_4 also yields (II), which in this case isomerises to *αγ-diphenyl-*Δ^{β}*-butene*, an oil, which gives an unstable dibromide and with $KMnO_4$ yields (III), BzOH, COPhMe, and (?) $CH_2Ph{\cdot}CO_2H$. The distyrene obtained by pyrolysis of polystyrene (mol. wt. 8000) contains no (II) (cf. Staudinger *et al.*, A., 1935, 740). *αγ*-Diphenylpropane, b.p. 124°/2 mm. [$(NO_2)_4$-derivative, m.p. 169°], is obtained by Clemmensen reduction of $COPh{\cdot}CH_2{\cdot}CH_2Ph$, into which it is reconverted by CrO_3 in hot AcOH. (IV) is also obtained from (II). M.p. are corr. R. S. C.

Configuration of certain diphenyl compounds indicated by their dipole moments.—See A., 1938, I, 437.

Catalytic condensation of Grignard reagents with hydrocarbons. M. S. Kharasch, W. Goldberg, and F. R. Mayo (J. Amer. Chem. Soc., 1938, **60**, 2004).—Formation of Ph_2 derivatives from MgArX and hydrocarbons involves the pre-formed Grignard reagent. Presence of at least catalytic amounts of H_2O and Mg are necessary, which indicates their participation in a chain reaction. Use of a min. amount of Et_2O is essential. The reaction is a general one. $CH_2Ph{\cdot}MgCl$ with C_6H_6 gives CH_2Ph_2 (29%) and $(CH_2Ph)_2$ (18%), with *m*-xylene gives 2 : 4-$C_6H_3Me_2{\cdot}CH_2Ph$ (17%), with mesitylene gives 2 : 4 : 6-$C_6H_2Me_3{\cdot}CH_2Ph$ (20%), but with *cyclo*hexane gives no benzyl*cyclo*hexane. MgPhBr with PhMe gives p-C_6H_4PhMe (about 10%) and Ph_2 (20%), with *m*-xylene gives $C_6H_3PhMe_2$ (9%), with PhCl gives C_6H_4PhCl (9%) and Ph_2 (39%), and with *cyclo*hexane gives Ph_2 (39%) (no phenyl*cyclo*hexane). MgMeI and C_6H_6 give only 0·06% of PhMe and 0·03% of *p*-xylene. R. S. C.

Mechanism of the Fittig reaction. O. Blum-Bergmann (J. Amer. Chem. Soc., 1938, **60**, 1999).—The formation of Ph radicals during the Fittig reaction is confirmed by the reaction of PhBr, C_6H_6, and Na in N_2 to give Ph_2, p-$C_6H_4Ph_2$ (I), and o-$C_6H_4Ph{\cdot}OH$, and by reaction of NaPh (from $HgPh_2$ and Na in C_6H_6) with PhBr to give Ph_2 and (I). (I) arises by disproportionation of Ph to C_6H_6 and C_6H_4. R. S. C.

Cracking of tetrahydronaphthalene with aluminium chloride. M. B. Turova-Polak and N. B. Lubimova (J. Gen. Chem. Russ., 1938, **8**, 538—543).—Tetrahydronaphthalene when distilled at 170—270° from $AlCl_3$ yields chiefly C_6H_6 and its homologues, together with some *cyclo*-pentane and -hexane. R. T.

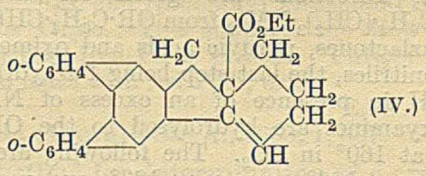
Dehydration of certain *cyclo*pentanol homologues. II. J. I. Denisenko (J. Gen. Chem.

Russ., 1938, **8**, 410—412).—α-Phenyl-β-1-hydroxy-*cyclo*pentylethane and anhyd. $H_2C_2O_4$ at 130—135° yield 1 : 2-trimethylene-1 : 2 : 3 : 4-tetrahydronaphthalene, from which 4 : 5-benzoindane is obtained by passing over C–Pt at 300° in a stream of CO_2 or H_2. R. T.

1 : 2 : 3 : 4-Dibenzphenanthrene. I. E. Bergmann (J. Amer. Chem. Soc., 1938, **60**, 1798—1799).—Unsuccessful attempts to synthesise 1 : 2 : 3 : 4-dibenzphenanthrene are described. β-9-Phenanthrylethylmagnesium bromide and 2-methyl*cyclo*hexanone give, with (?) a little 9-ethylphenanthrene, 1-*methyl*-2-9′-*phenanthrylethyl*-Δ^1-cyclo*hexene*, b.p. 220°/0·01 mm. (*picrate*, m.p. 124—125°; absorbs 2 Br), cyclised by $SnCl_4$ and HCl in C_6H_6 at room temp. to a *spirane*, b.p. 220°/0·01 mm. (*picrate*, m.p. 172°), which with Se at 300—320° gives poor yields of phenanthrene and a *hydrocarbon*, $C_{22}H_{14}$, m.p. 184° (*picrate*, m.p. 220°). Di*cyclo*hexenyl and 1 : 2-naphthaquinone at 180° give a resin, but 3-bromo-1 : 2-naphthaquinone does not react at 100° in $(CHCl_2)_2$. The K derivative of Et *cyclo*hexanone-2-carboxylate does not react with β-9-phenanthrylethyl chloride. R. S. C.

Magnetochemical investigations of hexa-arylethanes. E. Müller and W. Kruck (Ber., 1938, **21**, [*B*], 1778—1783).—Preliminary results show that in accordance with quantum-theoretical views the introduction of groups such as the chrysyl and phenanthryl residues which increase the energy of union also increase to a very marked extent the dissociability of hexa-arylated ethanes. The observations are not in themselves a complete verification of the quantum theories. 2-Benzoylchrysene and LiPh in C_6H_6 give *diphenyl*-2-*chrysylcarbinol*, m.p. 238°, converted by AcCl in boiling C_6H_6 into *diphenyl*-2-*chrysylmethyl chloride*, m.p. 194—195° (slight decomp.), which with Cu powder in C_6H_6 affords *ααββ-tetraphenyldi*-2-*chrysylethane*, m.p. 239° (decomp.) (also $+1C_6H_6$); this is dissociated to the extent of at least 65% in $C_{10}H_8$ at 125°. Diphenyl-9-phenanthrylcarbinol is transformed by AcCl in Et_2O saturated with HCl into diphenyl-9-phenanthrylmethyl chloride, m.p. 178°, converted by Hg in C_6H_6 at room temp. or by Cu powder in boiling C_6H_6 into a dimeric *product*, $C_{54}H_{38}$, m.p. 223—225° under N_2 but varying with the mode of heating. Me phenanthrene-3-carboxylate and LiPh in Et_2O give *diphenyl*-3-*phenanthrylcarbinol*, m.p. (crude) 80°, converted by MeOH–C_6H_6 or MeOH–$COMe_2$ into diphenyl-3-phenanthrylcarbinyl Me ether, m.p. 144—145°. This with AcCl in Et_2O gives diphenyl-3-phenanthrylmethyl chloride, m.p. 129—130°, which with Hg in C_6H_6 gives a dark red solution extremely sensitive to air; the corresponding *peroxide* has m.p. 195—196°. H. W.

1 : 2-*cyclo*Pentenotriphenylene. II. E. Bergmann and F. Bergmann (J. Amer. Chem. Soc., 1938, **60**, 1805—1807).—The compounds previously (A., 1936, 1371) considered to be *cyclo*pentenotriphenylene, 7-methyl-1 : 2-benzpyrene, and 1 : 2 : 3 : 4-dibenzfluorene are shown to be (? 9-)*methyl*-3 : 4-*benzpyrene* (I), 1 : 2 : 3 : 4-*dibenzfluorene* (II), and cyclo*pentenotriphenylene* (III), respectively. The adduct of 9-*cyclo*pentenylphenanthrene and maleic anhydride with $Pb(OAc)_4$, best in AcOH–Ac_2O at 75°, gives 1 : 2-cyclo*pentenotriphenylene*-3 : 4-*dicarboxylic anhydride*, m.p. 296°, which with basic Cu carbonate in boiling quinoline or soda-lime at 180—300° gives 1 : 2-cyclo*pentenotriphenylene*-3(or 4)-, m.p. 299—300° (*Me* ester, m.p. 197—198°), and -4(or 3)-*carboxylic acid*, m.p. 249° (*Me* ester, m.p. 117°), respectively. The former acid is converted by heating with Zn dust or as K salt alone at 320—350°, the latter by boiling with basic Cu carbonate in quinoline, into (III), b.p. 260—280°/2·5 mm. (picrate, m.p. 165—167°). The structure assigned to (II) is proved by its absorption spectrum and fluorescence. Di*cyclo*hexenyl and indene at 180° give *forms*, b.p. 180—185°/0·3 mm. and 185—190°/0·3 mm., of *dodecahydro*-1 : 2 : 3 : 4-*dibenzfluorene*, dehydrogenated by Se at 300° to (II). 9-Chloromethylphenanthrene (prep. from the carbinol by



(IV.)

$SOCl_2$ and $NPhMe_2$ in in C_6H_6 at 0°) and Et sodio-*cyclo*hexanone-2-carboxylate in PhMe give *Et* 2-9′-*phenanthrylmethyl*cyclo*hexanone*-2-*carboxylate*, m.p. 118—119°, converted by 2 : 1 (vol.) H_2O–H_2SO_4 into the *substance* (IV), m.p. 250°. R. S. C.

Synthesis of 4 : 9- and 4 : 10-dimethyl-1 : 2-benzanthracene. L. F. Fieser and R. N. Jones (J. Amer. Chem. Soc., 1938, **60**, 1940—1945).—Carcinogenic activity of 1 : 2-benzanthracene derivatives is connected with *meso* (9 or 10) and α (4, 5, or 8) substituents; 1 : 2 : 3 : 4-H_4-derivatives may also be active. Two new such aromatic compounds and their H_4-derivatives are prepared. 9 : 10-Dimethyl-1 : 2-benzanthracene and 1′ : 2′ : 3′ : 4′-tetrahydro-4 : 10-ace-1 : 2-benzanthracene are highly carcinogenic. The structure of 6-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene and 7-*o*-carboxybenzoyl-6-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (I) (modified prep.), m.p. 167·5—168° [Schroeter (A., 1921, i, 861), m.p. 160°], is proved by reactions detailed below and by oxidation of (I) by HNO_3 to 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$. With Zn–2N-NaOH (I) gives 7-*o*-*carboxybenzyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 168·9—169·1°, converted by $ZnCl_2$–AcOH–Ac_2O into 4-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benz*-9-*anthranyl acetate*, m.p. 150·5—151°, which with $MgBu^nBr$ gives 4-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benz*-9-*anthrone* (II), m.p. 151·5—151·7°. With MgMeCl (II) gives 4 : 9-*dimethyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 62·4 62·8° (*picrate*, m.p. 135·8—136·2°), which with S at 180—210° in N_2 gives 4 : 9-*dimethyl*-1 : 2-*benzanthracene*, m.p. 75·1—75·5° (*picrate*, m.p. 116—116·4°), but Se at 300° causes loss of the *meso*-Me and leads to 4-methyl-1 : 2-benzanthracene (III). With Zn–2N-NaOH (II) gives 4-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 82·3—82·9° (*picrate*, m.p. 158—158·2°), converted by Se at 290—300° into (III) [$C_6H_3(NO_2)_3$ additive *compound*, m.p. 163·5—164°]. MgMeCl and (II) give the *lactone*, m.p. 115—115·5°, of 7-α-*hydroxy*-α-*o*-*carboxyphenylethyl*-6-*methyl*-1 : 2 : 3 : 4-

tetrahydronaphthalene, reduced by Zn–Hg–AcOH–HCl–PhMe to 7-α-*o*-*carboxyphenylethyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, *forms*, m.p. 147—148° and 165·5—166°, respectively, cyclised by H_2SO_4 at room temp. to 4 : 10-*dimethyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benz*-9-*anthrone*, m.p. 112·8—113·4°. Zn dust in NaOH–PhMe reduces this to 4 : 10-*dimethyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 105—105·5° (*picrate*, m.p. 146—147°), dehydrogenated by S at 190—215° in N_2 to 4 : 10-*dimethyl*-1 : 2-*benzanthracene*, m.p. 114—114·4° (sinters at 113°) (*picrate*, m.p. 161·5—162°). M.p. are corr. R. S. C.

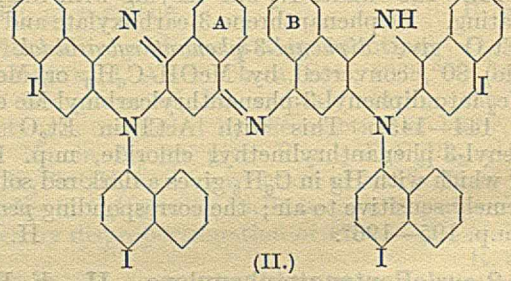
Mol. wt. of fichtelite.—See A., 1938, I, 502.

β-Phenylethylamine derivatives. Tertiary and quaternary salts. J. S. Buck, R. Baltzly, and W. S. Ide (J. Amer. Chem. Soc., 1938, **60**, 1789—1792).—Directions are given for the prep. of OR·C_6H_4·[CH_2]$_2$·NMe_2 from OR·C_6H_4·CHO by way of the azlactones, pyruvic acids and oximes, and arylacetonitriles, the last step being Pd-hydrogenation in MeOH in presence of an excess of $NHMe_2$. The alkoxyamines are hydrolysed to the OH-amine by HCl at 160° in CO_2. The following are described: 4-*o*-, m.p. 186°, -*m*-, m.p. 123°, and p-*ethoxy*-, m.p. 168°, 4-3′-*methoxy*-2′-*ethoxy*-, m.p. 140°, and 4-3′ : 4′-*diethoxy*-*benzylidene*-2-*phenyloxazolone*, m.p. 161°; *o*-*methoxy*-, m.p. 161°, *o*-, m.p. 164°, *m*-, m.p. 132°, and p-*ethoxy*-, m.p. 182°, 3-*methoxy*-2-*ethoxy*-, an oil, and 3 : 4-*diethoxy*-*phenylpyruvic acid*, m.p. 164°; m-*ethoxy*-, b.p. 141°/8 mm., 3-*methoxy*-2-*ethoxy*-, b.p. 133°/2 mm., and 4-*methoxy*-3-*ethoxy*-*phenylacetonitrile*, b.p. 151°/2·5 mm., m.p. 61·5°; dimethyl-β-phenylethylamine hydrochloride, m.p. 165° (corresponding methochloride, m.p. 192°); β-*o*-, m.p. 159·5° (221°), -*p*-, m.p. 176·5° (206°), and -m-*methoxy*-, m.p. 135° (158°), -3 : 4-, m.p. 197° (206°), and -2 : 3-*dimethoxy*-, m.p. 140° (180°), -*m*-, m.p. 137° (160°), -*p*-, m.p. 175° (193°), and -*o*-*ethoxy*-, m.p. 143° (211°), -3-*methoxy*-2-*ethoxy*-, m.p. 145° (182°), -3-*methoxy*-4-*ethoxy*-, m.p. 151° (173°), -4-*methoxy*-3-*ethoxy*-, m.p. 161·5° (162°), -3 : 4-*diethoxy*-, m.p. 138° (125°), -*o*-, m.p. 108° [254° (decomp.)], -*m*-, m.p. 164° (220°), and -*p*-hydroxy-, m.p. 181° [287° (decomp.)], -3 : 4-, m.p. 127° [263° (decomp.)], and -2 : 3-*dihydroxyphenyldimethylamine hydrochloride*, m.p. 96° (225°), the m.p. in parentheses being those of the corresponding arylethyltrimethylammonium chlorides. Temp. are corr. R. S. C.

Thermal rearrangement of *N*-chloroacetanilide in aqueous solution. A. R. Olson and J. C. Hornel (J. Org. Chem., 1938, **3**, 76—89; cf. A., 1937, II, 491).—In 20% aq. EtOH at 40° NPhClAc (I) reacts (*A*) with H· and Cl′ to give a steady-state concn. of Cl_2 and NHPhAc, which subsequently react to give *o*- and *p*-C_6H_4Cl·NHAc and HCl (cf. Orton *et al.*, Proc. C.S., 1909, **25**, 233), and (*B*) by condensation of 3 mols. of (I) to give an unknown compound (II) and two Cl′. With [Cl′] initially 0·04M and 0·005M about 70 and 25% respectively, of (I) disappears by reaction (*A*). (II) is an oxidising agent, and in acid solution oxidises I′ instantaneously, Br′ fairly rapidly, and Cl′ very slowly. The initial rate of formation of (II) ∝ initial (I) concn. and [H·], but independent of [Cl′], and is somewhat lowered by increasing [EtOH]. (II) decomposes slowly into a non-oxidising compound and a Cl′. H. G. M.

Associating effect of the hydrogen atom. III. Further examples of steric interference between vicinal groups. H. O. Chaplin and L. Hunter (J.C.S., 1938, 1034—1038).—Association factors are calc. cryoscopically in $C_{10}H_6$, or from wet m.p., as before (A., 1938, II, 179). Of 2 : 4 : 1- (I), 3 : 4 : 1- (II), and 2 : 3 : 1-$(NO_2)_2C_6H_3$·NHAc (III), (I) is unassociated, (II) associated, and (III) intermediate in properties. *Et* 4-*nitro*-3-*acetamidobenzoate*, m.p. 92° (from Ag salt), like *o*-NO_2·C_6H_4·NHAc (IV), is unassociated, but 2 : 3 : 5-NO_2·$C_6H_2Br_2$·NHAc and *Et* 2-*nitro*-3-*acetamidobenzoate*, m.p. 133°, are associated, as is 2 : 1 : 3-NO_2·C_6H_3Me·NHAc (from wet m.p. only). It thus appears that 3-substitution in (IV) hinders chelation (and favours association), owing to rotation of the NO_2-group into a position not coplanar with the C_6H_6 nucleus. Comparison between 1 : 8 : 2- and 1 : 6 : 2-$(NO_2)_2C_{10}H_5$·NHAc is difficult, owing to low solubility in $C_{10}H_8$, but the former is more associated (less chelated). In compounds of type 2 : 3 : 4-$(NO_2)_2C_6H_3X$·NHAc, it is suggested that X, if large, can orient the 3-NO_2 transversely to the nucleus, and favour chelation of the 2-NO_2; thus 2 : 3 : 4 : 1-$(NO_2)_2C_6H_2Br$·NHAc is much less, and 2 : 3 : 1 : 4-$(NO_2)_2C_6H_2Me$·NHAc rather less, associated than (III), although 2 : 3 : 4 : 1-$(NO_2)_2(OEt)C_6H_2$·NHAc is more associated. 2 : 5 : 4 : 1-$(NO_2)_2C_6H_2Br$·NHAc and 2 : 5 : 1 : 4-$(NO_2)_2C_6H_2Me$·NHAc are comparatively unassociated, and (from wet m.p. only) 2 : 3 : 4 : 1- and 3 : 5 : 4 : 1-$(NO_2)_2(OMe)C_6H_2$·NHAc are associated. Association–concn. curves and m.p. data are recorded. Attempted esterification (Fischer–Speier) of 2 : 3 : 1-$(NO_2)(NHAc)C_6H_3$·CO_2H gives *Et* 2-*nitro*-3-*aminobenzoate*, m.p. 48—49°, and the expected ester. E. W. W.

Catalytic phenylation of α-naphthylamine. H. H. Hodgson and E. Marsden (J.C.S., 1938, 1181—1182; cf. A., 1937, II, 408).—NH_4I, HI, and I catalyse the phenylation (*p*-tolyl- and α-naphthylation) of α-$C_{10}H_7$·NH_2 (I) with decreasing efficiency, the first giving the best yield (96%) of α-$C_{10}H_7$·NHPh, almost free from *apo*safranine-like dyes. *p*-C_6H_4I·NH_2



(II.)

and excess of (I) at 100° for 24 hr. yield two *dyes*, $C_{60}H_{33}N_5I_4$ (II), decomp. ~260°, and $C_{52}H_{29}N_5I_4$, *i.e.*, (II) without rings A and B, decomp. ~280° (main product), the former being obtained also from I and (I) at 50—55°. NH_2Ph and NH_2Ph,HI at 198° give only a little $NHPh_2$. A. T. P.

Introduction of nitrogen into the sterol molecule. II. Partial synthesis of norcholanylamine.

M. Vanghelovici (Bul. Soc. Chim. România, 1937, **19**, 35—42; cf. A., 1936, 982).—Et cholanate and N_2H_4,H_2O in EtOH yield *cholanhydrazide* (+EtOH), m.p. 195° (*Ac* derivative, m.p. 235°), converted by AcOH–$NaNO_2$ into the *azide*, m.p. 96—98° (decomp.), and thence (EtOH) into the *urethane*, m.p. 135°, which when distilled with CaO at 9 mm. gives *norcholanylamine*, m.p. 95° (*Ac* derivative, m.p. 177°; *hydrochloride*, decomp. 285°). J. D. R.

Manufacture of carbimides.—See B., 1938, 1016.

Preparation of benzenesulphonarylamides.—See B., 1938, 1100.

Conversion of *p*-substituted methylenebisarylamines and trimeric methylenearylamines into substituted 2-aminobenzylarylamines. T. R. Miller and E. C. Wagner (J. Amer. Chem. Soc., 1938, **60**, 1738—1741).—Conditions are detailed for the prep. of 2 : 4-NH_2·C_6H_3X·CH_2·NH·C_6H_4Y-*p* (X = Y = Me, Cl, or Br) in good yield from *p*-C_6H_4Y·NH_2 (large excess) and *p*-C_6H_4Y·NH_2,HCl with $(p\text{-}C_6H_4X\cdot NH)_2CH_2$ or $(p\text{-}C_6H_4X\cdot N\cdot CH_2)_3$. The prep. fails when X = Y = OMe or OEt, and gives tars when X ≠ Y. R. S. C.

Synthesis of naganine. O. J. Magidson, O. S. Madaeva, and M. V. Rubtzov (Chim. Farm. Prom., 1935, **2**, 89—94).—1 : 4 : 6 : 8-NH_2·$C_{10}H_4(SO_3H)_3$ is condensed in H_2O with *m*-nitrotoluoyl chloride, the NO_2 reduced (Fe) to NH_2, and the amine condensed with *m*-NO_2·C_6H_4·COCl. The new NO_2 is reduced and the amine condensed with $COCl_2$ in NaOAc to the Na salt of *mm'*-bis-[5-(4 : 6 : 8-trisulpho-1-naphthylcarbamyl)-*o*-tolylcarbamyl]carbanilide (naganine). Ch. Abs. (*c*)

Azo-dyes derived from quinol. C. Staehling and M. Bader (Bull. Soc. chim., 1938, [v], **5**, 1171—1178).—Gradual addition of $ClSO_3H$ to quinol in $CHCl_3$–C_5H_5N at 60° gives *dipyridinium phenylene*-p-*disulphate* (I), decomp. 170—180°, converted by NaOH into the *salt* $C_6H_4(O\cdot SO_3Na)_2,2H_2O$, decomp. 110°; the mother-liquors from (I) with aq. Na_2CO_3 give *Na* p-*hydroxyphenyl sulphate* (+$2H_2O$) (II) which becomes partly liquid at 248—250°. *p*-OH·C_6H_4·OBz in $CHCl_3$–C_5H_5N and $ClSO_3H$ afford *pyridinium* p-*benzoyloxyphenyl sulphate*, decomp. 124—134° [corresponding *Na* salt, melting partly at 256° (decomp.)]. Debenzoylation is readily effected by hot aq. Na_2CO_3. When coupled with the requisite ArN_2X, (II) affords Na 3-benzeneazo-, 3-*p*-toueneazo-, and 3-*p*-nitrobenzeneazo-4-hydroxyphenyl sulphate. *Na* 3-2′ : 5′-*dichlorobenzeneazo*-4-*hydroxyphenyl sulphate*, sublimes at 190°, decomposes ~250°, is readily converted by HCl into 2 : 5-*dichloro*-2′ : 5′-*dihydroxyazobenzene*, which changes in cryst. form at ~224° and melts ~246°. The following compounds are obtained similarly: *Na* 3-4′-*nitro*-2′-*methylbenzeneazo*-4-*hydroxyphenyl sulphate*, m.p. 190° (decomp.), and 4-*nitro*-2′ : 5′-*dihydroxy*-2-*methylazobenzene*, m.p. 206—208°; *Na* 3-4′-*anilino*-2′ : 5′-*diethoxybenzeneazo*-4-*hydroxyphenyl sulphate*, m.p. 248°, converted by HCl into a *substance*, m.p. 88—90°; *Na* 3-5′-*chloro*-2′-*phenoxybenzeneazo*-4-*hydroxyphenyl sulphate*, m.p. 170—172°, and 5-*chloro*-2′ : 5′-*dihydroxy*-2-*phenoxyazobenzene*, m.p. 204—206°. These dyes and those obtained correspondingly from 1 : 4-$C_{10}H_6(OH)_2$ are without tinctorial val. H. W.

Action of weak reducing agents on diazo-compounds. O. M. Golosenko (Prom. Org. Chim., 1938, **5**, 479—484).—The author's method of determination of diazo-compounds (A., 1937, II, 188) is of general application. R. T.

[Reaction of nitrosyl fluoborate with aniline.]—See A., 1938, I, 532.

Decomposition reactions of aromatic diazo-compounds. V. Reactions of benzenediazonium chloride with sulphur, selenium, and tellurium. W. A. Waters (J.C.S., 1938, 1077—1078; cf. A., 1938, II, 342).—Solid PhN_2Cl with Te and $CaCO_3$ in cold $COMe_2$ gives $TePh_2Cl_2$; S at > 50° affords COMe·CH_2Cl, Ph_2S, and (probably) Ph_2S_2, and Se on heating yields Ph_2Se. This supports the view (A., 1938, II, 52) that free Ph is present. PhN_2Cl does not appear to react with red P, B, or Si. E. W. W.

Depression of m.p.—See A., 1938, I, 507.

Cineole method for determination of *o*-cresol.—See B., 1938, 1013.

Mechanism of halogenation of phenols. E. A. Schilov (J. Gen. Chem. Russ., 1938, **8**, 519—523).—Polemical against Lichoscherstov *et al.* (A., 1938, II, 37). R. T.

Halogen derivatives of α-ethylpropylcresols.—See B., 1938, 1101.

Syntheses with *o*- and *p*-hydroxydiphenyls. II. Nitro- and amino-hydroxydiphenyls, their derivatives, and azo-dyes from hydroxydiphenyls. N. N. Voroshcov, jun., and A. T. Troschtschenko (J. Gen. Chem. Russ., 1938, **8**, 431—437).—*o*-C_6H_4Ph·OH and HNO_3 in AcOH at 0° give a mixture of 3-*nitro*- (I), m.p. 62° (*Me ether*, m.p. 72—73°), and 5-nitro-2-hydroxydiphenyl. Further nitration of (I) yields successively 3 : 5-dinitro- and *tetranitro*-2-*hydroxydiphenyl*, m.p. 182—183°. (I) is reduced ($SnCl_2$ in EtOH) to 3-*amino*-2-*hydroxydiphenyl* (II), m.p. 121—122·5°, which with AcCl in C_6H_6 (3 hr. at the b.p.) yields 6-*phenyl*-1-*methylbenzoxazole*, m.p. 69—70°; with BzCl the product is 1 : 6-*diphenylbenzoxazole*, m.p. 114—116°. (II), (I), and glycerol heated with H_2SO_4 yield 8-*hydroxy*-7-*phenylquinoline*, m.p. 142—144° (*hydrochloride*, m.p. 208—209°; *Cu* salt). 3-Amino- and 3-nitro-4-hydroxydiphenyl give similarly 8-*hydroxy*-5-*phenylquinoline*, m.p. 91—92° (*hydrochloride*, m.p. 212—226°; *Cu* salt). Diazotised (II) and β-$C_{10}H_7$·OH yield 2-*hydroxy*-3-β-*hydroxynaphthaleneazodiphenyl*, m.p. 211—211·5°; an analogous *compound* with *m*-$C_6H_4(OH)_2$ is described. 4-Hydroxydiphenyl gives *azo-dyes* with diazotised *p*-NH_2·C_6H_4·NO_2, m.p. 174—175°, α-$C_{10}H_7$·NH_2, m.p. 121—123°, and with tetrazotised benzidine, 3 : 3′-dimethyl- and 3 : 3′-dimethoxy-benzidine. R. T.

Relations between the chemical constitution of substituted phenols and of ascorbic acid and the size of their solubility products with antipyrine and pyridine.—See A., 1938, I, 518.

Arylphosphoric acid halides.—See B., 1938, 1018.

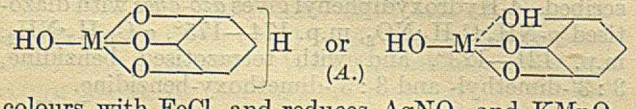
Manufacture of triaryl phosphates.—See B., 1938, 1015.

Substitution reactions and *meso*-derivatives of 1 : 2-benzanthracene. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1938, **60**, 1893—1896).—The 9-position of 1 : 2-benzanthracene (I) is shown to be remarkably inert. With $Pb(OAc)_4$ in AcOH at 100° (I) gives 52% of pure 1 : 2-benz-10-anthranyl acetate, but 10-methyl-1 : 2-benzanthracene gives only 10-*acetoxymethyl*-1 : 2-*benzanthracene*, m.p. 150·5—151·5° (17%), the 9-position being unattacked. Prep. by cyclisation methods of 10-anthranyl acetate, 3-methoxy-1 : 2-benz-10-anthranyl acetate, m.p. 194—194·5°, and 1-keto-1′ : 2′ : 3′ : 4′-tetrahydro-8 : 9-acephenanthrene, m.p. 143—145°, is improved. 10-*Methyl*-1 : 2-*benz*-9-*anthranyl* (II), m.p. 153·5—154°, and -3-*anthryl acetates* (III), m.p. 214—215°, are prepared. When $MgBu^{\alpha}Br$ and (III) are heated in Et_2O and then treated with Me_2SO_4–C_6H_6, 53% of 3 : 10-*dimethoxy*-1 : 2-*benzanthracene* (?), stable, m.p. 146—146·5°, and unstable *forms*, m.p. 84—87°, is obtained; by a similar reaction (II) gives 9-*methoxy*-10-*methyl*-1 : 2-*benzanthracene*, m.p. 143—144°. 1 : 2 : 5 : 6-Dibenzanthracene is best purified (to m.p. 266—266·5°) by treatment with $Pb(OAc)_4$, which by oxidation removes any 1 : 2 : 6 : 7-dibenzanthracene present. The structure of 10-nitro-1 : 2-benzanthracene, m.p. 164—165° (Barnett *et al.*, A., 1925, i, 821), is proved by PtO_2-hydrogenation to the 10-NH_2-derivative, m.p. 174·5—175·5°, which is also obtained from the 10-OH-compound (IV), NH_3, and $NaHSO_3$ in aq. dioxan at 150°. 10-Allyl-1 : 2-benzanthracene, I, and AgOBz in hot C_6H_6 give γ-1 : 2-*benz*-10-*anthranylpropane*-αβ-*diol dibenzoate*, m.p. 152·5—153·5°. With $Bu^{\gamma}OCl$ in Et_2O (IV) gives a Cl-*compound*, $C_{18}H_{18}OCl$, m.p. 197—198° (decomp.), converted by hot MeOH into a bimol. product, $C_{36}H_{22-24}O_2$, m.p. 261—263°, previously (A., 1937, II, 333) obtained directly from (IV). 3 : 4-Benzpyrene and methylcholanthrene with $Pb(OAc)_4$ give OAc-derivatives, m.p. 208·5—209° and 179·5—180·5°, respectively. M.p. are corr.

R. S. C.

Constitution of (A) bismuth pyrogallate, (B) antimony pyrogallate, (C) antimony subgallate. S. TAKAGI and Y. NAGASE (J. Pharm. Soc. Japan, 1936, **56**, 161—169, 170—174, 175—179).—(A) Pyrogallol (I) and $Bi(NO_3)_3$ in aq. AcOH give *pyrogallomonobismuthic acid* ($+H_2O$) (*A*; M = Bi) which forms a *Ba* salt but does not ppt. $Bi(OH)_3$ in alkaline solution and gives no colour with $FeCl_3$. *Bi* salts of the Me ether, amide, and anilide of (I) are described.

(B) (I) and $C_4H_4O_6K(SbO)$ in H_2O at 40—50° give *Sb pyrogallate* ($+0{\cdot}5H_2O$) (*A*; M = Sb), which gives



colours with $FeCl_3$ and reduces $AgNO_3$ and $KMnO_4$. Methylation (Me_2SO_4) gave (?) $C_6H_3Me_3$.

(C) Gallic acid and $C_4H_4O_6K(SbO)$ in boiling H_2O give *Sb subgallate*, $[OHSbO_3C_6H_2{\cdot}CO{\cdot}O]H_2$, $+2H_2O$, similar in properties to Sb pyrogallate. Methylation (Me_2SO_4) gave trimethylgallic acid. CH. ABS. (*c*)

Modes of reaction of organo-metallic compounds. II. Action of Grignard's compounds on phenyl allyl ether. A. LÜTTRINGHAUS, G. VON SÄÄF, and K. HAUSCHILD (Ber., 1938, **71**, [*B*], 1673—1681).—αδ-Dibromo-Δ^{β}-butene (I) [from butadiene (II) and B rin $CHCl_3$ at −15° to −18°] with NaI in $COMe_2$ yields I and (II), whilst with Zn or Mg in a suitable solvent it affords (II) in good yield. (I) and KOPh in MeOH afford *α-bromo-δ-phenoxy-*Δ^{β}*-butene* (III), b.p. 104—105°/0·07 mm., transformed by KOPh into αδ-diphenoxy-Δ^{β}-butene, m.p. 90°. (III) and $KMnO_4$ in $COMe_2$ containing $MgSO_4$ at −5° give *α-bromo-βγ-dihydroxy-δ-phenoxybutane*, m.p. 111·5°, further oxidised to $CH_2Br{\cdot}CO_2H$ and $OPh{\cdot}CH_2{\cdot}CO_2H$. (III) is transformed by Mg or MgBuBr into (II) and PhOH. Ph allyl ether (IV) and MgBuBr afford PhOH and Δ^{α}-*n*-heptene (dibromide, b.p. 98—100°/11 mm.; oxidised to hexoic acid). MgPhBr and (IV) give PhOH and allylbenzene. PhOH, pentadecene, and tetracosane are derived from Mg dodecyl bromide and (IV). Guaiacol allyl ether and MgBuBr afford guaiacol and heptene but no *o*-$C_6H_4(OH)_2$. Ph cinnamyl ether and MgPhBr give PhOH in 51% yield. $CH_2Ph{\cdot}OPh$ is little changed by MgBuBr at 80°.

H. W.

Preparation of diphenyl ether. M. A. ELENEVSKI and Z. G. ARTAMONOVA (J. Gen. Chem. Russ., 1938, **8**, 507—509).—A mixture of PhOH 23·5, PhCl 22·5, KOH 11·2, and $CuCO_3$ 0·5 g. is heated at the b.p. for 9 hr., so that PhCl distils, is separated from H_2O, and returned. The yield of Ph_2O is 59—64%.

R. T.

Action of gaseous hydrogen chloride on 5-nitroso-*o*-cresol and 6-nitrosothymol. A. ANGELETTI and A. OLIVERIO (Gazzetta, 1938, **68**, 359—363).—2 : 1 : 5-$OH{\cdot}C_6H_4Me{\cdot}NO$ with HCl in dry Et_2O gives the hydrochloride of 3 : 4-*dichloro*-5-*amino*-*cresol*, m.p. 158—159° (*Ac* derivative, m.p. 160°), which by diazotisation yields 1 : 3 : 4 : 2 : 5-$C_6HMeCl_2(OH)_2$ (*Me*$_2$ *ether*, m.p. 65°). 6-Nitrosothymol similarly gives the *hydrochloride*, m.p. 190—195° (decomp.), of 5-*chloro*-6-*aminothymol*, m.p. 115° (decomp.).

E. W. W.

Anomalous reaction of the sodium salt of 4-nitro-1-thiolnaphthalene with 2-chloro-1-nitronaphthalene and with *o*-chloronitrobenzene. H. H. HODGSON and E. LEIGH (J.C.S., 1938, 1031—1034).—$NO_2{\cdot}C_{10}H_6{\cdot}SNa$ (obtained by treating $C_{10}H_6Cl{\cdot}NO_2$ with EtOH–Na_2S_2, boiling the product with aq. EtOH–Na_2S–NaOH, and filtering off the insol. monosulphide) with $C_{10}H_6Cl{\cdot}NO_2$ gives in most cases the expected dinitrodinaphthyl sulphides. Thus 1 : 2- (I) and 1 : 4-$C_{10}H_6Cl{\cdot}NO_2$ (II) (using either compound and the SNa compound derived from the other) give 2 : 4′-*dinitro*-1 : 1′-*dinaphthyl sulphide*, m.p. 162—163°. Similarly (I) and 2 : 1-$C_{10}H_6Cl{\cdot}NO_2$ (III) give, by either route, 1 : 2′-*dinitro*-2 : 1′-*dinaphthyl sulphide*, m.p. 172—173°. 1 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}SNa$ and (II) give 1 : 4′-*dinitro*-2 : 1′-*dinaphthyl sulphide* (IV), m.p. 125—126°, but (III) and 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}SNa$ afford not (IV) but 4 : 4′-dinitro-1 : 1′-dinaphthyl

sulphide (A., 1937, II, 414). It is suggested that after separation of Cl′, the 4-H in 1-NO_2·$C_{10}H_6^+$ is very rapidly ionised (owing to the effects of NO_2 and of the positive 2-C pole), and that S (rendered less reactive by the 4-NO_2) then reacts at the new ionic centre. Similarly, *o*-C_6H_4Cl·NO_2 and 4 : 1-NO_2·$C_{10}H_6$·SNa give the anomalous product, p-*nitrophenyl* 4-*nitro*-1-*naphthyl sulphide*, m.p. 236—238°, also obtained from (II) and *p*-NO_2·C_6H_4·SNa, which with (I) and (III) gives p-*nitrophenyl* 2-*nitro*-1-, m.p. 121—122°, and 1-*nitro*-2-*naphthyl sulphide*, m.p. 122—123°, respectively. *o*-NO_2·C_6H_4·SNa with (I), (III), and (II) gives o-*nitrophenyl* 2-*nitro*-1-, m.p. 196—197°, 1-*nitro*-2-, m.p. 162—163°, and 4-*nitro*-1-*naphthyl sulphide*, m.p. 157—158°, respectively. Colour reactions of the sulphides with conc. H_2SO_4, $ClSO_3H$, and 26% oleum are given. E. W. W.

Purification of β-phenylethyl alcohol.—See B., 1938, 1018.

Active *cyclo*hexane compounds. M. Mousseron and R. Granger (Compt. rend., 1938, **207**, 366—368).—Interaction of MgAlkX with active 3-methyl*cyclo*hexanone affords *cis*- and *trans*-3-methyl-1-alkyl*cyclo*hexanols, the less volatile of which are obtained pure. The following are described: 3-methyl-, 1 : 3-dimethyl- (phenylcarbamate, m.p. 84°), 3-methyl-1-ethyl- (phenylcarbamate, m.p. 94°), 3-methyl-1-*n*-propyl- (phenylcarbamate, m.p. 111°), and 3-methyl-1-*n*-butyl-*cyclo*hexanol. The ratio between the optical rotation of the alcohols in EtOH or C_6H_6 and that without a solvent increases slightly in the order given above. The alcohols are dehydrated to the active isomeric *cyclo*hexenes, viz., methyl-, b.p. 102·5° and 104°/760 mm., 1 : 3-dimethyl-, b.p. 127°/760 mm., 1 : 3-dimethyl-Δ^3- (I), b.p. 129°/760 mm., 1-methyl-3-ethyl-, b.p. 148° and 150°/760 mm., 1-methyl-3-*n*-propyl-, b.p. 170° and 171°/760 mm., and 1-methyl-3-*n*-butyl-*cyclo*hexene, b.p. 180°/760 mm. These with H_2–Pt afford *cis*- and *trans*-*cyclo*hexanes; the following are described: 1 : 3-dimethyl-, b.p. 119·5° (optically inactive) and 123·5°/760 mm., 1-methyl-3-ethyl-, b.p. 147·5° and 148·5°/760 mm., and 1-methyl-3-*n*-propyl-*cyclo*hexane, b.p. 168·7° and 169·2°/760 mm. The less volatile isomeride has the *trans*-configuration (cf. A., 1936, 61). 1-Methyl-3 : 4-, b.p. 146·5°/760 mm., 1 : 3-dimethyl-2 : 3-, b.p. 152·5°/760 mm., and -3 : 4-, b.p. 152°/760 mm., 1-methyl-3-ethyl-3 : 4-, b.p. 174°/760 mm., and 1-methyl-3-*n*-propyl-3 : 4-epoxy*cyclo*hexane, b.p. 190°/760 mm., are prepared from the appropriate *cyclo*hexene and BzO_2H. 2-Amino-2 : 4-dimethyl-, b.p. 111°/20 mm., and -4-methyl-2-ethyl-*cyclo*hexanol, b.p. 120°/20 mm., are purified through the H tartrates. (I) is oxidised ($KMnO_4$) to active β-methyladipic acid. Vals. of [α] and other physical data are given. J. L. D.

Dipole moments and molecular structure. XIX. Dipole moments of anthracene derivatives and the stereochemical mechanism of addition and splitting reactions in the anthracene series. E. Bergmann and (Miss) A. Weizmann (J. Amer. Chem. Soc., 1938, **60**, 1801—1804; cf. A., 1936, 1183).—Dipole moments show that 9 : 10-addition of Cl_2 to 1 : 5-dichloroanthracene (I) and 9 : 10-diphenylanthracene is a reaction of the Cl_2 mol., since the product is the *cis*-derivative, but that 1 : 8-dichloroanthracene gives the *trans*-compound. 1 : 5-Dichloro-9 : 10-dihydroxy-9 : 10-dihydroanthracene, m.p. 210°, is the *cis*-diol, the isomeride, m.p. 244°, the *trans*-diol. The α- and β-forms of Me_2 9 : 10-dihydroanthracene-9 : 10-dicarboxylate (A., 1928, 1036) are *trans* and *cis*, respectively. 1-Chloroanthraquinone has a high dipole moment (1·9) due, probably, to induction or resonance. Prep. of the most of the compounds named is modified. 1 : 5 : 9 : 10-Tetrachloro-, m.p. 214—215°, and 1 : 5-dichloro-9 : 10-dibromo-9 : 10-dihydroanthracene, m.p. 220° (decomp.), are obtained from (I), which is prepared with 1 : 5-*dichloro*-9-*hydroxy*-9 : 10-*dihydroanthracene*, m.p. 102—103°, from 1 : 5-dichloroanthraquinone, Zn dust, and hot 20% aq. NH_3. The fission of 9 : 10-Cl_2-compounds does not appear to follow definite rules. R. S. C.

Structure of cholesteryl chloride. E. Bergmann (J. Amer. Chem. Soc., 1938, **60**, 1997—1998).—The absence of Walden inversion when cholesteryl chloride reacts with NaOAc and chloroandrosterone with NaOBz indicates that these chlorides can react in the allylic (Δ^4) form. R. S. C.

Bombicesterol. I. K. Kawasaki (J. Pharm. Soc. Japan, 1935, **55**, 758—774).—*Bombicesterol* (I), $C_{27}H_{46}O$, had m.p. 139—140°, $[\alpha]_D^{21·5}$ −31·5° (all rotations are in $CHCl_3$) and gave colour reactions of cholesterol. The *acetate* (I), m.p. 130·5°, $[\alpha]_D^{27}$ −44·2°, *benzoate*, m.p. 147°, $[\alpha]_D^{16}$ −14·1°, and *dibromide*, m.p. 114—115°, were prepared. *Bombicesteryl chloride*, m.p. 84—86°, with Na + C_5H_{11}·OH gave *bombicestene*, m.p. 91—92°, $[\alpha]_D^{26}$ −58·2° (*dibromide*, m.p. 91—93°), which was reduced catalytically to *bombicestane*, m.p. 79° (no depression with cholestane). *Bombicestanol*, m.p. 134—135°, $[\alpha]_D^{28}$ −10·6° (*acetate*, m.p. 130—131°, $[\alpha]_D^{17}$ +9·88°), *bombicestanone*, m.p. 152°, $[\alpha]_D^{28}$ +37·9°, and allo*bombicesterol*, m.p. 97°, were prepared by standard reactions. Oxidation of (I) gave a ketone probably identical with the methylheptanone obtained from cholesteryl acetate. Ch. Abs. (*c*)

Satisterol, $C_{27}H_{46}O$, m.p. 156°, and its Ac, m.p. 111°, EtCO, m.p. 106°, and Bz, m.p. 129°, derivatives.—See A., 1938, III, 772.

Sterols. XLII. Isolation of œstranediols from human non-pregnancy urine. R. E. Marker, E. Rohrmann, E. J. Lawson, and E. L. Wittle. **XLIII. 3(β)-Hydroxysteroids in human pregnancy urine.** R. E. Marker, S. B. Binkley, E. L. Wittle, and E. J. Lawson (J. Amer. Chem. Soc., 1938, **60**, 1901—1903, 1904—1905; cf. A., 1938, II, 408).—XLII. The carbinol fraction of the sterols of human non-pregnancy urine contains as 3(β)-OH-compounds mainly cholesterol and, amongst the compounds not pptd. by digitonin, *œstranediol*-A, m.p. 242° (*diacetate*, m.p. 160°), and -B, m.p. 204° (*diacetate*, m.p. 160°; also obtained by PtO_2-hydrogenation of œstrone in HCl–EtOH), oxidised by CrO_3 to *œstranedione*-A, m.p. 124°, and -B, m.p. 170°, and both converted by Pt-black in N_2 at 215—220° into equilenin and thus stereoisomeric at least at $C_{(5)}$ or $C_{(10)}$. Œstrone is unaffected by enzyme extracts from hog ovaries, ox

adrenal glands, and bull testes. In the pregnant woman œstrone is not utilised and is thus excreted in large amount, the reduction products being absent, whereas progesterone is utilised and is thus excreted solely as its reduction products. In the non-pregnant woman these relations are reversed: œstrone is absent from the urine, but its reduction products (at any rate the two diols) are present. Neoergosterol and *epi*neoergosterol are not pptd. by digitonin.

XLII. In confirmation of theory, saturated compounds of the coprostanol series with a 3(β)-OH are absent from human pregnancy urine (1000 gallons examined). The only 3(β)-OH-compounds present are cholesterol (4 mg. per gal.) and *allo*pregnane-3(β) : 20(α)-diol (1—1·5 mg. per gal.). R. S. C.

Preparation of œstradiol from urine of mares.—See B., 1938, 1101.

Sterols. XLI. Reduction of naphtholic steroids to phenolic steroids. Equilenin. R. E. Marker (J. Amer. Chem. Soc., 1938, **60**, 1897—1900; cf. A., 1938, II, 415).—The reduction of β-naphtholic sterols by Na–C_5H_{11}·OH to H_4-derivatives, in which ring A is benzenoid, is a general reaction (cf. Marker *et al.*, A., 1936, 1256; Windaus *et al.*, A., 1937, II, 99); larger amounts of neutral products are also formed. Correlation of configurations of sterols by the behaviour with digitonin and the m.p. is unreliable; the only valid correlation is obtained by chemical reactions. Equilenin (I) (modified purification), m.p. 257—258°, $[\alpha]_D^{25}$ +89°, and Na–C_5H_{11}·OH give a phenolic product which when benzoylated, oxidised (CrO_3), and then hydrolysed affords œstrone. $Al(OPr^{\beta})_3$ and (I) give α- (II), m.p. 248° (*Ac*$_2$, m.p. 124°, and *Bz* derivative, m.p. 215°), and β-dihydroequilenin (III), m.p. 215° (*Bz* derivative, m.p. 204° (cf. Marker *et al.*, A., 1937, II, 250). Wintersteiner's (II) (cf. A., 1937, II, 100) contained an active impurity (? α-œstradiol), since pure (II) and (III) have œstrogenic potencies of only 250 and 75—100 rat units per mg. Neither (II) nor (III) is pptd. by digitonin. With Na–C_5H_{11}·OH (II) gives a little α-œstradiol (IV), another phenol, m.p. 151—154°, and a neutral substance, m.p. 172°. (III) gives similarly β-œstradiol and other phenolic and neutral products; the benzoylated phenolic product with CrO_3 followed by hydrolysis gives œstrone and a *substance*, $C_{18}H_{20}O_2$, m.p. 222—225° [also obtained by oxidation of the mother-liquors from (IV)]. Œstrone benzoate and $Al(OPr^{\beta})_3$ give after hydrolysis α- and β-œstradiol. R. S. C.

Steric hindrance. III. Index of unsaturation in the *cyclo*pentene series. P. Duquénois (Bull. Soc. chim., 1938, [v], **5**, 1207—1208).—Hydnocarpic and chaulmoogric acid and their esters give theoretical Br vals. The *cyclo*pentene nucleus is therefore readily accessible to Br under the conditions of Volmar and Samdahl (B., 1928, 236). H. W.

***cyclo*Hexane series. I. Synthesis of nitriles.** G. Vasilu (Bul. Soc. Chim. România, 1937, **19**, 75—83; cf. A., 1938, II, 190).—*cyclo*Hexyl bromide (I) and CH_2Ph·CN in Et_2O with $NaNH_2$ yield cyclo*hexylphenylacetonitrile* (II), m.p. 60°, converted by further treatment with (I) and $NaNH_2$ in Et_2O into *di*cyclo*hexylphenylacetonitrile*, m.p. 133°, also formed with (II) from CH_2Ph·CN, (I) (2 mols.), and $NaNH_2$. Similarly from the appropriate CN·CHPhAlk are obtained α-cyclo*hexyl-α-phenyl-butyronitrile*, b.p. 179—180°/15 mm., and *-valeronitrile*, b.p. 190—191°/18 mm. Hydrolysis of (II) with H_2SO_4 yields cyclo*hexylphenylacetamide*, m.p. 174°, and with KOH–EtOH, cyclo*hexylphenylacetic acid*. J. D. R.

Benzilic acid rearrangement. J. J. Blanksma and W. H. Zaaijer (Rec. trav. chim., 1938, **57**, 883—885).—The velocity of the rearrangement (*k*) and the amount of BzOH formed (side reaction) in the action of NaOH or KOH on benzil in EtOH or MeOH at 100° have been measured by titrating with HCl and also determining the unchanged benzil. Rearrangement occurs slightly faster with NaOH than with KOH in 100% MeOH; 90% MeOH leads to increase in *k*. For NaOH, $k_{MeOH} > k_{EtOH}$. MeOH is the better solvent since EtOH gives some MeCHO and thence resin. Anisil under similar conditions gives anisic but practically no anisilic acid. A. Li.

Common basis of intramolecular rearrangements. IV. Correction: the benzilic acid rearrangement. F. C. Whitmore (J. Amer. Chem. Soc., 1938, **60**, 2002—2003).—The application of the author's theory (A., 1932, 1016) to the benzilic acid rearrangement is rendered invalid by later work of others. R. S. C.

Steric hindrance. II. Index of unsaturation in the cinnamic series. P. Duquénois (Bull. Soc. chim., 1938, [v], **5**, 1200—1207).—$CHPh{:}CH_2$ and $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ absorb Br quantitatively in 2 hr. in the dark. With $CHPh{:}CH{\cdot}CHO$, $CHPh{:}CH{\cdot}CO_2H$ and its esters bromination is incomplete in the dark but complete after 2 hr. in sunlight. In the dark the Br vals. of these latter compounds are not const.; the rate of fixation of Br is a function of the halogen concn. and is inversely ∝ the content of dissolved O_2. Steric hindrance appears to have a distinct relationship to the addition of Br. Inactivity is general among compounds with heterogenic conjugated double linkings. Addition takes place more readily with $CHPh{:}CH{\cdot}CO_2H$ than with its esters and is most difficult with CH_2Ph cinnamate. With cinnamyl cinnamate a supplementary passivity is observed, since after fixation of the first mol. of Br at the double linking of the alcoholic radical a relatively small space is left around the other ethylenic linking, thus greatly hindering the access of a new mol. of Br. Coumarin is always very incompletely brominated in spite of various photochemical stimuli. Cyclisation appears to increase the condition of saturation and the conjugated double linkings of this heterocyclic substance confer on it the properties of a nucleus. *CH_2Ph αβ-dibromo-β-phenylpropionate* has m.p. 95°. H. W.

Stereoisomeric enolic ethers, acetals, and the Claisen condensation. F. Arndt and L. Loewe [with E. Özsöy, M. Ögüt, A. Arslan, and L. Bagevi] (Ber., 1938, **71**, [*B*], 1631—1640).—CH_2Bz·CN is transformed by CH_2N_2 in Et_2O into trans-β-*methoxycinnamonitrile* (I), b.p. 111·5°/1 mm., m.p. 31°, con-

verted by boiling MeOH–NaOMe (2—4 mols.) in 1—5 hr. into a mixture, b.p. 116—126°/1 mm., of *cyanoacetophenone* Me_2 *acetal* (II), b.p. 111°/1 mm., m.p. 65·5°, and cis-β-*methoxycinnamonitrile* (III), b.p. 126°/1 mm. Neither (I) nor (III) is isomerised by heat. Transformation takes place through (II), since the same equilibrium is attained whether the starting point is (I), (II), or (III). NaOMe is pronouncedly catalytic. The enol ether (IV) of 2-hydroxythionaphthensulphone is quantitatively converted by warm NaOMe–MeOH into the corresponding acetal. Similarly the Me enol ether of p-$C_6H_4Me{\cdot}SO_2{\cdot}CH_2{\cdot}COMe$ quantitatively affords the acetal (V), p-$C_6H_4Me{\cdot}SO_2{\cdot}CH_2{\cdot}CMe(OMe)_2$, which does not undergo thermal re-conversion. In alkaline solution the equilibrium is completely on the acetal side. $CH_2Bz{\cdot}CN$ enolises spontaneously to a conjugated enol. (IV) and (V) on the contrary can be obtained only by indirect methylation with CH_2N_2 since the corresponding enols do not exist as they lack a conjugated system. The same constitutional factors are operative for the equilibria acetal–enol ether and keto–enol. As a further example of a conjugated enol ether $CH_2Bz{\cdot}CO_2Me$ is converted by CH_2N_2 into *Me* cis-β-*methoxycinnamate*, b.p. 124°/2 mm. The position of the equilibrium attained in boiling MeOH containing NaOMe is less readily ascertained owing to partial ester hydrolysis. If only 1 mol. of NaOMe is used the secondary change is not marked and the recovered ester is constitutionally pure enol ether. A transitory addition of OMe ion to at least a portion of the mols. is certain since the product has a lower and less const. b.p. and partly solidifies at −15°; obviously the pure *trans*-enol ether is solid and has a lower b.p. than the liquid *cis*-ether. With 4 mols. of NaOMe partial hydrolysis occurs with production of a solid Na salt and of a mixture of equimol. amounts of enol ether and acetal; repeated treatment and fractionation gives a product which is richer in acetal but not homogeneous. The chemistry of alkoxide catalysis and of the Claisen condensation is discussed in detail. H. W.

Derivatives of oleic acid. G. Roberti, P. Piutti, and D. Dinelli (Ric. sci. Progr. tecn., 1936, [ii], 7, II, 10—12; Chem. Zentr., 1936, ii, 3536).—Phenylstearic acid (cf. A., 1927, 560) and glyceryl tri(phenylstearate) (I) have been prepared. A 1 : 1 mixture of (I) with olive oil remains liquid at a low temp. and is recommended as a lubricant for combustion engines. A. H. C.

Racemisation of amino-acids.—See B., 1938, 1016.

***p-cyclo*Hexylphenoxyacetic acid and its derivatives.** D. Bodroux and A. Chatenet (Compt. rend., 1938, **207**, 364—366; cf. A., 1929, 1050).—Na *p-cyclo*hexylphenoxide with $CH_2Cl{\cdot}CO_2Na$ in boiling EtOH affords p-cyclo*hexylphenoxyacetic acid* (I), m.p. 151—152° [*Na* (+$3H_2O$), *Ba* (+$3H_2O$), *Ag*, and NH_4 (+H_2O) salt; the last with aq. NH_3–$CuSO_4$ at 80° affords the *Cu*,$4NH_3$ (+H_2O) derivative which at 100° gives the *Cu* salt; *Me* (II), m.p. 39°, and *Et*, m.p. 32°, esters, obtained only by the Ag salt method]. (II) with NH_3 in aq. EtOH at 75° affords p-cyclo*hexylphenoxyacetamide*, m.p. 169—170°. J. L. D.

Action of benzoic acid on vanadium pentoxide. J. F. Levy (Bol. Soc. Quím. Peru, 1938, 4, 108—115).—An extension of earlier work (A., 1938, II, 189). A small excess of BzOH with V_2O_5 at 249° gives *hypovanadous benzoate*, $V(OBz)_2$, also prepared from V and PhCHO at room temp.; with C_5H_5N and quinoline it gives the corresponding vanadates (cf. Katzoff and Roseman, A., 1936, 1350). F. R. G.

Fixation of active nitrogen by organic compounds. L. B. Howard and G. E. Hilbert (J. Amer. Chem. Soc., 1938, **60**, 1918—1924).—At. N, produced by a condensed or uncondensed discharge, and C_2Ph_2 give HCN, a brown, amorphous solid (I) of high m.p., (?) PhCN, and (?) a carbimide. (I) contains 16—18% of N, is stable to acid, generates NH_3 with alkali, with HNO_3 gives BzOH and an *acid*, $(C_{10}H_7O_5N)_x$, m.p. 215—220°, and probably contains N·C·N. Tetrahydronaphthalene and PhCN give similar products. R. S. C.

Industrial preparation of benzoyl chloride.—See B., 1938, 1013.

Estimation of isomeric nitrobenzoic acids. B. Flürscheim and E. L. Holmes (J.C.S., 1938, 1242).—A correction of a statement of Ingold and Smith (A., 1938, II, 324). A. T. P.

Titration of esters of *p*-hydroxybenzoic acid. F. Reimers (Dansk Tidsskr. Farm., 1938, **12**, 203—210).—Titration of p-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (I) as a dibasic (to p_H ~11) or monobasic (to p_H 6·8) acid, and direct titration of esters of (I), are unreliable. (I), from hydrolysis (aq. NaOH) of its esters, is determined accurately by the reaction: (I) + $3Br_2 \longrightarrow$ 2 : 4 : 6-$C_6H_2Br_3{\cdot}OH$ + 3HBr + CO_2, by addition of KBr–$KBrO_3$ in acid solution and determination of the excess of Br iodometrically. M. H. M. A.

Syntheses with *o*- and *p*-hydroxydiphenyls. I. 4- and 2-Hydroxydiphenyl-3-carboxylic acids and their derivatives. N. N. Voroshcov, jun., and A. T. Troschtschenko (J. Gen. Chem. Russ., 1938, **8**, 424—430).—p-$C_6H_4Ph{\cdot}OH$, KOH, and CO_2 (5 hr. at 200—250°/30 atm.) yield 4-*hydroxydiphenyl*-3-*carboxylic acid*, m.p. 215—216° (*Ac*, m.p. 151—152°, and *Bz* derivative, m.p. 174·5—175°). o-$C_6H_4Ph{\cdot}OH$ (I) (*Ac*, m.p. 64°, and *Bz* derivative, m.p. 62°) yields similarly 2-*hydroxydiphenyl*-3-*carboxylic acid* (II) m.p. 186—187° [*Ac*, m.p. 128—129°, and *Bz* derivative, m.p. 118—118·5°; *Me ether*, m.p. 54—56°; *Ph ether*, m.p. 90—92°; *anilide* (III), m.p. 120—121°; p-*toluidide* (IV), m.p. 148—149°; p-*chloroanilide*, m.p. 155—156°]. *Azo-dyes*, obtained by coupling (II) with diazotised p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, α-$C_{10}H_7{\cdot}NH_2$, and benzidine, and (III) and (IV) with p-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$, are described. R. T.

Pyrenecarboxylic acids and ethylanilides.—See B., 1938, 1018.

Condensations by sodium. XIV. Phthalic acids and some factors influencing yields of butyl- and dimethyl-malonic acids. A. A. Morton and F. Fallwell, jun. (J. Amer. Chem. Soc., 1938, **60**, 1924—1927; cf. A., 1938, II, 325).—In the C_6H_6–NaC_5H_{11}–CO_2 reaction m- and p-$C_6H_4(CO_2H)_2$ are formed from $C_6H_4Na_2$. Addition of NaC_5H_{11} to

C_6H_6 and NaOBz and subsequent reaction with CO_2 gives *o*-$C_6H_4(CO_2H)_2$. Addition of NaOBz after formation of the NaPh increases the yield of CPh_3·OH, but decreases that of *o*-$C_6H_4(CO_2H)_2$. Presence of Ni increases the yield of $CHBu(CO_2H)_2$ and (slightly) *o*-$C_6H_4(CO_4H)_2$, but not of $CMe_2(CO_2H)_2$. Adsorption of the various reactants on Na probably plays a part in controlling the direction of the reaction.

R. S. C.

Catalytic oxidation of naphthalene [to phthalic anhydride].—See B., 1938, 1018.

Polymerisation of phenylacetaldehyde. A. Müller (Seifens.-Ztg., 1936, **63**, 441—442; Chem. Zentr., 1936, ii, 3284; cf. A., 1934, 1301).—Polymerisation of CH_2Ph·CHO is considerable in diffuse autumn light (1 month) but is less in diffuse summer light than in the dark. Fixation of mobile electrons of the H atoms of the CH_2 in light of short λ is suggested rather than a polymerisation–depolymerisation equilibrium (cf. A., 1915, i, 261). A. H. C.

Condensation of $\Delta^{\alpha\gamma}$-butadiene with αβ-unsaturated compounds. I. Synthesis of Δ^3-tetrahydrobenzaldehyde, 6-methyl-Δ^3-tetrahydrobenzaldehyde, and their derivatives. N. Tschajanov (J. Gen. Chem. Russ., 1938, **8**, 460—474).—Δ^3-Tetrahydrobenzaldehyde (I) (*oxime*, b.p. 203—204°; *phenylhydrazone*, b.p. 207—208°/22 mm.; p-*nitrophenylhydrazone*, m.p. 163°; *compound* with NH_3, m.p. 105—107°) is obtained in 90% yield from $(CH_2{:}CH\cdot)_2$ and $CH_2{:}CH\cdot CHO$ (30 min. at 150°), together with its *trimeride*, m.p. 175—176°. (I) and H_2O_2 yield a *peroxide*, $\left(CH\ll\begin{matrix}CH\text{–}CH_2\\CH_2\cdot CH_2\end{matrix}\gg CH(OH)\cdot O\cdot\right)_2$, m.p. 90—91° (decomp.); in presence of H_2SO_4 and EtOH the product is *Et* Δ^3-*tetrahydrobenzoate*, b.p. 194—195°. (I) in $COMe_2$ and aq. KOH yield 1 : 2 : 5 : 6-*tetrahydrostyryl Me ketone*, b.p. 118—120°/10 mm. (*semicarbazone*, m.p. 135—136°); the product with COMeEt is γ-*keto*-β-*methyl*-Δ^α-*butenyl*-1 : 2 : 5 : 6-*tetrahydrobenzene*, b.p. 241—243°. $CHMe{:}CH\cdot CHO$ and $(CH_2{:}CH\cdot)_2$ (2 hr. at 160—180°) give 6-methyl-Δ^3-tetrahydrobenzaldehyde (*semicarbazone*, m.p. 169—170°; *oxime*, m.p. 64·5—65·5°; *phenylhydrazone*, b.p. 211—212°; p-*nitrophenylhydrazone*, m.p. 173—174°), which with $COMe_2$ in aq. KOH gives 6-*methyl*-1 : 2 : 5 : 6-*tetrahydrostyryl Me ketone*, b.p. 245·5—246·5° (*semicarbazone*, m.p. 144—145°). R. T.

Nitrobenzaldehydes of the di- and poly-aryl ether series.—See B., 1938, 1018.

Attempted resolution of phenyl αβ-dideuteroethyl ketone by an indirect method. J. B. M. Coppock, J. Kenyon, and S. M. Partridge (J.C.S., 1938, 1069—1074).—The system CHDRR′ does not appear to give rise to appreciable optical activity (cf. A., 1936, 840). (−)-α-Phenylallyl alcohol (I) (A., 1938, II, 275) with *p*-xenylcarbimide gives the (+)-*p*-xenylcarbamate, m.p. 134·8—135·2°, $[\alpha]_{5461}^{20}$ +131·1°, which is reduced by D_2 (Adams) to (+)-α-*phenyl*-βγ-*dideutero*-n-*propyl* p-*xenylcarbamate* (II), m.p. 137·9—138·4°, and by H_2 to (+)-α-phenyl-*n*-propyl *p*-xenylcarbamate (III), m.p. 138·3—138·7°; (II) and (III) have $[\alpha]_{5461}^{20}$ +148·8° and +150·4°, respectively (all in C_6H_6). Attempts to resolve (II) by fractional crystallisation are unsuccessful; more and less sol. crops show no difference in rotatory dispersion, and the slight differences in m.p. are also observed with (III). 3N-NaOH or -HCl does not hydrolyse (III), which with 30% (vol.) H_2SO_4 at 180° gives $(p\text{-}C_6H_4Ph\cdot NH_2)_2,H_2SO_4$, unchanged (III), and a heavy oil. Reduction of (I) by D_2 gives *phenyl*-αβ-*dideuteroethylcarbinol* (IV), of which the 3 : 5-*dinitrobenzoate* (recryst. thrice) had m.p. 52—53°, $[\alpha]_{5461}$ −45·57°, and is hydrolysed (KOH–EtOH) to (IV), b.p. 207°, α_{5461} +8·43°. This with CrO_3–AcOH gives *Ph* αβ-*dideuteroethyl ketone* (V), m.p. 19·5°, b.p. 208°, α_{5461} ±0·01°, when regenerated from the *semicarbazone*, m.p. 175°, α ±0·01° in AcOH or $COMe_2$. E. W. W.

Displacement of absorption bands of dyes with salt formation at the auxochrome groups. F. R. Storck (Helv. Phys. Acta, 1936, **9**, 437—466; Chem. Zentr., 1936, ii, 3782).—Quant. spectrographic examination of *p*-dimethylaminobenzylidene-acetophenone, -phenylacetonitrile, and -acetone, and auramine, and their N^V salts with HCl, H_2SO_4, $HClO_4$, Me_2SO_4, and MeI in H_2O or EtOH, shows that salt formation shifts the bands (extent depending on λ) towards the ultra-violet when the auxochrome is peripheral, and towards the red when central as in auramine. Dissociation of the pure solutions is so slight that the ionic contribution may be neglected.

A. H. C.

Condensation of *p*-dimethylaminobenzaldehyde with vanillylideneacetone and vanillylideneacetone derivatives. L. C. Raiford and M. M. Cooper (J. Org. Chem., 1938, **3**, 11—15).—The appropriate aldehyde with $COMe_2$ in EtOH–NaOH–H_2O affords 2-, m.p. 133—134°, 5-, m.p. 143—144°, and 6-, m.p. 145·5—146·5°, -*chloro*-, and 2-*bromo*-, m.p. 139—140°, -*vanillylideneacetone*. Vanillylideneacetone with *p*-$NMe_2\cdot C_6H_4\cdot CHO$ (I) in EtOH–NaOH–H_2O gives 4′-*dimethylamino*-4-*hydroxy*-3-*methoxydistyryl ketone*, m.p. 199°, together with some di-*p*-dimethylaminostyryl ketone (II). 2-, m.p. 186—187°, 5-, m.p. 203—204°, and 6- (+0·5H_2O), m.p. 95—110°, -*chloro*-, and 2-, m.p. 194—195°, 5-, m.p. 203—204°, and 6-, m.p. 185—185·5° (+0·5EtOH), m.p. 120—128° (decomp.), -*bromo*-4′-*dimethylamino*-4-*hydroxy*-3-*methoxydistyryl ketones* were similarly obtained, in most cases with larger amounts of (II). Better yields were obtained at room temp. than at 100° (bath), and when larger amounts of EtOH and NaOH than previously recommended were used. (II) is not formed by treating the foregoing mixed distyryl ketones with (I) under similar conditions. These derivatives are not formed from *p*-$NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot COMe$ and the appropriate vanillin derivative. H. G. M.

Synthesis of ketones from compounds of ethers with titanium tetrachloride. R. R. Galle (J. Gen. Chem. Russ., 1938, **8**, 402—409).—1-$C_{10}H_7\cdot OMe$ (I) with AcCl or BzCl in presence of $TiCl_4$ yields the corresponding 4-Ac or -Bz derivative; with 2-$C_{10}H_7\cdot OMe$ (II) the 1-Ac or -Bz derivative is obtained. (I), $(COCl)_2$, and $TiCl_4$ give a mixture of di-4-methoxy-1-naphthyl ketone and diketone, whilst with (II) the sole product is di-2-methoxy-1-naphthyl ketone. Thiophen, $(COCl)_2$, and $TiCl_4$ give di-2-thienyl ketone, and (largely) a stable Ti-containing

polymeric complex. $C_{10}H_7$·COR are not obtained from $C_{10}H_8$, RCOCl, and $TiCl_4$. R. T.

Preparation and reactions of magnesium 9-anthranyl bromide. W. E. Bachmann and M. C. Kloetzel (J. Org. Chem., 1938, **3**, 55—61).—Mg 9-anthranyl bromide (I) is obtained in good yield when the pure bromide is refluxed in Bu^{α}_2O–C_6H_6 (12 hr.), Bu^{α}_2O (0·5 hr.), or (generally best) in Et_2O (24 hr.) with pure, pulverised Mg activated by I or (better) EtBr (cf. Miller *et al.*, A., 1935, 741). In Bu^{α}_2O–C_6H_6 a *by-product*, m.p. 313—315°, sublimes at 250°/0·5 mm., was obtained. With I in Et_2O (I) gives 9-*iodoanthracene*, m.p. 82—83°, with MeI affords 9-methylanthracene, with CO_2 yields 9-anthroic acid in good yield, and with PhCN gives *Ph anthranyl ketimine*, m.p. 152—153°, sublimes at 195°/0·5 mm. (*hydrochloride*, m.p. 272—274°), also obtained (in Et_2O–C_6H_6) from MgPhBr and 9-cyanoanthracene, m.p. 174—175° [lit. 170—172°; prepared by heating the bromide with $Cu_2(CN)_2$ and C_5H_5N (220°, 9 hr.)], and hydrolysed with 36% HCl (sealed vessel, 145°, 80 hr.) to 9-benzoylanthracene. With $CHPh_2Br$ (I) in Bu^{α}_2O–C_6H_6 gives 9-*benzhydrylanthracene*, m.p. 204—205°, with $COPh_2$ affords *diphenylanthranylcarbinol*, m.p. 191—192°, and with fluorenone yields *anthranyldiphenylenecarbinol*, m.p. 205—206°. 9-Bromoanthracene (II) reacts readily with Li in anhyd. Et_2O giving Li anthranyl, converted by dil. HCl into anthracene (III). With maleic anhydride in boiling xylene (II) reacts more slowly than (III); the equilibrium favours formation of the adduct (94%) (cf. Barnett *et al.*, A., 1934, 1102).

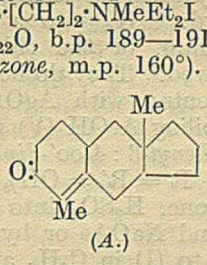
H. G. M.

Synthesis of materials possessing the odour of jasmone. W. Issagulianz (Riechstoffind., 1936, **11**, 84—86; Chem. Zentr., 1936, ii, 3373).—*Et*$_3$ *methyl*-n-*amylbutanetricarboxylate* (yield, 45%) gave tetrahydrojasmone (I) [semicarbazone, m.p. 142° (cf. Treff and Werner, A., 1933, 1296; 1935, 750; Ruzicka and Pfeiffer, A., 1934, 75)]. 3-*Methyl*-2-*isoamyl*-cyclo*pentanone*, b.p. 98—99°/8 mm. (*semicarbazone*, m.p. 156—157°), prepared similarly, has a stronger odour than (I). A. H. C.

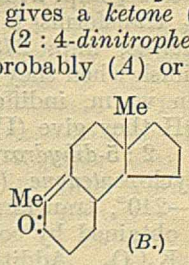
Condensation of acyclic aldehydes with cyclanic ketones. Condensation of formaldehyde and acetaldehyde with *cyclo*pentanone. H. Gault and J. Skoda (Compt. rend., 1938, **207**, 429—430; cf. A., 1923, i, 565).—CH_2O with an excess of *cyclo*pentanone (I) at a low temp. in presence of K_2CO_3 affords 2-*hydroxymethyl*- (II), b.p. 94°/2 mm. (*phenylhydrazone*, m.p. 96—97°; *Ac* derivative, b.p. 120—121°/15 mm.), and 2 : 2-*di*(*hydroxymethyl*)-cyclo*pentanone* (III), m.p. 25—27°, b.p. 146—148°/2 mm. (*phenylhydrazone*, m.p. 116—117°; Ac_2 derivative, b.p. 169—170°/16 mm.). (II) and (III) with H_2–Raney Ni afford 2-*hydroxymethyl*-, b.p. 137°/16 mm. (Ac_2 derivative, b.p. 131°/18 mm.), and 2 : 2-*di*-(*hydroxymethyl*)-cyclo*pentanol*, undistillable (Ac_2 derivative, b.p. 154—155°/5 mm.). (I) with MeCHO similarly affords 2-α-*hydroxyethyl*cyclo*pentanone*, b.p. 95°/1 mm., and more complex products. NaOH at room temp. converts (III) into a difficultly fusible insol. substance. J. L. D.

Liquid-phase reactions at high pressures. IV. Autocondensation of *cyclo*hexanone, and its condensation with aniline. R. H. Sapiro and S. P'eng (J.C.S., 1938, 1171—1174; cf. A., 1937, I, 417).—Autocondensation of *cyclo*hexanone (I) under pressure in absence of catalyst is studied further; the yield of 2-Δ^1-*cyclo*hexenyl*cyclo*hexanone (II) depends on temp. and pressure. Similar results are obtained with glass or SiO_2 tubes; the max. yields are 36·1 and 36·0%, respectively, at 100°/5000 atm. In presence of NH_2Ph, (I) affords its anil also, this being formed [but not (II)] even at 20°/1 atm. Both reactions are promoted by pressure, but they have opposite temp. coeffs. Yields of anils are recorded from equimol. mixtures of NH_2Ph and (I), its 2-Me derivative, *cyclo*pentanone, and COPhMe at 20—100° and 1 and 3500 atm. in absence of a condensing agent; COMeEt and $COEt_2$ do not react. (I) and NH_2Ph at <100° and 5000 atm. afford, in addition, some anil of (II). A. T. P.

Synthesis of substances related to the sterols. XX. Preparation of two tricyclic ketones. F. J. McQuillin and R. Robinson (J.C.S., 1938, 1097—1099).—*cis*-3(2)-Keto-9(10)-methyldecahydronaphthalene (A., 1937, II, 196; cf. *ibid.*, 413) with $NaNH_2$ in Et_2O and N_2, followed by COMe·$[CH_2]_2$·$NMeEt_2I$ (I) in EtOH, gives 2-*keto*-11-*methyl*-$\Delta^{1:13}$-*dodecahydroanthracene*, b.p. 149—151°/2 mm. (*semicarbazone*, m.p. 220°), which is dehydrogenated (Se at 360°) to anthracene. The crude condensation product from 2-methyl*cyclo*pentanone and (I) with $(NO_2)_2C_6H_3$·NH·NH_2 gives 2-*methyl*-2-γ-(*ketobutyl*)cyclo*pentanonebis*-2 : 4-*dinitrophenylhydrazone*, m.p. 201°, and with NaOEt–EtOH in Et_2O yields 5-keto-8-methyl-$\Delta^{4:9}$-tetrahydrohydrindene (A., 1937, II, 197), which is hydrogenated (Pd–$SrCO_3$) to 5-*keto*-8-*methylhydrindane*, b.p. 110°/12 mm. (*semicarbazone*, m.p. 190°). This is oxidised by alkaline $KMnO_4$ to a *dicarboxylic acid*, $C_{10}H_{16}O_4$, m.p. 158°, and with $NaNH_2$ and $COEt·[CH_2]_2·NMeEt_2I$ as before gives a *ketone* (II), $C_{15}H_{22}O$, b.p. 189—191°/13 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 160°). (II) is probably (*A*) or (*B*)



(*A.*)



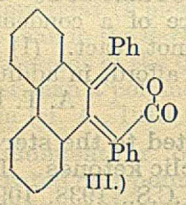
(*B.*)

(which could be used to construct the ætiocholane skeleton), and a hydrocarbon corresponding with (*B*), viz., 3′-*methyl*-4 : 5-*benzhydrindene* (III), m.p. 44° (*picrate*, m.p. 107°), has been synthesised (see below); (II) is, however, resistant to Se dehydrogenation, and identification is thus not possible. β-*o*-Tolylethyl chloride [the alcohol is obtained from *o*-C_6H_4Me·MgBr and $(CH_2)_2O$] with Mg and *cyclo*pentanone gives 1-β-*o*-*tolylethyl*cyclo*pentan*-1-*ol*, b.p. 141°/1 mm., converted by ice-cold 85% H_2SO_4 into 3′-*methyl*-6 : 7 : 8 : 9-*tetrahydro*-4 : 5-*benzhydrindene*, b.p. 97—99°/1 mm., dehydrogenated (Pd–C at 340—360°) to (III).

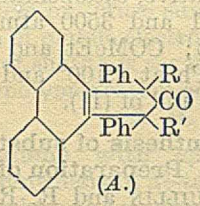
E. W. W.

Heteropolarity. XXXIII. Oxidation and reduction products of phencyclone and acecyclone.

W. Dilthey, S. Henkels, and M. Leonhard (J. pr. Chem., 1938, [ii], **151**, 97—126).—Passage of air through a solution of phencyclone (I) in C_5H_5N at 100° gives 9 : 10-*dibenzoylphenanthrene* (II), m.p. 206°, the constitution of which follows from its conversion by N_2H_4,H_2O in cold C_5H_5N into 3 : 6-*diphenyl*-4 : 5-oo′-*diphenylenepyridazine*, m.p. 340°, by molten P_2S_5 into 2 : 5-diphenyl-3 : 4-*oo*′-diphenylenethiophen, m.p. 204°, and by Zn–Hg in AcOH into 2 : 5-*diphenyl*-3 : 4-oo′-*diphenylenefuran*, m.p. 184°. (II) differs from the 9 : 10-dibenzoylphenanthrene, m.p. 317°, obtained by Willgerodt and Albert (A., 1911, i, 882) from phenanthrene, BzCl, and $AlCl_3$ in CS_2; a repetition of this work gave only a *dibenzoylphenanthrene*, m.p. 184°. The mother-liquors from (II)



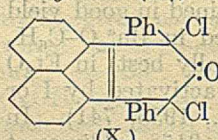
(III.)



(*A*.)

contain 3 : 6-*diphenyl*-4 : 5-oo′-*diphenylene*-2-*pyrone* (III), m.p. 273°, transformed by distillation with NaOH–CaO into 9-benzylphenanthrene, m.p. 154°, identical with the product from phenanthrene and CH_2PhCl in presence or absence of Zn dust. Oxidation of (I) by H_2O_2 in Ac_2O–AcOH gives mainly 2 : 5-*diacetoxy*-2 : 5-*diphenyl*-3 : 4-oo′-*diphenylene*cyclo*pentenone* (IV) (*A* ; R = R′ = OAc), m.p. 273°, also obtained by oxidation of (I) with $Pb(OAc)_4$ in AcOH, and together with a little (II). When heated or treated with conc. H_2SO_4 it is converted into (III). (IV) suspended in cold MeOH is transformed by HCl into 2 : 5-*dichloro*-2 : 5-*diphenyl*-3 : 4-oo′-*diphenylene*cyclo*pentenone* (V) (*A* ; R = R′ = Cl), m.p. 263°, also obtained from (I) and Cl_2 in addition to a second *dichloride*, m.p. 274° (probably *cis–trans* isomerides). PCl_5 transforms (I) in anhyd. C_6H_6 into a third *dichloride*, m.p. 278°. The m.p. of the chlorides diminish when they are preserved. They do not lose Cl in warm, indifferent solvents; with AgOAc in AcOH they give (IV). In boiling AcOH (V) passes into 2 : 5-*dihydroxy*-2 : 5-*diphenyl*-3 : 4-oo′-*diphenylene*cyclo*pentenone* (VI) (*A* ; R = R′ = OH), m.p. 239—240°, transformed by conc. H_2SO_4 into (III), also obtained by cold Ac_2O and NaOAc or by AcCl and K_2CO_3. Addition of Br to (I) in C_6H_6 affords 2 : 5-*dibromo*-2 : 5-*diphenyl*-3 : 4-oo′-*diphenylene*cyclo*pentenone* (*A* ; R = R′ = Br), m.p. 298°, transformed by boiling AcOH into (VI) and by KOAc in AcOH into (IV). (I) and I in CH_2Cl_2 yield 2 : 5-*di-iodo*-2 : 5-*diphenyl*-3 : 4-oo′-*diphenylene*cyclo*pentenone*, which immediately loses I in warm solvents and is converted by MeOH in $CHCl_3$ at room temp. into (III) accompanied by some (II); it is transformed by KOAc in boiling AcOH into dihydrophencyclone (*A* ; R = R′ = H), m.p. 314°.

Acecyclone (VII) suspended in PhCl is transformed by light and air into 7 : 8-*dibenzoylacenaphthylene* (VIII), m.p. 136—137°, whereas oxidation with BzO_2H in PhCl leads only to yellow, resinous products. N_2H_4,H_2O and (VIII) in EtOH give 2 : 5-*diphenyl*-3 : 4-1′ : 8′-*naphthylenepyridazine* (IX), m.p. 304—305° (*picrate*, m.p. 238°). Reduction (Zn–AcOH) of (VIII) gives 7 : 8-*dibenzoylacenaphthene*, m.p. 176°, converted by N_2H_4,H_2O into (IX). Treatment of (VII) with Cl_2 or PCl_5 in C_6H_6 yields *dichlorodihydroacecyclone* (X), m.p. 198° (decomp.), converted by insolation in C_6H_6 into (?) (VIII). Oxidation of (VII) by H_2O_2 in AcOH affords 3 : 6-*diphenyl*-4 : 5-1′ : 8′-*naphthylene*-2-*pyrone*, m.p. 253° [with some (VIII)], also obtained from (X) and KOAc in boiling AcOH. Reduction of (VII) with N_2H_4,H_2O in C_5H_5N or with Zn dust in AcOH affords 2 : 5-*diphenyl*-3 : 4-1′ : 8′-*naphthylene*cyclo*pentadienol*, m.p. 182—183°. Zn dust and boiling AcOH transform (VII) into greenish-yellow *tetrahydroacecyclone*, m.p. 229—230°, converted by boiling AcOH into a colourless *isomeride*, m.p. 229—230° (*oxime*, m.p. 176—178°).



(X.)

H. W.

Higher aromatic keto-fatty acids.—See B., 1938, 1016.

Syntheses in the pinane group. IV. Attempted synthesis of pinonic acid. Synthesis of *trans*-2 : 2-dimethyl-3-acetonyl*cyclo*butane-1-carboxylic acid. Constitution of Fujita's keto-carboxylic acid, $C_{10}H_{16}O_3$. Syntheses of nopinone and verbenone. P. C. Guha and P. L. N. Rao (Ber., 1938, **71**, [*B*], 1591—1595).—Largely a more detailed account of work previously abstracted (A., 1938, II, 283). The following appears new. Addition of EtOH (1 mol.) to pinyl dichloride in light petroleum affords a little *Et* trans-3-*carboxy*-2 : 2-*dimethyl*cyclo*butylacetate*, b.p. 161—162°/5 mm., 210—215°/15 mm. Norpinsemialdehyde condenses with $CH_2(CO_2H)_2$ to β-3-carboxy-2 : 2-dimethyl*cyclo*butyl-acrylic acid, which is reduced to the -propionic acid. Norpinyl dichloride appears to be transformed by ZnMeI under defined conditions into a diketone, m.p. 103—105°, which may be capable of transformation into verbenone. trans-3-*Carbethoxy*-2 : 2-*dimethyl*cyclo*butylacet-amide* and *-anilide* have m.p. 97° and b.p. 218—220° (slight decomp.)/3 mm., respectively. H. W.

Function of the cyano-group in tautomeric systems. F. Arndt and L. Loewe [with Z. Günter and F. Sipahi] (Ber., 1938, **71**, [*B*], 1627—1630).—The electromeric effect of CN is approx. the same as that of CO_2Alk. $CHCl_2{\cdot}CO{\cdot}NH_2$, NaOMe, and *p*-$C_6H_4Me{\cdot}SH$ in MeOH yield *di*-p-*tolylthiolacetamide* (I), m.p. 175° after softening, oxidised by H_2O_2 in AcOH to *di*-p-*toluenesulphonylacetamide*, m.p. 195° (decomp.), which does not give a colour with $FeCl_3$ in EtOH. (I) is transformed by P_2O_5 in boiling C_6H_6 followed by H_2O_2–AcOH into *di*-p-*toluenesulphonylacetonitrile*, m.p. 160°, readily sol. in alkali hydroxide and warm 2N-Na_2CO_3 and giving a brownish-pink colour with $FeCl_3$ in EtOH. The violent reaction with CH_2N_2 does not lead to a cryst. product. Reproducible enol vals. are obtained when the equilibrium solution of $CH_2Bz{\cdot}CN$ in EtOH at −15° is very rapidly treated with Br, the excess of which is immediately removed by β-$C_{10}H_7{\cdot}OH$. The val. is about one third < that of $CH_2Bz{\cdot}CO_2Et$. In EtOH it does not give a

colour with $FeCl_3$, indicating the presence of the enol exclusively in the *trans* form, $\begin{matrix} CPh{\cdot}OH \\ \| \\ N{:}C{-}CH \end{matrix}$.

H. W.

Condensations brought about by bases. III. General course of the Claisen type of condensation. C. R. HAUSER. **IV. Condensation of ethyl *iso*butyrate with benzoyl chloride, benzoic anhydride, and phenyl benzoate as examples of the Claisen type of condensation.** B. E. HUDSON, jun., R. H. DICK, and C. R. HAUSER (J. Amer. Chem. Soc., 1937, **60**, 1957—1959, 1960—1962; cf. A., 1938, II, 143).—III. All condensations of an enolate ion with compounds containing RCO by bases to give $\alpha\gamma$-diketones are classed as Claisen-type condensations. The mechanism of the reactions is discussed.

IV. When $Pr^{\beta}CO_2Et$ is added to CPh_3Na (prep. described) in Et_2O and shortly thereafter treated with BzCl, Bz_2O, or PhOBz, 50—55% yields of $CMe_2Bz{\cdot}CO_2Et$ are formed. EtOAc and CPh_3Na give 43% of $CH_2Ac{\cdot}CO_2Et$ in 3 min.; addition of EtOBz gives also a little $CH_2Bz{\cdot}CO_2Et$. Addition first of $EtCO_2Et$ and then of BzCl to CPh_3Na gives only high-boiling products, but simultaneous addition of $EtCO_2Et$ and PhOBz to CPh_3Na gives a poor yield of $CHMeBz{\cdot}CO_2Et$. EtOAc–EtOBz and $EtCO_2Et$–EtOBz give low yields of $CH_2Bz{\cdot}CO_2Et$ and $CHMeBz{\cdot}CO_2Et$, respectively. These reactions are considered to be Claisen-type condensations.

R. S. C.

Interaction between anthracene and succinic anhydride. E. BERGMANN and A. WEIZMANN (J.C.S., 1938, 1243—1244).—1′-Keto-1′ : 2′ : 3′ : 4′-tetrahydro-1 : 2-benzanthracene is prepared in similar manner to that described by Cook and Robinson (A., 1938, II, 227), who accord priority for the synthesis of 1′-methyl-1 : 2-benzanthracene to Fieser and Peters (A., 1933, 67). The orientation of β-2-anthroylpropionic acid (I) (*Et* ester, m.p. 138—140°) is proved by synthesis. 2-Acetylanthracene and Br in Et_2O at 0° give 2-*bromoacetylanthracene* (II), m.p. 155°; excess of Br yields a *Br*$_3$-compound, m.p. 162° (? 9 : 10-dibromo-2-bromoacetyl-9 : 10-dihydroanthracene). $CHNa(CO_2Et)_2$ and (II) form a product, converted by KOH–MeOH into (I). In preparing (I) from anthracene and $(\cdot CH_2{\cdot}CO)_2O$ some β-1-*anthroylpropionic acid*, m.p. 125°, is obtained. Anthracene, $CH_2Cl{\cdot}COCl$, and $AlCl_3$ in $C_2H_2Cl_4$ at 0° form a *bis-chloroacetylanthracene*, m.p. 205°.

A. T. P.

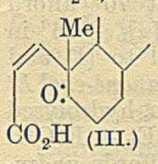
Phenacyl and *p*-substituted phenacyl esters. R. V. LUNDQUIST (J. Amer. Chem. Soc., 1938, **60**, 2000).—*Phenacyl heptoate*, *dichloroacetate*, and α-*bromo*-n-*butyrate*, oils, and *acetylsalicylate*, m.p. 105—105·5°, p-*bromo*-, m.p. 98·2—98·3°, and p-*chlorophenacyl dichloroacetate*, m.p. 93—93·8°, and p-*phenylphenacyl* α-*bromo*-n-*butyrate*, m.p. 103·5—104°, are prepared.

R. S. C.

Reaction of iodine monobromide with cholestenone and β-cholestanone. J. O. RALLS (J. Amer. Chem. Soc., 1938, **60**, 1744—1753).—The reaction of cholestenone (I) and cholestanone (II) with IBr is autocatalytic. These reactions and that of 2-bromocholestanone (III) are of the first order and are catalysed by HBr; moderate amounts of HBr decrease the total amount of halogen absorbed, but increase that organically bound. Br is the active ingredient of IBr. The catalytic effect of HBr is due to its increasing the enolisation of the ketone; the effect of larger amounts is due to some interference in the complex series of reactions. The ethylenic linking of (I) has no part in the reaction, as the oximes of (I) and (II) do not react. With IBr (II) gives mainly (III), m.p. 171·5°, with small amounts of Br_3-derivatives, (IV), m.p. 147°, and (V), m.p. 194°. (III) is unaffected by hot C_5H_5N. With IBr (III) gives (IV), proving the latter to be a 2 : *x*-Br_2-derivative. (V) is probably a 2 : 4-Br_2-derivative; with *o*-$C_6H_4(NH_2)_2$ it gives the *o-aminoanil*, m.p. 184°. With KOAc in EtOH–C_6H_6 (IV) gives a compound, m.p. 119°, and (V) gives a mixture, in which, however, a diosphenol could not be recognised.

R. S. C.

Transformations of brominated derivatives of cholesterol. V. Experiments with dibromocholestanone. H. H. INHOFFEN and HUANG-MINLON (Ber., 1938, **71**, [*B*], 1720—1730; cf. A., 1937, II, 423).—The action of C_5H_5N on 2 : 4-dibromocholestanone (I) at 135° gives a mixture of products from which $\Delta^{1:2\text{-}4:5}$-*cholestadien*-3-*one* (II), m.p. 111·5—112·5°, $[\alpha]_D^{23}$ +28·1° in $CHCl_3$ (*semicarbazone*, m.p. 230—231°), is isolated. Hydrogenation (Pd sponge in Et_2O) of (II) yields coprostanone whereas partial ozonisation affords the *acid*, $C_{26}H_{42}O_3$ (III), m.p. 207—207·5°, the structure of which is established by its absorption spectrum and its instability towards $KMnO_4$. Partial hydrogenation (Rupe's Ni in EtOH) of (II) yields $\Delta^{1:2}$-*coprosten*-3-*one*, m.p. 81—83° (clear at 85°), $[\alpha]_D^{22}$ +64·6° in $CHCl_3$ (*semicarbazone*, m.p. 207°), the spectrum of which shows that it is an αβ-unsaturated ketone. (I) is reduced by $Al(OPr^{\beta})_3$ in boiling C_6H_6–$Pr^{\beta}OH$ to 2 : 4-*dibromocholestan*-3-*ol*, m.p. 174—175° (*acetate*, m.p. 178—179°). This is unchanged by prolonged boiling with C_5H_5N even in presence of $AgNO_3$ or by KOBz in $Bu^{\beta}CO_2H$ but is transformed by KOBz in BzOH at 220° into 2-*benzoyloxycholestan*-3-*one* (IV), m.p. 198—199°, also obtained [together with an isomeric *benzoate* (V), m.p. 145—146°] from 2-bromocholestanone and KOBz in boiling $Bu^{\alpha}OH$–PhMe. Mild hydrolysis (KOH–EtOH–C_6H_6 at room temp.) of (IV) affords 2-*hydroxycholestan*-3-*one*, m.p. 125—127° after softening, reconverted (BzCl in C_5H_5N) into (IV) whereas KOH–MeOH in presence of H_2O_2 transforms (IV) into the previously described (*loc. cit.*) dicarboxylic acid (VI), m.p. 195—196°, also obtained similarly from (V). In the absence of H_2O_2 (IV) and (V) are converted by KOH–MeOH into cholestane-2 : 3-dione, m.p. 161—162°, and (VI).



(III.)

H. W.

Conversion of *trans*-dehydroandrosterone into pregnane derivatives. L. RUZICKA and H. F. MELDAHL (Nature, 1938, **142**, 399).—Δ^5-17-Ethinylandrostene-3-*trans*-17-diol (I) (A., 1937, II, 505) and AcOH in presence of Ac_2O, HgO, and BF_3,Et_2O give $\Delta^{5:20}$-20-acetoxypregnadiene-3-*trans*-17-diol (II), m.p. 175—177° (corr.). The 3-monoacetate of (I) also

adds AcOH forming $\Delta^{5:20}$-3-*trans*-20-diacetoxypregnadien-17-ol (III), m.p. 191—192° (corr.). Alkaline hydrolysis of (II) or (III) yields Δ^5-pregnene-3-*trans*-17-diol-20-one, m.p. 275—277° (corr.), $[\alpha]_D$ −78° in dioxan [oxime, m.p. 245—247° (corr.); 3-monoacetate (Ac_2O and C_5H_5N in the cold), m.p. 270—272° (corr.)]. L. S. T.

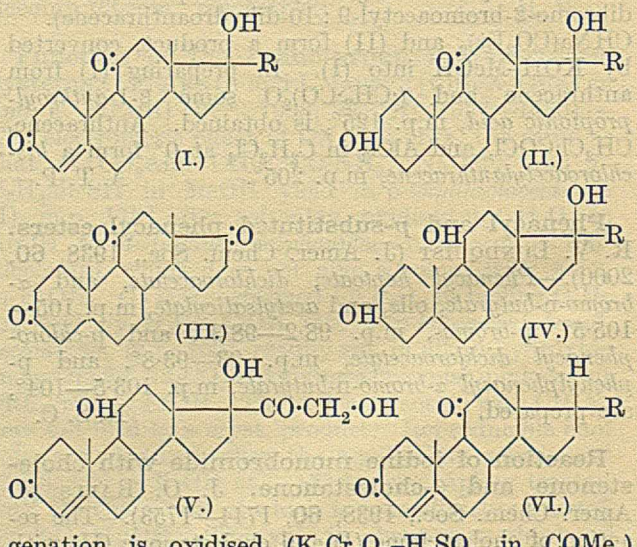
Δ^1-Androsten-17-ol-3-one, an isomeride of testosterone. A. Butenandt and H. Dannenberg (Ber., 1938, **71**, [*B*], 1681—1685).—Androstan-17-ol-3-one acetate in AcOH containing HBr is transformed by Br–AcOH at 20° into 2-*bromoandrostan*-17-*ol*-3-*one acetate* (I), m.p. 177—178°, hydrolysed by HCl–MeOH at room temp. to 2-bromoandrostan-17-ol-3-one (II), m.p. 181° (decomp.). From the products of the action of KOAc in AcOH on (I) or (II) at 200° the *oxime*, m.p. 213—215° (decomp.), of (III) (below) is isolated in very small yield with, in the case of (II), a *product*, (?) $C_{21}H_{28}O_3$, m.p. 208°. Addition of Δ^1-androstene-3 : 17-dione in EtOH to fructose undergoing fermentation by baker's yeast gives (83% yield) Δ^1-*androsten*-17-*ol*-3-*one*, m.p. 158—159°, $[\alpha]_D^{20}$ −42·3° in EtOH [*acetate* (III), m.p. 118—119°], which has pronounced œstrogenic properties. H. W.

Acetalising reactions with steroid ketones; new method of preparing testosterone and dihydrotestosterone. A. Serini and H. Köster (Ber., 1938, **71**, [*B*], 1766—1770).—Cholestanone (I), $CH(OEt)_3$, and EtOH–HCl in C_6H_6 at 70° afford *cholestanone Et*$_2$ *acetal*, m.p. 68—69·5°, $[\alpha]_D$ +26° in dioxan, hydrolysed by boiling dil. HCl to (I) and converted in boiling xylene into *cholestanone-enol Et ether*, m.p. 87—88°, $[\alpha]_D^{20}$ +63·1° in dioxan, hydrolysed to (I); the change is $\cdot C(OEt)_2 \rightarrow \gg C{\cdot}OEt + EtOH$. Similarly, androstane-3 : 17-dione (II) affords *androstane*-3 : 17-*dione* 3-*Et*$_2$ *acetal* (III), m.p. 121—123°, $[\alpha]_D^{20}$ +75·6° in dioxan, hydrolysed to (II) and passing in boiling xylene into *androstane*-3 : 17-*dione*-3-*enol Et ether*, m.p. 105—106°, $[\alpha]_D^{20}$ +126° in dioxan. Reduction (Na in Pr$^\alpha$OH) of (III) affords dihydrotestosterone, m.p. 176—177°, $[\alpha]_D^{20}$ +32° in EtOH. Androstene-3 : 17-dione (IV) (in C_6H_6), $CH(OEt)_3$, and EtOH–HCl at 75° yield directly *androstene*-3 : 17-*dione*-3-*enol Et ether*, m.p. 152°, $[\alpha]_D^{20}$ −89° in dioxan, hydrolysed by acid to (IV); it is also obtained from (IV) and $CMe_2(OEt)_2$ and is reduced (Na and Pr$^\alpha$OH) to testosterone-enol Et ether, m.p. 118—122°, which is hydrolysed to testosterone. Under somewhat different conditions (IV) and $CH(OEt)_3$ yield *androstene*-3 : 17-*dione*-3-*enol Et ether* 17-*Et*$_2$ *acetal*, m.p. 91—92·5°, $[\alpha]_D^{20}$ +141·6° in dioxan, hydrolysed to (IV). H. W.

Highly active esters of testosterone. K. Miescher, A. Wettstein, and E. Tschopp (Schweiz. med. Woch., 1936, **66**, 763—764; Chem. Zentr., 1936, ii, 3427).—Esters with fatty acids C_{1-18} are described. In the capon test, esters of acids C_{1-3} are equiv., higher esters having a more protracted but less intense action whilst in the rat test the propionate is the most active; lower esters are also active but the activity decreases rapidly with an increasing C chain. The possible ester character of the natural hormone is discussed and *esters* with the following acids are described: HCO_2H, m.p. 127—129°; AcOH, m.p. 140—142°; $EtCO_2H$, m.p. 121—123°; Pr$^\alpha CO_2H$, m.p. 111—113°; Pr$^\beta CO_2H$, m.p. 134—136°; Bu$^\alpha CO_2H$, m.p. 109—111°; Bu$^\beta CO_2H$, m.p. 138—140°; decoic, m.p. 55—57°; palmitic, m.p. 72—74°; stearic, m.p. 79—80°; BzOH, m.p. 198—200°. A. H. C.

Biochemical dehydrogenation in the testicular hormone series; bacterial oxidation of dehydroandrosterone to androstenedione. L. Mamoli and A. Vercellone (Ber., 1938, **71**, [*B*], 1686—1687).—Previous results (A., 1938, II, 103, 104) could not be repeated. Since aërobic bacteria cultivated in an impoverished yeast prep. are able to dehydrogenate dehydroandrosterone to Δ^4-androstenedione in excellent yield, it is probable that the dehydrogenation observed previously (*loc. cit.*) is due entirely to the presence of such micro-organisms. H. W.

Adrenal cortex. IV. Structures of compounds *C*, *D*, *E*, *F*, and *G*. V. Conversion of compound *E* into the series which contains four atoms of oxygen and into adrenosterone by the action of calcium hydroxide. H. L. Mason (J. Biol. Chem., 1938, **124**, 459—474, 475—479).—IV. Reichstein's formula (A., 1937, II, 506; cf. also A., 1936, 1382) for compound-*E* (his *Fa*), *i.e.*, (I) (R = $CO{\cdot}CH_2{\cdot}OH$), is adopted. The HIO_4 oxidation product of *E*, acid-5 (A., 1937, II, 25), now formulated as (I) (R = CO_2H) (the ethylenic linking does not react with BzO_2H), is converted (C_5H_5N–Ac_2O) into its *Ac*$_1$ derivative, m.p. 239—243°, $[\alpha]_{5461}^{25}$ +118·5±1·9° in EtOH (2 : 4-*dinitrophenylhydrazone*); as this is recryst. unchanged from aq. media it cannot be an easily hydrolysed enol acetate, and enolisation of the 3-CO group is thus excluded. With $H_2 + PtO_2$ and N-NaOH in EtOH, acid-5 gives *acid*-5B (II) (R = CO_2H), m.p. 290—293°, $[\alpha]_{5461}^{25}$ +42·5±2°, and an isomeric *acid*, $C_{20}H_{30}O_5$, m.p. 283—287°, respectively pptd. and not pptd. by digitonin. Further hydrogenation is indefinite. Residual material after hydrogenation is oxidised ($K_2Cr_2O_7$–H_2SO_4 in $COMe_2$) to ketone-3 (III), m.p. 179—181°, $[\alpha]_{5461}^{25}$ +191±1·5° in

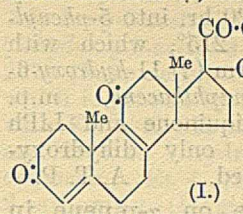


EtOH. The position of the fifth O in *E* is uncertain; it is assigned to $C_{(11)}$ on account of its inertness; thus acid-5B does not react with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 or MgMeI, and its Ac_2 derivative, m.p. 259—260°, $[\alpha]^{25}_{5461}$ −25·6±1·8° in EtOH, is not oxidised by CrO_3–AcOH. Compound-*C* (Reichstein's *C*), now formulated as (IV) (R = CO·CH_2·OH) (cf. A., 1937, II, 506—507), is oxidised by HIO_4 to CH_2O and an *acid* (IV) (R = CO_2H), m.p. 240—243°, $[\alpha]^{25}_{5461}$ +32·8±3·3° in EtOH, pptd. by digitonin. The oxidation product from acid-3 is not $C_{20}H_{30}O_3$ (A., 1936, 1117), but (III). Compound-*D* (Reichstein's *A*), now formulated as (IV) [R = CH(OH)·CH_2·OH], m.p. (+H_2O) 160—164° (uncorr.), m.p. (anhyd.) 165—167° [Reichstein's solidification and remelting (A., 1936, 473) not observed], is oxidised to impure (III), m.p. 160—161·5°. Aq. residues after removal of *E* contain *compound-F* (Reichstein's *M*; cf. A., 1937, II, 506) (V), m.p. 217—220°, $[\alpha]^{25}_{5461}$ +178°±2° (in EtOH?), converted by HIO_4 into CH_2O and an *acid*, $C_{20}H_{28}O_5$, m.p. 228—238°, and further by CrO_3 into ketone-4 (Reichstein's *G* or adrenosterone) (which the authors have not detected in cortex extracts). The liberation of 1 CH_4 by the last from MgMeI is attributed to enolisation of the hindered CO at $C_{(11)}$, not of that at $C_{(3)}$ (cf. acids 5 and 5A above). *Compound-G* (Reichstein's *D*), m.p. 228—236° (uncorr.), $[\alpha]^{25}_{5461}$ +83°±2° in EtOH, now formulated as (II) (R = CO·CH_2·OH), from fraction II, is oxidised by HIO_4 to acid-5B and CH_2O. *E* has about 1/5 the physiological activity of corticosterone. M.p. are corr. except where stated; m.p. >200° are with decomp.

V. Conversion from the $C_{21}O_5$ into the $C_{21}O_4$ series is effected. Compound-*E* (in EtOH) with saturated aq. $Ca(OH)_2$ in N_2 gives adrenosterone and acidic material. The latter with $K_2Cr_2O_7$–H_2SO_4–$COMe_2$ gives acid-1 (VI) (R = CO_2H) (cf. A., 1937, II, 459) [also obtained by oxidation of compound-*A* (VI) (R = CO·CH_2·OH)] and adrenosterone. *E* is 17-hydroxy-*A*. The possibility that acid-1 is derived from *A* or *B* (corticosterone; 11-dihydro-*A*), present as impurity in *E*, is excluded by the failure to obtain acid-1 from the *E* used and HIO_4 followed by CrO_3. *B* is unaffected by $Ca(OH)_2$. E. W. W.

Fission and fractionation of "corticosterone." M. Piccinini (Boll. Chim. farm., 1938, **77**, 489).—The following substances were isolated: *A*, $C_{21}H_{25}O_4$, m.p. 174—181·5°; *B*, $C_{21}H_{30}O_4$, m.p. 177—179° (physiologically active and identical with corticosterone); *C*, $C_{21}H_{34}O_5$, m.p. 245—250°; *F*, $C_{21}H_{30}O_5$, m.p. 214—220°; *G*, $C_{21}H_{32}O_5$, m.p. 228—238°. *A* and *B* are oxidised (HIO_4) to CH_2O and the acid $C_{20}H_{26}O_4$, m.p. 258—260°, and $C_{20}H_{28}O_4$, m.p. 255—258°, respectively. *C* and *G* are Reichstein's *C* and *D*, respectively (A., 1937, II, 506). Reactions indicating the groups present in some of the above substances are briefly described. F. O. H.

Sterols. XL. Origin and interrelationships of the steroidal hormones. R. E. Marker (J. Amer. Chem. Soc., 1938, **60**, 1725—1736; cf. A., 1938, II, 369).—Reasons are advanced against the view that steroidal hormones and bile acids are derived from cholesterol, notably the difficulty of introducing O into the ring-system and of oxidising the side-chain. Schemes are detailed, whereby the pregnane, androstane, and urane derivatives of C_{18}, C_{19}, and C_{21} types and the sterols in the cortical extract are derived according to definite rules from the common precursor, $\Delta^{4:8}$-pregnadiene-17 : 21-diol-3 : 11 : 20-trione (I) or its hydrate at $C_{(9)}$. Most of the proposed changes have counterparts in the laboratory. The rules account for all the products isolated and predict the occurrence of some more and absence of others. R. S. C.



(I.)

Leptospermone. I. L. H. Briggs, A. R. Penfold, and W. F. Short (J.C.S., 1938, 1193—1196; cf. B., 1926, 511).—"Leptospermol" is not a monobasic acid but is a β-diketone belonging to the same group as angustione and dehydroangustione (A., 1931, 487) and the authors rename it *leptospermone* (I), $C_{15}H_{22}O_4$. (I) has b.p. 146°/10 mm., contains 2 active H, gives an *anilino*-derivative, $C_{21}H_{27}O_3N$, m.p. 91°, a cryst. Cu salt, and an *anhydrophenylhydrazone* (II), m.p. 118°, containing a pyrazole ring. (I) and HNO_3–H_2SO_4 at 50° gives $CMe_2(CO_2H)_2$ only, whilst $KMnO_4$ at <45° affords $COPr^{\beta}_2$ and CH_2Pr^{β}·CO_2H. (I) and (II) are probably 2-*isovaleryl*-4 : 4 : 6 : 6-*tetramethyl*cyclo*hexane*-1 : 3 : 5-*trione* and $CO{\cdot}CMe_2{\cdot}C{\cdot}NPh \gg N$, respectively. A. T. P.
$CMe_2{\cdot}CO{\cdot}C{\cdot}CBu^{\beta}$

Semiquinone radicals in the indamine and indophenol groups.—See A., 1938, I, 521.

Compounds from aminoanthraquinones and αβ-unsaturated carbonyl compounds.—See B., 1938, 1019.

1 : 3-Dihalogeno-2-methylaminoanthraquinones.—See B., 1938, 1018.

Synthetic experiments in the rubrene series. E. Bergmann (J.C.S., 1938, 1147—1150; cf. A., 1936, 992, 1499).—1 : 2-Diphenyl*iso*benzfuran (I) and maleic anhydride form an adduct (II), converted by HCl–MeOH (followed by MeOH–KOH), or better by HBr–AcOH at 37° for 2 days, into 1 : 4-*diphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (III), m.p. 273—275° [free acid, m.p. 295° (decomp.) (*Bu H* ester, m.p. 238°)]. (II) and HCl–MeOH at 0°, followed by MeOH–KOH and then $SOCl_2$, give also a *dilactone* m.p. 250—252° (probably the *di-γ-lactone* of 1 : 4-dihydroxy-1 : 4-diphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-dicarboxylic acid). (III) and MgPhBr afford a keto-acid, cyclised by BzCl in 1-$C_{10}H_7Cl$ into 6 : 11-*diphenylnaphthacene*-5 : 12-*quinone* (IV), m.p. 282°. The use of conc. H_2SO_4 at room temp. as dehydrating agent yields (?) 6 : 11-*dihydroxy*-6 : 11-*diphenyl*-6 : 11-*dihydronaphthacene*-5 : 12-*quinone*, m.p. >360°. (IV) is obtained more readily from the *adduct*, yellow, m.p. 150° (reddish-black liquid), of (I) and α-naphthaquinone in xylene, and 40% HBr in AcOH at 37° for 2 days, 5 : 12-*dihydroxy*-6 : 11-*oxido*-6 : 11-*diphenylnaphthacene* (?), m.p. 150°, also being formed. 1-Phenylnaphthalene-2 : 3-dicarboxylic anhydride and

MgPhBr in PhMe form a keto-acid, converted by conc. H_2SO_4 at room temp. for 20 hr. into *5-phenylnaphthacene*-6 : 11-*quinone*, m.p. 215°, which with LiPh takes up one Ph only, to form (?) 11-*hydroxy*-6-*keto*-5 : 11-*diphenyl*-6 : 11-*dihydronaphthacene*, m.p. 248° (decomp.). Naphthacenediquinone and LiPh give no phenylated product, only dihydroxynaphthacenequinone being isolated. A. T. P.

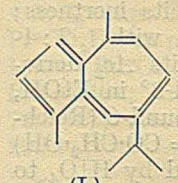
Action of acetic anhydride on α-pinene in presence of boric acid. I, II. M. Imoto (J. Soc. Chem. Ind. Japan, 1938, **41**, 209—212B; cf. Schmidt, B., 1925, 229).—I. *l*-α-Pinene (I), Ac_2O, and B_2O_3, heated at 90—95° for 14 hr., give unchanged oil, camphene, dipentene, limonene, and esters (22% yield) hydrolysed to borneol and *iso*borneol and fenchyl alcohol. *l*- and *d*-α-Pinene, Ac_2O, and cryst. H_3BO_3 in different proportions at 110—150° afford a larger yield of esters (37—58%).

II. A more detailed fractionation of the products of the latter reaction with (I) indicates the presence of all the above reaction compounds, together with *p*-cymene, some polymerised substance, and an unknown *alcohol*, $C_{10}H_{17}$·OH (*H phthalate*, m.p. 162—163°). A. T. P.

Caryophyllenes. VI. γ-Caryophyllene. G. R. Ramage and J. L. Simonsen. **VII. Experiments on the synthesis of caryophyllenic acid.** M. D. Owen, G. R. Ramage, and J. L. Simonsen (J.C.S., 1208—1211, 1211—1214).—VI. γ-Caryophyllene α-nitrosochloride and C_5H_5N give *oximino-γ-caryophyllene*, b.p. 162—167°/5 mm., reduced (Na–EtOH) to *aminodihydro-γ-caryophyllene* (I), b.p. 147°/13 mm., the Ac derivative of which on ozonolysis affords CH_2O and a *ketone* (II), $C_{16}H_{27}O_2N$, m.p. 139—140°, $[\alpha]_{5461}$ −58° in EtOAc. Hydrogenation of (I) yields *aminotetrahydro-γ-caryophyllene*, b.p. 147°/11 mm., which is deaminated and dehydrated to *dihydro-γ-caryophyllene*, b.p. 140°/24 mm., α_{5461} −26·1°, oxidised (O_3) to a liquid keto-acid, $C_{15}H_{26}O_3$ (*Ag* salt). Ozonolysis of acetamido-β-caryophyllene gives CH_2O and (II). It is suggested that β- and γ-caryophyllene are stereoisomerides.

VII. $CMe_2(CH_2{\cdot}OAc)_2$ and HBr give $CMe_2(CH_2Br)_2$ and the *α-bromo-γ-acetoxy*-compound, b.p. 85—95°/26 mm. The Br_2-compound and Et potassiomalonate afford *Et* 3 : 3-*dimethyl*cyclo*butane*-1 : 1-*dicarboxylate*, b.p. 118—119°/20 mm., hydrolysed to the *acid*, decomp. 162°, which is decarboxylated to 3 : 3-*dimethyl*cyclo*butanecarboxylic acid* (III), b.p. 204°/760 mm. (*p-phenacyl* ester, m.p. 92°). The acid and $SOCl_2$, followed by Br and MeOH, yield *Me* 1-*bromo*-3 : 3-*dimethyl*cyclo*butane*-1-*carboxylate*, b.p. 82—83°/14 mm. Debromination with $NPhEt_2$ gives *Me* 3 : 3-*dimethyl*cyclo*butanecarboxylate*, b.p. 70—80°/30 mm., and with KOH, 1-*hydroxy*-3 : 3-*dimethyl*cyclo*butane*-1-*carboxylic acid*, m.p. 83°, is obtained. $CMe_2{:}CO$ and CH_2N_2 give 3 : 3-*dimethyl*cyclo*butanone* (IV), b.p. 122—124°/770 mm. (*semicarbazone*, m.p. 234°). It is proposed to use (III) and (IV) for the synthesis of caryophyllenic acid. F. R. S.

Aromadendrene. II. C. B. Radcliffe and W. F. Short (J.C.S., 1938, 1200—1203).—Aromadendrone (I), obtained from *Eucalyptus rariflora* (30% yield) and *E. globulus* (37% yield), has m.p. 84·5—85°, $[\alpha]^{17}_{5770}$ +5·75° in EtOH, and forms α-, m.p. 195—196° (decomp.), and β-*semicarbazones*, m.p. 201·5—202·5° (decomp.), a p-*nitrophenylhydrazone*, m.p. 131°, and a *benzylidene* derivative, m.p. 66—66·5°. Reduction (Na) of (I) gives *aromadendrol*, b.p. 139—140°/10 mm., m.p. 54—59°, and of the oxime of (I) affords aromadendrylamine (*H oxalate*, m.p. 164—165°). With $KMnO_4$ aromadendrene gives (I), *aromadendrene glycol*, m.p. 118°, and an *acid*, m.p. 175—176° (decomp.). Dehydrogenation (S) of aromadendrene gives *S*-guaiacazulene in 6·3% yield. The provisional formula for (I) is suggested. F. R. S.



(I.)

Structure of triterpenes and related substances.—See A., 1938, I, 502.

Uncertain principles of lignin chemistry? E. Wedekind (Zellstoff-Faser, 1936, **33**, 14—15; Chem. Zentr., 1936, ii, 3679).—Treatment of beechwood alternately with Schweitzer's reagent and $H_2C_2O_4$ yields a product identical with Storch's beechwood lignin (A., 1936, 207) which is thus, contrary to Hilpert (cf. A., 1935, 550), not a reaction product of carbohydrate origin. A. H. C.

Resinols. V. β-Amyrenol and dehydro-β-amyrenol. Location of the unsaturated centres of the α- and β-amyrenols. J. H. Beynon, K. S. Sharples, and F. S. Spring (J.C.S., 1938, 1233—1236).—Oxidation (CrO_3) of β-amyrenyl benzoate gives *β-amyrenonyl benzoate*, m.p. 265°, $[\alpha]_D^{25}$ +126·6° in $CHCl_3$, hydrolysed to *β-amyrenonol* (I), m.p. 175°, $[\alpha]_D^{21}$ +113·2° in $CHCl_3$. *β-Amyrenonyl acetate*, m.p. 260—261°, $[\alpha]_D^{20}$ +157·9° in $CHCl_3$, is reduced (Pd–H_2) to β-amyrenyl acetate. Reduction (Na–C_5H_{11}·OH) of (I) yields a *product*, $C_{30}H_{50}O_2$,EtOH, m.p. 220—221°, which with Ac_2O gives *dehydro-β-amyrenyl acetate*, m.p. 208—209°, $[\alpha]_D^{20}$ +331° in $CHCl_3$. Oxidation (CrO_3) of dehydro-α-amyrenyl acetate affords an *acetate*, $C_{32}H_{50}O_4$, m.p. 312°, $[\alpha]_D^{24}$ +61·1° in $CHCl_3$. Light absorption data are given and the structures of the α- and β-amyrenols are discussed. F. R. S.

Toad venom. VIII. Structure of γ-bufotalin. M. Kotake and T. Kubota (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, **34**, 824—831).—EtOH extracts bufotalin and γ-bufotalin (I) from the skin of *Bufo vulgaris formosus*. (I) with 5% KOH–MeOH at 100° affords *Me* γ-iso*bufotalinate*, $C_{26}H_{36}O_5$, m.p. 190—191° (+1*EtOH*, m.p. 124—125°), which on further treatment with 5% KOH–EtOH at 100° gives *Me γ-bufotalinate* (II), m.p. 215°, which has aldehydic properties. With warm 2·5N-NaOH (II) gives γ-iso*bufotalinic acid*, m.p. 205°, isomeric with (I). The Ac derivative of (I) with O_3 in $CHCl_3$ below 0° affords CH_2O, $CHO{\cdot}CO_2H$, $H_2C_2O_4$, and *diacetylætio-γ-bufotalinic acid*, m.p. 225°. Anhydro-γ-bufotalin with Pd–H_2 in AcOH gives hexahydro-γ-bufotalin and an *isomeride*, m.p. 212—213°, of dihydroxycholanic acid. With CrO_3 in AcOH at 0° (I) affords a *substance*, $C_{24}H_{30}O_5$ or $C_{24}H_{32}O_5$, m.p. 252°. A structure is suggested for (I). J. L. D.

Soya-bean saponin. IV. K. Tsuda and S. Kitagawa (Ber., 1938, **71**, [*B*], 1604—1609; cf. A., 1938, II, 239).—Soyasapogenol *B* (I) is very slowly

oxidised by $KMnO_4$ in boiling $COMe_2$ to the *compound*, $C_{30}H_{48}O_3$, decomp. 218° (*monoxime*, decomp. 244°; *diacetate*, m.p. 146·5°). Methylhederagenin (II) (as typical triterpene alcohol) is converted by Cu-bronze at about 270° into CH_2O and methylhedragone, m.p. 203°, $[\alpha]_D^{19}$ +104·9° in $CHCl_3$, identical with the product of the oxidation of (II) with CrO_3 in AcOH. Analogously (I) and Cu-bronze at 270° yield CH_2O and the diketone, m.p. 253—255°, $[\alpha]_D^{22}$ +57·14° in $CHCl_3$ (*dioxime*, decomp. 266°), identical with that derived (*loc. cit.*) from (I) and CrO_3. Dihydrosoyasapogenol *C* and soyasapogenol *C* and *D* with Cu-bronze give CH_2O and the respective *monoketones*, $C_{29}H_{48}O$, m.p. 207° (*monoxime*, decomp. 213—215°), $C_{29}H_{46}O$, m.p. 215°, $[\alpha]_D^{20}$ +84·4° in $CHCl_3$ (*monoxime*, decomp. 231°), and $C_{29}H_{46}O_2$, m.p. 202° (*monoxime*, m.p. 223°). Betulin and dihydrobetulin (III) are unchanged when heated with Cu-bronze at 300°/4 mm. and 250—300°/3 mm., respectively. At 330° (III) affords the *keto-aldehyde*, $C_{30}H_{48}O_2$, decomp. 183—185°, $[\alpha]_D^{25}$ +11·45° in $CHCl_3$ (*dioxime*, decomp. 275°), corresponding with dihydrobetulonic acid. The action of Cu on triterpene alcohols, therefore, is a very simple means of preparing triterpene-ketones or -aldehydes and also affords a method for determining the position of their OH groups. H. W.

Condensation of furfuryl bromide with sodium phenoxide. R. Paul and H. Normant (Bull. Soc. chim., 1938, [v], **5**, 1148—1153).—Mainly an account of work already abstracted (A., 1937, II, 385). *o*-Furfurylphenol is converted by Me_2SO_4 and alkali into o-*furfurylanisole*, b.p. 136°/11 mm., reduced (H_2 at 110°/60 atm.–Raney Ni) to o-*tetrahydrofurfurylanisole*, b.p. 143—144°/11 mm. H. W.

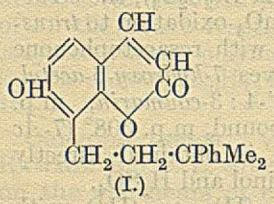
4-Benzoyl-2-phenylfuran. R. C. Fuson, C. L. Fleming, and R. Johnson (J. Amer. Chem. Soc., 1938, **60**, 1994—1997).—CHBz:CMeBz (modified prep.) reduces 0·5 mol. of SeO_2 in dioxan, giving 63% of 4-*benzoyl*-2-*phenylfuran* (I), m.p. 113·7—114°, which, unlike most furan derivatives, is stable to short treatment with acids, but is degraded by hot 10% NaOH to $(CH_2Bz)_2$. With NH_3–H_2O–EtOH at 130—140° (I) gives 4-*benzoyl*-2-*phenylpyrrole*, m.p. 213·7—215·5° [*oxime*, m.p. 188·5—191·5° (sinters at 171°)], and with boiling NH_2Ph gives the *anil*, m.p. 230·5—231°, hydrolysed to 4-*benzoyl*-1 : 2-*diphenylpyrrole*, m.p. 240—241° (*oxime*, m.p. 215·5—218·5°). Dypnone and SeO_2 give 2 : 4-diphenylfuran, but $(CMeBz)_2$ and CHBz:CHMe do not react. Nihydrogenation of (I) gives 2-*phenyl*-4-α-*hydroxybenzylfuran*, m.p. 128·1—129·1° (*benzoate*, m.p. 123·1—124·1°; p-*nitrobenzoate*, m.p. 109·5—109·8°). The *oxime*, m.p. 149—149·4°, of (I) and PCl_5 in Et_2O give 2-*phenyl*-4-*furoanilide*, m.p. 192—193°, hydrolysed to NH_2Ph and 2-*phenyl*-4-*furoic acid*, m.p. 208—209°, decarboxylated with difficulty (heating alone at 275°) to 2-phenylfuran. R. S. C.

Heterocyclic compounds. VII. Coumarins from resacetophenone and cyclic β-ketonic esters. VIII. Coumarins from alkyl*cyclo*hexanone-2-carboxylates and *trans*-β-decalone-3-carboxylate. N. A. Chowdhry and R. D. Desai (Proc. Indian Acad. Sci., 1938, **8**, **A**, 1—5, 12—19; cf. A., 1938, II, 198).—VII. Et *cyclo*hexanone-2-carboxylate, resacetophenone, and $POCl_3$ in boiling C_6H_6 give 7-*hydroxy*-6-*acetyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin* [7-*hydroxy*-6-*acetyl*-3 : 4-*tetramethylenecoumarin*], m.p. 237° (7-*Ac* derivative, m.p. 199°), the structure of which is proved by its giving a reddish-violet colour with $FeCl_3$–EtOH and by reduction by Hg–Zn dust and HCl to 7-hydroxy-6-ethyl-3 : 4-tetramethylenecoumarin. Et 4- (I) and 5-methyl*cyclo*hexan-1-one-2-carboxylate (II) give similarly 7-*hydroxy*-6-*acetyl*-4′-, m.p. 262°, and -5′-*methyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin*, m.p. 258°, respectively, reduced to 7-*hydroxy*-4′-, m.p. 252° (7-*Ac* derivative, m.p. 146°; *Me ether*, m.p. 158°), and -5′-*methyl*-6-*ethyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin*, m.p. 202° (7-*Ac* derivative, m.p. 167°; *Me ether*, m.p. 127°), respectively, which are also obtained directly from (I) or (II), 4-ethylresorcinol, and H_2SO_4 at room temp. Et *trans*-2-ketodecahydronaphthalene-3-carboxylate (III), m.p. 46°, b.p. 145—150°/6 mm. (modified prep. from *trans*-2-ketodecahydronaphthalene and $Et_2C_2O_4$), the structure of which is proved by $KMnO_4$-oxidation to *trans*-*cyclo*hexane-1 : 2-diacetic acid, with resacetophenone and $POCl_3$ in boiling C_6H_6 gives 7-*hydroxy*-6-*acetyl*-Δ²-trans-*octahydronaphtha*-2′ : 3′-4 : 3-*coumarin*, m.p. 250°, reduced to the 6-*Et* compound, m.p. 308° (7-*Ac* derivative, m.p. 172°), which is obtained directly from the ester by 4-ethylresorcinol and H_2SO_4.

VIII. Condensation of (I), (II), or (III) with phloroglucinol, orcinol, or pyrogallol to give coumarin derivatives is best effected by $POCl_3$, but for *m*-$C_6H_4(OH)_2$ and α-$C_{10}H_7$·OH H_2SO_4 is better. For Et 6-methyl*cyclo*hexan-1-one-2-carboxylate (IV), however, $POCl_3$ is more effective in all cases. Colour reactions indicate that the products from orcinol are 5-hydroxy-7-methyl- rather than 7-hydroxy-5-methylcoumarins as assumed by Sen *et al.* (A., 1928, 1254). Fries rearrangement of the tri- and tetra-cyclic acetoxycoumarins gives 8-acetylcoumarins, the structure of which is proved by independent synthesis (unpublished) of the 6-acetylcoumarins. The following are prepared by the above methods. 7-*Hydroxy*-, m.p. 217° (*Ac* derivative, m.p. 176°; *Me ether*, m.p. 123°), 7 : 8-, m.p. 256° (Ac_2 derivative; m.p. 179°; Me_2 *ether*, m.p. 154°), and 5 : 7-*dihydroxy*-4′-*methyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin*, m.p. 265° (Ac_2 derivative, m.p. 128°; Me_2 *ether*, m.p. 133°). 7-*Hydroxy*-, m.p. 202° (*Ac* derivative, m.p. 136°; *Me ether*, m.p. 118°), 7 : 8-, m.p. 231° (Ac_2 derivative, m.p. 214°; Me_2 *ether*, m.p. 123°), and 5 : 7-*dihydroxy*-5′-*methyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin*, m.p. 262° (Ac_2 derivative, m.p. 117°). 7-*Hydroxy*-, m.p. 205° (*Ac* derivative, m.p. 174°; *Me ether*, m.p. 112°), 7 : 8-, m.p. 227° (Ac_2 derivative, m.p. 140°), and 5 : 7-*dihydroxy*-6′-*methyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin*, m.p. 275° (Ac_2 derivative, m.p. 127°). 7-*Hydroxy*-8-*acetyl*-4′-, m.p. 135° (*semicarbazone*, m.p. 236°), and -5′-*methyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin*, m.p. 142° (*semicarbazone*, m.p. 232°). 5-*Hydroxy*-7 : 4′-, m.p. 250° (*Ac* derivative, m.p. 185°; *Me ether*, m.p. 140°), -7 : 5′-, m.p. 260° [called by Sen *et al.* (*loc. cit.*) 7-hydroxy-5 : 4-dimethyl- and given m.p. 249°] (*Ac* derivative, m.p. 134°; *Me ether*, m.p. 98°), and -7 : 6′-*dimethyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin*, m.p. 235° (*Ac* derivative, m.p. 124°). 4′-, m.p. 198°, 5′-, m.p. 173°, and 6′-*Methyl*-Δ¹-cyclo-

hexeno-1′ : 2′-4 : 3-α-*naphtha*-1 : 2-*pyrone*, m.p. 112°. 7-*Hydroxy*-, m.p. 245° (*Ac* derivative, m.p. 192°; *Me ether*, m.p. 178°), 7 : 8-, m.p. 267° (Ac_2 derivative, m.p. 200°), and 5 : 7-*dihydroxy*-Δ²-trans-*octahydronaphtha*-2′ : 3′-4 : 3-*coumarin*, m.p. 265° (Ac_2 derivative, m.p. 173°); 7-*hydroxy*-8-*acetyl*-Δ²-trans-*octahydronaphtha*-2′ : 3′-4 : 3-*coumarin*, m.p. 167° (*semicarbazone*, m.p. 258°); Δ²-trans-*octahydronaphtha*-2′ : 3′-4 : 3-α-*naphtha*-1 : 2-*pyrone*, m.p. 222°; and 5-*hydroxy*-7-*methyl*-Δ²-trans-*octahydronaphtha*-2′ : 3′-4 : 3-*coumarin*, m.p. 313° (*Ac* derivative, m.p. 184°). 4-Ethylresorcinol and (IV) give 7-*hydroxy*-6′-*methyl*-6-*ethyl*-Δ¹-cyclo*hexeno*-1′ : 2′-4 : 3-*coumarin*, m.p. 232° (*Ac* derivative; *Me ether*, m.p. 109°). R. S. C.

Natural coumarins. XXXVIII. Action of aluminium bromide and benzene on osthol. E. Späth and P. Kainrath (Ber., 1938, **71**, [*B*], 1662—1666).—Demethylation is accompanied by addition of C_6H_6 to the side-chain. Osthol is transformed by $AlBr_3$ in boiling C_6H_6 into *phenyldihydro-osthenol* (I), m.p. 171—172° (vac.), converted by an excess of CH_2N_2 in Et_2O or by KOH–Me_2SO_4 into the *Me ether*, m.p. 133—134°. (I) is hydrogenated (Pd sponge in AcOH at 16°) to *phenyltetrahydro-osthenol*, m.p. 126—127° (vac.), oxidised (HNO_3) to $(CH_2{\cdot}CO_2H)_2$. Oxidation of (I) in alkaline solution by H_2O_2 yields *γ-phenyl-γ-methylvaleric acid* (p-*xenylamide*, m.p. 97—98°; *anilide*, m.p. 115—117°); the acid is obtained synthetically by the action of $AlBr_3$ and abs. C_6H_6 on γ-*iso*hexolactone. *iso*Butyrophenone is treated with $CH_2Br{\cdot}CO_2Et$ and Zn filings and the product is boiled with 85% HCO_2H and then with KOH–MeOH, thereby giving a β-*phenyl-γ-methylpentenoic acid*, b.p. 120—130° (bath)/1 mm., hydrogenated (Pd sponge in AcOH) to β-*phenyl-γ-methylvaleric acid* (p-*xenylamide*, m.p. 101—103°). $CH_2(CO_2Et)_2$ is condensed with NaOEt and $CH_2Ph{\cdot}CHMe{\cdot}CH_2Br$ in EtOH and the product is hydrolysed, acidified, and decarboxylated to δ-*phenyl-γ-methylvaleric acid* (*anilide*, m.p. 74—76°). H. W.



(I.)

Natural coumarins. XXXIX. Constitution of umbelliprenin. E. Späth and F. Vierhapper (Ber., 1938, **71**, [*B*], 1667—1672).—*Angelica* seeds are extracted with Et_2O, the solution is evaporated, and the residue is treated with light petroleum of low b.p. The residue obtained from this solvent is subjected to a double lactone separation, whereby lactone closure is effected in each case with AcOH. The lactone fraction (about 0·25% of the drug) contains imperatorin with small amounts of *allo*imperatorin formed during the distillation, bergapten, and *umbelliprenin* (I) (= coumarin with the side-chain $Me{\cdot}[CMe{:}CH{\cdot}CH_2{\cdot}CH_2]_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}O{\cdot}$ at 6) m.p. 61—63°. It is converted by cold AcOH–H_2SO_4 into umbelliferone (identified also as its Me ether) and an intensely odoriferous, non-phenolic material (II) which is shown by micro-hydrogenation to be heterogeneous. (I) absorbs 4 H_2, showing the presence of three double linkings in the side-chain and one in the coumarin ring. Farnesol is conveniently identified as *di*-2-*naphthylfarnesylurethane*, m.p. 70—71°, which could not be obtained from (II). $CMe_2{:}CH{\cdot}CH_2Br$ and Na umbelliferone afford *umbelliferone γ-methyl*-Δ^β^-*butenyl ether*, m.p. 70—71°, in small yield. Attempts to obtain the farnesyl ether similarly did not give a cryst. product. H. W.

Structure of β- and γ-tocopherols. O. H. Emerson (J. Amer. Chem. Soc., 1938, **60**, 1741—1742).—Californian wheat-germ oil contains twice as much α- as β-tocopherol (I). CrO_3-oxidation of (I) and γ-tocopherol (II) gives Fernholz's acid (benzylthiuronium salt, m.p. 116—117°) (A., 1938, II, 186). At 360° in CO_2 (II) gives 2 : 3 : 5 : 1 : 2-$C_6HMe_3(OH)_2$. The tocopherols are thus closely related. R. S. C.

5-Chloro-2-hydroxy-3 : 6-dimethylthionaphthen.—See B., 1938, 1021.

Synthesis of the ephedrine of the pyrrolidine series. Q. Mingoia (Congr. int. Quim. pura apl., 1934, **9**, V, 174—180; Chem. Zentr., 1936, ii, 3908).—Mg pyrryl bromide and EtCOCl in H_2 yield 2-*propionylpyrrole* (I), m.p. 52°, and, after refluxing the reaction product, 3-*propionylpyrrole*, m.p. 110—111.° Bromination of (I) affords 2-(α-*bromopropionyl*)*pyrrole* (II), m.p. 131—133°; 2-(α-*chloropropionyl*)*pyrrole* (III), m.p. 90—92°, is obtained directly from CHClMe·COCl. With NH_2Me (II) or (III) gives 2-(α-*methylaminopropionyl*)*pyrrole*, m.p. 155—156° (*picrate*, m.p. 180—181°; *hydrochloride*), which when saturated with H_2 in AcOH in presence of PtO_2 yields the *ephedrine* of the pyrrolidine series (*picrate*, m.p. 145—147°; hydrochloride). A. H. C.

Synthesis of indole. K. Polyakova (Maslob. Shir. Delo, 1935, **11**, 452).—*o*-$C_6H_4Me{\cdot}NO_2$ and $Et_2C_2O_4$ give *o*-nitrophenylpyruvic acid, which is reduced to indole-2-carboxylic acid. The last decomposes to indole and CO_2. Ch. Abs. (*c*)

Alkylene derivatives of cyclic bases. I. Derivatives of 2-aminopyridine. T. M. Sharp (J.C.S., 1938, 1191—1193).—2-Aminopyridine, $NaNH_2$, and PhMe with the appropriate alkylene dibromide give the following compounds: αβ-*bis*-2-*pyridylaminoethane*, m.p. 134—135° (*dihydrochloride*, m.p. 239—241°), αε-*bis*-2-*pyridylamino*-n-*pentane*, m.p. 150° (*dihydrochloride*, m.p. 164°), αζ-*bis*-2-*pyridylamino*-n-*hexane*, m.p. 152—154° (*dihydrochloride*, m.p. 216—218°), αη-*bis*-2-*pyridylamino*-n-*heptane*, m.p. 104—105° (*dihydrochloride*, m.p. 203—205°), αθ-*bis*-2-*pyridylamino*-n-*octane*, m.p. 110—112° (*dihydrochloride*, m.p. 197—198°), αι-*bis*-2-*pyridylamino*-n-*nonane*, m.p. 140—141° (*dihydrochloride*, m.p. 136—139°), and ακ-*bis*-2-*pyridylamino*-n-*decane*, m.p. 122—124° (*dihydrochloride*, m.p. 149—152°). These compounds have a low toxicity, but are inactive in mouse trypanosomiasis. The expected compounds have not been obtained from CH_2I_2, $Br{\cdot}[CH_2]_3{\cdot}Br$, and $Br{\cdot}[CH_2]_4{\cdot}Br$. F. R. S.

Synthesis of xanthurenic acid and chromatographic experiments. L. Musajo (Ric. sci. Progr. tecn., 1936, [ii], **7**, II, 95—96; Chem. Zentr., 1936, ii, 3540; cf. A., 1935, 1007, 1268).—Fusion of 4-hydroxy-2-carboxy-, -2-carbethoxy-, or, better, -2-methyl-quinoline with KOH yields an acid identical with xanthurenic acid (probably 3 : 4-dihydroxyquinoline-2-

carboxylic acid). Chromatographic analysis on Al_2O_3 of a PhMe extract of urine of rats or rabbits fed on fibrin yields indirubin and a little indigo. A. H. C.

Quinoline derivatives of 2-amino-*p*-cymene. J. N. Le Conte (J. Elisha Mitchell Sci. Soc., 1935, **51**, 249—250).—8-*Methyl*-5-iso*propylquinoline*, b.p. 230—232°/190 mm., prepared from amino- (I) and nitro-cymene (Cohn and Gustavson's method), is reduced (Na–EtOH) to 8-*methyl*-5-iso*propyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b.p. 165—167°/27 mm. (I) gave with paraldehyde 2 : 8-*dimethyl*-5-iso*propylquinoline*, m.p. 78°, b.p. 179°/35 mm., 170°/25 mm., reduced to 2 : 8-*dimethyl*-5-iso*propyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 65°, with CH_2Ac_2, 2 : 4 : 8-*trimethyl*-5-iso*propylquinoline*, b.p. 177—178°/22 mm., and with $CH_2Ac{\cdot}CO_2Et$, 2-*hydroxy*-4 : 8-*dimethyl*-5-iso*propylquinoline*, m.p. 228—230° (in the last two cases after dehydrating the intermediate cymidides with H_2SO_4). 8-Substituted quinolines do not form methiodides; a *cymylisatin*, m.p. 174°, and 2-*chloro*-4 : 8-*dimethyl*-5-iso*propylquinoline*, m.p. 197°, are described. Ch. Abs. (*c*)

Catalytic condensation of acetylene with arylamines. XVII. Simultaneous condensation of arylamines with benzaldehyde and acetylene in presence of $HgCl_2$. XVIII. Condensation of acetylene with α- and β-naphthylamine in presence of $HgCl_2$. XIX. Condensation of acetylene with *o*-, *m*-, and *p*-toluidine in presence of CuBr. N. Kozlov (J. Gen. Chem. Russ., 1938, **8**, 413—418, 419—423, 475—476).—XVII. CHPh:NPh in EtOH, paraldehyde, and conc. HCl (5 hr. at 100°) yield 2-phenylquinoline, also obtained by saturating a mixture of PhCHO, NH_2Ph, and $HgCl_2$ with C_2H_2, at room temp.

XVIII. α- or β-$C_{10}H_7{\cdot}NH_2$ in EtOH and C_2H_2 in presence of $HgCl_2$ yield 2-methyl-7 : 8- or -5 : 6-benzquinoline; in $COMe_2$ the product is 2 : 4-dimethyl-7 : 8- or -5 : 6-benzquinoline.

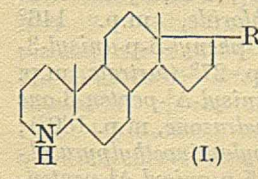
XIX. Condensation of toluidines with C_2H_2 is catalysed by CuBr as well as by CuCl. R. T.

Octahydropyridocoline–norlupinane relationship. II. G. R. Clemo, J. G. Cook, and R. Raper (J.C.S., 1938, 1183—1185).—Et hexahydroanthranilate and $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ give *Et* β-o-*carbethoxyhexahydroanilinopropionate*, b.p. 135—140°/1 mm., cyclised (K) to 4-*ketodecahydroquinoline*, b.p. 135—140°/15 mm. [*picrate*, m.p. 175°; *picrolonate*, m.p. 201° (decomp.); *Bz* derivative, m.p. 145°]. Reduction of the ketone by either the Wolff or the Clemmensen method affords *trans*-decahydroquinoline [*picrolonate*, m.p. 202° (decomp.)]; the Clemmensen method also gives an isomeric base (*picrate*, m.p. 169°). The *cis*-form of decahydroquinoline is converted by boiling HCl into the *trans*-form. Hence this cannot be used to test the hypothesis put forward (cf. A., 1936, 1526). *Et* 4-*methylpiperidine*-2-*carboxylate*, b.p. 70°/1 mm. (*picrate*, m.p. 142°), prepared from the acid, and γ-bromobutyronitrile give γ-2-*carbethoxy*-4-*methylpiperidinobutyronitrile*, b.p. 135°/1 mm., which is hydrolysed to *Et* γ-2-*carbethoxy*-4-*methylpiperidinobutyrate*, b.p. 136—138°/1 mm., cyclised to 1-*keto*-8-*methyloctahydropyridocoline*, b.p. 115—120°/15 mm. [*picrate*, m.p. 178° (decomp.)]. Reduction of the ketone by the Wolff method yields 8-*methyloctahydropyridocoline A*, b.p. 47—48°/1 mm. (*picrate*, m.p. 150°; *picrolonate*, m.p. 197°, and a small quantity of a second form; *methiodide*, m.p. 212°). Clemmensen reduction gives a *base B*, b.p. 47—48°/1 mm. (*picrate*, m.p. 189°, and a second form, m.p. 152°; *picrolonate*, m.p. 138°; *methiodide*, m.p. 181°). The bases are not interconvertible. F. R. S.

The 4-aminoacridine-1-carboxylic acid of Matsumura. K. Lehmstedt (Ber., 1938, **71**, [*B*], 1609—1610).—The nitroacridonecarboxylic acid obtained by Matsumura (A., 1938, II, 246) from 5-nitrodiphenylamine-2 : 2′-dicarboxylic acid is 3-nitroacridone-5-carboxylic acid since when decarboxylated and then treated with $NPhMe_2$ it gives 3-nitro-9-*p*-dimethylaminophenylacridine. The compounds obtained by Matsumura should therefore be re-numbered (his positions are placed in parentheses): 3(1)-*nitroacridone*-5(4)-*carboxyl chloride*, decomp. 299°; 3(1)-*aminoacridone*-5(4)-*carboxylic acid*, m.p. 289—290°; 3(1)-*aminoacridine*-5(4)-*carboxylic acid*, decomp. 273—274° (*hydrochloride*, decomp. 245—250°). H. W.

Complex salts of α-methyl-*o*-phenanthroline. P. Pfeiffer and W. Christeleit (J. pr. Chem., 1938, [ii], **151**, 127—133).—The introduction of 2-Me into the phenanthroline mol. has no marked influence on the ability of the two N to unite with metallic atoms. The colours of the salts may differ considerably from those of the simpler base. α-Methylphenanthroline gives a *perchlorate*, m.p. 205—208° (decomp.), a *picrate*, and a *platinichloride* ($+4H_2O$), which slowly becomes discoloured at 180°. The following complex *salts* are described: $[Fe(C_{13}H_{10}N_2)_3](ClO_4)_2$, which does not appear to exist in isomeric forms; $[Fe(C_{13}H_{10}N_2)_3]SO_4,12H_2O$; $[Ni(C_{13}H_{10}N_2)_3](ClO_4)_2$; $[Cu(C_{13}H_{10}N_2)Cl_2]$; $[Cu(C_{13}H_{10}N_2)_2](ClO_4)_2,2H_2O$; $[Ag(C_{13}H_{10}N_2)_2]NO_3$. H. W.

Sterol derivatives containing nitrogen in the nucleus. C. C. Bolt (Rec. trav. chim., 1938, **57**, 905—910).—Cholestenone with O_3 in AcOH, followed by H_2O, yields a CO-acid the oxime of which is reduced (Na–EtOH) to the corresponding NH_2-acid, isolated (by acidification with AcOH and extraction with Et_2O) as its *lactam*, m.p. 253—255°, $[\alpha]_D^{18}$ +44° in C_5H_5N (*Ac* derivative, m.p. 136—137°). Reduction (Na–$C_5H_{11}{\cdot}OH$) of the lactam yields the *amine* [(I), R = C_8H_{17}], m.p. 116—117°, $[\alpha]_D$ +48° in C_5H_5N (*Ac* derivative, m.p. 132—132·5°). Similarly testosterone acetate yields (with elimination of the Ac group) a *keto-acid*, $C_{18}H_{28}O_4$, m.p. 206·5—207° (*oxime*, m.p. 199—202°), *lactam*, m.p. 262—263°, $[\alpha]_D^{18}$ +33° in C_5H_5N (*Ac*$_2$ derivative, m.p. 164—167°), and *amine* [(I), R = OH], m.p. 202—203°, $[\alpha]_D^{18}$ +0·28° in C_5H_5N (*Ac*$_2$ derivative, m.p. 180·5—181·5°). M.p. are corr. A. Li.



(I.)

Hydantoins derived from the analogues of methyl β′β″-dichloro*iso*propoxyethyl ketone. B. B. Allen [with H. R. Henze] (J. Amer. Chem.

Soc., 1938, **60**, 1796—1797).—*Ph* α-β′β″-*dichloroisopropoxyethyl ketone* [prep. from $(CH_2Cl)_2CH{\cdot}O{\cdot}CHMe{\cdot}CN$ and MgPhBr], b.p. 169°/4 mm., or the corresponding alkyl ketones with KCN (1·25 mol.) and $(NH_4)_2CO_3$ (3 mols.) at 55—62° give 5-*phenyl*-5-α-β′β″-*dichloroisopropoxyethylhydantoin*, m.p. 187—188°, 5-*methyl*-, m.p. 229—230°, and 5-*ethyl*-5-α-β′β″-*dichloroisopropoxyethylhydantoin*, m.p. 198·5—199·5°, 5-α-β′β″-*dichloroisopropoxyethyl*-5-n-*propyl*-, m.p. 211·5—212·5°, -iso*propyl*-, m.p. 146·5—147·5°, -n-*butyl*-, m.p. 206·5—207·5°, -sec.-*butyl*-, m.p. 149·5—151°, -n-*amyl*-, m.p. 181—182°, and -iso-*amyl-hydantoin*, m.p. 187—187·5°. M.p. are corr. R. S. C.

Bromo-ethers derived from hydantoins having terminal ethylenic linkings in the 5 position. (Misses) D. A. Hahn, M. J. McLean, and H. T. Murphy (J. Amer. Chem. Soc., 1938, **60**, 1927—1929).—Both forms of Et 5-benzylidene-3-methylhydantoin-1-acetate (Litzinger, A., 1934, 534) with Br give not only the compound (I), $C_{17}H_{21}O_5N_2Br$, m.p. 113—113·5°, but also an *isomeride* (II), m.p. 92—94°, thereof. (I) and (II) are shown by their absorption spectra to be saturated hydantoins and are forms of *Et 5-ethoxy-5-α-bromobenzyl-3-methylhydantoin-1-acetate*. 5-Benzylidene-1 : 3-dimethylhydantoin gives similarly *forms*, m.p. 141—143° and 119·5—121·5°, respectively, of 5-*ethoxy*-5-α-*bromobenzyl*-1 : 3-*dimethylhydantoin*, which have similar absorption spectra. R. S. C.

Pyrazoline local anæsthetics. I. Derivatives of benzylidene- and anisylidene-acetone. H. B. Nisbet (J.C.S., 1938, 1237—1241).—Benzylideneacetone, $NHMe_2$, HCl, and CH_2O give 1-*dimethylamino*-5-*phenyl*-Δ⁴-*penten*-3-*one hydrochloride*, m.p. 157°, the *phenylhydrazone*, m.p. 169°, of which is isomerised (AcOH) to 1 : 5-*diphenyl*-3-β-*dimethylaminoethylpyrazoline hydrochloride*, m.p. 176°, and the *p*-tolylhydrazone to the 5-*phenyl*-1-p-*tolyl* compound, m.p. 177—178°. The following compounds have been similarly prepared: 1 : 5-*diphenyl*-3-β-*piperidinoethylpyrazoline hydrochloride*, m.p. 197°; p-*tolylhydrazone*, m.p. 199°, of 1-piperidino-5-phenyl-Δ⁴-penten-3-one hydrochloride; 5-*phenyl*-1-p-*tolyl*-, m.p. 212°, and -1-p-*ethoxyphenyl*-3-β-*piperidinoethylpyrazoline hydrochloride*, m.p. 192—193°; 1-*dimethylamino*-5-p-*anisyl*-Δ⁴-*penten*-3-*one hydrochloride*, m.p. 155° (p-*tolylhydrazone*, m.p. 170°; 1-*phenyl*-, m.p. 173°, and 1-p-*tolyl*-5-p-*anisyl*-3-β-*dimethylaminoethylpyrazoline hydrochloride*, m.p. 184°; 1-*diethylamino*-5-p-*anisyl*-Δ⁴-*penten*-3-*one hydrochloride*, m.p. 146° (*phenylhydrazone*, m.p. 171°); 1-*phenyl*-5-p-*anisyl*-3-β-*diethylaminoethylpyrazoline*, m.p. 27° (*tartrate*, m.p. 80°); 1-*di*-n-*propylamino*-5-p-*anisyl*-Δ⁴-*penten*-3-*one hydrochloride*, m.p. 150° (*phenylhydrazone*, m.p. 180°); 1-*phenyl*-5-p-*anisyl*-3-β-*di*-n-*propylaminoethylpyrazoline*, m.p. 63°; 1-*di*-n-*butylamino*-5-p-*anisyl*-Δ⁴-*penten*-3-*one hydrochloride*, m.p. 66—68° (*phenylhydrazone*, m.p. 167—168°); 1-*phenyl*-5-p-*anisyl*-3-β-*di*-n-*butylaminoethylpyrazoline*, m.p. 26—27°; 1-*piperidino*-5-p-*anisyl*-Δ⁴-*penten*-3-*one hydrochloride phenylhydrazone*, m.p. 188°; 1-*phenyl*-5-p-*anisyl*-3-β-*piperidinoethylpyrazoline*, m.p. 88° [*hydrochloride*, m.p. 215°, *acid sulphate*, m.p. 172° (decomp.), and *tartrate*, m.p. 115° (decomp.)]; p-*tolylhydrazone*, m.p. 176—177°, of 1-piperidino-5-*p*-anisyl-Δ⁴-penten-3-one hydrochloride; 1-p-*tolyl*-5-p-*anisyl*-3-β-*piperidinoethylpyrazoline hydrochloride*, m.p. 204°; 1-*dibenzylamino*-5-p-*anisyl*-Δ⁴-*penten*-3-*one hydrochloride*, m.p. 225—230° (decomp.) (*phenylhydrazone*, m.p. 235—240°); and 1-*phenyl*-5-p-*anisyl*-3-p-*dibenzylaminoethylpyrazoline* (?), b.p. 300—301°/1 mm. 1-Piperidino-5-*p*-anisyl-Δ⁴-penten-3-one hydrochloride with $NHPh{\cdot}NH_2$ does not give a hydrazone but a *ketazine* (*succinate*, m.p. 137°); it forms an *oxime*, m.p. 166° (*hydrochloride*, m.p. 208°). Increase in size, up to NPr^{α}_2, of the $NAlk_2$ group increases the local anæsthetic potency and to a smaller degree the toxicity. F. R. S.

Preparation of 2 : 6-dialkoxy-4-methyl-5-ethylpyrimidines. Y. F. Chi and D. Chin (J. Chem. Eng. China, 1938, **5**, 19—20).—4-Methyl-5-ethyluracil is transformed by $POCl_3$–PCl_5 at 120° into 2 : 6-*dichloro*-4-*methyl*-5-*ethylpyrimidine*, b.p. 130—131°/6 mm., m.p. 25—27°. This is converted by the requisite Na alkoxide in the appropriate alcohol at room temp. into 2 : 6-*dimethoxy*-, b.p. 118°/7 mm., and 2 : 6-*diethoxy*-, b.p. 138—139°/17 mm., -4-*methyl*-5-*ethylpyrimidine*. H. W.

Pyrimidines: molecular rearrangement of 2 : 6-dimethoxy-4-methyl-5-*n*-butylpyrimidine. Y. F. Chi, C. Wei, and N. S. Pan (J. Amer. Chem. Soc., 1938, **60**, 1719—1721).—2 : 6-*Dichloro*-4-*methyl*-5-n-*butylpyrimidine* [prep. from 4-methyl-5-*n*-butyluracil (I) by $POCl_3$–PCl_5 at 120°], b.p. 171°/23 mm., with NaOR in ROH gives 2 : 6-*dimethoxy*- (II), b.p. 159°/29 mm., -*diethoxy*-, b.p. 174°/27 mm., -*di*-n-*propoxy*-, b.p. 193—194°/23 mm., -*di*-n-*butoxy*-, b.p. 219°/29 mm., and -*diallyloxy*-4-*methyl*-5-n-*butylpyrimidine*, b.p. 192—193°/31 mm. At 250—270° (II) gives 1 : 3 : 4-*trimethyl*-5-n-*butyluracil* (III), m.p. 54—55°, also obtained from (I) by Me_2SO_4–NaOH. With MeI at 50° or 100° (I) is only partly rearranged, yielding 2-*keto*-6-*methoxy*-3 : 4-*dimethyl*-5-n-*butylpyrimidine* (IV), b.p. 183—184°/1 mm., 235—236° (decomp.)/31 mm., hydrolysed by hot dil. HCl to 3 : 4-*dimethyl*-5-n-*butyluracil*, m.p. 151—152°, and converted at 300—360° into (III). When kept in MeI at room temp. for 2 weeks, (I) gives a little (IV), probably formed by way of (III). R. S. C.

Pyrimidines: synthesis of 4-methyl-5-*n*-propylcytosine. Y. F. Chi and K. H. Chang (J. Amer. Chem. Soc., 1938, **60**, 1721—1723).—6-*Keto*-2-*thiol*-4-*methyl*-5-n-*propylpyrimidine* [prep. from $CHPr^{\alpha}Ac{\cdot}CO_2Et$, $CS(NH_2)_2$, and NaOEt], m.p. 209—209·5°, RHal, and NaOEt in EtOH at 100° give 6-*keto*-2-*methyl*-, m.p. 180—181°, -*ethyl*- (I), m.p. 92—93°, and -n-*propyl*-*thiol*-4-*methyl*-5-n-*propylpyrimidine*, m.p. 89—90°, hydrolysed by HBr or HCl to 4-*methyl*-5-n-*propyluracil*, m.p. 247—248°, which with $CH_2Cl{\cdot}CO_2Et$ gives *Et* 6-*keto*-4-*methyl*-5-n-*propylpyrimidine*-2-*thiolacetate*, m.p. 100—101° (corresponding *acid*, $+xH_2O$, m.p. 105—106°). With $POCl_3$ at 120—130° (I) gives 6-*chloro*-2-*ethylthiol*-4-*methyl*-5-n-*butylpyrimidine*, b.p. 165—166°/11 mm., converted by NH_3–EtOH at 160—170° into the 6-NH_2-compound, m.p. 86—87°, which with conc. HBr yields 4-*methyl*-5-n-*propylcytosine*, m.p. 317—

318° (decomp.) (*hydrobromide*, m.p. 253—254°; *hydrochloride*, m.p. 235°). R. S. C.

Complex salts of the alkali and alkaline-earth metals [with *o*-phenanthroline and dipyridyl].—See A., 1938, I, 529.

Anthraquinonylguanidines. M. Battegay (Congr. int. Quim. pura apl., 1934, **9**, IV, 337—351; Chem. Zentr., 1936, ii, 3299).—1-Amino-4-benzamidoanthraquinone and $CN{\cdot}NH_2$,2HCl in *m*-cresol (cf. A., 1932, 405; 1935, 1254) yield py-C-*amino*-4-*benzamido*-1 : 9-*anthrapyrimidine*, m.p. 295° (orange solution in H_2SO_4), dyeing cotton salmon-red from an orange-red vat. Treatment with BzCl and C_5H_5N in $PhNO_2$ for 1 hr. at 180° yields the C-*aminobenzoyl derivative* and a *compound*, $C_{36}H_{22}O_4N_4$, which dyes cotton yellow. Similarly 1 : 4-diaminoanthraquinone affords py-CC′-*diamino*-1 : 9 : 4 : 10-*anthradipyrimidine* (I), m.p. ⩽300°. (I) gives a yellow-red fluorescent solution in H_2SO_4 and a *nitrate*, $C_{16}H_{10}N_6$,2HNO_3. 1 : 5-Diaminoanthraquinone gives py-C-*amino*-5-*guanido*- (blue-red in H_2SO_4) and -5-*amino*-1 : 9-*anthrapyrimidine*, m.p. ⩽300°, which dye cotton brown after oxidation. A. H. C.

Indigotin. I. Nitration of indigotin. II. Ozonisation of indigotin. III. Reaction between indigotin, aromatic iodides, and potassium carbonate. J. van Alphen (Rec. trav. chim., 1938, **57**, 837—846, 911—914, 915—920).—I. Indigotin (I) is decomposed by HNO_3 alone, or in conc. H_2SO_4, 7% oleum, or glacial AcOH, but with HNO_3 in Ac_2O at −10° gives, according to the amount of HNO_3, 5′-*mono*-, 5 : 5′-*di*-, and 5 : 7 : 5′-*tri-nitro*-2-*acetoxydiindoxylyl*, converted by heating at 200—250° or by boiling with $PhNO_2$ into the *mono*-, di-, and *tri-nitroindigotins*, none of which melts below 300°. HNO_3 in $(Pr^nCO)_2O$ gives 5 : 5′-*dinitro*-2-n-*butyroxydi-indoxylyl*, which loses $PrCO_2H$ at 250°, whilst HNO_3 in AcCl gives 5-chloroisatin. 2 : 2′-Diacetoxy-2 : 2′-diindoxylyl with HNO_3 in Ac_2O at −10° yields 5 : 7 : 5′-*trinitro*-2 : 2′-*diacetoxydi-indoxylyl*, which when boiled with $PhNO_2$ gives the trinitroindigotin.

II. With 1 mol. of O_3 in dry $CHCl_3$, (I) yields an *ozonide* (decomp. 100—140°) which with H_2O gives isatin; excess of O_3 gives a less stable product which gives no isatin. O_3 in dry EtOAc, followed by H_2O, gives isatin, but in wet EtOAc yields isatinic anhydride.

III. When boiled with PhI, K_2CO_3, and Cu-bronze in $PhNO_2$, (I) gives (in poor yields) *o*-$NHPh{\cdot}C_6H_4{\cdot}CO_2H$ and *bis*-(1-*phenylindoxylyl*)*hydroxyacetic acid* (partly decomposed at 320°), which when heated gives acridine, CO_2, and H_2O, and is oxidised (CrO_3) to *bis*-1-*phenylindoxylyl ketone* (does not melt at <320°). The p-*tolyl*-, p-*anisyl*-, and p-*diphenylyl*-hydroxy-acids have similar properties. The mechanism of the reaction is discussed. A. Li.

Peganine. XIV. Pyracridone (= α-quinoquinolone). E. Späth and F. Kuffner (Ber., 1938, **71**, [*B*], 1657—1661).—Pyracridone (I) (Reissert, A., 1895, i, 244; Räth, A., 1931, 852) and α-quinoquinolone (Seide, A., 1925, i, 159) are shown to be identical with one another and to be hydrogenated (Pd-sponge in AcOH) to the H_4-base (II) obtained by Späth and Platzer (A., 1936, 215). They are therefore *o*-$C_6H_4{<}^{CO{\cdot}N{\cdot}CH:CH}_{N=C{\cdot}CH:CH}$. Further catalytic dehydrogenation of (II) gives (I), which is also obtained from 2-hydroxypyridine and isatoic anhydride. In the production of (I) from 2-chloropyridine and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ the initial step is the formation of *o*-2-pyridylaminobenzoic acid, which reacts in its tautomeric form *o*-$CO_2H{\cdot}C_6H_4{\cdot}N{:}C{<}^{NH{\cdot}CH}_{CH=CH}{>}CH$ to (I). H. W.

Carnosine nitrate, m.p. 227° (decomp.); anserine nitrate, m.p. 226° (decomp.).—See A., 1938, III, 739.

Chromic acid oxidation of uric acid. A. Lévêque and J. Moulin (Bull. Sci. Pharmacol., 1936, **43**, 213—220; Chem. Zentr., 1936, ii, 3146).—A mixture of 1 vol. of 1% $K_2Cr_2O_7$–H_2SO_4 and 5 vols. of saturated aq. K_2SO_4 is, unlike ordinary aq. $K_2Cr_2O_7$, stable at the b.p.; it oxidises uric acid to CO_2 and $CO(NH_2)_2$, the latter suffering further hydrolysis (84% after 24 hr., 100% in presence of Ag_2SO_4). Titration of excess of $K_2Cr_2O_7$ shows that 1 mol. of uric acid ≡ 6I and the method is therefore preferable to direct oxidation with I (1 mol. ≡ 2I). A. H. C.

Phthalocyanines and associated compounds. XIV. Metallic derivatives. P. A. Barrett, D. A. Frye, and R. P. Linstead (J.C.S., 1938, 1157—1163).—Excess of Li amyloxide and *o*-$C_6H_4(CN)_2$ give *Li*$_2$ *phthalocyanine*, whilst excess of the nitrile affords *Li H phthalocyanine*; the Li_2 compound is sol. in cold EtOH and may be used for the prep. of other phthalocyanines by double decomp. The following are described: (Pc = $C_{32}H_{16}N_8$), *Ag* (PcAg or ? PcHAg), *Hg*, *Sb*$_2$, *chloroantimony* (PcSbCl), and *chloroferric* (PcFeCl) *phthalocyanines*, and *Pd chlorophthalocyanine* ($C_{32}H_{15}N_8ClPd$). Fe^{II} phthalocyanine forms *hexaaniline*, *hexa-o-toluidine*, and *dipyridine additive compounds*. F. R. S.

Quinoline derivatives. V. T. N. Ghosh (J. Indian Chem. Soc., 1938, **15**, 240—242; cf. A., 1938, II, 296).—$CHAc_2{\cdot}CS{\cdot}NH{\cdot}CO_2H$ and $NHPh{\cdot}NH_2$ in EtOH give H_2S and 3 : β*δ*-*triketo*-2-*phenyl*-5-*γ*-n-*amyl*-Δ^4-1 : 2 : 4-*triazoline*, m.p. 105—106° (and an oil, possibly a further condensation product with $NHPh{\cdot}NH_2$), which with NH_2Ph at 160—170° gives β-*anilo*-3 : *δ*-*diketo*-2-*phenyl*-5-*γ*-n-*amyl*-Δ^4-1 : 2 : 4-*triazoline*, m.p. 205—207°, converted by H_2SO_4 at 110° into 3-*keto*-2-*phenyl*-5-2′ : 4′-*dimethylquinolyl*-3′-Δ^4-1 : 2 : 4-*triazoline*, m.p. 295°. 3 : β*δ*-Triketo-5-*γ*-*n*-amyl-Δ^4-1 : 2 : 4-triazoline with N_2H_4 in boiling EtOH gives the *azine*, m.p. 160°, and with NH_2Ph at 150—180° gives β-*anilo*-3 : *δ*-*diketo*-5-*γ*-n-*amyl*-Δ^4-1 : 2 : 4-*triazoline*, m.p. 226—227°, from which no quinoline derivative could, however, be obtained. R. S. C.

Action of nitric acid on derivatives of coumarono(2′ : 3′ : 3 : 2)indole. S. R. Cawley and S. G. P. Plant (J.S.C., 1938, 1214—1218).—The p-*nitrophenylhydrazone*, m.p. 186°, of tetrahydro-*γ*-pyrone does not undergo the Fischer reaction. Coumaranone and $NHPh{\cdot}NH_2$ give *coumarono*-(2′ : 3′ : 3 : 2)*indole*, m.p. 197°, which forms 1-*Ac*,

m.p. 156°, 1-*Bz*, m.p. 177°, and 1-*cinnamoyl* derivatives, m.p. 108—112°, and *Et coumarono*(2′ : 3′ : 3 : 2)-*indole*-1-*carboxylate*, m.p. 95°. Nitration of these derivatives in AcOH yields respectively 3(or 2)-*nitro*-2(or 3)-*acetoxy*-1-*acetyl*-, m.p. 142°, -1-*benzoyl*-, m.p. 185°, and -1-*cinnamoyl*-2 : 3-*dihydrocoumarono*-(2′ : 3′ : 3 : 2)*indole*, m.p. 157—159° [with *mononitro*-1-*cinnamoylcoumarono*(2′ : 3′ : 3 : 2)*indole*, m.p. 243—247°], and *Et* 3(or 2)-*nitro*-2(or 3)-*acetoxy*-2 : 3-*dihydrocoumarono*(2′ : 3′ : 3 : 2)*indole*-1-*carboxylate*, m.p. 120°. These NO_2-compounds do not give cryst. products with alkalis. *Coumaranone*-p-*nitrophenylhydrazone*, m.p. 192—194°, is converted (HCl) into 5-*nitrocoumarono*(2′ : 3′ : 3 : 2)*indole*, m.p. 270—275° (1-*cinnamoyl* derivative, m.p. 220°). *Coumaranone*-o-, m.p. 179—181°, and -m-*nitrophenylhydrazones*, m.p. 168—169°, do not form indoles. 3-*Acetylcoumarono*-(2′ : 3′ : 1 : 2)-β-*naphthindole*, m.p. 169°, gives (HNO_3–AcOH) a NO_2-derivative, m.p. 234—236°, and the corresponding 3-*Bz* compound, m.p. 201°, similarly yields a NO_2-derivative, m.p. 241—242°. F. R. S.

Cyanine dyes.—See B., 1938, 1104.

The new ergot alkaloids. A. Stoll and E. Burckhardt (Schweiz. med. Woch., 1936, **66**, 353—354; Chem. Zentr., 1936, ii, 3106; cf. A., 1935, 1256).—Following Kharasch *et al.* (A., 1936, 489), comparison of the m.p. and [α] of ergometrine, ergobasine, ergotocine, and their hydrochlorides shows them to be identical, small deviations (A., 1935, 1512) being due to resin-solvent impurities. A. H. C.

Synthetic anti-malarials [*N*-substituted 8-amino-6-methoxyquinolines, and some derivatives of quinine]. R. F. A. Altman (Rec. trav. chim., 1938, **57**, 941—963; cf. A., 1935, 1017, and Magidson *et al.*, A., 1934, 82, 417, 1230).—αω-Heptane-, -octane-, and -nonane-diols with conc. HCl at 95° in presence of petroleum (b.p. 90—120°) yield ω-chloro-heptan-, b.p. 120°/13·5 mm. (phenylcarbamate, m.p. 76—77°), -octan-, b.p. 139°/18·5 mm. (phenylcarbamate, m.p. 77°; m-*nitrophenylcarbamate*, m.p. 62°), and -nonan-α-ol, b.p. 146·5°/14 mm. (phenylcarbamate, m.p. 67°; *m*-nitrophenylcarbamate, m.p. 57°), which when heated in sealed tubes at 120—160° with $NHEt_2$ yield respectively ω-diethylamino-heptan-, b.p. 132°/9·5 mm., -octan-, b.p. 151°/12 mm. (*p*-nitrobenzoate, m.p. 74°), and -nonan-α-ol, b.p. 161·5°/12 mm. (*p*-nitrophenylcarbonate, m.p. 76—76·5°). These with $SOCl_2$ in C_6H_6 give the α-chloro-ω-diethylamino-compounds, b.p. 126°/15 mm., 130·5°/11 mm., and 145°/10 mm. respectively, which when heated in sealed tubes at 130—170° with a slight excess of 8-amino-6-methoxyquinoline afford 8-(ω-diethylamino-heptylamino)- (*dihydrochloride*, m.p. 115°), -octylamino)-, b.p. 206°/0·5 mm. (*dihydrochloride*, m.p. 112—113°; *dihydrobromide*, m.p. 84°), and -nonylamino)-6-methoxyquinoline, b.p. 218°/0·5 mm. (*dihydrochloride*, m.p. 105—106°; oxalate, m.p. 86°). These three compounds are very active against malaria in birds. They attack the gametes.

Treatment of quinine hydrochloride with $SOCl_2$ in $CHCl_3$ at 20° yields (unstable) quinine chloride monohydrochloride, decomp. 100°, and at 100° the *dihydrochloride*, m.p. 183° (decomp.), which when heated at 150° with $NHMe_2$ gives dimethylamino- [*picrolonate*, m.p. 170° (decomp.)], and with $NHEt_2$, diethylaminoquinine [*picrolonate*, m.p. 155° (decomp.)]. Quitenine with $SOCl_2$ at 100° gives the acid chloride of quitenine chloride monohydrochloride, m.p. 195—200° (decomp.), which yields with H_2O, *quitenine chloride dihydrochloride*, m.p. ~205° (decomp.), with MeOH the *Me*, m.p. 185—186° (decomp.), and with EtOH the *Et* ester *dihydrochloride*, m.p. ~206° (decomp.). These quinine derivatives are inactive against malaria. A. Li.

Alkaloids of Chinese gelsemium, Kou Wen. Y. F. Chi, Y. S. Kao, and Y. T. Huang (J. Amer. Chem. Soc., 1938, **60**, 1723—1724).—Mixed roots, stems, and leaves of Kou Wen contain koumine (formula, $C_{20}H_{22}ON_2$, confirmed), m.p. 168° [unaffected by Ac_2O; *hydrochloride*, m.p. 258°; *hydrobromide*, m.p. 268—269°; *sulphate*, m.p. 261—262°; *nitrate*, m.p. 249—250°; *platinichloride*, m.p. >310°; *methiodide*, anhyd. and $+H_2O$, m.p. 230° (decomp.)], gelsemine (I), (anhyd.) amorphous and ($+COMe_2$), m.p. 176—178° (hydrochloride, m.p. 303°; *nitrate*, m.p. 288°; *methiodide*, m.p. 284°), and koumidine, $C_{19}H_{25}O_4N_2$, new m.p. 299°. Chou's kouminine (A., 1932, 101; 1936, 618) was a mixture of (I) and other bases. R. S. C.

Veratrine alkaloids. III. Degradation of cevine. Question of coniine. W. A. Jacobs and L. C. Craig (J. Biol. Chem., 1938, **124**, 659—666; cf. A., 1937, II, 355, 473).—Distillation of cevine (I) with NaOH–CaO yields β-pipecoline, much product of higher b.p. which could not be investigated, and a fraction, b.p. 160°, now identified as 5-methyl-2-ethylpiperidine (II); the formation of coniine (III) could not be detected. Hydrogenation of 5-methyl-2-ethylpyridine (IV) gives a mixture of stereoisomeric piperidines the 3 : 5-dinitrobenzoyl derivative of which does not depress the m.p. of that of (II). Further (II) is dehydrogenated by Zn dust to (IV), identified as the picrate. Hence (III) is not a product of the distillation of (I) with NaOH–CaO or Zn dust and need not be further considered in the problem of the structure of the alkaloid. The dicyclic base $C_{10}H_{19}N$ obtained from the *tert.* base fraction of the NaOH–CaO distillation yields a picrate which does not depress the m.p. of that of 2-ethyloctahydropyrrocoline (Clemo and Metcalfe, A., 1937, II, 467) but the methiodide obtained from the base recovered from the picrate does not melt sharply so that the base appears to be a mixture of stereoisomerides. In the higher-boiling fractions a portion, b.p. 207°/760 mm., gave a picrate, analysis of which indicated the base to be $C_{11}H_{21}N$; its homogeneity is doubtful. Since the *tert.* base containing O (*loc. cit.*) reacts with MgMeI it appears to contain OH. From the fraction, b.p. 230—240°/760 mm., *crystals*, (?) $C_{11}H_{19}ON$, m.p. 153—156° after softening, separated. The slight basic fractions obtained by the distillation of (I) with Zn dust contain β-picoline but chiefly (IV), which gives *iso*cinchomeronic acid when oxidised. A small intermediate fraction appears to be 2 : 5-dimethylpyridine. H. W.

***Sophora* alkaloids. II. Alkaloids of the seeds of *S. tetraptera*.** L. H. Briggs and W. S. Taylor (J.C.S., 1938, 1206—1207).—The seeds are shown to

contain mostly matrine, a little methylcytisine, and a base [aurichloride, m.p. 186° (decomp.)]. F. R. S.

***Strychnos* alkaloids. C. Transformations of chlorostrychnine and its dihydro-compound.** H. LEUCHS and K. STEINBORN (Ber., 1938, **71**, [*B*], 1577—1585).—Strychnine dissolved in 12N-HCl at 0° is rapidly converted by Cl_2 in CCl_4 into chlorostrychnine (I), $C_{21}H_{21}O_2N_2Cl$, m.p. 235° (vac.) after softening (*perchlorate*), catalytically reduced (PtO_2 in 50% AcOH) to chlorodihydrostrychnine and some *trichlorostrychnine* (+0·5EtOH), m.p. 139—141° (decomp.) or m.p. (after resolidification, vac.) 206—208°, $[\alpha]_D^{20}$ —477°/*d* in $CHCl_3$ (*hydrochloride*; *hydrobromide*), hydrogenated (PtO_2 in 50% AcOH) to dihydrostrychnine. PhCHO, (I), and NaOEt in boiling EtOH afford *chlorobenzylidenestrychnine*, m.p. 252° (vac.) after softening, $[\alpha]_D^{20}$ —589°/*d* in $CHCl_3$, hydrogenated to *chlorobenzyldihydrostrychnine* (II), m.p. 216°, $[\alpha]_D^{20}$ —64·4°/*d* in $CHCl_3$; this is also obtained by chlorination of benzyldihydrostrychnine and is converted by NaOEt into two or more *iso*-bases which form isomorphous mixtures from which a *compound*, $C_{28}H_{28}O_2N_3Cl$, m.p. 246°, $[\alpha]_D^{20}$ —256°/*d* in $CHCl_3$, has been separated. (I) is oxidised by air in presence of Fehling's solution to *chloro-9-hydroxystrychnine* (*ψ-chlorostrychnine*) (+$3H_2O$), m.p. 130° (decomp.), or (anhyd.), m.p. 240°, $[\alpha]_D^{19}$ —132°/*d* in $CHCl_3$ free from EtOH, obtained also by the chlorination of *ψ*-strychnine, reduced by Zn dust and 2·5N-HCl to (I) and transformed by MeOH into *chloro-9-methoxystrychnine*, m.p. (indef.) 168—169° (vac.), $[\alpha]_D^{19}$ —117°/*d* in $CHCl_3$. Oxidation of (I) by $KMnO_4$ in $COMe_2$ at 0—2° gives *chlorostrychninonic acid*, m.p. 270° (indef.; decomp.), and *chlorodihydrostrychninonic acid*, m.p. 305° (decomp.). Chlorination of dihydrostrychnine yields *chlorodihydrostrychnine* (III), m.p. (air-dried or dried at 100°) 190° (decomp.) or, after long keeping, m.p. 208—210° after softening at 190°; this with PhCHO in KOH–EtOH gives *chlorobenzylidenedihydrostrychnine*, m.p. 275° (vac.), $[\alpha]_D^{20}$ —225°/*d* in $CHCl_3$, hydrogenated (PtO_2 in 50% AcOH) to (II). Restricted treatment of (III) with NaOMe in boiling MeOH leads to iso*chlorodihydrostrychnine* I, usually, m.p. 198°, occasionally m.p. 222° after softening at 198°, $[\alpha]_D^{19}$ —40·7°/*d* in $CHCl_3$ (*hydrochloride*; *hydrobromide*), hydrogenated (PtO_2 in 50% AcOH) to *iso*dihydrostrychnine; with PhCHO and NaOEt in boiling EtOH it yields iso*chlorobenzylidenedihydrostrychnine*, m.p. 217°, $[\alpha]_D^{19}$ —716°/*d* in $CHCl_3$ (*hydrochloride*), also obtained similarly from the non-isomerised chlorodihydro-base. More drastic treatment of (III) with NaOEt–EtOH affords iso*chlorodihydrostrychnine* II, m.p. about 250° (decomp.) or, after desiccation at 125°/15 mm., m.p. 325° (block) after softening at 270° and darkening at 320°, $[\alpha]_D^{22}$ —101°/*d* in abs. EtOH (*hydrochloride*; *hydrobromide*), which could not be catalytically hydrogenated. *iso*Bromodihydrostrychnine II is reduced (H_2–PtO_2–H_2O) to a substance, m.p. about 305°, $[\alpha]_D^{20}$ —265°/*d* in $CHCl_3$, which gives an amorphous *methiodide*; the *perchlorate*, *hydrochloride*, and *sulphate* are amorphous or freely sol. H. W.

Biuret reaction. VI. Protein–alkali–heavy metal compounds. H. JESSERER and F. LIEBEN (Biochem. Z., 1938, **297**, 369—378; cf. A., 1937, II, 478).—Zn, Hg^{II}, Mn, Bi, Cd, U, Ti, Cr, Pb, Al, and Sn do not combine with caseinogen (I) in aq. NaOH but Au and Co yield compounds containing respectively Au 10·3, Na 2·0, and N 11·17% and Co 3·21, Na 4·7, and N 11·3%. The at. ratio Cu : Au in the Cu and Au compounds of (I) is 3 : 1 and the Au compound takes up 67% of the Cu taken up by an equiv. amount of (I). Nascent H removes Au and Cu from combination with (I) without affecting the power of the protein to recombine with metals. W. McC.

Preparation and properties of thyroxyl derivatives of proteins. R. F. CLUTTON, C. R. HARINGTON, and M. E. YUILL (Biochem. J., 1938, **32**, 1119—1132).—See A., 1938, III, 854. The following are described: N-*carbobenzyloxy*-3 : 5-*di-iodothyronine Me ester*, m.p. 164·5°; N-*carbobenzyloxythyronyl-hydrazide*, m.p. 141°, *azide*, amorphous, and *-globulin*, and N-*carbobenzyloxythryroxyl-albumin* and *-globulin*.

A hæmoglobin from bile pigment. R. LEMBERG, J. W. LEGGE, and W. H. LOCKWOOD (Nature, 1938, **142**, 148—149).—Special treatment of a hæmoglobin–ascorbic acid solution yields a new "hybrid" hæmoglobin, now named *choleglobin* (I), which combines reversibly with O_2 or CO. The prosthetic group of (I) is an Fe–bile pigment compound closely related to verdohæmatin. L. S. T.

Hæmocuprein, a copper–protein compound of red blood-corpuscles. T. MANN and D. KEILIN (Nature, 1938, **142**, 148).—The isolation of bluish crystals of a Cu–protein compound, now named *hæmocuprein* (I) (N 14·35, S 1·12, Cu 0·34%), from the red blood-corpuscles of ox is described. In serum the Cu is also present as a blue Cu–protein compound similar to, if not identical with, (I). L. S. T.

Micro-analytical practice. E. ABRAHAMCZIK and F. BLÜMEL (Mikrochem., 1938, **24**, 268—277).—Various precautionary modifications in apparatus for org. microanalysis are described. A reagent-bottle with pipette sealed into a ground-over stopper, and a ground-over wash-bottle head, are described. E. W. W.

Micro-technique of organic qualitative analysis. F. SCHNEIDER and D. G. FOULKE (Ind. Eng. Chem. [Anal.], 1938, **10**, 445—447).—An extension and elaboration of the capillary and schlieren methods for solubility determination previously described (A., 1938, I, 209). F. N. W.

Determination of carbon and nitrogen in organic compounds by vacuum combustion. Application of this method in soil analysis. N. P. PENTSCHEV (Z. anal. Chem., 1938, **113**, 431—438).—An apparatus is described which enables the sample to be heated in a vac. with CuO, the gases evolved being circulated a few times over a heated CuO spiral, heated Cu gauze, and then P_2O_5 and finally being collected over Hg. The vol. of CO_2 + N_2 having been determined, the gases are further circulated over soda-lime and P_2O_5 and measured again over Hg. The method can be used for the combustion of ordinary org. compounds but is especially applicable to determination of C and N in

soils. The error due to CO_3'' present in the soil is corr. for either by pretreatment with H_3PO_4 or by a separate CO_3'' determination. J. W. S.

Colorimetric determination of ammonia with phenol and hypochlorite.—See A., 1938, I, 534.

Determination of sulphur by means of oxidising alkali melts.—See A., 1938, I, 533.

Constant-temperature bath for Stodola's acetylation micro-apparatus. H. G. Cassidy (Ind. Eng. Chem. [Anal.], 1938, **10**, 456).—The usual glycerol bath is replaced by an enclosed water-bath with reflux, containing a pocket sufficiently large to hold the micro-flask dipping in glycerol. F. N. W.

Determination of alkoxyl by the method of Vieböck and Schwappach. S. Kinsman and C. R. Noller (Ind. Eng. Chem. [Anal.], 1938, **10**, 424).—Difficulty experienced in applying the method (A., 1931, 107) is shown to be due to the fact that the recommended amount of Br is insufficient to oxidise all the IBr to HIO_3. When about twice the amount stated is used, accurate results are obtained. F. N. W.

Micro-determination of deuteroethyl alcohol. K. Hansen and O. Dybing (Biochem. Z., 1938, **298**, 110—114).—The results of a large no. of determinations of $C_2D_5{\cdot}OD$ by Hansen and Lövenskiold's modification (Norsk. Mag. Laegevidensk., 1934, 387) of Widmark's method (A., 1922, ii, 789) show that the empirically determined factor (1·170±0·002) to be used in the calculation is approx. 10% below the theoretical val. When 0·01N aq. $Na_2S_2O_3$ is used for titration 0·01 c.c. is equiv. to 1·17 μg. of $C_2D_5{\cdot}OD$. W. McC.

Determination of oxalic acid. A. Leulier and J. Dorcke (Bull. Soc. Chim. biol., 1938, **20**, 939—946).—$H_2C_2O_4$ can be removed from pure aq. solutions or complex solutions containing other org. acids, $CO(NH_2)_2$, etc. by extraction with Et_2O for 72 hr., and determined as oxalate with a max. error of ~5%, where the concn. is 15—35 mg. per l. A similar technique can be applied to urine provided that the p_H is maintained at 4—5 during the final pptn. in the presence of $COMe_2$ to prevent contamination with urinary pigments. P. G. M.

Determination of formaldehyde in dilute solutions and in the presence of interfering substances. O. Heim (Ind. Eng. Chem. [Anal.], 1938, **10**, 431).—To 10 c.c. of the aq. or aq.-EtOH solution (after 4 or 5 extractions with Et_2O–light petroleum) are added in rapid succession 100 c.c. of 0·1N-$AgNO_3$, 1 c.c. of 37% aq. HCl, and 3 c.c. of 25% aq. NaOH. After shaking for 10 min., the mixture is filtered, the ppt. washed with hot dil. HNO_3 and then with hot H_2O, and the filtrate and combined washings are titrated with 0·1N-NH_4CNS using Fe^{III} alum indicator. F. N. W.

Absorption spectrum of diacetyl.—See A., 1938, I, 492.

Manometric determination of amino-acids with ninhydrin in the Warburg apparatus. C. Schlayer (Biochem. Z., 1938, **297**, 395—397; cf. Van Slyke and Dillon, A., 1938, II, 211; Mason, *ibid.*, 252).—Warburg's apparatus is slightly modified, the NH_2-acid–ninhydrin (with KH_2PO_4 added) being boiled for 3 min. in the reaction vessel which is at 140°. If the vessel is not heated, the process takes several hr., but removal of any proteins present is then unnecessary. W. McC.

Microdetermination of thiocyanoacetic acid. J. V. Dubský and V. Šindelář (Mikrochem., 1938, **24**, 264—267).—The dark violet ppt. from $NCS{\cdot}CH_2{\cdot}CO_2Na$ and aq. $CuCl_2$ is a Cu^I–Cu^{II} *derivative*, $Cu^I{\cdot}S{\cdot}CH_2{\cdot}CO_2{\cdot}Cu^{II}{\cdot}OH,5H_2O$, of $SH{\cdot}CH_2{\cdot}CO_2H$, and in the absence of the latter may be used for the detection or determination of $NCS{\cdot}CH_2{\cdot}CO_2H$. With $CdSO_4$, the *salt* $(\cdot S{\cdot}CH_2{\cdot}CO_2\cdot)Cd$ is obtained. E. W. W.

Diazo-colour reactions. K. E. Jackson and W. M. Dehn (J. Amer. Pharm. Assoc., 1938, **27**, 576—578).—The substance is treated with AcOH and $NaNO_2$ and aq. NH_3 then added. The colours resulting from these two stages of the diazo-reaction, together with that of silk on which the colour is fixed, are tabulated for a series of pharmaceutical substances. F. O. H.

Gravimetric determination of the naphthols with formaldehyde. A. Castiglioni (Z. anal. Chem., 1938, **113**, 428—430).—The $C_{10}H_7{\cdot}OH$ is dissolved in a min. of 95% EtOH and the solution diluted with H_2O. An aliquot portion is treated with CH_2O and HCl, and heated for 3 hr. at 100°. The initially formed white ppt. [probably $CH_2(C_{10}H_6{\cdot}OH)_2$] turns red-brown or rose coloured according as α- or β-$C_{10}H_7{\cdot}OH$ is used. The ppt. is collected, washed, and dried at 100°. The final products are $OH{\cdot}CH(C_{10}H_6{\cdot}OH)_2$ and $CH_2<^{C_{10}H_6}_{C_{10}H_6}>O$ with α- and β-$C_{10}H_7{\cdot}OH$, respectively. The method is not applicable to the analysis of a mixture of α- and β-$C_{10}H_7{\cdot}OH$. J. W. S.

Methenamine [hexamethylenetetramine] as a qualitative reagent. K. E. Jackson and W. M. Dehn (J. Amer. Pharm. Assoc., 1938, **27**, 578—579).—The colour reactions given by $(CH_2)_6N_4$ (0·1 g. in 80 c.c. of conc. H_2SO_4) for various alkaloids, phenols, and other pharmaceutical substances are described. F. O. H.

Colorimetric determination of equilenin and dihydroequilenin. W. Marx and H. Sobotka (J. Biol. Chem., 1938, **124**, 693—698).—The alcoholic hormone solution (1·5 c.c.) is mixed in a 15-c.c. centrifuge tube with 1 c.c. of the reagent [10 mg. of diazotised *p*-nitrobenzeneazodimethoxyaniline (K salt) in 10 c.c. of H_2O] and 0·01N-Na_2CO_3 is added. After 1 hr. at room temp. the mixture is centrifuged and the supernatant liquid with excess of the reagent is poured off. The pptd. dye is dried, dissolved in C_6H_6 + EtOH, and determined colorimetrically in the blue solution. Œstrone, œstriol, and œstradiol do not couple readily under similar conditions. If more alkali is added to hasten the sluggish reaction, uncontrollable side reactions prevent the reproducible development of a suitable tint. The test indicates the complete absence of equilenin or dihydroequilenin from human pregnancy urine. H. W.