BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1940.

Elimination and metathetical reactions and the electronic theory of rearrangements. C. R. HAUSER (J. Amer. Chem. Soc., 1940, **62**, 933—941).—Eliminations, metatheses, and rearrangements of org. compounds containing OH or halogen are discussed. Those effected by electron acceptors (acids, heavy-metal salts) occur according to Whitmore's views, except that all the postulated steps may be simultaneous. Eliminations effected by bases occur by removal of H as proton, release of X (= halogen or OH) with a complete octet of electrons, and stabilisation of the mol. With strong bases (type I reactions) removal of H occurs before the other steps, but with weak bases (type II reactions) all three steps may be simultaneous. In a three-atom system stabilisation occurs by rearrangement to unsaturated products or by dimerisation, but in a two- or four-atom system unsaturated compounds are produced without rearrangement. Exchange reactions may occur as well as elimination, the anionic reagent attacking the C at the face most removed from X. Reactions of CO-compounds and their hydrates with bases are discussed in detail. R. S. C.

Bromination of propane. A. GUYER and A. RUFER (Helv. Chim. Acta, 1940, **23**, 533—541).—Thermal bromination of C_3H_8 is a chain reaction since it is decelerated by air, has an induction period, and the rate is altered by a change in the ratio of vol. to surface. The primary reaction is dissociation of Br followed by $C_3H_8 + Br \rightarrow C_3H_7 + HBr$, $C_3H_7 + Br_2 \rightarrow PrBr + Br$, $C_3H_8 + Br \rightarrow C_3H_7 + HBr$ . . . Under all circumstances very large amounts of $Pr^{\beta}Br$ are produced probably by the reactions, $Pr^{\alpha}Br \rightleftharpoons CHMe{:}CH_2 + HBr \rightleftharpoons Pr^{\beta}Br$. The formation of $CH_2(CH_2Br)_2$ and CMe_2Br_2 is probably due to further direct substitution whereas $CH_2Br{\cdot}CHMeBr$ probably arises by addition of Br to $CHMe{:}CH_2$. Higher and unsaturated bromides are also produced. Increase in temp. increases the proportion of $Pr^{\alpha}Br$ but only slightly augments the amount of polybromides. Unsaturated compounds are markedly increased, particularly with high [Br]. Formation of polybrominated propanes increases greatly with [Br]; this has little influence on the unsaturated compounds, formation of which is mainly a function of temp., and scarcely affects the ratio of $Pr^{\alpha}Br$ to $Pr^{\beta}Br$. With diminishing time of reaction the relative amounts of polybromides and unsaturated compounds are diminished. The bromides of Fe, Cu, Tl, or Zn on pumice favour the production of greater or smaller amounts of polybromide probably by accelerating the decomp. of $Pr^{\alpha}Br$ into $CHMe{:}CH_2$. The formation of unsaturated bromides is not greatly influenced by the catalysts which favour the production of tri- and tetra-bromides. H. W.

***iso*Butane from normal butane.**—See B., 1940, 343.

Catalytic alkylation of *iso*butane with gaseous olefines.—See B., 1940, 341.

Catalytic polymerisation of olefines.—See B., 1940, 343.

Separation of the isomeric hexenes by batch fractionation. A. ROSE (J. Amer. Chem. Soc., 1940, **62**, 793—795).—$\lesssim$400 theoretical plates are required for sharp fractionation of isomeric hexenes of similar b.p. R. S. C.

Attempted separation of isomeric hexenes by fractional distillation. F. C. WHITMORE, M. R. FENSKE, D. QUIGGLE, H. BERNSTEIN, T. P. CARNEY, S. LAWROSKI, A. H. POPKIN, R. B. WAGNER, W. R. WHEELER, and J. S. WHITAKER (J. Amer. Chem. Soc., 1940, **62**, 795—800).—The Podbielniak–Simons–Taylor column has an efficiency of ~15 theoretical plates and is ineffective for separation of hexene mixtures with b.p. ranges 1·5° or 2·7° (cf. Rose, preceding abstract). The work of Goldwasser *et al.* (A., 1939, I, 478, 479; II, 401) is erroneous. R. S. C.

Hydrogenation of octenes.—See B., 1940, 343.

Formation of αβ-dichloroethane from ethylene and hypochlorous acid.—See A., 1940, I, 260.

Preparation of *as*-tetrachlorodifluoroethane. W. T. MILLER (J. Amer. Chem. Soc., 1940, **62**, 993).—$CCl_2F{\cdot}CClF_2$ and $AlCl_3$ at 100° (5 hr.) give $CCl_3{\cdot}CClF_2$ and small amounts of C_2Cl_6 (more on longer heating). R. S. C.

Removal of substituents from vinyl polymerides. F. T. WALL (J. Amer. Chem. Soc., 1940, **62**, 803—806).—The fraction of Cl remaining in mixed vinyl chloride–vinyl acetate polymerides after treatment with Zn can be predicted using formulæ which are derived by statistical methods. W. R. A.

Nitration of ethane.—See B., 1940, 341.

Synthesis of *iso*propyl alcohol from propylene. I—III. M. KATUNO (J. Soc. Chem. Ind. Japan, 1940, **43**, 5—8B, 8—11B, 11—14B).—I. $Pr^{\beta}HSO_4$ is rapidly hydrolysed in H_2SO_4 without formation of $Pr^{\beta}{}_2O$ or C_3H_6 if the concn. of acid is $\gtrsim$40%; the $Pr^{\beta}OH$ is quantitatively obtained by distillation if the amount of H_2O used is that required for hydrolysis and formation of the azeotropic mixture. Absorption of C_3H_6 is best effected by 87% H_2SO_4, but is improved by use of 68% acid and a little Ag_2SO_4, which accelerates absorption.

II. Apparatus for the reactions $2C_3H_6 + H_2SO_4 \rightarrow Pr^{\beta}_2SO_4 \rightarrow 2Pr^{\beta}OH + H_2SO_4$ is described. The reaction mechanism is discussed.

III. Hydrolysis of $Pr^{\beta}_2SO_4$ is investigated. Formation of $Pr^{\beta}HSO_4$ is rapid in H_2O, but further hydrolysis to $Pr^{\beta}OH$ requires H^+ or OH'.

R. S. C.

Physical constants of pentan-γ-ol. F. C. Whitmore and J. D. Surmatis (J. Amer. Chem. Soc., 1940, **62**, 995).—EtCHO (prepared from $Pr^{\alpha}OH$ by Cu-dehydrogenation), b.p. 48·0°/736 mm., and MgEtCl–Et_2O give 60% of $CHEt_2{\cdot}OH$, b.p. 114·4°/740 mm. Commercial (Sharples) $CHEt_2{\cdot}OH$ yielded 27% of the pure alcohol. R. S. C.

Electrochemical oxidation of *n*-hexanol. W. R. Lowstuter and A. Lowy (Trans. Electrochem. Soc., 1939, **77**, Preprint 21, 263—270).—*n*-$C_6H_{13}{\cdot}OH$ (I), oxidised electrochemically, yields *n*-$C_5H_{11}{\cdot}CO_2H$ (II), *n*-$C_5H_{11}{\cdot}CO_2C_6H_{13}$, and small amounts of CO_2, CO, and a residue of high b.p. Max. current efficiency of 59·9%, calc. only as oxidation to (II), is obtained with an electrolytically prepared PbO_2 anode in 9% (I) in 5% H_2SO_4 at 12°, using a c.d. of 1·1 amp. per sq. dm.

D. F. R.

Preparation of unsaturated higher alcohols. IV. S. Komori (J. Soc. Chem. Ind. Japan, 1940, **43**, 34—35B; cf. A., 1939, II, 491).—Hydrogenation of unsaturated esters to unsaturated higher alcohols is well effected in presence of Cd chromite at 335°. *X*-Ray diagrams show that the catalyst does not contain CdO or Cr_2O_3. Co chromite may also be used, but Cd vanadate, tungstate, or molybdate is less satisfactory. R. S. C.

Phenolic sugar alcohols.—See B., 1940, 343.

Keten acetals. IV. Polymerides of keten diethyl acetal. P. R. Johnson, H. M. Barnes, and S. M. McElvain (J. Amer. Chem. Soc., 1940, **62**, 964—972; cf. A., 1938, II, 427).—$CH_2{:}C(OEt)_2$ (I) is stable in new Pyrex glass at 190—240° (6 hr.), in new soft glass in diffuse light at room temp., or in old glass washed with aq. alkali or in presence of $KOBu^{\gamma}$. Polymerisation occurs in acid-washed glass. Bz_2O_2 is without effect, but the following relative efficiency of catalysis is reported: $AlCl_3 > FeCl_3 > ZnCl_2 > CdCl_2 > CoCl_2 > NiCl_2 > BaCl_2$, $HgCl_2$, $CaCl_2$, the stability of the polymerides varying. $CdCl_2$ (0·06%) gives a wax, containing 45% of (I) and a white, solid *polymeride* (II), stable at 200° and to boiling 10% NaOH. Dil. acid at room temp. converts (II) into a red oil; boiling dil. acid gives a reddish-black glass (III) and CO_2. Little EtOH is lost in formation of (II), but more is lost during acid hydrolysis. (III) is sol. in, but unchanged by, aq. alkali. The amount of CO_2 evolved, analysis of (III), and $KMnO_4$ oxidation of (III) to CO_2 (80%) and AcOH indicate that (II) is about $(OEt)_2CMe{\cdot}[CH_2{\cdot}C(OEt)_2]_{21}{\cdot}CH_2{\cdot}C(OEt)_3$ and (III) about $COMe{\cdot}[CH{:}C(OH)]_{21}{\cdot}Me$. The insolubility indicates cross-linking (intermol. loss of EtOH) in (II), but this cannot be extensive owing to the high OEt content. 10% H_2SO_4 and (III) at 200° give only traces of $COMe_2$ and AcOH but 5% NaOH gives larger amounts thereof and a reddish-black substance (IV) (structure proposed), which on repeated hydrogenation (Raney Ni; 225°/200 atm.; 1% NaOH) gives a colourless solid (12%) with EtOH, AcOH, and a red oil. Polymerisation of (I) by 0·36% of $CdCl_2$ is exothermic and gives 13% of unstable dimeride, b.p. 61—62°/0·5 mm., probably $(OEt)_2CMe{\cdot}CH{:}C(OEt)_2$ (with 5% H_2SO_4 gives $COMe_2$ and with HCl–EtOH gives $CH_2Ac{\cdot}CO_2Et$), 20% of a trimeride (V), $CMe(OEt)_3$, EtOH, and a solid similar to (II). (V) may be $(OEt)_2CMe{\cdot}CH_2{\cdot}C(OEt)_2{\cdot}CH{:}C(OEt)_2$, but is isolated after distillation as (?) 1 : 1 : 3 : 3 : 5 : 5-hexaethoxy-*cyclo*hexane (VI), b.p. 91—92°/0·1 mm., with some EtOH. With 5% H_2SO_4, (VI) gives a little *s*-$C_6H_3(OEt)_3$ [not formed from (V)]. A trace of acid in boiling 95% EtOH converts (VI) into $CH_2Ac{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$. Absence of head-to-head polymerisation is confirmed by absence of $(CH_2{\cdot}CO_2H)_2$ when (IV) is oxidised with HNO_3 and is due to the strength of the anionoid centre in (I). $CHHal{:}C(OEt)_2$ and $CHal_2{:}C(OEt)_2$ are stable to light, $CdCl_2$, and Bz_2O_2. BF_3 or $BF_3{,}Et_2O$ converts $CHHal{:}C(OEt)_2$ slowly into a red oil. R. S. C.

Kinetics of decarboxylation in solution.—See A., 1940, I, 260.

Mechanism of polymerisation of vinyl acetate and methyl vinyl ketone.—See A., 1940, I, 263.

Chlorinations with sulphuryl chloride. III. (*a*) Peroxide-catalysed chlorination of aliphatic acids and acid chlorides. (*b*) Photochemical sulphonation of aliphatic acids. M. S. Kharasch and H. C. Brown (J. Amer. Chem. Soc., 1940, **62**, 925—929; cf. A., 1940, II, 72).—In absence of catalysts and in the dark, boiling aliphatic acids and acid chlorides do not react with SO_2Cl_2. In presence of peroxides (Bz_2O_2) chlorination occurs nearly quantitatively (except for AcOH or AcCl), preferentially at a C remote from the CO. Dilution with CCl_4 is advisable for the acids. Thus $EtCO_2H$ gives $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$ (55%) and $CHMeCl{\cdot}CO_2H$ (45%). EtCOCl gives $Cl{\cdot}[CH_2]_2{\cdot}COCl$ (60%) and $CHMeCl{\cdot}COCl$ (40%). $Pr^{\beta}CO_2H$ gives $CH_2Cl{\cdot}CHMe{\cdot}CO_2H$ (85%) and $CMe_2Cl{\cdot}CO_2H$ (15%). $Pr^{\beta}COCl$ gives $CH_2Cl{\cdot}CHMe{\cdot}COCl$ (80%) and $CMe_2Cl{\cdot}COCl$ (20%). $Pr^{\alpha}CO_2H$ gives $Cl{\cdot}[CH_2]_3{\cdot}CO_2H$ (45%), $CHMeCl{\cdot}CH_2{\cdot}CO_2H$ (45%), and $CHEtCl{\cdot}CO_2H$ (10%). $Pr^{\alpha}COCl$ gives $Cl{\cdot}[CH_2]_3{\cdot}COCl$ (30%), $CHMeCl{\cdot}CH_2{\cdot}COCl$ (55%), and $CHEtCl{\cdot}COCl$ (15%). $Bu^{\gamma}CO_2H$ gives *β-chloro-αα-dimethylpropionic acid*, m.p. 40—42°, b.p. 126—129°/30 mm. (*amide*, m.p. 108—109°), and $Bu^{\gamma}COCl$ gives the corresponding chloride, b.p. 85—86°/60 mm. AcOH gives >50% of $CH_2Cl{\cdot}CO_2H$, but AcCl does not react even in boiling PhCl. I catalyses reaction of EtCOCl at 70°, but only CHMeCl·COCl, formed by dissociation of SO_2Cl_2 into SO_2 and Cl_2, is obtained. In light and absence of catalysts sulphonation occurs, mainly at $C_{(\beta)}$. Boiling $EtCO_2H$ and SO_2Cl_2, when irradiated, give 37% of $SO_3H{\cdot}[CH_2]_2{\cdot}CO_2H$, $+ 0{\cdot}5H_2O$ (or more) (Ba salt, $+5H_2O$; anhydride, m.p. 76—77°); $Pr^{\alpha}CO_2H$ and $Bu^{\beta}CO_2H$ are also sulphonated (no details), but AcOH does not react. Sulphonation of *cyclo*hexane by SO_2Cl_2 in light is catalysed (5% yield) by AcOH.

R. S. C.

Purification of fatty esters of high mol. wt. L. O. Buxton and R. Kapp (J. Amer. Chem. Soc.,

1940, **62**, 986).—These esters are purified by dissolution in $(CH_2Cl)_2$, neutralisation by 38% KOH (amount determined by titration), filtration, and distillation. R. S. C.

Hydrolysis of fats and fatty acid esters.—See A., 1940, I, 260.

Mechanism of pyrolysis of castor oil. S. Ishikawa, T. Tosimitu, A. Miyata, J. Araki, and R. Someno (Sci. Rep. Tokyo Bunrika Daigaku, 1939, **3**, 273—285).—Pyrolysis of castor oil (I) in presence of SiO_2 or sea-sand (better than borax–pumice) at 480—500° gives *n*-C_6H_{13}·CHO and CH_2:CH·$[CH_2]_7$·CO_2H (II) with small amounts of *n*-C_6H_{13}·CH:C(C_5H_{11}-*n*)·CHO (2 : 4-*dinitrophenylhydrazone*, m.p. 128°), the corresponding alcohol, *n*-C_6H_{13}·CO_2H, and *n*-C_7H_{15}·OH. Addition of metal oxides, except possibly Mo_2O_5, to the SiO_2 does not improve the yield. The structure of (II) is confirmed by oxidation with $KMnO_4$ and O_3. (II) does not rearrange to CHMe:CH·$[CH_2]_6$·CO_2H. Citronellal at 420° gives only a little $\Delta^{3:8}$-*p*-menthadiene and *l*-menthol gives only a little Δ^3-*p*-menthene. Oleic acid gives no aldehyde. Pyrolysis of (I) follows conjugation of the OH with C:C. R. S. C.

Fatty acids. V. Preparation of methyl ricinoleate and ricinoleic acid by fractional crystallisation. J. B. Brown and N. D. Green (J. Amer. Chem. Soc., 1940, **62**, 738—740; cf. A., 1939, II, 4).—Crystallisation of Me ricinoleate (prep. from castor oil described) from $COMe_2$ at ~ −50° gives a 99·5%-pure ester, m.p. −4° or −4·5°, $[\alpha]_D^{32}$ +7·41° or $[\alpha]_D^{27}$ +5·19° in $COMe_2$. Hydrolysis and subsequent low-temp. crystallisation gives a 95·6%-pure acid, m.p. 5·5°, $[\alpha]_D^{26}$ +7·15° in $COMe_2$. R. S. C.

Chlorinated oils. T. Matsumoto and S. Iwai (J. Soc. Chem. Ind. Japan, 1940, **43**, 16—18B).—Addition of Cl_2 to linseed, sardine, or olive oil in CCl_4 occurs mainly at one ethylenic linking. Some evolution of HCl occurs and in this decomp. colloid formation, evidenced by increase in η, occurs. R. S. C.

Structure of pantothenic acid. R. J. Williams and R. T. Major (Science, 1940, **91**, 246).—The cryst. lactone, $C_6H_{10}O_3$, m.p. 91—92° (from Ba pantothenate concentrates), is α-hydroxy-ββ-dimethyl-γ-butyrolactone. Condensation with β-alanine gives physiologically-active pantothenic acid. L. S. T.

Calythrone. A. R. Penfold and J. L. Simonsen (J.C.S., 1940, 412—415).—The essential oil from *Calythrix tetragona* when extracted with aq. NaOH gives the *Na* salt, m.p. (+xH_2O) 110—111°, (anhyd.) 196°, of *calythrone* (I), $\begin{matrix}CMe{:}CMe\\CO\text{——}O\end{matrix}$>CH·$COBu^{\beta}$, b.p. 142°/14 mm. (*Cu* derivative, m.p. 208—210°), which is oxidised by aq. NaOH–NaOBr to $CHBr_3$, $Bu^{\beta}CO_2H$, dimethylmaleic anhydride (II), and a *Br$_2$-acid*, probably $CHBr_2$·CO·CMe:CMe·CO_2H, m.p. 129°. (I) has β-diketonic properties, due to the opening of the lactone ring; its *dioxime anhydride*, m.p. 135°, is considered to be CO<$\begin{matrix}CMe{:}CMe\\O\text{——}N\end{matrix}$>CH·$COBu^{\beta}$. (II) has pseudoketonic properties, giving a *semicarbazone*, m.p. 238° (when rapidly heated, 248°), and a *p-nitro*-, m.p. 214°, and a 2 : 4-*dinitro-phenylhydrazone*, decomp. 253—255°. These are sol. in aq. Na_2CO_3, and are therefore $\begin{matrix}CMe{:}CMe\\CO\text{——}O\end{matrix}$>C:NR, rather than $\begin{matrix}CMe{:}CMe\\CO\text{——}NR\end{matrix}$>CO. (II) is reduced catalytically to *meso*- and by Clemmensen reagent to *dl-s*-dimethylsuccinic acid, and is oxidised to $AcCO_2H$. With *p*-C_6H_4Ph·CO·CH_2Br and aq. KOH, followed by MeOH, (II) gives p-*phenylphenacyl Me dimethylmaleate*, m.p. 95°. E. W. W.

Long-chain acids. II. Aleuritic acid. P. C. Mitter and P. C. Dutta (J. Indian Chem. Soc., 1939, **16**, 673—676).—OPh·$[CH_2]_5$·Br and CH_2Ac·CO_2Et (2 mol.) with Na–EtOH give *Et* ω-*phenoxypentamethyleneacetoacetate*, b.p. 180°/3 mm., which with Na–Et_2O and COCl·$[CH_2]_8$·CO_2Et affords after hydrolysis (EtOH–KOH) o-*phenoxy*-ι-*keto-palmitic acid*, m.p. 89° (*Et* ester, b.p. 252°/2 mm., m.p. 50°). This with HBr–AcOH gives o-*bromo*-ι-*ketopalmitic acid*, m.p. 69°, in poor yield, which with AcOH–KOAc, followed by esterification (EtOH–HCl), yields *Et* o-*acetoxy*-ι-*ketopalmitate*, b.p. 219—220°/3 mm., m.p. 54—55°, which could not be satisfactorily reduced. F. R. S.

Dialkyl adipates. R. A. Feagan, jun., and J. E. Copenhaver (J. Amer. Chem. Soc., 1940, **62**, 869—870).—The following are prepared from ROH and the acid at 150—155° or acid chloride at slightly > room temp.: *di*-n-*amyl*, m.p. −14°, -*hexyl*, m.p. −9° to −7°, -*heptyl*, m.p. 3·8—4·5°, -*octyl*, m.p. 9·5—9·8°, -nonyl, m.p. 21·6° (lit. 17—18·5°), -*decyl*, m.p. 27·4°, -*undecyl*, m.p. 34·7°, -*dodecyl*, m.p. 39·3°, -*tridecyl*, m.p. 45·9°, -*tetradecyl*, m.p. 49·4°, -*pentadecyl*, m.p. 55°, -hexadecyl, m.p. 57·3° (lit. 53°), -*heptadecyl*, m.p. 61·8°, -*octadecyl*, m.p. 63·4°, -*nonadecyl*, m.p. 66·7°, and -*eicosyl*, m.p. 65·2°, *adipate*. There is only slight alternation in m.p., which are corr. R. S. C.

Polarimetric study of action of heat on crystalline *l*-malic acid. R. Descamps (Bull. Soc. chim. Belg., 1940, **49**, 1—20).—[α] of specimens of cryst. *l*-malic acid (I) heated at 85° to 120° increases with the time of heating, the curves being usually S-shaped and tending to an upper limit for temp. <100°, whilst those for temp. >100° show a max. The rotatory dispersion (λλ 5893—4358), which is anomalous in solutions of the unchanged substance, becomes less so as the heating proceeds. The products, as in the case of aq. solutions (cf. A., 1939, II, 468), are fumaric acid and one or more optically active dehydration products. Here also the Darmois rule is applicable. F. L. U.

Optical activity and chemical structure in tartaric acid. X. Influence of substituent and solvent effect. Y. Tsuzuki (Bull. Chem. Soc. Japan, 1940, **15**, 55—59).—Data on $[M]_D^{20}$ for compounds CHR<$\begin{matrix}O{\cdot}CH{\cdot}CO_2Et\\O{\cdot}CH{\cdot}CO_2Et\end{matrix}$ (*A*) in C_6H_6, EtOH, and *cyclo*hexane (I) are given. The lævorotation diminishes as the parachor of R increases, in accordance with the rule found (A., 1939, I, 357) for compounds *A* with CR′R″ for CHR, and the sequence of solvent effects is also the same, viz., C_6H_6 > EtOH > (I).

The following are described: Et_2 d-*butylidenedioxysuccinate* (R = Pr$^{\alpha}$), b.p. 160°/15 mm., $[\alpha]_D^{20}$ −55·80°; Et_2 d-iso*butylidenedioxysuccinate* (R = Pr$^{\beta}$), b.p. 160°/20 mm., $[\alpha]_D^{20}$ −54·17°; Et_2 d-*heptylidenedioxysuccinate*, b.p. 190°/16 mm., $[\alpha]_D^{20}$ −41·76°. Vals. of $[\alpha]_D^{20}$ in C_6H_6, EtOH, and (I) are also recorded. F. J. G.

Improved preparation of *DL*-threonic and -erythronic acids. J. W. E. Glattfeld and E. Rietz (J. Amer. Chem. Soc., 1940, **62**, 974—977).—CH_2:CH·CH_2·CN and Br in Bu$^{\gamma}$OH and light petroleum give the dibromide, converted by NaOEt–EtOH into CH_2Br·CH:CH·CN (55%), b.p. 80—85°/12 mm. The dibromide, prepared from CH_2:CH·CH_2·CO_2Et (I) by Br in Bu$^{\gamma}$OH, with NaOEt at 0° gives 60% of CH_2Br·CH:CH·CO_2Et (II). CH_2Cl·CH:CH·CO_2Et, similarly prepared in 65% yield, is hydrolysed and oxidised (OsO_4–$BaClO_3$) to *DL*-threonic acid (59%). At <35° (I) similarly gives β-hydroxybutyrolactone (35%), which with P_2O_5 in dioxan gives *iso*crotonolactone (53%) and thence *DL*-erythronolactone (45%). R. S. C.

Preparation of alkali bismuth saccharates. G. O. Doak (J. Amer. Pharm. Assoc., 1940, **29**, 108—111).—The following were prepared by interaction of $Bi(OH)_3$ with saccharic acid and the appropriate alkali in H_2O: K_2 *di-* (I), *Na di-*, *Na K di-* and K_2 *tri-bismuthylsaccharate*. (I) with 10% HCl affords *dibismuthylsaccharic acid*. (I) is more stable in H_2O or serum than the corresponding tartrate or gluconate. F. O. H.

Manufacture of formaldehyde.—See B., 1940, 343.

Aldehydic perfumes. III. Synthesis of β-hydroxynonaldehyde. S. Ishikawa and T. Sakurai (Sci. Rep. Tokyo Bunrika Daigaku, 1939, **3**, 287—289; cf. A., 1939, II, 406).—The aldehyde [2 : 4-*dinitrophenylhydrazone*, m.p. 124·6° (corr.)] is prepared from castor oil by oxidation by $KMnO_4$ to θικ-trihydroxystearic acid, m.p. 122—123°, and thence by Pb_3O_4–Ac_2O–AcOH. R. S. C.

Biochemical preparation of aliphatic ketones.—See A., 1940, III, 540.

Thermal decomposition of diacetyl.—See A., 1940, I, 259.

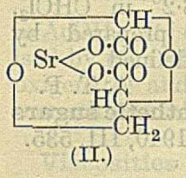
Reducing powers of various sugars with alkaline copper citrate reagent. H. S. Isbell, W. W. Pigman, and H. L. Frush (J. Res. Nat. Bur. Stand., 1940, **24**, 241—246).—Scales' method (A., 1919, ii, 435), modified by increasing the time of boiling to 6 min., is convenient for determining reducing sugars. Sugars with OH at $C_{(3)}$ *trans* to OH at $C_{(4)}$ and $C_{(5)}$ have the highest reducing power, whilst those with OH at $C_{(3)}$ or $C_{(4)}$ in the *cis* position have a lower reducing power. The configuration of OH at $C_{(2)}$ does not greatly affect the reducing power. When the glycosidic linkage of a disaccharide is at $C_{(3)}$ the mol. reducing power is < that of the corresponding monosaccharide, but if the linking is at $C_{(4)}$ or $C_{(6)}$ the reducing power is slightly > that of the monosaccharide. Under the conditions used the presence of $BaBr_2$ (6·5%) decreases the reducing val. by ~4%. J. W. S.

α- and β-Methyl lyxosides, mannosides, gulosides, and heptosides of like configuration. H. S. Isbell and H. L. Frush (J. Res. Nat. Bur. Stand., 1940, **24**, 125—151; cf. A., 1937, II, 177).—*d*-Lyxose refluxed with HCl–MeOH affords α-methyl- (I), m.p. 108° (cf. Phelps *et al.*, A., 1926, 501) [$CaCl_2$ *compound* (+$2H_2O$), $[\alpha]_D^{20}$ +31·3° in H_2O], and β-*methyl*-d-*lyxopyranoside*, m.p. 118°, $[\alpha]_D^{20}$ −128·1° in H_2O (*triacetate*, m.p. 88—89°, $[\alpha]_D^{20}$ −109·5° in $CHCl_3$); the latter and HIO_4 give a substance, $[\alpha]_D^{20}$ −125·5° [cf. product from (I), Maclay *et al.*, A., 1938, II, 430]. β-Methyl-*d*-mannopyranoside tetra-acetate and $Ba(OMe)_2$–MeOH, followed by Pr$^{\beta}$OH, yield β-*methyl*-d-*mannopyranoside Pr$^{\beta}$ alcoholate*, m.p. 74—75°, $[\alpha]_D^{20}$ −53·3° in H_2O, stable in presence of Pr$^{\beta}$OH vapour; Pr$^{\beta}$OH is lost at 105° in vac.; 70% of the Pr$^{\beta}$OH is lost at 77° in O_2. α-Methyl-*d*-α-galaheptopyranoside is prepared, identical with the compound named as the β-form (cf. Hann *et al.*, A., 1936, 193); nomenclatures are discussed. *d*-α-Galaheptose hydrate and Me_2SO_4–NaOH, then Ac_2O, give β-*methyl*-d-α-*galaheptopyranoside penta-acetate*, m.p. 171—173°, $[\alpha]_D^{20}$ +77·6° in $CHCl_3$, converted by $Ba(OMe)_2$–MeOH into β-methyl-*d*-α-galaheptopyranoside. *d*-α-Glucoheptose and HCl–MeOH give β- ($CaCl_2$ *compound*, +$2H_2O$, $[\alpha]_D^{20}$ −56·1° in H_2O) and α-*methyl*-d-α-*glucoheptopyranoside*, m.p. 106—107°, $[\alpha]_D^{20}$ +111·5° in H_2O (*penta-acetate*, m.p. 174—175°, $[\alpha]_D^{20}$ +107·4° in $CHCl_3$; cf. product, m.p. 169°, of Haworth *et al.*, A., 1932, 46), the latter being isolated by decomp. of its $CaCl_2$ *compound* (+H_2O), $[\alpha]_D^{20}$ +69·1° in H_2O. *d*-β-Galaheptose and HCl–MeOH give α-*methyl*-d-β-*galaheptopyranoside*, m.p. 154—155°, $[\alpha]_D^{20}$ −108° in H_2O (cf. Hann *et al.*, A., 1937, II, 178). Photomicrographs of the new glycosides are shown. The configurations of all asymmetric C in the pyranose ring affect the rate of hydrolysis. There is no fixed relationship between the configuration of the glycosidic C and the relative rates for hydrolysis of the α- and β-modifications. Aldopyranosides having *trans*-configurations for $C_{(1)}$ and $C_{(3)}$ are hydrolysed more slowly than the corresponding *cis*-forms. Mol. rotations of the methylglycopyranosides are compared and there is support for classifying the methyl-lyxopyranosides in the *d*-mannose rather than the *l*-gulose series. A. T. P.

Use of the benzyl radical in syntheses of methylated sugars. I. 4 : 6-Dimethylglucose. D. J. Bell and J. Lorber (J.C.S., 1940, 453—455).—The prep. of 4 : 6-dimethylglucose (I) (A., 1937, II, 484) is easily effected by converting the 2 : 3-diacetate of 4 : 6-benzylidene-α-methylglucoside (II) (Mathers *et al.*, A., 1933, 938) by KOH and CH_2PhCl in xylene at 95—100° into the 2 : 3-(CH_2Ph)$_2$ derivative (III), m.p. 93°, $[\alpha]_D^{20}$ −31·2° (all rotations in $CHCl_3$), of (II). Aq. HCl in boiling $COMe_2$ hydrolyses (III) to 2 : 3-*dibenzyl*-α-*methylglucoside*, m.p. 75—76°, $[\alpha]_D^{18}$ +18·8°. When methylated by Purdie's reagents, either directly or after treatment with Me_2SO_4–NaOH in $COMe_2$, this gives 2 : 3-*dibenzyl*-4 : 6-*dimethyl*-α-*methylglucoside*, b.p. 215—220° (bath)/0·03 mm., $[\alpha]_D^{18}$ +32·9°, which is debenzylated by Na in EtOH to 4 : 6-*dimethyl*-α-*methylglucoside*, b.p. 160° (bath)/0·5 mm. This [which with *p*-C_6H_4Me·SO_2Cl in C_5H_5N

gives its 2 : 3-di-*p*-toluenesulphonate, new m.p. 113° (cf. Mather *et al.*, A., 1933, 1037)] is hydrolysed by N-HCl at 100° to (I). E. W. W.

Cleavage of the carbon chain of β-glucosan by periodic acid. E. L. Jackson and C. S. Hudson (J. Amer. Chem. Soc., 1940, **62**, 958—961).—β-Glucosan (I) consumes 2 HIO_4, giving HCO_2H (1 mol.) and *L'*-oxy-*D*-methylenediglycollic dialdehyde, $[M]_D$ −15·0°, oxidised by Br–$SrCO_3$ to *Sr* L'-*oxy*-D-*methylenediglycollate* (II) (45%), $+5H_2O$, $+H_2O$, $[\alpha]_D^{20}$ +36·9° in H_2O, and anhyd., with smaller amounts of SrC_2O_4 and Sr *D*-glycerate. The accepted structure of (I) is thus confirmed. (I) is stable to 2·5N-HCl. R. S. C.


(II.)

Glucofuranosides and thioglucofuranosides. VII. Crystalline alkylfuranosides and dimethyl acetal of *d*-mannose. A. Scattergood and E. Pacsu (J. Amer. Chem. Soc., 1940, **62**, 903—910; cf. A., 1939, II, 407).—60% of α-methyl-*d*-mannofuranoside (I) is obtained from mannose Et_2 mercaptal (II) by $HgCl_2$–MeOH, Hg being a permissible reagent for removal of excess of $HgCl_2$ in this and other cases. In this and other preps. of (I) the mother-liquors contain β-methyl-*d*-mannofuranoside (III), m.p. 47°, $[\alpha]_D^{20}$ −12·6° in H_2O, isolated as $CaCl_2$ *compound*, $+3H_2O$, $[\alpha]_D^{20}$ −58·5° in H_2O, and recovered therefrom by $Ag_2C_2O_4$. $CaCl_2$ influences the α of (III). The tetra-acetate, m.p. 61—62°, of (I) has $[\alpha]_D^{20}$ −108·8° in $CHCl_3$, +120·3° in *cis*- and +105·3° in *trans*-$(CHCl:)_2$. The mercaptal method gives also α-*ethyl*-, m.p. 90°, $[\alpha]_D^{20}$ +105·0°, α-n-, m.p. 96°, $[\alpha]_D^{20}$ +96·0°, and α-iso-*propyl*-d-*mannofuranoside*, m.p. 96·7°, $[\alpha]_D^{20}$ +96·7° (all in H_2O). The penta-acetate of (II) with $HgCl_2$–MeOH gives a penta-acetate, hydrolysed by NaOMe–MeOH to *mannose* Me_2 *acetal*, m.p. 101°, $[\alpha]_D^{20}$ +0·6° in H_2O, stable in H_2O or alkali but converted in 0·05% HCl first into (I) and (III) (*k* 0·024) and then into *d*-mannose (*k* 0·00118). Introduction of the *F* term (A., 1940, II, 6) (= −4475) accounts for the [*M*] of the mannose derivatives. Fischer–Hirschfelder models are used to prove the contention (*loc. cit.*) that only one *cis*- and one *trans*-form of aldohexopyranoses are possible; the *cis*-form is unstable by repulsion. *F* must be due to the orientation about the C–O linkings of all the OH, probably owing to H linkings. R. S. C.

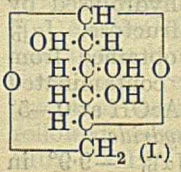
Monothioacetals of galactose. M. L. Wolfrom and D. I. Weisblat (J. Amer. Chem. Soc., 1940, **62**, 878—880).—*d*-Galactose Et_2 mercaptal penta-acetate and $POCl_3$ in boiling AcCl give aldehydo-1-*chloro*-1-*ethylthiol*-d-*galactose penta-acetate*, m.p. 111—113°, $[\alpha]_D^{22}$ −27° in $CHCl_3$, unstable, which with $CaSO_4$ and Ag_2CO_3 in MeOH or EtOH gives d-*galactose* Me_2, m.p. 119—120°, $[\alpha]_D^{22}$ +42·5° in $CHCl_3$, and Et_2 *monothioacetal penta-acetate*, m.p. 104—105°, $[\alpha]_D^{22}$ +50° in $CHCl_3$, hydrolysed by cold NaOMe–MeOH to d-*galactose* Me_2, m.p. 146—147°, $[\alpha]_D^{22}$ +50° in H_2O, and Et_2 *monothioacetal*, m.p. 155—156°, $[\alpha]_D^{22}$ +53° in H_2O, respectively, stable to hot Fehling's solution unless previously hydrolysed by acid (gives RSH).

N** (A., II.)

d-Galactose Me_2 acetal penta-acetate and AcCl at 0° give aldehydo-1-*chloro*-1-*methoxy*-d-*galactose penta-acetate*, m.p. 155—156°, $[\alpha]_D^{22}$ −38° → +15° in 24 hr. in $CHCl_3$, −53° → −42·5° in 10 hr. in C_6H_6. R. S. C.

Walden inversion in the altrose series. G. J. Robertson and W. Whitehead (J.C.S., 1940, 319—323).—4 : 6-Benzylidene-2 : 3-anhydro-α-methylalloside (I) with boiling aq. KOH gives 4 : 6-benzylidene-α-methylaltroside (II) (cf. A., 1935, 1225), which with *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N gives its 2 : 3-*di*-p-*toluenesulphonate* (III), m.p. 170—175°, $[\alpha]_D^{15}$ +46·9° in $CHCl_3$. With NaOMe–MeOH, this gives a quant. yield of 4 : 6-benzylidene-2 : 3-anhydro-α-methylmannoside (IV), identical with that obtained from 4 : 6-benzylidene-α-methylglucoside 2-*p*-toluenesulphonate (V) (*loc. cit.*). Thus hydrolysis of (III), like that of (V), involves Walden inversion at $C_{(3)}$. Hydrolysis of (IV) by aq. KOH gives a quant. yield of (II). 50% Aq. N_2H_4,H_2O at 110—120° opens the $(CH_2)_2O$ rings of (IV) and of (I) in 12 and 30 hr., respectively. The product from (IV) is 4 : 6-*benzylidene*-3-*hydrazino*-α-*methylaltroside*, m.p. 196°, $[\alpha]_D^{17}$ +53·7° in C_5H_5N, since with conc. HCl at room temp. it gives pyrazolyl-5-α-glycerol hydrochloride. The isomeride, from (I), is therefore 4 : 6-*benzylidene*-2-*hydrazino*-α-*methylaltroside*, m.p. 144°, $[\alpha]_D^{5}$ +67·96° in $CHCl_3$. The 3 : 6-anhydro-ring in altrose is formed from 2-*methyl*-α-*methylaltroside* 3-p-*toluenesulphonate* (VI), m.p. 118°, $[\alpha]_D^{15}$ +88·1° in $CHCl_3$, obtained by hydrolysing its 2 : 3-CHPh: derivative (*loc. cit.*) by dil. HCl in $COMe_2$ on the water-bath to const. rotation. The 4 : 6-Bz_2 derivative, m.p. 113°, $[\alpha]_D^{16}$ +94·69° in $CHCl_3$, of (VI) is hydrolysed by boiling MeOH–NaOMe to a dark product which after acidification gives 2-*methyl*-3 : 6-*anhydro*-α-*methylaltroside* (VII), m.p. 107—108°, $[\alpha]_D^{14}$ +105·1° in $CHCl_3$. Under milder conditions, *e.g.*, at room temp., (VI) only is obtained. Under no conditions is the theoretically possible 3 : 4-anhydro-compound obtained. With 2N-KOH at 100°, or 10% NaOMe–MeOH, (VII) is stable; with boiling 5% HCl, (VII) gives, with decomp., 2-*methyl*-3 : 6-*anhydroaltrose*, a syrup, $[\alpha]_D^{16}$ +81·27° in $CHCl_3$, +106·3° in H_2O. Methylation of (VII) by the Purdie reagents gives the fully methylated 2 : 4-*dimethyl*-3 : 6-*anhydro*-α-*methylaltroside*, a syrup, $[\alpha]_D^{18}$ +69·04° in $CHCl_3$. A further unsuccessful attempt to obtain a 3 : 4-anhydro-compound was made. With CPh_3Cl in C_5H_5N at 100°, (VI) gives its 6-*CPh*$_3$ derivative (VIII) [4-*acetate* (IX), m.p. 165°, $[\alpha]_D^{15}$ +72·4° in $CHCl_3$], in the form of a glass containing (VI). Alkaline hydrolysis of (IX) does not give a 3 : 4-anhydro-ring : mild agents give (VIII), while more powerful cause resinification. Apparently a Walden inversion from *trans*- to *cis*-formation is necessary before the 3 : 4-ring can be obtained. E. W. W.

Ring-structure of *D*-altrosan. N. K. Richtmyer and C. S. Hudson (J. Amer. Chem. Soc., 1940, **62**, 961—964).—*D*-Altrosan consumes 2 HIO_4, giving HCO_2H (1 mol.) and an aldehyde, oxidised to *L'*-oxy-*D*-methylenediglycollic acid, and thus is (I). R. S. C.


(I.)

Manufacture of fructose. I. Decomposition of fructose with acid. I. Determination of reaction constant at high temperature. K. FUJINO and Y. ARAO (Rept. Inst. Sci. Res. Manchoukuo, 1940, **4**, 17—24).—At 120° and in presence of acid, decomp. of fructose (I) increases with increase in time of heating, concn. of (I), and vol. of acid used. The rate of change, which is > that of glucose, is greatest at the beginning of the reaction.

I. A. P.

Structure of difructose anhydride III (difructofuranose 1 : 2′ : 2 : 3′-anhydride). E. J. MCDONALD and R. F. JACKSON (J. Res. Nat. Bur. Stand., 1940, **24**, 181—204; cf. Haworth *et al.*, A., 1932, 724).—Difructose anhydride I (difructofuranose 1 : 2′ : 2 : 1′-anhydride) or III (the 1 : 2′ : 2 : 3′-anhydride) (*A*) and Me_2SO_4–aq. NaOH at 70°, then MeI–Ag_2O, afford 3 : 4 : 6 : 3′ : 4′ : 6′-hexamethyldifructofuranose 1 : 2′ : 2 : 1′-anhydride, b.p. 170—175°/0·01 mm., $[\alpha]_D^{20}$ +23·7° in $CHCl_3$, and 3 : 4 : 6 : 1′ : 4′ : 6′-hexamethyldifructofuranose 1 : 2′ : 2 : 3′-anhydride, b.p. 161—165°/0·417 mm., $[\alpha]_D^{20}$ +157·9° in $CHCl_3$, respectively. The latter compound is hydrolysed by 0·8N-HCl at 95° to 3 : 4 : 6- (I) and 1 : 4 : 6-trimethylfructofuranose; oxidation (HNO_3) gives monobasic acids and thence esters, which are oxidised by acid $BaMn_2O_8$ to trimethylarabonolactone, derived from (I). (*A*) and CPh_3Cl–C_5H_5N at 80°, then at room temp., give 6 : 1′ : 6′-*tri*(*triphenylmethyl*)*difructofuranose* 1 : 2′ : 2 : 3′-*anhydride*, m.p. 127°, $[\alpha]_D$ +64·2° in $CHCl_3$, converted by Ac_2O–C_5H_5N at 100° (bath) into its triacetate, $[\alpha]_D$ +65·2° in $CHCl_3$, which is methylated by Me_2SO_4–aq. NaOH–$COMe_2$ to 6 : 1′ : 6′-*tri*(*triphenylmethyl*)-3 : 4 : 4′-*trimethyldifructofuranose* 1 : 2′ : 2 : 3′-*anhydride*, $[\alpha]_D^{24}$ +70·2° in $CHCl_3$. CPh_3 is removed from the latter by HBr–$CHCl_3$ at 0° and the anhydride formed is hydrolysed by 0·8N-HBr at 94° to partly methylated fructoses; these afford fructosides which are hydrolysed by 0·1N-HCl at 60° to 3 : 4-dimethyl- and 4-methyl-fructose, $[\alpha]_D^{26}$ −87·5° at equilibrium (glucosazone, m.p. 156°). Methyl-3 : 4-dimethylfructoside and HNO_3 (*d* 1·42) at 65—95° give the dibasic 3 : 4-dimethyl-lactol acid, also derived from 1 : 3 : 4-trimethylfructose (cf. Hibbert *et al.*, A., 1931, 827). The CPh_3 groups (see above) are substituents of the three primary OH. (*A*) is composed of two furanoid fructose residues, with two O bridges connecting $C_{(1)}$ and $C_{(2)}$ of one fructose residue with $C_{(2')}$ and $C_{(3')}$ of the other. Its great stability is due to the presence of a dioxan ring serving as connecting link between the two fructose groups. 6 : 6′-Ditriphenylmethyldifructofuranose 1 : 2′ : 2 : 1′-anhydride, m.p. 195°, $[\alpha]_D^{22}$ +20·35° in $CHCl_3$, and Ac_2O at 110° yield the 3 : 4 : 3′ : 4′-*tetra-acetate* (II), m.p. 194°, $[\alpha]_D^{20}$ +21·06° in $CHCl_3$, converted by Me_2SO_4–$COMe_2$–aq. NaOH into the $(CPh_3)_2$ Me_4 derivative, and thence by 0·8N-HBr at 95° into a substance which with HCl–MeOH affords fructosides, hydrolysed by 0·1N-HCl at 60° to 3 : 4-dimethylfructose, $[\alpha]_D^{20}$ −60·66° in H_2O. The latter is also obtained from triphenylmethyldimethylinulin, but is contaminated with 4-methylfructose. (II) and HBr–AcOH at 0—5° give *difructofuranose* 1 : 2′ : 2 : 1′-*anhydride* 3 : 4 : 3′ : 4′-*tetra-acetate*, m.p. 173°, $[\alpha]_D^{20}$ −9·9° in $CHCl_3$, methylated by Purdie's reagents to the 6 : 6′-Me_2 derivative, m.p. 127—128°, $[\alpha]_D$ +10·8° in $CHCl_3$, which is hydrolysed by 0·8N-HCl at 95° and the residue converted into fructosides which give 6-methylfructose (osazone, m.p. 183—184°). A mechanism is suggested by which the difructose anhydrides are formed during hydrolysis of inulin. Hexamethyldifructose anhydride II has m.p. 73°, b.p. 169—170°/0·43 mm., $[\alpha]_D^{20}$ −28·2° in $CHCl_3$. Constitutions of the disaccharides prepared by Schlubach *et al.* (A., 1933, 938) are ill-defined.

A. T. P.

Fission of methylglucosides of synthetic sugars by sweet almond emulsin.—See A., 1940, III, 535.

Synthesis of glycol glucosides. S. KARJALA and K. P. LINK (J. Amer. Chem. Soc., 1940, **62**, 917—920).—$(CH_2{\cdot}OH)_2$, acetobromoglucose (modified prep.; 86% yield), and Ag_2CO_3, later in C_6H_6, give ethylene glycol β-*d*-glucoside tetra-acetate, m.p. 105—106° [lit. 101—103° (corr.)], $[\alpha]_D^{23}$ −26·3° in H_2O, hydrolysed to the free glucoside, dimorphic, m.p. 117·5—118° and 136—137°, respectively, $[\alpha]_D^{22}$ −28·5° in H_2O, and converted by further similar reactions into ethylene glycol bis-β-*d*-glucoside octa-acetate, m.p. 169—170° (corr.) (lit. 170—171°), $[\alpha]_D^{23}$ −31·76° in $CHCl_3$. Similar reactions give *diethylene glycol* β-d-*glucoside*, m.p. 116·5—118°, $[\alpha]_D^{23}$ −22·4° in H_2O [*tetra-acetate*, m.p. 92—93° (corr.), $[\alpha]_D^{24}$ −27·62° in H_2O], and *bis*-β-d-*glucoside octa-acetate*, m.p. 125·5—126·5°, $[\alpha]_D^{22}$ −23·5° in $CHCl_3$ (gives an oil when hydrolysed), *propylene glycol* β-d-*glucoside*, m.p. 136—138°, $[\alpha]_D^{22}$ −25·5° in H_2O (*tetra-acetate*, m.p. 99—101°, $[\alpha]_D^{26}$ −6·8° in $CHCl_3$), triethylene glycol β-*d*-glucoside tetra-acetate, an oil, *methoxyethyl* β-d-*glucoside*, m.p. 139—140°, $[\alpha]_D^{23}$ −26·0° in H_2O (*tetra-acetate*, m.p. 65—67°, $[\alpha]_D^{23}$ −19·5° in $CHCl_3$), trimethylene glycol β-*d*-glucoside tetra-acetate, m.p. 97—98°, $[\alpha]_D^{26}$ −17·3° in $CHCl_3$, and bis-β-*d*-glucoside octa-acetate, m.p. 171—172°, $[\alpha]_D^{26}$ −15·8° in $CHCl_3$.

R. S. C.

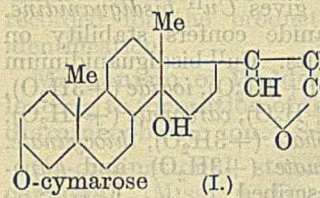
Scilliroside. A. STOLL and J. RENZ (Compt. rend., 1940, **210**, 508—509).—Alcoholic extracts (details given) of the dry powdered bulbs of red squill contain *scilliroside*, $C_{32}H_{46}O_{12}$,0·5H_2O, m.p. 168—170° (corr.; decomp.), $[\alpha]_D^{20}$ −59° in MeOH [*tetra-acetate*, m.p. 199° (corr.), $[\alpha]_D^{20}$ −49° in MeOH], which gives the Liebermann test, but neither the Legal nor Baljet test, and contains 1 Ac and a lactone ring. Hydrolysis (acid) liberates glucose but no cryst. aglucone. Spectrographic measurements indicate that its skeleton is a perhydro*cyclo*pentanophenanthrene together with a 6-atom lactone ring containing 2 double linkings (cf. Wieland *et al.*, A., 1936, 1252). Scilliroside acts like scillaren-*A* on the frog heart and is a powerful convulsant drug for rodents.

J. L. D.

Oleocyanin, $C_{27}H_{31}O_{15}Cl$.—See A., 1940, III, 462.

African arrow poison plants. I. *Adenium somalense*, Balf. fil. M. HARTMANN and E. SCHLITTLER (Helv. Chim. Acta, 1940, **23**, 548—558).—The dried roots are percolated with 70% MeOH and, after treatment with basic Pb acetate, the percolate is

treated with MeOH and $CHCl_3$. The portion sol. in $CHCl_3$ gives *somalin* (I), m.p. 197—198° or (+0·5H_2O) sintering at 133—136°, $[\alpha]_D^{19}$ +9·5° in EtOH. It gives a strongly positive Legal reaction and a dark blue Keller–Kiliani reaction in AcOH. It is hydrolysed to digitoxigenin (characterised by its acetate and by conversion into Me *iso*digitoxigenate) and cymarose. Pharmacologically (I) is more closely related to strophanthin than to digitoxin.



O-cymarose (I.)

H. W.

Viscosities of arabogalactan solutions. H. S. Owens (J. Amer. Chem. Soc., 1940, **62**, 930—932).—Prep. of arabogalactan (87·7% anhydrogalactose) from Western larch heartwood is described. η of 6—10% aq. solutions at 20°, 40°, and 60° is best expressed by Kunitz's equation (A., 1936, 1005) and indicates a spherical mol. in solution and a mol. wt. ≠2208, *i.e.*, $[C_5H_8O_4{\cdot}(C_6H_{10}O_5)_6]_2$. R. S. C.

Constitution of banana starch. E. G. E. Hawkins, J. K. N. Jones, and G. T. Young (J.C.S., 1940, 390—394).—Banana starch (I) resembles potato starch (II) in physical properties. It is hydrolysed normally by acid, giving only glucose. It is more resistant than (II) both to acetylation (either with Cl_2 and SO_2 catalysts, or using Ac_2O–C_5H_5N) and to methylation. The methylated product (III), whether prepared directly or via the acetate, has mol. wt. ~200,000 (based on η; cf. Hirst *et al.*, A., 1939, II, 359, 495), and on fractionation and hydrolysis gives 2 : 3 : 4 : 6-tetramethyl- (IV), 2 : 3 : 6-trimethyl-, and dimethylglucose only. The proportion of (IV) corresponds with a repeating unit of ~24 (22—26) glucose residues. Heated with 1% $H_2C_2O_4$ in MeOH–H_2O, (III) resembles rice starch (V) (*loc. cit.*, 495) in disaggregating smoothly to products of lower mol. wt. but unchanged chain length. The mol. structure in (I) and in (V) is thus essentially identical, both having glycosidic linkings. Methylated inulin, with 1 : 6-fructofuranoside linkings, is hydrolysed ~7 times as rapidly as (III). E. W. W.

Recrystallisation of cellulose and its derivatives. G. Gentola (Atti X Congr. Internaz. Chim., 1938, IV, 117—123).—The crystallinity of regenerated cellulose (I) depends on the concn. of the solution, the nature of the solvent and precipitant, the temp. and rate of coagulation, and the mechanical stresses involved. The general theory, which is exemplified by observations on regeneration of cellulose nitrate (N 13·2%), assumes that (I) and its derivatives in solution do not retain a strictly rectilinear configuration. F. O. H.

Mechanism of degradation of cellulose. S. M. Kaji and K. Venkataraman (Current Sci., 1940, **9**, 66—67).—A series of oxycelluloses (I) and hydrocelluloses (II) have been prepared by treating cellulose (III) with acids, oxidising agents, and ultra-violet light, and also by submitting (III) to singeing processes, heat-treatments, and mildew attack. Whilst four types of (I) have been distinguished, (II) seems to be of a single chemical type; correlations with the Haworth formula for (III) are suggested. Three possible series of reactions, after the fission of the 1 : 4-glucosidic linkings, are outlined in the degradation of (III) with the formation from (I) of (*a*) a dialdehyde, (*b*) a dicarboxylic acid, (*c*) a β-ketonic aldehyde or acid. W. R. A.

Trimethylamine oxide in different varieties of flesh and fish. IV. Mode of formation of formaldehyde from trimethylamine oxide. Y. Hattori (J. Pharm. Soc. Japan, 1940, **60**, 30—33).—NMe_3O is heated at 180° in a rapid current of moist air and the product is treated with dil. HCl. The solution when cautiously evaporated at a low temp. leaves very hygroscopic, colourless needles converted into dimethyl- and methoxydimethyl-ammonium platinichloride, m.p. 168°. The substance is stable in strongly acid (HCl) solution but not in dil. acid; the free base passes when gently heated into $NHMe_2$ and CH_2O. In absence of H_2O elimination of CH_2O from NMe_3O does not take place. Keeping of NMe_3,2H_2O over conc. H_2SO_4 at 10—12 mm. until const. in wt. leads to *hydroxytrimethylammonium hydroxide* (I), $NMe_3(OH)_2$, m.p. 201°, in which one OH is basic and the other is non-basic. (I) yields an *acetate*, OH·NMe_3·OAc, m.p. 49°, (non. cryst. *Ac* derivative), *picrate*, m.p. 202°, *benzoate*, m.p. 72°, (non-cryst. *Bz* derivative), *benzoyloxytrimethylammonium picrate*, m.p. 270°, *hydroxytrimethylammonium-phenylurethane*, m.p. 273°, *acetoxytrimethylammonium-phenylurethane*, m.p. 274°, and *trimethylammonium picrate phenylurethane*, m.p. 221·5°. The conversion of NMe_3O into CH_2O occurs through (I), which passes when heated into H_2O and NMe_2·OMe (volatile). This is stable towards heat when dry but reacts with H_2O at a low temp. giving OH·$NHMe_2$·OMe, which breaks down into $NHMe_2$, H_2O, and CH_2O. H. W.

Derivatives of diethylenetriamine [di-(β-aminoethyl)amine]. P. Job and J. Brigando (Compt. rend., 1940, **210**, 438—440; cf. A., 1927, 546).—Pentamminocobaltic chloride when warmed with $NH(CH_2{\cdot}CH_2{\cdot}NH_2)_2$ (= etn) gives (Co etn_2)Cl_3 from which all Cl is pptd. by $AgNO_3$ (cf. A., 1938, I, 403). Equimol. amounts of etn and $CuSO_4$ in H_2O give Cu_3etn_4; when the constituents react in varying proportions the equilibrium const. (*k*) is ~1·5 × 10^{-13} at room temp. A similar complex Ag salt is $[Ag\ etn_2]^+$, *k* being 1·07 × 10^{-8} at 22°. etn acts as a tervalent radical in the Co and Cu salts and is univalent in the Ag salt. J. L. D.

Amino-sugars. II. Action of dilute alkali on *N*-acylglucosamines. T. White (J.C.S., 1940, 428—437).—The view that *N*-acylglucosamines, after treatment with hot dil. alkali, give a red-purple coloration with Ehrlich's reagent, through formation of heterocyclic derivatives (by loss of H_2O), is confirmed. *N*-Acetylglucosamine (I) [improved prep. from glucosamine hydrochloride (II) and Ac_2O–AgOAc–MeOH] is stable to dil. alkali at room temp., but at the b.p. the change into a chromophoric product, now regarded as *2-methyl-4 : 5 : 2′ : 1′-glucopyrano-Δ²-oxazoline* (III), m.p. 70—75°, may be followed colorimetrically (cf. Morgan *et al.*, A., 1934, 910). (III) (prep. under various conditions de-

scribed) is hygroscopic and amorphous, and gives the Ehrlich test. It has $[\alpha]_D^{18}$ +30° in MeOH or H_2O (shows no mutarotation), is oxidised by Br in H_2O to glucosamine hydrobromide, and is hydrolysed by boiling 0·02N-MeOH–HCl to (I). With Me_2SO_4–NaOH, (III) gives *N*-acetylmethyl-3 : 4 : 6-trimethylglucosaminide (IV) (cf. Cutler *et al.*, A., 1938, II, 46); with MeI–Ag_2O–MeOH it is incompletely methylated. Ac_2O–C_5H_5N converts (III) into its 3′ : 4′ : 6′-*triacetate*, a hygroscopic glass, $[\alpha]_D^{18}$ +36·7° in $CHCl_3$. This is also obtained, m.p. 70°, $[\alpha]_D^{18}$ +54° in $CHCl_3$, from 1-bromo-*N*-acetylglucosamine 3 : 4 : 6-triacetate (Moggridge *et al.*, A., 1938, II, 266) with aq. NaOAc at 65° (mechanism of ring-formation suggested). With Me_2SO_4–CCl_4 in 60% NaOH at 75—100°, (I) gives (IV), steam-hydrolysed by 4N-HCl to 3 : 4 : 6-trimethylglucosamine hydrochloride, which with Ac_2O–AgOAc–MeOH gives N-*acetyl*-3 : 4 : 6-*trimethylglucosamine*, m.p. 234°, $[\alpha]_D^{18}$ +75° → +44·8° in H_2O. This with 0·02N-$Ba(OH)_2$ at 100° (bath) gives 2-*methyl*-4 : 5-2′ : 1′-(3′ : 4′ : 6′-*trimethylglucopyrano*)-Δ^2-*oxazoline*, a syrup, giving the Ehrlich test. *N*-α-Bromo- (V) with 0·1N-NaOH at 100° (15 min.) gives N-α-*hydroxy-propionylglucosamine* (VI), m.p. 217°, $[\alpha]_D^{18}$ +69·1° → 66·2° in H_2O. With 0·05N-NaOH or -$Ba(OH)_2$ at 100°, (V) gives 3-*keto*-2-*methyl*-5 : 6-2′ : 1′-*glucopyrano*-3 : 4 : 5 : 6-*tetrahydro*-1 : 4-*oxazine* (VII), m.p. 140—145°, $[\alpha]_D^{18}$ +19·4° in H_2O, giving the Ehrlich test. In 13% aq. NaOH, (VII) gives (VI). With boiling 1% MeOH–HCl, (VII) yields (II). Methylation of (VII) by MeI–Ag_2O gives a syrup. With Ac_2O–C_5H_5N, (VII) forms its 3′ : 4′ : 6′-*triacetate*, amorphous, $[\alpha]_D^{18}$ +32·1° in $CHCl_3$.

E. W. W.

Oxidation of aldoses by hypoiodite. VII. Glucosamine and *N*-acetylglucosamine. K. Myrbäck (Svensk Kem. Tidskr., 1940, **52**, 21—30; cf. A., 1940, II, 67).—Glucosamine (I) and its hydrochloride (II) can be determined as accurately as glucose by Bertrand's method. The change does not occur stoicheiometrically but the calculation of Cu to (I) is effected with the help of an empirical graph. In presence of NaOH (I) consumes much more I from OI′ than corresponds with the production of glucosamic acid (III), the amount increasing with [NaOH]. In presence of Na_2CO_3 or $NaHCO_3$ utilisation of 4 I occurs rapidly but the subsequent action is very slow. Br–H_2O oxidises (I) or (II) normally to (III), thus suggesting a betaine structure for (I). This view is confirmed by the observation that *N*-acetylglucosamine (IV), m.p. 204°, $[\alpha]_D$ +70·5° to +41·3° in H_2O (which is so slowly hydrolysed by alkali that betaine formation is excluded under the experimental conditions), behaves towards OI′ as a normal aldose. Exchange of OH at $C_{(2)}$ for NHAc has only a small influence on the rate of oxidation whereas the epimeric mannose is much more slowly oxidised. The behaviour of (IV) towards Fehling's solution depends greatly on experimental conditions. H. W.

Compound, $C_{21}H_{44}O_{12}N_6SSe_2$, decomp. 263—265°, from grain.—See A., 1940, III, 461.

Complex compounds of diguanide with bivalent metals. I. Copper diguanidines. P. Rây and P. N. Bagchi (J. Indian Chem. Soc., 1939, **16**, 617—620).—*Cu^{II} bisdiguanide dihydrate* when heated to 110° for 14 hr. gives *Cu^{II} bisdiguanidine*. Co-ordination with diguanide confers stability on many unstable simple Cu salts. Cu^{II} bisdiguanidinium chloride (+$2H_2O$), *bromide* (+$2H_2O$), *iodide* (+$3H_2O$), *fluoride* (+$4H_2O$), *nitrite* (+H_2O), *carbonate* (+$4H_2O$), *sulphite* (+$4H_2O$), *thiosulphate* (+$3H_2O$), *thiocyanate*, *dithionate* (+$2H_2O$), *chromate* (+$3H_2O$), and *hypophosphite* (+$2H_2O$) are described. F. R. S.

Production of amidines and their derivatives.—See B., 1940, 344.

Complex compounds of diguanide with tervalent metals. VI. Cobaltic trisdiguanidines. P. Rây and N. K. Dutt. **VII. Cobaltic trisphenyldiguanidines.** P. Rây and H. P. Bhattacharya (J. Indian Chem. Soc., 1939, **16**, 621—628, 629—633).—VI. Co combines with diguanide to form complex compounds similar to the corresponding Cr compounds (cf. A., 1938, II, 435): *Co^{III} trisdiguanide dihydrate*, *cobaltic trisdiguanidine*, *cobaltic trisdiguanidinium chloride*, *fluoride*, *bromide*, *iodide*, *thiocyanate*, *chlorate*, *perchlorate*, *borofluoride*, *nitrate*, *nitrite*, *chloroformate*, *carbonate*, *sulphate* (+$7H_2O$), *selenate* (+$7H_2O$), *chloroselenate*, *hydroxo-sulphite*, *sulphite* (+$7H_2O$), *chlorothiosulphate* (+$2{\cdot}5H_2O$), *thiosulphate*, *chlorochromate*, *chromate* (+$3H_2O$), *perchromate* (+$4H_2O$), *chlorophosphate*, *phosphate* (+$6H_2O$), *hydrosulphide* and *-polysulphide*, *iodate*, *chloroiodate* (+H_2O), *periodate* (+$3H_2O$), *oxalate*, and *camphorsulphonate*.

VII. *Co^{III} trisphenyldiguanide* forms a *trihydrate*, m.p. ~200° (decomp.), and *dihydrate* melts with decomp.; both are dehydrated to *Co^{III} trisphenyldiguanidine*, similar to the corresponding Cr compound. *Co^{III} trisphenyldiguanidinium chloride* (+$2{\cdot}5H_2O$), *bromide* (+H_2O), *iodide* (+H_2O), *sulphate* (+$10H_2O$), *nitrate* (+$0{\cdot}5H_2O$), *nitrite* (+$0{\cdot}5H_2O$), *carbonate* (+$2H_2O$), *thiosulphate* (+$7H_2O$), *thiocyanate* (+$3H_2O$), *dithionate* (+$2H_2O$), and *chromate* (+$2H_2O$) are also described. F. R. S.

Aliphatic arsinic acids. Arsenation of mono-, di-, and tri-chloroacetic and mono- and di-bromomalonic acids. A. R. Marquez (Rev. Fac. Cienc. Quím. La Plata, 1939, **14**, 217—228).—The yield of arsinoacetic acid (I) from $CH_2Cl{\cdot}CO_2H$ (1 mol.) and Na_3AsO_3 (*x* mols.) increases with *x* and reaches 100% when $x = 2$. The effect of varying the [NaOH] and time of reaction has been studied. The solubility of (I) in H_2O is recorded between 0° (0%) and 40° (98·5%). Reduction of (I) with NaH_2PO_2 in aq. H_2SO_4 yields arsenoacetic acid (NH_4 salt). The As in these acids is determined by the I liberated from KI in HCl. F. R. G.

***X*-Ray studies of mercury alkylthiol chlorides.** A. Johannson (Arkiv Kemi, Min., Geol., 1939, **13**, **A**, No. 14, 11 pp.).—$SR{\cdot}CH_2{\cdot}CO_2H$ are converted by 0·01M-H_2O_2 into $RSO{\cdot}CH_2{\cdot}CO_2H$, and thence by aq. $HgCl_2$ at 100° into $HgCl{\cdot}SR$, $CHO{\cdot}CO_2H$, and HCl. Thus are obtained *Hg Me*, m.p. >230°, *Et*, m.p. >230°, *Pr^{α}*, m.p. 182—183°, *Pr^{β}*, m.p. >230°, *Bu^{α}*, m.p. 175—176°, *Bu^{β}*, sinters at 215—220°, and *CHMeEt chloride*, m.p. 188—189°. *$HgBu^{\gamma}Cl$*, decomp. when heated, is obtained by working at room temp. throughout, since at 100° it decomposes mainly to

CH_2:CMe_2, HgS, and HCl. *X*-Ray consts. etc. are recorded for the products and may be used for identification. R. S. C.

Mechanism of Walden inversion in reactions leading to formation of the carbonato-diethylenediaminecobaltic ion.—See A., 1940, I, 266.

Co-ordinational stability of ethylene hydrocarbons. (Miss) A. Gelman (Ann. Sect. Platine, 1939, No. 16, 35—39).—The stability of complexes of the type $NH_4[PtCl_3,R]$ falls in the order R = CO > CH_2:CHPh > C_2H_4 > CH_2:CHMe = CH_2:CHEt. R. T.

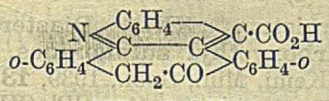
Compounds of platinum salts with ethylenic hydrocarbons.—See A., 1940, I, 267.

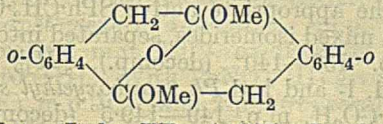
Compounds of platinum and iridium salts with acetonitrile.—See A., 1940, I, 267.

Ethylene compounds of platinum nitrochlorides.—See A., 1940, I, 267.

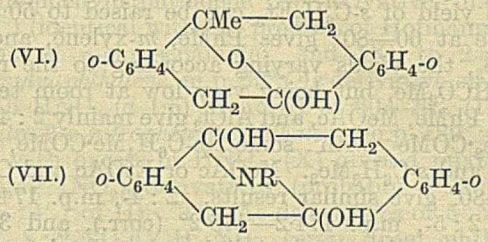
Low-temperature dehydrogenations. II. R. T. Arnold, C. Collins, and W. Zenk (J. Amer. Chem. Soc., 1940, **62**, 983—984).—Chloranil in boiling xylene converts 1-*p*-diphenylyl-, 1-*p*-diphenylyl-2-methyl-, 1-α- and 1-β-naphthyl-, and 1-*o*-tolyl-Δ^1-*cyclo*hexene into the derived aromatic compounds in 47, 72, 67, 72, and 72% yield, respectively (cf. A., 1939, II, 362). R. S. C.

Attempt to synthesise a substituted *cyclo*octatetraene. S. Wawzonek (J. Amer. Chem. Soc., 1940, **62**, 745—749).—3 : 4 : 7 : 8-*Dibenz*-$\Delta^{3:7}$-cyclo*octadiene*-1 : 5-*dione* (I) reacts as an aliphatic αε-diketone. $(CHPh{\cdot}CO_2H)_2$ is prepared from the dinitrile by boiling H_2SO_4–H_2O–AcOH (2 : 2 : 1). Diphensuccindane-9 : 12-dione with PCl_5 and later AcOH gives 9 : 12-dichloro-$\Delta^{9:11}$-diphenylsuccindadiene (II) (cf. A., 1922, i, 444) and 9 : 9 : 12 : 12-*tetrachloro*-Δ^{10}-*diphensuccindene* (III), *o*-C_6H_4<$CCl_2{\cdot}C$——$C{\cdot}CCl_2$>C_6H_4-*o*, m.p. 178—179°, converted by Zn dust in boiling AcOH into (II). With 12% O_3 in EtOH at −40°, (III) gives the ozonide, m.p. 191—193° (decomp.), converted by H_2–5% Pd–$BaSO_4$ at 2·3 atm. in EtOAc into (I), m.p. 203·5—204·5° [*dioxime*, m.p. 240—243° (decomp.); (*CHPh*:)$_2$ derivative, m.p. 244—246°], difficultly sol. in aq., but readily sol. in alcoholic, alkali to give a yellow solution becoming (reversibly) orange when heated. No colour is formed by (I) in PhN_2Cl–EtOH–alkali. With hot PCl_5, (I) gives the *dichlorodiphosphinic acid*, *o*-C_6H_4<$CCl(PO_3H_2){\cdot}CH_2$ / $CH_2{\cdot}CCl(PO_3H_2)$>C_6H_4-*o*, and with isatin and 20% KOH gives the *substance* (IV), m.p. 297° (gas). With Me_2SO_4 and 20% KOH in MeOH, (I) gives the *Me*$_2$ *ether* (V), m.p. 143—144°, unchanged by Br, but


(IV.)

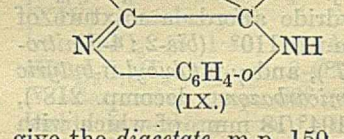

(V.)

hydrolysed to (I) by HBr–AcOH. In the Grignard machine, (I) shows only 1 CO and 1 active H. With MgMeI in boiling Et_2O–C_6H_6, (I) gives the *compound* (VI), m.p. 213—215°, and with boiling NH_3–H_2O–EtOH gives the *substance* (VII; R = H), m.p. 167° (gas), converted by HNO_3 or above the m.p. into (I).


(VI.)

(VII.)

With $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl–$Na_2CO_3$–EtOH–$H_2O$, (I) gives the *substance* (VII; R = $NH{\cdot}CO{\cdot}NH_2$), m.p. 210° (decomp.), converted by heat alone or with KOH into Δ^{10}-diphensuccindene and diphensuccindane. Zn–Hg–HCl–AcOH–H_2O or 20% KOH–Zn dust–EtOH reduces (I) to the glycol, *o*-C_6H_4<$CH_2{\cdot}C(OH)$——$C(OH){\cdot}CH_2$>C_6H_4-*o*, m.p. 148·5—149°, which with H_2SO_4– or HI–AcOH gives a yellow *substance*, m.p. >350°, and with $Pb(OAc)_4$ in C_6H_6 at 50° re-forms (I). Boiling Ac_2O–KOAc converts (I) into the *acetate* (VIII), m.p. 138—139°, of the monoenol, hydrolysed by alkali to (I) and oxidised by CrO_3–AcOH at 50—60° to *o*-$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$-*o*. With Br–AcOH, (VIII) gives a *Br-acetate*, m.p. 219—223° (gas), unchanged by KOAc–AcOH but converted by Br–$CHCl_3$ into a crude Br_2-derivative diacetate, m.p. 173—178° (gas), which with NH_3–EtOH–H_2O gives 3 : 4 : 7 : 8-*dibenz*-$\Delta^{3:7}$-cyclo*octadiene*-1 : 2 : 5-*trione*, m.p. 254—256° [phenazine *derivative* (IX), m.p. 283—285°], unaffected by Ac_2O–KOAc or –H_2SO_4 or H_2O_2–NaOH. (I) or (VIII) and H_2SO_4 (1 drop) in boiling Ac_2O give the *diacetate*, m.p. 150—151°, which yields a *Br*-derivative *diacetate*, m.p. 225—229°, obtained also from (VIII) by H_2SO_4–AcOH and unaffected by KOAc–AcOH or Br. R. S. C.


(IX.)

Oxidation of cyclic compounds by hydrogen peroxide catalysed by pervanadic acid. W. Treibs (Angew. Chem., 1939, **52**, 698—700).—A review. R. S. C.

Condensation of esters with aromatic hydrocarbons by means of aluminium chloride. J. F. Norris and P. Arthur, jun. (J. Amer. Chem. Soc., 1940, **62**, 874—877; cf. A., 1939, II, 372).—MeOAc and $AlCl_3$ give a 1 : 1 additive compound, m.p. 60°, which at 143° (rapidly at 170°) gives MeCl (0·7 mol.), at 184—200° gives HCl (0·38 mol.) and a residue, ? $AlCl_2{\cdot}OAc$ (I). EtOAc gives a similar compound, which gives EtCl (0·67 mol.) and (I). With C_6H_6 (2 mols.) and $AlCl_3$ (1·2 mols.), (I) (1 mol.) gives 42% of COPhMe. The liquid compound from $Bu^{\alpha}OAc$ gives 5% of $Bu^{\alpha}Cl$ and 1·26 mols. of HCl with much C_4H_8. $HCO_2Me,AlCl_3$, decomp. 110°, gives MeCl (88%) at 143°, followed by CO and HCl at 185°; the residue gives no PhCHO. HCO_2Et behaves similarly.

EtOAc, C_6H_6, and $AlCl_3$ (2 mols. required in this and similar reactions) at room temp. give PhEt (12·3%) and *m*-$C_6H_4Et_2$ (51·3%); longer treatment gives also a little *s*-$C_6H_3Et_3$. HCO_2Et gives the same products, but the yield of *s*-$C_6H_3Et_3$ can be raised to 50·5%. HCO_2Me at 60—80° gives PhMe, *m*-xylene, and *s*-$C_6H_3Me_3$, the yields varying according to the ratio C_6H_6 : HCO_2Me, but being very low at room temp. At 100° PhMe, MeOAc, and $AlCl_3$ give mainly 2 : 4 : 1-$C_6H_3Me_2$·COMe with some *p*-C_6H_4Me·COMe, *m*-xylene, and *s*-$C_6H_3Me_3$. MeOAc or EtOAc and C_6H_6 at 60—80° give similar results. 2 : 4-, m.p. 174·2—175·2°, 2 : 5-, m.p. 174·2—175·2° (corr.), and 3 : 4-dimethylacetophenone-2 : 4-dinitrophenylhydrazone, m.p. 255·2—255·8° (corr.), 2 : 4-, m.p. 154·6—154·8°, and 2 : 5-*dimethylacetophenone*-p-*nitrophenylhydrazone*, m.p. 159·8—160·1° (corr.), are described.

R. S. C.

Sulphonation and nitration reactions promoted by boron trifluoride.—See B., 1940, 342.

Production of pure hydrocarbons of the benzene series by distillation.—See B., 1940, 343.

Chain polymerisation of styrene.—See A., 1940, I, 259.

Constituents of some Indian essential oils. XXVII. Synthesis of *dl*-α-curcumene. F. D. Carter, J. L. Simonsen, and H. O. Williams (J.C.S., 1940, 451—453).—The *Et* ester, b.p. 157°/19 mm., of *dl*-γ-*p*-tolyl-*n*-valeric acid (improved prep.) and Na–EtOH give δ-p-*tolyl*-n-*amyl alcohol*, b.p. 151°/16 mm. (3 : 5-*dinitrobenzoate*, m.p. 80—81°), which is converted (NaCN–I) through the *chloride*, b.p. 141°/17 mm., into δ-p-*tolyl*-n-*hexoic acid* (I), b.p. 197°/20 mm. [*Me* (II), b.p. 167°/17 mm., and p-*phenacyl* esters, m.p. 70°]. Condensation ($AlCl_3$) of PhMe and glutaric anhydride affords a mixture of αγ-*di*-p-*toluoylpropane*, m.p. 110° (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 257°), and γ-p-*toluoyl*-n-*butyric acid*, m.p. 148—149° (*semicarbazone*, decomp. 218°), the *Me* ester, b.p. 192—194°/18 mm., of which with MgMeI yields δ-p-*tolyl*-Δ^{γ}-*hexenoic acid*, m.p. 80—81°. This acid is reduced (Pd–H_2) to (I), which could not be resolved owing to the instability of the alkaloidal salts. MgMeI and (II) give dl-β-*hydroxy*-ζ-p-*tolyl*-β-*methylheptane*, b.p. 164°/17 mm. (*xenylurethane*, m.p 84—85°), which with $KHSO_4$ is dehydrated to dl-α-*curcumene*, b.p. 134°/16 mm. (*nitrosate*, decomp. 114°), identical with the natural hydrocarbon (cf. Simonsen *et al.*, A., 1939, II, 516).

F. R. S.

Magnesium pentamethylphenyl bromide. H. Clement (Ann. Chim., 1940, [xi], **13**, 243—316; cf. A., 1939, II, 60).—Methylation of xylene by $AlCl_3$ and MeCl at 95° is a series of successive, not simultaneous, reactions so that it is possible to fix the most suitable durations (based on g. of HCl evolved) for the prep. of each derivative either in the best yield or for the readiest purification. C_6Me_5Br and Mg give C_6Me_5·MgBr if an alkyl halide is also present and this reacts normally with CO_2, CH_2O, MeCHO, and $COMe_2$. With $CH(OEt)_3$ it affords *pentamethylbenzaldehyde*, m.p. 130·5° (*oxime*), and with PhCHO it yields *pentamethylbenzhydrol*, m.p. 107·5°. Abnormal reactions occur with EtOAc which gives *pentamethylacetophenone*, m.p. 150—151°, and BzCl which yields *pentamethylbenzophenone*, m.p. 125° (*semicarbazone*, m.p. 170°), which is also obtained from EtOBz. A principal abnormal and a secondary normal reaction are given with HCO_2Et and AcCl.

H. W.

New isomeride of trinitrotoluene. M. Milone and A. Massa (Gazzetta, 1940, **70**, 196—201).—m-*Nitrophenyldinitromethane* (I), m.p. 124—125° (*K*, *Ag*, *Ba*, and *Pb* salts, deflagrating when heated; NH_4 salt), is obtained from $CHPh(NO_2)_2$ in HNO_3 (*d* 1·52) at room or higher temp. HNO_3 (*d* 1·4) has no action alone or in EtOH or AcOH; H_2SO_4–HNO_3 gives *p*-NO_2·C_6H_4·CO_2H. (I) is hydrolysed to *m*-NO_2·C_6H_4·CO_2H. In explosive properties (I) resembles 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$. The explosive power, and sensitiveness as detonators, of (I) and its salts are examined by the methods of Trauzl and of Berta. The compounds are inferior as detonators to those in common use.

E. W. W.

3 : 4′-Dinitrodiphenyl. W. A. Waters (J.C.S., 1940, 474).—The product (I), m.p. 137°, obtained by Hodgson *et al.* (A., 1940, II, 126°) from diazotised *m*-NO_2·C_6H_4·NH_2 and $PhNO_2$, is not 3 : 4′-dinitrodiphenyl (cf. Scarborough *et al.*, A., 1927, 236), which has m.p. 189°. (I) is presumably a mixture.

E. W. W.

Halogenation of *as*-diphenylethane. F. E. Sheibley and C. F. Prutton (J. Amer. Chem. Soc., 1940, **62**, 840—841).—Cl_2 converts $CHPh_2Me$ in quartz in light at 100—150° into a yellow liquid, which, when distilled, gives $CHPh_2Me$, $(CHPh{:})_2$, and αα-*dichloro*-ββ-*diphenylethylene* (I), m.p. 79—80° (corr.). The mechanism is: $CHPh_2Me \rightarrow CPh_2MeCl$ (rate-determining step) $\rightarrow CPh_2{:}CH_2 \rightarrow CPh_2Cl{\cdot}CH_2Cl \rightarrow CPh_2{:}CHCl \rightarrow CPh_2Cl{\cdot}CHCl_2 \rightarrow$ (I). The $(CHPh{:})_2$ is formed from the $CPh_2{:}CHCl$. Bromination and distillation give only small amounts of $(CHPh{:})_2$ and $(CPh_2{:}CH)_2$. (I) is hydrolysed completely (to $CHPh_2{\cdot}CO_2H$) only by KOH–MeOH at 150°. With PhOH at 225°, (I) gives *benzilic aldehyde Ph₂ acetal*, m.p. 111·5—112° (corr.). At 700° in SiO_2, $CHPh_2Me$ gives C_6H_6, PhMe, and $CHPh{:}CH_2$.

R. S. C.

Octadeca- (per-)chloroquaterphenyl. Preparation of deca- (per-)chlorodiphenyl. J. B. Wibaut, J. Overhoff, and K. Gratama (Rec. trav. chim., 1940, **59**, 298—302).—Commercial pentachlorodiphenyl and Cl_2, first at 100° and then with $FeCl_3$ and I at 200—300°, give $(C_6Cl_5)_2$ (I) (75%), m.p. 309° (corr.). 4-4′-Diphenylyldiphenyl [quaterphenyl] with $SbCl_5$, first at 220° and then at 270°, gives the Cl_{18}-derivative, m.p. 364—365° (corr.), sublimes at 340°/0·5 mm., the mol. wt. of which is determined by cryoscopy in (I) ($k = 36·0$).

R. S. C.

Stereochemistry. XXI. Diastereoisomeric phenyl β-carboxyethyl sulphoxides. B. Holmberg (Arkiv Kemi, Min., Geol., 1939, **13**, **A**, No. 15, 8 pp.).—The appropriate active $SPh{\cdot}CH_2{\cdot}CO_2H$ and H_2O_2 yield mixed isomerides, separated into d, d- and l, l-, m.p. 139—140° (decomp.), $[M]_D^{17}$ +397·8°, −397·1°, d, l- and l, d-*Ph* β-*carboxyethyl sulphoxide*, $PhSO{\cdot}CH_2{\cdot}CO_2H$, m.p. 149—149·5° (decomp.), $[M]_D^{17}$ +64·3°, −64·5° in abs. EtOH, the stereochemical prefixes referring to the C and S, respectively. Mix-

ture of the appropriate isomerides gives two inactive *acids*, m.p. 137—138°. Hot alkali racemises the C, but not the S. R. S. C.

α- and β-Phenylthiolethanesulphonic acid and the corresponding sulphones. I. HEDLUND (Arkiv Kemi, Min., Geol., 1939, **13**, **A**, No. 12, 14 pp.).—PhSNa and $CH_2Br{\cdot}CH_2{\cdot}SO_3Na$ in H_2O give β-*phenylthiolethanesulphonic acid*, $+2H_2O$, m.p. 48·5—49° (corr.) (*Cu*, $+4H_2O$, *Zn*, $+4H_2O$, *Ca*, and *Cd* salts), isolated as *Na* salt, $+H_2O$. The *Ba* salt, $+2H_2O$, is converted by $BaMnO_4$–CO_2 in H_2O into *Ph* β-*sulphoethyl sulphone*, $+2H_2O$ (*Ba* salt, $+H_2O$), which is hydrolysed by aq. $Ba(OH)_2$ at 100° mainly to $PhSO_2H$ and $OH{\cdot}[CH_2]_2{\cdot}SO_3H$, although some SO_2 is also evolved. β-$(MeCSH)_3$ (prep. modified to give 88% yield) and Cl_2 in H_2O give 35—45% of $CHMeCl{\cdot}SO_2Cl$, and thence $CHMeCl{\cdot}SO_3Na$, which with PhSNa in H_2O at 160° gives α-*phenylthiolethanesulphonic acid* (I), m.p. ($+H_2O$) 91·5—92°, ($+2H_2O$) 70—75° (*Na*, $+H_2O$, *Cu*, and sol. *Ba*, $+H_2O$, salts; loses SO_2 when kept over P_2O_5). Resolution of (II), best by brucine, gives the *Ba*, $+3H_2O$, $[M]_{5461}^{25}$ +289·1°, and *brucine* salt, $[M]_{5461}^{25}$ +266° in H_2O, of the *d*-acid and the *brucine* salt, $[M]_{5461}^{25}$ −288·8° to −290° in H_2O, of the *l*-acid. $BaMnO_4$ yields dl-, m.p. 74—75°, *d*- (*Ba* salt, $[M]_{5461}^{25}$ +34·7°), and *l*-Ph α-sulphoethyl sulphone (II) (*Ba* salt, $[M]_{5461}^{25}$ −36·3°). (I) is racemised by NaOH and more slowly by HCl at 100°. (II) is very rapidly racemised by alkali, but is stable to acid. R. S. C.

Oxidation of tetrahydronaphthalene in condensed phase.—See A., 1940, I, 259.

Synthesis of 2-phenylnaphthalenes. D. H. HEY and S. E. LAWTON (J.C.S., 1940, 374—383).—$2\text{-}C_{10}H_7Ph$ (I) is readily obtained in quantity from $2\text{-}C_{10}H_7{\cdot}NAc{\cdot}NO$ (II) and C_6H_6 (cf. Haworth *et al.*, A., 1940, II, 162). The optimum conditions for the prep. of (II) from $C_{10}H_7{\cdot}NHAc$ and nitrous fumes or NOCl in Ac_2O–AcOH are described. The yield of (I) is ≯25—30%, but the method is cheap. CrO_3 oxidises (I) to 2-phenyl-1 : 4-naphthaquinone (III). With HNO_3 (*d* 1·42) in AcOH, (I) gives 1-*nitro*- (IV), m.p. 127°, with some 1 : 5(?)-*dinitro*-2-*phenylnaphthalene*, m.p. 187—188°; under more drastic conditions, inseparable mixtures are formed. The constitution of (IV) is established by synthesis from diazotised $1 : 2\text{-}NO_2{\cdot}C_{10}H_6{\cdot}NH_2$. With hot $SnCl_2$–HCl–EtOH, (IV) gives 4-*chloro*-2-*phenyl*-1-*naphthylamine*, m.p. 79° (*Ac* derivative, m.p. 213°); with Fe in boiling AcOH, (IV) gives 2-*phenyl*-1-*naphthylamine* (V), m.p. 104° [*Ac* derivative (VI), m.p. 234°], converted by diazotisation in HCl and $Cu_2(CN)_2$, into 1-*chloro*-2-*phenylnaphthalene*, m.p. 82°. Attempted nitrosation of $1 : 2\text{-}NO_2{\cdot}C_{10}H_6{\cdot}NHAc$ was unsuccessful. With HNO_3 (*d* 1·45) in AcOH at 40°, (VI) gives the *Ac* derivative (VII), m.p. 230°, of 4-*nitro*-2-*phenyl*-1-*naphthylamine* (VIII), m.p. 155°, obtained from (VII) by hydrolysis. With $SnCl_2$–HCl–EtOH, (VIII) gives 2-*phenylnaphthylene*-1 : 4-*diamine*, m.p. 100—101° (Ac_2 derivative, m.p. 320°), oxidised by boiling 5% aq. CrO_3 to (III). With $PhNO_2$, (II) gives a mixture of 2-o- (IX), m.p. 101°, and 2-p-*nitrophenylnaphthalene* (X), m.p. 174°, separable only by vac.-sublimation or steam-distillation. With CrO_3–AcOH on the steam-bath, these yield respectively 2-o-, m.p. 164°, and 2-p-*nitrophenyl*-1 : 4-*naphthaquinone*, m.p. 223—224°. With excess of CrO_3 in boiling AcOH, (X) gives $p\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2H$. $SnCl_2$–HCl reduces (IX) to 2-o-aminophenylnaphthalene (*Ac* derivative, m.p. 204—205°) (identical with the product of Hofmann degradation of α-chrysenamide), and (X) to 2-p-*aminophenylnaphthalene*, m.p. 99° (*Ac* derivative, m.p. 206°). With HNO_3 (*d* 1·5) in AcOH at 60—70°, (IX) gives 1-*nitro*-2-o-*nitrophenylnaphthalene*, m.p. 189°; at 60—70° with excess of HNO_3, (X) gives a mixture containing $(NO_2)_3$-derivatives (probably 1 : 5 : 4′- and 1 : 8 : 4′-) of (I). The Ac derivatives of 5 : 2-, 6 : 2-, and $8 : 2\text{-}NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ (prep. from phthaloyl-2-naphthylamine improved by hydrolysing the nitrated product with HCl continuously added to boiling EtOH) are converted by nitrous fumes in AcOH–Ac_2O into 5-, m.p. 84° (decomp.), 6-, and 8-*nitronitrosoaceto*-2-*naphthalide*, both m.p. 86° (decomp.), and these by C_6H_6 into 5- (XI), m.p. 89°, 6- (XII), m.p. 146°, and 8-*nitro*-2-*phenylnaphthalene* (XIII), m.p. 69°. With Fe–HCl, (XI) gives 6-*phenyl*-1-*naphthylamine*, m.p. 142—143° (*Ac* derivative, m.p. 131°), and (XIII) gives 7-*phenyl*-1-*naphthylamine*, m.p. 94° (*Ac* derivative, m.p. 203°). With $SnCl_2$–HCl, (XII) gives 6-*phenyl*-2-*naphthylamine* (XIV), m.p. 132° (*Ac* derivative, m.p. 199°). $2 : 7\text{-}C_{10}H_6(NH_2)_2$, acetylated and treated in AcOH–Ac_2O with nitrous fumes, gives 2 : 7-*dinitrosodiacetamidonaphthalene*, m.p. 79° (decomp.), which with C_6H_6 yields 2 : 7-*diphenylnaphthalene*, m.p. 143°. The Ac_2 derivative, m.p. 334—335°, of $2 : 6\text{-}C_{10}H_6(NH_2)_2$ could not be nitrosated. With Br–AcOH, (I) gives 1-*bromo*-2-*phenylnaphthalene*, m.p. 66°, also obtained from (V) (Sandmeyer). $6 : 2\text{-}C_{10}H_6Br{\cdot}NHAc$ gives a *NO*-derivative, m.p. 82° (decomp.), which in C_6H_6 yields 6-*bromo*-2-*phenylnaphthalene*, m.p. 132°, also obtained from (XIV) (Sandmeyer). $1 : 2\text{-}C_{10}H_6Br{\cdot}OH$ is nitrated by HNO_3 (*d* 1·42) in AcOH to $1 : 6 : 2\text{-}(NO_2)_2C_{10}H_5{\cdot}OH$. $6 : 2\text{-}OMe{\cdot}C_{10}H_6{\cdot}NHAc$ gives a *NO*-derivative, m.p. 82° (decomp.), which in C_6H_6 yields 6-*methoxy*-, m.p. 148°, hydrolysed by HI–AcOH to 6-*hydroxy*-2-*phenylnaphthalene*, m.p. 175—176°. $7 : 2\text{-}OMe{\cdot}C_{10}H_6{\cdot}NHAc$ gives a *NO*-derivative, m.p. 85° (decomp.), yielding 7-*methoxy*-, m.p. 80°, and thence 7-*hydroxy*-2-*phenylnaphthalene*, m.p. 156°. With boiling Ac_2O, $7 : 2\text{-}OMe{\cdot}C_{10}H_6{\cdot}NH_2$ gives *diacetyl*-7-*methoxy*-2-*naphthylamine*, m.p. 129°. E. W. W.

Reactions in sunlight. IV. E. OLIVERI-MANDALÀ and E. DELEO (Gazzetta, 1940, **70**, 186—190; cf. A., 1939, II, 316).—Acenaphthene in $COMe_2$ in sunlight (at Messina) for 22 months gives acenaphthenone. Fluorene in $COMe_2$ in sunlight for 8 months gives fluorenone. E. W. W.

9-Methyl-3 : 4-benzfluorene. L. F. FIESER and L. M. JOSHEL (J. Amer. Chem. Soc., 1940, **62**, 957—958).—$1 : 2 : 3\text{-}C_{10}H_5Ph(CO)_2O$ and $AlCl_3$ in boiling C_6H_6 give 99% (HF gives much less) of 3 : 4-benzfluorenone-1-carboxylic acid and thence (basic Cu carbonate; 310—320°) 84% of 3 : 4-benzfluorenone. MgMeCl in Et_2O–C_6H_6 then gives 9-*methyl*-3 : 4-*benzfluoren*-9-*ol* (84%), m.p. 117·8—118·6°, which, when dehydrated in boiling AcOH, gives a *polymeride*, $(C_{18}H_{12})_x$, darkens at ~200°, m.p. 275—280°, but is

converted by boiling in AcOH and then hydrogenating (PtO_2) in AcOH into 9-*methyl*-3 : 4-*benzfluorene*, m.p. 80·8—82° (*picrate*, m.p. 128—128·5°), and a little polymeride. M.p. are corr. R. S. C.

Polycyclic aromatic hydrocarbons. XXII. C. L. Hewett. **XXIII.** J. W. Cook and (Mrs.) A. M. Robinson (J.C.S., 1940, 293—303, 303—304).—XXII. Carcinogenic activity, regarded as inherent in 3 : 4-benzphenanthrene derivatives (cf. A., 1938, II, 132, 438), especially when further substituted in the 1- and 2-positions, is observed in 1-*methyl*-3 : 4-*benzphenanthrene* (I), m.p. 77—78°, b.p. 210° (bath)/0·4 mm. [*picrate* (II), m.p. 112·5—113·5°], and in 2-iso*propyl*-3 : 4-*benzphenanthrene* (III), m.p. 91·5—92·5° (*picrate*, m.p. 116—117°), and is shared by the analogous 1 : 2-*dimethylchrysene* (IV), m.p. 127—128° (for prep. see below). In the prep. of (I), 3 : 4-benz-1-phenanthroic acid (*loc. cit.*) gives, via the chloride, the *anilide*, m.p. 215—216°, which with PCl_5 in $C_2H_2Cl_4$, followed by $SnCl_2$–HCl–Et_2O and hydrolysis, gives 3 : 4-*benz*-1-*phenanthraldehyde*, m.p. 81—82°, the *semicarbazone*, m.p. 220—222°, of which is heated with NaOEt at 180°, and the distilled *product*, b.p. 200—210°/0·4 mm., converted into (II), which in C_6H_6 passed through Al_2O_3 gives (I).

In the prep. of (III), 1 : 2-$C_{10}H_6Br$·CHO, which is obtained in good yield (cf. Mayer *et al.*, A., 1922, i, 740) from 1 : 2-$C_{10}H_6Br$·CH_2Br and $(CH_2)_6N_4$ in boiling AcOH, with CH_2Ph·CO_2Na–Ac_2O on the water-bath gives α-*phenyl*-β-2-(1-*bromonaphthyl*)*acrylic acid*, m.p. 211—212°, which with KOH at 260° forms 3 : 4-*benz*-2-*phenanthroic acid*, m.p. 236—237° (*Na* salt). With MeOH–HCl this forms its *Me* ester, m.p. 76—77°, converted by MgMeI–Et_2O, followed by NH_4Cl and ice, into 3 : 4-*benz*-2-*phenanthryldimethylcarbinol*, m.p. 139—140°, which with $C_6H_3(NO_2)_3$·OH in boiling EtOH gives the *picrate* (V), m.p. 113—113·5°, of 2-iso*propenyl*-3 : 4-*benzphenanthrene*, isolated from (V) in C_6H_6 by Al_2O_3, and hydrogenated (Pd–EtOH) to (III). Prep. of 1 : 2-*dihydro*-3 : 4-*benz*-1-*phenanthroic acid* (VI), m.p. 140·5—141·5°, is not very satisfactory. 1 : 2-C_{10}HBr·OAc and NaOEt–Et_2O–$Et_2C_2O_4$ give, after 16 hr. at room temp. and 2 hr. at the b.p. followed by treatment with dil. H_2SO_4 and heating of the ethereal extract at 200—210°/20 mm., *Et* 1-*bromo*-2-*naphthylmalonate*, b.p. 187—189°/0·3 mm., of which the Na derivative with CH_2PhCl–EtOH, followed by boiling with KOH–EtOH, gives, after decarboxylation of the dibasic acid, α-2-(1-*bromonaphthyl*)-β-*propionic acid* (VII), m.p. 131—132° (isolated through the *Me* ester, in the fraction of b.p. 210—220°/0·4 mm.). Attempted ring-closure of (VII) by KOH in quinoline at 250—260° for 2 hr. gives α-*phenyl*-β-2-(1-*bromonaphthyl*)*ethane*, b.p. 210°/0·3 mm. With KOH at 260° for 15 min., (VII) gives, after fractionation of the esterified product and hydrolysis of the fractions, mainly β-*phenyl*-α-2-(1-*hydroxynaphthyl*)*propionic acid*, m.p. 146·5—147·5°, with small amounts of (VI) and of 3 : 4-benz-1-phenanthroic acid.

The prep. of (IV) is effected by two routes. (i) 2 : 1-$C_{10}H_6Me$·CH_2Cl with Zn and aq. EtOH (water-bath) gives [with as-(2 : 2′-*dimethyl*-1 : 1′-*dinaphthyl*)-*ethane*, m.p. 177—178°] 1 : 2-$C_{10}H_6Me_2$ (VIII), which with Br in CS_2 gives 4-*bromo*-1 : 2-*dimethylnaphthalene* (IX), m.p. 39—40°, b.p. 190—195°/14 mm., isolated through the *picrate*, m.p. 108—109°. The constitution of (IX) is established by treating the Grignard derivative (X) with Me_2SO_4 and obtaining 1 : 2 : 4-$C_{10}H_5Me_3$. With $(CH_2)_2O$, (X) gives β-(3 : 4-*dimethyl*-1-*naphthyl*)*ethyl alcohol*, m.p. 65°, b.p. 150—152°/0·3 mm., of which the *chloride*, m.p. 44—45°, b.p. 140—145°/0·3 mm., with Mg and 2-methyl*cyclo*hexane in Et_2O gives, after treatment with ice and NH_4Cl, a *carbinol*, b.p. (impure) 195—200°/0·5 mm., dehydrated (P_2O_5) to a gum which resinifies when heated with Se. Chloromethylation of (VIII) by paraformaldehyde and HCl in AcOH at room temp. for 16 hr. (better than at 60° for 20 hr.) gives 3 : 4-*dimethyl*-1-*chloromethylnaphthalene* (XI), m.p. 70—71° (converted by Zn and aq. EtOH to 1 : 2 : 4-$C_{10}H_5Me_3$), with 3 : 4 : 3′ : 4′-*tetramethyl*-1 : 1′-*dinaphthylmethane*, m.p. 174—175°. With aq. KCN in boiling EtOH, (XI) gives, after hydrolysis, a large proportion of a neutral substance, and 3 : 4-*dimethyl*-1-*naphthylacetic acid*, m.p. 181—182°, of which the pure *nitrile*, m.p. 66·5—67·5°, b.p. 160—170°/0·5 mm., is obtained from (XI) and $Cu_2(CN)_2$ in CH_2Ph·CN at 160—170° and at 220°, and of which the *Na* salt with *o*-NO_2·C_6H_4·CHO and Ac_2O at 130° (7 hr.) gives α-(3 : 4-*dimethyl*-1-*naphthyl*)-*o-nitrocinnamic acid*, m.p. 213—214° (*NH_4* salt), reduced by $FeSO_4$–NH_3 to the *o-amino-acid*, m.p. 226—227° (*K* salt). The last with H_2SO_4–$NaNO_2$ and Cu powder, followed by heating at 70°, gives 1 : 2-*dimethylchyrsene*-7-*carboxylic acid*, m.p. 234—235°. This is decarboxylated by Cu powder in boiling quinoline to a product which, when distilled over Na at 200°/0·5 mm., gives (IV), oxidised by $Na_2Cr_2O_7$–AcOH to a quinone-like *substance*, m.p. 157—159°. (ii) Chrysaquinone with MgMeI and Et_2O, followed by ice and NH_4Cl, gives 1 : 2-*dihydroxy*-1 : 2-*dimethyl*-1 : 2-*dihydrochrysene* (XII), m.p. 154—155°. This heated with HI–AcOH gives a bimol. *product*, $C_{40}H_{32}$ (?), m.p. 258—260°, also obtained from (XII) and aq. HI–P at 175—180°. (XII) is unchanged by HCl–$CHCl_3$, and in AcOH with mineral acids or I is resinified. With HCl in cooled MeOH, (XII) gives 1 : 2-*dimethylchrysene* 1 : 2-*oxide* (XIII), m.p. 155—156°, which with HI in AcOH gives an *I*-compound, m.p. 115°, reduced by Zn–EtOH to (IV). With H_2–Pt in AcOH at 60—70°, (XIII) gives (IV), in poor yield. With H_2–Pd in $COMe_2$, (XIII) gives a quant. yield of 1 : 2-*dihydro*-1 : 2-*dimethylchrysene*, m.p. 104—104·5°, readily dehydrogenated to (IV).

In an attempt to synthesise 1 : 2 : 3 : 4-tetramethylphenanthrene, the corresponding -anthracene was obtained. 2-$C_{10}H_7Pr^{\alpha}$ with Br in $CHCl_3$ gives 2-α-*bromopropionylnaphthalene*, m.p. 81—82°, which with $CMeNa(CO_2Et)_2$ in C_6H_6 (first in freezing mixture, eventually boiling) gives, after hydrolysis, decarboxylation at 190—200°, Me esterification, and hydrolysis, β-2-*naphthoyl*-αβ-*dimethylpropionic acid*, m.p. 147·5—148·5°. The *Me* ester, m.p. 79·5—80°, b.p. 180—187°/1 mm., in C_6H_6 with MgMeI–Et_2O gives, after hydrolysis and acidification, γ-2-*naphthyl*-αβγ-*trimethylbutyrolactone*, m.p. 131—131·5°. This when boiled with Zn, aq. HCl, and PhMe gives γ-2-*naphthyl*-αβγ-*trimethylbutyric acid*, m.p. 124·5—125·5° (*Na*

salt), which with 80% (vol.) H_2SO_4 (water-bath) yields 4-*keto*-1 : 2 : 3-*trimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 190°/0·8 mm. The *carbinol* arising from the last and MgMeI, when dehydrated and heated with Pd, gives a mixture which cannot be purified. 1 : 2 : 3 : 4-*Tetramethylnaphthalene* (XIV), m.p. 106·5—107·5° (*picrate*, m.p. 182—183°), is obtained by chloromethylation of 2 : 3-$C_{10}H_6Me_2$ to 2 : 3-*dimethyl*-1-*chloromethylnaphthalene*, m.p. 86—87°, quant. reduction by Pd–H_2 in $COMe_2$ to 1 : 2 : 3-$C_{10}H_5Me_3$, new m.p. 27—28°, and chloromethylation to 2 : 3 : 4-*trimethyl*-1-*chloromethylnaphthalene*, m.p. 94—95°, which is hydrogenated to (XIV). In aq. HNO_3 at 175—180° (7 hr.), (XIV) gives a product converted through Ag salts and MeI into Me_6 mellitate. With succinic anhydride and $AlCl_3$ in $PhNO_2$, (XIV) yields α-(1 : 2 : 3 : 4-*tetramethyl*-6-*naphthoyl*)*propionic acid*, m.p. 196—197°, reduced by Zn–Hg in aq. HCl and PhOMe at the b.p. to γ-1 : 2 : 3 : 4-*tetramethylnaphthylbutyric acid*, m.p. 153·5—154·5°, which with 80% (vol.) H_2SO_4 (steam-bath) gives 5-*keto*-1 : 2 : 3 : 4-*tetramethyl*-5 : 6 : 7 : 8-*tetrahydroanthracene*, m.p. 178—179°. The *semicarbazone*, m.p. >270°, of the last with NaOMe at 180° gives 1 : 2 : 3 : 4-*tetramethyl*-5 : 6 : 7 : 8-*tetrahydroanthracene*, m.p. 127·5—128°, b.p. 180—185°/0·5 mm. This with Pt at 320—330° gives 1 : 2 : 3 : 4-*tetramethylanthracene* (XV), m.p. 135·5—136·5°, b.p. (crude) 200—220°/0·4 mm. (*picrate*, m.p. 165—166°). The structure of (XV) as an anthracene is shown by its reaction with maleic anhydride to an adduct (*acid*, dehydrated in xylene to the *anhydride*, $C_{22}H_{20}O_3$, decomp. 270—290°), which when sublimed at 300°/5 mm. regenerates (XV). With $Na_2Cr_2O_7$–AcOH, (XV) gives 1 : 2 : 3 : 4-*tetramethylanthraquinone*, m.p. 232—233°, shown to have a *p*-structure by its forming a vat dye with Zn–NaOH in dioxan (but not without the solvent), and by giving no reaction with *o*-$C_6H_4(NH_2)_2$.

XXIII. Carcinogenic activity in 5-alkyl-1 : 2-benzanthracenes decreases as the alkyl chain is lengthened. 5-Keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene with Grignard derivatives of alkyl bromides in Et_2O and C_6H_6, followed by ice and NH_4Cl, gives *tert.* carbinols, which when dehydrated by picric acid in EtOH yield picrates of 5-alkyl-7 : 8-dihydro-, dehydrogenated by Pt-black at 300—310° for 24 hr. to 5-alkyl-1 : 2-benzanthracenes, which are purified through their picrates. The following are described (m.p. of picrates given in parentheses): 5-*ethyl*-, m.p. 109—110° (159—160°), 5-n-*butyl*-, m.p. 69—70° (124—125°), 5-n-*amyl*-, m.p. 59—60° (90—91°), 5-n-*hexyl*-, m.p. 47—48° (86—87°), and 5-n-*heptyl*-7 : 8-*dihydro*-1 : 2-*benzanthracene* (XVI), m.p. 53—54° [80° (*dipicrate*)], and 5-n-*butyl*-, m.p. 81° (116—117°), 5-n-*amyl*- (XVII), m.p. 93° (85—86°), 5-n-*hexyl*- (XVIII), m.p. 72—73° (90—91°), and 5-n-*heptyl*-1 : 2-*benzanthracene*, m.p. 68° (82—83°). A *by-product*, $C_{25}H_{18}$ (XIX) (structure suggested), m.p. 116·5—117·5°, is formed in the dehydrogenation of (XVI). With *s*-$C_6H_3(NO_2)_3$, (XVII), (XVIII), and (XIX) form *complexes*, m.p. 112—113°, 116—117°, and 159—160°, respectively. E. W. W.

Synthesis of 2-methyl-3 : 4-benzphenanthrene. M. S. Newman and L. M. Joshel (J. Amer. Chem. Soc., 1940, **62**, 972—974).—$CHPh_2$·CHO, CN·CH_2·CO_2Et, and $NHEt_2$, first at room temp. and then at 100°, give after hydrolysis (H_2SO_4–AcOH–H_2O) and decarboxylation (200°) β-benzhydrylglutaric acid (I), m.p. 177·6—178·2° (*Me*$_2$ ester, m.p. 73·4—74·2°, b.p. ~180°/2 mm.), converted by HF at room temp. into 4-*keto*-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylacetic acid* (89%), m.p. 115·4—116·2° [also obtained from the anhydride of (I) by $AlCl_3$ in $(CHCl_2)_2$], which is reduced (Martin–Clemmensen) to 1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthylacetic acid, m.p. 140·2—140·8° (lit. 138—139°). MgMeCl in Et_2O–C_6H_6 and dehydrogenation by Pd–C at 290—320° then gives 2-methyl-3 : 4-benzphenanthrene, m.p. 70·4—71° (lit. 69·5—70°) (*picrate*, m.p. 141·8—143·2°). 2-Keto-1 : 2 : 9 : 10 : 11 : 12-hexahydro-3 : 4-benzphenanthrene and MgEtBr in C_6H_6 give an alcohol, which after dehydration by I and dehydrogenation by S at 230° gives 2-*ethyl*-3 : 4-*benzphenanthrene*, m.p. 50·4—51·2° [*picrate*, m.p. 78·4—80°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 105·6—106·6°]. M.p. are corr. R. S. C.

Synthesis of 1-methylchrysene and related compounds. M. S. Newman (J. Amer. Chem. Soc., 1940, **62**, 870—874).—Prep. of Ph·$[CH_2]_2$·CHPh·CN and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (I) is improved. Interaction of (I) with CHMeBr·CO_2Et–Zn–I, dehydration (I; 230°), and then hydrolysis (boiling KOH–EtOH) of the product gives α-2-*phenyl*-3 : 4-*dihydro*-1-*naphthylpropionic acid*, m.p. 210·2—210·6° (with a little *Et* α-1-*hydroxy*-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylpropionate*, m.p. 90·4—91·4°), reduced by H_2–Cu–Ba chromite in dioxan at 200°/127 atm. to α-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid*, m.p. 143—148° (147·6—148·8°). PCl_5–C_6H_6 and then $AlCl_3$–C_6H_6 at room temp. and later 50° give 2-keto-1-methyl-1 : 2 : 7 : 8 : 1*a* : 7*a*-hexahydrochrysene (II), which by reduction [$Al(OPr^{\beta})_3$–$Pr^{\beta}OH$], dehydration (I; 230°), and dehydrogenation (S; 240—250°) gives 1-*methylchrysene* (III) (36%), m.p. 117·2—117·8° [*picrate*, m.p. 142·6—143°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 172·6—173·6°]. Treatment of (II) with MgMeBr–Et_2O–C_6H_6, heating at 220°/vac., and dehydrogenation (S; 230—240°) gives 1 : 2-*dimethylchrysene*, dimorphic, m.p. 128·6—129·8° [*picrate*, m.p. 134·4—135·4° (decomp.); *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 158·6—159·4°], and some (III). Reactions starting from (I) and CHEtBr·CO_2Et give α-2-*phenyl*-3 : 4-*dihydro*-1-*naphthyl*-n-*butyric acid*, m.p. 156—159° (with 15% of $Pr^{\alpha}CO_2Et$), and 1-*ethylchrysene*, m.p. 91·4—92·4° [*picrate*, m.p. 99·2—100·6°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 125·2—125·8°], intermediates being oils. 2-Methylchrysene is slightly carcinogenic. M.p. are corr. R. S. C.

Physiologically active amines. III. *sec.* and *tert.* β-Phenylpropylamines and β-phenyl*iso*propylamines. E. H. Woodruff, J. P. Lambooy, and W. E. Burt (J. Amer. Chem. Soc., 1940, **62**, 922—924; cf. A., 1938, II, 271).—The following are prepared by (*a*) heating CHPh:NR with R′I to give CHPh:NRR′I and then hydrolysing with hot MeOH or EtOH, or (*b*) hydrogenating (Raney Ni; 3 atm.; EtOH) RCHO–NH_2R'–NaOAc or CHR:NR′ (CH_2O gives $NR'Me_2$, but other aldehydes give mixed *sec.*

and *tert.* amines). Figures in brackets are m.p. of the *hydrochlorides*. β-*Phenyl*-, b.p. 78—80°/6 mm. [135—136°], β-o-, b.p. 100—102°/6 mm. [137—138°], β-m-, b.p. 135—137°/18 mm. [142—143°], and β-p-*anisyl*-iso*propylmethylamine*, b.p. 117—119°/8 mm. [178·5—179·5°], β-*phenyl*-, b.p. 96—98°/18 mm. [148—159°], β-o-, b.p. 115—117°/8 mm. [199—200°], and β-p-*anisyl*-*propylmethylamine*, b.p. 127—128°/8 mm. [166·5—167·5°], β-o-, b.p. 104°/6 mm. [158—159°], β-m-, b.p. 140°/17 mm. [123—124°], and β-p-*anisyl*iso*propylethylamine*, b.p. 137°/9 mm. [156—157°], β-*phenyl*-, b.p. 127°/30 mm. [159—160°], and β-p-*anisyl*-*propylethylamine*, b.p. 137°/9 mm. [156—157°], β-*phenyl*-, b.p. 100°/12 mm. [159—161°], β-o-, b.p. 125°/10 mm. [157—158°], β-m-, b.p. 132°/10 mm. [134—135°], and β-p-*anisyl*-iso*propyldimethylamine*, b.p. 137°/13 mm. [161—162°], β-m-, b.p. 130°/12 mm. [175—176°], and β-p-*anisylpropyldimethylamine*, b.p. 129°/11 mm. [198—199°], methylephedrine, m.p. 86·5—87·5° [190—191°], β-*phenyl*-, b.p. 178°/13 mm. [198—199°], β-o-, b.p. 194°/9 mm. [130—131°], and β-m-*anisyl*-iso*propylbenzylamine*, b.p. 196°/10 mm. [143—144°], β-o-, b.p. 197°/10 mm. [dimorphic, m.p. 146—147° and 161—162°], β-m-, b.p. 181°/10 mm. [148—149°], and β-p-*anisylpropylbenzylamine*, b.p. 209—212°/13 mm. [154°]. R. S. C.

Preparation and properties of 6-halogeno-carvacrylamines from *p*-cymene. R. W. Bost and G. C. Kyker (J. Amer. Chem. Soc., 1940, **62**, 913—917).—Addition of 6 : 1 : 4 : 2-$NO_2{\cdot}C_6H_2MePr^{\beta}{\cdot}N_2Cl$ to CuCl–HCl at 0° and heating at 60° gives 2-*chloro*-6-*nitro*-p-*cymene* (Me = 1) (I) (77·5%), b.p. 132—133°/2 mm., and some 2-*nitro*-6-*hydroxy*-(?5-)6′-*nitrocarvacrylazo*-p-*cymene*, m.p. 186—187°. Mossy Sn, conc. HCl, and EtOH reduce (I) to 6-*chlorocarvacrylamine* (II), b.p. 134—136°/1 mm. [*hydrochloride*, softens at 210—220°, m.p. 225—226° (decomp.); *hydrobromide*, m.p. 231—232°; *nitrate*, m.p. 153°; *oxalate*, m.p. 155°; *di*-, m.p. 92—93°, and *tri*-*chloroacetate*, m.p. 157°; 2 : 4 : 6-*tri*-, m.p. 161°, and 3 : 5-*di*-*nitrobenzoate*, m.p. 133—134°; *picrate*, m.p. 151°; *H sulphate*, m.p. 166°; *benzene*-, m.p. 184°, and p-*toluene*-*sulphonate*, m.p. 193—194°; *Ac*, m.p. 117—118°, *Bz*, m.p. 139°, 3 : 5-*dinitrobenzoyl*, m.p. 197—198°, $PhSO_2$, m.p. 117·5°, p-$C_6H_4Me{\cdot}SO_2$, m.p. 115·5°, p-$C_6H_4Br{\cdot}SO_2$, m.p. 131·5°, m-$NO_2{\cdot}C_6H_4{\cdot}SO_2$, m.p. 129·5°, and *picryl* derivative, m.p. 150·5—151·5°], which yields 6-*chloro*-2-*carbamido*-p-*cymene*, m.p. 180—182° (decomp.; slow heating), 185—187° (decomp.; preheated to 160°), and as hydrochloride with aq. $NaNO_2$ at 0° gives 6 : 6′-*dichloro*-2 : 2′-*diazoamino*-p-*cymene*, m.p. 110°. Diazotisation of (II) and coupling gives azo-*dyes*, (m.p. as given) with β-$C_{10}H_7{\cdot}OH$, m.p. 202°, PhOH, m.p. 192—193°, *m*-$C_6H_4(OH)_2$, m.p. 233°, phloroglucinol, m.p. 278°, and 1 : 8 : 3 : 6-$(OH)_2C_{10}H_4(SO_3H)_2$, m.p. >300°. 6-*Bromo*-, m.p. 213—214° (decomp.), and 6-*iodo*-*carvacrylamine hydrochloride*, m.p. 244—245° (decomp.), are prepared as for (II). R. S. C.

Action of amines on 9-bromo-2-nitrofluorene. New and very sensitive colour reaction for pyridine. A. Novelli (Rev. Fac. Cienc. Quím. La Plata, 1939, **14**, 137—140).—9-Bromo-2-nitrofluorene (I) with $NHEt_2$ in EtOH gives 2 : 2′-dinitro-bisdiphenylene-ethylene, but the appropriate NH_2Ar affords 2-*nitro*-9-*phenyl*-, m.p. 164°, -9-p-*tolyl*-, m.p. 146—147°, -9-p-*nitrophenyl*-, m.p. 222—224° (decomp.), and -9-2′-*fluorenyl*-*fluorenylamine*, m.p. 186—187°. (I) heated with C_5H_5N or its derivatives and then diluted with H_2O and EtOH or $COMe_2$, with subsequent addition of aq. NH_3, gives an intense blue colour. F. R. G.

Constitution of sulphon-amides and -anilides. A. Baroni (R.C. Atti Accad. Ital., 1939, [vii], **1**, 46—49).—The parachors of 21 sulphon-amides and -anilides show that these have normal structures at 200°. In solution irregular deviations in [*P*] are observed. E. W. W.

Derivatives of sulphanilamide.—See B., 1940, 403, 404.

Sulphonamide derivatives of arylcarbamides. E. H. Cox (J. Amer. Chem. Soc., 1940, **62**, 743—744).—$NHAr{\cdot}CO{\cdot}NH_2$ (*A*) and $ClSO_3H$ at 0—10° give $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2Cl$ etc. (difficult to purify). $NHAr{\cdot}CO{\cdot}NHAc$ [prep. from (*A*) by AcCl–C_5H_5N at −10°, then 30°] and $ClSO_3H$ at 50° give $NHAc{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2Cl$ etc. The chloride is converted by 28% NH_3 or 30% $NHEt_2$ at 100° into the amide. Thus are obtained p-N′-*acetylcarbamido*-*benzene*-, m.p. 192—193°, -o-, m.p. 197—199°, and -m-*toluene*-*sulphonyl chloride*, m.p. 199—201°, p-*carbamido*-*benzene*-, m.p. 206—207° (*Ac* derivative, m.p. 246—247°), -o-, m.p. 223—225° (*Ac* derivative, m.p. 231—233°), and -m-*toluene*-*sulphonamide*, m.p. 209—210° (*Ac* derivative, m.p. 226—227°), p-*carbamido*-*benzene*-, m.p. 148—149°, -o-, m.p. 165—167°, and -m-*toluene*-*sulphondiethylamide*, m.p. 147—148°. R. S. C.

Action of amines on semicarbazones. A. B. Crawford (J. Roy. Tech. Coll., 1940, **4**, 607—616).—$CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$ and *p*-$NH_2{\cdot}C_6H_4{\cdot}N_2Ph$ (I) at 160° give NH_3, p-iso*propylidenesemicarbazidoazobenzene* (II) (12—15%), m.p. 210°, and $(NMe_2)_2$ with some $(NH{\cdot}CO{\cdot}NH_2)_2$. HCl in hot, aq. EtOH hydrolyses (II) to p-δ-*semicarbazidoazobenzene* (III), *p*-$NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Ph$, m.p. 237° (decomp.; red at ~210°) [*hydrochloride*, m.p. ~209° (decomp.), colour variable; *CHPh:* derivative, m.p. 217—218°]. Absorption spectra of (I) and (III) in EtOH and aq. HCl are in part correlated with structure. R. S. C.

Metallic complexes of *o*-substituted azo-dyes. J. L. Boyle, W. M. Cumming, and A. B. Steven (J. Roy. Tech. Coll., 1940, **4**, 617—632).—*o*-NH_2, *o*-CO_2H, and *o*-OAlk can take part in metal-lake formation of azo-dyes. The following lakes are prepared from pure intermediates. 1Cu : 1dye compounds with *p*-$C_6H_4R{\cdot}NH_2$ → β-$C_{10}H_7{\cdot}OH$ (R = NO_2 or SO_3H), NH_2Ph → 6 : 2-$SO_3H{\cdot}C_{10}H_6{\cdot}OH$, 2 : 5 : 1-$OH{\cdot}C_6H_3(NO)_2{\cdot}NH_2$ → β-$C_{10}H_7{\cdot}OH$ (I), 2 : 5 : 1-$OH{\cdot}C_6H_3(NO_2){\cdot}NH_2$ → 5 : 1-$SO_3H{\cdot}C_{10}H_6{\cdot}OH$ (II), and *o*-$C_6H_4R{\cdot}NH_2$ → β-$C_{10}H_7{\cdot}OH$ (R = OMe or CO_2H); 1Cu : 2(1 : 2-$PhN_2{\cdot}C_{10}H_6{\cdot}OH$); ? 4Cu : 3[5 : 2 : 1-$SO_3H{\cdot}C_6H_3(OH){\cdot}NH_2$ → β-$C_{10}H_7{\cdot}OH$]; 3Cu : 2dye compounds with 2 : 5 : 1-$OH{\cdot}C_6H_3(NO_2){\cdot}NH_2$ → 6 : 2-$SO_3H{\cdot}C_{10}H_6{\cdot}OH$ (III), 4 : 1 : 2 : 6-$SO_3H{\cdot}C_6H_2Me(NH_2)_2$ → *m*-$C_6H_4(NH_2)_2$ (IV), and 4 : 1 : 2-$NO_2{\cdot}C_6H_3(OH){\cdot}NH_2$ → 4 : 1 : 3-

$SO_3H{\cdot}C_6H_3(NH_2)_2$ (V); 2Cu : 1[*o*-$CO_2H{\cdot}C_6H_4{\cdot}NH_2$ → 2 : 3 : 6-$OH{\cdot}C_{10}H_5(SO_3H)_2$]; 1Cr : 1dye compounds with 5 : 2 : 1-$SO_3H{\cdot}C_6H_3(OH){\cdot}NH_2$ → β-$C_{10}H_7{\cdot}OH$, *o*-$CO_2H{\cdot}C_6H_4{\cdot}NH_2$ → β-$C_{10}H_7{\cdot}OH$, *o*-$CO_2H{\cdot}C_6H_4{\cdot}NH_2$ → 2 : 3 : 6-$OH{\cdot}C_{10}H_5(SO_3H)_2$, and (V); 2Cr : 3dye compounds with (I), (II), (IV), and *o*-$OMe{\cdot}C_6H_4{\cdot}NH_2$ → β-$C_{10}H_7{\cdot}OH$; 4Cr : 3(III). Formulæ are ascribed.

R. S. C.

Aromatic aminohydrazines.—See B., 1940, 345.

Nuclear methylation of phenol. T. Kennedy (Chem. and Ind., 1940, 297).—4 : 1 : 3 : 5-$OH{\cdot}C_6H_2Me(CH_2{\cdot}OH)_2$, prepared from *p*-cresol by CH_2O in aq. alkali, is hydrogenated (Cu chromite; dioxan) to mesitol, similarly obtained starting from a commercial mixed cresol.

R. S. C.

Deepening of colour of sodium nitrophenoxide solutions with elevation of temperature. T. L. Davis and J. L. Richmond (J. Amer. Chem. Soc., 1940, **62**, 756—761).—The thermotropic colour intensification and its retardation by Na_2CO_3 are similar for aq. *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}ONa$, the *m*-compound being somewhat less affected. The Na salts may be formed by addition of NaOH to give $\begin{matrix}CH{:}CH{\cdot}C(OH)_2\\CH{:}CH{\cdot}C{:}NO{\cdot}ONa\end{matrix}$ (and its *p*-analogue) and $\begin{matrix}CH(OH){\cdot}C(OH){:}CH\\CH{:}CH\text{———}C{:}NO{\cdot}ONa.\end{matrix}$ The colour is due to resonance of the ions.

R. S. C.

Syntheses of stilbene derivatives. I. New synthesis of *trans*-4 : 4′-dihydroxy-αβ-diethylstilbene. S. Kuwada and Y. Sasagawa (J. Pharm. Soc. Japan, 1940, **60**, 27—29; cf. Dodds *et al.*, A., 1939, II, 312).—Anisoin is converted by MgEtBr into *αβ-dianisylbutane-αβ-diol*, m.p. 113·5°, transformed by short treatment with warm 50% H_2SO_4 into αβ-dianisylbutan-α-one (I), b.p. 198—199°/1 mm. (*oxime*, m.p. 111°), whereas conc. H_2SO_4 yields much resinous matter. (I) and MgEtBr give a material from which a homogeneous cryst. product could not be extracted but which is dehydrated by PBr_3 in $CHCl_3$ to 4 : 4′-dimethoxy-αβ-diethylstilbene, m.p. 123—124°. This is demethylated (Späth) to *trans*-4 : 4′-dihydroxy-αβ-diethylstilbene, m.p. 168·5°, the absorption curve of which is closely similar to that of *trans*-αβ-dimethylstilbene.

H. W.

Structure of cannabidiol. II. Absorption spectra compared with those of various dihydric phenols. R. Adams, C. K. Cain, and H. Wolff. **III. Reduction and cleavage.** R. Adams, M. Hunt, and J. H. Clark (J. Amer. Chem. Soc., 1940, **62**, 732—734, 735—737; cf. A., 1940, II, 80).—II. Comparison of absorption spectra of *o*- and *m*-$C_6H_4(OR)_2$, 4 : 1 : 2- and 5 : 1 : 3-$C_6H_3Me(OR)_2$, 4 : 1 : 2- and 5 : 1 : 3-*n*-$C_5H_{11}{\cdot}C_6H_2(OR)_2$ (R = H or Me), cannabidiol (I) and its Me_2 ether indicates a resorcinol structure for (I). 4-n-*Amylpyrocatechol Me₂ ether*, b.p. 124—126°/4—5 mm., is prepared from the phenol by Me_2SO_4 and 10% NaOH–EtOH.

III. (I) is probably 4- or 2-*dihydro*-3′-p-*cymyl*-5-n-*amylresorcinol* (Me = 1′). Hydrogenation (PtO_2; 2—3 atm.; AcOH) of (I) gives *tetrahydrocannabidiol*, b.p. 188—190°/2·5 mm., oxidised by $KMnO_4$ in $COMe_2$ to *p*-menthane-3-carboxylic acid (Me = 1) [anilide, m.p. 152—152·5° (corr.) (lit. 148·5°)]. Dehydrogenation of (I) gives oils, probably containing a Ph_2 derivative. In C_5H_5N,HCl at 210—230° (much less well, $NH_2{\cdot}SO_3H$), (I) gives *p*-cymene and olivetol, b.p. (anhyd.) 170—175°/2 mm., m.p. (+H_2O) 41° [*bis*-3 : 5-*dinitrobenzoate*, m.p. 127—128° (corr.)].

R. S. C.

Claisen rearrangement. II. Kinetic study of rearrangement of 2 : 6-dimethylphenyl allyl ether in diphenyl ether solution. D. S. Tarbell and J. F. Kincaid (J. Amer. Chem. Soc., 1940, **62**, 728—731; cf. A., 1940, I, 30).—*m*-2-Xylenol and $CH_2{:}CH{\cdot}CH_2Br$ with hot NaOEt–EtOH give 85 and 15% or with Na in C_6H_6 give 55 and 45% of the *allyl ether* (I), b.p. 67—68°/2 mm., and 2 : 6-dimethyl-4-allylphenol (II), b.p. 90·5—91·4°/2 mm. (*phenylurethane*, m.p. 141—142·5°, obtained by PhNCO and dry HCl), respectively. At 171·6° in absence of air (I) gives 95% of (II) and 5% of a polymeride. In Ph_2O at 185·8°, 171·6°, or 156·9°, or alone at 171·6° or 185·8°, the rearrangement is of the first order, in agreement with findings that 10% of $NPhMe_2$ in Ph_2O increases the velocity by only ~15% (thus excluding a prototropic change as the slow step) and that 1 or 2% of AcOH increases it by 28 or 42%, respectively. *k* increases as the reaction proceeds with the more conc. solutions. The entropy of activation is −10·1 e.u. at 171·6°, comparison of which with that for *p*-$C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2$ (−9·5 under comparable conditions) indicates that rearrangement to the *o*- and *p*-positions has the same slow step. This is difficult to reconcile with chemical evidence for the cyclic mechanism, which also on Fisher–Hirschfelder models is impossible for the *p*-migration.

R. S. C.

***N*-Substituted aminophenols.**—See B., 1940, 345.

Alkylation of *o*-hydroxyazo-compounds and anomalous reduction of the ethers obtained. (Signa.) E. Ghigi (Gazzetta, 1940, **70**, 202—211, and Helv. Chim. Acta, 1940, **23**, 428—430).—The view of Fierz-David *et al.* (A., 1938, II, 317) that the OH of *o*-hydroxyazo-compounds cannot be alkylated is incorrect. 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}N{:}NPh$ (I) is converted into the Me ether (II) (cf. Charrier *et al.*, A., 1912, i, 812), which with $Na_2S_2O_4$ and NaOH in boiling EtOH gives 2-*anilino*-1-*naphthylamine* (III), m.p. 136—137°, converted by AcOH–$NaNO_2$ into 3-phenyl-αβ-naphthatriazole (cf. Charrier *et al.*, A., 1926, 848). PhCHO converts (III) into diphenylnaphthiminazole. With PhN_2Cl, (III) gives tarry products. With Et_2SO_4 in boiling 30% NaOH, (I) gives its Et ether, m.p. 79°, converted by $Na_2S_2O_4$ into (III). No definite products are obtained from (II) and Zn–AcOH. The acetate of (I) is reduced by $Na_2S_2O_4$ to 1 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}OH$. 4 : 1 : 3-$OH{\cdot}C_6H_3Me{\cdot}N_2Ph$ with Me_2SO_4–NaOH gives its *Me ether*, m.p. 53—54°, reduced by $Na_2S_2O_4$ to 6-*methoxy*-3-*methylhydrazobenzene*, m.p. 91—92° (*Ac*$_1$ derivative, m.p. 124—125°), which with boiling 10% H_2SO_4 gives 5-*methoxy*-2-*methylbenzidine*, m.p. 86—87° [sulphate, m.p. ~300°; *Ac*$_4$ derivative, m.p. 188—189°].

E. W. W.

[Interaction of] styrene and organic disulphides [in presence of] iodine. B. Holmberg (Arkiv Kemi, Min., Geol., 1939, **13**, **B**, No. 14, 6 pp.).—

R_2S_2 and CHPh:CH_2 (I) in presence of a little I (in C_6H_6 or other solvent, if solid) give *αβ-di-methyl-* (II), b.p. 149—150°/10 mm., *-ethyl-*, b.p. 163—164°/11 mm., *-(carbethoxyethyl)-*, b.p. 210—212°/3 mm., and *-phenyl-*, m.p. 57—58°, *-thiolethylbenzene*, SR·CHPh·CH_2·SR. Analogous condensations with other unsaturated components and of (I) with tetra- and *tri-thioglycollic acid*, $(CO_2H·CH_2·S)_2S$ (prep. from SH·CH_2·CO_2H by SCl_2), m.p. 122—124°, failed. Perhydrol and (II) in $COMe_2$ give the derived *di-sulphoxide*, *forms*, m.p. 122—124° (clear at 126°) and 130—131°. R. S. C.

Derivatives of 4 : 4′-diaminodiphenyl sulphide. —See B., 1940, 345.

Synthesis of sulphur-containing chemotherapeutic products. I. *p*-Nitrophenyl *p*-aminophenyl sulphoxide and sulphone. J. O. Gabel and F. L. Grinberg. **II. *p*-Nitrophenyl *p*-acetamidophenyl sulphide.** J. O. Gabel and A. L. Schpanion (J. Appl. Chem. Russ., 1939, **12**, 1481—1484, 1485—1489).—I. 4-Nitro-4′-acetamidodiphenyl sulphide (I) in AcOH and H_2O_2 (24 hr. at room temp., then 30 min. at 100°) give the *sulphoxide* (II), m.p. 210—211°, in 90% yield; when the final heating is prolonged to 3—3·5 hr. the product is the *sulphone* (III), m.p. 219—220° (yield 90—96%). (II) and (III) are hydrolysed (boiling 18% HCl) to 4-*nitro*-4′-*aminodiphenyl sulphoxide*, m.p. 132—134°, and *sulphone*, m.p. 167—169°, respectively.

II. Na_2S and *p*-$C_6H_4Cl·NO_2$ in EtOH (at the b.p.) yield a mixture of $(p\text{-}NO_2·C_6H_4)_2S$ and *p*-$NO_2·C_6H_4·S·C_6H_4·NH_2$-*p*. *p*-NHAc·$C_6H_4·SO_2Cl$ is reduced (Zn and aq. EtOH–HCl at 0° until evolution of H_2 ceases, then 25 min. at 100°) to *p*-NHAc·C_6H_4·SH, which with *p*-$C_6H_4Cl·NO_2$ in EtOH–NaOH gives (I) in good yield. R. T.

Reversibility of the rearrangement of *o*-hydroxysulphones. R. R. Coats and D. T. Gibson (J.C.S., 1940, 442—446).—Rearrangement (*A*) of *o*-hydroxysulphones to sulphino-ethers (cf. McClement *et al.*, A., 1937, II, 337) is reversible; the reverse change is much slower, but roughly of the same order. *o*-Nitrophenyl 1-sulphino-2-naphthyl ether, m.p. 116°, in aq. NaOAc at 50° for 5 hr. is converted (almost quant.) into *o*-nitrophenyl 2-hydroxy-1-naphthyl sulphone, m.p. 180—181° (2 forms) (cf. Levy *et al.*, A., 1932, 156); the conversion occurs in aq. $COMe_2$ and partly even in dry Et_2O–ligroin. 4′-Chloro-2-nitro-3′ : 5′-dimethyl-, new m.p. 131°, 2-nitro-4′ : 6′-dimethyl-, m.p. 153° (lit. 129°), 2-nitro-4′-methyl-, new m.p. 134°, and 6′-chloro-2-nitro-4′-methyl-2′-sulphinodiphenyl ether, m.p. 170°, rearrange to 5′-chloro-2-nitro-2′-hydroxy-4′ : 6′-dimethyl-, 2-nitro-2′-hydroxy-3′ : 5′-dimethyl-, 2-nitro-2′-hydroxy-5′-methyl-, and 3′-chloro-2-nitro-2′-hydroxy-5′-methyl-diphenyl sulphone respectively; the times for attaining equilibrium at the most favourable p_H in ~N./150 solution at 50±2° are 5, 250, 400, and 450 hr., respectively. Conversion of 2 : 4-dinitrophenyl 3-sulphino-*p*-tolyl ether, m.p. 140° (decomp.) (lit. 117—118°), into 2 : 4-dinitro-2′-hydroxy-5′-methyldiphenyl sulphone is rapid (2 hr.). Interconversion in either direction is facilitated by the positive character of the C atom *o* to NO_2 and attached to SO_2 (in the sulphone). The rate of conversion of 2-nitro-4′-hydroxy-2′-sulphinodiphenyl ether (*monohydrate*, 2 forms, m.p. 98°; not dehydrated by P_2O_5; cf. Kent *et al.*, A., 1934, 647) could not be determined, owing to the solubility of 2-nitro-2′ : 5′-dihydroxydiphenyl sulphone. Although *o*-nitrophenyl β-hydroxyethyl sulphone almost instantaneously gives β-*o*-nitrophenoxyethanesulphinic acid, new m.p. 124°, and 2-nitro-2′-hydroxy-5′-methoxydiphenyl sulphone affords 2-nitro-4′-methoxy-2′-sulphinodiphenyl ether, new m.p. 128°, no reverse reaction was obtained in either case. Theoretical aspects are discussed. The conversion medium may be NaOAc, HCO_2Na, or aq. $COMe_2$. The relative strengths of $PhSO_2H$ and *o*- and *p*-$C_6H_4Me·SO_2H$ are given. Rearrangement (*A*) occurs even in aq. NH_3, where co-ordination is impossible (cf. Heppenstall *et al.*, A., 1938, II, 320). A. T. P.

Condensation of phenol and ethylene oxide. R. A. Smith (J. Amer. Chem. Soc., 1940, **62**, 994).—OH·$[CH_2]_2$·OPh, b.p. 165°/80 mm., is best (94%) prepared from PhOH and $(CH_2)_2O$ in H_2 at 200°/2500 lb. R. S. C.

Decomposition of chlorosulphinic esters. M. P. Balfe and J. Kenyon (J.C.S., 1940, 463—464; cf. A., 1930, 598).—Aspects of the decomp. of semi-aromatic chlorosulphinates are reviewed (cf. Gerrard, A., 1940, II, 127). In presence of Cl′, derived either from the hydrochloride of *tert.* bases or by formation of the unstable intermediate additive compound, the chloride RCl is formed with inversion of configuration. In absence of *tert.* base, the chloride is formed with retention of configuration, probably by the intramol. mechanism suggested by Hughes *et al.* (A., 1937, II, 363). A. T. P.

Formation of phenol–formaldehyde resins. I. Condensation of guaiacol and formaldehyde. H. von Euler, E. Adler, and D. Friedmann (Arkiv Kemi, Min., Geol., 1939, **13**, **B**, No. 12, 7 pp.).—Guaiacol (I) (2·2 mols.), 40% aq. CH_2O (1 mol.), and a little HCl at 100° give (? 4 : 4′-) (II), m.p. 107—108°, and (? 4 : 2′-)*dihydroxy*-3 : 3′-*dimethoxydiphenylmethane*, m.p. 119—120°. 40% CH_2O (2 mols.), (I) (1 mol.), and 10% NaOH (1 mol.) at room temp. give a mixture of alcohols, probably 1 : 2 : 4-OH·C_6H_3(OMe)·CH_2·OH and 1 : 4 : 6 : 2-OH·$C_6H_2(CH_2·OH)_2$·OMe, and a little [4 : 3 : 5 : 1-OH·C_6H_2(OMe)$(CH_2·OH)]_2CH_2$, m.p. 148—149° (lit. 146·5—147°) [also obtained from (II) by CH_2O (2 mols.) and NaOH (2 mols.) at 40—50°]. R. S. C.

Steric course of dimerising reductions. N. A. Sörensen, J. Stene, and E. Samuelsen (Annalen, 1940, **543**, 132—142).—Reduction (method: Kuhn *et al.*, A., 1928, 281) of CHPh:CH·CHO gives approx. equal amounts of *meso-* (I), m.p. 156° (dibenzoate, m.p. 173—174°), and *r-hydrocinnamoin* (II), m.p. 107·5° (corr.); the reaction mixture is freed from (I) and the residual syrup treated with BzCl in C_5H_5N at 0°, whereby the *dibenzoate* (III), m.p. 165·5° (corr.), of (II) is formed. Hydrolysis (EtOH–NaOH) of (III) affords (II) whilst oxidation (O_3 in AcOH) gives PhCHO (1·6 mols.) and *r*-dibenzoyltartaric acid (+$2H_2O$), m.p. 112—114° resolidifying at 116—120° with m.p. 168—170°, m.p. (anhyd.) 174—175° (cf.

lit.) [anhydride, m.p. 175—177° (corr.)]. Contrary to Thiele (A., 1899, i, 616; cf. Farmer *et al.*, A., 1928, 151), distillation of (I) at atm. pressure gives *p*-$C_6H_4Ph_2$; reaction is considered to occur thus: (I) → [2 CHPh:CH·ĊH·OH ⟷ 2 OH·CH:CH·ĊHPh] → CHPh:CH·CH(OH)·CHPh·CH:CH·OH → *p*-$C_6H_4Ph_2$. Dimerising reductions of CHR:CH·CHO with Zn, Zn–Cu, Al–Hg, VSO_4, etc. are considered to give CHR:CH·ĊH·OH, which can dimerise (to the glycol) or rearrange (cf. above). H. B.

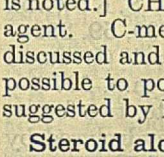
Ring-enlargement in the hydroaromatic series. I. Experiments with 3 : 3 : 5-trimethyl*cyclo*hexylmethylamine (dihydro*iso*phorylmethylamine). H. Barbier (Helv. Chim. Acta, 1940, **23**, 519—524).—*iso*Phorone is scarcely affected by $CH_2Cl·CO_2Et$ and NaOMe whereas dihydro*iso*phorone (I) yields *Et* 3 : 3 : 5-*trimethyl*cyclo*hexylglycidate*, b.p. 105°/4 mm., in 70% yield. This is converted by hydrolysis followed by distillation of the acid under diminished pressure into 3 : 3 : 5-*trimethyl*cyclo*hexanealdehyde*, b.p. 53°/4 mm., 201° (corr.)/730 mm. (*semicarbazone*, m.p. 132°). The corresponding *oxime*, b.p. 98°/4 mm., is dehydrated by boiling Ac_2O to the *nitrile*, b.p. 73°/4 mm., 226° (corr.)/730 mm., which is reduced (Na in boiling EtOH) to 3 : 3 : 5-*trimethyl*cyclo*hexylmethylamine*, b.p. 58°/4 mm., 202° (corr.)/728 mm. (*hydrochloride*, m.p. 245—250°). This is deaminated ($NaNO_2$ in dil. AcOH) to 1 : 1 : 3-*trimethyl*cyclo*heptene*, b.p. 38°/4 mm., 152° (corr.)/732 mm., 1 : 3 : 3 : 5-*tetramethyl*cyclo*hexanol*, b.p. 65°/4 mm., 185°(corr.)/729 mm., m.p. 82° [also obtained from (I) and MgMeI and dehydrated by *p*-$C_6H_4Me·SO_3H$ to *tetramethyl*cyclo*hexene*, b.p. 149·5° (corr.)/721 mm.], and a mixture of trimethyl*cyclo*heptanols which is oxidised and treated with $NH_2·CO·NH·NH_2$, thus leading to a homogeneous 3 : 5 : 5- or 3 : 3 : 5-*trimethyl*cyclo*heptanone*, b.p. 62°/4 mm. (*semicarbazone*, m.p. 174°), also obtained directly from (I) and CH_2N_2. H. W.

Ring-enlargement in the hydroaromatic series. II. Experiments with 2 : 2 : 6-trimethyl*cyclo*hexylmethylamine (dihydro*cyclo*geranylmethylamine). H. Barbier (Helv. Chim. Acta, 1940, **23**, 524—532).—*cyclo*Gernanonitrile is reduced (Raney Ni in PhMe at 110°/30—50 atm.) to a mixture of 2 : 2 : 6-*trimethyl*cyclo*hexylmethylamines* (I), b.p. 62°/4 mm., 212·5° (corr.)/732 mm. [*hydrochloride*; mercurichloride, m.p. 215°; platinichloride, m.p. 287° (decomp.)], and (II), b.p. 210·2° (corr.)/724 mm. [*hydrochloride*; mercurichloride, m.p. 161°; platinichloride, m.p. 265° (decomp.)], and (?) *di*(*dihydro*cyclo*geranyl*)-*amine*, b.p. 160°/4 mm. Deamination of (I) leads to 1 : 1 : 4-*trimethyl*-Δ³-cyclo*heptene* (III), b.p. 35°/4 mm., 165·5° (corr.)/732 mm., 2 : 2 : 6-*trimethyl*cyclo*hexylmethyl alcohol* (IV), b.p. 81°/4 mm. (*allophanate*, m.p. 172°), and a mixture of trimethyl*cyclo*heptanols (V). (IV) is characterised by successive conversions into dihydro*cyclo*citral, b.p. 62°/4 mm. (*semicarbazone*, m.p. 185°), and dihydro*cyclo*geranic acid, m.p. 82°. (II) yields a *cyclo*citronellol, b.p. 85°/4 mm. (allophanate, m.p. 132°). (V) is oxidised to a mixture from which is obtained 2 : 2 : 6- or 3 : 3 : 7-*trimethyl*cyclo*heptanone*, b.p. 58°/4 mm., 207°/733 mm. (*semicarbazone*, m.p. 190—192°); this is transformed by $CH_2Cl·CO_2Et$ and NaOMe in C_6H_6 into the glycidic ester, b.p. 115°/4 mm., which gives 2 : 2 : 6- or 3 : 3 : 7-*trimethyl*cyclo*heptanealdehyde*, b.p. 65—67°/4 mm. (*semicarbazone*, m.p. 121°). 2 : 5 : 5-*Trimethyl*-Δ²-cyclo*heptenone*, b.p. 66—68°/4 mm. (*semicarbazone*, m.p. 195—196°), obtained by the action of SeO_2 on (III), gives a *glycidic* ester, b.p. 124°/4 mm., which is transformed into (probably) 2 : 5 : 5-*trimethyl*-Δ²-cyclo*heptenealdehyde*, b.p. 72°/4 mm. (*semicarbazone*, m.p. 194°). H. W.

Reduction of 7-hydroxy-4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene with sodium and amyl alcohol. M. Miyasaka (J. Pharm. Soc. Japan, 1939, **59**, 278—282).—γ-(6-Methoxy-2-naphthyl)-butyric acid, m.p. 135°, and P_2O_5–C_6H_6 give 4-*keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 56° (*semicarbazone*, m.p. 235°), converted by $AlCl_3$ or $AlBr_3$ in C_6H_6 into the 7-*hydroxy*-4-*keto*-compound (I), m.p. 188° (*benzoate*, m.p. 155°), which with Na–C_5H_{11}·OH gives (probably) trans-, m.p. 189°, and cis-4 : 7-*dihydroxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*, m.p. 177° (7-*benzoate*, m.p. 111°; 3 : 5-*dinitrobenzoate*, m.p. 198°). (I) and H_2 (PtO_2 in AcOH) give 2-hydroxy-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene (3 : 5-*dinitrobenzoate*, m.p. 157°). 4-*Hydroxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-, m.p. 117° (*acetate*, m.p. 105°), and -1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-, m.p. 107°, and 2-*hydroxy*-5 : 6 : 7 : 8-*tetrahydro-phenanthrene*, m.p. 132° (*picrate*, m.p. 183°), are prepared. A. T. P.

Preparation of amino-alcohols.—See B., 1940, 345.

Speculation regarding the ring structure of sterols and related substances. (Sir) R. Robinson (J.C.S., 1940, 509—510).—It is doubtful whether the isoprene hypothesis can be applied to sterols. It is more probable that two identical progenitors (cf. *A*) together with a component introducing a side-chain combine to form different members of the group. It is suggested that group (*A*) may originate from tyrosine (I) or a protein containing (I) residues. [(By E. Walker.) The unfavourable effect of (I) on formation of ergosterol by yeast is noted.] CH_2O (or its equiv.) may be the methylating agent. C-methylation and group migration are discussed and a structural scheme is suggested. It is possible to postulate the formation of the precursor suggested by Marker (A., 1938, II, 415). A. T. P.



(*A.*)

Steroid alcohols.—See B., 1940, 405.

Hydrolysis of dicholesteryl ether by acid clay. T. Kawasaki (J. Pharm. Soc. Japan, 1939, **59**, 268—270; cf. A., 1940, II, 75).—Dehydration of cholesterol (I) by acid clay to dicholesteryl ether (II) is never complete, since (II) is similarly converted in C_6H_6 or CCl_4 into ~8% of (I). Yoder's conclusion (A., 1937, II, 16) that cholesterylenesulphonic acid is formed from (I) and floridin is erroneous. A. T. P.

Photochemical process in the formation of photopyrocalciferols. A. Windaus, K. Dimroth, and W. Breywisch (Annalen, 1940, **543**, 240—247).—Photo*iso*pyrocalciferol (I) is oxidised (CrO_3, AcOH, 0°—room temp.) to *photoisopyrocalciferone*, m.p. 79—

80°, $[\alpha]_D^{19}$ −116° in $CHCl_3$ [*semicarbazone*, m.p. ~210° (decomp.)], which, like *photopyrocalciferone*, m.p. 91°, $[\alpha]_D^{18}$ +197° in $CHCl_3$ (*semicarbazone*, decomp. ~210°), does not show absorption characteristic of an αβ-unsaturated ketone. Photopyrocalciferol (II) and (I) cannot, therefore, contain a 4 : 5 double linking. Ergosteryl acetate, photo*iso*pyrocalciferyl acetate (III), and the *iso*butyrate of (II) consume 3, 2, and 2 atoms of O, respectively, when titrated with BzO_2H in $CHCl_3$. Reduction (H_2, Pd-black, EtOAc) of (III) affords a H_4-derivative, an oil; hydrolysis followed by oxidation gives the corresponding ketone (*semicarbazone*, m.p. 197°). A tetrahydrophotocalciferol can be similarly obtained. These results indicate that (I) and (II) contain 2 double linkings (1 in side-chain, 1 in ring B). During the formation of (I) and (II) from pyrocalciferol, the second nuclear double linking is probably converted into a bridge (*e.g.*, between $C_{(5)}$ and $C_{(8)}$ or $C_{(9)}$) (cf. A., 1937, II, 376).

H. B.

Steroids and sex hormones. LXII. $\Delta^{5:17}$-3-*trans*-Hydroxy-17*a*-methyl-*D*-homoandrostadiene and its transformation products. L. Ruzicka and H. F. Meldahl (Helv. Chim. Acta, 1940, **23**, 513—518).—The conversion of Δ^5-17-acetylenylandrostene-3 : 17-diol diacetate into Δ^5-3 : 17*a*-diacetoxy-17*a*-methyl-*D*-homoandrosten-17-one (I), m.p. 191—193°, by HgO + $SnCl_4$, $SiCl_4$, or HgO + $FeCl_3$ in AcOH–Ac_2O is described. K_2CO_3 in boiling aq. MeOH hydrolyses (I) to the $(OH)_2$-compound, m.p. 273—275°, converted by N_2H_4,H_2O in C_5H_{11}·ONa at 200° into $\Delta^{5:17}$-3-trans-*hydroxy*-17a-*methyl*-D-*homoandrostadiene* (II), m.p. 162—164°, the *acetate*, m.p. 121—122°, of which is reduced (H_2, PtO_2, AcOH) to 3-trans-*acetoxy*-17a-*methyl*-D-*homoandrostane*, m.p. 128—129°, hydrolysed to the *alcohol*, m.p. 161—163°. (II) is oxidised by $Al(OBu^{\gamma})_3$ in boiling $COMe_2$–C_6H_6 to $\Delta^{4:17}$-17a-*methyl*-D-*homoandrostadien*-3-*one*, m.p. 156—158°, reduced (H_2, PtO_2, AcOH) to 17a-*methyl*-D-*homoandrostan*-3-*one*, m.p. 181—182°, and thence to 17a-*methyl*-D-*homoandrostane*, m.p. 107—109°, $[\alpha]_D$ 2°±2° in dioxan. All m.p. are corr. (vac.).

H. W.

Sterols. XX. Homogeneity of bessisterol and properties of its double linkings. S. Kuwada and S. Yosiki (J. Pharm. Soc. Japan, 1939, **59**, 282—284; cf. A., 1939, II, 431).—Bessisterol (I) fused with *p*-NPh:N·C_6H_4·COCl gives an ester, m.p. 237·5—239·5°. (I) affords a 3 : 5-dinitrobenzoate, two forms, m.p. 202·5—205·5° and 199·5—204·5°, hydrolysed by KOH–EtOH to (I), m.p. 175°, $[\alpha]_D^{23}$ −13·5° (acetate, m.p. 185°; benzoate, m.p. 202°). Hydrogenation of (I) gives bessistaenol, m.p. 113—115·5° (3 : 5-dinitrobenzoate, m.p. 206—209°; acetate, m.p. 115·5—117·5°). (I) is homogeneous. M.p. are corr.

A. T. P.

Sterols. XXI. Constitution of bessisterol. S. Kuwada and S. Yosiki (J. Pharm. Soc. Japan, 1940, **60**, 25—27).—Bessisterol (I) is oxidised by $Al(OPh)_3$ without change in the double linking to *bessistenone* (II), m.p. 180—181° (*semicarbazone*, decomp. 279·5°; *oxime*, decomp. 257°), the absorption spectrum of which in hexane has max. at 240 and 280—290 mμ. Hydrogenation (PtO_2 in EtOAc) of (II) gives bessistaenol (III), m.p. 113·5—115·5°. Reduction (Meerwein–Ponndorf) of (II) gives substances (IV), m.p. 209—211·5°, and (V), m.p. 175°, both of which are pptd. by digitonin from EtOH. (IV) is identical with the compound obtained by heating (I) with NaOEt in a sealed tube. (V) has the same composition, $C_{29}H_{48}O$,0·5H_2O, as (I) but differs somewhat from it in absorption spectrum and [α]; its 3 : 5-dinitrobenzoate and acetate are identical with those of (I). (III) is oxidised by a modified Oppenauer method to *bessistaenone* (VI), m.p. 116·5—120·5° (*oxime*, m.p. 186°; *semicarbazone*, decomp. 245·5°), which re-forms (III) when catalytically reduced. Its absorption curve has a max. at 280 mμ. It appears that Me at $C_{(10)}$ and OH at $C_{(3)}$ in (I) have the same steric arrangement as in cholesterol. Spectroscopic evidence negatives the presence of αβ-unsaturated CO in (II) and (VI) and appears to indicate the existence of a simple CO. If the readily reduced double linking in (I) is not in the neighbourhood of OH it must occupy a position quite different from that assumed previously in order to avoid conjugation. All m.p. are corr.

H. W.

Sterols. XIX. Sterol from *Coix* seeds. S. Kunada and S. Yosiki (J. Pharm. Soc. Japan, 1939, **59**, 203—204).—Extraction of the seeds of *Coix lacryma-jobi*, L. (var. *Frumentacea*, Makino), with Et_2O removes a fatty oil which when hydrolysed gives a sterol fraction which cannot be purified by the customary methods. It is therefore converted into the 3 : 5-*dinitrobenzoate*, m.p. 215—216° (corr.), $[\alpha]_D^{28}$ −7·3° in $CHCl_3$, which is hydrolysed to a *sterol* (I), $C_{29}H_{50}O$, m.p. 138·5° (corr.), $[\alpha]_D^{30}$ −19·5, the absorption spectrum of which shows max. at 280 and 287 mμ. (I) gives an *acetate*, m.p. 125° (corr.), $[\alpha]_D^{30}$ −37·2° in $CHCl_3$, and a *benzoate*, m.p. 147—149° (corr.), $[\alpha]_D^{31}$ −14·7° in $CHCl_3$. (I) absorbs 2 H_2 (PtO_2 in EtOAc) but the H_2-derivative, m.p. 140·5—142·5°, $[\alpha]_D^{32}$ +23·5° [which very obstinately retains 0·25H_2O; it does not give a colour with $C(NO_2)_4$ in $CHCl_3$ or with Ac_2O in conc. H_2SO_4], only could be isolated. Evidence is afforded in favour of the view that (I) is very closely related to β-sitosterol and possibly contains a small proportion of α-sitosterol.

H. W.

Sterols. XCVI. *allo*Pregnanediols from tigogenin. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1940, **62**, 898—900).—*ψ-Tigogenin*, m.p. 193—196° (prep. from tigogenin by Ac_2O at 195—200° and subsequent hydrolysis), and CrO_3–AcOH at 25—28° give $\Delta^{16:17}$-allo*pregnene*-3 : 20-*dione*, m.p. 210—212°, reduced by Na–EtOH to *allo*pregnane-3(β) : 20(α)-diol and by H_2–PtO_2 in AcOH at 3 atm. to *allo*pregnane-3(β) : 20(β)-diol (I). *ψ*-Tigogenin acetate and CrO_3–AcOH at 28° give a product which is reduced (H_2, PtO_2, AcOH) and then hydrolysed or oxidised (followed by hydrolysis) to (I) or *allo*pregnane-3(β)-ol-20-one, respectively. The β-configuration of the $C_{(3)}$·OH is thus confirmed.

R. S. C.

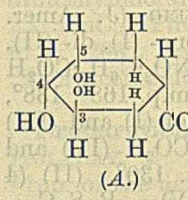
Lateral metallation of phenyl methyl sulphide. H. Gilman and F. J. Webb (J. Amer. Chem. Soc., 1940, **62**, 987—988).—PhSMe and $LiBu^a$ in Et_2O give after interaction with CO_2 35·2—43·5% of SPh·CH_2·CO_2H, but PhOMe gives 32·4% of

o-OMe·C_6H_4·CO_2H and 5·37% of $CO(C_6H_4$·OMe-*o*$)_2$. PhSEt gives *o*-SEt·C_6H_4·CO_2H. R. S. C.

Experiments on the synthesis of 1 : 2-dimethyl*cyclo*hexylacetic acid. F. C. Copp and J. L. Simonsen (J.C.S., 1940, 415—418; cf. A., 1939, II, 117).—2 : 3-Dimethyl*cyclo*hexanone (improved prep.) and $NaNH_2$–C_6H_6 (in N_2), then CH_2Br·CO_2Et, afford Et 6-keto-1 : 2- and *Et* 2-*keto*-3 : 4-*dimethyl*cyclo*hexyl*-*acetate*, b.p. 144°/16 mm., separated by condensing the former with $Et_2C_2O_4$ in EtOH–NaOEt at 0°; the resultant product, b.p. 160—180°/16 mm., and 10% aq. H_2SO_4 give keto-acids which afford an α-, m.p. 197—198°, and β-*semicarbazone*, decomp. 192° (softens at 187°), hydrolysed (dil. H_2SO_4) to α-6-*keto*-1 : 2-*dimethyl*cyclo*hexylacetic acid*, m.p. 107°, and a gum, respectively. 2-Methyl*cyclo*hexanone, $NaNH_2$–Et_2O (in N_2), and CH_2Br·CO_2Et afford a product, b.p. 130—145°/16 mm., converted by $Et_2C_2O_4$ into *Et* 6-*keto*-5-*carbethoxy*-2-*methyl*cyclo*hexylacetate*, b.p. 170—190°/20 mm., which is hydrolysed by 10% aq. H_2SO_4 to 2-*keto*-1-*methyl*cyclo*hexylacetic acid*, m.p. 77—78° (*semicarbazone*, decomp. 182°). Its *Et* ester (I), b.p. 142°/19 mm., $HCO_2C_5H_{11}$-*iso*, and Na in Et_2O give the hydroxymethylene derivative (*semicarbazone*, m.p. 151°). (I) and MeMgI afford an oil, hydrolysed by KOH–MeOH to the *lactone*, m.p. 73°, of 6-hydroxy-1 : 2-dimethyl*cyclo*hexylacetic acid, which is converted by Zn–Hg in HCl into one of the theoretically possible forms of dl-1 : 2-*dimethyl*cyclo*hexylacetic acid* (II), b.p. 153°/16 mm.; its p-*phenylphenacyl* ester (III), m.p. 61—62°, on admixture with the *d*-ester (IV) from hydroxyeremophilone benzoate or with (V) (below) has m.p. 62—64°. (II) is resolved partly through the *cinchonidine* salt, m.p. 141—142°, $[\alpha]_{5461}$ −95° in $CHCl_3$, into the *l*-acid [p-*phenylphenacyl* ester (V), m.p. 65—67°, $[\alpha]_{5461}$ −6° in EtOAc]; the latter mixed with (IV) in Et_2O affords a product, m.p. 62—63° [unchanged by (III)]. Acidification of the solution from the cinchonidine salt gives the *d*-acid (p-*phenylphenacyl* ester, m.p. 62—65°, $[\alpha]_{5461}$ +8° in EtOAc). In eremophilone and hydroxyeremophilone, the Me groups occupy the 1 : 10-positions; the ketones are not isoprene derivatives. A. T. P.

Resolution of *dl*-Δ²-*cyclo*geranic acid. D. J. Bennett, G. R. Ramage, and J. L. Simonsen (J.C.S., 1940, 418—419).—*dl*-Δ²-*cyclo*Geranic acid is resolved by the half-mol. method. The *cinchonine* salt, m.p. 204—206° (sinters at 183°), $[\alpha]_{5461}$ −15·4° in $CHCl_3$, gives the l-*acid*, m.p. 104°, $[\alpha]_{5461}$ −395·7° in EtOH; the acid, $[\alpha]_{5461}$ +200° in EtOH, from the more sol. salt is converted into the *cinchonidine* salt, m.p. 157—158°, $[\alpha]_{5461}$ +81·1° in $CHCl_3$, and thence into the d-*acid*, m.p. 104°, $[\alpha]_{5461}$ +395·7° in EtOH. Neither acid is identical with the acid, $C_{10}H_{16}O_2$, m.p. 83° (cf. A., 1939, II, 514). A. T. P.

Steric series. XXIII. Configuration of the tertiary carbon atom. III. K. Freudenberg, H. Meisenheimer, J. T. Lane, and E. Plankenhorn (Annalen, 1940, **543**, 162—171; cf. A., 1933, 502; 1934, 757).—In order to determine the mesoid or racemoid character of a compound, OH·$\overset{*}{C}$HR·$\overset{\dagger}{C}$HR′X, containing 2 asymmetric centres (configuration of * known, that of † unknown), it is necessary that R and R′ should be joined in a ring and that the *cis* or *trans* relationship of OH and X be known. Subsequent destruction of centre * (*e.g.*, CH·OH → CH_2) allows the configuration of centre † to be determined. These principles are applied to dihydroshikimic acid (*A*) (configuration of $C_{(3)}$ as in glucodesonic acid) (cf. Fischer *et al.*, A., 1937, II, 382), which is cleaved between $C_{(4)}$ and $C_{(5)}$ (after protection of $C_{(3)}$·OH as $C_{(3)}$·OMe), leading to



(*A*.)

CO_2Me·$\overset{*}{C}$H(OMe)·CH_2·$\overset{\dagger}{C}$H(CO_2Me)·CH_2·CO_2Me (*B*). This is converted by fuming HI at 180° into (probably) non-homogeneous *d*(+)-β-carboxyadipic acid, m.p. ~116°, $[\alpha]_D^{20}$ +12·6° (max.) in $COMe_2$ (crystallisation from EtOAc gives some *dl*-acid, m.p. 122—123°). 4 : 5-*iso*Propylideneshikimic acid (I), MeI, and Ag_2O in $COMe_2$ afford *Me* 3-*methyl*-4 : 5-iso*propylidene*-*shikimate*, b.p. 108—112°/0·4 mm., $[\alpha]_D^{20}$ −51·5° in EtOH, hydrolysed [30% AcOH at 100° (bath) followed by aq. $Ba(OH)_2$ at 50°] to 3-*methylshikimic acid*, m.p. 122—123°, $[\alpha]_D^{20}$ −190° in H_2O, which is reduced (H_2, Pd, H_2O) to 3-*methyldihydroshikimic acid* (II), m.p. 124·5°, $[\alpha]_D^{20}$ −22° in H_2O (*Me* ester, $[\alpha]_D^{20}$ −12° in EtOH). HI (*d* 1·7) at 50—55° converts (II) into (*A*), whilst oxidation [$Pb(OAc)_4$–AcOH followed by aq. K_2CO_3–$KMnO_4$] gives β-carboxy-δ-methoxyadipic acid [*Me*$_3$ ester (= *B*), b.p. 116° (bath)/0·1 mm., $[\alpha]_D^{20}$ +51·2° in $COMe_2$; *triamide*, m.p. 186°, $[\alpha]_D^{20}$ +33·5° in H_2O]. Fission of (II) with $Pb(OAc)_4$, conversion of the resultant dialdehyde into the dioxime, and dehydration to the dinitrile also affords, less well, a route to (*B*). Hydrolysis [aq. $Ba(OH)_2$] of Et αβ-dicyanobutane-δ-carboxylate (Leuchs *et al.*, A., 1909, i, 361) affords *dl*-β-carboxyadipic acid, resolved by brucine into the *l*-, m.p. 105—107°, $[\alpha]_D^{20}$ −15·5°, and *d*-acid, $[\alpha]_D$ +15·5° in $COMe_2$ (cf. above). H. B.

A little known reaction for benzoic acid. N. Schoorl (Pharm. Weekblad, 1940, **77**, 425—427; cf. Guerbet, A., 1920, ii, 517).—The sample is evaporated to dryness with HNO_3 (*d* 1·50), the residue dissolved in NaOH and reduced with 10% $SnCl_2$ and 4N-HCl. Sn is pptd. from the cold acid solution with Al, $NaNO_2$ is added, and the diazotised *m*-NH_2·C_6H_4·CO_2H coupled with β-$C_{10}H_7$·OH in aq. NH_3. The red azo-dye is also obtained from cinnamic acid; *o*- and *p*-OH·C_6H_4·CO_2H interfere. The reaction is sensitive to 0·1 mg. of BzOH. S. C.

Reactivity of atoms and groups in organic compounds. XX. Effect of substituents on the relative reactivities of the hydroxyl group in derivatives of benzoic acid. J. F. Norris and A. E. Bearse (J. Amer. Chem. Soc., 1940, **62**, 953—956; cf. A., 1939, II, 369).—The rate of formation of chlorides from BzOH and its derivatives with $SOCl_2$ shows that reactivity of the OH is inversely related to the reactivity of the acidic H. Thus the increasing activation by substitution is 2 : 6-$(OMe)_2$ > *p*-OMe > 2 : 4 : 6-Me_3 > 2 : 4 : 6-Et_3 > *o*-OMe > *p*- > *m*- > *o*-Me > H > *o*- > *m*-Cl > 2 : 6-Cl_2 > 2-chloro-6-nitro > *o*- > *m*-NO_2. *NN*-Dimethyl*cyclo*hexylamine and

C_5H_5N catalyse the reaction, particularly with *o*-substituted derivatives. R. S. C.

Alkanolamines. VIII. Reaction of ethanolamines with *p*-nitrobenzoic acid. M. Meltsner, D. Greenfield, and H. Rosenzweig (J. Amer. Chem. Soc., 1940, **62**, 991—992).—Mono- (I), di- (II), or tri-ethanolamine (1 mol.) with *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ (III) (1 mol.) at 100° gives the salts, m.p. 168°, 138°, and 116°, respectively. 1 mol. each of (I) and (III) under reflux give some *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (IV) and *di*(*ethanolamine*) p-*azoxybenzoate*, m.p. 130°. (II) (4 mols.) and (III) (1 mol.) at 180° give (IV). R. S. C.

Ferrisalicylic complexes. G. Illari (Annali Chim. Appl., 1940, **30**, 65—72).—Salicylic acid with $FeCl_3$ gives a violet-coloured complex, $C_6H_4(O{\cdot}FeCl_2){\cdot}CO_2H$, and, in presence of $NaHCO_3$, a violet-coloured complex $C_6H_4[O{\cdot}Fe(OH)_2]{\cdot}CO_2H$; the structures of these complexes are discussed (cf. A., 1931, 1022). In presence of 0·01N-HCl, a more intensely coloured complex, $C_6H_4(O{\cdot}FeCl_2){\cdot}CO_2FeCl_2$, is formed. F. O. H.

4 : 5-Dimethylacetylsalicylic acid. L. Birkofer (Z. physiol. Chem., 1939, **261**, 87—92).—1 : 2 : 4-$C_6H_3Me_2{\cdot}ONa$ and CO_2 at 170°/35 atm. give 4 : 5-*dimethylsalicylic acid*, m.p. 200° [*Ac* derivative (I), m.p. 122° or 112°; *Na* salt; *Me*, m.p. 33° (*Ac* derivative, m.p. 74—75°), and *Ph* ester, m.p. 85°]. (I) is extremely analgesic (rabbits, monkeys, humans), as bactericidal as aspirin, and less toxic orally (rabbits) and no more toxic intravenously (mice). R. S. C.

Chloralamides. Reaction of phosphorus pentachloride on choral-chlorosalicylamides and their methyl ethers, and the reactivity of the chlorine atom. N. W. Hirwe and K. N. Rana (J. Indian Chem. Soc., 1939, **16**, 677—680).—2 : 5 : 1-$OMe{\cdot}C_6H_3Cl{\cdot}CO{\cdot}NH{\cdot}CH(OH){\cdot}CCl_3$ (I) and PCl_5 give *α-chlorochloral-5-chloro-2-methoxybenzamide*, m.p. 144—145°, which with H_2O regenerates (I) and with the appropriate reagent gives α-methoxy-, *α-ethoxy-*, m.p. 137—138°, *α-anilino-*, m.p. 152—153°, o-, m.p. 148—149°, m-, m.p. 153—154°, and p-*toluidino-*, m.p. 169—170°, *α-phenoxy-*, m.p. 194—195°, and *α-benzoyloxy-chloral-5-chloro-2-methoxybenzamide*, m.p. 133—135°. *α-Chloro-*, m.p. 89—91°, α-methoxy-, *α-anilino-*, m.p. 147—148°, *α-phenoxy-*, m.p. 125—126°, o-, m.p. 153—154°, m-, m.p. 146—147°, and p-*toluidino-chloral-3 : 5-dichloro-2-methoxybenzamide*, m.p. 145—146°, are similarly prepared. F. R. S.

Metalation of alcohols and amines. H. Gilman, G. E. Brown, F. J. Webb, and S. M. Spatz (J. Amer. Chem. Soc., 1940, **62**, 977—979).—$CH_2Ph{\cdot}OH$ and $LiBu^a$ (~2 mols.) in Et_2O give after reaction with CO_2 8·7% of phthalide + *o*-$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$. $CH_2Ph{\cdot}OMe$ gives similarly *o*-$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}OMe$. $CHPh_2{\cdot}OH$ gives 18·6% of α-phenylphthalide. $CPh_3{\cdot}OH$, best in presence of Cu-bronze, gives 4·85% of the lactone of triphenylcarbinol-2 : 2′-dicarboxylic acid. NH_2Ph gives 4·2% of *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (I). $NHPh_2$ gives 10·9—14·7% of *o*-$NHPh{\cdot}C_6H_4{\cdot}CO_2H$. $NHPhBu^a$ gives 2% of N-n-*butylanthranilic acid*, m.p. 80—81°, also obtained from (I) by Bu^aBr–K_2CO_3. NPh_3 gives (Cu-bronze) mixed acids. Piperidine gives an oil. R. S. C.

Synthesis of growth-inhibitory polycyclic compounds. II. G. M. Badger and J. W. Cook (J.C.S., 1940, 409—412; cf. A., 1939, II, 315).—1 : 2-Benzanthracene and Br–CS_2 yield the 10-*Br-* (I), m.p. 147·5—148·5° (*picrate*, m.p. 155·5—156·5°), converted by $Cu_2(CN)_2$ in $CH_2Ph{\cdot}CN$ at 190—200° followed by hot aq. HCl, into the 10-CN-derivative, m.p. 187·5—188·5° (corr.) (cf. Fieser *et al.*, A., 1938, II, 493); the latter does not react with MeMgI and is not reduced by H_2–Pt or Zn–Hg in HCl–AcOH. It is hydrolysed by KOH–MeOH, but not by H_2SO_4–AcOH, to 1 : 2-*benz*-10-*anthramide*, m.p. 218—220°, Mg 1 : 2-benz-10-anthranyl bromide [from (I), EtBr, and Mg in Et_2O–C_6H_6] and $(CH_2)_2O$ give 10-β-*hydroxyethyl*-1 : 2-*benzanthracene*, m.p. 181·5—182·5°. 1 : 2-Benz-10-anthraldehyde (II) and ice-cold $KMnO_4$–$COMe_2$ yield 1 : 2-benz-10-anthroic acid (cf. Dansi, A., 1937, II, 285). 1 : 2-Benzanthracene, $COCl{\cdot}CO_2Et$, and $AlCl_3$ in $PhNO_2$ at 0°, then at room temp., give 1 : 2-*benzanthranyl*-10-*glyoxylic acid*, m.p. 175—176·5° (decomp.), reduced by Na–Hg in dil. NaOH to *α-hydroxy*-1 : 2-*benzanthranyl*-10-*acetic acid*, m.p. 187—191°, or by red P and HI (*d* 1·7) in AcOH to 1 : 2-benzanthranyl-10-acetic acid (III), m.p. 270—274° (previous sintering). 10-Chloromethyl-1 : 2-benzanthracene and KCN–aq. $COMe_2$ or $Cu_2(CN)_2$–$CH_2Ph{\cdot}CN$ at 180—190° followed by C_6H_6–conc. HCl afford 10-*cyanomethyl*-1 : 2-*benzanthracene*, m.p. 177—178°, hydrolysed by 15% KOH–EtOH to (III). (II) and CH_2N_2 in MeOH–Et_2O give (?) 1 : 2-*benzanthranyl*-10-*acetaldehyde*, m.p. 146—147° [*s*-$C_6H_3(NO_2)_3$ *complex*, m.p. 149—150°; *picrate*, m.p. 138·5—139·5°], oxidised by $Na_2Cr_2O_7$–AcOH to 1 : 2-benzanthraquinone. 9-Methyl-1 : 2-benzanthracene (IV) and Br–CS_2 afford a 10-*Br*-derivative, m.p. 122—123°, converted by $Cu_2(CN)_2$ in $CH_2Ph{\cdot}CN$ at 190—200° into 10-*cyano*-9-*methyl*-1 : 2-*benzanthracene*, m.p. 151·5—152°. $HCO{\cdot}NPhMe$, (IV), and $POCl_3$ in *o*-$C_6H_4Cl_2$ at 100° (bath) yield 9-*methyl*-1 : 2-*benz*-10-*anthraldehyde*, m.p. 111·5—112·5°. 6-Methyl-1 : 2-benzanthracene (V) and Br–CS_2 afford the 10-*Br*-derivative, m.p. 138—139° (oxidised by $Na_2Cr_2O_7$–AcOH to 6-methyl-1 : 2-benzanthraquinone), converted into 10-*cyano*-6-*methyl*-1 : 2-*benzanthracene*, m.p. 203·5—204·5°. (V) and paraformaldehyde in HCl–AcOH at 60° give a CH_2Cl compound, converted by KOAc–AcOH into 6-*methyl*-10-*acetoxymethyl*-1 : 2-*benzanthracene*, m.p. 168·5—169·5°, and thence by aq. EtOH–NaOH into the 10-*OH·CH*$_2$ compound, decomp. 220—230° (previous sintering). Tests [by A. Haddow] show that of the 10-substituted benzanthracenes examined, only 1 : 2-benz-10-anthraldehyde and Na 1 : 2-benz-10-anthroate (H_2O-sol.) produce a characteristic inhibition of growth, of moderate intensity; a definite effect is also noted with 10-cyano- and 10-cyano-6-methyl-1 : 2-benzanthracene. Introduction of OH and CO_2H groups is attended by marked loss of growth-inhibitory activity. Tests for carcinogenic activity are recorded. A. T. P.

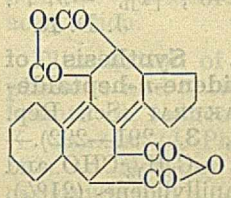
Optical study and synthesis of unsymmetrical phthaleins and their derivatives. L. C. Kin (Ann. Chim., 1940, [xi], **13**, 317—399).—Attempts to obtain methoxylated *o*-benzoylbenzoic acids by use of $AlCl_3$ under the customary conditions generally

give poor yields of impure products owing to elimination of Me but good results are secured by the use of $PhNO_2$ as solvent at <5°. Thus are obtained *o*-$C_6H_4Bz{\cdot}CO_2H$ (Me ester has m.p. 52°); 2-*p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$ (I), m.p. 145°, of which only one Me ester, m.p. 82°, could be isolated; o-4′-*hydroxy-*, m.p. 187—188°, and o-4′-*methoxy-2′-methyl-5′-isopropylbenzoylbenzoic acid*, m.p. 155—156°; *o*-2 : 4-, m.p. 164°, and *o*-3 : 4-dimethoxybenzoylbenzoic acid, m.p. 234°. By condensation of the requisite acid chloride with the necessary phenol or phenolic ether the following are obtained: α-phenyl-α-*p*-anisylphthalide, m.p. 115°, also obtained with *p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4Bz$, m.p. 134° (*diazine*, m.p. 161°), from (I) and MgPhBr; α-phenyl-α-*p*-hydroxyphenylphthalide, m.p. 171°; lactonic Me, m.p. 128°, and Me_2, m.p. 103°, ether of phenolphthalein; lactonic *Me_2 ether*, m.p. 122°, of phenolthymolphthalein; α-p-*hydroxyphenyl-α-4′-methoxy-2′-methyl-5′-isopropylphenylphthalide*, m.p. 195—200° after softening at 160°; lactonic *Me_2 ether*, m.p. 177°, of thymolphthalein; *phenolresorcinolphthalein Me_3 ether*, m.p. 230°; *phenolpyrocatecholphthalein Me_3 ether*, m.p. 98°; *phenolquinolphthalein Me_3 ether*, m.p. 176°; *thymolpyrocatecholphthalein Me_3 ether*, m.p. 158°; *thymolresorcinolphthalein Me_3 ether*, m.p. 168°; phenylpyrocatechol-, new m.p. 170—171°, phenylquinol-, m.p. 248°, *methylthymolpyrocatechol-*, m.p. 230°, *methylthymolresorcinol-*, m.p. 210—211°, *phenolthymol-*, m.p. 276°, phenolresorcinol-, m.p. 205°, *phenolpyrocatechol-* (*triacetate*, m.p. 148°), *phenolquinol-*, m.p. 240—245° (decomp.) after softening at 220°, *thymolpyrocatechol-*, m.p. 284°, and *thymolresorcinol-*, m.p. 284—285°, *-phthalein*. Reduction of the requisite phthalein with Zn dust and NaOH leads to the following *-phthalins*: *phenylpyrocatechol-*, m.p. 159°; *phenolthymol-*, m.p. 209°; *phenolresorcinol-*, m.p. 288—290°. 1 : 4-Di-*p*-hydroxybenzoylbenzene has m.p. 225°. Spectroscopic evidence proves that *o*-aroylbenzoic acids in solution are ketones and not OH-lactones. Phenolphthalein is not diketonic but quinonoid in alkaline solution. The intense coloration of the phthaleins is developed only if they contain at least two phenolic OH which may be present in the same aromatic nucleus. All the phthaleins contain the no. of active H required by their customary formulæ and Oddo's modifications are unnecessary. The stability of the different possible forms of the phthaleins varies with solvent, temp., p_H, and the structure of the rest of the mol. The presence of two phenolic OH attached to the same aromatic nucleus causes a more or less ready scission of the mol. in alkaline solution and the dihydric phenol is invariably liberated. The introduction of phenolic OH into the mol. of a phthalein has a profound influence on the colour in alkaline solution, and the position of OH relative to the other chromphores is also important. When the quinonoid grouping can be developed in two nuclei of a phthalein mol., a mixture of isomerides always appears to result. H. W.

Addition compounds of phthaleins and metallic salts. G. Sachs and L. Ryffel-Neumann (J. Amer. Chem. Soc., 1940, **62**, 993—994).—The following additive *compounds* are prepared: phenolphthalein,$SnCl_4$, +$PhNO_2$, m.p. 78—79°, +PhOMe, or +PhCN; phenolphthalein Me_2 ether (*A*) gives *A*,$SnCl_4$, m.p. 128°, 2*A*,$SnCl_4$, and *A*,$SbCl_5$; 3 : 6-dimethylfluoran (*X*) gives *X*,$SnCl_4$, *X*,$SnCl_4$,PhOMe, 2*X*,3$SnCl_4$,2PhOMe, m.p. 139° (decomp.), *X*,$SbCl_5$, m.p. 203°, and *X*,$SbCl_5$,HCl,AcOH, m.p. 203°; 2fluorescein,$SnCl_4$; fluorescein Me_2 ether,$SnCl_4$. R. S. C.

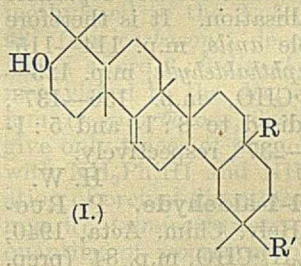
Preparation of aurintricarboxylic acid. D. A. Holaday (J. Amer. Chem. Soc., 1940, **62**, 989).—Prep. of the acid (97% pure) from $CH_2[C_6H_3(OH){\cdot}CO_2H]_2$, *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, and $NaNO_2$–H_2SO_4 is improved. R. S. C.

Total synthesis of a non-benzenoid steroid. L. W. Butz, A. M. Gaddis, E. W. J. Butz, and R. E. Davis (J. Amer. Chem. Soc., 1940, **62**, 995—996).—α-Δ^1-*cyclo*Hexenyl-β-Δ^1-*cyclo*pentenylacetylene and $(CH{\cdot}CO)_2O$ (1 mol.) at 130° give $\Delta^{8(14):9}$-*steradiene*-6 : 7 : 11 : 12-*tetracarboxylic dianhydride* (I), m.p. 249—251° (corr.; decomp.), converted by Pd–C in low yield into 1 : 2-*cyclo*pentenophenanthrene, m.p. 132—133° (corr.). R. S. C.

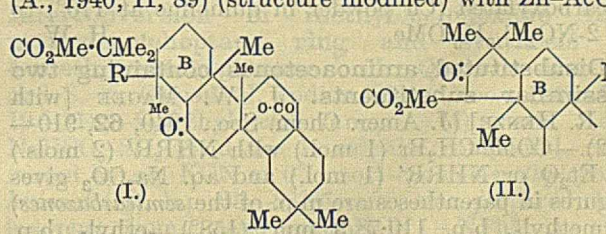

(I.)

Bile acids. LVII. M. Schenck (Z. physiol. Chem., 1939, **261**, 273—277).—The keto-oximinohydroxamic acid, $C_{24}H_{36}O_8N_2$ (cf. A., 1935, 213), and $KMnO_4$ give cilianic (? by way of bilianic) acid and ~0·3 equiv. of (N_2 + N_2O). R. S. C.

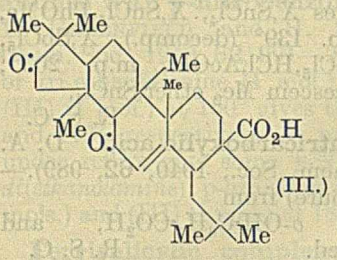
Saponins and sterols. XV. Dry distillation of ursolic acid with selenium, and its constitution. K. Fujii and S. Oosumi (J. Pharm. Soc. Japan, 1939, **59**, 264—268).—Ursolic acid (I) with Se at 330—350°/36 hr. gives sapotalene, 1 : 2 : 3 : 4-$C_6H_2Me_4$, 2 : 7-$C_{10}H_6Me_2$, 1 : 2 : 5 : 6-$C_{10}H_4Me_4$, and 1 : 5 : 6 : 2-$C_{10}H_4Me_3{\cdot}OH$ (cf. Drake *et al.*, A., 1936, 1386; Ruzicka *et al.*, A., 1937, II, 202). The appended structure for (I) (R or R′ = CO_2H or Me) indicates a skeleton structure similar to that of oleanolic acid. (I) and $ZnCl_2$–AcOH give ursylenic acid, m.p. 265° (corr.). A. T. P.


(I.)

Saponins. XV. Constitution of nitro-compounds of the oleanolic acid series. I. S. Kuwada and K. Takeda (J. Pharm. Soc. Japan, 1939, **59**, 294—298).—Me_3 nitro-oleanoltricarboxylate (A., 1940, II, 89) (structure modified) with Zn–AcOH at 100° yields the *Me_2* ester *lactone* [(I); R=$CH_2{\cdot}CO_2Me$], m.p. 229—232°, $[\alpha]_D^{24}$ +98·5°, which


(I.) (II.)

with boiling 10% MeOH–KOH gives a mixture of a *diketolactone Me* ester (II), decomp. 315—318°, $[\alpha]_D^{18}$ −37·7° (*monoxime*, decomp. 266—266·5°), and a *diketo-monocarboxylic acid* (III), decomp. 359—361°, $[\alpha]_D^{19}$ +73·4°. The nitroketonic ester (*loc. cit.*) (structure modified) is converted by Zn–AcOH into a *diketo-lactone* [as (II), CO_2Me = H], decomp. 306—308°, $[\alpha]_D^{24}$ +209·5° (*monoxime*, decomp. 298—300°), which with KOH–MeOH affords (III). Me_3 nitro-oleanintricarboxylate (*loc. cit.*) with boiling Zn–AcOH yields the *Me*$_2$ ester *lactone*, [(I); R = CO_2Me], m.p. 237—240°, $[\alpha]_D^{18}$ +97·7°. M.p. etc. are corr. J. D. R.



(III.)

Aldehydic perfumes. IV. Synthesis of α-vanillylidene- and α-salicylidene-*n*-heptaldehyde. S. Ishikawa and T. Sakurai (Sci. Rep. Tokyo Bunrika Daigaku, 1939, **3**, 291—292).—Vanillin or *o*-OH·C_6H_4·CHO with *n*-C_6H_{13}·CHO and NaOH in ~50% EtOH give α-vanillylidene- (21%), b.p. 119°/2 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 130·5° (corr.; block)], or α-salicylidene-*n*-heptaldehyde (36·7%), b.p. 124°/3·5 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 128·6° (corr.; block)], respectively. R. S. C.

Thermal decomposition of gaseous benzaldehyde.—See A., 1940, I, 259.

Nitration of 1-naphthaldehyde. P. Ruggli and E. Burckhardt (Helv. Chim. Acta, 1940, **23**, 441—445).—1-$C_{10}H_7$·CHO is converted by HNO_3 (*d* 1·52) at −15° mainly into $(NO_2)_2$-derivatives but by HNO_3 (*d* 1·47) at −5° to 0° into a mixture not separable from one another by crystallisation. It is therefore converted into the separable *anils*, m.p. 114—115° and 83—84°, of 8-*nitro*-1-*naphthaldehyde*, m.p. 123—124°, and 5 : 1-NO_2·$C_{10}H_6$·CHO, m.p. 136—137°, respectively, which are oxidised to 8 : 1- and 5 : 1-NO_2·$C_{10}H_6$·CO_2H, m.p. 236—237°, respectively. H. W.

Nitration of 2-naphthol-1-aldehyde. P. Ruggli and E. Burckhardt (Helv. Chim. Acta, 1940, **23**, 445—449).—2 : 1-OH·$C_{10}H_6$·CHO, m.p. 84° (prep. from β-$C_{10}H_7$·OH and HCO·NH_2 described), is converted by HNO_3 (*d* 1·47) at −5° to 0° into 6-*nitro*-2-*naphthol*-1-*aldehyde*, m.p. 239°, transformed by Me_2SO_4–KOH–MeOH into the *Me ether* (I), m.p. 174°, preferably obtained by nitration of 2 : 1-OMe·$C_{10}H_6$·CHO. (I) is oxidised ($KMnO_4$–KOH) to 6-*nitro*-2-*methoxy*-1-*naphthoic acid*, m.p. 187—188°, decarboxylated (Cu powder in quinoline at 170°) to 6 : 2-NO_2·$C_{10}H_6$·OMe. H. W.

Disubstituted aminoacetones containing two dissimilar substituents. J. W. Magee [with H. R. Henze] (J. Amer. Chem. Soc., 1940, **62**, 910—912).—COMe·CH_2Br (1 mol.) with NHRR′ (2 mols.) in Et_2O or NHRR′ (1 mol.) and aq. Na_2CO_3 gives (figures in parentheses are m.p. of the *semicarbazones*) *N*-methyl-, b.p. 110·7°/3 mm. (158°), -ethyl-, b.p. 123·5°/3 mm. (140°), and -benzyl-anilinoacetone, b.p. 187·9°/4·5 mm. (141°), N-*methyl*-, b.p. 129·5°/16 mm. (132°), -*ethyl*-, b.p. 113·8°/3 mm. (135°), -n-*propyl*-, b.p. 130°/6 mm. (125°), and -n-*butyl*-*benzylaminoacetone*, b.p. 147·5°/8 mm. (113°), N-o-, b.p. 137·3°/10 mm. (134°), and -p-*methylbenzylmethylaminoacetone*, b.p. 132·3°/9 mm. (133°), and -*cyclo*hexylmethylaminoacetone, b.p. 93·2°/4 mm. (171°). *N*-*cyclo*Hexylmethylamine is prepared by hydrogenating (Raney Ni) NHPhMe at 200°/233 atm. NHR·CH_2Ar are prepared by heating ArCHO and NH_2R at 100°, removing the H_2O formed, and hydrogenating the residue at 75°/133 atm. Temp. are corr. *n*, *d*, and parachors are recorded. R. S. C.

Condensation of methylzingerone. T. Kobayashi and T. Iwasaki (Sci. Rep. Tôhoku, 1940, **28**, 297—303).—Methylzingerone (β-3 : 4-dimethoxyphenylethyl Me ketone) (cf. Nomura, A., 1917, i, 570) and HCl in AcOH or EtOH at room temp./5 days give 1 : 3 : 5-*tri*-(β-3′ : 4′-*dimethoxyphenylethyl*)*benzene*, m.p. 144—145°, oxidised by aq. $KMnO_4$ at 100° (bath) to 1 : 3 : 5-$C_6H_3(CO_2H)_3$ and 3 : 4 : 1-$(OMe)_2C_6H_3$·CO_2H. A. T. P.

Hexahydroacetomesitylene. E. P. Kohler, T. L. Jacobs, and H. M. Sonnichsen (J. Amer. Chem. Soc., 1940, **62**, 785—793).—The CO of hexahydroacetomesitylene is slightly less hindered than that of acetomesitylene. Hydrogenation [Raney Ni, activated by $(NH_4)_2PtCl_6$; 250°/240 atm.; H_2O] of Na mesitylenecarboxylate gives mixed hexahydromesitylenecarboxylic (2 : 4 : 6-trimethyl*cyclo*hexane-1-carboxylic) acids, yielding an *amide* (I), m.p. 230°, and a mixed amide (II), m.p. 167°, containing (I). $NaNO_2$–AcOH and (I) give an *acid*, m.p. 86—87°; (II) gives a small amount of an acid (? impure), m.p. 114—117° (sinters at 100°). MgMeCl converts (I) into 2 : 4 : 6-*trimethylhexahydrobenzonitrile*, b.p. 66—71°/3 mm. 2 : 4 : 6-Trimethyl*cyclo*hexane-1-carboxyl chloride (III) (prep. by $SOCl_2$) and boiling MeOH give the *Me* ester, b.p. 90—96°/14 mm., which with MgMeCl gives a small amount of 1 : 3 : 5-*trimethyl*-2-iso*propenyl*cyclo*hexane* (IV), b.p. 70·8—71·2°/10 mm. MgMeCl and (III) in Et_2O–C_6H_6 give *hexahydroacetomesitylene* (V) (70%), b.p. 86—87°/9 mm. (obtained also in 55% yield by ZnMeCl), *hexahydromesityldimethylcarbinol* (VI) (16%), m.p. 67—69°, b.p. 106°/10 mm., and (IV) (5·5%). (V) reacts only slowly with MgRHal. MgMeI and (VI) give 1·12 mols. of CH_4. PhNCO dehydrates (VI), yielding $CO(NHPh)_2$; AcCl, Ac_2O, or NaOBr gives (IV). With HCl–EtOH, (VI) gives an unstable chloride, b.p. 94·6—97·1°/9 mm. O_3 yields CH_2O from (IV), but no (V) could be isolated. Br and (IV) in CCl_4 afford a product, which soon gives HBr and *inter alia* 1 : 3 : 5-*trimethyl*-2-β-*bromo*-α-*methylvinyl*cyclo*hexane*, m.p. 41—42°. 2 : 4 : 6 : 1-$C_6H_2Me_3$·COCl and MgMeCl give 90% of acetomesitylene and >1—2% of the alcohol. Na–CMe_2Et·OH reduces (V) to *hexahydromesitylmethylcarbinol*, b.p. 94—99·5°/8 mm. (*phenylurethane*, m.p. 132—134°). NaOBr and (V) give slowly *dibromoacetohexahydromesitylene*, m.p. 63—65°, and only a trace of acid. Condensation of (V) with aldehydes is difficult, but by use of $NaNH_2$–C_6H_6 the *CHPh*: derivative (VII), m.p. <0°, b.p. 148°/0·5 mm., is obtained; this gives a *dibromide*, m.p. 211—212° (slight decomp.), which with hot KOH–MeOH gives

90% of *αγ-diketo-γ-hexahydromesityl-α-phenylpropane*, m.p. 197—199°. Hydrogenation (PtO_2) of (VII) gives *β-phenylpropiohexahydromesitylene*, b.p. 180—182°/8 mm. MgPhBr converts (VII) into *ββ-diphenylpropiohexahydromesitylene*, m.p. 78—80°, which gives *enol peroxides*, m.p. 86—87° (VIII) (main product) and 119—121°. Hydrogenation (PtO_2) of (VIII) gives a *substance*, $C_{24}H_{30}O_2$, m.p. 86—87°, and thermal decomp. gives mainly a *hydrocarbon*, m.p. 200—205°. R. S. C.

Carbon suboxide in the Friedel–Crafts reaction. I. J. H. Billman, G. E. Tripp, and R. V. Cash (J. Amer. Chem. Soc., 1940, **62**, 770—771).—C_3O_2 (prep. described), C_6H_6, and $AlCl_3$ at ~4° and then at the b.p. give a little COPhMe (formed by way of $COPh{\cdot}CH_2{\cdot}CO_2H$) and much polymeric C_3O_2. R. S. C.

Chloromethylation of aryl ketones. R. C. Fuson and C. H. McKeever (J. Amer. Chem. Soc., 1940, **62**, 784—785).—The appropriate ketone, paraformaldehyde, and conc. HCl at 25—85° give 2 : 4-*dimethyl*-5-, m.p. 68·5—69°, and 2 : 4 : 6-*triethyl*-3-*chloromethylacetophenone*, m.p. 57—58°, 3-*chloromethyl-aceto*-, m.p. 74·5—75·5°, *-propio*-, m.p. 75—76°, -iso*butyro*-, b.p. 140°/2 mm., *-pivalyl*-, m.p. 54—55°, and *-benzoyl*-, m.p. 90—91°, *-mesitylene*, and 3-*chloromethylacetoisodurene*, m.p. 88·5—90°. *Pivalylmesitylene* has b.p. 97—97·5°/2·5 mm. R. S. C.

***C*-Alkylresorcinols. IV. Nuclear methylation of 4-acylresorcinols.** H. A. Shah and R. C. Shah (J. Indian Chem. Soc., 1940, **17**, 32—36; cf. A., 1939, II, 373).—Respropiophenone, MeI, and MeOH–KOH afford 2-*hydroxy*-4-*methoxy*-3-*methylpropiophenone* (I), m.p. 78—79°, demethylated by $AlCl_3$ at 135—140° or Ac_2O–HI (*d* 1·7) at 130—140° to 2 : 4-dihydroxy-3-methylpropiophenone, m.p. 128—130°, also obtained from 2 : 1 : 3-$C_6H_3Me(OH)_2$ (II) and EtCN (Hoesch). (I) and Ac_2O–NaOAc at 175—185° afford 7-*methoxy*-2 : 3 : 8-*trimethylchromone* (+H_2O), m.p. 69—70°, hydrolysed by boiling 5% aq. NaOH to (I) and 2 : 3 : 4 : 1-$OH{\cdot}C_6H_2Me(OMe){\cdot}CO_2H$. Resbutyrophenone similarly gives 2-*hydroxy*-4-*methoxy*-3-*methylbutyrophenone* (III), m.p. 82—84°, and thence the 2 : 4-$(OH)_2$-compound, m.p. 155—157° [also from (II) and PrCN], and 7-*methoxy*-2 : 8-*dimethyl*-3-*ethylchromone*, m.p. 43—45°, hydrolysed to (III) and 2 : 4 : 3 : 1-$(OMe)_2C_6H_2Me{\cdot}CO_2H$. 2 : 4-Dihydroxyphenyl benzyl ketone affords 2-*hydroxy*-4-*methoxy*-3-*methylphenyl benzyl ketone*, m.p. 110—111°, and thence the 2 : 4-$(OH)_2$-compound, m.p. 157—159° [also from (II) and $CH_2Ph{\cdot}CN$], and 7-*methoxy*-2 : 8-*dimethylisoflavone*, m.p. 140—142°. 2 : 4-Dihydroxybenzophenone and MeI–MeOH–KOH give 2-hydroxy-4-methoxy-3-methylbenzophenone, m.p. 125° (cf. Jones *et al.*, A., 1932, 852), which affords the 2 : 4-$(OH)_2$-compound and 7-*methoxy*-4-*phenyl*-8-*methylcoumarin*, m.p. 94—95°. A. T. P.

Structure and synthesis of bæckeol. G. R. Ramage and W. J. I. Stowe (J.C.S., 1940, 425—426; cf. A., 1939, II, 110).—1 : 2 : 4 : 6-$C_6H_2Me(OH)_3$ and $Pr^{\beta}CN$ with $ZnCl_2$–HCl–Et_2O at room temp. give 2 : 4 : 6-*trihydroxy*-3-*methyl*iso*butyrophenone*, m.p. 160—161° (+H_2O) or 161—162° (anhyd.), converted by CH_2N_2–Et_2O into its 4 : 6-*Me*$_2$ *ether*, m.p. 102—103° (acetate, m.p. 73°), identical with bæckeol. A. T. P.

Acetylation of α-bromo-ketones and their derivatives. R. P. Barnes and V. J. Tulane (J. Amer. Chem. Soc., 1940, **62**, 894—896).—Fused KOAc in boiling Ac_2O is a powerful acetylating agent. It converts $CHPhBr{\cdot}CO{\cdot}COPh$ (I) or $CHBrBz_2$ (II) into *αβ-diacetoxy-α-benzoyl-β-phenylethylene* (III), m.p. 133°, and CHPhBzBr (IV), benzoin or its acetate (V) into $(CPh{\cdot}OAc)_2$ (VI). KOAc–AcOH has no effect on (I), (II), or (V), converts (IV) into (V), and hydrolyses (III) to $CHBz_2{\cdot}OAc$. In cold, conc. H_2SO_4, (III) gives the oily, unstable di-enol, $OH{\cdot}CPh{:}C(OH){\cdot}COPh$, which in air yields $CO(COPh)_2$. Boiling AcOH hydrolyses (VI) to (V); alkali or conc. H_2SO_4 gives benzoin. Metathesis of Br for Ac precedes further acetylation. R. S. C.

Elimination of methyl from *o*-methoxyacetophenone and action of potassium hydrogen carbonate on resacetophenone and its derivatives. K. Okazaki (J. Pharm. Soc. Japan, 1939, **59**, 190—193).—5-Methoxy-6-acetyl-2-methylcoumarone-1-carboxylic acid is converted by NH_2Ph,HI and NH_2Ph at 95° into 5-hydroxy-6-acetyl-2-methylcoumarone, m.p. 112°. *p*-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$ is acetylated to *p-acetoxyphenylacetonitrile*, m.p. 49—50°, transformed (Fries) into 4-*hydroxy*-3-*acetylphenylacetonitrile* (I), m.p. 106° (*semicarbazone*, m.p. 218—219°). This is converted by MeI–K_2CO_3 in boiling $COMe_2$ into the 4-*OMe*-compound, m.p. 85—86°, which is demethylated to (I) by NH_2Ph,HI and NH_2Ph at 95°. 1 : 2 : 3 : 4-$C_6H_2Ac(OMe)_3$ is similarly converted into 2 : 1 : 3 : 4-$OH{\cdot}C_6H_2Ac(OMe)_2$, m.p. 83°. 2 : 6 : 4 : 1-$(OMe)_2C_6H_2Me{\cdot}CO_2Me$, $AlCl_3$, and AcCl yield *Me* 3-*hydroxy*-5-*dimethoxy*-2-*acetyl*-p-*toluate*, m.p. 123°, methylated to the 3 : 5-$(OMe)_2$-compound (II), m.p. 92° (*semicarbazone*, decomp. 215°). β-Orcinol and MeCN afford 3 : 6-*dimethylresacetophenone*, m.p. 153°, methylated to the *Me*$_2$ *ether* (III), b.p. 115—118°/3 mm. (*semicarbazone*, decomp. 206·5°). (II) and (III) give only traces of phenolic compounds when treated with NH_2Ph,HI and NH_2Ph. The Fries transformation of orcinol diacetate leads to 2 : 6-*diacetylorcinol*, m.p. 97° (*semicarbazone*, decomp. 215°), with a minor quantity of *iso*orcacetophenone, both of which are converted by $KHCO_3$ in a sealed tube at 180—190° into *p*-orsellinic acid. Under similar conditions resacetophenone is converted into 6-*hydroxy*-9-*methylfluorone*, decomp. 238° (*oximino*-compound, m.p. 200°), converted by NaOAc and boiling Ac_2O into 3 : 6-*diacetoxyxanthone*, m.p. 205°. H. W.

Stereochemistry of monocyclic rings. I. Interconversion of methyl*cyclo*hexane into methyl*cyclo*heptane ring and synthesis of 4-methyl*cyclo*heptanone. M. Qudrat-i-Khuda and S. K. Ghosh (J. Indian Chem. Soc., 1940, **17**, 19—31).—4-Methyl*cyclo*hexanone (I) and aq. $NaHSO_3$–SO_2 yield the H sulphite compound, converted by aq. KCN at 0° into 1-*cyano*-4-*methyl*cyclo*hexanol* (II), b.p. 65—68°/5 mm., also prepared, but less pure, from (I) and liquid HCN (+$NPhMe_2$). (II) and $SOCl_2$ in C_5H_5N, but better in dry C_6H_6, afford 1-*cyano*-4-*methyl*-Δ^1-cyclo*hexene* (III), b.p. 98—100°/5

mm., hydrolysed by boiling conc. HCl to 4-*methyl*-Δ^1-cyclo*hexene*-1-*carboxylic acid*, m.p. 132—133°, or by conc. H_2SO_4 at room temp. to the corresponding *amide*, m.p. 140°. (III) and Na–C_5H_{11}·OH at 160—170° afford 4-*methyl*cyclo*hexylmethylamine* (IV), b.p. 85—98°/34—35 mm. [*Bz* derivative, m.p. 93°; *hydrochloride*, m.p. 248—250° (decomp.; shrinks from 220°); *platinichloride*, m.p. 248° (decomp.)], and probably *di*-4-*methyl*cyclo*hexylmethylamine*, b.p. 155—165°/30—35 mm. (IV) and aq. $NaNO_2$–AcOH at 100° (bath) give (?) 4-methyl*cyclo*hexylcarbinol, 1-*methyl*-Δ^4-cyclo*heptene*, b.p. 69—70°/38 mm. (oxidised by aq. $KMnO_4$ to *γ-methylpimelic acid*, m.p. 56°), and 4-*methyl*cyclo*heptanol*, b.p. 105—106°/39—40 mm. (purified through the *H phthalate*, m.p. 95—97°); the latter and CrO_3–AcOH at room temp. for 10 days afford 4-*methyl*cyclo*heptanone* (*A*) [*semicarbazones*, m.p. 159° (V) (mainly), and m.p. 124°]. Et α-cyano-β-methylsuccinate, b.p. 148—150°/4 mm. (improved prep.), is converted by boiling conc. HCl into β-methylsuccinic acid, the Et ester, b.p. 106°/11 mm., of which with Na–EtOH at 140° (bath) affords β-*methylbutane*-αδ-*diol*, b.p. 120—122°/8 mm., converted by HBr at 140—145° (bath) into αδ-*dibromo*-β-*methylbutane* (VI), b.p. 125—128°/55 mm. This with $CHNa(CO_2Et)_2$–C_6H_6 affords *Et*$_2$ 3-*methyl*cyclo*pentane*-1 : 1-*dicarboxylate*, b.p. 120—122°/9—10 mm., and thence (aq. KOH–EtOH) the -dicarboxylic acid, m.p. 117—118° (decomp.) (*Ag* salt). The latter at 185—190° yields the -1-carboxylic acid, b.p. 92—94°/7—8 mm. (*Ag* salt). (VI) and KCN–EtOH afford β-*methyladiponitrile*, b.p. 138—140°/30 mm., converted by HCl into β-methyladipic acid [Et ester (VII), b.p. 130—132°/14 mm.], also obtained from 4-methyl*cyclo*hexanol and aq. $KMnO_4$ at 100° (bath). (VII) and Na–EtOH give *γ-methylhexane*-αζ-*diol*, b.p. 158—160°/15 mm., whence (as above) αζ-*dibromo*-*γ-methylhexane*, b.p. 145—148°/55—60 mm., *γ-methylsuberonitrile*, b.p. 160—164°/20 mm., and *γ-methylsuberic acid*, m.p. 146°. Its Ca salt and Fe, distilled in dry N_2, at 300—350° afford (*A*), b.p. 105—110°/45—50 mm. [semicarbazone (V)], also obtained from (I) and CH_2N_2. A. T. P.

3-Methyl-2-hexyl-Δ^2-*cyclo*pentenone. L. J. Briusova and S. Kore (J. Appl. Chem. Russ., 1939, **12**, 1457—1461).—Heptaldehyde is reduced (Raney Ni in EtOH, at 55°) to heptanol (98% yield). Mg heptyl bromide with lævulic acid yields *γ-methyl*-*γ-undecolactone*, b.p. 140—140·5°/3 mm., which when heated with H_3PO_4 gives 3-methyl-2-hexyl-Δ^2-*cyclo*pentenone. R. T.

Polymethylbenzenes. XXV. Reaction between dimethylacrylic acid and the trimethylbenzenes. L. I. Smith and W. W. Prichard (J. Amer. Chem. Soc., 1940, **62**, 771—777; cf. A., 1939, II, 306).—$CMe_2{:}CH{\cdot}CO_2H$ (I), ψ-cumene (II), and $AlCl_3$ at −10° give β-3 : 4 : 5-*trimethylphenyl*isovaleric *acid* (III) (50—60%), m.p. 111—112° (*Me* ester, b.p. 130—130·5°/6 mm.), with some durene and other acids, rearrangement occurring. (III) is sole product from 1 : 2 : 3-$C_6H_3Me_3$ (IV), (I), and $AlCl_3$ at −10°. Oxidation of (III) by $KMnO_4$ in aq. KOH gives only α-3 : 4 : 5-*tricarboxyphenyl*isobutyric *acid*, m.p. 192—194° (Me_x ester, an oil). 1 : 2 : 4 : 5-$C_6H_2Me_3$·COMe and MgMeI in Et_2O–N_2 give an oily carbinol; the derived (HCl–light petroleum) chloride is condensed with $CHNa(CO_2Et)_2$, hydrolysed to the dicarboxylic acid, m.p. 143·5—148·5° (decomp.), and then decarboxylated at 160° to yield β-2 : 4 : 5-*trimethylphenyl*-isovaleric *acid*, m.p. 79—81°, which is partly isomerised to (III) by $AlCl_3$. $CMe_2{:}CH{\cdot}COCl$ (V), (IV), and $AlCl_3$ at −10° give 2 : 3 : 4-*trimethyl*-β-iso*propylidene*-*acetophenone*, b.p. 138—139°/6 mm., oxidised by $KMnO_4$ to 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$ and cyclised by $AlCl_3$–HCl in CS_2 to 3 : 3 : 5 : 6 : 7-*pentamethylhydrindone*, m.p. 103·5—104° (*oxime*, m.p. 196—196·5°), which is obtained in 99% yield from (III) by conc. H_2SO_4 at room temp. (II), (V), and $AlCl_3$ in CS_2 give 2 : 4 : 5-*trimethyl*-β-iso*propylideneacetophenone* (VI), b.p. 131—131·5°/6 mm., oxidised to 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$ and cyclised to 3 : 3 : 4 : 5 : 7-*pentamethylhydrindone*, m.p. 54—55·5°. Addition of Br to (I), conversion by PCl_5–C_6H_6 into the Br_2-chloride, b.p. 77—82° (some decomp.)/5 mm., and condensation with (II) by $AlCl_3$–CS_2 gives αβ-*dibromo*-2 : 4 : 5-*trimethyl*isovalerophenone, m.p. 74—76°, also obtained from (VI) by Br–Et_2O, and cyclised by $AlCl_3$ to 2-*bromo*-3 : 3 : 4 : 5 : 7-*pentamethylhydrindone*, m.p. 102—104°. *p*-Xylene, (I), and $AlCl_3$ at 0° give mainly (? 2 : 5-)*dimethylphenyl*isovaleric *acid*, m.p. 108—110°, cyclised to (? 3 : 3 : 4 : 7-)*tetramethylhydrindone*, m.p. 52—53°. *s*-$C_6H_3Me_3$ gives similarly a β-*dimethylphenyl*isovaleric *acid*, m.p. 110—111°, cyclised to a *tetramethylhydrindone*, m.p. 62—63°. Mesityl oxide with (II) and $AlCl_3$ at 0° gives 1 : 1 : 3 : 4 : 5 : 7-*hexamethylindene*, m.p. 87·5—88·5°, but with PhOH, ψ-cumenol, or *p*-$C_6H_4Br{\cdot}OH$ in conc. H_2SO_4 or H_2SO_4–AcOH at 0°, *p*-$C_6H_4Cl{\cdot}OH$–$AlCl_3$, *p*-$C_6H_4Cl{\cdot}OMe$–$PhNO_2$–$AlCl_3$, or *p*-$C_6H_4(OMe)_2$–$AlCl_3$–CS_2 gives no identifiable product. *o*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$ and MgMeI–Et_2O give a carbinol, m.p. 43—44°, converted by HCl and $CaSO_4$ in C_6H_6 into a halogen-free substance, m.p. 95—96°. R. S. C.

3 : 3 : 5 : 6 : 7-Pentamethylhydrindone and 4 : 4 : 5 : 6 : 8-pentamethylhydrocarbostyril. L. I. Smith and W. W. Prichard (J. Amer. Chem. Soc., 1940, **62**, 778—780).—Beckmann rearrangement (PCl_5–$POCl_3$) of 3 : 3 : 5 : 6 : 7-pentamethylhydrindoxime gives only mixtures. 3 : 3 : 5 : 6 : 7-Pentamethylhydrindone gives ($NaNO_3$–H_2SO_4–$CHCl_3$; −5°) mainly the 4-NO_2-, m.p. 94—94·5°, and thence (Zn dust–AcOH) the 4-NH_2-, double m.p. 84° and 101—102°, and ($NaNO_2$–10% H_2SO_4; $CuSO_4$) the 4-*OH*-derivative, m.p. 183—185° (*oxime*, m.p. 183—185°, with PCl_5–$POCl_3$ gives an amorphous solid). 1 : 2 : 4 : 5-$C_6H_2Me_3{\cdot}NH_2$ and $CMe_2{:}CH{\cdot}COCl$ in hot C_6H_6 give the *amide*, m.p. 107·5—108°, cyclised by $AlCl_3$ at 100° to 4 : 4 : 5 : 6 : 8-*pentamethylhydrocarbostyril*, m.p. 209—210°, which resists hydrolysis by $Ba(OH)_2$ at 150—250°. R. S. C.

Synthesis of 1-keto-2 : 3-dimethylnaphthindene. E. F. Arcangeli (R. C. Atti Accad. Ital., 1939, [vii], **1**, 55—59).—2-$C_{10}H_7Ac$ (I) and $CHMeBr{\cdot}CO_2Et$ with Zn in C_6H_6 give, after treatment with H_2SO_4, (I) and *Et* β-*hydroxy*-β-2-*naphthyl*-α-*methyl*-n-*butyrate*, b.p. 275—280°/62 mm., which when heated with P_2O_5 for 2 hr. gives 1-*keto*-2 : 3-*dimethyl*-α(or -β)-*naphthindene* (II), m.p. 129·5—130°, b.p.

229—230°/34 mm. With conc. H_2SO_4, crude (II) gives (I). E. W. W.

Preparation of substituted ketimines. R. Cantarel (Compt. rend., 1940, **210**, 403—405).—$COPh_2$ vapour with NH_3 in presence of ThO_2 at 380° gives $CPh_2{:}NH$ (I), b.p. 160°/13 mm. Many aldehydes and ketones in EtOH saturated with NH_3 containing Ni at 70° (under 8—9 kg. per sq. cm. H_2 pressure) give the corresponding amines in high yield, but $COPh_2$ gives only traces of $CHPh_2{\cdot}OH$ and $CHPh_2{\cdot}NH_2$; the latter is formed quantitatively by reducing (I) (H_2). Equimol. amounts of (I) and primary amines give NH_3 and the appropriate imine. The following are new: *benzhydrylidene-β-phenylethylamine*, m.p. 35°, and *-cyclohexylamine*, m.p. 49°. $CPh_2{:}N{\cdot}CHPh_2$ with H_2–catalyst gives *dibenzhydrylamine* (~100%), m.p. 143°. J. L. D.

Steroid ketones.—See B., 1940, 404, 405.

Sterols. XCVII. Sarsasapogenin. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1940, **62**, 900—902).—Sarsasapogenin acetate with MgEtBr in Et_2O–C_6H_6 gives a *diol*, $C_{29}H_{50}O_3$, m.p. 159—161·5° [*diacetate* (I), m.p. 87·5—89°], and with MgMeI gives a *diol*, $C_{28}H_{48}O_3$, m.p. 179—181·5° (*di-p-nitrobenzoate*, m.p. 192—194°). CrO_3 in ~90% AcOH at 90° oxidises (I) to a product, hydrolysed (NaOH) to 3-hydroxyætiobilianic acid. The Me_2 ester thereof with aq. MeOH–NaOH (1 mol.) gives the Me_1 ester, m.p. 211—213°, the *acetate*, m.p. 181·5—183·5°, of which gives an oily chloride, converted by CH_2N_2 into a *diazo-ketone*, $C_{23}H_{33}O_5N_2$, m.p. 159—160° (decomp.). Ag_2O in EtOH at 70—80° then gives an oil, which by hydrolysis, acetylation, heating (250°), and hydrolysis gives ætiocholan-3(β)-ol-17-one (II), *form*, m.p. 117—119°. Identity of (II) with the product of Ruzicka *et al.* (form, m.p. 151—152°, A., 1934, 1221) is proved by prep. of the semicarbazone, m.p. 241—242·5° (decomp.), and reduction by Na–$C_5H_{11}{\cdot}OH$ to ætiocholane-3(α) : 17(α)-diol (III). Partial hydrolysis (MeOH–KOH) of the diacetate of (III) followed by oxidation (CrO_3) and hydrolysis gives (mainly) *ætiocholan-17-ol-3-one*, m.p. 139—141°, which with Br–HBr–AcOH affords a product converted by boiling C_5H_5N into testosterone. R. S. C.

Sterols. XCV. Acid isomerisation of ψ-sapogenins to sapogenins. R. E. Marker and E. Rohrmann (J. Amer. Chem. Soc., 1940, **62**, 896—898).—Clemmensen reduction of ψ-sarsasapogenone gives deoxysarsasapogenin. HCl–EtOH at 25° converts ψ-sarsasapogenin, ψ-tigogenin, and ψ-chlorogenin into sarsasapogenin, tigogenin, and chlorogenin, respectively, but has no effect on dihydro-ψ-sarsasapogenin. The naturally occurring saponin glucosides may be derived from the ψ-forms or the keto-diol form, *e.g.*, $\cdot CMe{\cdot}CHR\rangle CH{\cdot}OH$ ($\cdot CH{-}CH_2$ / R = $CHMe{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}OH$). R. S. C.

Total synthesis of the sex hormone, equilenin, and its stereoisomerides. W. E. Bachmann, W. Cole, and A. L. Wilds (J. Amer. Chem. Soc., 1940, **62**, 824—839).—Equilenin (I) and three stereoisomerides thereof are synthesised. Results already reported (A., 1939, II, 261) are amplified, the following being new. Prep. of 6 : 1-$OMe{\cdot}C_{10}H_6{\cdot}NH_2$ (from the Ac derivative), 6 : 1-$OMe{\cdot}C_{10}H_6{\cdot}[CH_2]_2{\cdot}OH$ [76—84% from 1 : 6-$C_{10}H_6I{\cdot}OMe$, EtBr, Mg, and $(CH_2)_2O$ in Et_2O–C_6H_6], 6 : 1-$OMe{\cdot}C_{10}H_6{\cdot}[CH_2]_2{\cdot}Br$ (I) (by PBr_3–C_6H_6), 6 : 1-$OMe{\cdot}C_{10}H_6{\cdot}[CH_2]_3{\cdot}CO_2H$ (II) [75—89% from (I), $CH_2(CO_2Et)_2$, NaOEt, etc.], and 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (III) [90—95% from (II) by $SOCl_2$–C_5H_5N–Et_2O, followed by $SnCl_4$–C_6H_6] is modified. $Me_2C_2O_4$, (III), and NaOMe in C_6H_6 give *Me* 1-*keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*glyoxylate*, m.p. 138—140° (Pyrex) or 134—135° (soda glass), converted at 180°, best when mixed with powdered glass, into Me 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-carboxylate, double m.p. 110—111° (nearly completely) and 125—126·5°, and thence by MeI–NaOMe–MeOH into the 2-Me derivative (IV), m.p. 84·5—85°. Hydrolysis of (IV) by aq. MeOH–KOH affords 1-keto-7-methoxy- (V), m.p. 109—110°, which with 42% HBr gives 7-hydroxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, m.p. 193—196° (air), 195·5—197·5° (after resolidification, 197—197·5°; vac.). With Zn, I, and $CH_2Br{\cdot}CO_2Me$ in C_6H_6–Et_2O, (IV) gives *Me* 1-*hydroxy*-2-*carbomethoxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-1-*acetate* (85—90%), m.p. 125—125·5° [hydrolysed by alkali to (V)], which with $SOCl_2$–C_5H_5N (with or without C_6H_6), followed by KOH–MeOH, gives the *anhydride* (VI), m.p. 233—234°, of *syn*-2-carboxy-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro-1-phenanthrylideneacetic acid and the anti-*acid* (VII), m.p. 216—217° (gas) (*Me*$_2$ ester, m.p. 113·5—114°). Na–Hg in aq. KOH then gives α- (VIII) (45%), m.p. 231—232°, and β-2-*carboxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-1-*acetic acid* (IX) (55%), m.p. (+$x C_6H_6$) ~145° or 150°, (anhyd.) 213—214°, obtained similarly in 33 and 43% yield, respectively, from (VI) or in 44—47 and 40—43% yield, respectively, without isolation of the unsaturated compounds. The *Me*$_2$ ester, m.p. 114—115·5°, of (IX) is hydrolysed by N-NaOH (1 mol.) in hot MeOH to the 2-*carbomethoxy*-1-*acetic acid*, m.p. 211—212°, converted (Arndt–Eistert) into *Me* β-2-*carbomethoxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-1-*propionate*, m.p. 101—102°. Cyclisation by NaOMe in C_6H_6–N_2 then yields 97% of 16-*carbomethoxy*-dl-*equilenin Me ether*, m.p. 181—182° (vac.; after softening), converted by boiling HCl–AcOH–H_2O–N_2 into *dl*-equilenin (X), m.p. 276—278° (vac.) [once 287—288° (vac.), sometimes 265°] [*benzoate*, m.p. 248·5—249·5° (vac.); *acetate*, m.p. 153—154° (159·5—160° after resolidification; vac.)], and its *Me ether*, m.p. 185—186·5° (vac.) [converted by MgMeI, followed by $KHSO_4$ at 160—170°, into 7-methoxy-3′ : 3′-dimethyl-1 : 2-*cyclo*pentenophenanthrene (XI)]. Esterification of (X) in dioxan–C_5H_5N–N_2 and crystallisation gives d-*equilenin* l-*menthoxyacetate* (XII), m.p. 174—174·5°, $[\alpha]_D^{20}$ +18° in C_6H_6, hydrolysed to *d*-equilenin, which is proved to be identical with the natural product by means of 6 derivatives [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 206—207° (corr.)], absorption spectrum, and physiological action. l-*Equilenin*, m.p. 250—251° (vac.), 258—259° (vac.; corr.), $[\alpha]_D^{20}$ −85° in dioxan [d-*menthoxyacetate* (XIII), m.p. 174·5—175° (vac.), $[\alpha]_D^{20}$

—16° in C_6H_6], is obtained similarly from (X) or the residues from (XII) (after hydrolysis). A 1 : 1 mixture of (XII) and (XIII) has m.p. 151—152° (vac.). By similar methods (VIII) gives *Me* 2-*carbomethoxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-1-*acetate*, dimorphic, m.p. 86—89° and 126—126·5°, the 2-*carbomethoxy*-1-*acetic acid* (XIV), m.p. ~110—112° (gas) and then 137—138°, α-2-*carboxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-1-*propionic acid*, m.p. 89—89·5°, 16-*carbomethoxy*-dl-iso*equilenin Me ether*, m.p. 149—149·5° (air), 152·5—153·5° (vac.), dl-iso*equilenin Me ether*, m.p. 127—127·5° (vac.), 130—130·5° (vac.) after resolidification [gives (XI) in 3% yield], and dl-iso*equilenin*, m.p. 223—224° (vac.) [*acetate*, m.p. 159—160° (vac.); *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 186—187° (vac.)]. (XIV) gives l-*menthyl* l-α-2-*carbomethoxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-1-*acetate* (XV), m.p. 139·3—139·8°, $[\alpha]_D^{30}$ −152° in C_6H_6, converted into the *Me*$_2$ ester, m.p. 110—110·3°, $[\alpha]_D^{30}$ −151° in C_6H_6, and *Me H* ester, m.p. 130°, 159—160° after resolidification, of the *l*-acid and thence into *Me*$_2$ l-α-2-*carbomethoxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthryl*-1-*propionate*, m.p. 103—103·5°, 16-carbomethoxy-*d*-*iso*equilenin, m.p. 147—150°, and d-iso*equilenin*, m.p. 257—258° (vac.), 265—266° (vac.; corr.), $[\alpha]_D^{29}$ +147° in dioxan, +173° in abs. EtOH [Me ether, m.p. 118·5—119·5°; *acetate*, dimorphic, m.p. 146—147° (vac.) (149—149·5°) and 127—128°, $[\alpha]_D^{24}$ +137 ± 7°, +129·4° in abs. EtOH], identical with 14-*epi*equilenin (Hirschmann *et al.*, A., 1939, II, 76). Hydrolysis (KOH–MeOH) of the residues after separation of (XV) and methylation (CH_2N_2) gives Me *dl*-, m.p. 125·5—126°, and *d*-α-2-carbomethoxy-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthryl-1-acetate, m.p. 108—109° or 110—110·5°, Me *d*-α-2-carbomethoxy-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthryl-1-propionate, m.p. 103—103·5°, $[\alpha]_D^{29}$ +122°, and l-iso*equilenin*, dimorphic, m.p. 272—273° (vac.) and 257—258° (vac.), $[\alpha]_D^{28}$ −147° in dioxan, −162° in abs. EtOH. Œstrogenic units are *d*- 30 and *l*-equilenin 400, *d*- and *l*-*iso*equilenin >500 μg.

R. S. C.

Hydroxyquinones. I. Synthesis of dyes of the polyporic acid series. M. Asano and Y. Kameda (J. Pharm. Soc. Japan, 1939, **59**, 291—293).—*p*-$C_6H_4Me{\cdot}N_2Cl$ with NaOAc and *p*-benzoquinone (I) in EtOH at <5° yields 2-mono- (II), m.p. 137—139°, and 2 : 3 : 5-*tri*-p-*tolyl*-p-*benzoquinone*, m.p. 197—199°. 2-Phenyl-*p*-benzoquinone and PhMe or (II) and C_6H_6 with $AlCl_3$ yield 2-*phenyl*-5-p-*tolylbenzoquinone*, m.p. 171—173°, reduced (Zn–AcOH) to 2-*phenyl*-5-p-*tolylquinol*, m.p. 151—153°, the 3 : 6-Br_2-derivative, m.p. 195—197° (prep. in $CHCl_3$), of which is hydrolysed by 10% MeOH–KOH to 3 : 6-*dihydroxy*-2-*phenyl*-5-p-*tolylbenzoquinone*, m.p. 246—248°. *p*-$OMe{\cdot}C_6H_4{\cdot}N_2Cl$ and (I) similarly give 2-anisyl-*p*-benzoquinone, m.p. 112—113°, which with C_6H_6 and $AlCl_3$ yields 2-*phenyl*-5-p-*anisylbenzoquinone*, (III), m.p. 177—183° (corresponding *quinol*, m.p. 157—158°). With NH_2Et in EtOH, (III) in EtOAc yields 3 : 6-*di*(*ethylamino*)-2-*phenyl*-5-*anisylbenzoquinone*, m.p. 256°, which is hydrolysed by 50% H_2SO_4 to 3 : 6-*dihydroxy*-2-*phenyl*-5-*anisylbenzoquinone*, m.p. 261—263°.

J. D. R.

Constitution and synthesis of embelin. M. Asano and K. Yamaguti (J. Pharm. Soc. Japan, 1940, **60**, 34—38, and Proc. Imp. Acad. Tokyo, 1940, **16**, 36—38).—Contrary to Hasan *et al.* (A., 1931, 1158) embelin (I) is 3 : 6-*dihydroxy*-2-*undecyl*-p-*benzoquinone* (II), and not the dodecyl derivative (III). In this series identification by the method of mixed m.p. is untrustworthy and the identity of (I) with synthetic (II) is established by the Debye–Scherrer diagrams. 3 : 4 : 5-$(OMe)_3C_6H_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ is condensed with $C_{10}H_{21}I$ and NaOEt in EtOH to *Et* α-3 : 4 : 5-*trimethoxybenzoyl-laurate*, m.p. 46°, which does not give a colour with $FeCl_3$ in EtOH and is converted by boiling 1% KOH–EtOH into 3 : 4 : 5-*trimethoxylaurophenone*, m.p. 65° (p-*nitrophenylhydrazone*, m.p. 96°). This is reduced by Na–boiling $C_5H_{11}{\cdot}OH$ to 3 : 5-*dimethoxydodecylbenzene*, b.p. 165°/0·3 mm. (demethylated to 3 : 5-*dihydroxydodecylbenzene*, m.p. 81°), which is oxidised ($Na_2Cr_2O_7$ in AcOH at 85—90°) to 6-*methoxy*-2-*dodecyl*-p-*benzoquinone* (IV), m.p. 74°. NH_2Me in EtOH at 0° transforms (IV) into 3 : 6-*di*(*methylamino*)-2-*dodecyl*-p-*benzoquinone*, m.p. 147°, which is converted by 50% H_2SO_4 at 100° into 3(or 6)-*methylamino*-6(or 3)-*hydroxy*-2-*dodecyl*-p-*benzoquinone*, m.p. 163—164°; this with boiling 50% H_2SO_4–AcOH yields (III), m.p. 142° (*dibenzoate*, m.p. 96—96·5°), which does not depress the m.p. of (I), from which it differs in Debye–Scherrer diagram. Reductive acetylation of (III) affords 2 : 3 : 5 : 6-*tetra-acetoxydodecylbenzene*, m.p. 120°. Tridecoic acid, m.p. 39·5° (*p*-toluidide, m.p. 87·5—88°), is obtained by oxidation of (III) with H_2O_2 and dil. KOH. 3 : 4 : 5-$(OMe)_3C_6H_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ and $C_9H_{19}I$ afford *Et* α-3 : 4 : 5-*trimethoxybenzoylundecoate*, m.p. 39—40°, and thence successively 3 : 4 : 5-*trimethoxyundecophenone*, m.p. 51—52°, 3 : 5-*dimethoxyundecylbenzene*, b.p. 170°/1 mm. (3 : 5-*dihydroxyundecylbenzene*, m.p. 69—71°), 6-*methoxy*-, m.p. 78—79°, and 3 : 6-*di*(*methylamino*)-, m.p. 147—148°, -2-*undecyl*-p-*benzoquinone*, and (II), m.p. 143—144° (*dibenzoate*, m.p. 97°). 2 : 3 : 5 : 6-*Tetra-acetoxyundecylbenzene* has m.p. 124°.

H. W.

2-Acetoxymethyl-1 : 4-naphthaquinone, m.p. 110°, and -naphthalene, m.p. 61°; 2-methylnaphthaquinone monoxime, m.p. 165°.—See A., 1940, III, 431.

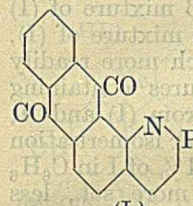
Compounds having antihæmorrhagic activity. L. F. Fieser, M. Tishler, and W. L. Sampson (J. Amer. Chem. Soc., 1940, **62**, 996).—Application of the vitamin-K_1 synthesis (A., 1940, II, 96) gives 2-geranyl-, 2-farnesyl, and 2-*phytyl*-1 : 4-*naphthaquinone* (I) [all have -*K*-activity, (I) fully at 50 μg.], 2 : 3 : 5-*trimethyl*-6-*phytylbenzoquinone*, an oil (no -*K*-activity; *quinol diacetate*, m.p. 56°; with $SnCl_2$–AcOH–HCl gives α-tocopherol), 2-*methyl*-3-*phytyl*-5 : 8-*dihydro*-1 : 4-*naphthaquinone* (active at 5—6 μg.). -K_1 gives the βγ-H_2-derivative (active at 6 μg.; quinol diacetate, m.p. 57—58°) and βγ : 5 : 6 : 7 : 8-H_6-derivative (slightly active; quinol diacetate, m.p. 53°). 2-Methyl-5 : 8-dihydro-1 : 4-naphthaquinol and the adduct from toluquinone and $(CH_2{:}CH)_2$ are active at 8-μg. doses. A by-product in the synthesis of -K_1 is a *ketone*, $C_{31}H_{48}O_2$ (absorption max. at 253 and 300 mμ.; 2 : 4-dinitrophenylhydrazone, m.p. 107—

108°; 1 active H), active at 50 μg., which is reduced by $Al(OPr^{\beta})_3$ to a *diol*, (?) $C_{31}H_{52}O_2$, and by pyrolysis gives a little -K_1. The isomeric *naphthotocopherol* (absorption max. at 246 and 320 mμ.; *p*-nitrobenzoate, m.p. 84—85°) is active at 3 × 10^{-4}-g. doses and gives on oxidation a *OH-quinone*. 2-*Methyl*-3-*farnesyl*-1 : 4-*naphthaquinone* is less active than -K_1. R. S. C.

Action of nitric acid on anthracene. IV. [Nitroanthraquinones.] R. Oda (J. Soc. Chem. Ind. Japan, 1940, **43**, 14—15B).—2 : 7-Dinitro- (I) is separated from 2-nitro-anthraquinone by dissolution in NaOH–$COMe_2$, but cannot be recovered therefrom. Hot, aq. Na_2SO_3, best with C_5H_5N, converts (I) into the 2-NH·SO_3Na derivative. When a mixture of (I) and anthraquinone is boiled in NH_2Ph for 10 min. and then cooled, both solids separate, but, if boiling is continued for 3—4 hr. (also in *p*-C_6H_4Me·NH_2 containing a little C_5H_5N), the (I) remains in solution as a mol. compound and is recovered by HCl.

R. S. C.

1-Amino-2-methylanthraquinone in relation to phthaloylation and Schiff's base. G. B. Crippa (Atti X Congr. Internaz. Chim., 1938, IV, 842—850).—Largely an account of work previously abstracted (A., 1939, II, 181, 379). Condensation of 1-amino-2-anilomethylanthraquinone with COPhMe affords a *substance*, m.p. 130—135°, probably (I). F. O. H.



(I.)

1 : 3 : 8-Trihydroxyanthraquinone. W. K. Anslow, J. Breen, and H. Raistrick (J.C.S., 1940, 427—428).—Emodic acid (see A., 1940, II, 135) is decarboxylated by quinoline–Cu chromite at 225—230° in O_2-free N_2 to 1 : 3 : 8-trihydroxyanthraquinone, new m.p. 287—288°, purified through its triacetate, new m.p. 194—195°. Methylation (Me_2SO_4–$COMe_2$–2N-NaOH) gives 1 : 3 : 8-*trimethoxyanthraquinone*, m.p. 195—196°. A. T. P.

Constitution of carviolin, a colouring matter of *Penicillium carmino-violaceum*, Biourge. H. G. Hind (Biochem. J., 1940, **34**, 577—579).—Demethylation of carviolin (I) (A., 1940, II, 99) with HBr–AcOH yields a Br_1-compound, $C_{15}H_9O_5Br$, m.p. 248°, which with aq. AcOH–AgOAc gives *demethylcarviolin*, $C_{15}H_{10}O_6$, m.p. 278—280°. Methylation of (I) yields a Me_3 ether, m.p. 186°, identical with ω-hydroxyemodin Me_4 ether, indicating that (I) is an ω-hydroxyemodin Me_1 ether. Successive oxidation (Pb_3O_4 in conc. H_2SO_4) and reduction (SO_2–H_2O) of (I) gives a compound showing the absorption bands of a 1 : 4 : 5 : 8-tetrahydroxyanthraquinone.

P. G. M.

Elimination reactions and their steric course. W. Hückel, W. Tappe, and G. Legutke (Annalen, 1940, **543**, 191—230; cf. A., 1939, II, 147).—*l*-Menthyl *p*-toluenesulphonate (I) and EtOH–NaOEt afford (cf. A., 1939, II, 120) *trans*-Δ^2-menthene (II), b.p. 55·5°/16 mm., which has α_D +107°, $[\alpha]_D^{20}$ +132·1° (cf. Read *et al.*, A., 1939, II, 79), when carefully fractionated (over Na; reduced pressure in N_2). The oxide, b.p. 83—84°/17 mm., from (II) and BzO_2H in $CHCl_3$, is converted by 5% $HClO_4$ into the very viscous menthanediol, $[\alpha]_D^{20}$ +33° in EtOH, which is oxidised (cold aq. $KMnO_4$ + K_2CO_3) to a lactonic *acid*, $C_{10}H_{16}O_4$, m.p. 192° (sinters 182°), and non-cryst. material. Δ^3-Menthene (III) is rapidly racemised by boiling EtOH–*p*-C_6H_4Me·SO_3H whilst (II) is similarly little affected; (III) is also oxidised much more rapidly than (II) by BzO_2H (cf. Meerwein *et al.*, A., 1926, 722). These methods are applied to the determination of the amount of (II) in admixture with (III). Thus, *l*-menthyl chloride (IV) and NaOEt give a little (II) [not obtained wholly free from unchanged (IV)]; (I) and EtOH in presence and absence of $CaCO_3$ afford mixtures, α + 78° and +35°, respectively, each containing 32% of (II). The amounts of (II) in the mixtures obtained from *d*-neomenthyl chloride and EtOH–NaOEt, *d*-neomenthylamine (V) and HNO_2, *l*-menthyl xanthate (thermal decomp.), and *d*-neomenthyl xanthate (prep. described; decomp. at 185—220°) are ~25, 20, 28, and 80%, respectively. Some inactive menthan-4-ol (VI) is also formed from (V) and HNO_2; the intermediate *d*-neomenthyl ion presumably rearranges to the *tert.*-4-menthyl ion which then adds OH^- [to give (VI)] or eliminates H^+ [forming inactive (III)]. Racemisation of (III) by EtOH–*p*-C_6H_4Me·SO_3H probably occurs owing to the formation of (VI) (as ester). The possible production of the *l*-menthyl ion from (I) in EtOH, and subsequent loss of H^+ to give (II) and (III) is discussed. The reaction between (IV) and NaOEt is considered to be of the following type: $OEt^- + H{\cdot}CR_2{\cdot}CR_2Cl$ (H and Cl in *trans* position) → $OEt^- \; H^+ \cdots CR_2{\cdot}CR_2 \cdots Cl^- \rightarrow$ $EtOH + \overset{-}{C}R_2{\cdot}\overset{+}{C}R_2 + Cl^-$; Tschugaev's xanthate method is held to be strictly analogous, SMe^- reacting as OEt^-. The formation of menthenes and octahydronaphthalenes from (i) menthyl and decahydronaphthyl esters, respectively, in EtOH or EtOH + $CaCO_3$, and (ii) the corresponding amines and HNO_2, is of type *E* 1 (Hughes *et al.*, A., 1937, I, 467). Elimination reactions of type *E* 2 (cf. *loc. cit.*; Hanhart *et al.*, A., 1927, 650) are: (i) the above esters with NaOAlk, (ii) exhaustive methylations (above amines), and (iii) thermal decomp. of the xanthates.

The *p*-toluenesulphonate, m.p. 72°, of *trans*-decahydro-α-naphthol, m.p. 49°, with boiling EtOH–NaOH gives 90% of *trans*-$\Delta^{1:2}$-octahydronaphthalene (VII) and 10% of the $\Delta^{1:9}$-isomeride (VIII). The *p*-toluenesulphonate, m.p. 98°, of *trans*-decahydro-α-naphthol, m.p. 63°, similarly affords (VII), whilst the *p*-toluenesulphonate, m.p. 96°, of *cis*-decahydro-α-naphthol, m.p. 93°, yields (VIII). Thermal decomp. of the corresponding xanthates gives approx. 4 : 1, 1 : 4, and 9 : 1 mixtures, respectively, of (VII) and (VIII). *trans*-Δ^2-Octahydronaphthalene, b.p. 62°/22 mm., new m.p. −14° [oxidised (alkaline $KMnO_4$) to *trans-cyclo*hexane-1 : 2-diacetic acid], is obtained from the *p*-toluenesulphonates, m.p. 110° and 66°, of *trans*-decahydro-β-naphthol, m.p. 53° and 75°, respectively, with EtOH–NaOEt or $Pr^{\beta}OH$–$NaOPr^{\beta}$. In many of these reactions with NaOAlk a little free decahydronaphthol and alkyl ether are also formed (cf. following abstract). Borneol *p*-toluenesulphonate with EtOH–NaOEt gives mainly borneol. Ozonolysis of menthenes of α +78° to +104° in AcOH at 0° affords mainly active "hydroxymenthylic acid" (*semicarbazone*, m.p. 153°, $[\alpha]_D^{21}$ +4·6° → +8° in 10% Na_2CO_3). An

inactive *semicarbazone*, m.p. 163°, is obtained from menthenes of α ~30°. H. B.

Walden inversion. V. Walden inversion in the formation of ethers. W. Hückel and H. Pietrzok (Annalen, 1940, **543**, 230—239; cf. A., 1940, II, 135).—*l*-Menthyl chloride (I) and boiling EtOH + $CaCO_3$ give some menthene but no menthyl Et ether; with MeOH + $CaCO_3$ at 180—190° (autoclave)/65 hr., a 27 : 73 mixture of *trans*-Δ^2- and Δ^3-menthene and a smaller amount of a 2 : 3 mixture of *l*-menthyl and *d*-neomenthyl Me ether are formed. No ether is obtained from (I) and EtOH–NaOEt but *l*-menthyl *p*-toluenesulphonate gives (cf. A., 1939, II, 120) small amounts of *l*-menthol and *d*-neomenthyl Et ether, b.p. 83—84°/14 mm., α_D +26·05°. Borneol, α_D +4·6°, yields an inactive *p-toluenesulphonate*, m.p. 80·5°, which with boiling EtOH + $CaCO_3$ affords camphene and a smaller amount of camphene hydrate Et ether, b.p. 86—89°/14 mm. The decahydro-β-naphthyl Et, b.p. 112°/15 mm., and Pr^{β} ethers, b.p. 114°/15 mm., obtained (cf. A., 1940, II, 227) with *trans*-Δ^2-octahydronaphthalene from the *p*-toluenesulphonate of *trans*-decahydro-β-naphthol, m.p. 53°, are both cleaved by NaEt to *trans*-decahydro-β-naphthol, m.p. 75°, showing that complete Walden inversion has occurred in their formation. Reaction mechanisms are discussed. H. B.

Fenchene series. X. Isomerisation of α-fenchene. G. Komppa and G. A. Nyman (Annalen, 1940, **543**, 111—118; cf. A., 1938, II, 371).—Short treatment (7—15 min.) of α-fenchene (I) (*dl*-form used at its b.p.) with $KHSO_4$ gives β- (II) and γ-fenchene (III); the formation of little or no (I) from fenchyl alcohol and $KHSO_4$ (or other acidic reagents) is thus partly due to the foregoing isomerisation. Dehydration of 2-methyl-α-fenchocamphorol by distillation affords (I) but $KHSO_4$ at 150—160° (short time) gives (II) and (III). Contrary to Wallach (A., 1899, i, 65), active (II) ("*D*-*d*-fenchene"), which contains a variable amount of (III), is not converted by EtOH–H_2SO_4 into pure *l*-(I) ("*D*-*l*-fenchene"); 2N-H_2SO_4 or $KHSO_4$ in boiling EtOH gives *l*-(I), *l*-methylsantene, and *iso*fenchol Et ether. Structures are proved by oxidation [except for (III) which gives an adduct with PhN_3]. H. B.

Bornyl chloride and its isomerides. I. V. I. Liubomilov, B. N. Rutovski, and T. V. Scheremeteva (J. Gen. Chem. Russ., 1939, **9**, 2067—2074).—The velocity of hydrolysis of bornyl chloride (with KOPh at 200—210°) is ⩾ that of the liquid chlorides obtained by saturation of *d*-pinene with HCl. Fractionation of the mixture of hydrocarbons obtained by heating the mixture of monochlorides with KOPh gives camphene, limonene, dipentene, isomeric fenchenes, and a new dicyclic *terpene*, $C_{10}H_{16}$, b.p. 157·8—158·5°/750 mm., $[\alpha]_D$ −7·87°, the acetate of which is hydrolysed to an *alcohol*, $C_{10}H_{17}$·OH, b.p. 86—88°/10 mm. (*phenylurethane*, m.p. 88—89°). This is oxidised (CrO_3) to a ketone [*oxime*, m.p. 132·5—133°; *semicarbazone*, m.p. 217—219° (decomp.)]. With HCl it gives a solid hydrochloride, which rapidly liquefies at room temp. R. T.

Lupanetriol and its oxidation. E. R. H. Jones and R. J. Heakins (J.C.S., 1940, 456—457).—Lupeol and OsO_4 in Et_2O, followed by decomp. (Na_2SO_3) of the Os complex, give *lupanetriol*, $C_{30}H_{52}O_3$, m.p. 278—284° (decomp.), $[\alpha]_D^{20}$ +2·1° in C_5H_5N (*diacetate*, m.p. 174°, $[\alpha]_D^{20}$ +4·5° in $CHCl_3$), which is oxidised by $Pb(OAc)_4$ to norlupanonol, m.p. 230°, identical with the oxidation product (CrO_3) of lupenyl acetate. This proves the presence of an exocyclic CH_2 in lupeol and betulin. F. R. S.

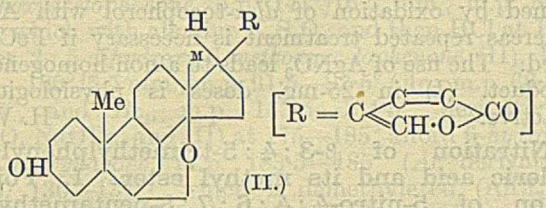
Paprika colouring matter. XI. Isomerisation phenomena. L. Zechmeister and L. von Cholnoky (Annalen, 1940, **543**, 248—257; cf. A., 1937, II, 384).—When a solution of chromatographically homogeneous capsanthin (I) in C_6H_6 is kept at ~20°, some isomerisation of (I) to neocapsanthins *A*, *B*, and *C* occurs; the amounts (determined colorimetrically after chromatographic separation), in the order quoted, after 7 and 13 days are in the ratio 92 : 8 : 0 : 0 and 62 : 16 : 15 : 7, respectively. The neocapsanthins are similarly more labile; *A* in C_6H_6 at room temp./15 days gives a 54 : 46 mixture of (I) and *A*, whilst *B* affords a 50 : 38 : 12 mixture of (I), *A*, and *B*. Isomerisation occurs much more readily in boiling C_6H_6; equilibrium mixtures containing ~80 and ~65% of (I) are formed from (I) and *A*, respectively, after 30—45 min. Similar isomerisation of (I) is effected still more rapidly by 1% of I in C_6H_6 at ~20°. The neocapsanthins are more sol., less cryst., and show absorption at shorter λ; (I), *A*, *B*, and *C* have $[\alpha]_C$ (in C_6H_6) 0±5—10°, +89°, +21±5°, and +27±10°, respectively. Acylation of the OH groups of (I) causes a marked change in the tendency for isomerisation and adsorption. Capsanthin dipalmitate (II), new m.p. 95° (corr.), resembles physalien (A., 1940, II, 138); it is converted in boiling light petroleum (b.p. 70°) into ~35% (equilibrium) of the oily neocapsanthin dipalmitates-I and -II. The same equilibrium mixture is also formed with I and also when a mixture of the dipalmitates-I and -II is used. Capsorubin, $[\alpha]_C$ ±0° in C_6H_6, resembles (I) and gives neocapsorubins *A* and *B*, $[\alpha]_C$ −134° and −69° in C_6H_6, respectively, whilst its dipalmitate affords neocapsorubin dipalmitates-I and -II. H. B.

Carotenoids of purple bacteria. V. Rhodoviolascene. P. Karrer and H. Koenig (Helv. Chim. Acta, 1940, **23**, 460—468; cf. A., 1936, 248, 340, 1561; 1938, II, 277).—Oxidation of rhodoviolascene (I) with $KMnO_4$ yields bixindialdehyde and an incompletely identified dialdehyde which is free from OMe; a revision of the formula suggested tentatively for (I) is therefore essential. H. W.

Constituents of *Nephromopsis stracheyi*, f. *ectocarpitma*, Hue. III. M. Asano and M. Taniguti (J. Pharm. Soc. Japan, 1939, **59**, 216; cf. A., 1935, 863; 1939, II, 97).—Chromotography (Al_2O_3) of acid *B* (*loc. cit.*) results in the isolation of *l*-protolichesteric acid, m.p. 103—106°, $[\alpha]_D^{10}$ −12·4°, converted by CH_2N_2 into the pyrazoline derivative, $C_{21}H_{36}O_4N_2$, m.p. 60—61°, $[\alpha]_D^{12}$ −288·2°. H. W.

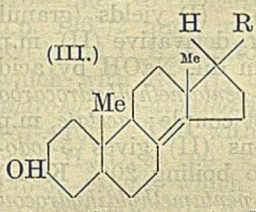
Constituents of "senso." X. Isomeric anhydrogamabufotalins. H. Kondo and S. Ohno

(J. Pharm. Soc. Japan, 1939, **59**, 186—189; cf. A., 1939, II, 438).—The action of 5% H_2SO_4–EtOH on gamabufotalin (I) gives a *compound*, $C_{24}H_{32}O_4,H_2O$, m.p. 125—127° (decomp.), which passes at 110°/high vac. into anhydrogamabufotalin (II) of m.p. 204°.



(II.)

Dry HCl in EtOH–Et_2O converts (I) into anhydrogamabufotalin (III) of m.p. 260°, with small amounts of a chlorinated material. Conc. H_2SO_4 and (I) at room temp. give a non-cryst. product from which (II) and (III) can be extracted. (II) yields a non-cryst. acetate but a cryst. (*mono*-)p-*nitrobenzoate*. The amorphous *acetate* and p-*nitrobenzoate* of (III) are diacyl compounds. Isomerisation of (II) to (III) is therefore accompanied by the formation of a new *sec.* OH. The spectra of (II) and (III) show a max. absorption at 290—300 mμ. so that the unsaturated δ-lactone has remained intact. Catalytic hydrogenation of (II) and (III) results in the absorption of ~4 H_2 with production of the corresponding acids, $C_{24}H_{40}O_4$, m.p. 210—212° [from (II)] and m.p. 199—201° [from (III)], which are isomeric with dihydroxycholanic acid. The neutral compounds which are obtained with the acids and their acyl derivatives are non-cryst. but the *p*-nitrobenzoate derived from (II) is a diacyl and that from (III) is a monoacyl derivative. It is very probable that (II) has an oxide ring between a *tert.* and a *sec.* OH of the sterol nucleus and that during conversion into (III) with opening of the oxide ring the elimination of the *tert.* OH takes place as 1 H_2O. (II) and its hydrogenation product do not contain a double linking in the sterol nucleus and can give only monoacyl derivatives. The position and configuration of the OH on the sterol nucleus is not clearly defined. Since cinobufagin and bufotalin acetate after hydrolysis give only monoacyl derivatives, the products of their hydrolysis probably contain an oxide ring. H. W.



Configurations of the $C_{(2)}$ and $C_{(3)}$ hydroxyl groups in gitogenin and digitogenin. K. Ganapathi (Current Sci., 1940, **9**, 18—19; cf. A., 1940, II, 14; Noller, A., 1939, II, 546; Marker *et al.*, *ibid.*, 548).—Assuming the pptn. with digitonin to have the same significance for the steroid sapogenins as for the sterols (Noller), it is to be concluded that OH at $C_{(3)}$ in gitogenin (I) and digitonin (II) is of the β-configuration, *i.e.*, *cis* to Me at $C_{(10)}$. By the other OH at $C_{(2)}$ occupying the two possible positions *cis* and *trans* with reference to Me at $C_{(10)}$ two forms are possible in which the two OH (which are *cis* to each other in both forms) are unsymmetrical or symmetrical respectively about the plane of the C atoms 2, 3, 5, and 9. (These two forms correspond with those of *B* and *A* respectively of 2 : 3-dihydroxy-*trans*-decahydronaphthalene.) By analogy with the above from *B*, the sapogenins would be expected to isomerise to the *trans*-form on treatment with acid if these OH possessed the unsymmetrical configuration. Since this has not been observed it is concluded that in (I) and (II) the OH at $C_{(3)}$ and $C_{(2)}$ (which are in *cis* positions to each other) are *cis* and *trans* respectively with respect to Me at $C_{(10)}$. H. W.

Saponins and sterols. XIV. Anhydro-compounds of ursolic acid. K. Fujii and S. Oosumi (J. Pharm. Soc. Japan, 1939, **59**, 237—239; cf. A., 1940, II, 99).—The " chloride " obtained from ursolic acid by PCl_5 is reduced by Zn dust in AcOH to a neutral substance. Me ursolate (I) and PCl_5 give a non-cryst. product, reduced by Zn dust–AcOH to the anhydro-ester, *Me ursylenate*, $C_{31}H_{48}O_2$, m.p. 163—165°, isomerised by Zn–Hg–HCl–AcOH to *Me* iso*ursylenate*, m.p. 164—167°, and hydrolysed by NaOH–KOH–EtOH–H_2O (1 : 2 : 16 : 4) at 145—150° to *ursylenic acid* (II), m.p. 266—268° (unchanged by Zn–Hg–HCl–AcOH). Me oleanolate, (I), and the Me ester of sanguisorbigenin are similarly hydrolysed. H_2–Pd–C reduces (II) to *ursenic acid*, $C_{30}H_{48}O_2$, m.p. 203—205° (*Me* ester, m.p. 138—140°). R. S. C.

Pachymic acid, a new constituent of " Bukuryo " (*Poria cocos*, Wolf.). I. S. Nakanishi, M. Yamamoto, and H. Ikeda (J. Pharm. Soc. Japan, 1939, **59**, 273—276).—An ether extract of " Bukuryo " (*P. cocos* = *Pachyma Hoelen*, Rumph; a Chino-Japanese drug) gives *pachymic acid*, $C_{30}H_{44}O_5$, m.p. 300° (*acetate*, m.p. 225°; *Me* ester, m.p. 175°, and its *acetate*, m.p. 155°), monobasic and containing one lactone group, one double linking, and one OH. A. T. P.

Hydroxylation of furan ring. Y. Obata (J. Agric. Chem. Soc. Japan, 1940, **16**, 187—191).—Pyromucic acid tetrabromide with moist Ag_2O gives an acidic substance which easily decomposes into $H_2C_2O_4$ and a resin. Oxidation with $KMnO_4$ gives 2 mols. of $H_2C_2O_4$. Since oxidation with $Pb(OAc)_4$ yields $CHO{\cdot}CO_2H$ it is concluded the substance contains the grouping $CO_2H{\cdot}CH(OH){\cdot}CH(OH){\cdot}$. J. N. A.

Reduction of a mixture of benzaldehyde and crotonaldehyde. Z. C. Glacet (Compt. rend., 1940, **210**, 479—480).—PhCHO and $CHMe{:}CH{\cdot}CHO$ with Mg–AcOH give 5-*hydroxy*-2-*phenyl*-3-*methyl*- or 3-*hydroxy*-2-*phenyl*-5-*methyl*-2 : 3 : 4 : 5-*tetrahydrofuran* (I), b.p. 105—108°/0·5 mm. [*Ac* derivative (II), b.p. 112°/0·6 mm.]. (II) when heated at 150—175°/40 mm. pressure, or (I) when dehydrated with $CuSO_4$ (poor yield), gives 2-*phenyl*-3-*methyl*-2 : 3-*dihydro*- or 2-*phenyl*-5-*methyl*-4 : 5-*dihydro-furan*, b.p. 99—100°/13 mm. J. L. D.

Bromination of pyromucic acid. Y. Obata (J. Agric. Chem. Soc. Japan, 1940, **16**, 184—186).—Pyromucic acid with Br vapour or with Br in Et_2O at 0° gives only δ-bromopyromucic acid; with dry Br below 0° it yields pyromucic acid tetrabromide, m.p. 159·5—160° (decomp.). J. N. A.

Reaction of bromine with furfuraldehyde and related compounds. E. E. Hughes and S. F.

ACREE (J. Res. Nat. Bur. Stand., 1940, **24**, 175—180). —The mechanism of the reaction of Br in aq. solution with equimols. of furfuraldehyde (I), methylfurfuraldehyde (II), or furoic acid (III) is discussed. With (I) and (III) there is no decrease in acidity at any time during the reaction, but with (II), >2 equivs. of acid (methylfuroic or other acid) are formed per mol. of Br consumed. Equimols. of (I) and Br in H_2O at 0° give a compound which affords a (?) bisphenylhydrazone, m.p. 155°, of a hydroxy- or keto-dihydrofurfuraldehyde; the reaction consists in addition of 2 OH to a positive double linking and formation of 2 equivs. of HBr. With the addition of minor side reactions, (II) and (III) behave similarly to (I). A. T. P.

2-Furfurylpropylamine and *di*-2-furfuryl *tert.* amines. J. E. ZANETTI and J. T. BASHOUR (J. Amer. Chem. Soc., 1940, **62**, 742—743).—Addition of the appropriate furfurylalkylamine to 2-furfuryl bromide in Et_2O with some cooling gives ~80% of *di*-2-*furfuryl*-*methyl*-, b.p. 100—102°/5 mm. (153—154°), -*ethyl*-, b.p. 109—110°/5 mm. (149—151°), -n-*propyl*-, b.p. 115—117°/5 mm. (147—148°), -n-*butyl*-, b.p. 126—128°/5 mm. (105—106°), and -n-*amyl*-, b.p. 137—139°/5 mm. (103—105°), -*amine* and NN-*di*-2-*furfurylaniline*, m.p. 31—32°, b.p. 163—167°/5 mm. (137—141°), figures in parentheses being m.p. of the *hydrochlorides*. 2-*Furfuryl*-n-*propylamine*, b.p. 80—81°/20 mm. (*hydrochloride*, m.p. 138—140°), is prepared (method: A., 1940, II, 19). R. S. C.

Lichen pigments of the pulvic acid series. VI. Synthesis of atromentic acid. M. ASANO and S. HUZIWARA (J. Pharm. Soc. Japan, 1939, **59**, 284—286; cf. A., 1935, 1238).—*pp'*-Dimethoxydiphenylketipinodinitrile (I) and HI (*d* 1·7) in AcOH give atromentic acid (II), converted by Ac_2O–H_2SO_4 into the Ac_2 derivative, m.p. 270—271°, of the lactone (cf. Kögl *et al.*, A., 1928, 1250, 1251). (I) and 60% H_2SO_4–AcOH give *pp'*-dimethoxypulvic anhydride (III), m.p. 266—268°, and some corresponding acid, m.p. 212°; the latter is also obtained from the Et ester, m.p. 160° [from (I)–H_2SO_4–EtOH]. (III) and HI–AcOH give (II). A. T. P.

Lichen pigments of the pulvic acid series. VII. Reduction of vulpic acid. M. ASANO and Y. ARATA (J. Pharm. Soc. Japan, 1939, **59**, 286—290; cf. A., 1935, 1238).—Vulpic acid (I) and Na–Hg (CO_2) afford Me dihydrocornicularate, m.p. 67°, and *dihydro*- (II), m.p. 194—196° (*benzoate*, m.p. 138—139°), and iso*dihydro-vulpic acid* (III), m.p. 123—127°. Boiling aq. $Ba(OH)_2$ and (II) or (III) give *dihydropulvic acid* (IV), m.p. 208—210°, converted by Ac_2O into *cornicularlactone carboxylic acid*, m.p. 218—219° [*Me* ester (V), m.p. 170—172°]. Distillation of (IV) at 210°/6 mm. gives *cornicularlactone* (VI), m.p. 136—136·5°. (V) and Na–Hg (CO_2) give a H_2-derivative [boiling aq. $Ba(OH)_2$ gives phenylsuccinic acid] and *Me* α*δ*-*diphenyladipate*, m.p. 139—142° (*acid*, m.p. 247—250°). With Na–Hg (CO_2) (VI) gives α*δ*-diphenylvalerolactone and with Zn–AcOH dihydro-cornicularlactone and -cornicularic acid. Vulpic acid absorbs H_2 (Pd–C) slowly to give (II). Pulvinone and Na–Hg (CO_2) give dihydropulvinone, m.p. 215—219° (benzoate, m.p. 140—141°) (cf. Claisen *et al.*, A., 1895, i, 373). A. T. P.

α-Tocopherolquinone. P. KARRER and A. GEIGER (Helv. Chim. Acta, 1940, **23**, 455—459).—Homogeneous α-tocopherolquinone (I) is readily obtained by oxidation of *dl*-α-tocopherol with $AuCl_3$ whereas repeated treatment is necessary if $FeCl_3$ is used. The use of $AgNO_3$ leads to a non-homogeneous product. (I) in 25-mg. doses is physiologically inactive. H. W.

Nitration of β-3 : 4 : 5-trimethylphenyl*iso*valeric acid and its methyl ester. I. Formation of 5-nitro-4 : 4 : 6 : 7 : 8-pentamethyldihydrocoumarin. L. I. SMITH and W. W. PRICHARD (J. Amer. Chem. Soc., 1940, **62**, 780—784).—3 : 4 : 5-$C_6H_2Me_3$·CMe_2·CH_2·CO_2Me and KNO_3–H_2SO_4–$CHCl_3$ at −15° to 5° give 53% of 5-*nitro*-4 : 4 : 6 : 7 : 8-*pentamethyldihydrocoumarin* (I), m.p. 152·5—153° [also obtained in 20% yield from the corresponding acid by HNO_3 (*d* 1·6)], and 45% of a *substance*, $C_{15}H_{20}O_6N_2$, m.p. 125—125·5°. (I) yields (granulated Zn–AcOH–H_2O) the 5-NH_2-derivative (II), m.p. 125—125·5°, which, pptd. from dil. NaOH by acid, gives 5-*hydroxy*-4 : 4 : 6 : 7 : 8-*pentamethylhydrocarbostyril*, m.p. 193—194° (does not couple; *acetate*, m.p. 207—208°). By diazo-reactions (II) gives 5-*iodo*-, m.p. 131·5—132·5° (loses I to boiling 20% KOH), and 5-*hydroxy*-4 : 4 : 6 : 7 : 8-*pentamethyldihydrocoumarin*, m.p. 207—208° (*Me ether*, m.p. 132—132·5°, resists further methylation, benzoylation, and fission by 20% KOH). R. S. C.

Pyrone series. Attempted oxidation of chromanones with selenium dioxide. I. D. CHAKRAVARTI and J. DUTTA (J. Indian Chem. Soc., 1939, **16**, 639—644).—Condensation of the appropriate phenol with Cl·$[CH_2]_2$·CO_2H in KOH gives the phenoxypropionic acid, cyclised in C_6H_6 with P_2O_5. The following are described: β-(p-*chloro*-, m.p. 138—139°, β-(o-*chloro*-, m.p. 108—109°, β-(p-*nitro*-, m.p. 118—119°, β-(o-*nitro*-, m.p. 121—122°, β-(o-*methyl*-, m.p. 94—95°, and β-(*p*-methyl-phenoxy)-, m.p. 146°, and β-(2)-*naphthoxy*-, m.p. 144—145°, and β-(1)-naphthoxy-propionic acid, m.p. 147—148°; 6-*chloro*-, m.p. 106° (3-*veratrylidene* derivative, m.p. 151—152°), 8-*chloro*-, m.p. 65° (3-*veratrylidene* derivative, m.p. 110—111°), 6-*nitro*-, m.p. 176—177° (3-*veratrylidene* derivative, m.p. 190—191°), 8-*nitro*-, m.p. 126—127° (3-*veratrylidene* derivative, m.p. 179—180°), β-*naphtha*-, b.p. 185—187°/9 mm. [*semicarbazone*, m.p. 227° (decomp.)], α-naphtha-, m.p. 104° (3-*veratrylidene* derivative, m.p. 169—170°), 8-*methyl*-, 125—130°/9 mm. [*semicarbazone*, m.p. 230—231° (decomp.)], and 6-methyl-chromanone, b.p. 118—126°/6 mm. (3-*veratrylidene* derivative, m.p. 131—132°). The chromanones are not oxidised with SeO_2 to chromones, although the flavanones and chalkones are oxidised with SeO_2 to the flavones. 5-*Chloro*-2-*hydroxy*-3′ : 4′-*dimethoxychalkone*, m.p. 174°, is oxidised to 6-*chloro*-3′ : 4′-*dimethoxyflavone*, m.p. 194°, and the 3-*chloro*-*chalkone*, m.p. 163—164°, similarly affords the 8-*chloro*-*flavone*, m.p. 110° (decomp.). 3-*Nitro*-2-*hydroxy*-3′ : 4′-*dimethoxy*-5-*methylchalkone*, m.p. 175°, yields 8-*nitro*-3′ : 4′-*dimethoxy*-6-*methylflavone*, m.p. 244—245° (decomp.). F. R. S.

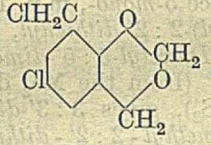
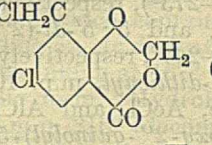
Syntheses of 5 : 6- and 5 : 8-dihydroxyflavone and constitution of primetin. Z. Horii (J. Pharm. Soc. Japan, 1939, **59**, 209—214).—Primetin is shown to be 5 : 8-*dihydroxyflavone* (I). 1 : 2 : 6-$C_6H_3Ac(OH)_2$ is converted by CH_2N_2 in Et_2O into 2-*hydroxy*-6-*methoxyacetophenone*, b.p. 141°/16·5 mm., m.p. 57—58°, which with alkaline $K_2S_2O_8$ and then HCl at 100° gives 2 : 5-*dihydroxy*-6-*methoxyacetophenone* (II), b.p. 155—160°/5·5 mm., m.p. 91·5—92·5° (*Ac*$_2$, m.p. 66·5—67·5°, and *Bz*$_2$, m.p. 153·5—154·5°, derivatives). Bz_2O, NaOBz, and (II) at 175—185° afford 6-*hydroxy*-5-*methoxyflavone*, m.p. 183·5—185° (*Ac* derivative, m.p. 136—137°), which is demethylated ($AlCl_3$ in $PhNO_2$ at 100° or by 20% HCl or HI) to 5 : 6-*dihydroxyflavone* (III), m.p. 189—191° (*Ac*$_2$ derivative, m.p. 165—166·5°). Alternatively (II) is completely methylated to 2 : 5 : 6-*trimethoxyacetophenone* (IV), b.p. 163·5°/11 mm., which is condensed with EtOBz and Na and then hydrolysed by HI to (III). (IV) is partly demethylated by NH_2Ph,HI and NH_2Ph at 120—130° to 6-*hydroxy*-2 : 5-*dimethoxyacetophenone*, b.p. 136°/2 mm., m.p. 61·5—62·5°, transformed by BzCl and C_5H_5N into the *benzoate*, m.p. 120—121°, which with $NaNH_2$ in dry PhMe at 100° gives 6-*hydroxy*-2 : 5-*dimethoxy*-ω-*benzoylacetophenone*, m.p. 167—168°. This with NaOAc and glacial AcOH, or conc. H_2SO_4 at 100°, gives 5 : 8-*dimethoxyflavone*, m.p. 145·5—146·5°, which is unaffected by boiling 20% HCl but is partly demethylated by $AlCl_3$ in boiling CS_2 to 5-*hydroxy*-8-*methoxyflavone*, m.p. 210° (*acetate*, m.p. 176°), which does not depress the m.p. of the Me ether of (I). H. W.

Flavones, flavanones, and flavonols derived from hydroxyquinol. G. Bargellini and G. B. Marini-Bettolo (Gazzetta, 1940, **70**, 170—178).—1 : 2 : 4 : 5-$C_6H_2Ac(OMe)_3$ with boiling conc. HCl gives 2 : 1 : 4 : 5-OH·$C_6H_2Ac(OMe)_2$ (I). With PhCHO in EtOH–KOH, followed by CO_2, (I) gives 2-*hydroxy*-4 : 5-*dimethoxychalkone* (II), m.p. 98°, and, especially when the amount of KOH and the temp. are increased, 6 : 7-*dimethoxyflavanone* (III), m.p. 170—171°, also obtained by heating (II) in dil. HCl–EtOH. When heated with dil. KOH and treated with CO_2, (II) gives 6 : 7-dimethoxyflavone. With H_2O_2 in EtOH–KOH, (II) or (III) yields 6 : 7-*dimethoxyflavonol*, m.p. 198°, which with HI gives a red product. With anisaldehyde, (I) similarly gives 2-hydroxy-4 : 5 : 4′-trimethoxychalkone (cf. Bargellini *et al.*, A., 1911, i, 855) and 6 : 7 : 4′-*trimethoxyflavanone*, m.p. 154°. SeO_2 in C_5H_{11}·OH oxidises (IV) to 6 : 7 : 4′-trimethoxyflavone, whilst H_2O_2 yields 6 : 7 : 4′-*trimethoxyflavonol*, m.p. 230°, with (in presence of excess of H_2O_2) 2 : 4 : 5 : 1-OH·$C_6H_2(OMe)_2$·CO_2H. With veratraldehyde, (I) gives, by similar methods, 2-*hydroxy*-4 : 5 : 3′ : 4′-*tetramethoxychalkone*, m.p. 152°, and 6 : 7 : 3′ : 4′-*tetramethoxy-flavanone*, m.p. 161°, -*flavone*, m.p. 219°, and -*flavonol*, m.p. 228°, and with piperonal, 2-*hydroxy*-4 : 5-*dimethoxy*-3′ : 4′-*methylenedioxychalkone*, m.p. 189°, and 6 : 7-*dimethoxy*-3′ : 4′-*methylenedioxy-flavanone*, m.p. 176°, -*flavone*, m.p. 250°, and -*flavonol*, m.p. 258°. E. W. W.

Synthesis of derivatives of diphenylene dioxide. XV. α-Keto- (or -hydroxy-)β-(or -γ-)morpholylalkyldiphenylene dioxides. M. Tomita (J. Pharm. Soc. Japan, 1939, **59**, 205—206; cf. A., 1939, II, 442).—Treatment of 2 : 6-di-β-halogeno-α-ketoethyldiphenylene dioxide with morpholine gives 2 : 6-*di*-α-*keto*-β-*morpholinoethyldiphenylene dioxide*, m.p. 195° (*hydrochloride*, m.p. >300°), reduced (Na–Hg or H_2–PtO_2) to 2 : 6-*di*-α-*hydroxy*-β-*morpholinoethyldiphenylene dioxide*, m.p. 202°. The following are obtained analogously : 3 : 7-*dimethyl*-2 : 6-*di*-α-*keto*-, m.p. 171° (*hydrochloride*, m.p. >300°), and -α-*hydroxy*-, m.p. 242°, -β-*morpholinoethyldiphenylene dioxide*; 2 : 6-*di*-α-*keto*-, m.p. 176° (*hydrochloride*, m.p. >280°), and -α-*hydroxy*-, m.p. 199°, -γ-*morpholinopropyldiphenylene dioxide*; 2 : 6-*di*-α-*keto*-, m.p. 184° (*hydrochloride*, m.p. >280°), and -α-*hydroxy*-, m.p. 220—232°, -β-*morpholinopropyldiphenylene dioxide*. The properties of these compounds are similar to those of the piperidino-derivatives (*loc. cit.*). H. W.

Photolysis of rhodamine. E. Baur (Atti X Congr. Internaz. Chim., 1938, **4**, 417).—Anaërobic irradiation of rhodamine (I)-3B, -3G, or -6G adsorbed on colophony (II) sol affords CH_2O. The non-Et-esterified forms of (I) [*e.g.*, (I)G] do not yield CH_2O. The effect is independent of the nature of the alkyl group. (I)G gives CH_2O when (II) is replaced by MeOH, PrOH, and other alcohols, probably owing to ester formation during irradiation. F. O. H.

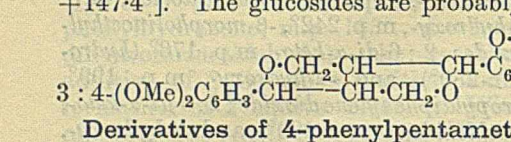
Proof of structure of 6-chloro-8-chloromethyl-1 : 3-benzdioxan by oxidation. C. A. Buehler, B. C. Bass, R. B. Darling, and M. E. Lubs (J. Amer. Chem. Soc., 1940, **62**, 890—894).—Passage of HCl into *p*-C_6H_4Cl·OH in 40% CH_2O–conc. HCl–H_2SO_4 at 40° gives 6-*chloro*-8-*chloromethyl*-1 : 3-*benzdioxan* (I), m.p. 103°, which with CrO_3–AcOH gives

(I.)  (II.) 

6-*chloro*-8-*chloromethyl*-1 : 3-*benzdioxan*-4-*one* (II), m.p. 181—182°, hydrolysed by NaOH to 5-*chloro*-2-*hydroxy*-3-*hydroxymethylbenzoic acid* (III), m.p. 166·5—167° (purple $FeCl_3$ colour). $KMnO_4$ oxidises (I) in boiling AcOH–H_2O to 6-*chloro*-8-*aldehydo*-1 : 3-*benzdioxan*-4-*one* (IV), m.p. indefinite (reduces Tollens' reagent), 5-*chloro*-2-*hydroxy*-3-*aldehydobenzoic acid* (V), +H_2O, m.p. 217—221°, 5-*chloro*-2-*hydroxy*-*isophthalic acid* (VI), +H_2O, m.p. 238—240° (red $FeCl_3$ colour; *Et*$_2$ ester, m.p. 50—51°), and small amounts of (II) and 6-*chloro*-8-*aldehydo*-1 : 3-*benzdioxan* (VII), m.p. 138—138·5° (*phenylhydrazone*, m.p. 152·5—155°). (V) and (VI) are formed by oxidation of (IV), which is formed by way of (II) and (VII). The dioxanone ring of (IV) is easily ruptured : titration with alkali gives (V), NH_2OH,HCl and 10% NaOH give the *oxime*, m.p. 199·5—200·5°, of (V), and H_2–Raney Ni in EtOAc at 2·5 atm. gives (III). *a*-OH·C_6H_4·CO_2H, $CHCl_3$, and aq. NaOH at 80° give 3 : 2 : 1-CHO·$C_6H_3(OH)$·CO_2H, converted by Cl_2 in AcOH into an anhyd. *form*, m.p. 226°, of (V), which with $KMnO_4$ in AcOH–H_2O gives an anhyd. *form*, m.p. 245—246°, of (VI). R. S. C.

Forsythin as isomeride of phillyrin (philyroside). Its constitution. T. Kaku, H. Ri, and

N. Hara (J. Pharm. Soc. Japan, 1939, **59**, 248—255).—Forsythin exists in α-, m.p. 154—155°, and β-forms, m.p. 184—185°, $[\alpha]_D$ (both) +64·6° (63·9°) in C_5H_5N, +48·4° (48·5°) in EtOH, of which the former is identical with phillyrin. CH_2N_2 or Me_2SO_4 converts forsythegenol into *epi*pinoresinol Me_2 ether [$(NO_2)_2$-derivatives, (i) m.p. 230°, $[\alpha]_D$ +119·7°, (ii) *forms*, m.p. 161—162° (unstable) and 180°, $[\alpha]_D$ +147·4°]. The glucosides are probably



R. S. C.

Derivatives of 4-phenylpentamethylene oxide and sulphide.—See B., 1940, 346.

Oxidation of thiophen-sulphur by calcium hypochlorite solutions.—See A., 1940, I, 268.

Thiophen series. LI. Atophan-like derivatives of dithienyl and diphenyl. W. Steinkopf and H. J. von Petersdorff (Annalen, 1940, **543**, 119—128; cf. A., 1939, II, 443).—Isatin (I), *p*-C_6H_4Ph·COMe, and 28% KOH with a little EtOH at 110° (bath) give 2-p-*diphenylylquinoline*-4-*carboxylic acid*, m.p. 289—290°, decarboxylated (soda-lime) to 2-p-*diphenylylquinoline*, m.p. 175—177°. $(C_6H_4$·COMe-$p)_2$ and (I) similarly give 4 : 4′-*di*-(4″-*carboxy*-2″-*quinolyl*)*diphenyl*, m.p. >320°, whence 4 : 4′-*di*-2″-*quinolyldiphenyl*, m.p. 314—315°. 2 : 2′-Dithienyl, AcCl, and $TiCl_4$ in C_6H_6 at 100° (bath) afford 5-*acetyl*-, m.p. 114·5—115·5°, and 5 : 5′-*diacetyl*-2 : 2′-*dithienyl*, m.p. 231—232°, converted (as above) into 5-*mono*-, m.p. 237—238°, and 5 : 5′-*di*-(4″-*carboxy*-2″-*quinolyl*)-2 : 2′-*dithienyl*, amorphous (*Me*$_2$ ester, m.p. 271—273°), respectively, whence 5-*mono*-, m.p. 142—143°, and 5 : 5′-*di*-(2″-*quinolyl*)-2 : 2′-*dithienyl*, m.p. 243—244°, respectively. 3 : 3′-*Diacetyl*-5 : 5′-*dimethyl*-2 : 2′-*dithienyl*, m.p. 109—111° (from the Me_2 derivative, AcCl, and $AlCl_3$ in CS_2), gives 3 : 3′-*di*-(4″-*carboxy*-2″-*quinolyl*)-5 : 5′-*dimethyl*-2 : 2′-*dithienyl*, hygroscopic, m.p. 209° (decomp.), +AcOH, m.p. 222—224°. 2 : 5 : 2′ : 5′-Tetramethyl-3 : 3′-dithienyl, AcCl, and $TiCl_4$ in C_6H_6 afford the 4 : 4′-Ac_2 derivative, m.p. 90—91°; 2-phenylthiophen similarly yields 5-*phenyl*-2-*acetothienone*, m.p. 115—118°, whence 5-*phenyl*-2-4′-*carboxy*-2′-*quinolylthiophen*, m.p. 230—231°. Acetylthiophthen and (I) give 2(or 3)-4′-*carboxy*-2′-*quinolylthiophthen*, m.p. 260—262° (blackening), whence 2(or 3)-2′-*quinolylthiophthen*, m.p. 214—215°. Many of the compounds show luminescence in Hg light. H. B.

Thiophen series. LII. Derivatives of 3-bromo- and 2 : 3-dibromo-thiophen. W. Steinkopf and, in part, H. J. von Petersdorff (Annalen, 1940, **543**, 128—132).—3-Bromothiophen (I), b.p. 154—160° [from 2 : 3-dibromothiophen (II), EtBr, and Mg in Et_2O and subsequent hydrolysis], with $Hg(OAc)_2$ in AcOH at 50—55° and the b.p. gives the 2 : 5-*di*- and 2 : 4 : 5-*tri*-*acetoxymercuri*-derivatives, respectively, converted (usual method) into 3-*bromo*-2 : 5-*di*-*iodo*- (III), m.p. 55—56°, and -2 : 4 : 5-*tri*-*iodo*-*thiophen*, m.p. 156—157°, respectively. An excess of Br rapidly converts (III) into tetrabromothiophen. 3-Bromothiophen-2-sulphonic acid (*amide*, m.p. 163—164°) is formed from (I) and cold $ClSO_3H$. 2 : 3-Dibromo-5-iodothiophen, m.p. 58—58·5° [from (II), HgO, and I in C_6H_6], with Cu-bronze at 240° affords 4 : 5 : 4′ : 5′-*tetrabromo*-2 : 2′-*dithienyl*, m.p. 181° (with Br gives hexabromo-2 : 2′-dithienyl). The di-, tri-, and tetra-chloro-2 : 2′-dithienyl of Eberhard *et al.* (A., 1894, i, 117; 1896, i, 16) are the 5 : 5′-, 3 : 5 : 5′-, and 3 : 5 : 3′ : 5′-derivatives, respectively. H. B.

Some reactions of Δ^{β}-γ-lactones. E. Walton (J.C.S., 1940, 438—442).—The statement of Lukeš *et al.* (A., 1929, 824) that lactones of type $\begin{matrix}CH{:}CR'\\CH_2{\cdot}CO\end{matrix}>O$ (*A*) with amines give not pyrrolidones of type $\begin{matrix}CH_2{\cdot}CH_2\\CO{-}NR\end{matrix}>R'{\cdot}OH$, but open-chain amides, NHR·CO·$[CH_2]_2$·COR′, is incorrect. Their "lævulanilide" obtained from Δ^{β}-angelicalactone (I) (*A*; R′ = Me) and NH_2Ph at 180°, is identical with 2-hydroxy-1-phenyl-2-methyl-5-pyrrolidone (II) (*loc. cit.*), which with Br–H_2O gives the corresponding 1-p-*bromophenyl* compound, m.p. 159—161° (decomp.), also obtained from (I) and *p*-$C_6H_4Br{\cdot}NH_2$ (III). Succinanil with MgMeI in C_6H_6 also gives (II) (mixed m.p.). γ-Phenyl-Δ^{β}-crotonolactone (IV) (*A*; R′ = Ph) with conc. aq. NH_3 gives 2-hydroxy-2-phenyl-5-pyrrolidone (V), and with 33% aq. NH_2Me, NH_2Et, and NH_2Pr^{α} gives 2-*hydroxy*-2-*phenyl*-1-*methyl*- (VI), m.p. 130—135° (decomp.) [also obtained from succinomethylimide (VII) (cf. Lukeš *et al.*, A., 1928, 897)], -1-*ethyl*-, m.p. 85—87°, and -1-n-*propyl*-5-*pyrrolidone*, m.p. 85—86°. These products (in the formation of which there are colour changes from green through blue, violet, and red, to yellow) are all amphoteric, dissolving in 6N-HCl and in 2N-NaOH. In the latter, (V) is decomposed, but (VI) may be refluxed unchanged for 5 min., and its homologues are also stable; the compounds are, however, hydrolysed by aq. HCl or EtOH–HCl to $CH_2Bz{\cdot}CH_2{\cdot}CO_2H$ and NH_2R. With boiling NH_2Ph, (IV) gives 2-*hydroxy*-1 : 2-*diphenyl*-5-*pyrrolidone*, m.p. 148—149°, which with Br–H_2O forms 2-*hydroxy*-2-*phenyl*-1-p-*bromophenyl*-5-*pyrrolidone*, m.p. 166°, also obtained from (III) and (IV). *p*-$C_6H_4Me{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ and Ac_2O at 100° give γ-p-*tolyl*-Δ^{β}-*crotonolactone* (VIII), m.p. 111°, which with conc. aq. NH_3 at 100° gives 2-*hydroxy*-2-p-*tolyl*-5-*pyrrolidone*, m.p. 165—167° (decomp.), previously regarded as an open-chain amide. With 33% aq. NH_2Me, (VIII) gives 2-*hydroxy*-2-p-*tolyl*-1-*methyl*-5-*pyrrolidone*, m.p. (+0·5H_2O) 92—93°, (anhyd.) 132—140° (decomp.), also obtained from (VII) and *p*-$C_6H_4Me{\cdot}MgBr$ in C_6H_6. *p*-$C_6H_4Br{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ with Ac_2O at 100° gives γ-p-*bromophenyl*-Δ^{β}-*crotonolactone*, m.p. (impure) 115—130° (decomp.), which with warm aq. NH_3 and with 33% aq. NH_2Me gives respectively 2-*hydroxy*-2-p-*bromophenyl*-5-*pyrrolidone*, m.p. 169—171° (decomp.), and -1-*methyl*-5-*pyrrolidone*, m.p. 145—148° (decomp.) [also obtained from (VII) and *p*-$C_6H_4Br{\cdot}MgBr$]. Similarly γ-p-*anisyl*-Δ^{β}-*crotonolactone*, m.p. 110—111° (obtained as before) gives 2-*hydroxy*-2-p-*anisyl*-5-*pyrrolidone*, m.p. 133—135°, and -1-*methyl*-5-*pyrrolidone*, m.p. 88—92° [not obtained from (VII)]. The above pyrrolidones are hydrolysed by HCl as before. Attempts to confirm the presence of OH in (VI) were unsuccessful, there being no reaction with Me_2SO_4,

Ac_2O, or PhNCO, and AcCl causing elimination of H_2O to give an unsaturated product. E. W. W.

Derivatives of substituted succinic acids. IV. Action of alkaline sodium hypobromite on some α-alkyl-α′-arylsuccinamides. J. A. McRae and (Miss) N. A. McGinnis (Canad. J. Res., 1940, **18**, B, 90—95).—The NH_4 salt of phenylmethylsuccinic acid when heated at 180° gives *α-phenyl-α′-methylsuccinimide*, m.p. 109°, which with NH_3–EtOH affords the *-amide*, m.p. 224—225°. This amide with NaOBr is converted into 6-phenyl-5-methyldihydrouracil, m.p. 192—195° (lit. 185°), not identical with the corresponding *5-phenyl-6-methyl* compound (I), m.p. 224°. *β-Amino-α-phenylbutyric acid*, m.p. 248°, prepared from Me α-phenylcrotonate and NH_2OH, with KCNO yields β-ureido-α-phenylbutyric acid, which when heated is converted into (I). *β-Cyano-β-phenyl-α-n-hexylpropionic acid*, m.p. 166°, obtained from heptylidenephenylacetonitrile and KCN, is difficult to hydrolyse and the succinic acid is directly converted into *α-phenyl-α′-n-hexylsuccin-imide*, m.p. 52°, by heating the NH_4 salt, and thence with NH_3–EtOH into the *-amide*, m.p. 233° (decomp.). This amide with NaOBr gives *β-phenylureido-α-n-hexylpropionic acid*, m.p. 144—145° (decomp.). *α-Phenyl-α′-benzylsuccin-imide*, m.p. 131°, is converted (NH_3–EtOH) with difficulty into the *-amide*, m.p. 216°, which with NaOBr has given a substance, m.p. 219°, which could not be characterised. F. R. S.

Identification of organic compounds. II. Piperidyl derivatives of aromatic halogenonitro-compounds. (Miss) M. K. Seikel (J. Amer. Chem. Soc., 1940, **62**, 750—756; cf. A., 1940, II, 160).—Conditions are defined for conversion of aromatic halogenonitro-compounds into piperidino-derivatives. The following compounds are described, the piperidino-group being inserted, unless otherwise stated, by replacement of halogen. 1-Chloro-2 : 4-dinitro-5-, m.p. 114—114·5° (lit., 117—118°, 119°), 1 : 3-dibromo-2 : 4-dinitro-5-, m.p. 129—129·5°, 1-*chloro*-4-*nitro*-3-[from 1 : 3 : 4-$C_6H_3Cl(NO_2)_2$ (I) or -$C_6H_3Cl_2{\cdot}NO_2$ (II), 1 : 2 : 3 : 5-$C_6H_2Cl(NO_2)_3$ or -$C_6H_2Cl_2(NO_2)_2$], m.p. 125·5°, 1 : 3-*dichloro*-5-*nitro*-(?)2- [from 1 : 3 : 2 : 5-$C_6H_2Cl_2(NO_2)_2$], m.p. 86·5—87·5°, 1 : 3-*dichloro*-5-*nitro*-4-, m.p. 57—58°, 1-*chloro*-2 : 3-*dinitro*-4- [from 1 : 4 : 2 : 3-$C_6H_2Cl_2(NO_2)_2$], m.p. 91—92°, 1-*chloro*-2 : 5-*dinitro*-4-, m.p. 71·5—72·5°, 1 : 2-*dichloro*-4-*nitro*-3-, m.p. 73—74°, 1 : 3-*dichloro*-4-*nitro*-5-, m.p. 41—42°, 1 : 2-*dichloro*-3 : 5-*dinitro*-6-, m.p. 95—96°, and 1 : 3-*dibromo*-4-*nitro*-5-, m.p. 70—71°, -1′-*piperidinobenzene*; 1-*nitro*-2 : 5- [from (I) or (II)], m.p. 77·5—78·5°, 1-*chloro*-3-*nitro*-4 : 6- [from 1 : 2 : 4 : 5-$C_6H_2Cl_2(NO_2)_2$ or -$C_6H_2Cl_3{\cdot}NO_2$], m.p. 103·5—104° and (+ piperidine) ~125°, 1 : 2-*dinitro*-3 : 5-, m.p. 173—173·5°, 1 : 2-*dinitro*-3 : 6-, m.p. 167—167·5°, 1-*chloro*-3-*nitro*-2 : 6-, m.p. 93·5—94°, 1-*chloro*-4-*nitro*-3 : 5-, m.p. 88·5—89·5°, 1-*chloro*-3 : 5-*dinitro*-2 : 6-, m.p. 188·5—189°, 1-*chloro*-3 : 5-*dinitro*-2 : 4-, *forms*, m.p. 142·5—143° and (stable) 146·5—147·5°, 1-*chloro*-2 : 6-*dinitro*-3 : 5-, m.p. 190°, 1-*bromo*-4-*nitro*-3 : 5-, m.p. 87·5—88°, and 1-*bromo*-2 : 4-*dinitro*-3 : 5-, m.p. 224—225°, *-dipiperidinobenzene*; 1-o-, m.p. 38—39° (hydrochloride, m.p. 210·5—212°), and 1-*m*-nitrobenzylpiperidine, m.p. 10—13° (hydrochloride, m.p. 202·5—205°). *s*-$C_6H_3(NO_2)_3$ and piperidine give an unstable additive compound, m.p. 60—62° (decomp. 110—120°). 1 : 3 : 5-$C_6H_3Cl(NO_2)_2$ dissolves, forming an additive compound, which is not isolated. 1 : 3 : 5-$C_6H_3Cl_2{\cdot}NO_2$, 1 : 2 : 6- and 1 : 4 : 2-$C_6H_3MeCl{\cdot}NO_2$ do not react. R. S. C.

Quinuclidine derivatives.—See B., 1940, 406.

Oxalates of ammonium–pyridine platinum compounds.—See A., 1940, I, 267.

***N*^{1}*N*^{4}-Nicotinoyl derivatives of sulphanilamide.** T. C. Daniels and H. Iwamoto (J. Amer. Chem. Soc., 1940, **62**, 741—742).—N^4-*Nicotinoyl-* (I), m.p. 257—258° (N^1-*Ac* derivative, m.p. 255—256°), and thence N^{1}N^4-*dinicotinoyl-sulphanilamide*, *forms*, m.p. 222° and 248°, are prepared from *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ by nicotinoyl chloride in C_5H_5N at 100° or from nicotinanilide by $ClSO_3H$ (first at <15° and then at 60°) etc. (nomenclature: A., 1938, II, 439). The pharmacological properties of (I) are promising. R. S. C.

Pyridine sulphanilamides.—See B., 1940, 405.

Phenylpyridines.—See B., 1940, 346.

Mechanism of formation of indoxyl *in vivo* from *o*-nitrobenzene derivatives.—See A., 1940, III, 519.

β-Indolylacetic acids.—See B., 1940, 346.

Syntheses in the indole series. I. Synthesis of indolyl-3-glyoxylic acid and of *r*-3-indolylglycine. J. W. Baker (J.C.S., 1940, 458—460).—Mg indolyl iodide and $CO_2Me{\cdot}COCl$ give *Me indolyl-3-glyoxylate* (I), m.p. 224°, which contains a prototropic pentad system, yielding an *Ac* derivative, m.p. 130°, and a *xenylurethane*, shrinking at 167° to a clear liquid at 200°, of the enolic form. Hydrolysis (NaOH) of (I) affords the *acid*, m.p. 216° (decomp.), also obtained either by hydrolysis or treatment with HNO_2 of the *amide*, m.p. 252° (slight decomp.). Methylation (MeOH–Na–MeI) of (I) gives *Me* 1-*methylindolyl-3-glyoxylate*, m.p. 82·5°, and reduction (Al–Hg) yields *Me indolyl-3-glycollate*, m.p. 82·5°. Oximation of (I) affords *oxime-A*, m.p. 174°, and *-B*, m.p. 143°; the former is reduced (Al–Hg in Et_2O) to *Me α-aminoindolyl-3-acetate*, m.p. 118°, which is hydrolysed (NaOH) to r-3-*indolylglycine*, m.p. 221° (decomp.). F. R. S.

***Amanita* toxins. V. Constitution of phalloidine.** H. Wieland and B. Witkop (Annalen, 1940, **543**, 171—183).—Phalloidine (I), $C_{30}H_{39}O_9N_7S$ (cf. Lynen *et al.*, A., 1938, II, 66; method of isolation modified), $[\alpha]_D$ +62·3° in EtOH, is hydrolysed by 30% H_2SO_4 in CO_2 at 100° (bath) to *l*-cysteine (isolated partly as cystine owing to subsequent autoxidation), *l*-alanine, *l*-hydroxyproline *b*, m.p. 241° (decomp.), $[\alpha]_D^{20}$ −57·4° in H_2O (Leuchs *et al.*, A., 1920, i, 85), and l-*hydroxytryptophan* [*α-amino-β-2-keto-2 : 3-dihydro-3-indolylpropionic acid*] (II), m.p. 249—253° (decomp.), $[\alpha]_D^{20}$ +39·2° in N-NaOH. Quant. results indicate that (I) is the hexapeptide derived by loss of $6H_2O$ [(I) does not contain free NH_2 or CO_2H] from 1, 2, 2, and 1 mol., respectively, of the above NH_2-

acids. Hydrolysis of (II) by short treatment with hot aq. $Ba(OH)_2$ gives (probably) *o*-$NH_2{\cdot}C_6H_4{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (couples with β-$C_{10}H_7{\cdot}OH$); (II) gives the Folin–Denis but not the Hopkins–Cole reaction. H. B.

Synthesis of nitrogen ring compounds. XIX. Synthesis of *iso*quinolines having *N*-hetero-ring in 1-position. S. Sugasawa, K. Sakurai, M. Fujisawa, and N. Sugimoto (J. Pharm. Soc. Japan, 1940, **60**, 39—42).—Et quinaldinate and 3 : 4-$(CH_2O_2)C_6H_3{\cdot}CH_2{\cdot}CHMe{\cdot}NH_2$ at ~220° give *quinaldin*-β-3 : 4-*methylenedioxyphenyl*-α-*methylethylamide*, m.p. 125°, cyclised by $POCl_3$ in hot PhMe to 6 : 7-*methylenedioxy*-1-2′-*quinolyl*-3-*methyl*-3 : 4-*dihydro*isoquinoline, m.p. 143°. The corresponding dimethiodide is transformed into the methochloride, which is catalytically reduced to 6 : 7-methylenedioxy-1-2′-1′-methyl-1′ : 2′ : 3′ : 4′-tetrahydroquinolyl-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, characterised as the *dipicrate*, m.p. 214—215°. *Quinaldin*-β-3 : 4-*methylenedioxyphenylethylamide*, m.p. 108°, is similarly cyclised to 6 : 7-*methylenedioxy*-1-2′-*quinolyl*-3 : 4-*dihydro*isoquinoline, m.p. 121°, which gives only resinous products with $C_2H_4Br_2$. Catalytic reduction of 6 : 7-dimethoxy-1-3′-pyridyl-3 : 4-dihydroisoquinoline dimethochloride gives the non-cryst. 6 : 7-dimethoxy-1-1′-methyl-3′-piperidyl-2-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline (*dipicrate*, decomp. 207·5°; platinichloride, decomp. 224°). β-Nicotinhomoveratrylamide is catalytically reduced to 1-*methyl*-3-*piperidylhomoveratrylamide*, m.p. (crude) ~95° (*picrate*, decomp. 230°), cyclised by $POCl_3$ in dry PhMe to non-cryst. 6 : 7-*dimethoxy*-1-1′-*methyl*-3′-*piperidyl*-3 : 4-*dihydro*isoquinoline (*dipicrolonate*, decomp. 243°). *Chloroacet*-β-*methoxy*-β-3 : 4-*methylenedioxyphenyl*-α-*methylethylamide*, b.p. 179°/3·5 mm., from the amine and $CH_2Cl{\cdot}COCl$ in $COMe_2$ at 0°, is transformed by piperidine in C_6H_6 into *piperidinoacet*-β-*methoxy*-β-3 : 4-*methylenedioxyphenyl*-α-*methylethylamide* (*methiodide*, decomp. 197—198°), cyclised by $POCl_3$ in boiling PhMe to 6 : 7-*methylenedioxy*-1-*piperidinomethyl*-3-*methyl*isoquinoline, m.p. 140° (*methiodide*, decomp. 201—202°). H. W.

Hydrogenation under pressure of 6-hydroxyquinoline and its derivatives. K. Miyaki and H. Kataoka (J. Pharm. Soc. Japan, 1939, **59**, 222—224).—6-Hydroxyquinoline is hydrogenated (20% Ni–kieselguhr in abs. EtOH) at 140°/80—100 atm. (initial pressure) to the 1 : 2 : 3 : 4-tetrahydride, m.p. 160°, whereas at 180° the product is the *decahydride*, separated into a solid, m.p. 185°, and a liquid, b.p. 93—98°/0·005 mm., portion. 6-Acetoxyquinoline in *cyclo*hexane at 140° yields the *tetrahydride*, b.p. 130—140°/0·01 mm. 6-Acetoxy-1-benzoyl- in abs. EtOH at 250° is converted into 6-*hydroxy*-1-*hexahydrobenzoyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 210°, whilst 6-*methoxy*-1-*hexahydrobenzoyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 75—76°, is obtained from the corresponding Bz derivative. H. W.

5 : 5-Dimethylhydantoins containing a NRR′ substituent. H. R. Henze and J. W. Magee (J. Amer. Chem. Soc., 1940, **62**, 912—913).—$COMe{\cdot}CH_2{\cdot}NRR'$, KCN, and $(NH_4)_2CO_3$ in 50% EtOH at 55—65° give 68—92% yields of 5-*methyl*-5-N-*methyl*-, m.p. 190°, -*ethyl*-, m.p. 171°, and -*benzylanilinomethylhydantoin*, m.p. 213°, 5-*methyl*-5-N-*benzyl*-N-*methyl*-, m.p. 204°, -*ethyl*-, m.p. 165°, -n-*propyl*-, m.p. 157°, and -n-*butyl*-*aminomethylhydantoin*, m.p. 169°, 5-*methyl*-5-N-o-, m.p. 177°, and -p-*methylbenzyl*-N-*methylaminomethylhydantoin*, m.p. 178°, and 5-*methyl*-5-N-cyclo*hexyl*-N-*methylaminomethylhydantoin*, m.p. 199°. M.p. are corr. R. S. C.

Colour in relation to chemical constitution of the organic salts and metallic derivatives of oximinodiphenylthiohydantoin. S. Dutt and B. M. S. Agarwal (Proc. Indian Acad. Sci., 1940, **11**, A, 96—105).—Protracted action of $NaNO_2$ on 1 : 3-diphenylthiohydantoin in AcOH at room temp. gives unchanged material, an unidentified yellow *substance*, m.p. 245°, and *oximino*-1 : 3-*diphenylthiohydantoin* (I), m.p. 174°. (I) is bright yellow when solid or in solution in non-hydroxylic org. media but gives an intense crimson colour on addition of alkali or org. bases, thus resembling violuric acid. The change is attributed to the conversion of the oximino-ketonic into the nitroso-enolic form: $CS<^{NPh{\cdot}C(:N{\cdot}OH)}_{NPh{\cdot}CO} \rightarrow CS<^{NPh{\cdot}C(NO)}_{NPh{\cdot}C(OH)}$. (I) gives *salts* with NH_2Me, m.p. 120°, $NHMe_2$, m.p. 148°, NMe_3, m.p. 152°, NH_2Et, m.p. 156°, $NHEt_2$, m.p. 179°, NEt_3, m.p. 87°, NH_2Bu^{β}, m.p. 167°, C_5H_5N, m.p. 139°, piperidine, m.p. 158°, nicotine, m.p. 132°; the *K*, m.p. 167°, *Na*, m.p. 188°, and NH_4, m.p. 112°, salts are described. H. W.

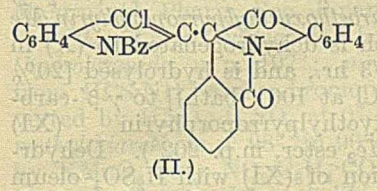
Dicyclic heterocyclic compounds with a hetero-atom common to both cycles. V. Prelog (Arh. Kemiju, 1939, **12**, 97—105).—A review. R. T.

Polarisation in heterocyclic rings with aromatic character. IV. Polarisation in the glyoxaline ring. E. Ochiai and M. Sibata (J. Pharm. Soc. Japan, 1939, **59**, 256—260; cf. A., 1939, II, 451).—2 : 4-Dimethylglyoxaline, PhCHO, and $ZnCl_2$ at 180—185° give 2-*styryl*-4-*methylglyoxaline*, decomp. 147—148° (*picrate*, decomp. 248°). 2-*Styryl*-1 : 1 : 4-*trimethylglyoxalinium iodide*, m.p. 248·5° (corresponding *picrate*, m.p. 166·5°), is obtained from 1 : 1 : 2 : 4-*tetramethylglyoxalinium iodide*, hygroscopic (corresponding *picrate*, m.p. 126·5°), by PhCHO and a little piperidine at 150—165°, but 2-*styryl*-3 : 4-*dimethylthiazolinium iodide*, m.p. 227° (corresponding *picrate*, m.p. 163·5°), is obtained at 100°. 2 : 4-Diphenylglyoxaline and aq. CH_2O at 140—160° give 2 : 4-*diphenyl*-5-*hydroxymethylglyoxaline* (I), decomp. 179°, and 5 : 5′-*methylenedi*-(2 : 4-*diphenylglyoxaline*) (II), $+1{\cdot}5H_2O$, m.p. 256° (*dipicrate*, decomp. 212°). In boiling decahydronaphthalene (I) gives (II) and CH_2O. Hydrogenation of 5-nitro-4-methylglyoxaline in acid gives the unstable 5-NH_2-compound (*CHPh* derivative, m.p. 216°), but hydrogenation in presence of $CH_2(COMe)_2$ gives 4 : 4′ : 6′-*trimethylglyoxalino*-1 : 5-1′ : 2′-*pyrimidine*, $+H_2O$, m.p. 80·5—82° (*picrate*, decomp. 201°). These condensations are anticipated from considerations of resonance. R. S. C.

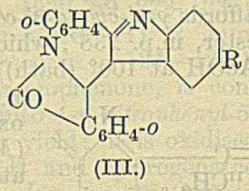
Indigo. V. Benziminazole derivative isomeric with indigo. J. van Alphen (Rec. trav. chim., 1940, **59**, 289—297; cf. A., 1939, II, 285).—2-Methylbenziminazole (I) (*phthalate*, m.p. 190°)

with o-$C_6H_4(CO)_2O$ (II) at 200° gives 2-1′ : 3′-*diketo*-2′-*hydrindylidenebenziminazole*, m.p. >350° (*nitrate*, m.p. 184°), also obtained by boiling (I) with an excess of o-$C_6H_4(CO_2H)_2$. Heating (I) with isatin (III) or acenaphthenequinone gives 3-2′-*benziminazolylmethyleneindoxyl*, m.p. >350°, and 7-*keto*-8-2′-*benziminazolylmethylene*-7 : 8-*dihydroacenaphthene*, m.p. 295°. 2-Ethyl- (*phthalate*, m.p. 197°) and 2-benzyl-benziminazole (IV) (*phthalate*, m.p. 177°) do not condense with (II), but (IV) and (III) at 180° give 3-α-2′-*benziminazolylbenzylideneindoxyl*, +EtOH, m.p. 264°. R. S. C.

Benzoyl derivatives of indigotin. V. H. DE DIESBACH, O. JACOBI, and C. TADDEI (Helv. Chim. Acta, 1940, **23**, 469—484; cf. A., 1937, II, 78, 120).—Indigotin (I) is converted by hot BzCl into the substance (II) (Dessoulavy, Diss., Neuchâtel, 1909),

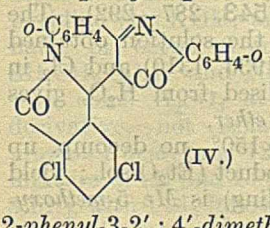


(II.)



(III.)

which is transformed by boiling NH_2Ph into o-NHBz·C_6H_4·CONHPh, m.p. 280°, 2 : 3-diphenylquinazolone, m.p. 159°, the *quinoline* derivative [(III), R = H], m.p. 255—256°, and a mixture of bases which gives a *Bz*$_2$ derivative, $C_{41}H_{27(29)}O_3N_3$, m.p. ~300°, hydrolysed (conc. H_2SO_4) to a mixture of bases, $C_{27}H_{19(21)}ON_3$. This when diazotised and coupled with β-$C_{10}H_7$·OH gives a *dye*, $C_{37}H_{26(24)}O_2N_4$, m.p. 215—255°. When the diazo-solution is kept it yields a *ppt.*, $C_{27}H_{20}O_3N_2$, m.p. >300°, the mother-liquors from which contain a stable diazo-salt which couples with β-$C_{10}H_7$·OH to the *product*, $C_{37}H_{26(24)}O_3N_4$, m.p. 276°. The mixed bases and their derivatives are resistant to alkali at 400° and are either indifferent to oxidising agents or yield only o-$C_6H_4(CO_2H)_2$. Similar products are not formed from other primary aromatic amines. (II) and boiling p-C_6H_4Me·NH_2 give a mixture separated by boiling EtOH–NaOEt into a compound [(III), R = Me], m.p. 264°, and an *acid*, $C_{23}H_{18}O_2N_2,H_2O$, m.p. 210°, re-cyclised by heat or by solvents of high b.p. to the *compound*, $C_{23}H_{16}ON_2$, m.p. 263°. (II) and boiling p-C_6H_4Cl·NH_2 yield the quinoline *derivative* [(III), R = Cl], m.p. 293°, which loses Cl and suffers profound decomp. with alkali at 400°. m-C_6H_4Me·NH_2 and (II) afford *benzoylanthranil*-m-*toluidide*, m.p. 224°, which passes at 330° into 2-*phenyl*-3-m-*tolyl*-4-*quinazolone*, m.p. 139°. Similarly (II) and β-$C_{10}H_7$·NH_2 at 200° afford *benzoylanthranil*-β-*naphthalide*, m.p. 258°, which passes at 300° into 2-*phenyl*-3-2′-*naphthyl*-4-*quinazolone*, m.p. 184°. (II) appears sometimes unchanged by boiling o-C_6H_4Me·NH_2, sometimes converted into ill-defined compounds; α-$C_{10}H_7$·NH_2 behaves similarly. Boiling *as-m*-xylidine and (II) give a *compound*, $C_{24}H_{16}ON_2$, m.p. 278°, and 2-*phenyl*-3-2′ : 4′-*dimethylphenyl*-4-*quinazolone*, m.p. 130° (*picrate*, m.p. 202°). (II) passes slowly at ~250° into BzCl and Ciba-yellow. (I) and o-C_6H_4Cl·COCl yield a mixture, m.p. 258°, converted by conc. H_2SO_4 into Höchst yellow U and a further similar dye with an additional Cl in the Ph nucleus. (I) and 2 : 4 : 6 : 1-$C_6H_2Cl_3$·COCl give *dichlorinated Höchst yellow U* (IV), m.p. >300°. H. W.

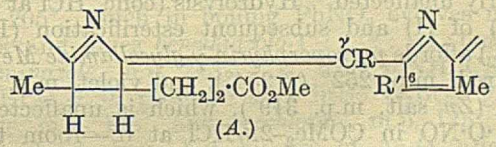


(IV.)

1 : 1′-Di(methylthiol)-3 : 3′-bis*iso*indolenylidene.—See B., 1940, 349.

Constitution of yeast ribonucleic acid. Guanineuridylic acid. J. M. GULLAND (Chem. and Ind., 1940, 321—324).—A reply to Tipson *et al.* (A., 1940, II, 27) concerning the entity of guanineuridylic acid. H. W.

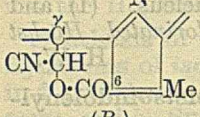
Chlorophyll. XCV. Partial syntheses in the chlorin and purpurin series. H. FISCHER and M. STRELL (Annalen, 1940, **543**, 143—161).—Purpurin 3 (=γ-formylpyrrochlorin) Me ester (I) (A., 1937, II, 470) with AcOH–HI at 70°, and subsequent reoxidation of the leuco-compound, gives γ-formylpyrroporphyrin Me ester, m.p. 246° (cf. A., 1940, II, 109); reduction with H_2–Pd in $COMe_2$ affords *mesopurpurin* 3 *Me* ester, m.p. 155°. When (I) is shaken with a very large excess of 30% MeOH–KOH, γ-formyl-2-vinylpyrroporphyrin [*Me* ester, m.p. 208° (cryst. *oxime*)] is formed; short treatment with boiling conc. MeOH–KOH gives 2-vinylpyrroporphyrin. The amorphous oxime, m.p. 145°, of (I) is dehydrated by boiling Ac_2O + anhyd. K_2CO_3 (? NaOAc) to *γ-cyanopyrrochlorin Me* ester (II) (*A*, R = CN, R′ = H), m.p. 205°,



(*A*.)

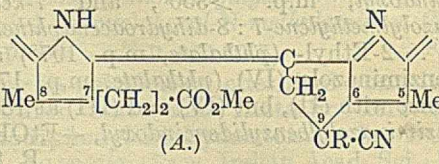
converted (HI) into pyrroporphyrin and γ-cyanopyrroporphyrin (III). The CN of (II) could not be hydrolysed; boiling 20% MeOH–KOH for 1 hr. affords (III). Catalytic reduction of (II) in AcOH gives first (30 hr.) the meso-compound and then decomp. products. Purpurin 7 Me_3 ester (IV), NH_2Et, and anhyd. K_2CO_3 in C_5H_5N for 4 days (shaking) give a complex mixture of chlorins (a *compound*, m.p. 201°, is extracted by 10% HCl after treatment with Et_2O–CH_2N_2); purpurin 5 Me_2 ester (V) reacts similarly but (I) is largely unchanged. $CH_2(CN)_2$ and (I) in C_5H_5N at 100° (bath) yield *γ-β′β′-dicyanovinylpyrrochlorin Me* ester [*A*, R = CH:C(CN)$_2$, R′ = H], m.p. 222°, decomposed by AcOH–HI. $CH_2(CN)_2$, (V), and anhyd. Na_2CO_3 in C_5H_5N at room temp./2 days give the *compound*, $C_{38}H_{38}O_4N_6$ [*A*, R = CH:C(CN)$_2$, R′ = CO_2H (note hydrolysis)], m.p. >320°, converted by hot C_5H_5N into a compound resembling (spectrum) rhodochlorin, by MeOH–KOH into vinylrhodoporphyrin, and by AcOH–HI into a substance similar (spectrum) to chloroporphyrin e_5 Me_1 ester (VI); the neopurpurin reaction (A., 1939, II, 288; cf. A., 1940, II, 141) is negative. An extremely light-sensitive substance (extraction no. 22) is obtained from (IV), $CH_2(CN)_2$, and NH_2Et in dioxan at 100° (bath). Anhyd. HCN and (V) in $CHCl_3$–C_5H_5N + anhyd. K_2CO_3 give, after 5—6 days at room temp. and extraction of the Et_2O solution

with 21% HCl (whereby hydrolysis of the original 6-CO_2Me may occur), the lactonic *nitrile* (as *B*), $C_{35}H_{35}O_4N_5$, m.p. >300°, converted by AcOH–HI into first a substance resembling (VI), and then rhodoporphyrin. Mesopurpurin 5 and HCN react similarly. The *cyanohydrin*, $C_{34}H_{37}O_3N_5$, which eliminates HCN when heated, from (I) in C_5H_5N + anhyd. K_2CO_3, is hydrolysed (MeOH–HCl at room temp.) to ? *Me_2 pyrrochlorin-γ-glycollate* (*A*, R = OH·CH·CO_2Me; R′ = H), m.p. 243° (can be benzoylated; free acid is unstable and loses HCO_2H when reduced to the meso-derivative), ? *Me pyrrochlorin-γ-glycollamide*, m.p. 215°, and γ-formylpyrroporphyrin. HCN and (IV) do not react. H. B.

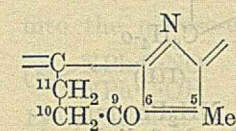

(*B.*)

Chlorophyll. XCVI. Total synthesis of phæoporphyrin a_5. H. Fischer, E. Stier, and W. Kanngiesser. **XCVII. Synthesis of deoxophylloerythrin derivatives, an *iso*mesoporphyrin, and an *iso*rhodin.** H. Fischer and W. Kanngiesser (Annalen, 1940, **543**, 258—270, 271—287).—XCVI. γ-Formylpyrroporphyrin Me ester cyanohydrin (I) is converted by MeOH–HCl–SO_2 at 40°/48 hr. into Me_2 pyrroporphyrin-γ-glycollate (II), new m.p. 281°, and some (impure) Me_2 pyrroporphyrin-γ-glyoxylate (III) (cf. A., 1940, II, 109). Pyrroporphyrin-γ-glycollic acid (IV) with 2N-HCl at 70° gives γ-formylpyrroporphyrin (V) whilst *iso*chloroporphyrin e_4 is similarly unaffected. Hydrolysis (conc. HCl at room temp.) of (I) and subsequent esterification (Et_2O–CH_2N_2) affords *pyrroporphyrin-γ-glycollamide Me* ester (VI), red, m.p. 252° (? 254°), and violet, m.p. 251°, forms (*Zn* salt, m.p. 319°), which is unaffected by C_5H_{11}·O·NO in $COMe_2$–2N-HCl at 0°—room temp. Boiling 2N-HCl converts (IV) into pyrroporphyrin but at 100° (bath), (IV) and (VI) give (V). Reduction [H_2, Pd-black, HCO_2H, 100° (bath)] of (VI), atm. reoxidation of the product, and esterification (CH_2N_2) affords *pyrroporphyrin-γ-acetamide Me* ester (VII), m.p. 318°, which loses NH_3 at 320° (bath) and yields phylloerythrin. Successive hydrolysis (15% HCl at 45°/48 hr.) and esterification (CH_2N_2) of (VII) gives *iso*chloroporphyrin e_4 Me_2 ester (VIII). These results coupled with previous work (A., 1936, 1272) constitute a total synthesis of phæoporphyrin a_5. Oxidation ($KMnO_4$, $COMe_2$, C_5H_5N) of (II) yields (III) whilst reduction (H_2, Pd, HCO_2H, 90—95°; subsequent atm. reoxidation) of (III) affords (VIII) and a little (II).

XCVII. Oxidation ($KMnO_4$, C_5H_5N, room temp./3—4 days) of free phylloporphyrin gives pyrroporphyrin-γ-carboxylic acid (Me_2 ester, m.p. 242—244°), (V), and γ-hydroxymethylpyrroporphyrin. *γ-Carbamylpyrroporphyrin Me* ester, m.p. 287°, is obtained by successive hydrolysis (conc. H_2SO_4 at 70°) and esterification (MeOH–HCl) of the γ-CN-derivative. γ-Formylpyrroporphyrin Me ester (IX) and $MeNO_2$ in C_5H_5N–$NHEt_2$ afford *γ-β′-nitrovinylpyrroporphyrin Me* ester (+1 mol. of $MeNO_2$), m.p. 271°. *γ-β′-Cyano-β′-carbomethoxyvinylpyrroporphyrin Me* ester, m.p. 240° [from (IX) and CN·CH_2·CO_2Me in C_5H_5N + piperidine], when fused with $(CH_2·CO_2H)_2$ at 210°/3 min. yields *9-cyano-9-carbomethoxydeoxophylloerythrin Me* ester (*A*, R = CO_2Me), m.p. 246°, converted by 50% H_2SO_4 at room temp./2 days followed by Et_2O–CH_2N_2 into *9-cyanodeoxophylloerythrin Me* ester (*A*, R = H), m.p. 270°. γ-β′-


(*A.*)

Cyano-β′-carbethoxyvinylpyrroporphyrin Me ester (X) and $CHN_2·CO_2Et$ at 100° (bath) give a *compound*, $C_{41}H_{45}O_6N_5$, m.p. 205—208°, which probably contains a *cyclo*propane ring. Reduction (H_2, PtO_2, dioxan) of (X) (as Zn salt), decomp. of the product (in Et_2O) with 20% HCl, and subsequent esterification (CH_2N_2) affords *γ-β′-cyano-β′-carbethoxyethylpyrroporphyrin Me* ester, m.p. 238°, which is dehydrogenated to (X) in AcOH at 100° (bath)/3 hr., and is hydrolysed [20% HCl at 100° (bath)] to γ-β′-carboxyethylpyrroporphyrin (XI) (Me_2 ester, m.p. 202°). Dehydration of (XI) with H_2SO_4–oleum (cf. A., 1928, 1383) gives pyrroporphyrin-6 : γ-propan-9-one [*iso*mesorhodin] (XII) (as *B*) (*Me* ester, m.p. >325°, blackens ~248°) and *iso*mesoverdin [better obtained from (XII) in AcOH at 50°, whereby loss of 2 H between $C_{(10)}$ and $C_{(11)}$ occurs], both of which form oximes (spectroscopic evidence).


(*B.*)

H. B.

Derivatives of cyameluric acid. Probable structures of melam, melem, and melon. C. E. Redemann and H. J. Lucas (J. Amer. Chem. Soc., 1940, **62**, 842—846).—The Pauling–Sturdivant formula (cf. A., 1940, II, 110) for cyameluric acid (I) is confirmed by reactions which are often analogous to those of cyanuric acid. (I) gives *salts*, $CuNH_4(C_6O_3N_7)$,NH_3 and $Hg_3(C_6O_3N_7)_2$. The K_3 salt (dried at 150°) and PCl_5 at 100°, later 139°, give *cyameluryl trichloride* (II) (93%), $C_6N_7Cl_3$, also obtained from (I) and PCl_5 at 218°. The anhyd. Na_3 salt and CH_2PhCl at 156° give *tri-N-benzyl cyamelurate*, m.p. 283—284° (corr.), hydrolysed by 6N-KOH to $CH_2Ph·NH_2$. With $CH_2Ph·OH$, (II) gives CH_2PhCl and (I). CH_2N_2 and (I) give *Me*, $C_6H_2O_3N_7Me$, and on further treatment *Me_3 cyamelurate*, $C_6O_3N_7Me_3$, +1·5H_2O. With 15N-NH_3, NH_3–Et_2O, or liquid NH_3, (II) gives mixtures. Probably melam is [3 : 5-$C_3N_3(NH_2)_2]_2NH$, melem is $C_6H_7(NH_2)_3$, and melon is a large, planar, cyclic polymeride with C·N·C· linkings. R. S. C.

Wing-pigments of butterflies. V. Degradation of deiminoleucopterin. H. Wieland and A. Tartter (Annalen, 1940, **543**, 287—292).—The material pptd. by Et_2O from the solution obtained from deiminoleucopterin (A., 1933, 1310) and Cl_2 in MeOH at ~0°, when crystallised from H_2O, gives *deiminoleucopterin glycol Me_1 ether*, $C_{22}H_{26}O_{19}N_{12}$,3H_2O, darkens ~150°, no decomp. up to 260°; the main reaction product (Et_2O-sol.; yield increased by less rigorous cooling) is *Me 5-methoxyuramil-7-oxalate*,

$CO<^{NH\cdot CO}_{NH\cdot CO}>C(OMe)\cdot NH\cdot CO\cdot CO_2Me$, m.p. 195°, which is hydrolysed (boiling 3N-HCl) to MeOH (2 mols.) and 1 mol. each of NH_3, $H_2C_2O_4$, and alloxan. H. B.

αβ-Di-4-morpholinoethane.—See B., 1940, 347.

Absorption spectra of *N*-substituted auramine dyes. G. Brewer and J. Schnitzer (J.C.S., 1940, 461—463).—The absorption spectra of auramine, *N*-phenyl-, *N*-α-naphthyl-, *N*-β-naphthyl-, and N-2-*anthryl-auramine*, their hydrochlorides and picrates (except that of *N*-2-anthrylauramine) are recorded over the range 2500—5500 A. A. J. M.

Polarisation in heterocyclic rings with aromatic character. V. Substitution of aromatic hetero-rings with directly united phenyl chain. E. Ochiai, Y. Tunoda, I. Nakayama, and G. Masuda (J. Pharm. Soc. Japan, 1939, **59**, 228—235).—4-*Phenyl*-5-*methylthiazole*, b.p. 110—111°/2 mm. (*hydrobromide*, m.p. 197°; *picrate*, m.p. 124—125°), from $HCS\cdot NH_2$ and α-bromopropiophenone, is converted by HNO_3–H_2SO_4 at 0° into 4-p-*nitrophenyl*-5-*methylthiazole*, m.p. 98°, in 90% yield; it is oxidised by $KMnO_4$ to p-$NO_2\cdot C_6H_4\cdot CO_2H$ and hydrogenated to 4-p-*aminophenyl*-5-*methylthiazole*, m.p. 80° (*acetate*, m.p. 144°). Under similar conditions 4-phenylthiazole affords 4-p-*nitrophenylthiazole*, m.p. 180° (96% yield), reduced to 4-p-*aminophenylthiazole*, m.p. 99° (*acetate*, m.p. 165°). 4 : 5-*Diphenyl*-2-*methylthiazole*, m.p. 51—52°, yields 4 : 5-*di*-p-*nitrophenyl*-2-*methylthiazole*, m.p. 183°. Regardless of the type of thiazole, NO_2 always enters the p-position in the C_6H_6 nucleus and is not influenced by the position of the nucleus. Nitration of 2 : 5-diphenylpyrazine yields two isomeric 2 : 5-*dinitrophenylpyrazines*, m.p. 172—173° and decomp. 292°, respectively; since they are resistant to oxidation their constitution has not been established but they are not identical with 2 : 5-*di*-m-*nitrophenylpyrazine*, m.p. 249°, obtained from *m*-nitro-ω-aminoacetophenone. 2-Phenyl-4 : 6-dimethylpyrimidine (I) reacts only slowly with HNO_3–H_2SO_4 at 0°, giving a small amount of a $(NO_2)_1$-compound, m.p. 155—156°; this is catalytically reduced to the $(NH_2)_1$-derivative, m.p. 88—90° (*picrate*, decomp. 199—200°; *acetate*, m.p. 130—132°), which gives a $(OH)_1$-compound, m.p. 125—127°, not identical with 2-*p*-hydroxyphenyl-4 : 6-dimethylpyrimidine. Fuming HNO_3 in AcOH transforms (I) into a *compound*, $C_{24}H_{18}O_2N_6$, m.p. 167—170°. 2-*Phenyl*-4 : 6-*distyrylpyrimidine*, from (I), PhCHO, and $ZnCl_2$ at 150°, has m.p. 158·5—159°. H. W.

Sulphur derivatives of pyridine. (Synthesis of 2 : 3-pyridothiochromanone.) M. Colonna (Gazzetta, 1940, **70**, 154—159).—5-*Nitro*-2-*pyridylthiol-acetic acid*, m.p. 105° [obtained from 5-nitro-2-thiolpyridine (I), KOH, and $CH_2Cl\cdot CO_2K$ on the water-bath, or better from 2-chloro-5-nitropyridine and $SH\cdot CH_2\cdot CO_2H$ and $NaHCO_3$ in EtOH at the b.p.], with conc. H_2SO_4 at 150—180° gives a thioindigo derivative, not isolated. β-(5-*Nitro*-2-*pyridyl*)*thiol-propionic acid*, m.p. 125° [obtained from a neutralised mixture of (I) and $Cl\cdot[CH_2]_2\cdot CO_2H$ heated at 100° for 3 hr.], with PCl_5 followed by $AlCl_3$ in C_6H_6 at the b.p. gives 5′-*nitropyrido*-2′ : 3′-3 : 2-*thiochromanone*, m.p. 107°. 5 : 5′-Dinitro-2 : 2′-dipyridyl sulphide with $K_2Cr_2O_7$–H_2SO_4 in AcOH gives the corresponding *sulphone*, m.p. 185—187°. E. W. W.

Cyanine dyes.—See B., 1940, 406, 408.

Polarisation in heterocyclic rings with aromatic character. VIII. Polarisation in the benzene ring. E. Ochiai and T. Nishizawa (J. Pharm. Soc. Japan, 1940, **60**, 43—48).—The activity of $C_{(2)}$ in thiazole towards nucleophilic reagents is paralleled by that of $C_{(1)}$ in benzthiazole (I). $NaNH_2$ and (I) in decahydronaphthalene at 140° afford (mainly) 1-aminobenzthiazole, m.p. 130° (monoacetate, m.p. 187°; *hydrochloride*, decomp. 235—236°; *picrate*, m.p. 265°), 2 : 2′-diaminodiphenyl disulphide, m.p. 93° (*Ac*$_2$ derivative, m.p. 169°), and a *compound*, m.p. 194°, possibly a dibenzthiazolyl or dibenzthiazole, which does not yield a picrate. 1-Methylbenzthiazole (II) condenses with PhCHO and $ZnCl_2$ at 160—170° to 1-styrylbenzthiazole, m.p. 111—112°, reduced (Pd–C in EtOH) to 1-β-*phenylethylbenzthiazole*, b.p. 180° (bath)/0·5 mm., m.p. 62°. 1-*Aminobenzthiazole* (III) and CH_2BzBr in EtOH at 100° afford *benzthiazolo*-1′ : 2′-2 : 1-4-*phenylglyoxaline hydrobromide*, m.p. 263° (corresponding *base*, m.p. 100°). CH_2BzBr and (II) readily give the *product*, $C_{16}H_{14}ONBrS$, m.p. 233°, which with $NaHCO_3$ yields a very unstable material which passes into a red, amorphous mass; this gives the red diazo-reaction and a bluish-violet Ehrlich test. A uniform product is likewise not obtained from (II) and CH_2AcCl. Picryl chloride and (III) yield 1-*picramidobenzthiazole*, m.p. 205°, which in boiling $PhNO_2$ evolves nitrous fumes and gives *benzthiazolo*-1′ : 2′-2 : 1-4 : 6-*dinitrobenziminazole*, m.p. 243°. (I), from o-$NH_2\cdot C_6H_4\cdot SH$ and HCO_2H in presence of a little H_3BO_3, gives a *picrate*, m.p. 168°, and *perchlorate*, m.p. 135°. (II), obtained as above but by use of Ac_2O, affords a *picrate*, m.p. 153·5°. (III), m.p. 130° (*hydrochloride*, decomp. 236°; *acetate*, m.p. 187°), is obtained by bromination of $NHPh\cdot CS\cdot NH_2$ or by catalytic reduction (Pd–C in AcOH) of o-$NO_2\cdot C_6H_4\cdot CNS$. H. W.

Preparation of quinine iodo-hydriodide. S. N. Naumov and C. B. Medinski (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 32, 1—6).—20 g. of KI in 100 ml. of H_2O are added to a solution of quinine sulphate 5, H_2SO_4 5, and $Fe(NH_4)_2(SO_4)_2,12H_2O$ 30 g. in 800 ml. of H_2O, and the product is twice recryst. from 1% H_2SO_4 in 85% EtOH. R. T.

Alkaloids of *Stemona tuberosa*, Loureiro. II. Tuberostemonine. H. Kondo, K. Suzuki, and M. Satomi. **IV. Stemonidine.** K. Suzuki (J. Pharm. Soc. Japan, 1939, **59**, 177—186).—II. *Tuberostemonine* (I) has been obtained as the cryst. *hydrobromide*, m.p. 120° (decomp.), *aurichloride*, and *perchlorate*, m.p. 242° (decomp.), from which the cryst. *base*, $C_{22}H_{33}O_4N$ (not $C_{19}H_{29}O_4N$), m.p. 86—88° [or, + 1MeOH, m.p. 65—88° (decomp.)], is isolated. (I) is a non-phenolic, *tert.* base devoid of OMe, NMe, or active H. It contains a lactone group but does not react with NH_2OH or p-$NO_2\cdot C_6H_4\cdot NH\cdot NH_2$. It yields a *methiodide* (+1H_2O), m.p. 236—238° (decomp.), *methochloride*, (+2H_2O), m.p. 172°, *methylmethosulphate*, m.p. 253° (decomp.), and a *methylauri-*

chloride (+H_2O), m.p. 140° after softening at 125°. (I) is not affected by Ac_2O in CO_2 but under the customary conditions it is converted into a neutral, amorphous substance which gives Ehrlich's pyrrole reaction in the cold. (I) is unaffected by boiling 30% H_2SO_4 or by HCl–EtOH. The function of 2 O in (I) is not elucidated. Dry distillation of (I) with Zn dust gives vapours which turn a pine shaving moistened with HCl red; this reaction is not given by the base itself. Oxidation with Ag_2O leads to a neutral *compound*, $C_{22}H_{29}O_4N$, m.p. 178°, which contains a lactone group and gives Ehrlich's pyrrole reaction. (I) therefore contains a pyrrolidine ring which is dehydrogenated to a pyrrole ring. Attempts to obtain an additive product with maleic anhydride were unsuccessful. Possibly (I) is identical with the alkaloid, $C_{22}H_{33}O_4N$, m.p. 86—87°, from *Stemona sessilifolia* (Schild, A., 1936, 350) although (I) cannot be catalytically hydrogenated (PtO_2 in EtOH) and does not give a cryst. dehydrogenated product when treated with I or MeI according to Schild.

IV. Stemonidine (II) is a *tert.* base since it does not react with Zerevitinov's reagent or Ac_2O and does not give Liebermann's reaction. Complete analysis of the compound, m.p. 248°, shows it to be the methiodide. Of the 5 O of (II) two are present in a lactone and one in a OMe group; the function of the remaining two is unknown. Distillation of (II) with Zn dust gives a pyrrole derivative which is readily hydrogenated (Pd–C in AcOH) to a liquid base; probably the pyrrole nucleus is not preformed in (II). I or MeI converts (II) into the hydriodide or methiodide; dehydrogenation does not appear to take place. Oxidation of (II) by $KMnO_4$ (≡3 O) in $COMe_2$ gives a base characterised by a *methiodide*, $C_{19}H_{29}O_5N$,MeI, m.p. 235°. Aq. $KMnO_4$ (≡7·9 O) in H_2O at 60° gives a quaternary base (*aurichloride*, $C_{19}H_{29}O_5NMeAuCl_4$, m.p. 158°). When oxidised by $KMnO_4$ (≡13·5 O) in dil. H_2SO_4 at 10° (II) yields a neutral *substance* (III), $C_{16}H_{23}O_5N$, m.p. 208°, $[\alpha]_D$ −58·3°, and a *compound* (IV), $C_{11}H_{17}O_4N$, m.p. 202°, $[\alpha]_D$ −24·17° (*semicarbazone*, m.p. 258°). (III) contains a lactone group and OMe but is not a pyrrole derivative and does not react with CO reagents. (IV) contains OMe but is not a lactone; it strongly reduces ammoniacal Ag solution but does not give the pyrrole reaction. 25% HCl–AcOH and EtOH saturated with HCl are without action on (II). Dehydrogenation of (II) by 40% Pd–asbestos at 260—290° gives a non-cryst. dehydro-*base* (which contains OMe and a lactone group, gives the diazo-reaction, and yields an *oxime* and a *methiodide*, $C_{17}H_{23}O_4N$,MeI, decomp. 227—228°), a neutral pyrrole derivative which gives the pine shaving and Ehrlich reaction, and an (impure) acid which gives a dark green colour with $FeCl_3$. H. W.

Alkaloids of fumariaceous plants. XXIV. *Corydalis ochotensis*, Turcz. XXV. *Corydalis pallida*, Pers. R. H. F. Manske (Canad. J. Res., 1940, **18**, B, 75—79, 80—83).—XXIV. The following substances have been isolated: protopine (I), cryptocavine, ochotensine, aurotensine, ochotensimine (*methiodide*, decomp. 225°, $[\alpha]_D^{22}$ +49·2° in MeOH, identical with Me ether methiodide of ochotensine; *dihydromethine*, $C_{23}H_{27}O_4N$, m.p. 92°), alkaloid F 49, $C_{19}H_{23}O_4N$, m.p. 228° (decomp.), fumaric acid, and maltol (?).

XXV. Capaurine, *d*- and *dl*-tetrahydropalmitine, (I), capauridine, capaurimine (F 50), $C_{20}H_{23}O_5N$, m.p. 212°, $[\alpha]_D^{24}$ −287° in $CHCl_3$ (phenolic; one OH and three OMe), and alkaloid F 51, $C_{20}H_{23}O_4N$, m.p. 171° (one OH and three OMe), have been isolated. Methylation of capaurimine gives capaurine *O*-Me ether, the *dl*-form of which is identical with capauridine *O*-Me ether, and alkaloid F 51 similarly affords *dl*-tetrahydropalmatine, not identical with the known *dl*-bases of the same formula. F. R. S.

Conessine series. V. Reduction of nitroconessine to conessineoxime and conversion of the oxime into mono[hydr]oxyconessine. S. Siddiqui and V. Sharma (Proc. Indian Acad. Sci., 1939, **10**, A, 417—422; cf. A., 1937, II, 527).—Hydrogenation (Pt-black in MeOH at room temp.) of nitroconessine gives *conessineoxime* (I), $C_{24}H_{41}ON_3$, m.p. 230—232°, $[\alpha]_D^{29}$ −26·3° in abs. EtOH, +9·5° in $CHCl_3$, better obtained by use of an excess of Na–Hg in EtOH–AcOH. (I) yields a *carbonate*, $C_{24}H_{41}ON_3,2H_2CO_3,4{\cdot}5H_2O$, m.p. >360°, *dihydrochloride*, m.p. 349° (decomp.), *dihydriodide*, m.p. 331°, *picrate*, m.p. 254° (decomp.) after blackening at 251°, *platinichloride*, m.p. 292°, and *methiodide*, m.p. 258° (decomp.) after changing colour at 242°. (I) is transformed by HNO_2 into N_2O and monohydroxyconessine (II), m.p. 200°, $[\alpha]_D^{30}$ +11·5° in EtOH, also produced from (I) and CH_2O–HCO_2H at 100°. (I) and Br (≡2 atoms) appear to yield a Br-derivative. (III) is converted by Br into a product, decomp. 232° after shrinking at 200°, which is transformed by prolonged heating with EtOH or H_2O into monohydroxyconessine dihydrobromide. H. W.

Constitution of matrine. XXII. Gen-alkaloids of matrine and *d*-lupanine. E. Ochiai, Y. Ito, and M. Maruyama (J. Pharm. Soc. Japan, 1939, **59**, 270—273; cf. A., 1939, II, 460).—*N-iso*Amylpiperidine or 2-methylindolizidine and 3% H_2O_2–$COMe_2$ give *oxides*, m.p. 135° (+0·75H_2O) (*picrate*, m.p. 117°), and an oil (*picrate*, m.p. 164°), respectively, but *N-iso*amylpiperidone, treated similarly, is unchanged. *d*-Lupanine (I) and 3% H_2O_2 give a monoxide (*dipicrate*, m.p. 189°; *perchlorate*, m.p. 247°; *aurichloride*, m.p. 216°; *methiodide*, m.p. 137°) [cf. matrine (II)]. (I) and PCl_5–K_2S in xylene give d-*thiol-lupanine*, m.p. 102° (*picrate*, m.p. 225°), but (II) is unchanged by similar treatment. The lactam ring of (I) is not broken by KOH–EtOH, but (II) is hydrolysed. A. T. P.

Menispermaceæ alkaloids (formerly, alkaloids of *Sinomenium* and *Cocculus*). L. Alkaloids of *Stephania Sasakii*, Hayata. I. M. Tomita (J. Pharm. Soc. Japan, 1939, **59**, 207—208; cf. Kondo *et al.*, A., 1939, II, 459).—The following are obtained from the roots of *S. Sasakii*: (*a*) a cryst. base, decomp. 103° (as C_6H_6 adduct), which agrees in chemical reactions and physical consts. with cepharanthine and is degraded (Hofmann) to cepharanthine-α- and -β-methine; (*b*) a *base* (I), $C_{38}H_{40}O_7N_2$, m.p. 115—117°, $[\alpha]_D^{20}$ −57·4° in $CHCl_3$ [*hydrochloride* (+2H_2O), m.p. 222—225° (decomp.)],

which is insol. in aq. NH_3, alkali carbonate or hydroxide and contains 4OMe. The *methiodide*, m.p. 220°, is transformed by hot alkali hydroxide into the *methine* base, $C_{40}H_{44}O_7N_2,H_2O$, m.p. 110—114°, $[\alpha] \pm 0°$; (*c*) a phenolic *base* (II), $C_{36}H_{36}O_7N_2$, m.p. 210°, $[\alpha]_D^{20}$ —36·7° in $CHCl_3$ (*hydrochloride*, m.p. 264°), which contains 2 OMe and is converted by CH_2N_2 into a *Me_2 ether*, m.p. 160—165°, with 4 OMe which differs from (I). (I) and (II) are very similar chemically, particularly in their colour reactions. H. W.

Organic arsenicals.—See B., 1940, 404, 406.

Gallium triphenyl. H. Gilman and R. G. Jones (J. Amer. Chem. Soc., 1940, **62**, 980—982).—*Ga triphenyl* (prep. in 82% yield from $HgPh_2$ and Ga in N_2 at 130°), m.p. 166°, is moderately reactive. With PhCHO in boiling C_6H_6 it gives 70% of $CHPh_2$·OH. With COPh·CH:CHPh it gives 85% of COPh·CH_2·$CHPh_2$. With BzCl in C_6H_6 it gives 79% and in light petroleum 68·4% (as oxime) of $COPh_2$ (cf. $TlPh_3$, which gives only $TlPh_2Cl$). It does not react with $COPh_2$ (3 mols.) in boiling xylene, but an excess of $GaPh_3$ gives 35% of $CHPh_3$. With CH_2PhCl it gives an oil containing CH_2Ph_2 (yields 9% of $COPh_2$). It does not react with PhCN. It gives no colour with Michler's ketone in C_6H_6, unless it is present in excess; it probably forms a complex with the NMe_2. R. S. C.

Reaction of mercuric acetate with *p*-phenetidine and *p*-anisidine. M. Ragno (Annali Chim. Appl., 1940, **30**, 72—78).—*p*-Phenetidine with $Hg(OAc)_2$ in AcOH–EtOH yields an *adduct*, OEt·C_6H_4·NH_2,$Hg(OAc)_2$, m.p. 137°; similarly treated, *p*-anisidine yields 3-*acetomercuri*-p-*anisidine*-N-*mercuriacetate acetate*, m.p. 148—149° (decomp.), which with aq. KI affords 3-*mercuri*-p-*anisidine iodide* and, with aq. KBr, the corresponding *bromide* (I), m.p. 165°. The structure of the compounds is indicated by bromination of (I) to 3 : 5-dibromoanisidine. F. O. H.

[Preparation of] organic mercury derivatives of basic triphenylmethane dyes. L. Chalkley (Science, 1940, **91**, 300; cf. A., 1925, i, 1108; 1929, 1322).—Derivatives of the basic dye are mercurated, and then converted into the dye, *e.g.*, 4 : 4′-bisdimethylaminotriphenylacetonitrile is readily mercurated, and the mercurated nitrile converted into the corresponding Hg malachite-green by means of a photochemical reaction. The Hg in this compound is relatively stable to $(NH_4)_2S$ which, in presence of aq. NH_3, gives an org. Hg^{II} sulphide. L. S. T.

Mercuration of cholesterol. R. H. Levin and M. A. Spielman (J. Amer. Chem. Soc., 1940, **62**, 920—921).—The product, m.p. 200—205°, obtained (Merz, A., 1926, 723) from cholesterol by $Hg(OAc)_2$–AcOH, is the 6-HgCl-derivative, since the derived 6-iodocholesterol, m.p. 156—158° (*benzoate*, m.p. 214—215°), is hydrolysed by $CuCl_2$–$NaHCO_3$–H_2O at 225° (not by milder reagents) into 6-ketocholestanol (3 : 5-*dinitrobenzoate*, m.p. 226—228°), isolated as benzoate. R. S. C.

Hydroxyquinolines. IV. Mercurated derivatives of 8-hydroxyquinoline. F. Pirrone (R. C. Atti Accad. Ital., 1939, [vii], **1**, 50—54).—8-Hydroxyquinoline (I) heated in AcOH with $Hg(OAc)_2$ (II) gives its ?-*acetatomercuri*-derivative, m.p. ⱷ360°, which with HCl gives a *compound*, $C_9H_6ONHgCl$, m.p. 205°, and with aq. NH_3 a *compound*, $C_9H_7O_2NHg$. In H_2O, (I) and excess of (II) give 8-*hydroxy*-??-*bisacetatomercuriquinoline*. If the AcOH formed is progressively neutralised by NaOH, the *Na* derivative of the ???-trisacetatomercuri-derivative is obtained. E. W. W.

Chemical structure in the protein series. A. Weidinger (Collegium, 1940, 1—37).—A review.

Melanins, their chemistry and significance. W. L. C. Veer (Chem. Weekblad, 1940, **37**, 214—222).—A review. S. C.

Effect of denaturing agents on myosin. I. Sulphydryl [thiol] groups as determined by porphyrindin titration. J. P. Greenstein and J. T. Edsall. **II. Viscosity and double refraction of flow.** J. T. Edsall and J. W. Mehl (J. Biol. Chem., 1940, **133**, 397—408, 409—429).—Amplification of previous work (A., 1939, III, 869). The porphyrindin titration and the significance of η for solutions of large, very asymmetrical mols. are discussed. The chemical and physical effects are uncorrelated. Methionine + cysteine account for 95% of the S of myosin. R. S. C.

Number of peptide linkages in insulin.—See A., 1940, III, 498.

Gas-volumetric semi-micro-determination of carbon. Wet method for aliphatic and cyclic compounds. E. Berl and W. Koerber (Ind. Eng. Chem. [Anal.], 1940, **12**, 245—246).—The sample is oxidised with H_2CrO_4 and a Hg catalyst, and the CO_2 evolved is measured in a gas burette. J. D. R.

Determination of chlorine, bromine, and iodine in organic compounds by hydrogenation. A. Slooff (Rec. trav. chim., 1940, **59**, 259—283).—Cl, Br, and/or I in org. compounds are determined by heating the compound in H_2, passing the vapours over Ni foil at 800°, absorbing the HHal in solid Na_2CO_3, and (after destruction of NaCN and NaCNS, if necessary) titrating the Na halide formed. In 31 cases the error is <0·4%. Published data are used to show by calculation that decomp. of HCl and HBr in excess of H_2 is negligible and that at 800° there is 2% of dissociation of HI, which, however, is reduced to <1% (considered negligible) by cooling to 700°. R. S. C.

Determination of elements in organic substances. L. Rosenthaler (Pharm. Acta Helv., 1939, **14**, 215—216; cf. A., 1937, II, 358).—Cl and Br are liberated from many org. compounds by treatment with saturated aq. $KMnO_4$ and H_2SO_4. Cl may be detected with *m*-$C_6H_3Me(NH_2)_2$ (forms at first drops, then needles, and finally aggregates; Br does not react) and Br with fluorescein paper. Numerous compounds which liberate H_2S by the action of nascent H are described. In some cases, *e.g.*, $EtSO_3Na$, cystine, cysteine, a positive reaction [with $Pb(OAc)_2$] is obtained but no H_2S is evolved. The liberation of CO_2 by the action of H_2SO_4 on org. substances is also discussed. E. H. S.

Determination of organic nitrogen. J. Cartiaux (Ann. Chim. Analyt., 1940, [iii], **22**, 92).—N is converted into NH_4^+ by treatment of the sample with 5 c.c. of conc. H_2SO_4 and two to four 10—20-c.c. portions of H_2O_2 in the manner described. The method gives better results than the usual H_2SO_4 + Hg attack, and is particularly suitable for leather, wool, tobacco, and vegetable products. L. S. T.

Electrolytic method of oxidising arsenic and phosphorus for their determination in organic compounds. C. B. Di Capua (Atti X Congr. Internaz. Chim., 1938, III, 401—406).—The compound is dissolved in 70% H_2SO_4 and the solution introduced into a sintered glass crucible dipping into 70% H_2SO_4. The solution is then electrolysed using a Pt wire anode immersed in the crucible and a Pt foil cathode in the outer vessel. The H_3AsO_4 and H_3PO_4 produced are subsequently pptd. as $MgNH_4AsO_4$ and $MgNH_4PO_4$, respectively. J. W. S.

Identification of paraffins. Analysis of paraffinic mixtures by means of Raman spectra. A. V. Grosse, E. J. Rosenbaum, and H. F. Jacobson (Ind. Eng. Chem. [Anal.], 1940, **12**, 191—194).—The sample is freed from aromatic and ethylenic constituents, carefully fractionated, and the Raman spectra of the individual narrow cuts are photographed. For qual. analysis this spectrum is matched with the characteristic lines of pure isomerides known to be present in the mixture. Quant. analysis is carried out, with an accuracy of 5—10%, by visual estimation of the relative intensities of the Raman lines. The method has been applied to the isomeric pentanes, hexanes, and heptanes, and to mixtures prepared by the addition of olefines to paraffins in presence of $AlCl_3$. J. D. R.

Colorimetric determination of primary mononitroparaffins. E. W. Scott and J. F. Treon (Ind. Eng. Chem. [Anal.], 1940, **12**, 189—190).—A sample of aq. $EtNO_2$ is treated with NaOH, acidified (HCl), and aq. $FeCl_3$ added. The red colour produced is compared colorimetrically with a standard solution of similar concn. The method succeeds with $PrNO_2$ and $BuNO_2$, but with $Pr^{\beta}NO_2$ and $Bu^{\beta}NO_2$ the colour fades too rapidly, whilst with $MeNO_2$ no colour is produced. J. D. R.

Oxidation with dichromate and its microanalytical applications. I. General principles. II. Micro-determination of ethyl alcohol. L. Thivolle and G. Sonntag (Bull. Soc. Chim. biol., 1939, **21**, 1353—1368, 1369—1380).—I. Oxidisable substances are determined in strongly acid medium by adding a 2—3 c.c. excess of ~ 0·1N-$K_2Cr_2O_7$ and a few drops of 0·1% diphenylbenzidine in 70% H_2SO_4 and titrating with 0·002N-$K_4Fe(CN)_6$ until the colour vanishes.

II (cf. Nicloux *et al.*, A., 1935, 116; 1936, 535; 1937, II, 317). EtOH is oxidised in the cold with excess of $K_2Cr_2O_7$ in HNO_3 and the excess is titrated as above. The error is >0·5% when the amount of EtOH is 1—3 mg. or 1—2% when it is <0·5 mg. W. McC.

Rapid qualitative test for alcoholic hydroxyl group. Use of nitrato- and perchloratocerate anions as test reagents. F. R. Duke and G. F. Smith (Ind. Eng. Chem. [Anal.], 1940, **12**, 201—203).—The test substance in H_2O is treated with a solution of $(NH_4)_2Ce(NO_3)_6$ (I) in aq. HNO_3 or $H_2Ce(ClO_4)_6$ (II) in aq. $HClO_4$. A red colour indicates an alcohol. With substances insol. in H_2O a solution in dioxan is employed and (II) cannot be used because of reduction of the reagent. Acids, aldehydes, ketones, esters, and hydrocarbons do not interfere. Amines, amine hydrochlorides, substances with chromophoric groups, readily oxidisable substances, and phenols interfere. Aq. solutions of 2—4% BuOH give positive tests with (I) and 1—2% with (II). J. D. R.

Hydroxamic acids in qualitative organic analysis. D. Davidson (J. Chem. Educ., 1940, **17**, 81—84).—Tests involving the formation of hydroxamic acids are described for alcohols, ethers, aldehydes, esters, carboxylic and sulphonic acids, phenols, oximes, NO_2-compounds, amides, acid chlorides, and anhydrides. L. S. T.

Detection of organic compounds. L. Rosenthaler (Pharm. Acta Helv., 1939, **14**, 218—221).—(*a*) MeOH does not react with HNO_3 (65%) at room temp. (differentiation of MeOH and EtOH). (*b*) The reaction depending on the formation of a blue colour from glycerol with $K_2Cr_2O_7$ and HNO_3 is not sp.; many other alcohols and sugars react similarly. (*c*) For the identification of phenols the colour of the melt and the alkali solution of the reaction product with *o*-sulphobenzoic anhydride is a very sensitive test. 15 examples are given. (*d*) By the use of Na alizarinsulphonate as indicator, the formation of H ions by the action of neutral Hg salt solutions on HCN can be detected in 1 μg. of HCN per c.c. An improvement on the Vortmann method is given. The sample is heated with aq. NaOH and $FeSO_4$, the mixture is filtered, acidified, $NaNO_2$ is added, and, after warming and cooling, aq. NH_3 and $(NH_4)_2S$ are added (nitroprusside reaction). (*e*) Characteristic light brown, ball-shaped masses are formed when a solution of theophylline in aq. NH_3 is treated with solid TlOAc. (*f*) The blue colour formed from aromatic *o*-$(OH)_2$-compounds and K_2CO_3 and $FeSO_4$ is discussed. Ascorbic and dihydroxymaleic acids react similarly but the reaction mixture is decolorised by HCl. (*g*) The oxidation of many org. compounds by $Fe_2(SO_4)_3$ is detected by the reaction of the $Fe^{\cdot\cdot}$ formed (after addition of H_3PO_4) with $(CMe{:}N{\cdot}OH)_2$ and aq. NH_3. 2·5 c.c. of a solution containing 1 μg. of pyrocatechol give a positive reaction. E. H. S.

Detection of small amounts of mustard gas. A. S. Jousma (Pharm. Weekblad, 1940, **77**, 246—249).—Mustard gas (I) is adsorbed on a granule of active C, which is then heated (below redness) in a stream of H_2 washed with $KMnO_4$ solution to remove H_2S, and the gas is passed over a red-hot Pt wire and through a paper containing $Pb(OAc)_2$, on which a brown or black stain is produced. The method is very sensitive and will detect (I) in C which has been exposed to the vapour for only 5 sec. S. C.

Analytical procedures employing Karl Fischer reagent. IV. Determination of acid anhydrides.

D. M. Smith, W. M. D. Bryant, and J. Mitchell, jun. (J. Amer. Chem. Soc., 1940, **62**, 608—609; cf. A., 1940, II, 146).—A procedure for the determination of carboxylic anhydrides (described) depends on the complete hydrolysis of the anhydride to acid in presence of excess of H_2O, and subsequent titration of the residual H_2O with Karl Fischer reagent. The method is best suited for acyclic aliphatic anhydrides. Analytical data are recorded for ten anhydrides. W. R. A.

Potentiometric determination of glucose with potassium ferricyanide in sodium carbonate solution. H. T. S. Britton and L. Phillips (Analyst, 1940, **65**, 149—152).—$K_3Fe(CN)_6$ in ~0·4M. aq. Na_2CO_3 can be titrated potentiometrically with glucose solution at 92—94°. The inflexion in the potential curve extends over 0·4—0·5 v. 1 mol. of glucose requires 5·9 mols. of $K_3Fe(CN)_6$ for oxidation. J. W. S.

Micro-determination of glucose, free and conjugated glucuronic acid. I. Determination of free and conjugated glucuronic acid in presence of glucose in aqueous solution. S. Kakinuma (J. Pharm. Soc. Japan, 1939, **59**, 244—246).—This is effected by the method of Ogata *et al.* (*ibid.*, 1929, **49**, 541) after first removing the glucose (⩾1%) by yeast. R. S. C.

Objective microphotometry. Photometric analysis of picrates of organic bases. P. Krumholz and E. Krumholz (Natuurwetensch. Tijds., 1940, **22**, 27—28).—The picrate of a base or of a hydrocarbon (*e.g.*, anthracene) is heated with 0·2N-NaOH in 80% EtOH and the Na picrate determined microphotometrically. The error is ~0·5%. S. C.

Determination of primary, secondary, and tertiary amines and ammonia present together. K. G. Mizutsch and A. J. Savtschenko (Prom. Org. Chim., 1940, **7**, 24—25).—The mixture of hydrochlorides is dissolved in 30 ml. of H_2O, and 25 ml. of EtOH are added, followed by 3 g. of $NaNO_2$,$Co(NO_2)_2$ in 50 ml. of H_2O at 0°. The ppt. of NH_4 cobaltinitrite is collected after 15 min., washed with EtOH, and NH_3 determined in the usual way. Primary amines are determined as the difference between total NH_2-N as found by Van Slyke's method and NH_3-N. *tert.* Amine is determined by Kjeldahl distillation after treating the solution with excess of HNO_2 (2 hr. at 15—20°). *sec.* Amines are given by difference between total N and NH_3-, NH_2-, and *tert.* amine-N. R. T.

Colorimetric micro-determination of arginine and of mono-substituted derivatives of guanidine. Application to protein hydrolysates. C. Dumazert and R. Poggi (Bull. Soc. Chim. biol., 1939, **21**, 1381—1388; cf. Jean, A., 1934, 672).—EtOH–glycerol mixture is added, after addition of aq. NaOH, α-$C_{10}H_7$·OH, and NaOBr, and the arginine in 2 c.c. of protein hydrolysate is determined by a modification of Weber's method (A., 1930, 755). The error is ±2%. A colorimeter or step photometer is used. Since the reaction is not usually affected by the nature of the substituent when one NH_2 only of guanidine is substituted, methylguanidine, agmatine, octopine, synthalin (I), and arcaine (II) are determined in the same way, (I) and (II) yielding colour intensity double that given by equiv. amounts of the other substances. W. McC.

Azides as reagents for the identification of organic compounds. XVII. *p*-Nitrobenzazide and *p*-nitrophenylcarbimide as reagents for identification of amines. P. P. T. Sah (Rec. trav. chim., 1940, **59**, 231—237; cf. A., 1940, II, 32).—*p*-Nitrobenzazide or *p*-NO_2·C_6H_4·NCO in PhMe afford new N-*aryl*-N′-p-*nitrophenylcarbamides* from the following: *o*-, m.p. 201°, *m*-, m.p. 205° (decomp.), and *p*-C_6H_4Me·NH_2, m.p. 259°; *m*-xylidine, m.p. 215°; *o*-NO_2·C_6H_4·NH_2, m.p. 256°; *o*-C_6H_4Cl·NH_2, m.p. 233°; *o*-C_6H_4Br·NH_2, m.p. 228°; *o*-, m.p. 224°, *m*-, m.p. 272°, and *p*-C_6H_4I·NH_2, m.p. 288°; *o*-, m.p. 212°, and *p*-OH·C_6H_4·NH_2, m.p. 235° (decomp.); *o*-, m.p. 191°, and *p*-OMe·C_6H_4·NH_2, m.p. 229° (decomp.); *o*-, m.p. 178—179°, and *p*-OEt·C_6H_4·NH_2, m.p. 202° (decomp.); α-$C_{10}H_7$·NH_2, m.p. 236°; *p*-C_6H_4Ph·NH_2, m.p. 235—236°; *o*-, m.p. 186°, *m*-, m.p. 195—196°, and *p*-NH_2·C_6H_4·CO_2Et, m.p. 254—255°; 2 : 1 : 4-, m.p. 260° (decomp.), 3 : 1 : 4-, darkens at 245°, chars and decomp. at 260°, 4 : 1 : 2-, m.p. 261—262°, 3 : 1 : 2-, m.p. 278° (decomp.), 5 : 1 : 2-, m.p. 246—247°, 4 : 1 : 3-, m.p. 263—264°, and 6 : 1 : 3-NO_2·C_6H_3Me·NH_2, m.p. 283—284°; 1 : 3 : 4-, m.p. 209—210°, 1 : 5 : 2-, m.p. 264°, and 1 : 6 : 3-C_6H_3MeCl·NH_2, m.p. 246°; 1 : 3 : 4-, m.p. 204—205°, 1 : 5 : 2-, m.p. 268—269°, and 1 : 6 : 3-C_6H_3MeBr·NH_2, m.p. 248—249°; 1 : 5 : 2-, m.p. 264°, and 1 : 6 : 3-C_6H_3MeI·NH_2, m.p. 239°; NH_2Ac, m.p. 295—296°; NH_2Bz, m.p. 260°; NHPhMe, m.p. 123°; NHPhAc, m.p. 254—255°; *cyclo*hexylamine, m.p. 169—170°. M.p. are corr. A. T. P.

Azides as reagents for the identification of organic compounds. XVIII. *o*-Nitrobenzazide as reagent for identification of phenols. P. P. T. Sah and W. Yin (Rec. trav. chim., 1940, **59**, 238—245; cf. A., 1940, II, 32).—*o*-Nitrobenz-hydrazide, m.p. 119°, affords the -azide, decomp. ~44°, which gives o-*nitrophenylurethanes* (generally of lower m.p. than the *m*- and *p*-isomerides) from the following phenols in ligroin, $NPhMe_2$ being an effective catalyst for the *o*-substituted compounds: PhOH, m.p. 96—98°; *o*-, m.p. 113—114°, *m*-, m.p. 85—86°, and *p*-cresol, m.p. 97—98°; 1 : 2 : 4-, m.p. 117—119°, 1 : 4 : 5-, m.p. 90—91°, and 1 : 3 : 4-xylenol, m.p. 99—101°; *o*-, m.p. 124°, *m*-, m.p. 158°, and *p*-NO_2·C_6H_4·OH, m.p. 175°; *o*-, m.p. 109—110°, *m*-, m.p. 96—97°, and *p*-C_6H_4Cl·OH, m.p. 126—127°; *o*-, m.p. 122°, *m*-, m.p. 91—92°, and *p*-C_6H_4Br·OH, m.p. 129—130°; *o*-, m.p. 150—151°, *m*-, m.p. 98—100°, and *p*-C_6H_4I·OH, m.p. 133—135°; 2 : 4 : 1-$C_6H_3Cl_2$·OH, m.p. 123°, and -$C_6H_3Br_2$·OH, m.p. 121—122°; 2 : 4 : 6 : 1-$C_6H_2Cl_3$·OH, m.p. 153—155°, and -$C_6H_2Br_3$·OH, m.p. 172—174°; *o*-, m.p. 136—138°, *m*-, m.p. 99—100°, and *p*-OMe·C_6H_4·OH, m.p. 156°; α-, m.p. 130°, and β-$C_{10}H_7$·OH, m.p. 143°. M.p. are corr. A. T. P.

Determination of phenols by means of benzoic anhydride. A. Leman (Bull. Soc. chim., 1940, [v], **7**, 105—113; cf. A., 1939, II, 196).—The sample is heated for 1 hr. at 100° with a solution of Bz_2O in anhyd. C_5H_5N (100 g. in 100 c.c.); H_2O is added and

the heating is continued with frequent shaking for a further hr. after which the mixture is cooled and titrated with N-KOH (phenolphthalein). With coloured samples a spot test on phenolphthalein paper is used. In confirmation the ester is separated from the neutralised solution and washed with H_2O, which is added to the solution; this is then treated with a measured vol. of N-H_2SO_4 and back-titrated with N-KOH. A blank test is necessary. As with acetylation in C_5H_5N, benzoylation of phenols is quant. and is somewhat more precise but less rapid. Treatment with *o*-$C_6H_4(CO)_2O$ in C_5H_5N is almost without effect on phenols or naphthols. In their mixtures with primary alcohols it is therefore possible to determine total OH by Bz_2O and primary alcoholic OH by *o*-$C_6H_4(CO)_2O$–C_5H_5N. Amended m.p. are cited for the following benzoates: Ph, m.p. 69·1°; *o*-, m.p. 17°, *m*-, m.p. 53·6°, and *p*-, m.p. 70°, -tolyl; *p*-xylenyl, m.p. 59·5°; thymyl, m.p. 31·2°; dibenzoates of *o*-, m.p. 85·1° and *p*-$C_6H_4(OH)_2$, m.p. 202·5°.

H. W.

Identification of organic compounds. III. Chlorosulphonic acid as a reagent for characterisation of aromatic ethers. E. H. Huntress and F. H. Carten (J. Amer. Chem. Soc., 1940, **62**, 603—604).—The following are prepared (method; A., 1940, II, 160). p-*Methoxy*-, m.p. 110—111°, *p*-ethoxy-, m.p. 149—150°, p-n-*propoxy*-, m.p. 116—117°, p-n-*butoxy*-, m.p. 103—104°, 4-methoxy-3-methyl-, m.p. 137°, 4-methoxy-2-methyl-, m.p. 129—130°, 2-methoxy-5-methyl-, m.p. 182°, 4-*ethoxy*-3-*methyl*-, m.p. 148—149°, 4-*ethoxy*-2-*methyl*-, m.p. 110—111°, 2-ethoxy-5-methyl-, m.p. 138—138·5°, 2-n-*propoxy*-4-*methyl*-, m.p. 126—127°, 4-n-*butoxy*-5-*methyl*-, m.p. 95—96°, 3 : 4-, m.p. 135—136°, 2 : 4-, m.p. 166—167°, and 2 : 5-*dimethoxy*-, m.p. 148°, 3 : 4-, m.p. 162—163°, 2 : 4-, m.p. 184—185°, and 2 : 5-*diethoxy*-, m.p. 154—155°, 2 : 3 : 4-*trimethoxy*-, m.p. 123—124°, 3-chloro-4-methoxy-, m.p. 130—131°, 5-chloro-2-methoxy-, m.p. 150—151° (lit. 154°), 3-*bromo*-4-*methoxy*-, m.p. 139—140°, 5-*bromo*-2-*methoxy*-, m.p. 147—148°, 5-*fluoro*-2-*methoxy*-, m.p. 174—175°, 3-*chloro*-4-*ethoxy*-, m.p. 132—133°, 5-*chloro*-2-*ethoxy*-, m.p. 134—134·5°, 3-*bromo*-4-*ethoxy*-, m.p. 134—135°, 5-*bromo*-2-*ethoxy*-, m.p. 144—144·5°, and *p*-*p*′-bromophenoxy-, m.p. 130—131°, -benzenesulphonamide; 4-, m.p. 156—157°, and 7-*methoxy*-, m.p. 150—151°, 4-, m.p. 164—165°, and 7-ethoxy-, m.p. 161—163° (lit. 155°), -naphthalenesulphonamide; Ph_2 ether 4 : 4′-disulphonamide, m.p. 159°; αβ-*diphenoxyethane*-, m.p. 228—229°, and αγ-*diphenoxypropane*-, m.p. 244—245°, -4 : 4′-*disulphonamide*.

R. S. C.

Potentiometric titration of quinol, *p*-aminophenol, and *p*-methylaminophenol with complex chlorides of quadrivalent iridium. S. G. Bogdanov and S. E. Krasikov (Ann. Sect. Platine, 1939, No. 16, 77—80).—Quinol, *p*-NH_2·C_6H_4·OH, and *p*-NHMe·C_6H_4·OH are titrated with 0·01N-K_2IrCl_6 or -$(NH_4)_2IrCl_6$.

R. T.

Separation and determination of isomeric menthols. R. T. Hall, J. H. Holcomb, jun., and D. B. Griffin (Ind. Eng. Chem. [Anal.], 1940, **12**, 187—188).—From a mixture of *l*-menthol, *d*-neomenthol (I), and *d*-*iso*menthol (II), (I) is separated by fractional distillation followed by acetylation and hydrolysis of the recryst. acetate, and (II) by fractional distillation and crystallisation. Total menthol in mixtures is determined by acetylation and determination of the sap. val. of the acetate using KOH in $(CH_2·OH)_2$. Use of $(CH_2·OH)_2$ in place of EtOH greatly reduces the time of saponification.

J. D. R.

Cantharides. I. Titration of cantharidin. B. P. Hecht and L. M. Parks (J. Amer. Pharm. Assoc., 1940, **29**, 71—77).—Purified cantharidin (I), m.p. 214—214·5° (uncorr.), cannot be titrated quantitatively in presence of EtOH; in this respect, it resembles $C_6H_4(CO)_2O$ and Bz_2O. Titration of (I) and other anhydrides is effected by adding 0·5N-KOH in EtOH, removing EtOH, and back-titrating with 0·1N-HCl. Cantharidic acid has dissociation const. 5×10^{-9}, whilst the degree of hydrolysis of 0·005M-K cantharidate in H_2O at 25° is 2·28%.

F. O. H.

Diliturates of physiologically important bases. C. E. Redemann and C. Niemann (J. Amer. Chem. Soc., 1940, **62**, 590—593).—Properties of 5-nitrobarbiturates of 71 org. bases are recorded. The salts of lower aliphatic amines, proteinogenic amines, and some NH_2-acids are very sparingly sol. and are excellent for quant. separation from some mixtures. The bases are readily recovered by double decomp., which also serves best for formation of the salts. The Mg (0·1 mmol. per l.), Ba, Sr, Ca, Cu, and K (separation from Na) salts are very slightly sol.

R. S. C.

Reactions of diethylbarbituric acid and pyrazolone derivatives with silver proteinate, silver nitrate, and ferric chloride. V. Zanotti (Boll. Chim. farm., 1940, **79**, 117—120).—Colour reactions are described.

F. O. H.

Action of a copper–iodine reagent on alkaloids. Precipitation and colour reactions. M. Péronnet and J. Guénin (J. Pharm. Chim., 1940, [ix], **1**, 142—147).—Aq. solutions of many alkaloids, but not glucosides or barbiturates, give ppts. when treated with a Cu_2I_2 reagent, which is more sensitive than I–KI. Ppts. obtained with sparteine, quinine, and cocaine contain Cu; they are readily hydrolysed and decompose at 60°. The ppt. obtained with eserine dissolves in aq. NH_3 with violet-red colour. Ephedrine and adrenaline give violet and red colours, respectively.

J. L. D.

Action of heat on hæmoglobin and reversible stages in coagulation of proteins.—See A., 1940, III, 380.

Colour reaction of phenarsazine chloride J. Delga (J. Pharm. Chim., 1940, [ix], **1**, 73—76).—Phenarsazine chloride (I) or oxide with the $AgNO_3$ reagent (10% aq. $AgNO_3$: AcOH = 1 : 1) (5 c.c.) at 100°/10 min. gives a yellow or orange colour depending on the concn. 0·04 mg. can be detected. Many other As derivatives do not give the reaction. (I) ni H_2O (1 in 125,000) is detected similarly.

J. L. D.