BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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AUGUST, 1943

A., II.—ORGANIC CHEMISTRY

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A., II.—Organic Chemistry

AUGUST, 1943.

I.—ALIPHATIC.

Chlorination of methane. Nitration of methane.—See B., 1943, II, 205.

Production of ethylene and ethylene chlorohydrin.—See B., 1943, II, 206.

Photochemical reactions between vinyl chloride and chlorine or bromine, leading to the formation of $\alpha\alpha\beta$-trichloroethane and $\alpha\beta$-dibromochloroethane.—See A., 1943, I, 206.

Synthesis of olefine hydrocarbons by catalytic condensation and dehydration of aliphatic aldehydes. V. I. Komarewsky and T. H. Kritschevsky (*J. Amer. Chem. Soc.*, 1943, **65**, 547—548).—In presence of Cr_2O_3 or, less well, Al_2O_3 at 330—365°/20 atm., $CH_2R{\cdot}CHO$ gives $CH_2R{\cdot}CH(OH){\cdot}CHR{\cdot}CHO$, dehydrated to $CH_2R{\cdot}CH{:}CR{\cdot}CHO$; at 385—410°/20 atm., decomp. to $CH_2R{\cdot}CH{:}CHR + CO$ occurs (cf. A., 1942, II, 127). Complex products are also formed. Presence of H_2 leads to saturated products. Thus, in presence of Cr_2O_3 at 400° (N_2) EtCHO gives $CHMe{:}CHEt$ (40%) and $CHEt{:}CMe{\cdot}CHO$ (18·7%); $Pr^{\alpha}CHO$ at 400° (H_2) gives $CHEt{:}CHPr^{\alpha}$ (**I**) (51%), $CHPr^{\alpha}{:}CEt{\cdot}CHO$ (**II**) (4%), and $CHEtBu^{\alpha}{\cdot}CHO$ (**III**) (4·9%), at 365° (H_2) gives (**I**) (35%), (**II**) (15·5%), and (**III**) (10·4%), at 360° (N_2) gives (**I**) (15%) and (**II**) (45%), and at 330° (N_2) gives (**I**) (6%), (**II**) (40·2%), and (**III**) (8·1%); $Bu^{\alpha}CHO$ at 400° (N_2) gives $CHPr^{\alpha}{:}CHBu^{\alpha}$ (32%); $n\text{-}C_5H_{11}{\cdot}CHO$ at 408° (H_2) gives $CHBu^{\alpha}{:}CH{\cdot}C_5H_{11}\text{-}n$ (39%). In absence of a catalyst, $Pr^{\alpha}CHO$ is unchanged at 402° (H_2). At 400° in presence of Al_2O_3 (N_2), $Pr^{\alpha}CHO$ gives (**I**) (17%) and (**II**) (15%), but in presence of Cr_2O_3–Ni (H_2) gives (**I**) (50%) and $n\text{-}C_7H_{16}$ (50%). EtCHO gives also δ-methyl-*n*-heptene (10%), b.p. 112—115°, and $Pr^{\alpha}CHO$ gives also an *undecene* (5%). R. S. C.

Catalytic polymerisation of acetylene. Preparation of vinylacetylene.—See B., 1943, II, 206.

Addition of hydrogen fluoride to acetylenic compounds. A. L. Henne and E. P. Plueddeman (*J. Amer. Chem. Soc.*, 1943, **65**, 587—589).—Combination of HF with low-boiling acetylenes (≯4 C) is best (75% yield of difluoride) effected by boiling the acetylene (1 mol.) into HF in a Cu flask at 0°. C_5H_8 or C_6H_{10} is best dropped into HF stirred at −50°. Higher acetylenes (1 mol.) are dropped into a solution of HF (5 mols.) in Et_2O or $COMe_2$ (1 mol.) at 0° and the mixture is then kept at room temp.; the oxonium compounds, $Et_2O,2HF$ and $COMe_2,2HF$, are good solvents for the reagents and products but the combined HF is not available for addition; yields are 70—75% for rapid and 85—90% for slow addition; any unsaturated impurity is removed by a further reaction. ββ-Difluoro-butane, f.p. −117·3°, b.p. 30·92°/10 mm., -*n*-pentane, f.p. −93°, b.p. 59·7°/20 mm., -*n*-hexane, f.p. −82·5°, b.p. 87·4°/20 mm., -*n*-heptane, f.p. −62·2°, b.p. 112·7°/20 mm., and -*n*-octane (**I**), f.p. −53·2°, b.p. 137·5°/20 mm., CF_2EtPr^{α}, f.p. −89·3°, b.p. 87·4°/20 mm., and δδ-*difluoro*-n-*octane* (**II**), f.p. −45·9°, b.p. 137·3°/20 mm., are thus prepared. CF_2Et_2, f.p. −94·0°, b.p. 60·2°/20 mm., and *n*-heptylene difluoride, f.p. −82°, b.p. 119·7°/20 mm., are prepared from the corresponding dichlorides. Markovnikov's rule is valid: *e.g.*, $CMe{:}C{\cdot}C_5H_{11}$ gives 87% of (**I**) and 13% of (**II**) as determined by the f.p. curve. Further reactive groups in the acetylene often interfere: $\Delta^{\alpha\theta}$-nonadi-inene gives *ββθθ-tetrafluoro*-n-*nonane*, f.p. −2·3°/20 mm., b.p. 82°/20 mm., and some *βθ-difluoro*-$\Delta^{\alpha\theta}$-*nonadiene*, f.p. 1·19°/4 mm., b.p. 87°/20 mm., but $\Delta^{\alpha\zeta}$-heptadi-inene is completely resinified. Other physical data of the products are recorded. *n* is valuable as a criterion of purity. R. S. C.

Catalytic decomposition of ethyl alcohol in presence of magnesium oxide.—See A., 1943, I, 205.

Condensation of epichlorohydrin with ethylene glycol; new polyfunctional derivatives. M. S. Kharasch and W. Nudenberg (*J. Org. Chem.*, 1943, **8**, 189—193).—Epichlorohydrin (**I**) condenses with $(CH_2{\cdot}OH)_2$ in presence of conc. H_2SO_4 at room temp. and subsequently at 100° to *α-chloro-γ-β′-hydroxyethoxypropan-β-ol* (**II**), b.p. 135—139°/3 mm. (yield 56%). (**II**) is transformed by $OH{\cdot}[CH_2]_2{\cdot}ONa$ (**III**) into *αγ-di-β-hydroxyethoxypropan-β-ol*, b.p. 188—192°/2—3 mm., m.p. 30°, more conveniently obtained from (**I**) and (**III**). KOH–EtOH at 2° transforms (**II**) into *αβ-epoxy-γ-β′-hydroxyethoxypropane* (**IV**), b.p. 92—94°/2 mm., converted by boiling H_2O into *γ-β′-hydroxyethoxypropane-αβ-diol*, b.p. 162—164°/3 mm., also obtained from (**II**) and boiling aq. Na_2CO_3; this is transformed by paracetaldehyde and a little 50% H_2SO_4 into *2-methyl-4-β-hydroxyethoxymethyl*-1 : 3-*dioxolen*, b.p. 113—115°/8 mm. (**IV**) is transformed by conc. aq. NH_3 into *α-amino-γ-β′-hydroxyethoxypropan-β-ol*, b.p. 141—144°/2—4 mm., and by $NHMe_2$ into the α-NMe_2-compound, b.p. 102—105°/1—2 mm. *2-Hydroxymethyl*-1 : 4-*dioxan* (**V**), b.p. 92—93°/8 mm., is obtained by treating (**IV**) with conc. H_2SO_4 at room temp. and then at 100°; the 3 : 5-*dinitrobenzoate* has m.p. 106—108° (decomp.). KOH–EtOH and (**II**) afford *α-ethoxy-γ-β-hydroxyethoxypropan-β-ol*, b.p. 115—122°/2 mm., and (**V**). H. W.

Dipole moments of derivatives of ethylene glycol and glycerides.—See A., 1943, I, 193.

Utilisation of aliphatic nitro-compounds. VIII. Nitrotriols (nitroglycerols) prepared from simple aldehydes. C. A. Sprang [with E. F. Degering] (*J. Amer. Chem. Soc.*, 1943, **65**, 628).—$NO_2{\cdot}CH_2{\cdot}CHEt{\cdot}OH$ (from $MeNO_2$ and EtCHO) (1 mol.), 40% aq. CH_2O (1 mol.), and K_2CO_3 in EtOH at room temp. give *β-nitro-β-hydroxymethyl*-n-*pentane-αγ-diol*, m.p. 141°. *β-Nitro-β-hydroxymethyl*-n-*hexane*-, m.p. 154—156°, -n-*nonane*-, m.p. 145—147°, and -ε-*methyl*-n-*hexane*-1 : 3-*diol*, m.p. 144—146°, are similarly prepared. R. S. C.

Production of *iso*propyl ether.—See B., 1943, II, 207.

Action of polyhalogenated derivatives on organomagnesium compounds. G. Sanna [in part with S. Spano] (*Gazzetta*, 1942, **72**, 305—312).—$CCl_3{\cdot}SCl$ with MgEtBr in Et_2O gives *CCl_3 Et sulphide*, b.p. 85°/10 mm., and $(CCl_3{\cdot}S)_2$ (**I**), and with MgPhBr gives *Ph CCl_3 sulphide*, b.p. 135°/10 mm., (**I**), and Ph_2. $CCl_3{\cdot}SO_2Cl$ with MgEtBr in Et_2O gives *CCl_3 Et sulphone* and $CCl_3{\cdot}SOEt$, and with MgPhBr gives *Ph CCl_3 sulphone*, m.p. 121°, and Ph_2. E. W. W.

Sulphonium compounds. II. Derivatives of nitric and of organic acids. F. E. Ray and G. J. Szasz (*J. Org. Chem.*, 1943, **8**, 121—125).—Me_2S and $MeNO_3$ at room temp. slowly afford *trimethylsulphonium nitrate* (corresponding *mono*- and *di-picrate*, m.p. 199° and 70—75° respectively). MeEtS and $MeNO_3$ give a non-cryst. product transformed into SMe_3 picrate. Evidence of formation of a sulphonium compound from $EtNO_3$ and Me_2S was not obtained. $SEt_3{\cdot}NO_3$ could not be obtained pure from $EtNO_3$ and Et_2S but the product is convertible into SEt_3 picrate, m.p. 115°; the change is accelerated by C_5H_5N. Impure HCO_2SMe_3 is derived from Me_2S and HCO_2Me. Me stearate when heated with Me_2S for 200 hr. at 70° yields some solid and the product affords SMe_3 dipicrate. No visible change occurs between cottonseed oil and Me_2S but the aq. extract gives a picrate, m.p. 90° to a red liquid. H. W.

Sulphonation of β-methylallyl chloride. Mobility of the olefinic linking in unsaturated sulphonic acids. C. M. Suter and F. G. Bordwell (*J. Amer. Chem. Soc.*, 1943, **65**, 507—517).—$CH_2{:}CMe{\cdot}CH_2Cl$ (**I**) (1·73 mols.) and dioxan,SO_3 (2·13 mols.) in $(CH_2Cl)_2$ at 0° give a solution (*A*), which with NH_2Ph gives exothermally 20% of NH_2Ph,H_2SO_4 (**II**) + *NH_2Ph phenylsulphamate* (**III**) (see below) with 80% of mixed monosulphonates; passing NH_3 into (*A*) gives similar mixed NH_4 salts. Purification of the NH_4 (*B*) or NH_2Ph (*C*) salts yields products which give AgCl with warm $AgNO_3$ but no SO_4'' with $KMnO_4$ and thus are $CH_2Cl{\cdot}C(:CH_2){\cdot}CH_2{\cdot}SO_3M$ (*D*); crude (*B*) give ~20% of SO_4'' and thus contain ≮25% of $CH_2Cl{\cdot}CMe{:}CH{\cdot}SO_3NH_4$ (*E*), and crude (*B*) or (*C*) with aq. HNO_3–$AgNO_3$ at 100° give only ~65% of AgCl, indicating presence of ~35% of $CHCl{:}CMe{\cdot}SO_3M$. The (**II**) and (**III**) are derived from *β-methyl-β-chloromethylethionic anhydride* (**IV**), $CH_2Cl{\cdot}CMe<\begin{matrix}CH_2{\cdot}SO_2\\O—SO_2\end{matrix}>O$ (see below). (*B*) yield nearly pure *benzylthiuronium* salts, m.p. 103—105° and 123—128°, derived from (*D*) and (*E*), respectively, or vice versa. A 1 : 1 mixture (*F*) of $CH_2{:}C(CH_2Cl)_2$ and $CHCl{:}CMe{\cdot}CH_2Cl$ [obtained from (**I**) by Cl_2] with boiling aq. Na_2SO_3 gives *Na α-chloro-β-methyl-Δ^{α}-propene-γ-sulphonate*, decomp. 305—310° [and some disulphonate (**V**); with NaOH, but not $AgNO_3$, gives Cl′; with cold $KMnO_4$ gives no SO_4''], and thence the *benzylthiuronium* salt, m.p. 123·5—125°, and, by way of the acid chloride, the *amide*, m.p. 68—69°. With PCl_5 or $POCl_3$ and then Et_2O–NH_3, (*B*) give *γ-chloro-β-methyl-Δ^{α}-propene-α-sulphonamide*, m.p. 75·5—77°, which with O_3 gives 40% of H_2SO_4 but only 2% of CH_2O. With aq. Na_2SO_3, (*B*) give

salts (**VI**), converted by $POCl_3$ into $SO_2Cl{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}SO_2Cl$, m.p. 78—79°, also obtained from (**V**) by PCl_5. The rearrangement occurs during prep. of (**V**) or (**VI**), since (*a*) (**V**) yields the corresponding dibenzylthiuronium salt, dimorphic, m.p. 139—141° and 158—159°, and (*b*) with O_3 gives 69% of CH_2O but only 9% of SO_4''. Rearrangement also occurs during prep. of OPh-derivatives: with PhOH in boiling 33% NaOH, (*B*) give *Na α-phenoxy-β-methyl-Δ$^{\alpha}$-propene-γ-sulphonate* (**VII**), darkens 340°, decomp. 345—350° (derived *benzylthiuronium* salt, m.p. 145—146°), also obtained from (**IV**) by PhOH and NaOH at 100° and from (**I**) by $ClSO_3H$, followed by NaOPh. Its structure is proved by oxidation by aq. Br to $C_6H_2Br_3{\cdot}OH$ and failure to give SO_4'' with $KMnO_4$. It is partly isomerised in hot AcOH, yielding then SO_4'' with $KMnO_4$ and CH_2O with O_3. With K_2CO_3 and PhOH in $COMe_2$ and then aq. Na_2SO_3, (*F*) gives *Na γ-phenoxy-β-methylenepropane-α-sulphonate*, dimorphic, m.p. 226—230° (derived *benzylthiuronium* salt, m.p. 117—118°), which with $KMnO_4$ at 0° and then the b.p. gives $OPh{\cdot}CH_2{\cdot}CO_2H$, with O_3 gives CH_2O (45%), with Br gives ≯ a trace of $C_6H_2Br_3{\cdot}OH$, and in hot 10% NaOH rearranges to (**VII**). With SO_3 in $(CH_2Cl)_2$ at 0°, (**I**) gives (**IV**) (50%), m.p. 66—68°, stable at −5° but not at room temp. (vac.), which in H_2O is acidic (litmus), yields SO_4'' but not Cl' immediately, and is only slightly unsaturated, but in aq. alkali is highly unsaturated, yielding Cl' and SO_4'' quantitatively when heated therein. R. S. C.

Manufacture of formic acid.—See B., 1943, II, 207.

Ozonisation of acetic acid and acetic anhydride. H. Paillard and E. Briner (*Helv. Chim. Acta*, 1942, **25**, 1528—1533).—AcOH is very slightly attacked by O_3 yielding AcO_2H, which in presence of H_2O is decomposed with formation of H_2O_2. Ac_2O is even more slowly attacked. The bluish colour of a solution of O_3 in AcOH disappears when O_3 is removed and the ultra-violet absorption spectrum becomes identical with that prior to ozonisation. AcOH is therefore a very suitable solvent for ozonisation reactions. J. W. S.

Derivatives of aldol and crotonaldehyde. II. α-Chlorocrotyl acetate. E. Späth and H. Schmid (*Ber.*, 1940, **73**, [*B*], 243—248). —The product of the action of AcCl on $CHMe{:}CH{\cdot}CHO$ at 35—40° is identified as α-chlorocrotyl acetate, b.p. 64—66°/8·5 mm., since it is readily hydrolysed by cold H_2O to $CHMe{:}CH{\cdot}CHO$ (identified as the semicarbazone) and converted by ozonisation in EtCl with treatment of the product with H_2O containing Zn dust, quinol, and $AgNO_3$ into MeCHO; the yield of MeCHO is approx. equal to that obtained under similar conditions from $CHMe{:}CH{\cdot}CH(OAc)_2$. Pr$^{\alpha}$CHO and AcCl afford *α-chloro-n-butyl acetate*, b.p. 51—52°/9·5 mm. H. W.

Preparation and properties of trifluoromethyl compounds. J. H. Simons and E. O. Ramler (*J. Amer. Chem. Soc.*, 1943, **65**, 389—392).—$(CF_3{\cdot}CO_2)_2Ba$ and boiling PCl_3 give *trifluoroacetyl chloride* (**I**) (53%), m.p. −146°, b.p. −27°, and thence the known $CF_3{\cdot}CO{\cdot}NH_2$. PBr_3 at 190° gives similarly *trifluoroacetyl bromide* (59·3%), m.p. −136°, b.p. −5°. With C_6H_6–$AlCl_3$ at ~5°—room temp., (**I**) yields *trifluoroacetophenone* (43%), m.p. ~−40°, b.p. 75°/37 mm., 152°/730 mm., which is sol. in 10% aq. KOH, giving BzOH and a gas (? CHF_3), yields a cryst. $NaHSO_3$ compound, rapidly gives CHF_3 if a neutral solvent is present, gives a 2 : 4-dinitrophenylhydrazone, m.p. 94·5—95·5°, does not give a cyanohydrin, with PCl_5 at 175° yields *ββ-dichloro-ααα-trifluoro-β-phenylethane* (48·5%), b.p. 89—90° (resistant to SbF_3), and with MgPhBr–Et_2O gives *diphenyltrifluoromethylcarbinol* (46%), m.p. 74—74·5°, b.p. 157°/17 mm. $CPhF_3$ (133), Fe (1 g.), and Br (24 c.c.) at, successively, 60—70°, 56°, and 60° give *m*-$C_6H_4Br{\cdot}CF_3$ (**II**) (52%), b.p. 151—152°, hydrolysed by boiling 80% H_2SO_4 to *m*-$C_6H_4Br{\cdot}CO_2H$; use of more Fe leads to 25% of (**II**) and 8% of 3 : 4 : 1-$C_6H_3Br_2{\cdot}CF_3$, b.p. 102—104°/25 mm., hydrolysed to 3 : 4 : 1-$C_6H_3Br_2{\cdot}CO_2H$. In Et_2O, (**II**) gives a Grignard reagent (100%), which with Me_2SO_4–Et_2O at the b.p. gives $CPhF_3$ (65%) and *m*-$C_6H_4Me{\cdot}CF_3$ (9·1%), b.p. 127° (hydrolysed to *m*-$C_6H_4Me{\cdot}CO_2H$). $CF_3{\cdot}COI$ could not be prepared. An excellent yield of $CPhF_3$ is obtained from $CPhCl_3$ by HF at high temp./>1 atm. F is detected by pptn. by $Ce(NO_3)_3$–AcOH. R. S. C.

Resolution and rates of hydrolysis of *dl*-α-bromopropionic acid and its glycine derivatives. A. F. Chadwick and E. Pacsu (*J. Amer. Chem. Soc.*, 1943, **65**, 392—402).—Yields by resolution of *dl*-$CHMeBr{\cdot}CO_2H$ (**I**) by alkaloids are low because of decomp. of the salts. *dl*-α-Bromopropionylglycine ions are equally unstable. *dl*-α-Bromopropionylglycylglycine is resolved by quinine in 0·8% EtOAc solution, yielding a Na salt, $[\alpha]_D^{20}$ +27·7° in H_2O, and an acid, $[\alpha]_D^{20}$ −18·0°. The kinetics of the first- and second-order reactions involved in removal of Br from the ions are investigated; mechanisms are discussed. Decomp. of the solid brucine salts is measured; that of (**I**) yields *dl*-lactylglycinelactone. R. S. C.

Synthesis of methacrylic acid. T. White (*J.C.S.*, 1943, 238—239). —By careful control of conditions, Me *iso*propenyl ketone may be oxidised by strongly alkaline aq. NaOCl to $CH_2{:}CMe{\cdot}CO_2H$, the Me ester of which with the appropriate alcohol gives the *ethylene di-*, b.p. 122—126°/15 mm., and the n-*hexyl* esters, b.p. 86—88°/17 mm. F. R. S.

Normal addition of hydrogen bromide to Δ$^{\beta}$-butenoic, Δ$^{\gamma}$-pentenoic, and Δ$^{\delta}$-hexenoic acid in hexane. A. Michael and H. S. Mason (*J. Amer. Chem. Soc.*, 1943, **65**, 683—686).—Mixtures of $Br{\cdot}[CH_2]_{3-4}{\cdot}CO_2H$ with $CHMeBr{\cdot}[CH_2]_{2-3}{\cdot}CO_2H$ are analysed by the much faster reaction of the *sec.* bromides with $AgNO_3$–HNO_3–H_2O–EtOH at 27°. When O_2 and peroxides are rigidly excluded, addition of HBr to $CH_2{:}CH{\cdot}[CH_2]_{1-3}{\cdot}CO_2H$ is 88—100% (in one case 75%) "normal." R. S. C.

Wandering of halogen atoms in carbon chains and rings. V. C. D. Nenitzescu, I. G. Gavat, and D. Cocora (*Ber.*, 1940, **73**, [*B*], 233—237).—Addition of Δ$^{\alpha}$-hexenoic acid (**I**) in C_6H_6 to $AlCl_3$ in C_6H_6 at 45—50° yields exclusively *δ-phenylhexoic acid*, b.p. 143°/1 mm. (*chloride*, b.p. 138°/11 mm.; *amide*, m.p. 75°). Under similar conditions but with CS_2 as solvent (**I**) and $AlCl_3$ give a mixture of partly halogenated Δ$^{\beta}$- and Δ$^{\gamma}$-acids, converted by hydrolysis followed by ozonisation into some $(CH_2{\cdot}CO_2H)_2$ but no Pr$^{\alpha}CO_2H$. Migration of the double linking occurs in a direction opposite to that of the classical Fittig reaction. This isomerisation is not general since Δ^{1}-*cyclo*hexenecarboxylic acid is not thus affected. *β*-Methyl-Δ$^{\alpha}$-hexenoic acid, $AlCl_3$, and C_6H_6 give *δ-phenyl-β-methylhexoic acid* (**II**), b.p. 138—140°/1·5 mm. (*chloride*, b.p. 119°/5 mm.; *amide*, m.p. 78°). *δ-Phenylpentan-β-ol*, b.p. 124—125°/15 mm., obtained by reduction of the corresponding ketone, is converted by PBr_3 into the corresponding *bromide*, b.p. 115°/10 mm., which is condensed with $CH_2(CO_2Et)_2$; the product is hydrolysed and decarboxylated to (**II**). Unexpectedly, sorbic acid, $AlCl_3$, and C_6H_6 afford (**II**). H. W.

Esters of methylneopentylacetic acid. F. C. Whitmore, J. D. Surmatis, and J. N. Haimsohn (*J. Amer. Chem. Soc.*, 1943, **65**, 487). —*Et*, b.p. 176·8°/734 mm., *Pr$^{\alpha}$*, b.p. 196·6°/734 mm., *Bu$^{\alpha}$*, b.p. 213·8°/734 mm., and n-*hexyl αγγ-trimethyl*-n-*valerate*, b.p. 247·2°/734 mm., are obtained from the acid by $SOCl_2$ and then ROH (excess). R. S. C.

A monomeric aldehyde peroxide (*iso*carboxylic acid). H. J. Backer and J. Strating (*Ber.*, 1940, **73**, [*B*], 316—317).—Mainly comment on the work of Rieche *et al.* (A., 1940, II, 63). Previous work (A., 1934, 662; 1935, 498) has shown that 3-*tert.*-butyl-2 : 5-dihydrothiophen 1 : 1-dioxide gives an ozonide, hydrolysed to an *iso*carboxylic acid, convertible by alkali into $CMe_3{\cdot}CO{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CO_2H$. A. T. P.

Fatty acids. XII. Preparation of α- and β-linoleic acids by debromination in various solvents. Chemistry of these acids. J. S. Frankel and J. B. Brown (*J. Amer. Chem. Soc.*, 1943, **65**, 415—418; cf. A., 1943, II, 151).—The following nomenclature is adopted for linoleic acids: no prefix = the *cis-cis* acid (**I**) (Br_4 no. 102·9); α- the mixture obtained from the tetrabromides (**II**), m.p. 114—115°; β- product from liquid tetrabromides obtained by brominating (**I**) or the α-acid; crystallisation acid = product obtained by crystallising the acids from semi-drying oils; isomeric acids (*cis-trans* or *trans-cis*) = acids giving only liquid tetrabromides. Et_2O is the best solvent for debromination; Pr$^{\beta}_2O$ and dioxan are also satisfactory; MeOH leads to Me esters; C_5H_5N is difficult to remove from the product; AcOH leads to acids of low I val. and Br_4 no.; light petroleum is useless. C_5H_5N leads to acids of correct Br_4 no. but low m.p. In MeOH liquid tetrabromides give only 40—60% of distillable acid, probably owing to polymerisation, but the yield from (**II**) is nearly quant. Oxidation of the α-acid gives ~50% of sativic acids, but little or none is obtained from the β-acid. α- and β-Acids contain 1·0—1·2 and 1·9—6·4% of conjugated acid. The β- differs from the α-acid mainly in containing only 15—53% of (**I**), 32—70% of isomeric acids, and 6—22% of much altered acids. The isomeric acids are not *trans-trans*, since they give no tetrabromide, m.p. 78°. With two samples of β-acid the I val. rises with time, but this is only partly due to conjugation. β-Acid, obtained by debromination in C_5H_5N, had m.p. −2°. Crystallisation of the β-acid at low temp. has not been effected. R. S. C.

Heat-polymerisation of triglycerides. I. Tristearin and triolein. N. L. Phalnikar and B. V. Bhide (*J. Univ. Bombay*, 1943, **11**, **A**, Part 5, 77—82).—Distillation of tristearin at 30 mm. yields stearic acid (58), tristearin (22), and stearone with traces of hydrocarbons (26%), with a negligible residue. Triolein similarly gives nonoic and oleic acids, triolein, and hydrocarbons with a trace of ketones, with a residue yielding on hydrolysis sebacic and oleic acids, and polymerised acid fractions, mol. wt. 553, 443, 539, and 634. In each case much acraldehyde and some CO_2 are evolved. A. Li.

Condensations. XIX. Alkylation of β-keto-esters with alcohols and ethers in presence of boron trifluoride. J. T. Adams, B. Abramovitch, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1943, **65**, 552—554; cf. A., 1943, II, 119).—Passing BF_3 into ROH (1 mol.) or R_2O (0·5 mol.) and $COR'{\cdot}CH_2{\cdot}CO_2R''$ gives $COR'{\cdot}CHR{\cdot}CO_2R''$; side-reactions are dehydrogenation of ROH or dealcoholation of R_2O to give olefines (which may polymerise), exchange of R'' for R, and further reaction of the product. Time and temp. of reaction greatly affect the yield and under suitable conditions the yield of $CHPr^{\beta}Ac{\cdot}CO_2Et$ (**I**), b.p. 97—98°/20 mm., by use of Pr$^{\beta}$OH is

increased to 67% cf. A., 1940, II, 374). Et α-*cyclo*hexylacetoacetate, b.p. 146—148°/20 mm., is obtained in 32—34% yield and with 5% NaOH gives *cyclo*hexylacetone. $CH_2Ac{\cdot}CO_2Et$ (**II**) with $Bu^{\gamma}OH$ or $EtOBu^{\gamma}$ (in this and other cases also BF_3) gives 6—14% of $CHBu^{\gamma}Ac{\cdot}CO_2Bu^{\gamma}$ (and unsaturated hydrocarbons) and thence (H_2SO_4–AcOH) $COMe{\cdot}CH_2Bu^{\gamma}$ (23%), b.p. 123—126°. $CMe_2Et{\cdot}OH$ and (**II**) give an ester, hydrolysed to $CMe_2Et{\cdot}CH_2{\cdot}COMe$. $(CH_2Ph)_2O$ and (**II**) at −70° to −10° give 18% of $CH_2Ph{\cdot}CHAc{\cdot}CO_2Et$, b.p. 164—166°/12 mm. $CHMeAc{\cdot}CO_2Et$ and Pr^{β}_2O at 24° give $CMePr^{\beta}Ac{\cdot}CO_2Et$ (55%), b.p. 98—98·5°/15 mm., and $COMe{\cdot}CHMePr^{\alpha}$ (*semicarbazone*, m.p. 107—107·5°). Alkylation does not occur with (*a*) (**II**) and $Bu^{\alpha}OH$, $Bu^{\beta}OH$, *sec.*-BuOH, Et_2O, or Pr^{β}_2O, (*b*) $CH_2Bz{\cdot}CO_2Et$ and $Pr^{\beta}OH$, Et_2O, or Pr^{β}_2O, (*c*) (**I**) and Pr^{β}_2O, or (*d*) $CH_2(CO_2Et)_2$ or $MeNO_2$ and Pr^{β}_2O or $Bu^{\gamma}OH$; (**II**) and BuOH give $CH_2Ac{\cdot}CO_2R$ (R = Bu^{α} or Bu^{β}). R. S. C.

Stereochemical relationships of the θ*ι*-oxidostearic acids and the θ*ι*-dihydroxystearic acids. D. Atherton and T. P. Hilditch (*J.C.S.*, 1943, 204—208).—When the two isomeric forms of θ*ι*-oxidostearic acid are treated with Et_2O–HCl, chlorohydroxystearic acids are produced which in presence of alkali re-form the original oxido-acid. Hence the inversion, which occurs when either of the θ*ι*-$(OH)_2$-acids is converted into the chlorohydroxy-acids and the latter, through the oxido-compounds, into the isomeric form of the $(OH)_2$-acid, must take place during replacement of OH by Cl. This leads to the conclusion that no inversion takes place during the conversion of oleic and elaidic acid into the θ*ι*-$(OH)_2$-acids, m.p. 95° and 132°, respectively, by means of BzO_2H, AcO_2H, or Caro's acid. F. R. S.

Oxidation of resorcinol by hydrogen peroxide in presence of tungstic acid sol as catalyst. B. C. Kar (*J. Indian Chem. Soc.*, 1942, **19**, 499—500).—Oxidation of resorcinol with H_2O_2, in presence of tungstic or molybdic acid sol, gives CO_2 and maleic acid. The kinetics of the reaction are studied. A. T. P.

Autocondensation of oxalacetic acid. F. L. Breusch and R. Tulus (*Rev. Fac. Sci. Istanbul*, 1942, **A**, **6**, 144—149).—Oxalacetic acid (**I**) in cryst. form occurs only as the *cis*- and *trans*-enolic modifications but in aq. solution is present also in the keto-form and, under certain conditions, as keto-hydrate (**II**). This latter form is subject to autocondensation with a second mol. of (**I**) to products which resemble citric acid and give the $CBr_3{\cdot}CO{\cdot}CHBr_2$ reaction. In conc. aq. solution the production of (**II**) is favoured by conc. alkalis, in dil. aq. solution by $Ca^{\cdot\cdot}$. H. W.

Preparation of lower aldonic acids by oxidation of sugars in alkaline solution. H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1942, **29**, 227—232).—Directions are given for the prep. of *l*-erythronic (**I**), *d*-threonic (**II**), *d*-lyxonic, *l*-xylonic, and *d*-arabonic acid (**III**) by oxidation with O_2 of the appropriate sugar in alkaline solution. (**III**) is obtained in ∼70% yield in agreement with the results of previous investigators; with the other aldonic acids lower yields are obtained which do not differ greatly from those obtained by oxidation with air. The simplicity of the method is a great recommendation. (**I**) and (**II**) are separated as their brucine salts, the optical rotations of which are represented by: $[\alpha]_D^{20} = -28{\cdot}4 - 0{\cdot}85C + 0{\cdot}025C^2$ in which C is the g. of anhyd. brucine *l*-erythronate in 100 ml. of aq. solution, and $[\alpha]_D^{20} = -28{\cdot}5 - 0{\cdot}9C + 0{\cdot}025C^2$ in which C is the g. of anhyd. brucine *d*-threonate in 200 ml. of aq. solution. H. W.

Synthesis of some α-acyltetronic acids. W. Baker, K. D. Grice, and A. B. A. Jansen (*J.C.S.*, 1943, 241—242).—α-Acetyltetronanilide (improved prep.) is hydrolysed in cold alkaline solution to α-acetyltetronic acid (**I**), which condenses with aldehydes in AcOH and a little piperidine in poor yield to give α-(β′-*phenylacrylyl*)-, m.p. 138—140°, α-(β′-*phenylpropionyl*)-, m.p. 131°, α-(β′-p-*anisylacrylyl*)-, m.p. 164°, α-(β′-*styrylacrylyl*)-, m.p. 178—182° [reduced (H_2–Ni) to α-(δ′-*phenylvaleryl*)-, m.p. 81·5—82·5°], and α-(β′-2-*furylacrylyl*)-*tetronic acid*, m.p. 146—148° [reduced to the α(β′-2-*tetrahydrofurylpropionyl*)-acid, m.p. 73·5—74°]. The oxime of (**I**) undergoes the Beckmann transformation (PCl_5–PCl_3) to α-*acetamidotetronic acid*, m.p. 170°. F. R. S.

Diethyl acetal of γ-methyl-Δ$^{\gamma}$-butenal. D. Kritchevsky (*J. Amer. Chem. Soc.*, 1943, **65**, 487).—$CH_2{:}CMe{\cdot}CH_2{\cdot}MgCl$ and $CH(OEt)_3$ in boiling Et_2O give $CH_2{:}CMe{\cdot}CH_2{\cdot}CH(OEt)_2$ (24%), b.p. 154—155°, and then β-*methyl*-Δ$^{\beta}$-*butenaldehyde*-p-*nitro*-, m.p. 157°, and -2 : 4-*dinitro-phenylhydrazone*, m.p. 181°, and -*semicarbazone*, m.p. 204—205°. R. S. C.

Ultra-violet absorption spectra of tagetone and related ketones.—See A., 1943, I, 191.

β-Alkylthiolethylamines and the corresponding carbamides, sulphoxides, and sulphones. K. W. Brighton and E. E. Reid (*J. Amer. Chem. Soc.*, 1943, **65**, 458—459).—Adding RSH and then $Br{\cdot}[CH_2]_2{\cdot}NH_2$,HBr to NaOEt–EtOH and then boiling gives β-n-*butyl*-, b.p. 211°, β-n-, b.p. 231°, and β-iso-*amyl*-, b.p. 231°, β-n-*hexyl*-, b.p. 252°, and β-n-*heptyl-thiolethylamine*, b.p. 270°, which yield their respective *hydrochlorides*, m.p. 118°, —, 167°, 131°, and 121°, *carbamide* derivatives, m.p. 91°, 101°, 111°, 99°, and 95°, *sulphoxide hydrochlorides*, m.p. 112°, 121°, —, 127°, and 123°, and *sulphone hydrochlorides*, m.p. 211°, 221°, —, 238°, and 230°. R. S. C.

Iron pentacarbonyl as solvent and reaction medium.—See A., 1943, I, 198.

High mol. wt. aliphatic compounds of nitrogen and sulphur. B. A. Hunter (*Iowa State Coll. J. Sci.*, 1942, **17**, 85—87; cf. A., 1941, II, 279, 283).—The following have been prepared: N-n-*octadecyl-ammonium nicotinate*, m.p. 78—79°, -nicotinamide, m.p. 91—92°, -*pyrrole*, m.p. 74—75°, 2 : 5-*dimethyl*-1-n-*octadecyl*-, m.p. 39—40°, and 1-n-*dodecyl-pyrrole*, b.p. 138—140°/1 mm., 1-n-*octadecyl*-, m.p. 107—108° (Et_2 ester, m.p. 33—33·5°), and 1-n-*dodecyl-pyrrole*-3 : 4-*dicarboxylic acid* (Et_2 ester, b.p. 240—243°/5 mm.). n-$C_{12}H_{25}{\cdot}NH_2$ with HNO_2 gives some n-$C_{12}H_{25}{\cdot}OH$ with n-Δ$^{\alpha}$-$C_{12}H_{24}$, converted into n-αβ-$C_{12}H_{24}Br_2$, b.p. 156—158°/6 mm. Nitration of n-$C_{12}H_{25}{\cdot}CO_2H$ yields presumably n-α-$NO_2{\cdot}C_{12}H_{14}{\cdot}CO_2H$ (*Et* ester, b.p. 150—160°/1 mm.). Contrary to Collin *et al.* (A., 1933, 1141), n-$C_{18}H_{37}{\cdot}SH$ has m.p. 31°. Contrary to the principles of homology, n-$C_{12}H_{25}{\cdot}SH$ with Na yields $(n\text{-}C_{12}H_{25})_2S$. Fuming H_2SO_4 sulphonates n-$C_{17}H_{35}{\cdot}CO_2H$ at 50° and n-$C_{17}H_{35}{\cdot}CN$, the Ba salt being isolated in the former case. F. R. G.

Action of thionyl chloride on urethanes. L. C. Raiford and H. B. Freyermuth (*J. Org. Chem.*, 1943, **8**, 174—178).—Under the conditions of Warren *et al.* (A., 1935, 854), the production of an allophanate from $NH_2{\cdot}CO_2Et$ or $NH_2{\cdot}CO_2Bu^{\alpha}$ (**I**) could not be confirmed. (**I**) and $SOCl_2$ in boiling C_6H_6 afford *Bu*$^{\alpha}$ *allophanate*, m.p. 149—150°, with a small amount of cyanuric acid. The action of $SOCl_2$ with *N*-aryl-substituted urethanes to give uretediones is sp., as far as tested, for the Ph derivative. Compounds containing "negatively" substituted Ph suffer no change when refluxed with the reagent but tar is formed when the substituent is alkyl. β-$C_{10}H_7{\cdot}NH{\cdot}CO_2Et$ (**II**) is slowly transformed by $SOCl_2$ at 0° into *Et* 1-*chloro*-2-*naphthylaminoformate*, m.p. 94—95°, and *Et* 2-*naphthyl-iminochlorosulphinate*, m.p. 133—134°, which loses SO_2 when preserved particularly in sunlight and partly regenerates (**II**) when boiled with EtOH. *Et* 4-*chloro*-1-*naphthylaminoformate*, m.p. 143—144°, is obtained similarly from α-$C_{10}H_7{\cdot}NH{\cdot}CO_2Et$; it is hydrolysed by KOH–EtOH to 4 : 1-$C_{10}H_6Cl{\cdot}NHAc$, m.p. 97—98°. H. W.

Amino-acids and their derivatives. V. Synthesis of α-amino-α-methylbutyric acid and α-amino-α-*iso*propylbutyric acid. L. Li, K. Lin, Y. Huang, and S. Kang. **VI. Synthesis of α-amino-α-ethylvaleric acid.** L. Li, K. Lin, Y. Huang, and A. Y. L. Huang. **VII. Synthesis of α-amino-δ-methyl-α-*iso*amylhexoic acid (α-aminodi*iso*amylacetic acid).** Y. Huang, K. Lin, L. Li, and M. Lu (*J. Chinese Chem. Soc.*, 1942, **9**, 1—13, 14—30, 31—40).—V. $CN{\cdot}CHEt{\cdot}CO_2Et$ (**I**) and NaOEt–EtOH–MeI give $CN{\cdot}CMeEt{\cdot}CO_2Et$, b.p. 90·5—94°/18·5 mm., which with conc. H_2SO_4 at 37° (50 hr.) affords *Et* α-*carbamyl*-α-*methylbutyrate*, m.p. 46—46·5° [corresponding butyric acid, m.p. 99° (decomp.)]. Bromination in $CHCl_3$–aq. NaOH at −12° to −15° then yields the *N*-Br-derivative, converted by 30% aq. KOH at 50—70° into Et α-amino-α-methylbutyrate, b.p. 65—66°/20 mm. (picrate, new m.p. 151·5—152·5°; *phenylcarbamyl* derivative, m.p. 114°; free butyric acid, m.p. 308°). A product, b.p. 95·5°/13·5 mm., containing 91% of (**I**), prepared from $CN{\cdot}CHNa{\cdot}CO_2Et$ and EtBr–EtOH, reacts with $Pr^{\beta}Br$–NaOEt–EtOH to give $CN{\cdot}CEtPr^{\beta}{\cdot}CO_2Et$, b.p. 105—108·5°/15 mm., and thence (conc. H_2SO_4 at 100° for 25 min.) Et α-carbamyl-α-*iso*propylbutyrate, m.p. 88°; its *N*-Br-derivative and 30% aq. KOH at 60° afford *Et* α-*amino*-α-iso*propylbutyrate*, b.p. 52°/4·3 mm. (*hydrochloride*, m.p. 136·5—138°). The corresponding butyric *acid*, m.p. 283° (decomp.), affords a *chloroacetyl* derivative, m.p. 177·5°, a *phenylcarbamyl* compound, m.p. 181° (decomp.), and thence 1-*phenyl*-4-*ethyl*-4-iso*propyl-hydantoin*, m.p. 115·5—116·5°.

VI. $CN{\cdot}CHPr{\cdot}CO_2Et$ and Et–I–NaOEt–EtOH give $CN{\cdot}CEtPr{\cdot}CO_2Et$ (**II**); pure (**II**) is converted by conc. H_2SO_4 at 100° (bath) into *Et* α-*carbamyl*-α-*ethylvalerate* (**III**), m.p. 86·5°; aq. KOH gives the corresponding *acid* (**IV**), m.p. 139·5—140°, also obtained from (**II**) by 26% aq. KOH at 120°, followed by conc. H_2SO_4 at 100° (bath). (**III**) and Br–10% aq. NaOH–$CHCl_3$ at −12° to −15° give the *N*-Br-derivative (**V**), converted by 30% aq. KOH at 50—60° into *Et* α-*amino*-α-*ethylvalerate*, b.p. 61°/3·8 mm. (*hydrochloride*, m.p. 80—86°). (**V**) with NaOMe–MeOH at room temp. overnight, then at 80°, affords *Et* α-*carbomethoxyamino*-α-*ethylvalerate* (**VI**), b.p. 92—93·5°/5 mm. Br–MeOH and (**IV**)–NaOEt–EtOH at 0°, followed by NaOMe, at room temp. overnight, then at 80°, yield *Me* α-*amino*-α-*ethylvalerate*, b.p. 94°/6·5 mm. (*hydrochloride*, m.p. 133—134°; *phenylcarbamyl* derivative, m.p. 122—124°), and some α-*carbomethoxyamino*-α-*ethylvalerate* (**VII**), m.p. 112° (decomp.) [obtained also from (**IV**) and Br–MeOH–NaOMe at 20°]. α-*Amino*-α-*ethylvaleric acid*, m.p. 303° (sealed capillary) (*chloroacetyl*, m.p. 191—192°, *carbamyl*, decomp. 187—187·5°, and *hydantoin* derivative, m.p. 145·5—146·5°), is obtained by hydrolysis of its Me or Et ester, by heating the respective hydrochloride with Ag_2CO_3, or by hydrolytic decomp., using aq. $Ba(OH)_2$ at 120—125° or 120—140°, of (**VI**) and (**VII**), respectively.

VII. $CN{\cdot}C(CH_2Bu^{\beta})_2{\cdot}CO_2Et$, b.p. 157°/16 mm., and conc. H_2SO_4 at 100° (bath) give *Et* α-*carbamyl*-δ-*methyl*-α-iso*amylhexoate*, m.p.

65—66° (*acid*, m.p. 140—143°; di*iso*amylacetamide, new m.p. 118—118·5°), thence the *N*-Br-derivative (**VIII**), converted by 10% aq. NaOH at 25—30°, then at <20°, into *carbethoxydiisoamylmethylcarbimide* (**IX**), b.p. 126·5—127°/~5·5 mm. (NH_2Ph gives the *phenylcarbamido*-derivative, *Et α-phenylcarbamido-δ-methyl-α-isoamylhexoate*, m.p. 118—119°). (**IX**) refluxed with fuming HCl yields, through the *hydrochloride*, m.p. 280—282° (decomp.), *α-amino-δ-methyl-α-isoamylhexoic acid* (*α-aminodiisoamylacetic acid*) (**X**), m.p. 290° (decomp.) [*phenylcarbamyl* derivative, m.p. 177° (decomp.); *chloroacetyl* compound, m.p. 153°]. (**IX**) and α-amino-γ-methyl-α-*iso*butyl valerate in N-NaOH at 70—80° afford N-(*carboxydiisobutylmethyl*)-N′-(*carbethoxydiisoamylmethyl*)*carbamide*, m.p. 184—185°. (**VIII**) and NaOMe–MeOH at 80—83° yield *Et α-carbomethoxyamino-δ-methyl-α-isoamylhexoate*, b.p. 132—133°/~4·3 mm., hydrolysed by refluxing with aq. $Ba(OH)_2$ at 120—125° to (**X**). A. T. P.

Synthesis of *dl*-serine. C. E. Redemann and R. N. Icke (*J. Org. Chem.*, 1943, **8**, 159—161).—Passage of $OH\cdot[CH_2]_2\cdot OEt$ over Cu chromite heated at 310—330° in a vertical Pyrex tube gives $OEt\cdot CH_2\cdot CHO$ in 30—35% yield. This is converted into *dl*-serine, m.p. 243—244° (decomp.) after darkening at 228° (corr.), by the modified Strecker reaction. H. W.

Characteristic reaction possibilities of natural compounds containing sulphur. A. Schöberl (*Angew. Chem.*, 1940, **53**, 227—232).—A lecture.

Aliphatic carbodi-imides. II. E. Schmidt and W. Striewsky (*Ber.*, 1940, **73**, [*B*], 286—293).—Simplified methods for the prep. of $OMe\cdot CH_2\cdot CNS$ (**I**) and $OEt\cdot CH_2\cdot CNS$ are given. NH_2Me transforms (**I**) in Et_2O into N-*methyl*-N′-*methoxymethylthiocarbamide*, m.p. 76—77°, converted by HgO in dry Et_2O into *methylmethoxymethylcarbodi-imide* (**II**), b.p. 35·5—36·5°/ 10 mm., which slowly becomes acid when preserved yielding a solid which does not regenerate (**II**) when distilled. Similar methods are used in the prep. of N-*methyl*-N′-*ethoxymethyl*-, m.p. 83—84°; N-*methoxymethyl*-N′-n-*propyl*-, m.p. 58·5—59·5°; N-*methoxymethyl*-N′-iso*propyl*-, needles, m.p. 80·5—81·5°, or, less frequently, plates, m.p. 73—75° when rapidly heated or m.p. 80—81° softens at 73—75° when slowly heated; N-*ethoxymethyl*-N′-iso*propyl*-, m.p. 77—78°; N-*methoxymethyl*-N′-iso*hexyl*-, m.p. 35·5—37°; N-cyclo*hexyl*-N′-*methoxymethyl*-, m.p. 103—104°, and N-cyclo*hexyl*-N′-*ethoxymethyl*-, m.p. 109—110°, *-thiocarbamide*. These are converted respectively into *methylethoxymethyl*-, b.p. 46—47°/10 mm.; *methoxymethyl*-n-*propyl*-, b.p. 61·5—62·5°/10 mm.; *methoxymethyl*iso*propyl*-, b.p. 52—53°/10 mm.; *ethoxymethyl*iso*propyl*, b.p. 62·5—63·5°/10 mm.; *methoxymethyl*iso*hexyl*-, b.p. 97—98°/10 mm.; cyclo*hexylmethoxymethyl*-, b.p. 109—110°/10 mm.; and cyclo*hexylethoxymethyl*-, b.p. 117·5—118·5°/10 mm., *-carbodi-imide*. H. W.

Hydrogenation of adiponitrile.—See B., 1943, II, 209.

[Manufacture of] unsaturated ether nitriles, cyanoalkyl ethers of monohydric alicyclic alcohols, and cyanoalkyl ethers of ether alcohols.—See B., 1943, II, 208.

II.—SUGARS AND GLUCOSIDES.

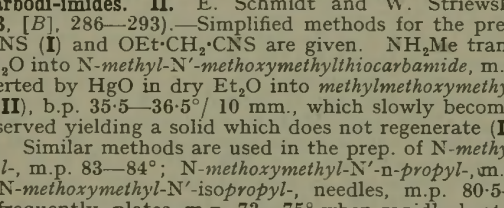
Carbohydrate formation in nature.—See A., 1943, III, 534.

Lead tetra-acetate oxidations in the sugar group. III. Triphenylmethyl ethers of β-methyl-*D*-arabinopyranoside and of α-methyl-*L*-fucopyranoside. Determination of their structures. R. C. Hockett and D. F. Mowery, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 403—409; cf. A., 1939, II, 407, 493).—β-Methyl-*D*-arabinopyranoside (**I**) (0·133) with CPh_3Cl (0·16 mol.) in C_5H_5N at 23° (18 days) gives the 2-*CPh_3 ether* (**II**) (40%), m.p. 143—145°, [α] −79·7° in EtOH, −75·8° in $CHCl_3$, and 2 : 3-(*CPh_3*)$_2$ *ether* (**III**) (6%), m.p. 191—192°, [α] −81·7° in $CHCl_3$, −58·6° in C_5H_5N, and a syrup, which with Ac_2O–C_5H_5N at 0° gives the 3-*CPh_3 ether* 2 : 4-*diacetate* (**IV**), m.p. 202—203°, [α] −107·6° in $CHCl_3$. In boiling NaOMe–MeOH, (**IV**) gives *β-methyl*-D-*arabinopyranoside* 3-*CPh_3 ether* (**V**), +2MeOH, m.p. 157—159°, [α] −103·7° in $CHCl_3$, −93·3° in MeOH, which resists the action of $Pb(OAc)_4$ in C_5H_5N (proof of structure). The structure of (**II**) could not be thus determined, since reaction in C_5H_5N is so fast that the difference for β-methyl-*D*-glucopyranoside and (**I**) is indistinct. AcOH causes perceptible hydrolysis of the CPh_3 ethers, but can be used as solvent for rate determinations if allowance is made for this consumption of reagent; thus, (**II**) is shown to contain the *cis*-glycol grouping. (**III**) gives *β-methyl*-D-*arabinopyranoside* 2 : 3-(*CPh_3*)$_2$ *ether* 4-*acetate*, m.p. 193—194°, [α] −98·8° in $CHCl_3$, $[\alpha]_D^{26}$ −109·7° in C_5H_5N; when kept in AcOH at 60°, this loses the CPh_3 to give a solution which is attacked by $Pb(OAc)_4$ at a rate characteristic of *trans*-glycols, thus establishing the structure of (**III**). $CPh_3\cdot OAc$ is unaffected by $Pb(OAc)_4$–AcOH. CPh_3 is removed from (**III**) by AcOH at 60° but not from (**IV**) at room temp. CPh_3Cl converts (**V**), but not (**II**), into (**III**). 50% of (**III**) is obtained by using 4 mols. of CPh_3Cl per mol. of (**I**). α-Methyl-*L*-fucopyranoside gives 81·5% of the 2-CPh_3 ether, m.p. 127—128° (corr.), [α] −58·0° in $CHCl_3$ (cf. A., 1934, 635) (3 : 4-*diacetate*, m.p. 208—210°, [α] −37·5° in $CHCl_3$), the structure of which is proved as above and confirmed by the similarity of its $[M]_D$ to that of (**II**). The OH at $C_{(2)}$ is thus the most reactive *sec.* OH. Unless otherwise stated, [α] are $[\alpha]_D^{20}$. R. S. C.

Mutarotation of β-*D*-altrose. N. K. Richtmyer and C. S. Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 740—741).—β-*D*-Altrose exhibits mutarotation which is very rapid at first (cf. A., 1935, II, 135; also Austin *et al.*, A., 1934, 759). Its initial $[\alpha]_D^{20}$ is, by extrapolation, ~−69°, its final $[\alpha]_D^{20}$ +33·1°, in H_2O. R. S. C.

Hydrogenation of invertible saccharides.—See B., 1943, II, 209.

Synthesis of disaccharide acetates in the mannose series. E. A. Talley, D. D. Reynolds, and W. L. Evans (*J. Amer. Chem. Soc.*, 1943, **65**, 575—582).—Acetobromomannose (**I**), β-*D*-mannose 1 : 2 : 3 : 4-tetra-acetate, $CaSO_4$, Ag_2O, and I in $CHCl_3$ give 6-β-D-*mannosido*-6-β-D-*mannose octa-acetate* (39%), m.p. 152—153° (corr.), $[\alpha]_D^{25}$ +19·6° in $CHCl_3$, which is shown to be the normal form by constancy of [α] in HCl–$CHCl_3$ and by hydrolysis by NaOMe–MeOH or acid to 6-β-*D*-mannosido-β-*D*-mannose, softens 70°, decomp. 90—95° (*phenylosazone*, m.p. 122—128°); absence of I leads mainly to a syrup, probably containing ortho-esters. β-*D*-Glucose 1 : 2 : 3 : 4-tetra-acetate (**II**) with (**I**) and $CaSO_4$ in $CHCl_3$ (presence of I leads mainly to the normal acetate) yields d- (**III**), m.p. 168—169° (corr.), $[\alpha]_D^{30}$ +17·1° in $CHCl_3$, and l-(β-D-*glucoside* 1 : 2 : 3 : 4-*tetra-acetate*)-D-*mannose* 3′ : 4′ : 6′-*triacetate* 6 : 1′ : 2′-*orthoacetate* (**IV**), m.p. 174—174·5° (corr.), $[\alpha]_D^{32}$ −27·6° in $CHCl_3$, and a residue, whence very dil. HCl and hot H_2O yield an amorphous normal octa-acetate (**V**), softens 83—87°, $[\alpha]_D^{23}$ +33·5°. (**III**) and (**IV**) are stereoisomerides at C* of the orthoacetate (*A*; Ac_4Gl = glucose tetra-acetate residue linked to C* by $C_{(6)}\cdot O$), since acid removes eight and alkali removes seven Ac. Moreover, in HCl–$CHCl_3$, $[\alpha]_D^{28}$ of (**III**) and (**IV**) changes very rapidly to +44° and +43°, respectively, the rate being independent of the [HCl] provided that 1 mol. of HCl is present; this is followed by a slower decrease in [α], the rate of which is dependent on the [HCl]. In HBr–$CHCl_3$, there is a similar very rapid rise in [α], followed by a slower further rise at a rate dependent on the [HBr]. The rapid rises are due to hydrolysis to (**II**) + acetochloro- or acetobromo-mannose (**VI**), respectively; this is confirmed by the crude product formed in HBr showing the darkening and evolution of HBr characteristics of (**VI**). The subsequent slower changes are due to decomp. of (**II**), which in HCl- or HBr–$CHCl_3$ shows a decrease and rise, respectively, of [α] at rates similar to those found for (**III**) and (**IV**). The normal acetate structure of (**V**) is shown by removal of 8 Ac by alkali, by stability in HCl–$CHCl_3$, and by conversion by HBr–AcOH–Ac_2O at −2° into *acetobromo*-6-β-D-*mannoside*-D-*glucose* (**VII**), m.p. 172—172·5° (rapid heating), decomp. ~182°, $[\alpha]_D^{30}$ +151·5° in $CHCl_3$ [yields two trisaccharides (not yet described)]. With AgOAc–AcOH–I–$CaSO_4$ in $CHCl_3$, (**VII**) yields an acetate (**VIII**), softens 90—94°, $[\alpha]_D^{25}$ +43°. Purification of (**V**) or (**VIII**) by "flowing" chromatography on Al_2O_3 (freed from alkali by AcOH) yields pure 6-β-D-*mannosido*-β-D-*glucose octa-acetate* (normal form), softens 90—95°, $[\alpha]_D^{19}$ +38·9° in $CHCl_3$, from which alkali removes eight Ac. R. S. C.



(*A*.)

Synthesis of an epimeric pair of trisaccharides containing mannose units. E. A. Talley and W. L. Evans (*J. Amer. Chem. Soc.*, 1943, **65**, 573—574).—β-*D*-Mannose or -glucose 1 : 2 : 3 : 4-tetra-acetate with acetobromo-6-β-*D*-mannosido-*D*-glucose, $CaSO_4$, Ag_2O, and I in $CHCl_3$ gives 12-β-D-*mannosido*-epi-β- (**I**) (46%), m.p. 112—113° (corr.), $[\alpha]_D^{23}$ +14·3° in C_6H_6, +11·2° in $CHCl_3$, and *-β-gentiobiose hendeca-acetate* (58%), m.p. 118—119° (corr.), $[\alpha]_D^{24}$ +20·2° in $CHCl_3$, respectively, insol. in Et_2O. The possible identity of (**I**) with the trisaccharide acetate from "Konjac" mannan (Nishida *et al.*, A., 1930, 1413) is discussed. R. S. C.

Synthetic glycosides of strophanthidin. F. C. Uhle and R. C. Elderfield (*J. Org. Chem.*, 1943, **8**, 162—169).—Strophanthidin is converted by acetobromoglucose in anhyd. dioxan containing Ag_2CO_3, anhyd. $MgSO_4$, and I into *strophanthidin* β-d-*glucoside tetra-acetate*, m.p. 240—250°, softens at ~165° dependent on rate of heating, $[\alpha]_D^{27}$ +24° in $CHCl_3$. *Strophanthidin* β-d-*galactoside tetra-acetate* has m.p 236—237° (decomp.), softens at 230°, $[\alpha]_D^{28}$ +16° in $CHCl_3$, β-d-*xyloside triacetate*, m.p. 240—250° (decomp.) after softening, $[\alpha]_D^{28}$ −10° in $CHCl_3$, and β-l-*arabinoside triacetate*, m.p. ~200° (decomp.), softens at ~155° greatly dependent on rate of heating. The acetates are hydrolysed by $Ba(OMe)_2$ in MeOH to *strophanthidin* β-d-*glucoside*, m.p. 234—236° (decomp.), softens at 228°, $[\alpha]_D^{28}$ +21° in H_2O, β-d-*xyloside*, m.p. 152—154° (decomp.), $[\alpha]_D^{28}$ +7° in 95% EtOH, β-l-*arabinoside*, m.p. ~210° (decomp.) after softening, $[\alpha]_D^{30}$ 31° in EtOH, and non-cryst. β-*d*-galactoside. Pharmacologically the glycoside acetates are considerably less potent than the glycosides, which, in turn, are more potent than the aglycons. Introduction of Ac into the latter causes greatly increased activity whereas acetylation of the sugar compound lowers activity in most cases. The activity of the glycosides falls

within the same general range whereas that of their acetates varies over a much wider range. H. W.

Constitution of the polysaccharide synthesised by the action of crystalline muscle-phosphorylase. W. Z. Hassid, G. T. Cory, and R. M. McCready (*J. Biol. Chem.*, 1943, **148**, 89—96).—The *polysaccharide* (**I**), $[\alpha]_D$ +150° in N-NaOH, synthesised by the action of cryst. muscle-phosphorylase on glucose 1-phosphate is similar in properties to that formed by potato-phosphorylase and to the amylose fraction from potato starch. It is sparingly sol. in H_2O and rapidly retrogrades from solution; it produces a more intense blue colour with I than do natural starches and in contrast to the latter is almost completely hydrolysed to maltose by β-amylase. It does not activate muscle-phosphorylase. The methylated synthetic muscle-polysaccharide gives 0·6% of tetramethylglucose on hydrolysis, indicating a chain length of ~200 units. The main product of hydrolysis is 2 : 3 : 6-trimethylglucose; a small amount of dimethylglucose is also present. (**I**) appears to consist of long, unbranched chains in which the glucopyranose units are joined by α-glucosidic linkings between $C_{(1)}$ and $C_{(4)}$. H. W.

Solution viscosities of the amylose components of starch. J. F. Foster and R. M. Hixon (*J. Amer. Chem. Soc.*, 1943, **65**, 618—622).—The dependence of η in $(CH_2{\cdot}NH_2)_2$ on concn. is determined for amylose pptd. from maize, potato, tapioca, and lily bulb starch by BuOH, "cryst." amylose and amylodextrin from maize, amylose extracted from maize by hot H_2O, and synthetic starch. The results fully confirm the deductions from titration by I (Bates *et al.*, A., 1943, II, 157). Synthetic starch behaves anomalously in both cases, probably owing to heterogeneity. R. S. C.

Determination of the liquefaction of starch. K. Mayer (*Z. physiol. Chem.*, 1939, **262**, 29—36).—The liquefaction of starch by enzyme solutions which contain saccharifying enzymes can be studied by using as substrate starch which has been oxidised by I. This material is not attacked by saccharifying amylases. H. W.

Changes of starch during oxidation. F. F. Farley (*Iowa State Coll. J. Sci.*, 1942, **17**, 57—59; cf. A., 1938, II, 474).—Hydrolysis of maize starch (**I**) paste oxidised by Br produces 50·7% glycuronic anhydride equiv. and the presence of glycuronic acid units was confirmed by its isolation. Oxime formation is equiv. to a *sec.* OH in 65—75% of the glucose anhydride units. CO_2H groups are produced in excess of the uronic acid units and there is evidence for splitting of hexose units at a glycol grouping. A mechanical theory of the electrolytic oxidation of (**I**) granules by alkaline NaOCl is proposed; industrial application of the theory depends on cheap power and the discovery of a suitable anode to replace Pt. F. R. G.

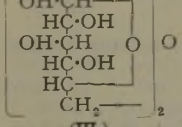
Configuration of starch and the starch–iodine complex. I. Dichroism of flow of starch–iodine solutions. R. E. Rundle and R. R. Baldwin. **II. Optical properties of crystalline starch fractions.** R. E. Rundle and D. French (*J. Amer. Chem. Soc.*, 1943, **65**, 554—558, 558—561).—I. After staining with I, blue-staining starch pastes and the BuOH-ppt. (**I**) from maize or potato starch show dichroism of flow (qual. observation described); red-staining starches, waxy maize and glutinous rice starches show only traces of dichroism; glycogen and the residue from (**I**) purified by adsorption on cellulose show no dichroism. The dichroic solutions absorb light with its electric vector parallel to the flow lines more strongly than if the vector is normal thereto. The dichroism requires that the long axes of the I mols. be parallel to the long axes of the starch–I complex; of two possible structures, one (*A*) is that in which the starch forms a helix enclosing the I (cf. Freudenberg, A., 1940, II, 120).

II. The cryst. amylose of Kerr *et al.* (A., 1943, II, 156) consists of optically negative, probably uniaxial platelets; after staining with I, these are highly dichroic, light with its electric vector in the plane of the platelets being the more weakly absorbed. The birefringence of (**I**) is very similar; (**I**) forms rosettes of flattened spherocrystals and probably consists of the platelets of Kerr *et al.* with the normals in one plane. These results are in best accord with structure (*A*); a three-dimensional structure is proposed. R. S. C.

Oxidation of cellulose; reaction of cellulose with periodic acid. H. A. Rutherford, F. W. Minor, A. R. Martin, and M. Harris (*J. Res. Nat. Bur. Stand.*, 1942, **29**, 131—141).—In the early stages of the oxidation of cellulose by HIO_4 (when ~1% of the glucose residues is attacked) the reaction is confined to the oxidation of *sec.* OH groups to CHO and results in the rupture of the C chain between $C_{(2)}$ and $C_{(3)}$ of the glucose unit. In accordance with this mechanism 2 CHO result from each mol. of HIO_4 consumed. ·CHO of periodic acid-oxycellulose (**I**) can be converted into ·CO_2H, titration of which provides an independent check on the content of the former. (**I**) is characterised by its susceptibility to further attack by alkaline solutions. The alkali-sensitivity of these materials, as measured by solubility in hot, dil. NaOH and by cuprammonium fluidity, appears ∝ CHO content. Alkali-lability practically ceases with the complete transformation of ·CHO into ·CO_2H. This suggests that the sensitivity of (**I**) to alkali does not depend solely on the rupture of the glucose ring between $C_{(2)}$ and $C_{(3)}$ but is related to the sp. instability towards alkali of the dialdehyde formed during the oxidation. H. W.

Fractionation of cellulose acetate. A. M. Sookne, H. A. Rutherford, H. Mark, and M. Harris (*J. Res. Nat. Bur. Stand.*, 1942, **29**, 123—130).—By fractional pptn. by EtOH from $COMe_2$ solution 2 kg. of technical cellulose acetate has been separated into 15 fractions varying in degree of polymerisation from 30 to 380. The distribution of chain lengths in the initial material (excepting the first fraction) is deduced from the viscosimetrically-determined chain lengths of the fractions. The first fraction is not completely sol. in $COMe_2$ or $OH{\cdot}[CH_2]_2{\cdot}OMe$ and therefore no estimate of the degree of polymerisation can be obtained. A large proportion of the ash and haze-producing materials is contained in this first fraction. All the other fractions have very low ash contents and with the exception of the fractions of very low degree of polymerisation the Ac contents are const. A phase diagram showing some of the solubility relationships of the starting material and several of the fractions is given. H. W.

Formation of anhydro-structures by alkaline deacylation of a partly substituted cellulose acetate *p*-toluenesulphonate. T. S. Gardner and C. B. Purves (*J. Amer. Chem. Soc.*, 1943, **65**, 444—449).—A cellulose acetate *p*-toluenesulphonate (A., 1942, II, 397) containing 0·196 primary and 0·054 *sec.* p-$C_6H_4Me{\cdot}SO_3$ per glucose residue with an excess of N-NaOH in MeOH gives an anhydrocellulose (**I**), analysis of which and of the derived (Ac_2O–C_5H_5N; 60°) acetate (**II**) suggests presence of 0·060 OMe, 0·007 p-$C_6H_4Me{\cdot}SO_3$, and 0·183 anhydro-groups per glucose residue. With 2·3% HCl–MeOH at 130° (40—50 hr.), (**II**) gives the equilibrium mixture (0·025 mol.) of α- and β-3 : 6-anhydroglucofuranoside and an anhydrodihexose (**III**) (0·022 mol.) [Me_6 derivative (**IV**), b.p. 136—140°/10^{-3} mm., $[\alpha]_D^{20}$ +94° in $CHCl_3$]. (**III**) probably has the structure shown, since (**IV**) is stable to hydrolysis and methanolysis and having regard to the current interpretation of the action of alkali on *p*-toluenesulphonates. Since (**I**) has a chain-length ~200 and swells, but does not dissolve, in 5—17% aq. NaOH, cuprammonium or Triton F solution, or org. solvents, it probably contains many (**III**) units joined by 1 : 4- and crossed linkings. R. S. C.


(III.)

III.—HOMOCYCLIC.

Physical data of monoalkyl*cyclo*-pentenes and -pentanes. A. W. Schmidt and A. Gemassmer (*Ber.*, 1940, **73**, [*B*], 359—366).—Grignard synthesis from AlkCl and *cyclo*pentanone gives 1-alkyl-Δ^1-*cyclo*pentenes, hydrogenated (PtO_2–AcOH) to *cyclo*pentanes (cf. A., 1939, II, 361). The following are prepared: 1-*octyl*-, m.p. −36·5°, b.p. 110—111°/11 mm., -*decyl*-, m.p. −16·5°, b.p. 111°/0·05 mm., -*dodecyl*-, m.p. −2·5°, b.p. 117°/0·1 mm., -*tetradecyl*-, m.p. 11·5°, b.p. 128—130°/0·05 mm., -*hexadecyl*-, m.p. 24·5°, b.p. 148—150°/0·05 mm., and -*octadecyl*-Δ^1-cyclo*pentene*, m.p. 30·5°, b.p. 178—180°/0·05 mm.; n-*octyl*-, m.p. −44·5°, b.p. 106°/10 mm., -*decyl*-, m.p. −23·5°, b.p. 117—118°/0·06 mm., -*dodecyl*-, m.p. −7·5°, b.p. 116—117°/0·05 mm., -*tetradecyl*, m.p. 8°, b.p. 129°/0·05 mm., -*hexadecyl*-, m.p. 19·5°, b.p. 149°/0·05 mm., and -*octadecyl*-cyclo*pentane*, m.p. 28°, b.p. 180°/0·05 mm. Other physical consts., *e.g.*, *d* and η, are recorded, and some m.p. curves are shown. A. T. P.

Production of aromatic hydrocarbons.—See B., 1943, II, 210.

Poly*iso*propylbenzenes. I. Preparation and properties of two di-, two tri-, and one tetra-*iso*propylbenzene. A. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 320—323).—In presence of 96% H_2SO_4 at 30—40° C_6H_6 and C_3H_6 give $C_6H_4Pr^{\beta}_2$ (1 : 3- : 1 : 4- 58·6 : 41·4 pts.), $C_6H_3Pr^{\beta}_3$ (1 : 2 : 4- : 1 : 3 : 5- 83·7 : 16·3 pts.), $C_6H_4Pr^{\beta}_4$ (only 1 : 2 : 4 : 5-), and alkyl sulphates. In presence of $AlCl_3$ at 60°, there are formed $C_6H_4Pr^{\beta}_2$ (1 : 3- : 1 : 4- 65·4 : 34·6 pts.), $C_6H_3Pr^{\beta}_3$ (only 1 : 3 : 5-), and $C_6H_2Pr^{\beta}_4$ (only 1 : 2 : 4 : 5-). Physical properties of the products are given. R. S. C.

Rearrangements in the Friedel–Crafts alkylation of benzene. H. Gilman and R. N. Meals (*J. Org. Chem.*, 1943, **8**, 126—146).—Examination of the literature shows that primary alkyl compounds give both primary and *sec.*-alkylbenzenes and higher temp. favour the formation of the latter. *sec.*-Alkyl compounds afford *sec.* and never primary alkylbenzenes. *iso*Alkyl compounds appear to have little tendency to form *iso*alkylbenzenes and give largely *tert.*-alkylbenzenes which are the exclusive products from *tert.*-alkyl compounds. Under mild experimental conditions C_6H_6 and a primary *n*-alkyl bromide in presence of $AlCl_3$ give a mixture of alkylbenzenes in which Ph is probably attached to each C of the alkyl residue. The evidence obtained does not indicate any appreciable branching of the alkyl chain under the experimental conditions used. n-$C_6H_{13}Br$ and C_6H_6 in presence of $AlCl_3$ give α-, β-, and γ-phenylhexane and n-$C_{12}H_{25}Br$ affords a mixture of dodecylbenzenes in which α- and ζ-phenyldodecane have been identified. The α-Ph derivatives have been isolated from C_6H_6 and n-$C_{14}H_{29}Br$, n-$C_{16}H_{33}Br$, and n-$C_{18}H_{37}Br$. The α-phenylalkanes are prepared

synthetically by Clemmensen reduction of the appropriate Ph alkyl ketone or by the Wurtz–Fittig reaction. *sec.*-Alkylbenzenes are obtained from the appropriate ketone and Grignard reagent followed by dehydration of the carbinol with 60% H_2SO_4 and subsequent reduction of the olefine by Na and EtOH. The hydrocarbons are finally transformed into their sulphonamides or derivatives thereof. The following are described: n-*hexadecyl*-, b.p. 202—213°/7 mm., n-*tetradecyl*-, b.p. 188—189°/6 mm., n-*dodecyl*-, b.p. 164°/4 mm., n-*heptyl*-, b.p. 240—244°/1 atm., and n-*hexyl-benzene*, b.p. 220—222°/1 atm.; *β-phenyldodecan-β-ol*, b.p. 174—177°/7 mm.; *γ-phenyldodecan-γ-ol*, b.p. 168°/5 mm.; *γ-phenyldodecan-δ-ol*, b.p. 170°/4 mm., *ε-phenyldodecan-ε-ol*, b.p. 166—168°/5 mm., *ζ-phenyldodecan-ζ-ol*, b.p. 169—170°/6 mm., *β*-phenylhexan-*β*-ol, b.p. 120°/10 mm., and *γ*-phenylhexan-*γ*-ol, b.p. 134°/27 mm., *β*-, b.p. 160—162°/5 mm., *γ*-, b.p. 165°/7 mm., *δ*-, b.p. 153—154°/5 mm., *ε*-, b.p. 156—157°/6 mm., and *ζ*-, b.p. 161°/9 mm., -phenyldodecene, *β*-, b.p. 125—130°/42 mm., and *γ*-, b.p. 125—130°/56 mm., -phenylhexene; *β*-, b.p. 161°/7 mm., *γ*-, b.p. 171°/13 mm., *δ*-, b.p. 164°/17 mm., *ε*-, b.p. 158°/7·5 mm., and *ζ*-, b.p. 153°/6 mm., -phenyldodecane, *β*-, b.p. 208·7—210°/741 mm., and *γ*-, b.p. 200—203·5°/1 atm., -phenylhexane; *hexadecyl*-, m.p. 97°, *tetradecyl*-, m.p. 97·5—98°, *dodecyl*-, m.p. 97·5°, *α-methylundecyl*-, m.p. 99°, *α-ethyldecyl*-, m.p. 56°, *α*-n-*propylnonyl*-, m.p. 60°, *heptyl*-, m.p. 90·5°, *hexyl*-, m.p. 86°, and *α-methylamyl*-, m.p. 83°, *-benzenesulphonamides*; *α-ethyldecyl*-, m.p. 103°, *α*-n-*propylnonyl*-, m.p. 112—112·5°, *α*-n-*butyloctyl*-, m.p. 107—107·5°, and *α*-n-*amylheptyl*-, m.p. 128°, *-β-naphthalenesulphonamides*; *acetamido*-derivatives, m.p. 91°, 76°, and 127°, respectively, of *α*-, *β*-, and *γ-hexylbenzene* and corresponding *diacetamido*-compounds, m.p. 200—202°, 178°, and 199—201°, respectively. H. W.

Polymerisation of styrene in presence of 3 : 4 : 5-tribromobenzoyl peroxide. C. C. Price and B. E. Tate (*J. Amer. Chem. Soc.*, 1943, **65**, 517—520).—3 : 4 : 5 : 1-$C_6H_2Br_3{\cdot}CO_2H$ [best (60%) prepared from *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ according to Sudborough (A., 1894, i, 244)] with $SOCl_2$ and then Na_2O_2–C_6H_6 at 0·5° gives *di*-3 : 4 : 5-*tribromobenzoyl peroxide* (**I**) (18%), m.p. 183—185°. With (**I**) in C_6H_6 or dioxan, $CH_2{:}CHPh$ (**II**) gives *polymers*, $C_6H_2Br_3(C_8H_8)_{12}O_3$, $C_6H_2Br_3(C_8H_8)_{15}O_7$, and $C_6H_2Br_3(C_8H_8)_{36}O_{19}$. Presence of one $C_6H_2Br_3$ per mol. indicates the reaction mechanism, but the source of the O is unknown. Very little Br is introduced into polystyrene (**III**) by (**I**) in C_6H_6. *k* for removal of (**I**) from C_6H_6 at 80° in presence of (**II**) is 0·0102—0·0108, but in presence of (**III**) is 0·0019. Bz_2O_2 and (**II**) in dioxan give a *polymer*, $Ph(C_8H_8)_{31}O_3$, only slightly degraded by boiling conc. HCl–AcOH. O-free (**III**) is unaffected by peroxide-containing dioxan in light. R. S. C.

Ester groups in polystyrene made with chloro- and bromo-benzoyl peroxides. P. D. Bartlett and S. G. Cohen (*J. Amer. Chem. Soc.*, 1943, **65**, 543—546).—Styrene and (*p*-$C_6H_4Br{\cdot}CO_2)_2$ (**I**) (explodes at 148°) in boiling C_6H_6 give polymers containing 10·7% (**II**) and 11·5% of Br. (**II**) is stable to boiling 20% aq. KOH (cf. Price *et al.*, A., 1942, II, 304), but, when boiled for a long time with NaOEt–EtOH, yields 53% of *p*-$C_6H_4Br{\cdot}CO_2H$ and a residue containing 36% of the Br. Thus, (**II**) contains ~36% of the (**I**) as *p*-C_6H_4Br and ~64% as *p*-$C_6H_4Br{\cdot}CO_2$. Hydrolysis of (**II**) by NaOEt–EtOH–PhMe with later addition of H_2O is less satisfactory. Styrene and (*p*-$C_6H_4Cl{\cdot}CO_2)_2$ (decomp. 138°) at 81—84° and then 100—103° give a polymer containing 0·096% of Cl, which by hydrolysis by NaOEt–EtOH–PhMe with later addition of H_2O is shown to contain ~12% of *p*-C_6H_4Cl, but the Cl content (0·015%) of the monomer renders this result uncertain. R. S. C.

Addition of triphenylmethyl to β-methyl-Δ$^{\alpha}$-buten-γ-inene. A. F. Thompson, jun., and D. M. Surgenor (*J. Amer. Chem. Soc.*, 1943, **65**, 486—487).—CPh_3Cl, Hg, and $CH{:}C{\cdot}CMe{:}CH_2$ in C_6H_6–N_2 at room temp. give *aaayyy-hexaphenyl-δ-methyl-*Δ$^{\beta\gamma}$*-hexadiene* (47%), m.p. 184—185·5° [contains 2 C:C (H_2–PtO_2–AcOH)], which with O_3 in EtOAc at 0°, then H_2–Pd–$CaCO_3$, and finally Ag_2O gives $CPh_3{\cdot}CO_2H$ and $COMe{\cdot}CH_2{\cdot}CPh_3$. R. S. C.

Dialkylation of naphthalene. II. Synthesis of 2 : 6-diphenylnaphthalene. C. C. Price and A. J. Tomisek (*J. Amer. Chem. Soc.*, 1943, **65**, 439—440; cf. A., 1943, II, 126).—Phenylsuccinic anhydride (prep. from the acid by AcCl), Ph_2, and $AlCl_3$ in boiling CS_2 give *4-β-carboxy-α-phenylpropionyldiphenyl*, m.p. 175·5—176°, oxidised by $KMnO_4$ to *p*-$C_6H_4Ph{\cdot}CO_2H$ and reduced by Zn–Hg–conc. HCl–AcOH–C_6H_6 to *β-phenyl-γ-4-diphenylylbutyric acid*, m.p. 120·5—121°, which with, successively, $SOCl_2$, $AlCl_3$–CS_2, Zn–Hg–HCl–AcOH–C_6H_6, and Se at 290—320° gives 2 : 6-$C_{10}H_6Ph_2$, m.p. 233—234°, thus proving the structures of the products of Boudroux (A., 1929, 1050) and Pokrovskaja *et al.* (A., 1940, II, 161). R. S. C.

Electronic distribution and chemical reactivity in condensed unsaturated hydrocarbons. N. Svartholm (*Arkiv Kemi., Min., Geol.*, 1942, **15**, **A**, No. 13, 13 pp.).—A discussion of the $C_{10}H_8$ mol. indicates that a picture of the electron distribution can be obtained by a comparison of separate superposition diagrams for unexcited and singly excited structures. This method is applied to anthracene, phenanthrene, chrysene, 1 : 2-benzanthracene (**I**), pyrene, 1 : 2 : 3 : 4- and 1 : 2 : 5 : 6-dibenzanthracene, and 3 : 4-benzpyrene. A closer quantum-mechanical study of electron distribution in (**I**) gives a superposition diagram in general agreement with the simpler treatment. Electron distributions in (**I**) and the three last-named compounds are briefly correlated with chemical reactivity. A. J. E. W.

Action of magnesium methyl iodide on methyl α-phenylcinnamate. Synthesis of 2-phenyl-1 : 1-dimethylindene. C. F. Koelsch and P. R. Johnson (*J. Amer. Chem. Soc.*, 1943, **65**, 565—567).—$CHPh{:}CPh{\cdot}CO_2H$ (**I**) (from $CH_2Ph{\cdot}CO_2H$, PhCHO, and NaOAc in Ac_2O) with MeOH–H_2SO_4 gives the Me ester, which with MgMeI in Et_2O gives $CHPh{:}CPh{\cdot}CMe_2{\cdot}OH$ (**II**) (50%), m.p. 69—70° (lit. 68°) (absorbs Br; gives no CHI_3). $Ph{\cdot}[CH_2]_2{\cdot}CO_2H$ [obtained (85%) by electrolytic reduction of (**I**)] gives the Me ester, b.p. 168°/8 mm., which with MgMeI–Et_2O yields *γδ-diphenyl-β-methylbutan-β-ol* (86—88%), m.p. 68—69°, dehydrated by H_2SO_4–AcOH at 100° to *αβ-diphenyl-γ-methyl-Δ$^{\beta}$-n-butene* (**III**), b.p. 150°/10 mm. Oxidation of (**III**) by CrO_3–AcOH at room temp. gives $CH_2Ph{\cdot}COPh$, but Br in $CHCl_3$, later boiling AcOH, gives *2-phenyl*-1 : 1-*dimethylindene* (**IV**) (45%), m.p. 61—62°, also obtained in ~10% yield from (**II**) by H_2SO_4–AcOH and oxidised by CrO_3–AcOH to *α-o-carboxyphenyl-isobutyrophenone* (**V**), m.p. 210—211° (stable to $KMnO_4$). The products of Earl *et al.* (A., 1931, 340) formulated as (**IV**) and (**V**) are 3-phenyl-1 : 1-dimethylindene and *α-o-benzoylphenylisobutyric acid*, respectively. R. S. C.

Thermal isomerisation of indene derivatives. C. F. Koelsch and P. R. Johnson (*J. Amer. Chem. Soc.*, 1943, **65**, 567—573).—Pyrolysis of 1 : 3- (**I**), 1 : 2- (**II**), or 2 : 3-diphenylindene (**III**) at 450° in N_2 gives an equilibrium mixture, (**I**) 8—20%, (**II**) 4—6%, (**III**) 47—65%, which is unchanged by further pyrolysis (cf. A., 1940, II, 355). The still readier isomerisation, (**III**) ⇌ (**III**), prevents deduction whether the Ph migrates from $C_{(3)}$ or $C_{(1)}$. The possibility of migration from $C_{(1)}$ is proved by three examples. (i) At 490° 1 : 1 : 3-triphenylindene [prepared by interaction of $CPh_2{:}CH{\cdot}MgBr$ with $COPh_2$ to give $CPh_2{:}CH{\cdot}CPh_2{\cdot}OH$ (in AcOH gives $CPh_2{:}C{:}CPh_2$) and subsequent dehydration by H_2SO_4–AcOH; 64% yield] gives 86% of 1 : 2 : 3-triphenylindene (and a red gum), which is also obtained from 2 : 3-diphenylindone by MgPhBr, followed by AcOH + H_2SO_4 (1 drop). (ii) Rapid pyrolysis of 3′-phenyl*spiro*fluorene-9 : 1′-indene (**IV**) at 490° gives, probably reversibly, 80% of 9-phenyl-1 : 2 : 3 : 4-dibenzfluorene and 17% of unchanged (**IV**). (iii) 1 : 3-Diphenyl-1-methylindene (prep. from 3-phenyl-3-methylindan-1-one by MgPhBr and then H_2SO_4–AcOH), m.p. 59—60°, at 470° gives irreversibly 82% of a mixture of 2 : 3-*diphenyl*-1- (**V**), m.p. 106·5°, and 1 : 2-*diphenyl*-3-*methylindene* (**VI**), m.p. 91°, and an oil which with CrO_3–AcOH yields *o*-$C_6H_4Bz_2$, *o*-$C_6H_4Bz{\cdot}CO_2H$ (**VII**), and BzOH; the (**VII**) is derived from 1 : 3-diphenyl-3-methylindene, formed to a small extent by migration of Me. Structures are proved as follows. Crude $CHMeBr{\cdot}CHBr{\cdot}CO_2H$ (prep. from $CHMe{:}CH{\cdot}CO_2H$ and Br in Et_2O at 10—15°) with C_6H_6 and $AlCl_3$ gives $CHPhMe{\cdot}CHPh{\cdot}CO_2H$, m.p. 182—183° (lit. 180—181°), which with hot PCl_5– and then $AlCl_3$–C_6H_6 gives *2-phenyl-3-methylindanone* (70%), m.p. 84·5—86°, b.p. 196—200°/13 mm.; with MgPhBr and then 1% H_2SO_4–AcOH this gives 79% of (**V**). 2 : 3-Diphenylindanone similarly yields 70% of (**VI**). Me migrates only if the ring contains also Ph. 3-Methylindone, b.p. 91—92°/24 mm. [$OMe{\cdot}C_6H_4{\cdot}CH{:}$ derivative, m.p. 114—115° (lit. 113°); picrate, m.p. 76—77°], in 1% H_2SO_4–AcOH at room temp. yields a non-volatile, oily polymeride, depolymerised by distillation with a few drops of H_2SO_4 at 1 atm., but is unchanged by pyrolysis at 490° (cf. Mayer *et al.*, A., 1921, i, 554). 2-Hydrindone and MgMeI give 2-methylindan-2-ol (**VIII**) (73%), m.p. 52—53° (lit. 52°), anhydrobis-2-hydrindone (**IX**), m.p. 173—176°, and a product, m.p. 156—157°, probably obtained from (**IX**) and MgMeI; dehydration of (**VIII**) in boiling C_6H_6 by P_2O_5 (H_2SO_4–AcOH gives a polymeride) gives 2-methylindene (55%), b.p. 97—99°/24 mm. (unstable picrate, m.p. 79—79·5°), unchanged by pyrolysis at 490°. At 490° 3-phenyl-1 : 1-dimethylindene (**X**), m.p. 50—51°, b.p. 184—187°/27 mm. [(? 2-)*NO*$_2$-derivative, m.p. 141—142°], gives ~63% of unchanged (**X**) and 26% of 3-phenyl-1 : 2- (**XI**) + 1-phenyl-2 : 3-dimethylindene (**XII**), since the oily mixture with CrO_3–AcOH at room temp. yields *o*-$C_6H_4Bz{\cdot}CMe_2{\cdot}CO_2H$ (**XIII**) and *2-acetylbenzophenone* (**XIV**), m.p. 99° [*disemicarbazone*, m.p. 214—216° (decomp.)], whereas (**X**) gives only (**XIII**) and (**XII**) gives only (**XIV**). Pyrolysis of (**XII**) also gives (**X**), (**XI**), and (**XII**). 60% of unchanged 2-phenyl-1 : 1-dimethylindene is recovered after pyrolysis at 490°, but the oily fraction yields *o*-$C_6H_4Bz{\cdot}CO_2H$ (indicating migration of Ph from $C_{(2)}$), and possibly (**XIII**), which would arise from (**X**). Migration from $C_{(2)}$ thus occurs if $C_{(1)}$ is fully substituted, but a secondary rearrangement then occurs. A mobile H on the indene is essential for the migration. The reaction mechanisms are discussed. R. S. C.

Resonance structure of anthracene and phenanthrene. C. V. Jonsson (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 14, 9 pp.).—The electron distributions, bond strengths, and resonance energies (*R*) in $C_{10}H_8$, anthracene (**I**), and phenanthrene (**II**) are considered. A simplified quantum-mechanical treatment is employed in which only unexcited and singly excited canonical structures are included; the no. of structures to be considered is thus reduced to 52 for (**I**)

or (**II**). For (**I**) and (**II**), respectively, $R = 4{\cdot}54$ and $4{\cdot}78$ e.v., and vals. of the exchange integral (which are probably several % too high) are $1{\cdot}60$ and $1{\cdot}63$. The relative strength of a linking can be estimated by counting the no. of possible unexcited structures in which it occurs. A less reliable estimate of the probable electron density at a given atom may be made by counting the no. of singly excited structures in which ineffective linkings start from that atom. A. J. E. W.

Dehydrogenation. VII. S. C. Sen-Gupta (*J. Indian Chem. Soc.*, 1942, **19**, 467—472).—With C_6H_6 ($AlCl_3$), the anhydride of 1-carboxy-*cyclo*hexyl-1-acetic acid (at room temp., then at 60—65°) [or the acid chloride of Me 1-carboxy*cyclo*hexyl-1-acetate (at room temp.)] yields 1-*phenacyl*- (**I**), m.p. 117—118° (*semicarbazone*, m.p. 132—133°), [or its *Me* ester, b.p. 165—170°/3 mm., m.p. 65—66°], reduced (Clemmensen) to 1-*β-phenylethyl*-cyclo*hexane*-1-*carboxylic acid*, m.p. 93° (*Et* ester, b.p. 111—112°/5 mm.; *anilide*, m.p. 130—131°), cyclised by 75% (vol.) H_2SO_4 to 1-*keto*-, b.p. 145°/3 mm. (*semicarbazone*, m.p. 187—188°), which on Clemmensen reduction yields 1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 2-spirocyclo*hexane*, b.p. 115—117°/3 mm. Se-dehydrogenation of this yields phenanthrene. 1-p-*Methylphenacyl*- (prep. as above), m.p. 129—130° (*semicarbazone*, m.p. 166°; *Me* ester, b.p. 180—182°/5 mm., m.p. 65—66°), similarly yields 1-β-p-*tolylethyl*-cyclo*hexane*-1-*carboxylic acid*, m.p. 99—100° (*Et* ester, b.p. 115—116°/6 mm.; p-toluidide, m.p. 128—129°), and 1-*keto*-7-*methyl*-, b.p. 158—160°/4 mm. (*oxime*, m.p. 139—140°), and 7-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 2-spirocyclo*hexane*, b.p. 155—156°/8 mm., dehydrogenated to 3-methylphenanthrene, whilst 1-p-*ethylphenacyl*-, m.p. 117—118° (*semicarbazone*, m.p. 144°; *Me* ester, b.p. 202—203°/7 mm.), gives 1-β-p-*ethylphenylethyl*-cyclo*hexane*-1-*carboxylic acid*, m.p. 87—88° (*Et* ester, b.p. 104—105°/6 mm.), and 1-*keto*-7-*ethyl*-, b.p. 195—197°/9 mm. (*semicarbazone*, m.p. 203—204°), and 7-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 2-spirocyclo*hexane*, b.p. 168—169°/8 mm., dehydrogenated to 3-ethylphenanthrene. In no case was any anthracene derivative obtained. A. Li.

Aromatic cyclodehydration. X. 10-Phenyl-9-alkyl- or -9-aryl-anthracenes. C. K. Bradsher and E. S. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 451—452; cf. A., 1941, II, 127).—Crude *o*-$C_6H_4Cl{\cdot}CPh_2{\cdot}OH$ with red P and I in boiling AcOH gives *o*-$C_6H_4Cl{\cdot}CHPh_2$ (47·5%), converted by CuCN in C_5H_5N at 200° into *o*-$CN{\cdot}C_6H_4{\cdot}CHPh_2$ (**I**) (81%), m.p. 82—84° (lit. 89°). With MgPhBr, (**I**) gives an imine, hydrolysed only by boiling HCl to *o*-$C_6H_4Bz{\cdot}CHPh_2$ (60%), m.p. 84—86°, which in boiling 34% aq. HBr–AcOH (81% yield) or with 2 drops of H_2SO_4 in AcOH at 100° (95% yield) gives 9 : 10-diphenylanthracene, m.p. 247—248°. With MgRI, (**I**) gives similarly 9-phenyl-10-methyl- (50%), m.p. 112·5—113·5°, and -10-ethyl-anthracene (47·5%), m.p. 107—108·5°. R. S. C.

Condensation of unsaturated amines with aromatic compounds. Preparation of β-substituted phenylethylamines. A. W. Weston, A. W. Ruddy, and C. M. Suter (*J. Amer. Chem. Soc.*, 1943, **65**, 674—677).—In presence of $AlCl_3$ (3 mols.), but not of BF_3–Et_2O or conc. H_2SO_4, at 0° and later the b.p., $CH_2{:}CH{\cdot}CH_2{\cdot}NH_2$ (1 mol.) and C_6H_6 (excess) give 85—94% of $CHPhMe{\cdot}CH_2{\cdot}NH_2$ (**I**), b.p. 97—98°/19 mm. [m.p. 143—144·5° (lit. 146—147°, 123—124°); this and other m.p. in parentheses refer to the hydrochlorides]. PhF and PhMe give similarly mainly β-p-*fluorophenyl*- (59%), b.p. 105—106°/22 mm. (m.p. 149—150°), and β-p-*tolyl*-n-*propylamine* (90%), b.p. 116—117°/22 mm. (m.p. 174—176°), respectively, orientations being proved by oxidation to impure *p*-$C_6H_4F{\cdot}CO_2H$ and *p*-$C_6H_4(CO_2H)_2$, respectively. Condensation with PhOMe was unsuccessful. *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NMe{\cdot}CH_2{\cdot}CH{:}CH_2$ [prep. from *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NHMe$ by $CH_2{:}CH{\cdot}CH_2Cl$ (**II**) and KOH in a little EtOH; 89% yield], b.p. 190—193°/12 mm., and Na in $Bu^{\alpha}OH$ give 48% of $CH_2{:}CH{\cdot}CH_2{\cdot}NHMe$, b.p. 65°. 33% NH_2Et and (**II**) give $CH_2{:}CH{\cdot}CH_2{\cdot}NHEt$ (43%), b.p. 82—84°, and *ethyldiallylamine*, b.p. 129—130°. $CH_2{:}CH{\cdot}CH_2{\cdot}NMe_2$, b.p. 61—64°, is obtained (~30%) by shaking $NHMe_2$,HCl with (**II**) and aq. NaOH at >1 atm. 33% NH_2Me and $CH_2{:}CMe{\cdot}CH_2Cl$ in warm EtOH give *methyldi-β-methylallylamine* (78%), b.p. 145—145·5°, and *methyl-β-methylallylamine* (15%), b.p. 86—86·5°; $NHMe_2$ gives *dimethyl-β-methylallylamine* (41%), b.p. 82·4—82·6°/750 mm. The appropriate substituted allylamine with C_6H_6 and $AlCl_3$ gives β-phenyl-*n*-propyl-methyl- (**III**) (47%), b.p. 86—87°/10 mm. [m.p. 145—145·5° (lit. 148—159°)], -ethyl- (77%), b.p. 93°/10 mm. (m.p. 158·5—159·5°), -n-*butyl*- (66%), b.p. 121—123°/12 mm. (m.p. 154—155·5°), -*dimethyl*- (62%), b.p. 79—80°/10 mm. (m.p. 221—222·5°), and -*di*-n-*butyl-amine* (45%), b.p. 148—150°/12 mm., and β-*phenyl*-iso*butyl-amine* (84%), b.p. 75—76°/5 mm. (m.p. 200—201·5°), -*methylamine* (70%), b.p. 84—85°/9 mm. (m.p. 218·5—219·5°), and -*dimethylamine* (83%), b.p. 87—88°/10 mm. (m.p. 199—200°). $CHPhMe{\cdot}CH_2Br$ with NH_3–EtOH at 80—90° gives 32% of (**I**) and much $CH_2{:}CPhMe$ (**IV**), and with NH_2Me–EtOH at 5° gives 32% of (**III**) and 51% of (**IV**). The oral toxicity of most of the hydrochlorides to mice is recorded. R. S. C.

***N*-Benzylamides as derivatives for identifying the acyl groups in esters.**—See A., 1943, II, 248.

Derivatives of 1 : 2 : 4 : 5-tetrachlorobenzene. I. Nitro- and amino-compounds. A. T. Peters, F. M. Rowe, and D. M. Stead (*J.C.S.*, 1943, 233—235).—2 : 3 : 5 : 6 : 1-$C_6HCl_4{\cdot}NH_2$ (**I**), m.p. 107—108° (lit. 90°) (improved prep.) (*diazonium zincichloride*; *azo-β-naphthol*, m.p. 212°; Ac_1, m.p. 213—214°, and Ac_2 derivative, m.p. 175—176°), is diazotised by $NO{\cdot}SO_4H$ at 60°. With 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}COCl$–$PhNO_2$, (**I**) affords 2 : 3 : 5 : 6-*tetrachloro*-2′-*hydroxy*-3′-*naphthanilide*, m.p. 232°. Diazotised (**I**) with aq. NaOAc at room temp. (4 days) yields 3 : 4 : 6-trichlorobenzene-2-diazo-1-oxide, m.p. 117—118° (decomp.). 2 : 3 : 5 : 6 : 1 : 4-$C_6Cl_4(NO_2)_2$ (**II**) (modified prep.) and Sn–HCl–EtOH or $Na_2S_2O_4$–aq. EtOH give the corresponding diamine, m.p. 222—223° [Ac_1 (**III**), m.p. 276°, and Ac_4 derivative, m.p. 205—209°]. Diazotisation ($NO{\cdot}SO_4H$) of (**III**), followed by coupling, gives 2 : 3 : 5 : 6-*tetrachloro*-4-*aminobenzeneazo-β-naphthol*, m.p. 257—258° (decomp.). (**II**) with aq. $Na_2S_2O_4$–EtOH, or 2·8N-EtOH–NH_3 at 110—120°, yields 2 : 3 : 5 : 6-*tetrachloro*-4-*nitroaniline*, m.p. 216—217° [AcCl–PhMe at 110—120° gives the Ac_1, m.p. 252—253°, and boiling Ac_2O–H_2SO_4 yields the Ac_2 derivative, m.p. 168—169°, reduced by $Na_2S_2O_4$–aq. EtOH to 2 : 3 : 5 : 6-*tetrachloro*-4-*aminodiacetanilide*, m.p. 194—195°]; diazotisation ($NO{\cdot}SO_4H$ at 60°) and coupling then gives the *azo-β-naphthol*, m.p. 282—284° (decomp.), and the *azo*-2′-*hydroxy*-3′-*naphthanilide*, m.p. 296° (decomp.). 2 : 3 : 5 : 6-*Tetrachloro*-4-*nitro*-2′-*hydroxy*-3′-*naphthanilide* has m.p. 269—270°. 4 : 2 : 3 : 5 : 6 : 1-$NO_2{\cdot}C_6Cl_4{\cdot}OMe$ (**IV**), m.p. 112—113° (lit. 105—106°), prepared from 2 : 3 : 5 : 6 : 1-$C_6HCl_4{\cdot}OMe$ and HNO_3 (*d* 1·5) at 0°, or from (**II**) and 0·2N-NaOMe, is reduced by $Na_2S_2O_4$–aq. EtOH to the corresponding amine (**V**), m.p. 107—108° (Ac_2 derivative, new m.p. 105—106°; *azo-β-naphthol*, m.p. 204—205°; 2 : 3 : 5 : 6-*tetrachloro*-4-*methoxy*-2′-*hydroxy*-3′-*naphthanilide*, m.p. 208°). 2 : 3 : 5 : 6 : 1-$C_6HCl_4{\cdot}OH$ and HNO_3 (*d* 1·5)–AcOH at 10° give 2 : 3 : 5 : 6-*tetrachloro*-4-*nitrophenol*, m.p. 148—149° (decomp.) (*acetate*, m.p. 113—114°), also obtained in small yield during amination of (**II**), and in the prep. of (**IV**) by NaOMe. Diazotised (**V**) with aq. NaOAc at room temp. yields 2 : 3 : 5 : 6-*tetrachlorobenzene*-4-*diazo*-1-*oxide*, explodes at 131° (darkens at 120°), converted by Ac_2O into 2 : 3 : 5 : 6 : 1 : 4-$C_6Cl_4(OAc)_2$, and by β-$C_{10}H_7{\cdot}OH$ in 1% NaOH into 2 : 3 : 5 : 6-*tetrachloro*-4-*hydroxybenzeneazo-β-naphthol*, m.p. 264—265° (decomp.), also obtained from the diazo-oxide derived from 4 : 2 : 3 : 5 : 6 : 1-$NO_2{\cdot}C_6Cl_4{\cdot}N_2HSO_4$ (replacement of NO_2). A. T. P.

Ethyl *p*-aminobenzenesulphonate. L. A. Walter (*J. Amer. Chem. Soc.*, 1943, **65**, 739).—*Et sulphanilate*, m.p. 78—80°, unstable, is prepared by hydrogenating (PtO_2; 30—40 lb.; HCl–EtOH) *p*-$NO_2{\cdot}C_6H_4{\cdot}SO_3Et$ and is isolated as unstable *hydrochloride*. R. S. C.

Derivatives of 2 : 5-diaminobenzenesulphonamide. A. R. Goldfarb and B. Berk (*J. Amer. Chem. Soc.*, 1943, **65**, 738—739).—5 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}SO_2Cl$ (**I**) (from *p*-$C_6H_4Cl{\cdot}NO_2$ and $ClSO_3H$ at 120—130°), m.p. 85—87°, with 28% aq. NH_3 gives the amide (**II**), m.p. 184—185°, which with $CuSO_4$–$(NH_4)_2CO_3$–28% aq. NH_3 at 120° gives 5 : 2 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}SO_2{\cdot}NH_2$ (86%), m.p. 208°, reduced (alkaline $Na_2S_2O_4$) to 2 : 5 : 1-$(NH_2)_2C_6H_3{\cdot}SO_2{\cdot}NH_2$ (70%), m.p. 184°. With $CaCO_3$–CO_2 in boiling NH_2Ph, (**II**) gives 5 : 2 : 1-$NO_2{\cdot}C_6H_3(NHPh){\cdot}SO_2{\cdot}NH_2$, m.p. 168—169°, and thence ($Na_2S_2O_4$ or H_2–Raney Ni–EtOH) 5-*amino*-2-*anilinobenzenesulphonamide*, m.p. 164°. $OH{\cdot}[CH_2]_2{\cdot}NH_2$ (excess), (**I**), and KOH in H_2O give, with cooling, 2-*chloro*-5-*nitro*- (58%), m.p. 133—135°, or, without cooling, 5-*nitro*-2-β-*hydroxyethylamino*- (73%), m.p. 119—120°, converted as above into 5-*nitro*-2-*amino*-, m.p. 149—150°, 2 : 5-diamino- (*dihydrochloride*, m.p. 184°), and 5-*amino*-2-β-*hydroxyethylamino*-, m.p. 162—163°, -*benzenesulphon*-β-*hydroxyethylamide*. R. S. C.

Alkylphenols.—See B., 1943, II, 210.

***o*- and *m*-Tolyl butyrate. Preparation and properties.** B. E. Mirza and G. D. Advani (*J. Univ. Bombay*, 1943, **11**, **A**, Part 5, 87—91).—*o*- and *m*-Cresol with PrCOCl yield respectively *o*- (58) and *m*-tolyl butyrate (72·6%). Physical data are given. A. Li.

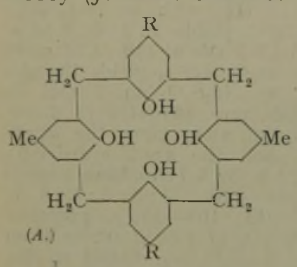
Nitrosation of phenols. XIX. The three cresols and their methyl ethers. Some semicarbazide reactions. H. H. Hodgson and E. A. C. Crouch (*J.C.S.*, 1943, 221—223).—HNO_2 reacts normally with *o*- and *m*-cresol to give 5 : 1 : 2- (**I**) and 6 : 1 : 3-$NO{\cdot}C_6H_3Me{\cdot}OH$ (**II**), respectively; *p*-cresol similarly affords 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}OH$. $NO{\cdot}SO_4H$ and *o*-$C_6H_4Me{\cdot}OMe$ in AcOH at 0°, then at room temp. for 3 days, yield 3 : 5 : 1 : 2-$(NO_2)_2C_6H_2Me{\cdot}OH$ (**III**), but at ≯−5° give 5-*nitroso*-o-*tolyl Me ether* (**IV**), m.p. 53·5°. (**I**) and (**IV**) are oxidised by dil. HNO_3 at 40° to (**III**). *m*-$C_6H_4Me{\cdot}OMe$ similarly gives 6 : 1 : 3-$NO_2{\cdot}C_6H_3Me{\cdot}OH$ (**V**) or 6-*nitroso*-m-*tolyl Me ether* (**VI**), m.p. 22°. Oxidation (dil. HNO_3) of (**II**) and (**VI**) gives (**V**). (**VI**) and NH_2OH,HCl–NaOAc–β-$C_{10}H_7{\cdot}OH$–aq. EtOH afford 4-*methoxy*-2-*methylbenzeneazo-β-naphthol*, m.p. 193°; (**IV**) does not react similarly. *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ with (**IV**) or (**VI**) gives 4′-*nitro*-4-*methoxy*-3-, m.p. 187·5°, or 4′-*nitro*-4-*hydroxy*-2-*methyldiazoaminobenzene*, m.p. 205° (decomp. from 185°), respectively. With $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl and NaOAc in MeOH, (**IV**) yields probably 4 : 3 : 1-$OMe{\cdot}C_6H_3Me{\cdot}N(OH){\cdot}N{:}N{\cdot}CO{\cdot}NH_2$, converted by boiling NH_2Ph into 4-*methoxy*-3-*methylhydrazobenzene*-N-*diazocarboxylamide*, m.p. 238°, whereas (**VI**) affords 5-*methoxy*-2-*methylbenzene*-*diazoaminocarboxylamide*, m.p. 230°, unchanged by boiling NH_2Ph.

The difference in reactivity of (**IV**) and (**VI**) is ascribed to the different anionoid character of the O atoms of the NO-groups. A. T. P.

Oxidation of resorcinol by hydrogen peroxide in presence of tungstic acid sol as catalyst.—See A., 1943, II, 217.

Preparation of 4-nitroresorcinol. N. B. Parekh and R. C. Shah (*J. Univ. Bombay*, 1943, **11**, **A**, Part 5, 101—103).—2 : 4 : 1-$(OH)_2C_6H_3{\cdot}CO_2H$ with HNO_3 (*d* 1·42) at room temp. yields 5 : 2 : 4 : 1-$NO_2{\cdot}C_6H_3(OH)_2{\cdot}CO_2H$ (Me ester similarly prepared), decarboxylated by AcOH–HCl–H_2O in a sealed tube at 140—145° to 4 : 1 : 3-$NO_2{\cdot}C_6H_3(OH)_2$, m.p. 122° (cf. lit.). A. Li.

Indirect phenol–aldehyde condensations. J. B. Niederl and J. S. McCoy (*J. Amer. Chem. Soc.*, 1943, **65**, 629—631).—Contrary to Koebner (B., 1933, 514), 4 : 1 : 3 : 5-$OH{\cdot}C_6H_2Me(CH_2{\cdot}OH)_2$ (**I**) and *p*-cresol with a little conc. HCl at room temp. (exothermic reaction rising to 63°) or with HCl gas in AcOH give a *product*, $C_{32}H_{32}O_4,H_2O$ (*A*; R = Me), m.p. 215° (*tetra-acetate*, m.p. 125°). *p*-$C_6H_4Br{\cdot}OH$ and (**I**) in HCl–AcOH give a similar product (*A*; R = Br), m.p. 210° (*tetra-acetate*, m.p. 111°). The "blocked" *m*-4-xylenol and (**I**) in HCl–AcOH give 3 : 5-di-(2′-hydroxy-3′ : 5′-dimethylbenzyl)-*p*-cresol, m.p. 116° (*triacetate*, m.p. 143°). The products do not couple with *o*-$C_6H_4Me{\cdot}N_2Cl$. R. S. C.



Interconversion of hexœstrol and *iso*hexœstrol [dimethyl ethers]. D. A. Peak and W. F. Short (*J.C.S.*, 1943, 232).—When undried H_2S is passed slowly through *iso*hexœstrol Me_2 ether or hexœstrol Me_2 ether at 305—310° (bath) interconversion occurs. *iso*Hexœstrol is unchanged by C_5H_5N–piperidine at 250° and Ac_2O at 250° (after hydrolysis), and is completely decomposed by H_2S at 300°. A. T. P.

Factors determining the course and mechanism of Grignard reactions. VI. Synthesis of hexœstrol dimethyl ether (γδ-dianisylhexane). M. S. Kharasch and M. Kleiman (*J. Amer. Chem. Soc.*, 1943, **65**, 491—493).—Adding *p*-$OMe{\cdot}C_6H_4{\cdot}CHEtBr$ (**I**) (prep. *in situ*) in PhMe at −80° to MgPhBr and $CoCl_2$ (5 mol.-%) in Et_2O at −20° to −10° gives $(p\text{-}OMe{\cdot}C_6H_4{\cdot}CHEt)_2$ (**II**) (41%) and Ph_2 (40%). Use of 15 mol.-% of $CoCl_2$ gives 27% of (**II**), of $NiCl_2$ (5 mol.-%) gives 14%, of $FeCl_3$ (5 mol.-%) gives 29%, but of $CrCl_3$, $MnCl_2$, or $CuCl_2$ (5 mol.-%) gives none. Replacing MgPhBr by pure MgMeBr (+15 mol.-% of $CoCl_2$) gives 27% of (**II**). Thus, (**I**) and ·CoCl give *p*-$OMe{\cdot}C_6H_4{\cdot}CHEt{\cdot}$, which then dimerises. R. S. C.

Formation of 3 : 4-dimethoxy-6-ethylphenol by the ozonisation of methyl 3 : 4-dimethoxy-6-ethylcinnamate. E. Späth and M. Pailer (*Ber.*, 1940, **73**, [*B*], 238—242).—The product of the action of HCN on 1 : 3 : 4-$C_6H_3Et(OMe)_2$ in presence of $AlCl_3$ and HCl is shown to be 3 : 4 : 6 : 1-$(OMe)_2C_6H_2Et{\cdot}CHO$ (**I**) by the formation of *m*-hemipinic acid on vigorous oxidation. (**I**) and $CH_2(CO_2H)_2$ in AcOH at 100° afford 3 : 4-*dimethoxy*-6-*ethylcinnamic acid*, m.p. 169—171°. The *Me* ester, m.p. 96°, is transformed by ozonisation in $CHCl_3$ and treatment of the product with boiling aq. $AgNO_3$ and Zn dust into 3 : 4 : 6 :1-$(OMe)_2C_6H_2Et{\cdot}CO_2H$, 3 : 4-*dimethoxy*-6-*ethylphenol* (**II**), b.p. 100° (bath)/0·04 mm. (*benzoate*, m.p. 88—90°), and (**I**). 2 : 5 : 4 : 1-$(OH)_2C_6H_2(OMe){\cdot}COMe$ is reduced (Zn–Hg and HCl) to 2-*methoxy*-5-*ethylquinol*, m.p. 151—153° (vac.), which is methylated to (**II**). It is improbable that (**II**) is formed from (**I**) by H_2O_2 liberated during decomp. of the ozonide. It is more probable that partial decomp. of the ozonide occurs during passage of O_3 and the products are further changed by O_3. H. W.

Polyhalogeno-*o*-anisidines and their derivatives. W. S. W. Harrison, A. T. Peters, and F. M. Rowe (*J.C.S.*, 1943, 235—237).—1 : 2 : 4 : 5-$C_6H_2Cl_4$ and aq. NaOH–MeOH at 160° give 2 : 4 : 5 : 1-$C_6H_2Cl_3{\cdot}OH$ (**I**) and thence $(Me_2SO_4$–aq. NaOH) 2 : 4 : 5 : 1-$C_6H_2Cl_3{\cdot}OMe$ (**II**). (**I**) and HNO_3 (*d* 1·43)–AcOH give the 2-NO_2-compound, m.p. 92—93° (lit. 81°), and (**II**)–HNO_3 (*d* 1·5) at 5—10° afford 3 : 4 : 6-*trichloro*-2-*nitroanisole* (**III**), m.p. 19—21°, b.p. 288°. (**III**) and Fe–aq. AcOH–EtOH yield 3 : 4 : 6-*trichloro*-o-*anisidine* (**IV**), m.p. 61—62°; its Ac_1 (AcCl–PhMe), m.p. 181—182°, or Ac_2 derivative (Ac_2O–C_5H_5N), m.p. 128—129°, and HNO_3 (*d* 1·5) at <10° give 3 : 4 : 6-*trichloro*-5-*nitro*-o-*acetanisidide* (**V**), m.p. 237°, hydrolysed by H_2SO_4 at 100° (bath) to the *amine* (**VI**), m.p. 121—122° (Ac_2 derivative, m.p. 142—143°). (**IV**) or (**VI**) and HNO_3 (*d* 1·5)–AcOH at <10° give 2 : 3 : 5-*trichloro*-4-*nitro*-6-*methoxy*-N-*nitroaniline*, m.p. 116—117° (decomp.), converted by boiling AcOH into 2 : 3 : 5-*trichloro*-6-*methoxy*-p-*benzoquinone*, m.p. 159°. Diazotised (**IV**) [$NO{\cdot}SO_4H$ at 100° (bath)] and β-$C_{10}H_7{\cdot}OH$ in AcOH or aq. NaOH give the *azo-β-naphthol*, m.p. 166°. (**IV**) can also be diazotised through the hydrochloride (prep. by HCl–$CHCl_3$), and after 24 hr. at 0° demethylation occurs and 3 : 4 : 6-*trichlorobenzene*-2-*diazo*-1-*oxide* (**VII**), m.p. 118° (decomp.) [also obtained from the diazonium sulphate from (**IV**) and aq. NaOAc at 5—10°], is obtained. EtOH at 150° converts (**VII**) into (**I**); (**VII**) with alkaline β-$C_{10}H_7{\cdot}OH$ yields 2 : 3 : 5-*trichloro*-6-*hydroxybenzeneazo*-β-*naphthol*, m.p. 226—228°. Decomp. of the diazonium salt from 2 : 4 : 3 : 5 : 1-$NH_2{\cdot}C_6HClBr_2{\cdot}OMe$ is also accompanied by demethylation, giving 4-chloro-3 : 5-dibromobenzene-2-diazo-1-oxide; thus halogen in position 6 is not necessary for demethylation. (**VI**) (diazotised, using $NO{\cdot}SO_4H$) gives 3 : 4 : 6-trichloro-5-nitrobenzene-2-diazo-1-oxide and thence 2 : 3 : 5-*trichloro*-4-*nitro*-6-*hydroxybenzeneazo*-2′-*hydroxy*-3′-*naphthanilide* (**VIII**), m.p. 285°. (**VI**) diazotised and coupled in AcOH, or even in AcOH–H_2SO_4, affords 2 : 3 : 5-*trichloro*-4-*nitro*-6-*methoxybenzeneazo*-2′-*hydroxy*-3′-*naphthanilide*, m.p. 282°, and a little (**VIII**). Reduction (Fe–aq. AcOH–EtOH at 70°) of (**VI**) gives 3 : 4 : 6-*trichloro*-2 : 5-*diaminoanisole*, m.p. 121—122° [2 : 5-Ac_2 derivative, m.p. 342° (decomp.); 2-*Ac* derivative, m.p. 202°, obtained by reducing (**V**), gives 2 : 3 : 6-*trichloro*-5-*methoxy*-4-*acetamidobenzeneazo*-β-*naphthol*, m.p. 267—268°]. 2-*Diacetyl*-3 : 4 : 6-*trichloro*-5-*amino*-o-*anisidine*, m.p. 142°, is obtained by reducing the corresponding 5-NO_2-compound. (**IV**) and Br–AcOH at 15° yield 3 : 4 : 6-*trichloro*-5-*bromo*-o-*anisidine*, m.p. 101° (*Ac* derivative, m.p. 236—237°; *azo*-β-*naphthol*, m.p. 195°; the derived diazo-oxide yields 2 : 3 : 5-*trichloro*-4-*bromo*-6-*hydroxybenzeneazo*-2′-*hydroxy*-3′-*naphthanilide*, m.p. 274°). (**IV**) and dry Cl_2 in $CHCl_3$ give tetrachloro-*o*-anisidine, m.p. 95°, and thence 2 : 3 : 4 : 5-*tetrachloro*-6-*methoxybenzeneazo*-β-*naphthol*, m.p. 204°. A. T. P.

Action of sulphuryl and benzenediazonium chlorides on aromatic thioethers. A. V. Rege, J. W. Airan, and S. V. Shah (*J. Univ. Bombay*, 1943, **11**, **A**, Part 5, 83—86).—4 : 4′-Dihydroxy-3 : 3′-diacetyl- (**I**) and -dicarboxy- (**II**), and 2 : 2′-dihydroxy- (**III**) and 2 : 2′-dihydroxy-3 : 3′-dicarboxy-dinaphthyl sulphide (**IV**) with PhN_2Cl in aq. NaOH at ~0° yield respectively 4-*benzeneazo*-2-*acetyl*-1-*naphthol*, m.p. 136°, 4-benzeneazo-1-hydroxy-2-naphthoic acid, 1 : 2-$PhN_2{\cdot}C_{10}H_6{\cdot}OH$, and 1-benzeneazo-2-hydroxy-3-naphthoic acid. With SO_2Cl_2 in C_6H_6, (**I**) and (**II**) yield respectively 4 : 2 : 1-$C_{10}H_5ClAc{\cdot}OH$ and 1 : 4 : 2-$OH{\cdot}C_{10}H_5Cl{\cdot}CO_2H$; (**III**) gives no isolable product and (**IV**) does not react. $C_{10}H_8$ with SO_2Cl_2 in Et_2O yields 1-$C_{10}H_7Cl$ and 1 : 4-$C_{10}H_6Cl_2$. A. Li.

Interaction of indene and styrene bromohydrins with sodium sulphite. Cleavage of alkali sulphonates with sodium in liquid ammonia. C. M. Suter and H. B. Milne (*J. Amer. Chem. Soc.*, 1943, **65**, 582—584).—Indene bromohydrin (**I**) and hot aq. Na_2SO_3 give *Na indan*-2-*ol*-1-*sulphonate* (**II**) (83%) [characterised by conversion by Ac_2O into the *acetate* (of the Na salt), m.p. 235—236° (corr.)] and ~2% of *trans*-indene glycol. The reaction may occur by way of indene oxide (**III**), since with Na_2SO_3 this gives chiefly (**II**) but $NaHSO_3$ affords (at 80—90°) a mixture of *cis*- and *trans*-glycols and a little (**II**). Crude $OH{\cdot}CHPh{\cdot}CH_2Br$ (**IV**) with hot aq. Na_2SO_3 gives *Na* β-*hydroxy*-β-*phenylethane*-α-*sulphonate* (**V**) (derived *p*-chlorobenzylthiuronium salt, m.p. 182—183°) with some $OH{\cdot}CHPh{\cdot}CH_2{\cdot}OH$ and $Ph{\cdot}[CH_2]_2{\cdot}SO_3Na$ (**VI**) [derived from $CH_2{:}CHPh$ or $CHPhMeBr$ present in the (**IV**); derived *p*-chlorobenzylthiuronium salt, m.p. 197°]. With Ac_2O, (**V**) gives the acetate, which at 180—200° gives AcOH and $CHPh{:}CH{\cdot}SO_3Na$, the *p*-chlorobenzylthiuronium salt, m.p. 199°, derived therefrom being also obtained from $(CHPh{:}CH{\cdot}SO_3)_2Ba$. Aq. NaCN and (**I**) give only 1-indanone and the glycols. Na in liquid NH_3 reduces (**II**) (proof of structure), (**III**), or (**I**) [by way of (**III**)] to 2-indanol. Na in liquid NH_3 reduces sulphonates containing $S{\cdot}C{\cdot}Ar$ or $S{\cdot}C{\cdot}C{:}CH_2$, but not saturated aliphatic sulphonates; *e.g.*, $CH_2Ph{\cdot}SO_3Na$ gives PhMe, Na_2SO_3, and a little $(CH_2Ph)_2$; $CHPhMe{\cdot}SO_3Na$ gives PhEt; $CH_2{:}CMe{\cdot}CH_2{\cdot}SO_3Na$ gives Na_2SO_3 and (?) $CH_2{:}CMe_2$; but *p*-$C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}SO_3Na$, (**V**), and (**VI**) are unaffected. R. S. C.

Rôle of neighbouring groups in replacement reactions. VI. *cyclo*-Hexylene ethyl orthoacetate. S. Winstein and R. E. Buckles (*J. Amer. Chem. Soc.*, 1943, **65**, 613—618).—The reaction mechanisms previously indicated (A., 1943, II, 117) are confirmed. *cis*- (**I**) or *trans-cyclo*Hexane-1 : 2-diol (**II**) with $CMe(OEt)_3$ and a trace of *p*-$C_6H_4Me{\cdot}SO_3H$ (**III**) gives 65—70% of *Et* cis- (**IV**), b.p. 92—93°/10 mm., and trans-*cyclohexylene Et* 1 : 2-*orthoacetate*, $[CH_2]_4\langle{}^{CH{\cdot}O}_{CH{\cdot}O}\rangle CMe{\cdot}OEt$, b.p. 95—96°/10 mm., respectively, yielding (**I**) and (**II**), respectively, by hydrolysis. Hydrolysis of (**IV**) is measured by change in the miscibility temp. of (**IV**)–EtOH–H_2O with mineral oil; at room temp. it is very slow in NaOEt–EtOH, very rapid with (**III**)–EtOH, but has a half-reaction time ~25 min. in 2% AcOH. 51% of (**IV**) is recovered after interaction of *trans*-2-acetoxy*cyclo*hexyl *p*-toluenesulphonate with KOAc–EtOH if H_2O is rigidly excluded and AcOH formed is removed. Acid hydrolysis of (**IV**) in aq. EtOH yields 95·5% of *cis*-2-acetoxy*cyclo*hexanol and 4·5% of (**I**); in AcOH containing a little H_2O the yields are 92 and 8%, respectively. With (**III**) and Ac_2O in hot AcOH, (**IV**) gives an ester hydrolysed to (**I**); with KOAc–Ac_2O–AcOH, (**IV**) gives a product, hydrolysed to pure (**II**); with Ac_2O–AcOH a product is obtained, which by hydrolysis yields mostly (**II**); Ac_2O alone at 130° leads to 43% of pure *trans*-diacetate (**V**) and a residue, hydrolysed to (**II**) (cf. Post *et al.*, A., 1938, II,

123), but at room temp. gives, after hydrolysis, mainly (**I**) [no (**V**) is formed]. With HCl–LiCl–AcOH at room temp., (**IV**) gives *trans*-2-chloro-1-acetoxy- (68%) and *cis*-1 : 2-diacetoxy-*cyclo*hexane (32%). *trans*-2-Ethoxy*cyclo*hexanol (prep. from the oxide by H_2SO_4–EtOH; 80% yield), b.p. 86—86·5°/15 mm., with H_2SO_4–Ac_2O gives the *acetate*, b.p. 91—92°/10 mm. R. S. C.

Tervalent carbon. II. Unsymmetrical hexa-aryldimethyl peroxides. E. L. Buhle, (Sr.) M. L. Whalen, and F. Y. Wiselogle (*J. Amer. Chem. Soc.*, 1943, **65**, 584—586; cf. A., 1942, II, 13).—Treating CPh_3Cl (1 mol.) + CAr_3Cl (1 mol.) with Hg–C_6H_6–N_2 for 17 hr. and oxidising the filtrate in air yields mainly $CPh_3{\cdot}O_2{\cdot}CAr_3$. This is the sole product (60—62%) when CAr_3Cl is *p*-$C_6H_4Ph{\cdot}CPh_2Cl$ (**I**) or (*p*-$C_6H_4Ph)_2CPhCl$ (**II**), and (**I**) + (**II**) give only (65%) *diphenyl*-p-*xenylmethyl phenyldi*-p-*xenylmethyl peroxide*, m.p. 175° (instantaneous). The peroxide is formed from the free radicals, for 1 mol. each of CPh_3Cl and (*p*-$C_6H_4Ph)_3CCl$ (**III**) give mainly $(CPh_3)_2O_2$ and [(*p*-$C_6H_4Ph)_3C]_2O_2$ with 13% of *CPh*$_3$ *tri*-p-*xenylmethyl peroxide* (**IV**), m.p. 148°; this is because widely differing degrees of dissociation of C_2Ar_6 give differing concns. of CAr_3; thus, use of 3 mols. of CPh_3Cl and 1 mol. of (**III**) increases the yield of (**IV**) to 36%. *CPh*$_3$ *diphenyl*-p-*xenylmethyl*, m.p. 177° (decomp.; instantaneous), and *phenyldi*-p-*xenylmethyl peroxide*, m.p. 186° (instantaneous), are described. Structures of the peroxides are proved by cleavage by Na–Hg, HI, or red P–I–AcOH. R. S. C.

Preparation of methoxyphenylacetic acids. H. A. Weidlich and M. Meyer-Delius (*Ber.*, 1940, **73**, [*B*], 325—327).—Me 3 : 4-methylenedioxymandelate (**I**) and Zn–HCl–AcOH afford a *substance*, $C_{22}H_{20}O_9$, m.p. 256—257° (darkens) (*Me*$_2$ ester, m.p. 95—96°), and 25% of homopiperonylic acid (**II**), m.p. 128—129°. (**II**) is obtained in 96% yield from (**I**) and H_2–Pd–HBr–AcOH. *Me* o-*methoxymandelate*, m.p. 46°, and the *p*-isomeride are similarly hydrogenated at 55—60° and room temp., respectively, to *o*-, m.p. 124°, and *p*-OMe·$C_6H_4{\cdot}CH_2{\cdot}CO_2H$, m.p. 85—86°, respectively; $BzCO_2Et$ affords $OH{\cdot}CHPh{\cdot}CO_2H$, which is unaffected under various conditions. A. T. P.

Effect of heat on mandelic acid. W. R. Angus and R. P. Owen (*J.C.S.*, 1943, 249—250).—$OH{\cdot}CHPh{\cdot}CO_2H$ (but not its *O*-acyl derivatives or esters) undergoes change in structure and composition on being melted (the f.p. curve of mixtures of the *r*- and *l*-acids cannot thus be determined by the usual methods) probably owing to internal ester formation. The extent and products of condensation appear to be governed by the temp. and method of heating. A. T. P.

Stability of racemates. Mandelic acid and its derivatives. W. R. Angus and R. P. Owen (*J.C.S.*, 1943, 227—230).—M.p. or f.p. curves for mixtures of active and *r*-mandelic, acetyl- and propionylmandelic acids, and of Me, Et, and Bu$^\beta$ mandelates have been determined. Racemate stability is increased by acylation and by esterification. The f.p. of the active acids are considerably higher than those of the corresponding *r*-acids, whilst the f.p. of the *r*-esters are a few degrees higher than those of the active forms. O-*Propionyl*-r- (+2H_2O), m.p. ~50°, anhyd. m.p. 51·2°, and -l-*mandelic acid*, m.p. 70—71°, $[\alpha]_D^{15}$ −124·5° in EtOH (vals. for other solvents given), were prepared from the mandelic acid and EtCOCl. O-*Benzoyl*-r-*mandelic acid*, m.p. 114—115°, is similarly prepared. C. R. H.

Resolution of enantiomorphs. II. Liquid–liquid extraction. E. Shapiro and R. F. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 777—779).—Partial resolution of $OH{\cdot}CHPh{\cdot}CO_2H$ (**I**), $OAc{\cdot}CHPh{\cdot}CO_2H$ (**II**), *o*-$NO_2{\cdot}C_6H_4{\cdot}CH(OR){\cdot}CO_2H$ (R = H and Ac), and $HCO{\cdot}NH{\cdot}CHPh{\cdot}CO_2H$ has been achieved by fractional distribution of the brucine salts between H_2O and $CHCl_3$. Multiple extractions gave a 10% resolution of (**I**) and (**II**). (**I**) has been partly resolved by a countercurrent extraction column. W. R. A.

Addition of phenol ethers to substituted cinnamic acids. B. D. Patel and K. V. Bokil (*J. Univ. Bombay*, 1943, **11**, **A**, Part 5, 92—100).—With the appropriate phenol ethers in presence of 80% H_2SO_4 at room temp. $CPhMe{:}CH{\cdot}CO_2Et$ yields *Et* β-*phenyl*-β-p-*anisyl*-, b.p. 210—217°/12 mm. (free *acid*, m.p. 100—102°; *Me* ester, b.p. 200—205°/5 mm.), -β-p-*ethoxyphenyl*-, b.p. 200—210°/8 mm. (free *acid*, b.p. 270—275°/20 mm.; *Me* ester, b.p. 185—195°/7 mm.), and -β-6-*methoxy*-m-*tolyl*-*butyrate*, b.p. 210—218°/14 mm. (free *acid*, m.p. 118°; *Me* ester, b.p. 190—200°/8 mm.), *p*-$C_6H_4Me{\cdot}CMe{:}CH{\cdot}CO_2Et$ yields *Et* β-p-*anisyl*-, b.p. 230—235°/10 mm. (free *acid*, m.p. 130°; *Me* ester, b.p. 210—215°/6 mm.), -p-*ethoxyphenyl*-, b.p. 220—228°/6 mm. (free *acid*, m.p. 112°; *Me* ester, b.p. 210—220°/9 mm.), and β-6-*methoxy*-m-*tolyl*-β-p-*tolylbutyrate*, b.p. 205—215°/6 mm. (free *acid*, m.p. 130—132°; *Me* ester, b.p. 220—225°/10 mm.; *anilide*, m.p. 140—141°), *p*-OMe·$C_6H_4{\cdot}CMe{:}CH{\cdot}CO_2Et$ yields *Et* β-p-*anisyl*-β-p-*ethoxyphenyl*-, b.p. 240—250°/11 mm. (free *acid*, m.p. 99—100°; *Me* ester, b.p. 245—255°/9 mm.), and β-6-*methoxy*-m-*tolyl*-*butyrate*, b.p. 245—250°/12 mm. (free *acid*, m.p. 120°; *Me* ester, b.p. 235—240°/9 mm.), *p*-OEt·$C_6H_4{\cdot}CMe{:}CH{\cdot}CO_2Et$ yields *Et* β-*ethoxyphenyl*-β-6-*methoxy*-m-*tolylbutyrate*, b.p. 250—260°/8 mm. (free *acid*, m.p. 103—104°; *Me* ester, b.p. 245—250°/10 mm.), *o*-OMe·$C_6H_4{\cdot}CMe{:}CH{\cdot}CO_2Et$ yields *Et* β-o-*anisyl*-β-p-*anisylbutyrate*, b.p. 230—235°/10 mm. (free *acid*, m.p. 118—119°), and 6 : 3 : 1-OMe·$C_6H_3Me{\cdot}CMe{:}CH{\cdot}CO_2H$ (from 4 : 6-dimethylcoumarin and Me_2SO_4 in NaOH at 50°) yields β-p-*anisyl*-, m.p. 158° (*Me* ester, m.p. 86—87°, b.p. 240—250°/20 mm.), β-p-*ethoxyphenyl*-, m.p. 148° (*Et* ester, m.p. 72°; *anilide*, m.p. 149°), and β-6-*methoxy*-m-*tolyl*-β-4-*methoxy*-m-*tolylbutyric acid*, m.p. 157° (*Et* ester, m.p. 84°; *Me* ester, m.p. 84—85°; *anilide*, m.p. 144°). α- and β-$C_{10}H_7{\cdot}OH$ with $CH_2Ac{\cdot}CO_2Et$ and 80% H_2SO_4 at room temp. yield respectively 4-methyl-1 : 2-α- (85) and -1 : 2-β-α-naphthapyrone (70% yield), converted by Me_2SO_4 and EtOH–NaOH into β-1-*methoxy*-2-, m.p. 137° (*Et*, b.p. 280—290°/9 mm., and *Me* ester, b.p. 280—285°/14 mm.), and β-2-*methoxy*-1-*naphthylcrotonic acid*, m.p. 188—189°, respectively, neither of which, like $CPh_2{:}CH{\cdot}CO_2H$, adds phenol ethers under the above conditions. A. Lr.

Synthetic anthelmintics. VI. β-*p*-Anisyl-γ-alkylbutyrolactones. K. Paranjape, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1943, **11**, **A**, Part 5, 104—110).—*p*-OMe·$C_6H_4{\cdot}COPr$, $CH_2Br{\cdot}CO_2Et$, and Zn in boiling PhMe give *Et* β-*hydroxy*-β-p-*anisylhexoate*, b.p. 155°/25 mm. (free *acid*, b.p. 168°/25 mm.), dehydrated (P_2O_5 in C_6H_6) to *Et* β-p-*anisyl*-Δ$^\beta$-*hexenoate*, b.p. 170°/20 mm., the free *acid*, b.p. 210°/25 mm. (anilide, m.p. 110°), from which (10% KOH at room temp.) with 60% H_2SO_4 at room temp. yields β-p-*anisyl*-γ-*ethyl*-γ-*butyrolactone*, b.p. 185°/20 mm., demethylated (HBr–AcOH) to the *OH*-*lactone*, b.p. 198°/35 mm. Similarly obtained are β-*hydroxy*-β-p-*anisyl*-*heptoic*, b.p. 190°/30 mm. (*Et* ester, b.p. 160°), -*nonoic*, b.p. 235°/45 mm. (*Et* ester, b.p. 220°/50 mm.), -*octadecoic*, m.p. 65° (*Et* ester, m.p. 58°), and -*eicosanoic acid*, m.p. 71° (*Et* ester, m.p. 60°), β-p-*anisyl*-Δ$^\beta$-*heptenoic*, b.p. 195°/20 mm. (*Et* ester, b.p. 170°/20 mm.; anilide, m.p. 105°), -*nonenoic*, b.p. 240°/25 mm. (*Et* ester, b.p. 225°/45 mm.; anilide, m.p. 101°), -*octadecenoic*, m.p. 48° (Et ester, decomposes when heated; anilide, m.p. 68°), and -*eicosenoic acid*, m.p. 76° (*Et* ester, m.p. 68°), β-p-*anisyl*-γ-*propyl*-, b.p. 186°/16 mm., -n-*amyl*-, b.p. 245°/30 mm., -*tetradecyl*-, b.p. 299°/25 mm., and -*hexadecyl*-γ-*butyrolactone*, m.p. 58°, and β-p-*hydroxyphenyl*-γ-*propyl*-, b.p. 220°/35 mm., -n-*amyl*-, m.p. 44°, -*tetradecyl*-, m.p. 45°, and -*hexadecyl*-γ-*butyrolactone*, m.p. 78—79°. p-*Anisyl hexyl ketone* (from $C_6H_{13}{\cdot}COCl$, PhOMe, and $AlCl_3$) has b.p. 240°/50 mm. A. Lr.

Esters of dihydrochaulmoogric acid and dihydrochaulmoogryl alcohol. K. Burschkies (*Ber.*, 1940, **73**, [*B*], 405—408).—Et chaulmoograte is hydrogenated (PtO_2–EtOH) to *Et dihydrochaulmoograte*, b.p. 210—220°/0·05 mm. [aq. NaOH–EtOH gives the free *acid* (**I**), m.p. 71°, whence ($SOCl_2$) the *chloride* (**II**), b.p. 205—215°/0·1—0·2 mm.], converted by Na–EtOH at 120° (after initial reaction) into *dihydrochaulmoogryl alcohol* (**III**), m.p. 29—30°, b.p. 180°/0·2 mm. The appropriate alcohol and (**II**) in N_2 give *cholesteryl* (prep. in C_6H_6), m.p. 94°, Δ^4-*octadecenyl* [also from (**I**)], b.p. 256—270°/0·1 mm., and *CH*$_2$*Ph* [from (**I**)], b.p. 220—230°/0·2 mm., *dihydrochaulmoograte*. (**III**) and the respective chloride in C_5H_5 and N_2 afford *dihydrochaulmoogryl oleate*, b.p. 250—260°/0·15 mm., and *cinnamate*, b.p. 255—265°/0·05 mm. A. T. P.

Peptides of dehydrogenated amino-acids. D. G. Doherty, J. E. Tietzmann, and M. Bergmann (*J. Biol. Chem.*, 1943, **147**, 617—637).—N-NaOH and acetyldehydrophenylalanine azlactone (**I**) are added successively to a suspension of glycine in $COMe_2$; after several hr. the solution yields acetyldehydrophenylalanylglycine, m.p. 194—195°, when treated with N-HCl. The following are obtained similarly: *acetyldehydrophenylalanylphenylserine*, m.p. 226—228° (decomp.), converted by Ac_2O and anhyd. NaOAc at 40° into the *azlactone* (**II**), m.p. 184—186°, of acetyldehydrophenylalanyldehydrophenylalanine (**III**); *benzoyldehydrophenylalanylglycine* (**IV**), m.p. 208—209° (corr.); *benzoyldehydrophenylalanylphenylserine* (**V**), m.p. 180° (decomp.); *acetyldehydroleucylglycine*, m.p. 185—187°, by hydrolysis of the *Et* ester, m.p. 130—132°, obtained from $NH_2{\cdot}CH_2{\cdot}CO_2Et$ and *acetyldehydroleucine azlactone*, b.p. 68—69°/0·15 mm. [corresponding *acid*, m.p. 155—157°, and its *amide*, m.p. 205—207° (corr.)]. *trans*-Phenylserine Et ester and carbobenzyloxyglycine chloride afford *carbobenzyloxyglycylphenylserine Et* ester, m.p. 149—151°, hydrolysed by NaOH–MeOH at room temp. to *carbobenzyloxyglycyl*-dl-*phenylserine*, m.p. 161—163°; the *azlactone*, m.p. 141—142°, of this substance (corresponding *amide*, m.p. 164—166°) yields *carbobenzyloxyglycyldehydrophenylalanine*, m.p. 168—170°. *Acetyldehydrophenylalanyl*-l-*alanine*, m.p. 195—196° (decomp.), $[\alpha]_D^{33·5}$ +69·6° in C_5H_5N, -l-*phenylalanine*, m.p. 213—215° (decomp.), $[\alpha]_D^{28}$ +37·6° in C_5H_5N, and -l-*tyrosine*, m.p. 228·5—229·5° (decomp.) (becomes discoloured at 221°), $[\alpha]_D^{30}$ +45·0° in C_5H_5N, are described. Acetyl-*dl*-phenylalanylglycine is transformed by Ac_2O, PhCHO, and NaOAc into the *azlactone*, m.p. 206—207° (corr.), of *acetyl*-dl-*phenylalanyldehydrophenylalanine*, m.p. 209—211° (decomp.), softens at 206°. Similarly, acetyldehydrophenylalanylglycine gives the azlactone, m.p. 184—186° [corresponding *acid*, m.p. 204—205°, and *amide*, m.p. 229° (corr.)], of (**III**). (**IV**), PhCHO, Ac_2O, and NaOAc or (**V**), Ac_2O, and NaOAc yield the *azlactone*, m.p. 188—190°, of *benzoyldehydrophenylalanyldehydrophenylalanine*, m.p. 180—181° (decomp.) (*amide*, m.p. 199°). The acetylated *azlactone*, m.p. 193—194° (softens at 165°), of *acetyldehydrophenylalanyldehydrotyro-*

sine, m.p. 218° (decomp.), is obtained similarly. (**IV**), *p*-OH·C_6H_4·CHO, Ac_2O, and NaOAc give the *acetylazlactone*, m.p. 231—233° (corresponding *azlactone*, m.p. 235—238°), of *benzoyldehydrophenylalanyldehydrotyrosine*, m.p. 164—166° (decomp.) [*amide*, m.p. 228° (decomp.)]. The *azlactone*, m.p. 171—173°, of *acetyldehydroleucyldehydrophenylalanine*, m.p. 215—216° (decomp.), has been prepared. *Carbobenzyloxyglycyldehydrophenylalanyl-l-glutamic acid*, m.p. 177—179° (decomp.), $[\alpha]_D^{20}$ −28·0 in C_5H_5N, and *-phenylserine*, m.p. 168—170°, are described. (**II**) and the required NH_2-acid give *acetylbis(dehydrophenylalanyl)-glycine*, decomp. 216° after becoming discoloured at 205°, *-l-alanine*, m.p. 215—216° (decomp.), $[\alpha]_D^{20}$ −255·1°, $[\alpha]_D^{20}$ 282·9° in C_5H_5N, *-l-leucine*, m.p. 235—236° (decomp.), softens at 225°, $[\alpha]_D^{32}$ −245·6° in C_5H_5N, *-l-phenylalanine*, m.p. 229—230° (decomp.), darkens at 256°, $[\alpha]_D^{8}$ −172·2° in C_5H_5N, *-l-tyrosine*, m.p. 172—173·5° (decomp.), $[\alpha]_D^{33}$ +133·6° in C_5H_5N, *-l-proline*, m.p. 203—204° (decomp.), $[\alpha]_D^{19}$ +60·6°, $[\alpha]_D^{20}$ +50·6° in C_5H_5N, *-phenylserine*, m.p. 223—225° (decomp.), and *-l-glutamic acid*, m.p. 209—210° (decomp.), $[\alpha]_D^{30}$ −182·6°. *l*-Cystine and (**I**) give *bis(acetyldehydrophenylalanyl)-l-cystine*, m.p. 212—213° (decomp.), $[\alpha]_D^{30\cdot5}$ −19·5° in C_5H_5N. *Acetylbis(dehydrophenylalanyl)dehydrophenylalanine*, m.p. 233—235°, is converted into *acetyltris(dehydrophenylalanyl)-l-phenylalanine*, m.p. 201—202°, becomes yellow at 172—173°, $[\alpha]_D^{30}$ −35·4° in C_5H_5N, and *-phenylserine*, m.p. 199° (decomp.); this gives *acetyltris(dehydrophenylalanyl)dehydrophenylalanine azlactone*, m.p. 247—249° (decomp.), converted into *bis(acetyldehydrophenylalanyldehydrophenylalanyl)-l-cystine*, m.p. 209—211°, $[\alpha]_D^{30}$ −82·3°, $[\alpha]_D^{20}$ −86·1° in C_5H_5N. M.p. are corr. H. W.

Chlorination of benzoic acid. H. G. Biswas and S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1942, **19**, 497—498).—BzOH with aq. $KClO_3$–HCl affords 3 : 4 : 1- and 2 : 5 : 1-$C_6H_3Cl_2$·CO_2H, separable through their Ba salts. A. T. P.

Ester group in polystyrene made with chloro- and bromo-benzoyl peroxides.—See A., 1943, II, 223.

Polymerisation of styrene in presence of 3 : 4 : 5-tribromobenzoyl peroxide.—See A., 1943, II, 223.

Isomorphism of organic compounds. V. Nitrobenzoic acids and substituted benzoic acids. H. Lettré (*Ber.*, 1940, **73**, [*B*], 386—390; cf. A., 1938, II, 324).—M.p. curves show that 1 : 1 compounds are formed from: *o*-NO_2·C_6H_4·CO_2H and BzOH (**I**), *m*- (**II**) or *p*-C_6H_4Me·CO_2H (**III**), or *m*-C_6H_4Cl·CO_2H (**IV**); *m*-NO_2·C_6H_4·CO_2H and (**I**), (**II**), (**III**), (**IV**), *o*-C_6H_4Me·CO_2H, *o*-C_6H_4Cl·CO_2H, *o*- or *m*-C_6H_4Br·CO_2H, *m*-C_6H_4I·CO_2H, or *p*-OH·C_6H_4·CO_2H; *p*-NO_2·C_6H_4·CO_2H and (**I**), (**III**), or *p*-C_6H_4R·CO_2H (R = Cl, Br, I, or OH). In the other cases investigated, mixed crystal or eutectic formation is noted. A. T. P.

Michael reactions. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 437—439).—Attempts to effect Michael reactions with CH_2:CH·CN (**I**) or CH_2:CH·CO_2Me (**II**) with NaOR–ROH led to addition of ROH. Thus, MeOH + a trace of NaOMe with (**II**) at 30—35° gives OMe·[CH_2]$_2$·CO_2Me (77%), b.p. 137—143°, and EtOH with (**I**) gives *β-ethoxypropionitrile* (89%), b.p. 170—173°. However, Michael reactions with these and similar compounds proceed well in absence of a solvent, when a trace of NaOR–ROH is used at <50°. Thus, CH_2Ph·CN (**III**) with (**II**) gives *γ-carbomethoxy-α-phenyl-* [20—23%; 24% obtained by $NaNH_2$ in an excess of (**III**)], b.p. 187—190°/18 mm., with CHMe:CH·CO_2Et gives *γ-carbethoxy-α-phenyl-β-methyl-* (63—68%), b.p. 170—175°/10 mm., with CMe_2:CH·CO_2Et affords *γ-carbethoxy-α-phenyl-ββ-dimethyl-*, b.p. 195—200°/23 mm., with CHPh:CH·CO_2Et gives γ-carbethoxy-αβ-diphenyl-, forms, m.p. 100—101° and 59—60°, with Me_2 maleate give *βγ-dicarbomethoxy-α-phenyl-* (50%), b.p. 198—203°/10 mm., and with Et_2 maleate gives *βγ-dicarbethoxy-α-phenyl-* (52—58%; 46% in EtOH), b.p. 185—187°/1 mm., *-butyronitrile*. With (**I**), (**III**) gives *α-phenyl-* [20—33%; 36 and 25% in Et_2O and an excess of (**III**), respectively], b.p. 198—200°/12 mm., with CH_2:CH·CH_2·CN gives *α-phenyl-β-methyl-* (76%), b.p. 193—197°/14 mm., and with *p*-OMe·C_6H_4·CH:CH·CN gives *α-phenyl-β-*p*-anisyl-* (72%), m.p. 135—136°, *-glutaronitrile*. CHPh:CH·CN with (**III**) gives *αβ-diphenylglutaronitrile* (81—87%), m.p. 101—103°, with CH_2Ph·CO_2Et gives *γ-carbethoxy-βγ-diphenylbutyronitrile* (50%), m.p. 118—121°, with *p*-OMe·C_6H_4·CH_2·CN gives *β-phenyl-α-*p*-anisylglutaronitrile* (26%), m.p. 140—142°, and with m-*aminophenylacetonitrile* (**IV**), b.p. 183—187°/13 mm., gives *β-phenyl-α-*m*-aminophenylglutaronitrile, forms*, m.p. 120—122° (33%) and 152—154° (17%). (**IV**) is obtained (50—55%) from *m*-NO_2·C_6H_4·CH_2·CN by Fe in 5% AcOH, not $SnCl_2$ or Sn–HCl, and gives a picrate, m.p. 200° (decomp.), and *Ac* derivative, m.p. 100—102°. R. S. C.

3 : 4-Dimethoxyphenylsuccinic acid. K. P. Dave, J. J. Trivedi, and K. S. Nargund (*J. Univ. Bombay*, 1943, **11**, **A**, Part 5, 111—112).—3 : 4 : 1-$(OMe)_2C_6H_3$·CHO with CN·CH_2·CO_2Na and 10% NaOH at 40° yields *α-cyano-β-*3 : 4-*dimethoxyphenylacrylic acid*, m.p. 200° (*Me* ester, m.p. 122°), the *Et* ester, m.p. 152°, of which with aq. EtOH–KCN gives a product hydrolysed (dil. HCl) to 3 : 4-*dimethoxyphenylsuccinic acid*, m.p. 130° [Me_2 ester, m.p. 65°; *anhydride*, m.p. 124°, whence the *anilic*, m.p. 151°, and *p-toluidinic acid*, m.p. 158—159°, and *imide*, m.p. 172° (softens at 163°)]. A. Li.

Diene syntheses. V. E. Lehmann (*Ber.*, 1940, **73**, [*B*], 304—309; cf. A., 1938, II, 488).—CH_2:CH·CH_2·MgBr and CH_2:CH·CH_2Br–BzCl yield *phenyldiallylcarbinol* (**I**), b.p. 119—120°/13 mm.; *o-tolyldiallylcarbinol* (**II**) has b.p. 131—132°/10 mm. (**I**) or (**II**) and $SOCl_2$–$CHCl_3$ give the carbinyl chlorides, converted by distillation with NaOH at 270—280° into δ-phenyl- or δ-*o*-tolyl-$\Delta^{\alpha\gamma}$-heptatriene, respectively, and thence by (:CH·CO)$_2$O in C_6H_6 at 105—110° into *3-phenyl-*, m.p. 174° (slow heating) (*anhydride*, m.p. 157·5°), or *3-o-tolyl-3-allyl-*Δ^4*-tetrahydrophthalic acid*, m.p. 236—237° (previous sintering), respectively. The $NaHSO_3$ compound of 2-*m*-4′-xylyl-2-methyl-Δ^3-tetrahydrobenzaldehyde (A., 1935, 978) and aq. KCN yield the corresponding cyanohydrin, which with HCl affords *2-m-4′-xylyl-2-methyl-*Δ^3*-tetrahydro-mandelamide, forms*, m.p. 213—214° and 158·5—159°, hydrolysed [boiling NaOH–EtOH (6 days)] to the *-mandelic acid*, m.p. 149° [Ac_2O–AcOH at 100° (bath) yields the *anhydride*, forms, m.p. 105—106° and 83—83·5°], hydrogenated (Pd–$BaSO_4$–AcOEt) to *2-m-4′-xylyl-2-methylhexahydromandelic acid*, m.p. 182°. A. T. P.

Alkyl β-nitroalkyl phthalates.—See B., 1943, II, 211.

Synthesis of 2 : 4-dimethoxy- and -dihydroxy-*iso*phthalic acids. (Miss) K. S. Radha and R. C. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 495—496).—3 : 2 : 4 : 1-CHO·$C_6H_2(OMe)_2$·CO_2H (A., 1939, II, 22) and $KMnO_4$–10% aq. NaOH yield 2 : 4-*dimethoxy*iso*phthalic acid*, m.p. 222—223° (*Me*$_2$ ester, m.p. 78—80°; 1-*Me H* ester, m.p. 150—151°), demethylated by $AlCl_3$ in boiling light petroleum to 2 : 4-*dihydroxy*iso*phthalic acid*, m.p. 179—181°. A. T. P.

Preparation of aldehydes by disruptive oxidation of the ethylene linking. R. R. Davies and H. H. Hodgson (*J.S.C.I.*, 1943, **62**, 90—92).—Alkaline $KMnO_4$ is preferable to CrO_3 for the oxidation of stilbene derivatives to aldehydes, whilst CrO_3 is much superior for the oxidation of R·CH:CHMe to R·CHO. Higher yields (piperonal from *iso*safrole; vanillin from *iso*eugenol) are obtained when dispersing agents are present, and this is attributed to ephemeral formation of double compounds with the aldehyde when produced.

Ethers of protocatechualdehyde.—See B., 1943, II, 211.

Reaction of Grignard reagents with oximes. II. Action of aryl Grignard reagents with mixed ketoximes. K. N. Campbell, B. K. Campbell, and E. P. Chaput. **III. Mechanism of the action of magnesium aryl halides on mixed ketoximes. New synthesis of ethyleneimines.** K. N. Campbell, B. K. Campbell, J. F. McKenna, and E. P. Chaput (*J. Org. Chem.*, 1943, **8**, 99—102, 103—109; cf. A., 1939, II, 366).—II. CArAlk:N·OH (**I**) and MgArX (**II**) yield β-NH_2-alcohols. (**II**) is prepared in Et_2O and the solvent is removed by heating to 150—155°; PhMe is added to the residue followed by dropwise addition of (**I**) in PhMe at 150°. The following (m.p. of the hydrochloride and Bz derivatives, respectively, being in parentheses) are prepared thus or from COAr·CH_2·NH_2 and (**II**): β-amino-α-phenyl-α-*p*-tolyl-, m.p. 104—105° (183—184°; 142—143°), -α-phenyl-α-naphthyl-, m.p. 159—160° (232—234°; 193—194°), -α-phenyl-α-*p*-anisyl-, m.p. 134° (162—163°; —), and *-α-phenyl-α-*p*-di-phenylyl-ethanol*, m.p. 86—88° (220—222°; 193—195°); β-amino-α-phenyl-α-*p*-tolylpropanol, m.p. 74—75° (239°; 195—196°); *β-amino-αα-diphenylbutanol*, m.p. 77—78° (259°; 209—211°).

III. Evidence is adduced to show that ethyleneimines are intermediates in the above conversion of (**I**) into β-NH_2-alcohols. If the reaction between CPhEt:N·OH and MgPhBr is effected by using a conc. Grignard reagent and hydrolysing the reaction complex with acid and ice, NH_2·CHMe·CPh_2·OH (**III**), m.p. 103—104°, is obtained in 30—40% yield. If no acid is used in the hydrolysis or if the complex is hydrolysed with acid at 0°, immediately made basic with aq. NH_3, and extracted the product is 2 : 2-*diphenyl-3-methylethyleneimine* (**IV**), m.p. 74·5—75° [*hydrochloride*, m.p. 139—140°; picrate, m.p. 199—200°; NHPh·CS derivative, m.p. 126·5—127°; *derivative*, $C_{22}H_{17}O_3N_2$·CO_2H, m.p. 190—192°, from 3 : 1 : 2-NO_2·$C_6H_3(CO)_2O$]. (**IV**) is isolated in better yield when the Grignard reaction is effected in PhMe at 135—145° and the complex is hydrolysed without use of acid or the acid solution kept very cold and worked up immediately. If the acid mixture is kept or allowed to get warm both (**III**) and (**IV**) are obtained. If the Grignard reaction is carried out in Et_2O and the mixture hydrolysed without use of acid (**IV**) and much unchanged oxime result. (**IV**) reduces $KMnO_4$ very slowly. It is rapidly hydrolysed by warm 2N-H_2SO_4 or 6N-HCl to (**III**) or to COMe·$CHPh_2$, NH_3, and (**III**) if the reaction is prolonged. (**III**) is converted by $SOCl_2$ in $CHCl_3$ followed by KOH–EtOH into (**IV**). MgPhBr and CPhPr$^{\alpha}$:N·OH in PhMe at 150° afford 2 : 2-*diphenyl-3-ethylethyleneimine*, m.p. 44·5—45° (*hydrochloride*, m.p. 144·5—145°; 1-$C_{10}H_7$·NH·CO, m.p. 184—185°, and non-cryst. NHPh·CS derivative); it is hydrolysed by 3N-H_2SO_4 to NH_2·CHEt·CPh_2·OH. H. W.

αβ-Unsaturated amino-ketones. VIII. Reaction of primary amines with 1 : 3-diketones and bromine derivatives of phenyl styryl ketone. Ethyleneimines. N. H. Cromwell, R. D. Babson, and C. E. Harris. **IX. Colour and constitution.** N. H. Cromwell and

R. S. Johnson (*J. Amer. Chem. Soc.*, 1943, **65**, 312—315, 316—319; cf. A., 1943, II, 243).—VIII. CH_2Bz_2 (1 mol.) with boiling $CH_2Ph{\cdot}NH_2$ (**I**) or *cyclo*hexylamine (**II**) (2 mols.) and a drop of conc. HCl gives *Ph β-benzylamino-*, m.p. 101° (*hydrobromide*, m.p. 172—174°, obtained by HBr–Et_2O–C_6H_6 and hydrolysed in H_2O), or *β-cyclohexylamino-*, m.p. 78°, *-styryl ketone*, respectively, which both decolorise Br–$CHCl_3$, are sol. in 6N-HCl, and are hydrolysed therein to CH_2Bz_2. $COMe{\cdot}CH_2Bz$ gives similarly *Ph β-benzylamino-*, m.p. 62°, and *β-cyclohexylamino-propenyl ketone*, m.p. 54° (with $COMe{\cdot}CH_2Bz$ gives an oil), sol. in dil. acids and hydrolysed therein to $COMe{\cdot}CH_2Bz$. (**I**) or (**II**) (4 mols.) with $CHPhBr{\cdot}CHBr{\cdot}COPh$ (1 mol.) in EtOH or $CHPh{:}CBr{\cdot}COPh$ (2 mols.) in Et_2O at 0° gives 2-*benzoyl*-3-*phenyl*-1-*benzyl*- (**III**), m.p. 108°, or -1-*cyclohexyl-ethyleneimine* (**IV**), m.p. 107°, respectively, unaffected by Br–$CHCl_3$ or H_2–Raney Ni at 50 lb.; (**IV**) is accompanied by a mixture, m.p. 85—90°, of, probably, (**IV**) and $CH_2Ph{\cdot}CBz{:}N{\cdot}C_6H_{11}$. $CHPh{:}CBr{\cdot}COPh$ (1 mol.) with (**I**) (1 mol.) in Et_2O–light petroleum at −10° to −5° gives *Ph α-bromo-β-benzylamino-β-phenylethyl ketone* (**V**), m.p. 75—77° (decomp.) [*hydrobromide* (**VI**), m.p. 157—159° (decomp.), separates from C_6H_6], which generates ionic Br in EtOH–$AgNO_3$, slowly in aq. HNO_3–$AgNO_3$, and not in H_2O, with tetrahydroquinoline in EtOH at room temp. slowly or with C_5H_5N in warm EtOH yields (**III**), and in C_6H_6 slowly gives (**III**) also. With dry HBr–C_6H_6, (**III**) gives (**VI**), with dry HCl–C_6H_6–Et_2O at 0° or 6N-aq. HCl at 85° gives *Ph α-chloro-β-benzylamino-β-phenylethyl ketone hydrochloride* (**VII**), m.p. 167—169° (decomp.), but with dry HCl–Et_2O gives the *hydrochloride*, m.p. 129—131° (decomp.), of (**III**). (**VII**) is converted into (**III**) by C_5H_5N in warm MeOH, whilst (**III**) and boiling 15% H_2SO_4 gives the *betaine*, $^+NH_2(CH_2Ph){\cdot}CHPh{\cdot}CH(COPh){\cdot}O{\cdot}SO_3^-$, m.p. 218° (with small amounts of PhCHO and $COPh{\cdot}CO{\cdot}CH_2Ph$), insol. in H_2O or EtOH, sol. in KOH–EtOH or aq. Na_2CO_3, whence it is regenerated by acid, and converted by hot KOH–aq. EtOH into (**III**). In aq. HCl at 85°, (**IV**) gives *Ph α-chloro-β-cyclohexyl-amino-β-phenylethyl ketone hydrochloride*, m.p. 187—189° (decomp.). PhCHO and 33% aq. NH_2Me give exothermally $CHPh{:}NMe$ (70%), b.p. 183—185°, hydrogenated (Raney Ni) in EtOH at room temp./45 lb. to $NHMe{\cdot}CH_2Ph$, b.p. 184—186°. M.p. are determined in a preheated bath.

IX. Absorption spectra of the compounds discussed above and *loc. cit.* support the structure assigned. In EtOH, $Ph{\cdot}[CH_2]_2{\cdot}COPh$ (**VIII**) and $CHPh{:}CH{\cdot}COPh$ (**IX**) have max. at 3275 and 3350 A. and ε 0·0418 and 2·040 × 10^{-3}, respectively; in C_6H_6, (**IX**) has a max. at 3275 A. and ε 1·468 × 10^{-3}. NHR at $C_{(\alpha)}$ of (**IX**) gives visible colour and absorption at 3500—4100 A. with a max. at ~4000 A. and ε 2—3 × 10^{-3} in EtOH, the max. being at shorter λ and ε slightly increased in C_6H_6. NHR at $C_{(\beta)}$ of (**IX**) has little effect on colour or the position of the max. but greatly increases ε (14—20 × 10^{-3} at 3500 A.). α-Br in (**IX**) has little effect on the position of the max. but decreases ε (0·876 × 10^{-3} at 3300 A.), but simultaneous presence of NRR′ at $C_{(\beta)}$ has great effect (ε 18·5 × 10^{-3} at 4025 A.). Absorption of the imines closely resembles that of (**VIII**); *e.g.*, (**III**) has a max. at 3275 A. and ε 0·0623 × 10^{-3} in EtOH. Resonance accounts for most of these results. R. S. C.

Polymethylbenzoylnaphthoic acids. R. H. Martin (*J.C.S.*, 1943, 239—241).—1 : 2-$C_{10}H_6(CO)_2O$ (**I**), 1 : 2 : 3-$C_6H_3Me_3$ (**II**) (excess), and $AlCl_3$ at room temp. give 1-(3′ : 4′ : 5′-*trimethylbenzoyl*)-2-*naphthoic acid* (**III**), m.p. 273—274° [Ac_2O–C_5H_5N gives the *acetoxy-lactone* (**IV**), $C_{23}H_{20}O_4$, m.p. 231—232°, hydrolysable to (**III**)], and 2-(3′ : 4′ : 5′-*trimethylbenzoyl*)-1-*naphthoic acid* (**V**), m.p. 191—192° (*acetoxy-lactone*, m.p. 161·5—162·5°; *benzoyloxy-lactone*, m.p. 191·5—192·5°). (**III**) or (**V**) with KOH at 260—280° or 280—340° gives 3 : 4 : 5 : 1-$C_6H_2Me_3{\cdot}CO_2H$ and 2- or 1-$C_{10}H_7{\cdot}CO_2H$, respectively. 2 : 1-$C_{10}H_6Me{\cdot}COCl$ and (**II**)–$AlCl_3$–CS_2 at 0°, then at room temp., give 1-(3′ : 4′ : 5′-*trimethylbenzoyl*)- (**VI**), m.p. 150—151°, and 1-(2′ : 3′ : 4′-*trimethylbenzoyl*)-2-*methylnaphthalene*, m.p. 108—108·5°. (**VI**) and SeO_2–H_2O at 235°, followed by Ac_2O–C_5H_5N, yield (**IV**). (**I**), 1 : 2 : 3 : 4-$C_6H_2Me_4$, $AlCl_3$, and $PhNO_2$ at 0° (12 hr.), then at room temp. (60 hr.) afford 2-(2′ : 3′ : 4′ : 5′-*tetramethylbenzoyl*-1-*naphthoic acid*, m.p. 241·5—242·5°, converted by BzCl and a little conc. H_2SO_4 at 100° (bath) into (probably) 5 : 6 : 7 : 8-*tetramethyl*-1 : 2-*benzanthraquinone*, m.p. 203—203·5°. Prep. of 1 : 2 : 3 : 4-$C_6H_2Me_3Br$ is modified; 1 : 2 : 3 : 4-$C_6H_2Me_3{\cdot}MgBr$ and (**I**) give a difficultly separable mixture of acids. A. T. P.

Alkylation of ethyl 3-methyl-Δ²-*cyclo*hexenone-4-carboxylate (Hagemann's ester) and related substances. L. I. Smith and G. F. Rouault (*J. Amer. Chem. Soc.*, 1943, **65**, 631—635).—Adding piperidine to $CH_2Ac{\cdot}CO_2Et$ (2 mols.) and paraformaldehyde (1 mol.) with cooling, heating at 100°, and treating the resulting crude Et_2 3-methyl-Δ²-*cyclo*hexenone-4 : 6-dicarboxylate (**I**) with boiling NaOEt–EtOH (1 mol.; 2 mols. give 10%) gives Et 3-methyl-Δ²-*cyclo*hexenone-4-carboxylate (**II**) (40—50%), b.p. 142—144°/15 mm. [semicarbazone, m.p. 165—167° (lit. 169°)] (cf. A., 1896, i, 393; 1939, II, 412). In boiling aq. H_2SO_4, (**I**) gives 3-methyl-Δ²-*cyclo*hexenone (**III**) (24%); b.p. 75—77°/10 mm., in H_2SO_4–AcOH–H_2O gives (**III**) (44%) and (**II**) (8%), and in H_2O at 200° gives (**III**) (25%) and (**II**) (21%). NaOMe–MeI–MeOH at 5°, later 20°, and finally the b.p. converts (**II**) into 2 : 3-dimethyl-Δ²-*cyclo*hexenone (**IV**) (37%), b.p. 90—96°/14 mm. [semicarbazone, sinters 200—205°, m.p. 222° (lit. 225°)], and its 4-CO_2Et-derivative (**V**) (17%), b.p. 138—142°/12 mm.; MeBr at <10° gives 49% of (**IV**). EtBr, (**II**), and NaOEt in boiling EtOH give the 4-CO_2Et-derivative (55%) (**VI**), b.p. 141—143°/9 mm. (*semicarbazone*, m.p. 160—164°), of 3-methyl-2-ethyl-Δ²-*cyclo*hexenone (**VII**) (27%), b.p. 82—85°/9 mm. (*semicarbazone*, m.p. 190—194°) [obtained from (**VI**) in 62% yield by KOH–EtOH]. Perhydrogeranyl bromide, (**II**), and NaOEt in boiling EtOH give only (49%) *Et* 3-*methyl*-2-*perhydrogeranyl*-Δ²-*cyclohexenone*-4-*carboxylate*, b.p. 182°/4 mm. (*semicarbazone*, m.p. 85·5—87°, formed slowly), and thence (KOH–EtOH) 3-methyl-2-perhydrogeranyl-Δ²-*cyclo*hexenone (54%), b.p. 153—154°/3 mm. (*semicarbazone*, m.p. 93—95°). Condensing $CH_2Ac{\cdot}CO_2Et$ with MeCHO by piperidine at the b.p. and hydrolysing the product by 25% (vol.) H_2SO_4 gives 3 : 5-dimethyl-Δ²-*cyclo*hexenone (19%), b.p. 81°/9 mm, its 4-CO_2Et- (6%), b.p. 146°/12 mm., and 4 : 6-$(CO_2Et)_2$-derivative (a little), b.p. 205°/11 mm. Pd–C *d* (A., 1940, II, 351) at 200° converts (**IV**) into *o*-3-xylenol (53%), but other reagents were unsuccessful. R. S. C.

Reactions catalysed by aluminium chloride. XIX. Synthesis of stereoisomeric 1-keto-9-methyldecahydronaphthalenes. C. D. Nenitzescu, E. Cioranescu, and V. Przemetzky (*Ber.*, 1940, **73**, [*B*], 313—315; cf. A., 1939, II, 268).—$CO_2Me{\cdot}[CH_2]_2{\cdot}COCl$, 1-methyl-Δ¹-*cyclo*hexene, and $AlCl_3$ in $PhNO_2$ at room temp. (2 days) give Me γ-keto-γ-2-methyl-Δ¹-*cyclo*hexenylbutyrate, b.p. 150—160°/15 mm., converted by N_2H_4,H_2O–NaOEt–EtOH at 180° into γ-2-methyl-Δ¹-*cyclo*hexenylbutyric acid (**I**), b.p. 159—160°/9 mm., 175°/20 mm. [*p*-bromophenacyl ester, m.p. 78° (lit. 65—66°)]. Prolonged warming with alkali causes migration of the double linking in (**I**), and the product then affords a colourless NN′-*di*-p-*dimethylaminophenyl-carbamide*, m.p. 148° (cf. Zetzsche *et al.*, A., 1939, II, 467). The chloride of (**I**) with $AlCl_3$ in *cyclo*hexane at 0°, then at room temp., and finally at 40°, yields (cf. Linstead *et al.*, A., 1938, II, 268) *cis-*, b.p. 92—93°/5 mm. [*semicarbazone*, m.p. 223° (decomp.)], and *trans*-8-methyl-1-ketodecahydronaphthalene, b.p. 82—83°/5 mm. (*semicarbazone*, m.p. 185°). A. T. P.

Oxidation of cholesterol. Isolation of 1-keto-2 : 13-dimethyl-Δ$^{9:14}$-dodecahydro-7-phenanthrol.—See A., 1943, II, 235.

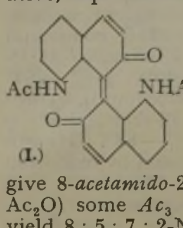
Monomeric fluorenone peroxide. G. Wittig and G. Pieper (*Ber.*, 1940, **73**, [*B*], 295—297; cf. A., 1939, II, 22).—Fluorenone (**I**) and ~1·5N-Et_2O–H_2O_2 + P_2O_5 at room temp. give the monomeric *fluorenone peroxide* (**II**), $C_{12}H_8{>}C(\overset{+}{O}{\cdot}\overset{-}{O})$, m.p. 108—108·5°, converted by Ac_2O–AcOH–H_2SO_4 at 0° for 48 hr. into (**I**) and the lactone, m.p. 94—95° [also obtained from (**I**) and Ac_2O–H_2O_2–H_2SO_4], of *o*-$OH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO_2H$-*o*. A. T. P.

Condensation of acyloins with ethyl acetate. R. B. Woodward and E. R. Blout (*J. Amer. Chem. Soc.*, 1943, **65**, 562—565).—Adding $Pr^{\alpha}CO_2Et$ and then EtOAc to Na wire in Et_2O, evaporating, and heating the residue at 100° gives 2-*ethyl*-4-n-*propyl*cyclo*pentane*-1 : 2-*dione* (**I**) (32%), m.p. 119·4—120·5°. This structure, contrary to that proposed by Bouveault *et al.* (A., 1907, i, 479; 1910, i, 92), is proved by rapid neutralisation of 1 NaOH, formation of a reddish-violet colour with $FeCl_3$ (enolisation), and similarity of its absorption (max. at 255 mμ.; log ε 4·12) in EtOH to that (max. at 258 mμ.; log ε 4·08) of dimethyldihydroresorcinol. The autoxidation of (**I**) in air is characteristic of alkyl-substituted cyclic β-diketones. The other reactions (*loc. cit.*) of (**I**) are also explained by this structure and analogous structures apply to the other products described by Bouveault *et al.* The condensation involves the reactions, $OH{\cdot}CHPr^{\alpha}{\cdot}CO{\cdot}CHEt{\cdot}COMe \rightleftharpoons COPr^{\alpha}{\cdot}CH(OH){\cdot}CHEt{\cdot}COMe \rightarrow$ 3-hydroxy-2-ethyl-4-*n*-propyl-Δ⁴-*cyclo*pentenone → (**I**). R. S. C.

Electrolytic preparation of quinhydrone. R. E. Ely (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 284—285).—Quinol is oxidised electrolytically in H_2O to a 75% yield of 98% pure quinhydrone. J. D. R.

Effects of environment and aggregation on absorption spectra of dyes.—See A., 1943, I, 192.

Dinaphthones. A. Rieche and W. Rudolph (*Ber.*, 1940, **73**, [*B*], 335—342).—8 : 2-$NHAc{\cdot}C_{10}H_6{\cdot}OH$ and aq. $FeCl_3$–HCl (or CuO–$PhNO_2$) at 70° afford 1 : 1′-(8 : 8′-*diacetamido*-2 : 2′-*dinaphthone*) (**I**), m.p. 332° (phenylhydrazone, m.p. 314°), reduced (Zn in aq. NaOH or AcOH) to 8 : 8′-*diacetamido*-2 : 2′-*dihydroxy*-1 : 1′-*dinaphthyl* (**II**), m.p. 289—290°; Me_2SO_4 then yields (probably) the 2 : 8 : 2′ : 8′-Me_4 derivative, m.p. 244—245°. (**II**) is reconverted into (**I**) by $K_3Fe(CN)_6$–aq. NaOH, and with conc. HCl at 180° affords 1 : 1′-dinaphthylene-2 : 8′-2′ : 8-dioxide (**III**), m.p. 242°. 8 : 2-$C_{10}H_6Cl{\cdot}OH$ and aq. $K_3Fe(CN)_6$–NaOH yield impure 1 : 1′-(8 : 8′-dichloro-2 : 2′-dinaphthone), m.p. 168—193°, converted by aq. $Na_2S_2O_4$–NaOH at 70°, through the corresponding dinaphthol, into (**III**). 8 : 2-$NHAc{\cdot}C_{10}H_6{\cdot}OH$ and Ac_2O–NaOAc–AcOH give 8-*acetamido*-2-*acetoxynaphthalene* (**IV**), m.p. 184°, and (excess of Ac_2O) some Ac_3 compound, m.p. 98—99°. (**IV**) and SO_2Cl_2–C_6H_6 yield 8 : 5 : 7 : 2-$NHAc{\cdot}C_{10}H_4Cl_2{\cdot}OAc$, m.p. 212°, hydrolysed by aq.



(I.)

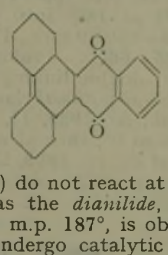
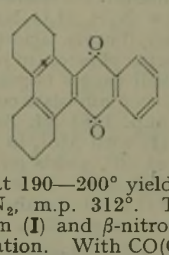
NaOH to 5 : 7-*dichloro*-8-*acetamido*-2-*naphthol*, m.p. 263°, which is oxidised by aq. $K_3Fe(CN)_6$–aq. NaOH at 90° to 1 : 1′-(5 : 7 : 5′ : 7′-*tetrachloro*-8 : 8′-*diacetamido*-2 : 2′-*dinaphthone*), m.p. 304° (decomp.). 2 : 7 : 8-$(OH)_2C_{10}H_5$·NHAc and aq. $FeCl_3$–HCl at 70° afford 1 : 1′-(8 : 8′-diacetamido-7 : 7′-dihydroxy-2 : 2′-dinaphthone), m.p. 310°.

A. T. P.

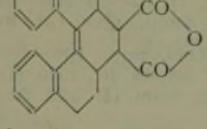
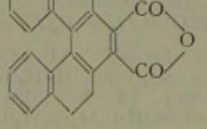
Aromatic hydrocarbons and their derivatives. XXX. Syntheses in the perylene series. E. Clar (*Ber.*, 1940, **73**, [*B*], 351—353; cf. A., 1940, II, 273).—1-β-Naphthoxyanthraquinone and $AlCl_3$–NaCl at 140°, then at 200°, give 12 : 6′-*oxido*-1′ : 2′ : 1 : 2-*benzperylene* (**I**), m.p. 280—281°, and 12 : 6′-*oxido*-1′ : 2′ : 1 : 2-*benzperylene*-3 : 10-*quinone* (**II**), $C_{24}H_{10}O_3$; (**II**) is also obtained by oxidising (**I**) with CrO_3 or, better, with air in AcOH or xylene. When O_2 is passed through the above $AlCl_3$ melt, (**II**) is obtained, with a little (**I**). (**I**) forms an adduct with $(CH{\cdot}CO)_2O$ much more readily than perylene.

A. T. P.

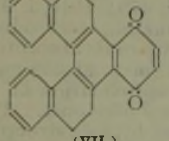
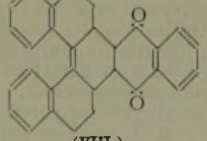
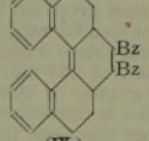
Mechanism of the diene reaction. F. Bergmann, H. E. Eschinazi, and M. Neeman (*J. Org. Chem.*, 1943, **8**, 179—188).—Di*cyclo*hexenyl (**I**) and *p*-$OC_6H_4{:}O$ (5 : 1) at 100° afford isomeric *adducts*, $C_{30}H_{40}O_2$, m.p. 247° and 212°, converted by KOH–EtOH at room temp. into *enols*, m.p. 327° and 310—312°, respectively. (**I**) and 1 : 4-naphthaquinone (5 : 1) at 100° afford the *substance* (**II**), m.p. 207—208°, converted by KOH–EtOH into a quinone, m.p. 248°, and by AcOH–conc. HBr into the *compound* (**III**), m.p. 234—235°. Fumaric

(II.)   (III.)

acid and (**I**) do not react at 100° but at 190—200° yield an adduct identified as the *dianilide*, $C_{28}H_{22}O_2N_2$, m.p. 312°. The *adduct*, $C_{20}H_{26}O_2N$, m.p. 187°, is obtained from (**I**) and β-nitrostyrene; it does not undergo catalytic hydrogenation. With $CO(CH{:}CHPh)_2$ at 180—190° (**I**) yields the double *adduct*, $C_{41}H_{50}O$, m.p. 208—209°.

(V.)   (VI.)

Maleic anhydride and 3 : 4 : 3′ : 4′-tetrahydro-1 : 1′-dinaphthyl (**IV**) give the adduct (**V**), m.p. 256°, converted by CH_2N_2 into the corresponding *Me*$_2$ ester, m.p. 168°, which is isomerised and hydrolysed by boiling BuOH–NaOBu to an *acid*, m.p. 239°; a second isomeric

(VII.) (VIII.) (IX.)

adduct, m.p. 260°, is formed in small amount. Condensation in boiling $PhNO_2$ leads to the *substance* (**VI**), m.p. 275°. (**IV**) and *p*-$OC_6H_4{:}O$ at 125—150° afford the *substance* (**VII**), m.p. 268°, which is unchanged by HBr–AcOH. (**IV**) and 1 : 4-naphthaquinone (1 : 2) at 130° give the *adduct* (**VIII**), m.p. 226°. *trans*-$(CHBz)_2$ and (**IV**) do not react in boiling C_6H_6 but at 200° the *compound* (**IX**), m.p. 236—238°, is slowly formed; it is dehydrated by boiling Ac_2O containing H_3PO_4 (*d* 1·75) to the corresponding *furan*, $C_{36}H_{28}O$, m.p. 272—273°.

H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

Oxidation of cholesterol. Isolation of 1-keto-2 : 13-dimethyl-$\Delta^{9:14}$-dodecahydro-7-phenanthrol and preparation of derivatives. H. Köster and W. Logemann (*Ber.*, 1940, **73**, [*B*], 298—304).—The product obtained from the mother-liquors after oxidising cholesteryl acetate dibromide and separating dehydroandrosterone and pregnenolone acetates is heated with dil. H_2SO_4; the resulting compound with Ac_2O at 120° for 2 hr. affords 1-*keto*-2 : 13-*dimethyl*-$\Delta^{9:14}$-*dodecahydro*-7-*phenanthryl acetate*, (**I**), m.p. 128—129°, $[\alpha]_D^{20}$ −87° [*oxime*, m.p. 166—169°; *semicarbazone*, m.p. 243° (decomp.)], hydrolysed (aq. H_2SO_4–MeOH at 50—60°) to 1-*keto*-2 : 13-*dimethyl*-$\Delta^{9:14}$-*dodecahydro*-7-*phenanthrol* (**II**), m.p. 133—134°, $[\alpha]_D^{20}$ −88°. Hydrogenation (1·6 mols. of H_2; PtO_2–AcOH) of (**I**) (followed by oxidation with CrO_3–90% AcOH) gives the *acetate*, m.p. 144—145°, $[\alpha]_D^{20}$ −12·2° (*oxime*, m.p. 154—156°), of 1-*keto*-2 : 13-*dimethylperhydro*-7-*phenanthrol*, m.p. 128—129° (3 : 5-*dinitrobenzoate*, m.p. 192—193·5°); these are probably identical with the compounds obtained from β-ergostenyl acetate by Achtermann (A., 1934, 1000). (**II**) and $Al(OPr^{\beta})_3$ in boiling PhMe–*cyclo*hexanone yield 1 : 7-*diketo*-2 : 13-*dimethyl*-$\Delta^{9:14}$-*dodecahydrophenanthrene*, m.p. 140—141°, $[\alpha]_D^{20}$ +128°. (**I**) and boiling MgMeI–C_6H_6–Et_2O afford 1 : 7-*dihydroxy*-1 : 2 : 13-*trimethyl*-$\Delta^{9:14}$-*dodecahydrophenanthrene*, m.p. 162·5—163°, oxidised by $Al(OPr^{\beta})_3$–PhMe–*cyclo*hexanone to 7-*keto*-1 : 2 : 13-*trimethyl*-Δ^{8}-*dodecahydro*-1-*phenanthrol* (**III**), m.p. 195·5—196·5°, $[\alpha]_D^{20}$ +94·1°. CH_2CK (prep. in liquid NH_3) with (**I**) in C_6H_6–Et_2O yields 1 : 7-*diketo*-2 : 13-*dimethyl*-1-*acetylenyl*-$\Delta^{9:14}$-*dodecahydrophenanthrene*, m.p. 217—218·5°, $[\alpha]_D^{20}$ −108·5°, converted by $Al(OPr^{\beta})_3$ into 7-*keto*-2 : 13-*dimethyl*-1-*acetylenyl*-Δ^{8}-*dodecahydro*-1-*phenanthrol* (**IV**), m.p. 131—132°, $[\alpha]_D^{20}$ +77·7°. [α] are in $CHCl_3$. (**III**) and (**IV**) have no physiological activity.

A. T. P.

Dehydration of cholesterol in liquid sulphur dioxide. R. H. Levin (*J. Amer. Chem. Soc.*, 1943, **65**, 627—628).—In (liquid) SO_2 at 100—140°, cholesterol gives 9—33% of dicholesteryl ether, m.p. 203—205° (cf. lit.) [*tetrabromide*, m.p. 164—166° (decomp.)]. Presence of anhyd. $CuSO_4$ gives 54% at 100° and 40% at 135°, of $CuSO_4{,}5H_2O$ gives 76% at 100° but resins at 135°, of powdered glass gives 29% (remainder resinified), of $CuCl_2$ gives 26%, and of S gives 18%. Cu, Raney Ni, $FeSO_4$, $CaSO_4$, and Na_2CO_3–$Cu_3(PO_4)_2$ inhibit the reaction.

R. S. C.

Bile acids and related substances. XX. Attempted preparation of Δ^9-cholenic acid. H. B. Alther and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 492—511; cf. A., 1938, II, 497).—Me 12(β)-hydroxy- is oxidised by CrO_3 in AcOH at 18° to Me 12-keto-cholanate, m.p. 107—108°, $[\alpha]_D^{16}$ +87·7°±1° in $COMe_2$; a form of m.p. 152° (Ohta, A., 1939, II, 371) has not been encountered. It is hydrolysed and then brominated in AcOH (stable to CrO_3) to a mixture of acids separated by Et_2O into 11(α)- (**II**), m.p. 196—197° (decomp.), $[\alpha]_D^{15}$ +31·9°±2° in $CHCl_3$ [*Me* ester (**III**), m.p. 60—64°, $[\alpha]_D^{19}$ +26·6°±2° in $COMe_2$], and 11(β)- (**IV**), m.p. 171—174° (decomp.), $[\alpha]_D^{15}$ +16·3° ±2° in $CHCl_3$, -bromo-12-ketocholanic acid. (**IV**) yields a *Me* ester (**V**), m.p. 77—79°, $[\alpha]_D^{17}$ +19·8°±2° in $COMe_2$, also isolable when the crude acid is used. (**V**) and boiling C_5H_5N afford *Me* 12-*keto*-Δ^9-*cholenate* (**VI**), m.p. 89—90°, $[\alpha]_D^{20}$ +93·1°±2° in MeOH, which when pure invariably separates as needles from the slowly cooling solutions but, when crude, sometimes gives leaflets, m.p. 72—74°. Its prep. is rendered difficult by a very tenacious impurity and its homogeneity is best judged by the height of the absorption max. in the ultra-violet. The prep. of (**VI**) from (**III**) and boiling C_5H_5N, collidine, or NaOAc and from mixtures of (**III**) and (**V**) is described. 12-*Keto*-Δ^9-*cholenic acid* has m.p. 145—146°. Hydrogenation (PtO_2 in AcOH) of (**VI**) gives a mixture of Me cholanate and Me 12(β)-hydroxycholanate. Reduction of crude (**VI**) by N_2H_4,H_2O and NaOEt at 170° with subsequent methylation affords a mixture of Me cholanate (**VII**) and Δ^9- (**VIII**) and Δ^{11}-cholenate (**IX**) whereas pure (**VI**) yields a mixture of (**VIII**) and (**IX**). BzO_2H in $CHCl_3$ oxidises crude (**VIII**) to Me 11 : 12-, m.p. 97—98° [from (**IX**)], and a *Me* 9 : 11-*oxidocholanate*, m.p. 74·5—76°, $[\alpha]_D^{15}$ +18·8°±2° in $COMe_2$; the last with boiling H_2SO_4–MeOH followed by CH_2N_2 gives a (?) *Me choladienate*, m.p. 88—90°, and with boiling AcOH affords a substance, m.p. 184—198°. Reduction (H_2, PtO_2, AcOH) of (**VIII**) + (**IX**) gives (**VII**). M.p. are corr. (block); limit of error ±2°.

H. W.

Bile acids and related substances. XIX. Methyl 3(α)-hydroxy-Δ^{11}-norcholenate and 3(α)-hydroxy-Δ^{11}-bisnorcholenate. P. Grandjean and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 482—492).—Me 3(α)-hydroxy-Δ^{11}-cholenate and MgPhBr give the non-cryst. carbinol which with Ac_2O–C_5H_5N at 18° affords *diphenyl*-3(α)-*acetoxy*-Δ^{11}-*norcholenylcarbinol* (**I**), m.p. 151—153°, $[\alpha]_D^{14}$ +47·3°±3° in $COMe_2$. (**I**) is dehydrated by boiling AcOH to *diphenyl*-3(α)-*acetoxy*-Δ^{11}-*bisnorcholenylethylene* (**II**), m.p. 142—143°. Successive treatments of (**I**) with Br–$CHCl_3$, CrO_3–AcOH, and Zn dust–AcOH give mainly (**II**) with little acid. *Me* 3(α)-*acetoxy*-Δ^{11}-*norcholenate* (**III**), m.p. 133—134°, $[\alpha]_D^{15}$ +56·2°±2° in $COMe_2$, is best obtained by direct oxidation of (**II**) by excess of CrO_3 followed by esterification (CH_2N_2) and re-acetylation. (**III**) is hydrogenated (PtO_2 in AcOH) to Me acetylnorlithocholate, m.p. 159—160°, and converted by HCl–MeOH in $CHCl_3$ at 18° into *Me* 3(α)-*hydroxy*-Δ^{11}-*norcholenate* (**IV**), m.p. 140—141°. (**IV**) and MgPhBr afford the non-cryst. carbinol; the non-cryst. acetate is dehydrated by boiling AcOH to the resinous diphenyl-3(α)-acetoxy-Δ^{11}-ternorcholenylethylene. This is oxidised by CrO_3 and the acidic portion methylated and acetylated to *Me* 3(α)-*acetoxy*-Δ^{11}-*bisnorcholenoate*, m.p. 99—100°, $[\alpha]_D^{13}$ +10·7°±2° in $COMe_2$. *Me* 3(α)-*hydroxy*-Δ^{11}-*bisnorcholenate* has m.p. 107—108°. M.p. are corr. (block); limit of error ±2°.

H. W.

Bile acids and related substances. XXII. 11-Keto- and 11(α)-hydroxy-cholanic acid. H. Reich and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 562—585).—Me Δ^{11}-cholenate (**I**) is converted by HOBr into a difficultly separable mixture (**II**) of substances which is therefore directly oxidised (CrO_3) and then debrominated (Zn dust). Chromatographic (Al_2O_3) fractionation of the product leads to a little (**I**), mainly *Me* 11-*ketocholanate* (**III**), m.p. 88—89°, $[\alpha]_D^{19}$ +46·0°±1° in $COMe_2$, and Me 12-keto-Δ^9-cholenate, m.p. 88—90°.

The change can be effected by HOBr in aq. Bu$^{\gamma}$OH or, more conveniently, by NHAcBr in aq. Bu$^{\gamma}$OH or aq. $COMe_2$. HOCl or chloramine-*T* in presence of a trace of acid may also be used whereby similar intermediates with Cl for Br are formed. The constitution of (**III**) is established from the known position of the double linking in (**I**) and the non-identity of (**III**) and Me 12-ketocholanate. CO in (**III**) is very non-reactive and cannot be detected by the usual reagents, but (**III**) is slowly hydrogenated (PtO_2 in AcOH) to *Me* 11(*α*)-*hydroxycholanate* (**IV**), m.p. 87—88°, $[\alpha]_D^{18}$ +49·8° ±2° in $COMe_2$, quantitatively reoxidised (CrO_3) to (**III**). The most conclusive preliminary evidence of the configuration of (**IV**) is found in attempts to separate (**II**) chromatographically with very active Al_2O_3, which yield Me 11 : 12-dibromocholanate, *Me* 11(*α*) : 12(*α*)-*oxidocholanate* (**V**), m.p. 64·5—65·5°, $[\alpha]_D^{20}$ +47·5±9° in $COMe_2$, and an amorphous Br-compound, probably Me 9 : 11-dibromo-12-hydroxycholanate. (**V**) differs from the 11(*β*) : 12(*β*)-ester obtained by oxidising (**I**) with CrO_3. Hydrogenation (Raney Ni) of (**V**) gives Me cholanate and (**IV**). (**IV**) is slowly transformed by Ac_2O in C_5H_5N at 100° into a non-cryst. *acetate* and by AcOH–HCl into a mixture mainly of (**I**) and *Me* Δ^9-*cholenate*, leaflets, m.p. 49·5—50°, or needles, m.p. 67—67·5°, $[\alpha]_D^{14}$ +39·15°±1° in $COMe_2$ [most conveniently obtained from (**IV**) and $POCl_3$ in C_5H_5N at room temp.]. The following oxidations with NHAcBr are recorded : *trans*-androsterone to androstanedione (**VI**) in 58·5% yield; androstanediol to (**VI**) in 82·5% yield; Me 12(*β*)-hydroxy- to Me 12-ketocholanate in high yield; Me deoxycholate to Me diketocholanate; deoxycorticosterone to an entirely neutral product, probably Δ^4-pregnen-21-al-3 : 20-dione; progesterone is scarcely attacked and cryst. products are not obtained from 21-acetoxy-Δ^4-pregnene-17(*β*) : 20-diol-3-one and substance *J*. M.p. are corr. (block).

H. W.

Bile acids and related substances. XXIV. Esters of 3(*β*)-hydroxy-11-keto- and 3(*β*) : 11(*α*)-dihydroxy-cholanic acid. J. Press, P. Grandjean, and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 598—606).—Me 3(*β*)-acetoxy-Δ^{11}-cholenate (**I**) is transformed by NHAcBr in aq. $COMe_2$ at 20° into a difficultly separable mixture converted by oxidation (CrO_3), debromination (Zn dust), and chromatography (Al_2O_3) into (**II**), *Me* 11-*keto*-3(*β*)-*acetoxycholanate* (**II**), m.p. 173—174°, $[\alpha]_D^{17}$ +56·4°±2° in $COMe_2$, and *Me* 12-*keto*-3(*β*)-*acetoxy*-Δ^9-*cholenate* (**III**), m.p. 192—193°, $[\alpha]_D^{20}$ +73·9°±4° in $COMe_2$. (**III**) is closely similar to *Me* 12-*keto*-3(*β*)-*acetoxycholanate*, m.p. 184—186°, $[\alpha]_D^{19}$ +77·9°±2° in $COMe_2$, from which it is best differentiated by its ultra-violet absorption spectrum. (**II**) is rather more readily obtained by cautious hydrogenation (AcOH containing a little PtO_2) of Me 3 : 11-diketocholanate and separation of the products by digitonin, thus giving much *Me* 3(*β*)-*hydroxy*-11-*ketocholanate* (**IV**), m.p. 152—153°, $[\alpha]_D^{21}$ +39·4°±2° in $COMe_2$, with little 3(*α*)-OH-ester. (**IV**) is acetylated to (**II**). Energetic reduction of (**II**) leads to *Me* 11(*α*)-*hydroxy*-3(*β*)-*acetoxycholanate*, m.p. 139—140°, $[\alpha]_D^{20}$ +50·0°±2° in $COMe_2$, oxidised to (**II**). (**I**) and Br in $CHCl_3$ give *Me* 11 : 12-*dibromo*-3(*β*)-*acetoxycholanate*, m.p. 172—175°. M.p. are corr. (block); limit of error ±2°.

H. W.

Bile acids and related substances. XXI. 12-Keto-3(*α*)-acetoxy- and 3(*α*)-hydroxy-Δ^9-cholenic acid. E. Seebeck and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 536—562).—The greatest difficulty in the prep. and investigation of 3(*α*)-hydroxy-Δ^9-cholenic acid (**I**) is its isomorphism with 3(*α*)-hydroxy-Δ^{11}-cholenic and lithocholenic acid. These acids are very difficult to separate and characterise, the only certain method being by chromatography after acetylation, methylation, and treatment with BzO_2H. An approx. determination of each component in a mixture may thus be effected. The (**I**) of Chakravorty *et al.* (A., 1940, II, 179) is shown to be non-homogeneous. 12-Keto-3(*α*)-acetoxycholanic acid is brominated according to Longwell *et al.* (*ibid.*, 95), and the product is separated with difficulty into 11(*β*)-bromo-12-keto-3(*α*)-acetoxycholanic acid (**II**), m.p. 220—222°, $[\alpha]_D^{17}$ +39·2°±2° in $COMe_2$, and the corresponding 11(*α*)-acid (**III**), m.p. 179—182°. (**II**) and (**III**) with CH_2N_2 in Et_2O afford *Me* esters (**IV**), m.p. 160—161°, $[\alpha]_D^{18}$ +37·5° ±1° in $CHCl_3$, and (**V**), forms, m.p. 100—101°, and 159—161° $[\alpha]_D^{19}$ +47·3°±2° in $CHCl_3$, respectively. The isolation of (**II**) is not always reproducible and the esters can be obtained directly from the crude brominated product whereby (**V**) is copiously but (**IV**) sparingly secured. (**VI**) is readily transformed by boiling C_5H_5N into *Me* 12-*keto*-3(*α*)-*acetoxy*-Δ^9-*cholenate* (**VI**), m.p. 145—147°, $[\alpha]_D^{20}$ +110·8°±2° in $CHCl_3$, $[\alpha]_D^{18}$ +101·4°±1·5° in $COMe_2$, the homogeneity of which is best established by its ultra-violet absorption spectrum; (**V**) under similar conditions is little affected by C_5H_5N but passes into (**VI**) in boiling collidine. (**VI**) with 1% HCl–MeOH at 18° gives *Me* 3(*α*)-*hydroxy*-12-*keto*-Δ^9-*cholenate* (**VII**), m.p. 115—116°, $[\alpha]_D^{14}$ +93·2°±2° in $COMe_2$, hydrolysed by alkali to the acid, m.p. 173—174°, $[\alpha]_D^{15}$ +96·1°±5° in $COMe_2$ [*semicarbazone*, m.p. 270° (decomp.)], which is acetylated by boiling AcOH–Ac_2O to 12-keto-3-acetoxy-Δ^9-cholenic acid, m.p. 205—206°, $[\alpha]_D^{18}$ +99·2°±2° in $COMe_2$ (cf. Longwell *et al.*, *loc. cit.*). (**VII**) is oxidised by CrO_3 in AcOH to *Me* 3 : 12-*diketo*-Δ^9-*cholenate*, m.p. 131—132°, $[\alpha]_D^{19}$ +71·6°±2° in $COMe_2$. Non-homogeneous (**VI**) is reduced by N_2H_4,H_2O and NaOEt–EtOH at 180° to a mixture (**VIII**), m.p. 132—134°, $[\alpha]_D^{13}$ +62·6°±2° in $COMe_2$, of *Me* 3(*α*)-*acetoxy*-Δ^9- (**IX**), and -Δ^{11}-cholenate (**X**) and Me acetyl-lithocholate (**XI**). (**VIII**) and excess of BzO_2H in $CHCl_3$ give *Me* 9 : 11-*oxido*-3(*α*)-*acetoxycholanate* (**XII**), m.p. 121—122°, $[\alpha]_D^{13}$ +44·1°±2° in $COMe_2$ (main product), and Me 11 : 12-oxido-3(*α*)-acetoxycholanate, m.p. 140—142°. Similar reduction of pure (**VI**) leads to a mixture (**XIII**) containing (**IX**) and (**X**) but apparently no (**XI**). Hydrogenation (Raney Ni in MeOH) of (**XII**) gives inconclusive results but (**XI**) is obtained by treatment of (**XIII**) with H_2–PtO_2 in AcOH. Me 11(*α*)-hydroxy-3(*α*)-acetoxycholanate, m.p. 146—148°, is transformed by $SOCl_2$ or $POCl_3$ in anhyd. C_5H_5N at room temp. into (**IX**), m.p. 138—140°, $[\alpha]_D^{14}$ +62·9°±2° in $COMe_2$, converted by BzO_2H in $CHCl_3$ into (**XII**) and hydrolysed by KOH in boiling EtOH to (**I**), m.p. 190—192°, $[\alpha]_D^{13\cdot5}$ +46·9°±2° in abs. EtOH (*acetate*, m.p. 176—179°, $[\alpha]_D^{13}$ +60°±2° in $COMe_2$; *Me* ester, m.p. 105—107°, $[\alpha]_D^{13\cdot5}$ +45·3°±2° in $COMe_2$) (Me lithocholate has $[\alpha]_D^{13}$ +32·8°±2° in $COMe_2$). (**IX**) is oxidised by CrO_3 in AcOH at 40° to (**VI**). Non-cryst. materials are obtained from (**XII**) and boiling HCl–AcOH followed by methylation and acetylation of the crude product. M.p. are corr. (block); limit of error ~±2°.

H. W.

Bile acids and related substances. XXV. Esters of 3-keto- and 3(*α*)- and 3(*β*)-hydroxy-Δ^{11}-ætiocholenic acid. A. Lardon and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 607—619).—3(*α*) : 12(*β*)-Dihydroxyætiocholanic acid is converted by successive treatments with CH_2N_2 and Ac_2O–C_5H_5N at 100° into *Me* 3(*α*) : 12(*β*)-*diacetoxy-ætiocholanate*, m.p. 149—150°, $[\alpha]_D^{25}$ +149·8°±1·5° in $COMe_2$. This is converted by HCl–MeOH at 18° into *Me* 3(*α*)-*hydroxy*-12(*β*)-*acetoxyætiocholanate*, m.p. 141—142°, $[\alpha]_D^{17}$ +143·6°±3° in $COMe_2$, oxidised by CrO_3 in AcOH at 18° to *Me* 3-*keto*-12(*β*)-*acetoxyætiocholanate* (**I**), m.p. 95—96°, $[\alpha]_D^{16}$ +138°±2° in $COMe_2$. Alkaline hydrolysis of (**I**) followed by re-esterification yields the 12(*β*)-*OH*-ester (**II**), m.p. 144—145°, $[\alpha]_D^{16}$ +105·9°±2° in $COMe_2$. BzCl and abs. C_5H_5N in C_6H_6 at 20° followed by MeOH–C_5H_5N and AcOH convert (**II**) into *Me* 3-*keto*-12(*β*)-*benzoyloxycholanate* (**III**), unstable transparent granules, m.p. 148—150°, or stable granules or prisms, m.p. 197—198°, $[\alpha]_D^{19}$ +117·9°±3° in $COMe_2$; in an individual experiment in which the treatment with AcOH was omitted the product appeared to be the corresponding Me_2 *acetal*, m.p. 115—117°, $[\alpha]_D^{16}$ +105·7°±2° in $COMe_2$, converted by boiling aq. AcOH into (**III**). (**III**) at 330—340°/12 mm. and later at 380—400°/12 mm. gives *Me* 3-*keto*-Δ^{11}-*ætiocholenate* (**IV**), m.p. 133—135°, $[\alpha]_D^{16}$ +79·1°±2° in $COMe_2$, hydrogenated (PtO_2 in AcOH) to Me 3-ketoætiocholanate and reduced [$Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$] to *Me* 3(*α*)-(**V**), m.p. 122—124°, $[\alpha]_D^{16}$ +77·7°±2·5° in $COMe_2$, and *Me* 3(*β*)-*hydroxy*-Δ^{11}-*ætiocholenate* (**VI**), m.p. 131—133°, $[\alpha]_D^{16}$ +70·7°±2° in $COMe_2$. The 1 : 1 compound of (**V**) and (**VI**) has m.p. 142—143°. (**V**) or (**VI**) is oxidised by CrO_3 in AcOH to (**IV**). *Me* 3(*α*)- and 3(*β*)-*acetoxy*-Δ^{11}-*ætiocholenate* have m.p. 99—100°, $[\alpha]_D^{17}$ +87·7°±2° in $COMe_2$, and m.p. 70—72°, $[\alpha]_D^{21}$ +62·5°±2° in $COMe_2$, respectively. M.p. are corr. (block).

H. W.

Bile acids and related substances. XXIII. Esters of 3 : 11-diketo-, 3(*α*)-hydroxy-11-keto- and 3(*α*) : 11(*α*)-dihydroxy-cholanic acid. A. Lardon and T. Reichstein [with, in part, P. Grandjean] (*Helv. Chim. Acta*, 1943, **26**, 586—598).—Me 3-keto-Δ^{11}-cholenate (**I**) in $COMe_2$ is treated with aq. NHAcBr at room temp. and the crude product is oxidised (CrO_3 in AcOH), debrominated (Zn dust in AcOH), and separated (Al_2O_3) into unchanged (**I**), *Me* 3 : 11-*diketocholanate* (**II**), m.p. 82—84°, $[\alpha]_D^{17}$ +61·7°±2° in $COMe_2$, and *Me* 3 : 12-*diketo*-Δ^9-*cholenate* (**III**), m.p. 130—131°, $[\alpha]_D^{15}$ +71·7°±2° in $COMe_2$. The brominated product from (**I**) contains *Me* 11 : 12-*dibromo*-3-*ketocholanate*, m.p. 136—138°, and (probably) *Me* 11(*α*) : 12(*α*)-*oxido*-3-*ketocholanate*, m.p. 122—124°. Similar bromination, oxidation, and debromination of Me 3-acetoxy-Δ^{11}-cholenate leads to *Me* 11-*keto*-3(*α*)-*acetoxycholanate* (**IV**), m.p. 132—133°, $[\alpha]_D^{17}$ +67·1° ±2° in $COMe_2$, and *Me* 12-*keto*-3(*α*)-*acetoxy*-Δ^9-*cholenate* (**V**), m.p. 149—150°, $[\alpha]_D^{17}$ +102·5°±1·5° in $COMe_2$. (**IV**) is converted by alkaline hydrolysis, esterification, and oxidation into (**II**) and (**V**) similarly into (**III**). (**IV**) is hydrogenated (PtO_2 in AcOH at 20°) to *Me* 11(*α*)-*hydroxy*-3(*α*)-*acetoxycholanate* (**VI**), m.p. 146—148°, $[\alpha]_D^{17}$ +70·7°±2° in $COMe_2$, reoxidised to (**IV**). Acid hydrolysis followed by methylation and reacetylation of (**VI**) gives a product, m.p. 135—137°, $[\alpha]_D^{15}$ +59·7°±2° in $COMe_2$, which, although apparently homogeneous, is probably a mixture of Me 3(*α*)-acetoxy-Δ^9- and -Δ^{11}-cholenate. M.p. are corr. (block).

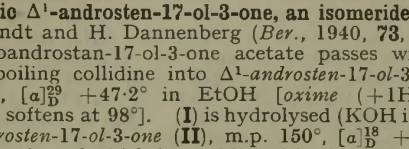
H. W.

Preparation of homologues of 3-hydroxy-12-ketocholanic acid. E. Schwenk, B. Riegel, R. B. Moffett, and (Miss) E. Stahl (*J. Amer. Chem. Soc.*, 1943, **65**, 549—551).—*Deoxycholic acid* 3-*H succinate* (prep. in C_5H_5N), m.p. 231—232°, $[\alpha]_D$ +51·5° (*Me*$_2$ ester, m.p. 98—100°), with CrO_3–AcOH at room temp. and then boiling aq. alkali gives 3-hydroxy-12-ketocholanic acid, $[\alpha]_D$ +86·6° (lit. +110°) (3-*H succinate*, m.p. 242—244°; 3-*acetate Me* ester, m.p. 148·5—150°). Similarly, *nordeoxycholic acid* 3-*H succinate*, m.p. 241—242°, $[\alpha]_D$ +54·8°, gives 3-*hydroxy*-12-*ketonorcholanic acid* 3-*H succinate* (77·3%), m.p. 257—258°, and thence the free *acid*, m.p. 250—251°, $[\alpha]_D$ +69·7° (3-*acetate*, m.p. 207·8—209·5°, $[\alpha]_D$ +99·7°), the *semicarbazone*, decomp. ~250—275°, of which with NaOEt–EtOH at 180—200° gives norlithocholic acid (>44%), m.p. 183—

183·5° (cf. lit.). *Bisnordeoxycholic acid 3-H succinate*, m.p. 234—235°, $[\alpha]_D$ +33·9°, gives 3-*hydroxy*-12-*ketobisnorcholanic acid*, m.p. 298—299°, $[\alpha]_D$ +84·6° [3-*acetate*, m.p. 246—247°, $[\alpha]_D$ +65·9°; *semicarbazone*, decomp. ~210—230° (gas)], by way of its 3-*H succinate*, m.p. 252—254°. Crude 3-hydroxy-12-ketoætiodeoxycholic acid 3-H succinate, m.p. 161—169°, gives 3-*hydroxy*-12-*ketoætiocholanic acid*, m.p. 213—215°, $[\alpha]_D$ +127·2° (3-*acetate*, m.p. 205—206°). [α] are in dioxan. M.p. are corr. R. S. C.

Authentic Δ^1-androsten-17-ol-3-one, an isomeride of testosterone. A. Butenandt and H. Dannenberg (*Ber.*, 1940, **73**, [*B*], 206—208).—2-Bromoandrostan-17-ol-3-one acetate passes without isomerisation in boiling collidine into Δ^1-*androsten*-17-*ol*-3-*one acetate* (**I**), m.p. 122°, $[\alpha]_D^{29}$ +47·2° in EtOH [*oxime* (+1H_2O), m.p. 112° (decomp.), softens at 98°]. (**I**) is hydrolysed (KOH in boiling MeOH) to Δ^1-*androsten*-17-*ol*-3-*one* (**II**), m.p. 150°, $[\alpha]_D^{18}$ +53·3° in EtOH, the constitution of which is established by its absorption spectrum, and by its oxidation (CrO_3 in AcOH) to Δ^1-*androstene*-3 : 17-*dione*, m.p. 138—139°, $[\alpha]_D^{19}$ +144·0° in EtOH, which is reduced (Na–Pr$^\beta$OH) to *iso*androstane-3 : 17-diol, m.p. 163—164° (diacetate, m.p. 122°). According to the Fussgänger test (**II**) belongs to the most active class of compounds of the androsterone series whereas in the other tests it is much inferior to testosterone. The pronounced œstrogenic activity previously ascribed to the Δ^1-unsaturated compounds of the androstane series appears to be confined to the isomeric "hetero-Δ^1-compounds." H. W.

Sterols. CLIII. Sapogenins. LXV. Kryptogenin, a new type of sapogenin from *Beth* root. R. E. Marker, R. B. Wagner, D. P. J. Goldsmith, P. R. Ulshafer, and C. H. Ruof (*J. Amer. Chem. Soc.*, 1943, **65**, 739).—Roots of *Trillium erectum* contain about equal amounts of diosgenin (**I**) (A., 1941, III, 62) and *kryptogenin* (**II**), $C_{27}H_{42}O_4$, m.p. 187—189°. With Na–Pr$^\beta$OH, (**II**) gives (**I**) (isolated



(II.)

as acetate) and with H_2–PtO_2 in Et_2O + AcOH (a little) gives the 5 : 6-H_2-derivative, m.p. 169—171°, which with CrO_3–AcOH gives 3-dehydrotigogenoic acid. The structure shown is assigned to (**II**). No details are given. R. S. C.

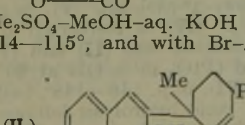
V.—TERPENES AND TRITERPENOID SAPOGENINS.

Inversion of menthone with hydrogen chloride in benzene. A. Weissberger and D. S. Thomas, jun. (*J. Amer. Chem. Soc.*, 1943, **65**, 402—403).—Inversion of *l*-menthone (**I**) by HCl in C_6H_6 at 20·0 + 0·1° is shown kinetically to proceed by way of a complex, (**I**) + 2HCl. R. S. C.

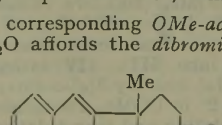
Synthetic production of camphor from pinene. IV. Oxidation of borneols to camphor. B. G. S. Acharya, R. C. Shah, and T. S. Wheeler (*J. Univ. Bombay*, 1943, **11**, **A**, Part 5, 113—115).—Methods of oxidising borneol to camphor are reviewed. 96% of camphor is obtained from *iso*borneol with 35% HNO_3–50% H_2SO_4 at 75—85°. A. Li.

Reaction of β-naphthol with dienes. J. C. Salfeld (*Ber.*, 1940, **73**, [*B*], 376—385).—β-$C_{10}H_7$·OH (**I**) and α-phellandrene at 130° give an *adduct* (**II**), $C_{20}H_{24}O$, m.p. 139—140° (p-*nitrobenzoate*, m.p. 164—165°). (**I**) and Me sorbate at 180° yield the *lactone*, 2 : 3-$C_{10}H_6$·CH·CH_2·CH:CHMe (**III**), m.p. 102—103°, which with O——CO

Me_2SO_4–MeOH–aq. KOH gives the corresponding *OMe-acid*, m.p. 114—115°, and with Br–AcOH–Et_2O affords the *dibromide*, m.p.



(II.)



(IV.)

222—224° [Zn–EtOH gives (**III**)]. With $\Delta^{1:3}$-*cyclo*hexadiene, (**I**) affords an *adduct*, $C_{16}H_{16}O$, b.p. 175—178°/1 mm. (*picrate*, m.p. 121°; p-*nitrobenzoate*, m.p. 171—172°). (**II**) with Se at 275°, or with HCl–MeOH, gives the *compound* (**IV**), m.p. 105—106° (*picrate*, m.p. 126—127°), also obtained in small amount from (**I**), α-phellandrene, and $ZnCl_2$–AcOH at 0° (2 days), then at room temp. (1 day), and then at 100° (bath) (1 hr.). Br–AcOH converts (**IV**) into a Br_1-derivative, m.p. 130—132°. (**II**) is hydrogenated (Pd–C; EtOH; 1 mol. of H_2) to a H_2- (p-*nitrobenzoate*, m.p. 135—136°) or (3 mols. of H_2) H_6-derivative (p-*nitrobenzoate*, m.p. 177—179°). The *p*-nitrobenzoate of (**II**) and BzO_2H in $CHCl_3$ give an *oxide*, $C_{27}H_{27}O_5N$, m.p. 179—180°, hydrolysed by KOH–MeOH to a *compound*, $C_{20}H_{24}O_2$, m.p. 153—154° (non-cryst. *acetate*). (**III**) similarly affords an *oxide*, $C_{16}H_{14}O_3$, m.p. 144—145°. A. T. P.

Triterpenediols. VI. Faradiol and arnidiol. J. Zimmermann (*Helv. Chim. Acta*, 1943, **26**, 642—647; cf. A., 1941, III, 714).—The isolation of faradiol (**I**), m.p. 236—237°, $[\alpha]_D$ +44·5° in $CHCl_3$ (diacetate, m.p. 163—167°, $[\alpha]_D$ +55·5° in $CHCl_3$), and arnidiol (**II**), m.p. 257°, $[\alpha]_D$ +82·7° in $CHCl_3$ (diacetate, m.p. 193°, $[\alpha]_D$ +80·4° in $CHCl_3$), from arnica, sunflower, and coltsfoot is described. The *diketone* obtained by oxidation of (**I**) has m.p. 242° and that from (**II**), m.p. 254° (*dioxime*, m.p. 268°). The *diacetates* of *dihydrofaradiol* and *-arnidiol* have m.p. 196° and 210°, respectively. Dihydro-faradiol and -arnidiol give the same *diketone*, m.p. 182° (*dioximine*, m.p. 253—254°). (**I**) is distinguished from (**II**) by the position of the double linking and the steric position of the OH groups in the mol. (**I**) diacetate is isomerised by 90% HCO_2H to a *substance*, $C_{34}H_{54}O_4$, m.p. 255°, $[\alpha]_D$ +89·6°. Triterpenes could not be obtained from the disc florets, fruits, recepticle, stalk, and upper stem, pericarp, or seeds of sunflower but only from the ray florets. The same sitosterol glucoside is present in all parts of the plant; it is characterised by its *tetra-acetate*, m.p. 168°. H. W.

Carotenoids from the blossoms of the chrysanthemum. Chrysanthemaxanthin.—See A., 1943, III, 615.

Cardanol derivatives.—See B., 1943, II, 212.

VI.—HETEROCYCLIC.

Condensation of 2-furylacetic acid with *o*-nitrobenzaldehyde. E. D. Amstutz and E. R. Spitzmiller (*J. Amer. Chem. Soc.*, 1943, **65**, 367—369).—K 2-furylacetate, *o*-NO_2·C_6H_4·CHO, and Ac_2O at, best (100·7% of crude ketone), 75° give cis- (**I**) (42·6%), m.p. 192—192·4° (corr.), and trans-*o*-*nitro*-α-2-*furylcinnamic acid* (**II**) (23·2%), m.p. 137·6—138·2° (corr.), configurations referring to Ph and furyl. With a trace of I in $PhNO_2$ at 210°, (**II**) gives <58% of (**I**). Decarboxylation of (**I**) and (**II**) gives cis- (**III**), b.p. 152—154°/3 mm., and trans-β-*o*-*furylstyrene* (**IV**) (15%), m.p. 92·8—93·6° (corr.), respectively. In quinoline at 230°, (**III**) gives a trace of crystals, possibly (**IV**). With $FeSO_4$–aq. NH_3, (**II**) gives *o*-*amino*-α-2-*furylcinnamic acid* (78%), m.p. 156°, which resists "Pschorr" ring-closure. R. S. C.

Tetrahydropyranyl amino-alcohols. G. H. Harnest and A. Burger (*J. Amer. Chem. Soc.*, 1943, **65**, 370—372).—(CHMeCl·CH_2)$_2$O does not react with $CHNa(CO_2Et)_2$ (**I**) or NaI–$COMe_2$. Tetrahydropyran-4-carboxylic acid is obtained in 52% yield by successive condensation of (Cl·$[CH_2]_2$)$_2$O with (**I**), hydrolysis (KOH–aq. EtOH), and decarboxylation (175—185°). With $SOCl_2$ it gives the acid chloride, b.p. 93—95°/21 mm., and thence (CH_2N_2–Et_2O) 4-*diazo*-, m.p. 42—45° (decomp.), and (48% aq. HBr–Et_2O at 0°) 4-*bromoacetyltetrahydropyran*, lachrymatory, m.p. 50—53°. With NHR_2 (2·5 mols.) in Et_2O at room temp., this (1 mol.) gives 4-*diethylamino*-, m.p. 152—155°, 4-*piperidino*-, m.p. 177—179°, and 4-*morpholinoacetyltetrahydropyran hydrochloride*, m.p. 214—219°, reduced by H_2–PtO_2 in EtOH to 4-α-*hydroxy*-β-*diethylamino*-, m.p. 140·5—142°, *-piperidino-* (**II**), m.p. 208—210° (*acetate hydrochloride*, m.p. 211—213°), and *-morpholino-ethyltetrahydropyran hydrochloride*, m.p. 213—216° (*acetate hydrochloride*, m.p. 223—225°). NH_3–Et_2O and (**I**) give the amide, dehydrated by P_2O_5 at 180—280°/20 mm. to 4-cyanotetrahydropyran, b.p. 100—102°/25 mm. Et 4-cyanotetrahydropyran-4-carboxylate has b.p. 130—134°/23 mm. (cf. lit.). (**II**) is analgesic. Some tetrahydropyranylhydantoins are mild anticonvulsants, but not hypnotic. M.p. are corr. R. S. C.

Vitamin-*E*. XL. Synthesis and properties of 4-hydroxy-3 : 4 : 5-trimethyl-1-*iso*propylcoumaran. L. I. Smith and J. A. King (*J. Amer. Chem. Soc.*, 1943, **65**, 441—444; cf. A., 1941, II, 326).—Adding Na and then $COMePr^\beta$ to $Pr^\beta CO_2Et$ gives $CH_2(COPr^\beta)_2$ (28%), b.p. 62—63°/3 mm., which with NaOEt–EtOH and then O:C_6HMe_3:O at <25° (later 0°) gives δ-2: 5-*dihydroxy*-3 : 4 : 6-*trimethylphenyl*-βζ-*dimethyl*-n-*heptane*-γε-*dione* (76%), m.p. 135—135·5°. With a drop of H_2SO_4 in AcOH this gives α-5-*acetoxy*-2-iso*butyroxy*-3 : 4 : 6-*trimethylphenyl*-γ-*methylbutan*-β-*one* (**I**), m.p. 113°, or with boiling HCl–EtOH gives 4-*hydroxy*-3 : 5 : 6-*trimethyl*-1-iso*propylbenzfuran*, m.p. 118° (*acetate*, m.p. 69—70°), also obtained similarly from (**I**), and reduced by H_2–Raney Ni at 125°/1300 lb. to 4-*hydroxy*-3 : 5 : 6-*trimethyl*-1-iso*propyl*-1 : 2-*dihydrobenzfuran* (**II**), m.p. 112° (*acetate*, m.p. 72—73°). Aq. $AuCl_3$ or $FeCl_3$ oxidises (**II**) to 2 : 3 : 5-*trimethyl*-6-β-*hydroxy*iso*amyl*-1 : 4-*benzoquinone*, an oil, reduction of which by $Na_2S_2O_4$–H_2O–MeOH or boiling Zn–AcOH yields (**II**) directly, no quinol being obtainable. R. S. C.

Condensation of α-substituted acetoacetates with phenols. VI. Condensation of phenols with ethyl acetosuccinate. VII. Condensation of substituted phenols with ethyl acetosuccinate. R. H. Shah and N. M. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 481—485, 486—488).—VI. CO_2Et·CHAc·CH_2·CO_2Et has been condensed with phenols in the presence of different catalysts. Resorcinol yields ($POCl_3$ or P_2O_5) Et 7-hydroxy-4-methylcoumarin-3-acetate [acetate (**I**), m.p. 98°; benzoate, m.p. 138° (lit. 127°)], or ($AlCl_3$) the free

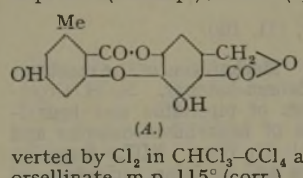
acid [*acetate* (**II**), m.p. 199—200°; *benzoate*, m.p. 190—191°]. (**II**) is decarboxylated by Cu-bronze in boiling quinoline. (**I**) is converted by $AlCl_3$ at 120—125° into 7-hydroxy-8-acetyl-4-methylcoumarin-3-acetic acid. Orcinol ($POCl_3$ or H_2SO_4) yields the Et ester, m.p. 206° (lit. 198—200°) (*acetate*, m.p. 91—92°), of *5-hydroxy-4 : 7-dimethylcoumarin-3-acetic acid*, m.p. 270° (*acetate*, m.p. 183—184°). Pyrogallol yields (conc. H_2SO_4, H_2O-cooling) 7 : 8-*dihydroxy-4-methylcoumarin-3-acetic acid*, m.p. 270° (*acetate*, m.p. 224—225°), or [H_2SO_4 (ice-cooling) or $POCl_3$] its Et ester, m.p. 206° (lit. 186°) (*acetate*, m.p. 123—124°). Phloroglucinol yields (80% H_2SO_4) 5 : 7-*dihydroxy-4-methylcoumarin-3-acetic acid*, m.p. >285° (*acetate*, m.p. 169—170°) or ($POCl_3$) its *Et* ester, m.p. 250° (*acetate*, m.p. 114—115°). α- and β-$C_{10}H_7$·OH yield respectively *4-methyl-α-*, m.p. 253—254° ($AlCl_3$, $POCl_3$, or 80% H_2SO_4), or its Et ester, m.p. 141° (lit. 137°), and *-β-*naphthapyrone-3-acetic acid (conc. H_2SO_4) (Et ester, m.p. 101°). *m*-Cresol yields (conc. H_2SO_4) *Et* 4 : 7-*dimethylcoumarin-3-acetate*, m.p. 106° (free *acid*, m.p. 193—194°).

VII. With CO_2Et·$CHAc$·CH_2·CO_2Et, Me β-resorcylate yields (80% H_2SO_4) Me 7-hydroxy-4-methylcoumarin-6-carboxylate; 2 : 1 : 3-$C_6H_3Ac(OH)_2$ yields ($POCl_3$) *Et 7-hydroxy-8-acetyl-4-methylcoumarin-3-acetate*, m.p. 167—168° (*acetate*, m.p. 221—223°), or (80% H_2SO_4) the free *acid*, m.p. 262—263°; 2 : 1 : 3-$C_6H_3Bz(OH)_2$ yields ($POCl_3$) *Et 7-hydroxy-8-benzoyl-4-methylcoumarin-3-acetate*, m.p. 196—197° (*acetate*, m.p. 177°; free *acid*, m.p. 255°); 4 : 1-$C_{10}H_6Cl$·OH yields (conc. H_2SO_4) Et 6-chloro-4-methyl-1 : 2-α-naphthapyrone-3-acetate, m.p. 185—186° (lit. 181—184°), or (80% H_2SO_4) the free *acid*, m.p. 276—277° (*anilide*, m.p. 265—266°); 4 : 1 : 3-$C_6H_3Cl(OH)_2$ yields ($POCl_3$ or conc. H_2SO_4) Et 6-chloro-7-hydroxy-4-methylcoumarin-3-acetate (*acetate*, m.p. 169°; free *acid*, m.p. 263°), but 4 : 1 : 3-$C_6H_3Br(OH)_2$ gives ($POCl_3$) Et 7-hydroxy-4-methylcoumarin-3-acetate. The effect of substituents on the reaction is discussed. A. LI.

Constitution of evodionol. F. N. Lahey (*Univ. Queensland Papers, Dept. Chem.*, 1942, **1**, No. 20, 14 pp.).—Evodionol (**I**) is shown to be *7-hydroxy-5-methoxy-6-acetyl-2 : 2-dimethyl-1 : 2-benzpyran* (cf. *Univ. Queensland Publication*, 1940, **1**, 17). With NH_2OH,HCl and $BaCO_3$ (excess) in boiling EtOH (not other conditions) it gives an *oxime*, m.p. 89° (green $FeCl_3$ colour; brown *Cu* compound proves the presence of OH·C·C·C:N·OH), and with PhCHO and NaOH in ~50% EtOH at room temp. gives a *CHPh:* derivative (**II**), m.p. 94° (brown $FeCl_3$ colour). Dihydroevodionol (the derived chroman) (**III**) gives similarly an *oxime*, m.p. 132° (violet $FeCl_3$ colour; brown *Cu* derivative, cf. above), a *CHPh:* (**IV**), m.p. 118° (red $FeCl_3$ colour), and, by boiling HNO_3–H_2O–EtOH, the 8-NO_2-derivative, m.p. 158·5°, a 2 : 4-dinitrophenylhydrazone, m.p. 188°, and acetate, m.p. 84—85°. The Me ether (**V**) of (**I**) gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 135°, and *CHPh:* derivative (**VI**), m.p. 114°. The Me ether of (**III**) gives a 2 : 4-dinitrophenylhydrazone, m.p. 169°, and *CHPh:* derivative (**VII**), m.p. 104°; its *oxime*, m.p. 160—161°, is converted by $SOCl_2$ into the *amide*, $C_{15}H_{21}O_4N$, m.p. 172°, from which, however, only a trace of amine is formed by hydrolysis. H_2–PtO_2 at 2 atm. reduces (**II**) to *tetrahydrobenzylidene-evodionol* [*7-hydroxy-5-methoxy-6-β-phenylpropionyl-2 : 2-dimethylchroman*], m.p. 88° (reddish-brown $FeCl_3$ colour), hydrolysed by 40% KOH–EtOH at 230—250° to the known 7-hydroxy-5-methoxy-2 : 2-dimethylchroman, m.p. 103°, and Ph·$[CH_2]_2$·CO_2H; this proves the structure of (**I**) except for the position of the Ac. Hydrogenation of (**VI**) gives similarly the known 5 : 7-dimethoxy-6-β-phenylpropionyl-2 : 2-dimethylchroman, an oil (oxime, m.p. 129·5°), which proves the structure of (**I**) except for the position of the free OH. The dibasic acid (**VIII**), $C_{15}H_{18}O_8$, obtained from (**I**) by $KMnO_4$–$COMe_2$ (*loc. cit.*) is termed *evodionic acid*; at 140—150° it yields a glassy acid (**IX**) and small amounts of AcOH, 4 : 2 : 6 : 1-OH·$C_6H_2(OMe)_2$·COMe (and thence the Me_3 ether), and 3 : 5 : 1-$C_6H_3(OMe)_2$·OH (**X**) [yields *s*-$C_6H_3(OMe)_3$; more formed at 250°; also obtained from (**IX**)]; (**IX**) is converted by MeOH–H_2SO_4 into 3 : 5 : 4 : 1-$(OMe)_2C_6H_2Ac$·O·CMe_2·CO_2Me, m.p. 76°, which is similarly obtained from (**VIII**) and is synthesised from 4 : 2 : 6 : 1-OH·$C_6H_2(OMe)_2$·COMe by CMe_2Br·CO_2Me and K_2CO_3 in $COMe_2$; these products confirm the structure of (**I**). In boiling 25% NaOH, (**I**), but not (**IV**), yields $COMe_2$, confirming the 2 : 2-dimethyl-1 : 2-benzpyran structure. O_3 in CCl_4 converts (**V**) into *6-hydroxy-2 : 4-dimethoxy-3-acetylbenzaldehyde*, m.p. 76—77° (red $FeCl_3$ colour; reduces $AgNO_3$–NH_3), converted by MeI–K_2CO_3–$COMe_2$ into 2 : 4 : 6-*trimethoxy-3-acetylbenzaldehyde*, m.p. 84° (no $FeCl_3$ colour), which with $KMnO_4$ in aq. $COMe_2$ yields 2 : 4 : 6-*trimethoxy-3-acetylbenzoic acid*, m.p. 149—150°, and thence (heat at 160°) 2 : 4 : 6 : 1-$C_6H_2(OMe)_3$·COMe. Interaction of (**VIII**) with KOBr is re-interpreted thus: 1 : 3 : 2 : 5 : 6-CO_2H·$C_6HAc(OMe)_2$·O·CMe_2·CO_2H (**VIII**) → 6 : 2 : 4 : 1 : 3-CO_2H·CMe_2·O·$C_6H(OMe)_2(CO_2H)_2$ → 3 : 5 : 2 : 4 : 1-$(OMe)_2C_6HBr_2$·O·CMe_2·CO_2H, which with Na–Hg yields 3 : 5 : 1-$C_6H_3(OMe)_2$·O·CMe_2·CO_2H (**XI**). (**XI**) is synthesised from (**X**) by CMe_2Br·CO_2Me in NaOEt–EtOH (later hydrolysis by KOH–EtOH) and, when heated with soda-lime, gives *s*-$C_6H_3(OMe)_3$ and an oil, possibly 1 : 3 : 5-$C_6H_3(OMe)_2$·OPr^β, which is also an oil when prepared from (**X**) by $Pr^\beta I$–K_2CO_3–$COMe_2$. Pyrolysis of 3 : 5 : 4 : 1-$(OMe)_2C_6H_2Ac$·O·CMe_2·CO_2H also gives a little *s*-$C_6H_3(OMe)_3$. Aq. $KMnO_4$ oxidises (**VII**) in $COMe_2$ to 5 : 7-*dimethoxy-2 : 2-dimethylchroman-6-glyoxylic acid*, m.p. 169° (decomp.) (2 : 4-dinitrophenylhydrazone), BzOH, and 5 : 7-*dimethoxy-2 : 2-dimethylchroman*, an oil, identified by conversion by HCl–$Zn(CN)_2$–Et_2O into the known 8-CHO derivative (semicarbazone, m.p. 217°; 2 : 4-dinitrophenylhydrazone, m.p. 242°). Boiling (**II**) or (**IV**) in 10% H_2SO_4 containing some EtOH gives *5-methoxy-8 : 8-dimethyl-1 : 2-pyrano*[3 : 2-g]-*flavanone* [*5-methoxy-2′ : 2′-dimethylpyrano-5′ : 6′ : 6 : 7-flavanone*], m.p. 126°, and its 6 : 7-[3′ : 4′-]H_2-derivative, m.p. 145—146°, respectively. 5 : 7-Dihydroxy-6-acetyl-2 : 2 -dimethylchroman (improved prep.) with MeI and K_2CO_3 in boiling $COMe_2$ gives, after 2 hr., *5-hydroxy-7-methoxy-6-acetyl-2 : 2-dimethylchroman* (**XII**), m.p. 88° (2 : 4-*dinitrophenylhydrazone*, m.p. 192°), isomeric with (**I**), or, after 12 hr., the 5 : 7-Me_2 ether, m.p. 91°, identical with the Me ether of (**III**). 2 : 6-Dibromobenzoquinonechloroimide gives, as expected, a positive test with (**XII**), but not with (**I**) or (**III**). R. S. C.

Spectrographic study of evodionol and its derivatives.—See A., 1943, I, 191.

Chemical constituents of lichens found in Ireland. *Lecanora parella*, Ach. Constitution of variolaric acid. D. Murphy, J. Keane, and T. J. Nolan (*Sci. Proc. Roy. Dublin Soc.*, 1943, **23**, 71—82).—Extraction of the lichen with $COMe_2$ gives variolaric acid (**I**), new formula $C_{16}H_{10}O_7$, m.p. 296° (decomp.) after darkening, which gives a purple colour with $FeCl_3$, no colour with $CaOCl_2$, and a blue colour with 2 : 6-dichloro-*p*-benzoquinonechloroimide. When kept in 10% KOH at room temp. (**I**) affords ochric acid, $C_{16}H_{12}O_8$, m.p. 221—223° with evolution of CO when rapidly heated, and when boiled with 50% aq. KOH it gives a *substance* (**II**), $C_{14}H_{14}O_5$, m.p. 194—195°, insol. in aq. $NaHCO_3$, and a *compound* (**III**), $C_{15}H_{14}O_7$, m.p. 188·5° (decomp.) when slowly heated or m.p. 194—196° (decomp.) when rapidly heated. (**II**) with Me_2SO_4 in cold or boiling aq. NaOH gives a *Me_1 ether*, m.p. 128—129°, whereas CH_2N_2 gives a non-cryst. product. With excess of CH_2N_2 (**III**) gives a *Me_4 derivative*, m.p. 108—109°, whilst with a restricted proportion a *Me_1* ester, m.p. 217—218°, results. (**II**) and (**III**) do not give cryst. acetates. (**I**) and Ac_2O containing a little conc. H_2SO_4 at room temp. afford a *diacetate*, m.p. 245—246° after darkening. (**I**) is transformed by an excess of CH_2N_2 in $COMe_2$ at room temp. into its *Me_2 ether*, m.p. 260—261° (blackens), converted by boiling with 10% or 50% aq. KOH into the *substance*, $C_{16}H_{10}O_6(OMe)_2$, m.p. 246° (decomp.); hence (**I**) contains 2 aromatic OH but no CO_2H.



(*A*.)

With KOH–MeOH (**I**) gives a *Me_1* ester (**IV**), $C_{16}H_{11}O_7(OMe)$, $1·5H_2O$, m.p. 243° (decomp.), converted by CH_2N_2 into its *Me_3 ether*, m.p. 181—182°. When fused with KOH (**I**) gives orcinol and 3 : 5 : 1-$(OH)_2C_6H_3$·CO_2H. (**IV**) is converted by Cl_2 in $CHCl_3$–CCl_4 at room temp. into Me 2 : 4-dichloro-*o*-orsellinate, m.p. 115° (corr.). *Me* 2 : 6-*dichloro*-p-*orsellinate* has m.p. 167—169°. Hence (**I**) is (*A*). The lichen also contains mannitol. H. W.

Pyridines.—See B., 1943, II, 212.

Reduction of 3-acetylpicolines. A. Dornow and H. Machens (*Ber.*, 1940, **73**, [*B*], 355—358).—3-Acetyl-2-methylpyridine (**I**) and N_2H_4.H_2O at 125° give the hydrazone, which with a little KOH at 150° gives *2-methyl-3-ethylpyridine*, b.p. 67—69°/14 mm. (*picrate*, m.p. 140—141°; *methiodide*, m.p. 136°), also obtained by Clemmensen reduction of (**I**). Similarly prepared (Wolff–Kishner) is 2 : 6-*dimethyl-3-ethylpyridine* (**II**), b.p. 75°/13 mm. (*picrate*, m.p. 122°). Et 2 : 6-dimethylpyridine-3-carboxylate and boiling EtOAc–NaOEt (free from EtOH) give after hydrolysis by 10% HCl 3-acetyl-2 : 6-dimethylpyridine (**III**), reduced to (**II**). Hydrogenation (PtO_2–H_2O) of (**III**) gives 2 : 6-*dimethyl-3-α-hydroxyethylpyridine* (**IV**), m.p. 69°, also obtained by Clemmensen reduction of (**III**), or similarly from the corresponding 3-CH_2Br·CO compound after treatment with AcOH–KOAc. (**IV**) and CrO_3–AcOH give (**III**). 2-Methyl-3-α-hydroxyethylpyridine has b.p. 142°/12 mm. A. T. P.

3 : 4-Substituted pyridines. II. β-4-Pyridylpropionic acid. J. R. Stevens and R. H. Beutel (*J. Amer. Chem. Soc.*, 1943, **65**, 449—451; cf. A., 1942, II, 328).—CN·CH_2·CO·NH_2 (**I**) with CO_2Et·CO·CH_2·CO_2Et and piperidine (**II**) in warm MeOH gives *Et* 2 : 6-*dihydroxy-3-cyanopyridine-4-carboxylate*, softens 120°, liquid at 150°, isolated as *piperidine* salt (36%), m.p. 180—181°; with $CO(CH_2$·$CO_2Et)_2$, and (**II**) in boiling MeOH it gives *Et* 2 : 6-*dihydroxy-3-cyano-4-pyridylacetate* (31·5%), m.p. 239°. CO_2Et·$[CH_2]_2$·COCl and CHNaAc·CO_2Et in C_6H_6 give *Et_2 β-keto-α-acetyladipate* (18·4%), b.p. 65—76°/5 × 10^{-3}—10^{-4} mm., converted by NH_3–Et_2O at 0° into *Et_2 β-ketoadipate* (**III**) (60%), b.p. 65—70°/10^{-3} mm. With NHPh·NH_2 at 100°, (**III**) gives *1-phenyl-3-β-carbethoxyethylpyrazolone* (86%), m.p. 107·5°, and with (**I**) and (**II**) in EtOH at 85° gives *Et* β-2 : 6-*dihydroxy-3-cyano-4-pyridylpropionate* (36·5%), m.p. 247°, hydrolysed by conc. HCl at 150° to β-2 : 6-*dihydroxy-4-pyridylpropionic acid*, m.p. 268—269°. With $POCl_3$ at 175° this gives β-2 : 6-*dichloro-4-pyridyl-* (57%), m.p. 127°, sublimes 115°/10^{-3} mm., and thence (H_2–$PdCl_2$–C; MeOH; 30 lb.) β-4-*pyridyl-propionic*

acid (77%), m.p. 208°. OEt·$[CH_2]_2$·Br, (**III**), and NaOEt–EtOH give *Et_2 β-keto-α-β′-ethoxyethyladipate* (20%), b.p. 90°/5 × 10^{-4} mm., which could not be condensed with (**I**). R. S. C.

Synthesis of pyridinium ethanols. IV. Syntheses with carbethoxymethylpyridinium bromide. F. Krohnke (*Ber.*, 1940, **73**, [*B*], 310—312; cf. A., 1939, II, 104).—$CO_2Et·CH_2·NC_5H_5Br$ (**I**) and *m*-$NO_2·C_6H_4·CHO$ in aq. NaOH–EtOH at 0° give *β-hydroxy-α-carboxy-β-m-nitrophenylethylpyridinium betaine*, *m*-$NO_2·C_6H_4·CH(OH)·CH(CO_2^-)·N^+C_5H_5$, m.p. 157° (decomp.); the o-C_6H_4Cl analogue decomposes at 145—147° (*picrate*, m.p. 119—120°). (**I**) and 2 : 5 : 1-$C_6H_3Cl_2·CHO$ in aq. NaOH–EtOH at 0° afford *β-hydroxy-α-carbethoxy-β-2 : 5-dichlorophenylethylpyridinium bromide*, m.p. 148° (decomp.), converted by aq. NaOH at room temp. into the corresponding *betaine*, m.p. 140° (decomp.). (**I**) and aq. NaOH–EtOH at 0° give a 1 : 1 *compound*, m.p. (vac.) 110°, of $C_5H_5N^+·CH_2·CO_2^-$ and NaBr. A 1 : 1 *compound*, m.p. 158—159°, of NHPh·CO·$CH_2·NC_5H_5Br$ (A., 1939, II, 208) and *m*-$NO_2·C_6H_4·CHO$ is prepared in EtOH–N-NaOH at 0°. A. T. P.

Action of dipyridinium radicals on *para*-hydrogen.—See A., 1943, I, 204.

Reduction of quinoline and substituted quinolines in liquid ammonia. C. M. Knowles and G. W. Watt (*J. Amer. Chem. Soc.*, 1943, **65**, 410—412).—Passing H_2 into quinoline, 5-nitro- (**I**) or -amino-, or 8-amino-quinoline in NH_3 containg an excess of NH_4Br at −33·5° gives, without development of colour, 1 : 4-dihydroquinoline (**II**) [isolated as the *dimeride*, m.p. >80° (decomp.), of the Ac_2 derivative], the *trimeride*, m.p. >157° (decomp.), of 5- (**III**), or the *dimeride*, m.p. >125° (decomp.), of 8-amino-1 : 4-dihydroquinoline (**IV**), respectively. Reduction by Na in NH_3 gives the same products more rapidly, but colours develop prior to the blue due to Na; however, products were isolated as the *dimeride*, m.p. >100° (decomp.), of the benzoate of (**II**), the Et_4 derivative, m.p. >160° (decomp.), of (**III**) [from (**I**)], and the Bz_3 derivative, m.p. >148° (decomp.), of (**IV**); the Bz_3 derivative, m.p. >95° (decomp.), of (**III**) is also used for isolation. Na reduces 8-nitroquinoline in NH_3, yielding (**IV**), which is isolated as the Et_4 derivative, m.p. >155° (decomp.), but H_2 gives a gum unless Et_2O is used as diluent. Cessation of reduction at the H_2-stage precludes the 1 : 2-H_2-structure for the products. R. S. C.

Quinoline derivatives.—See B., 1943, III, 160.

αβ-Unsaturated amino-ketones. VI. Mechanisms of the reactions of *sec.*-amines with αβ-unsaturated α-bromo-ketones. N. H. Cromwell and D. J. Cram. **VII. Reaction of piperidine and benzylmethylamine with bromine derivatives of benzylidene-acetone and -acetophenone.** N. H. Cromwell and I. H. Witt. **VIII. Reaction of primary amines with 1 : 3-diketones and bromine derivatives of benzylideneacetophenone. Ethyleneimines.** N. H. Cromwell, R. D. Babson, and C. E. Harris (*J. Amer. Chem. Soc.*, 1943, **65**, 301—308, 308—312, 312—315; cf. A., 1942, II, 149).—VI. Contrary to the literature (A., 1941, II, 271), *sec.*-amines add to compounds, >C:CBr·COR, to give α-bromo-β-amino-ketones, which readily dissociate into their components and, under the influence of strong bases, rearrange to α-NH_2-ketones. The rearrangement probably proceeds by reversible formation (inhibited by presence of acid) of a salt, $\left[>N<\begin{matrix}CH— \\ CH·COR\end{matrix}\right]Br$, which by interaction with other reagents leads to varied types of products. Tetrahydro*iso*quinoline (**I**) (prep. from *iso*quinoline by H_2–Cu chromite in EtOH at 180°/1800 lb.) and CHPh:CBr·COMe [prep. from CHPhBr·CHBr·COMe (**II**) by NaOAc in boiling 95% EtOH], m.p. 30—31°, b.p. 114—117°/1 mm., in light petroleum–Et_2O at −15° give *α-bromo-β-tetrahydroisoquinolino-β-phenylethyl Me ketone* (**III**) (91%), m.p. 102—103°, which rapidly generates ionic Br in EtOH but only slowly in HNO_3–EtOH. With boiling NaOEt–EtOH, (**III**) gives a *tetrahydroisoquinolino-β-phenylvinyl Me ketone* (92%), m.p. 90—91°, unaffected by (**I**) in EtOH. *αβ-Bistetrahydroisoquinolino-β-phenylethyl Me ketone* (**IV**), m.p. 169—170°, is obtained exothermally from (**I**) and (**III**) (75%) or (**II**) (63·4%) in EtOH. Tetrahydroquinoline (**V**) reacts with neither (**II**) nor (**III**). In EtOH at room temp. (**III**) and (**V**) give *β-tetrahydroquinolino-α-tetrahydroisoquinolino-β-phenylethyl Me ketone* (43·7%; 30·5% formed in Et_2O), m.p. 107—109°, which in boiling 15% H_2SO_4 is hydrolysed to tetrahydro*iso*quinolinoacetone (**VI**) (*hydrochloride*, m.p. 213—215°), also obtained from (**I**) and $CH_2Cl·COMe$. In EtOH at 0° morpholine and (**III**) give (**IV**) (27·9%) and an inseparable mixture of α-tetrahydro*iso*quinolino-β-morpholino-β-phenylethyl Me ketone, (**IV**), and perhaps αβ-dimorpholino-β-phenylethyl Me ketone; a mixture is also formed in Et_2O; hydrolysis of the mixture gives (**VI**) as sole isolable product. Piperidine and (**III**) in Et_2O at 60° give only 5·3% of *β-piperidino-tetrahydroisoquinolino-β-phenylethyl Me ketone* (**VII**), m.p. 150—51°; in EtOH only (**IV**) (19%) is isolated. α-Bromo-β-morpholino-β-phenylethyl Me ketone (**VIII**) and (**I**) in Et_2O at 0° give (**IV**); in EtOH only 5·9% is obtained. α-Bromo-β-piperidino-β-phenylethyl Me ketone (**IX**) and (**I**) in Et_2O or EtOH at 0° give (**VII**) (36·4 and 40·3%, respectively), which in 15% H_2SO_4 at 100° gives PhCHO, piperidinoacetone [oxime, m.p. 122—123° (lit. 104°)], and a little $CH_2Ph·CO·COMe$. In EtOH, (**V**) and (**IX**) give exothermally 48·5% of (**VII**) (in Et_2O, 12·7%). In EtOH at room temp. (1 day), (**III**) gives (**IV**) (26%) and then, by treatment of the filtrate with morpholine at room temp., αβ-dimorpholino-β-phenylacetone (**X**) (5·5%), and 95% of the residual (**III**) is recovered. Similarly, (**VIII**) in EtOH with subsequent treatment with (**I**) gives (**X**) (15·3%) and then (**IV**) (31·4%). With H_2–PtO_2 in C_6H_6 at 28°/1·2 atm., α-bromo-β-piperidino-β-phenylpropiophenone gives piperidine (**XI**) and Ph·$[CH_2]_2$·COPh; with I–KI–acid, complex condensation products containing no Br or N are formed. α-Bromo-β-piperidino-β-phenylpropiophenone with H_2–PtO_2 in C_6H_6 at ~28°/1·2 atm. gives 82·7% of CH_2Bz_2. α-Bromobenzylideneacetophenone and dry HBr–Et_2O at −5° give CHPhBr·CHBr·COPh; α-piperidinobenzylideneacetophenone and dry HBr–C_6H_6 at 0° give piperidine hydrobromide.

VII. COMe·CH_2Bz (1 mol.), (**XI**) (2 mols.), and conc. HCl (1 drop) at the b.p. give a small yield of *γ-piperidino-α-phenyl-Δβ-buten-α-one*, m.p. 97—98°, which in dil. HCl gradually gives COMe·CH_2Bz (nearly 100%). β-Piperidinobenzylideneacetophenone does not condense with CH_2Bz_2. CHPh:CBr·COMe (**XII**) and (**XI**) in Et_2O–light petroleum at −30° give (**IX**), m.p. 80—82°, which gives ionic Br more rapidly in EtOH than in HNO_3–EtOH and with boiling NaOEt–EtOH gives *α-piperidino-β-phenylvinyl Me ketone*, m.p. 56—58° (hydrolysed by acid to $CH_2Ph·CO·COMe$). With (**IV**) in EtOH, (**IX**) gives α-piperidino-β-tetrahydroquinolino-β-phenylethyl Me ketone, m.p. 126—127°. CHPhBr·CHBr·COMe (**XIII**) and (**XI**) in EtOH at room temp. give αβ-dipiperidino-β-phenylethyl Me ketone, m.p. 121—122°. *αβ-Di(benzylmethylamino)-β-phenylethyl Me ketone*, m.p. 106—108°, is obtained from NHMe·CH_2Ph (**XIV**) by (**XII**) in Et_2O–light petroleum at −5° or (**XIII**) in EtOH. CHPh:CBr·COPh (**XV**) and (**XIV**) in Et_2O–light petroleum at 0° give *α-bromo-β-benzylmethylamino-β-phenylpropiophenone* (**XVI**), m.p. 109—110° (slowly releases I from HI; readily gives ionic Br in EtOH), converted by NaOEt–EtOH into *α-benzylmethylamino-β-phenylacrylophenone*, m.p. 73—75°, which in 5% HCl gives $CH_2Ph·COBz$. *αβ-Di(benzylmethylamino)-β-phenylpropiophenone*, m.p. 142—144°, is obtained (*a*) from (**XIV**) and (**XV**) in moist Et_2O, (*b*) with (?) an *isomeride*, m.p. 102—103°, from (**XIV**) and (**XVI**), or (*c*) in poor yield, with (?) 3-*benzylmethylamino*-2 : 4 : 5-*triphenyl*-1-*methyl*-Δ^3-*pyrroline*, m.p. 118—120°, from (**XIV**) and CHPhBr·CHBr·COPh in EtOH. In EtOH, (**XVI**) (1 mol.) and (**V**) (2 mols.) give *α-benzylmethylamino-β-tetrahydroquinolino-β-phenylpropiophenone*, m.p. 150—153°, hydrolysed by acid to ω-benzylmethylaminoacetophenone (*oxime*, m.p. 96—97°), which is also obtained from $COPh·CH_2Br$. M.p. are corr. and determined in a preheated bath.

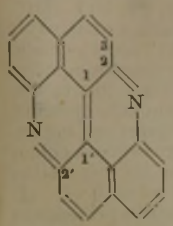
VIII. See A., 1943, II, 232. R. S. C.

5 : 5-Disubstituted hydantoins. H. R. Henze, L. M. Long, R. J. Speer, and T. R. Thompson (*J. Amer. Chem. Soc.*, 1943, **65**, 323—325).—Data of Marsh *et al.* (A., 1940, II, 289) are erroneous. H_2–PtO_2 in EtOH reduces 5-phenyl- to 5-*cyclo*hexyl-5-methylhydantoin, m.p. 214·6—215·8°. *p*-$NH_2·C_6H_4·COMe$, KCN, and $(NH_4)_2CO_3$ in 50% EtOH at 57—60° give 5-p-*aminophenyl*-5-*methylhydantoin*, m.p. 186—188°. Bucherer's method fails with *p*-$NMe_2·C_6H_4·COPh$, but KCN and $(NH_4)_2CO_3$ in fused NH_2Ac at 140° yield di-5-*p*-dimethylaminophenylhydantoin (38%) (colourless), m.p. 276—280°. Mesityl oxide gives a poor yield of 5-methyl-5-β-methylpropenylhydantoin, having a low m.p. (identified by hydrogenation to the Buβ compound), and 3-hydroxy-3 : 5 : 5-trimethylpyrrolidone, which is identified by conversion into 2-hydroxy-αγ-dimethyl-γ-valerolactone (**I**) and is also obtained from diacetoneamine by aq. KCN. $COMe·CH_2·CMe_2·OH$ gives (**I**), 5 : 5-dimethyl- (probably formed by way of $COMe_2$) and 5-*methyl*-5-β-*hydroxy*isobutyl-*hydantoin*, m.p. 180—181°, and a substance, (?) *α-ureido-αγ-dimethyl-γ-valerolactone*, m.p. 209—210°. M.p. are corr. R. S. C.

Synthesis of pyrazolesulphanilamides. II. G. Sanna [in part with (Signa.) V. Sollai] (*Gazzetta*, 1942, **72**, 313—317; cf. Sanna, *Rend. Sem. Fac. Sci. Cagliari*, 1940, **10**).—Antipyrine (**I**) with $ClSO_3H$ gives the chloride (**II**), m.p. 191°, of 1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone*-4-*sulphonic acid*, m.p. 277° [NH_4 salt, m.p. 277°; Cu salt; *amide*, m.p. 229° [239°]). With $CO(NH_2)_2$, (**II**) gives NN′-*bis*-(1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone*-4-*sulphon*)*carbamide*, m.p. 165°. With 2-aminopyridine (**III**), (**II**) in H_2O at 100°, or at the m.p., gives 1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone*-4-*sulphon*-2′-*pyridylamide*, m.p. 244°. (**II**) and (**III**) under other conditions [in EtOH?] give a substance, m.p. 96°. *p*-NHAc·$C_6H_4·SO_2Cl$ and 4-aminoantipyrine give the Ac derivative, m.p. 267°, of 4-p-*aminobenzenesulphonamidoantipyrine*, m.p. 213°. (**I**) and $ClSO_3H$ at 70°, followed by cooling, addition of H_2O, and reduction by Zn, give 4-*thiolantipyrine*, b.p. 135°/5 mm. E. W. W.

Dinaphthylenedi-imine and dehydrodinaphthylenedi-imine. A. Rieche, W. Rudolph, and R. Seifert (*Ber.*, 1940, **73**, [*B*], 343—350).—1 : 1′-(8 : 8′-Diacetamido-2 : 2′-diaphthone) and boiling aq. H_2SO_4 (130°) give *dehydrodinaphthylenedi-imine* (*dinylin*) (**I**), m.p. 312°

(sulphate, m.p. 279—280°; *ferrichloride*; $CuCl_2$, $CoCl_2$, $ZnCl_2$, and $SnCl_2$ salts), also obtained from 2 : 2′-diamino-8 : 8-dimethoxy-1 : 1′-dinaphthyl and $FeCl_3$ or $AlCl_3$. (**I**) with H_2O and Al_2O_3 gel or SiO_2 gel at ~300° in H_2 gives 1 : 1′-dinaphthylene 2 : 8′-2′ : 8-dioxide, with $NaNO_3$–H_2SO_4 at ⩾4°, then at room temp., affords a *NO*$_2$-derivative, m.p. 344°, and with Br–AcOH gives a *Br*$_2$-compound, m.p. >360°. Aq. NaOH–$Na_2S_2O_4$ at 60° converts (**I**) into (probably) a H_2-derivative, m.p. ~310°, which forms salts with mneral acids. (**I**) and boiling NH_2Ph yield 3-*anilinodinylin*, m.p. 262°. 1 : 1′-(5 : 7 : 5′ : 7′-Tetrachloro-8 : 8′-diacetamido-2 : 2′-dinaphthone) and boiling H_2O–H_2SO_4 (1 : 2) give 5 : 7 : 5′ : 7′-*tetrachlorodinylin*, m.p. >360°. A. T. P.



(I.)

Transformation of some oximinopyrroles into pyrimidine derivatives, Ciamician's reaction, and the constitution of nitrosopyrroles and pyrrole-aldehydes. T. Ajello (*Gazzetta*, 1942, **72**, 325—333).—The action of PCl_5 on 4-oximino-2 : 3 : 5-triphenylpyrrole (**I**) to give β-benzamido-αβ-diphenylacrylamide and thence 6-hydroxy-2 : 4 : 5-triphenylpyrimidine (cf. *ibid.*, 1940, **70**, 460) proceeds by way of the hydrochloride of (**I**), which loses H_2O to give 4-chloroimino-2 : 3 : 5-triphenylpyrrole, as is shown by Zn reduction to the 4-NH_2-compound. With PCl_5, 3-oximino-2 : 5-diphenylpyrrole gives *β-benzamido-β-phenylacrylamide*, m.p. 85° (*oxime*, m.p. 182°, and *hydrazone*, m.p. 196°, both reduced to 6-amino-2 : 4-diphenylpyrimidine, m.p. 120°), which when heated in AcOH or EtOAc slowly gives 6-hydroxy-2 : 4-diphenylpyrimidine. It is suggested that in the Ciamician reaction, a 2-CHCl. compound is intermediately formed. Nitrosopyrroles may have a *NN′*-oxide bridge, and an oxide bridge may explain the non-reactivity of pyrrole-aldehydes. E. W. W.

Two heterovitamins-B_1. P. Baumgarten and A. Dornow (*Ber.*, 1940, **73**, [*B*], 353—355).—Mainly a discussion of previous work (A., 1940, II, 291) and of structures. A. T. P.

Triazines.—See B., 1943, II, 213.

Nucleic acids. XV. Synthesis of nucleotides (muscle-adenylic acid, cytidylic acid). H. Bredereck, E. Berger, and J. Ehrenberg (*Ber.*, 1940, **73**, [*B*], 269—273).—Adenosine is converted by CPh_3Cl in dry C_5H_5N at 100° into triphenylmethyladenosine, $[\alpha]_D^{20}$ −17·6° in C_5H_5N, transformed by Ac_2O–C_5H_5N at room temp. into the *diacetate*, which is hydrolysed by acid to adenosine diacetate, m.p. 181—181°. This is converted by PPh_2·OCl in C_5H_5N followed by hydrolysis into muscle-adenylic acid in very small yield. Cytidine nitrate and CPh_3Cl in anhyd. C_5H_5N afford triphenylmethylcytidine, similarly transformed into cytidylic acid, identified as the brucine salt, $[\alpha]_D^{20}$ −15·3° in 35% EtOH. H. W.

Sedimentation and diffusion behaviour of nucleic acid preparations. H. G. Tennent and C. F. Vilbrandt (*J. Amer. Chem. Soc.*, 1943, **65**, 424—428).—The sedimentation velocity, diffusion consts., and apparent sp. vol. of eight nucleic acid preps. are determined and used to calculate mol. wts., frictional ratios, shape factors, and (for 5 preps. giving measurable sedimentation consts.) mol. dimensions. Three Na thymonucleates, prepared under very mild conditions, exist in solution as very long mols., having mol.wt. ~500,000. Thymonucleic and yeast nucleic acid, pancreas polynucleotide, and Ba thymate have mol. wt. 3000—7000. The cross-sectional diameter is ~15 A., in agreement with *X*-ray dimensions (16 × 7 A.). R. S. C.

Polymorphism of riboflavin.—See A., 1943, I, 178.

Aryldiazomorpholides. R. A. Henry and W. M. Dehn (*J. Amer. Chem. Soc.*, 1943, **65**, 479—480).—*Benzene-* (**I**), m.p. 29—30°, o-, m.p. 32—33°, and p-*toluene-*, m.p. 49·5—50·5°, *naphthalene-α-*, m.p. 82—83°, and *-β-* (**II**), m.p. 99·5—100·5°, m-*xylene*-2-, an oil, *diphenyl*-4-, m.p. 110·5—111°, m-, m.p. 83—84°, and p-*nitrobenzene-*, m.p. 137·5—138·5°, o-, m.p. 20—22°, m-, an oil, and p-*chlorobenzene-*, m.p. 54—55°, 2 : 5-*dichlorobenzene-*, m.p. 76—77°, m-, m.p. 33—34°, and p-*bromobenzene-* (**III**), m.p. 89·5—90°, p-*iodobenzene-*, m.p. 140·5—141·5°, m-*chlorotoluene*-6-, m.p. 59—60°, m-*bromotoluene*-4-, m.p. 48·5—49·5°, 2 : 6-*dibromotoluene*-4-, m.p. 87—88°, p-*anisole-* (**IV**), m.p. 69—70°, and p-*morpholinobenzene-* (**V**), m.p. 209—211°, *-diazomorpholide* and *diphenyl*-pp′-, m.p. 253—255°, and 3 : 3′-*dimethyldiphenyl*-4 : 4′-*bisdiazomorpholide*, m.p. 140·5—141·5°, are prepared. Excepting (**IV**), they are stable when solid. In conc. HBr or HCl, (**V**) gives 4-p-*bromophenylmorpholine hydrobromide*, m.p. 114·5—115·5°, or hydrochloride, decomp. 192—194°, respectively. With C_6H_6 and AcOH (1 mol.) or, better, C_6H_6–$AlCl_3$, they give Ph_2 derivatives. They are unaffected by Ac_2O. With aq. HIO_4, (**III**) gives I, *p*-C_6H_4BrI (7%), *p*-C_6H_4I·NO_2, and tar. With SO_2, (**I**), (**II**), and (**III**) give *products*, m.p. 142—143·5°, 181—182·5°, and 155—156°, respectively, insol. in but decomposed by hot conc. HCl, sol. and slowly decomp. in cold aq. alkali. In boiling aq. NaOH, the product from (**III**) gives *p*-C_6H_4Br·SO_2H. M.p. are corr. R. S. C.

High mol. wt. aliphatic compounds of nitrogen and sulphur.—See A., 1943, II, 218.

Thiazans.—See B., 1943, II, 212.

Transformation of pyrrole- into *iso*oxazole-derivatives. T. Ajello and (Signa.) C. Petronici (*Gazzetta*, 1942, **72**, 333—342).—2 : 3 : 5-Trimethylpyrrole with Na and C_5H_{11}·O·NO gives the Na salt (**I**) of 4-*oximino*-2 : 3 : 5-*trimethylpyrrole*, amorphous, which is isolated by action of aq. CO_2. With boiling 0·5N-HCl, (**I**) gives 3-*acetyl*-4 : 5-*dimethylisooxazole* (**II**), b.p. 190—195°/759 mm. [*oxime* (**III**), m.p. 180° (168°?) (*Bz* derivative, m.p. 123°); *semicarbazone* (**IV**), m.p. 249°; *phenylhydrazone*, m.p. 156°; *azine*, m.p. 124°], which with boiling aq. HNO_3 gives 4 : 5-*dimethylisooxazole*-3-*carboxylic acid*, m.p. 154°. With NH_2OH,HCl in H_2O–EtOH at 100°, (**I**) gives *γ-methylhexane-βδε-trione trioxime* (**V**), m.p. 168° (*Bz*$_3$ derivative, m.p. 138°). With boiling KOH–EtOH–H_2O, (**V**) gives the *oxime*, m.p. 73°, of 3-*methyl*-4-*β-keto*-sec.-*butyl*-1 : 2 : 5-*oxadiazole*, an oil (*semicarbazone*, m.p. 165°), which is hydrolysed by boiling 50% KOH–EtOH to AcOH and 3-*methyl*-4-*ethyl*-1 : 2 : 5-*oxadiazole*, an oil (oxidised to 3-methyl-1 : 2 : 5-oxadiazole-4-carboxylic acid). With EtOH–HCl, (**V**) gives, after brief heating, (**III**), and, after longer heating, (**II**). With aq. NH_2·CO·NH·NH_2,HCl at 100°, (**I**) gives *γ-methylhexane-βδε-trione βε-disemicarbazone δ-oxime*, m.p. 234°, hydrolysed by boiling conc. HCl to (**IV**). E. W. W.

Absorption and resonance in dyes.—See A., 1943, I, 192.

Effects of environment and aggregation on absorption spectra of dyes.—See A., 1943, I, 192.

Colour and constitution of polymethine dyes.—See A., 1943, I, 192.

VII.—ALKALOIDS.

Veratrine alkaloids. XV. Rubijervine and *iso*rubijervine. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, **148**, 41—50).—Accumulated analytical data indicate that jervine, rubijervine (**I**), and probably germine are C_{27} alkaloids built up on the same general hydrocarbon ring which is probably identical with or closely related to that of the sterols. The isolation of (**I**), m.p. 240—242°, $[\alpha]_D^{25}$ +19·0° in EtOH, from the final viscous mother-liquors from the hellebore roots by hydrolysis followed by treatment with $CHCl_3$ is described. (**I**) is accompanied by iso*rubijervine*, $C_{27}H_{43}O_2N$, m.p. 235—237°, $[\alpha]_D^{25}$ +6·5° in EtOH, or (+EtOH), m.p. 215—217° (*hydrobromide*, sinters >275°, softens to a resin at 290—295°). (**I**) gives a *hydrobromide*, m.p. (indef.) 265—270°, a *hydriodide*, m.p. 293—296° after softening, and an Ac_2 derivative, m.p. 160—163°. The basic fraction obtained by dehydrogenation (Se) of (**I**) is essentially 5-methyl-2-ethylpyridine; there is no evidence of cevantharidine. The neutral fraction contains a relatively large *hydrocarbon* fraction $C_{18}H_{18}$, m.p. 74—77° [*picrate*, m.p. 131—132°; additive *compound*, m.p. 144—145°, with *s*-$C_6H_3(NO_2)_3$], probably a methyl*cyclo*pentenophenanthrene (suggested also by absorption spectrum), and a *phenol*, $C_{18}H_{18}O$, m.p. 136—138°. H. W.

Veratrine alkaloids. XVI. Formulation of jervine. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1943, **148**, 51—55).—Analyses of jervine (**I**), m.p. 237—238° after softening, $[\alpha]_D^{25}$ −147° in EtOH, its hydrochloride, parallelograms, m.p. 330—334° (decomp.) after changing to needles at 280°, *hydriodide*, m.p. 302—305°, nitroso-, m.p. 250—253°, *N*-acetyl-, m.p. 224—225°, softens at 210°, and diacetyl-jervine, m.p. 147—153° from dil. $COMe_2$ or 154—163° from MeOH, support the formula $C_{27}H_{39}O_3N$ for the base. (**I**) liberates 4 mols. of CH_4 at 95° (Zerevitinov) and hence probably contains 1 reactive and 2 sluggish OH. (**I**) is reduced by Na in BuOH to *tetrahydrojervine*, m.p. 227—229°, which does not yield a sparingly sol. sulphate, but by H_2–PtO_2 in AcOH to a mixture of isomerides from which *tetrahydrojervines*, m.p. 228—232° (sparingly sol. sulphate) and m.p. 210—212°, are isolated. H. W.

Veratrine alkaloids. XVII. Germine; its formulation and degradation. L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1943, **148**, 57—66; cf. Poethke, A., 1938, II, 35).—It is shown that germine (**I**) is $C_{27}H_{43}O_8N$ and is therefore isomeric with cevine (**II**). The mother-liquor from the directly crystallising alkaloids of *Veratrum album* is hydrolysed and treated with $CHCl_3$, giving a cryst. compound of $CHCl_3$ and (**I**) contaminated with rubijervine, which is removed by crystallisation from MeOH. (**I**) (+2MeOH), m.p. ~220° after softening (decomp.) at ~163—173°, $[\alpha]_D^{25}$ +5·0° in 95% EtOH, contains 8 active H (Tschugaev–Zerevitinov) as does (**II**). (**I**) and $COMe_2$ in EtOH containing HCl afford *acetonyl*-[iso*propylidene*-]*germine*, m.p. 235—239° (decomp.) after softening and becoming discoloured [*hydrochloride*, m.p. 275° (decomp.), shrinks at 255°]. The mother-liquors from (**I**) contain iso*germine*, m.p. 260°, darkens >245°, sinters >250°, $[\alpha]_D^{25}$ +46·5° in EtOH. (**I**) is oxidised by CrO_3–H_2SO_4 at room temp. and subsequently at 95° to Me_4 hexanetetracarboxylate, m.p. 63—64°, $[\alpha]_D^{25}$ +21° in MeOH, obtained previously from (**II**); no indication of the production of the precursor of decevinic acid was obtained. The main, volatile basic product of the dehydrogenation (Se) of (**I**) is 5-methyl-2-ethylpyridine. The volatile hydrocarbon fraction prob-

ably contains $C_{18}H_{18}$. The undistilled dehydrogenation mixture affords cevanthridine and cevanthrol.

Protoveratrine is hydrolysed to a cryst. *alkamine*, $C_{27}H_{43}O_9N$, which is shown to contain a double linking by reduction to *dihydroprotoverine*, $C_{27}H_{45}O_9N$. Similarly (**I**) affords *dihydrogermine*. These *tert.* bases, like (**II**) and solanidine, must be hexacyclic compounds. H. W.

Adsorption in relation to constitution. Adsorption of alkaloids by silica gel.—See A., 1943, I, 199.

VIII.—ORGANO-METALLIC COMPOUNDS.

Mercuri-compounds.—See B., 1943, III, 161.

Modern methods of preparative organic chemistry. I. Syntheses with organic lithium compounds. G. Wittig (*Angew. Chem.*, 1940, **53**, 241—247).—A review.

IX.—PROTEINS.

Structure of the protein molecule.—See A., 1943, I, 194.

Periodic structure of proteins. A. G. Ogston (*Trans. Faraday Soc.*, 1943, **39**, 151—158).—The theory of Bergmann and Niemann (A., 1937, III, 168; 1938, III, 210) is examined mathematically, and the numerical conditions that must be fulfilled by a regular periodic structure are established. A simple diagrammatic test, requiring full analytical data and applicable to complex structures, is described. F. L. U.

Absence of β-alanine from proteins. M. A. Pollack (*J. Amer. Chem. Soc.*, 1943, **65**, 484—485).—Since the hydrolysates from silk fibroin, horse hæmoglobin, ovalbumin, gelatin, casein, and lactoglobulin possess no growth-promoting properties for yeast, the proteins do not contain β-alanine. R. S. C.

Simple method for the approximate estimation of the isoelectric point of soluble proteins.—See A., 1943, III, 517.

Denaturation of fibrinogen by anticoagulants.—See A., 1943, III, 372.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Oxidative degradation of halogen-substituted spruce-lignins. W. Lautsch and G. Piazolo (*Ber.*, 1940, **73**, [*B*], 317—320).—Bromolignin and boiling $Co(OH)_3$ (from $CoSO_4,7H_2O$–aq. $NaOH$–H_2O_2) +10% aq. KOH (in O_2) afford 6-bromovanillin (8% yield), m.p. 176°, and a little vanillin. Iodolignin, obtained by the action of KI–I on the OAc·Hg-compound, similarly yields 10% of 5-iodovanillin (cf. Freudenberg *et al.*, A., 1940, II, 352). Structural aspects are discussed. A. T. P.

Fine structure of lignins.—See A., 1943, I, 195.

XI.—ANALYSIS.

Micro-analytical determination of oxygen. J. Unterzaucher (*Ber.*, 1940, **73**, [*B*], 391—404).—Schütze's method (A., 1940, II, 199) is improved. A. T. P.

Determination of sulphur in organic compounds by hydrogenation. W. Theilacker and W. Schmid (*Angew. Chem.*, 1940, **53**, 255—256).—The ter Meulen method is improved by using platinised SiO_2 wool with a modified absorption train. A SiO_2 reaction tube is necessary only for cyclic S compounds (*e.g.*, thianthren), where bright red heat is needed. M. H. M. A.

Micro-extraction and micro-titration of fatty acids. D. Stretten and G. F. Grail (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 300).—8—20-mg. samples of fatty acids are titrated using 0·16N-NaOH delivered from a micrometer-driven micro-burette, α-naphtholphthalein indicator, and 90% MeOH as solvent for acid and alkali. A micro-extraction apparatus for extraction of fatty acids is described. J. D. R.

Separation of acetic, butyric, lactic, and *d*-gluconic acid. S. Preiss (*Biochem. Z.*, 1940, **306**, 130—136).—In a modification of the procedure of Wiegner and Magasanik (A., 1922, ii, 532), $PrCO_2H$ and most of the AcOH are separated from the other acids by repeated distillation. When the residue is contuously extracted with Et_2O for 24 hr., lactic acid and the remainder of the AcOH are removed and determined after evaporation of the Et_2O, by addition of excess of alkali and titration with acid. *d*-Gluconic acid (insol. in Et_2O) is determined in the same way in the residue from the Et_2O extraction. W. McC.

Ascorbic acid. I. Detection and estimation. W. R. Fearon and E. Kawerau (*Sci. Proc. Roy. Dublin Soc.*, 1943, **23**, 103—110).—Available methods for the detection and determination of ascorbic acid (**I**), dehydroascorbic acid (**II**), and "bound" ascorbic acid are classified and discussed. (**I**) is detected by the development of a violet colour with o-$C_6H_4(NO_2)_2$ and 20% NaOH; the test is not given under defined conditions by (**II**), glutathione, cysteine, creatinine, or uric acid and only more slowly by reducing sugars. (**II**) in solution buffered to pH 4 gives a stable, grass-green colour when gently boiled; the test is not given by (**I**) or by any of the familiar biological acids, sugars, proteins, and related substances. (**I**) is determined by titration with standard $Fe^{'''}$ solution in presence of AcOH; 1% KCNS is used as indicator. (**I**) can also be determined by titration with I using xylene as a partition indicator. H. W.

***N*-Benzylamides as derivatives for identifying the acyl group in esters.** O. C. Dermer and J. King (*J. Org. Chem.*, 1943, **8**, 168—173).—Many esters and free acids can be converted into cryst. *N*-benzylamides by boiling $CH_2Ph·NH_2$ in presence of salt catalysts (*e.g.*, NH_4Cl). The method fails for esters of inorg. acids, sulphonic acids, CO-acids, polynitro-aromatic acids, and some halogenated fatty acids. Esters of alcohols of high mol. wt. may require preliminary methanolysis. The amides formed by OH-acids, OAlk-acids, and polybasic acids, or by their respective esters, constitute excellent identifying derivatives whereas those from fatty acids melt too low and too close together to be useful. The following *-benzylamides* are new: *α-methyl*-n-*butyr-*, m.p. 47·5—48·5°; iso*valer-*, m.p. 53—54°; m-*tolu-*, m.p. 74·5—75·5°; *α-ethyl*-n-*butyr-*, m.p. 76—77°; *phenoxyacet-*, m.p. 84·5—86·0°; *myrist-*, m.p. 89—90°; p-*aminobenz-*, m.p. 89—90°; *glycoll-*, m.p. 103—104°; o-*iodobenz-*, m.p. 109—110°; *anilinoacet-*, m.p. 113—114°; *diglycoll-*, m.p. 124·0—124·5°; *anthranil-*, m.p. 124—125°; *ethylmalon-*, m.p. 137—138°; *diethylmalon-*, m.p. 137·5—138·5°; m-*hydroxybenz-*, m.p. 141—142·5°; 2-*furylacryl-*, m.p. 145—146°; n-*butylmalon-*, m.p. 148—149°; *male-*, m.p. 149—150°; *pimel-*, m.p. 153—154°; *sebac-*, m.p. 166·0—167·5°; *phenylethylmalon-*, m.p. 167—168°; *citr-*, m.p. 169—170°; *glutar-*, m.p. 169·5—170°; p-*nitrophenylacet-*, m.p. 185—186°; *adip-*, m.p. 188—189°; *phenylsuccin-*, m.p. 189—190°; *naphthal-*, m.p. 196·5—197·5°; *fumar-*, m.p. 203·5—205°; *cinnam-*, m.p. 225—226°; *terephthal-*, m.p. 264—266°. *β-Benzylaminopropionbenzylamide hydrochloride* (from $CH_2{:}CH·CO_2Me$) has m.p. 236—237°. M.p. are corr. H. W.

Chromatography as a means of separating amino-acids. J. L. Wachtel and H. G. Cassidy (*J. Amer. Chem. Soc.*, 1943, **65**, 665—668; cf. A., 1942, II, 249).—Details are given for separating glycine, leucine, phenylalanine, and tyrosine by chromatography on C from H_2O. The mixture is separated on one column into (*a*) the first two and (*b*) the second two acids named and these pairs are then separated on further columns. Some of the tyrosine is lost by decomp. R. S. C.

Sugar analysis by alkaline ferricyanide method. Determination of ferrocyanide by iodometric and other procedures. D. T. Englis and H. C. Becker (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 262—264).—$K_4Fe(CN)_6$ is oxidised with I in acid solution in presence of PO_4''' or F′ to remove Fe and prevent the reverse reaction. Room temp. with 60—75% excess of I for 15 min. is used, and the vol. is adjusted to give $[K_3Fe(CN)_6]$ <0·01M. The excess of I is titrated with $Na_2S_2O_3$. A comparison of the results obtained on the reduction of alkaline $K_3Fe(CN)_6$ by glucose and fructose, by direct oxidation of $K_4Fe(CN)_6$ by I, by indirect determination of $K_3Fe(CN)_6$ iodometrically, and by direct oxidation of $K_4Fe(CN)_6$ with $Ce(SO_4)_2$ shows good agreement and indicates that the by-products of the primary oxidation of sugars have a negligible effect on any of the methods used to determine $K_3Fe(CN)_6$ consumed. J. D. R.

Micro-colorimetric determination of tryptophan. H. W. Eckert (*J. Biol. Chem.*, 1943, **148**, 205—212).—The sample is dissolved in 1·2N-HCl and treated with 1% $NaNO_2$; after 30 min. 4% $NH_2·SO_3NH_4$ is added followed after 10 min. with 10 c.c. of H_2O and finally 0·1% $NH_2·[CH_2]_2·NH·C_{10}H_7$-α,2HCl (**I**). The red colour attains max. intensity in 30—60 min. If the material is colourless, the blank consists of 1·2N-HCl treated in the same way. If the sample gives a colour other than red, a close approximation may be secured by adding a small amount of Na_2SO_3 to the coloured solution after the reading on the colorimeter is taken. After the red colour has disappeared the blank reading is made. Similarly the addition of KH_2PO_4 and $NaNO_2$ will discharge the red colour, or the sample may be treated exactly and described except that in the last step 5 c.c. of H_2O are added in place of (**I**). If these methods are inadequate, the mixtures are extracted with Bu$^{\alpha}$OH and the filtered extracts are examined colorimetrically. H. W.

Spectrophotometric analysis of tissue staining.—See A., 1943, III, 554.

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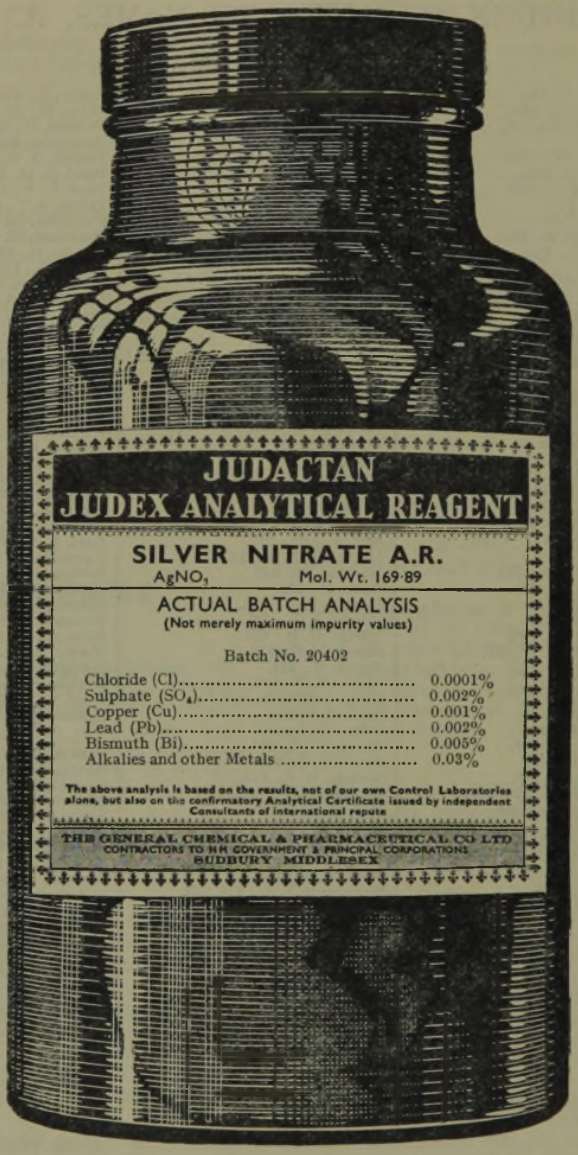
ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL

BATCH

ANALYSIS



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Chemical Manufacturers, Judex Works, Sudbury, Middlesex

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