BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JANUARY, 1941.

I.—ALIPHATIC.

Reaction of hydrogen atoms with butane.—See A., 1941, I, 16.

Manufacture of butadiene.—See B., 1940, 779.

Nitration of aliphatic hydrocarbons. P. G. Stevens and R. W. Schiessler (*J. Amer. Chem. Soc.*, 1940, **62**, 2885—2886). —*l*-CHMeEt·C_5H_{11}-*n*, α_D^{25} −6·5°, and HNO_3 (*d* 1·075) at 130° give *l*-*n*-C_5H_{11}·CMeEt·NO_2, b.p. 106·5—107°, α_D^{25} −0·65° (−0·70°). The mechanism of such nitrations is briefly surveyed. R. S. C.

β-Dioximes and trialkyl*iso*oxazoles from nitroparaffins. S. B. Lippincott (*J. Amer. Chem. Soc.*, 1940, **62**, 2604—2606). —$EtNO_2$ (1), NH_2Pr^a or $NHEt_2$ (1), and H_2O (0·5 mol.) at room temp. give 15% of *βδ-dioximino-γ-methyl*-n-*pentane*, m.p. 132·2±0·1° (with hot, dil. H_2SO_4 gives 1 mol. of NH_2OH). Pr^aNO_2, NH_2Bu^a or NH_2Pr^a, and H_2O give 57% of *γε-dioximino-δ-ethyl*-n-*heptane*, m.p. 135·4±0·1°, converted by boiling 3N-H_2SO_4 or dil. NaOH into 3 : 4 : 5-*triethyliso*oxazole, b.p. 215·3±0·2°/761 mm. Bu^aNO_2, NH_2Bu^a, and H_2O give *δζ-dioximino*-ε-n-*propyl*-n-*nonane* (37%), m.p. 116·6±0·2°, converted by boiling 2N-H_2SO_4 into 3 : 4 : 5-tri-*n*-propyl*iso*oxazole (96%), b.p. 255·2±0·2°. A mechanism for conversion of nitroparaffins into *iso*oxazoles by way of dioximes is proposed. R. S. C.

Manufacture of alcohols from olefines.—See B., 1940, 779.

Catalytic dehydrogenation of alcohols in the liquid phase using ethylene as a hydrogen acceptor. W. Reeve and H. Adkins (*J. Amer. Chem. Soc.*, 1940, **62**, 2874—2876).—Dehydrogenation of liquid aliphatic alcohols (≮C_4) by C_2H_4 in presence of mixed Cu–Zn–Ni–Ba chromite (prep. described) at 280°/70—130 atm. gives 26—77% of the aldehyde or ketone. Examples are $Bu^{\alpha}OH$, $Bu^{\beta}OH$, $CH_2Bu^{\gamma}·OH$, *n*-C_6H_{13}·OH, $CHEtBu^{\alpha}·CH_2·OH$, $C_{12}H_{25}$·OH, heptan-β- and -δ-ol. Cu chromite is necessary for formation of aldehyde, the other metals (particularly Ba) minimise deactivation of the catalyst, and Zn and Ni minimise condensation of the aldehyde. The reaction is best stopped before all the alcohol is dehydrogenated, as otherwise much aldehyde is lost by condensation. R. S. C.

Rearrangement of unsaturated αδ-glycols. II. *cis*- and *trans*-forms of βε-dimethyl-Δ$^{\gamma}$-hexene-βε-diol. J. R. Johnson and O. H. Johnson (*J. Amer. Chem. Soc.*, 1940, **62**, 2615—2620; cf. A., 1933, 47).—Me_2 maleate and MgMeBr (6 mols.) in Et_2O, first at −30° to −35° and then at ≯10°, give *cis*-$(OH·CMe_2·CH{:})_2$ (**I**) (35%), m.p. 69—70° (configuration confirmed by reactions described below; cf. Bourguel *et al.*, A., 1925, i, 883; 1928, 989, 1353; 1929, 317; 1930, 574), and a mixture (50%), shown to contain γγ-dimethylcrotonolactone (**II**) (~15%) and β-(? α-)methyl-γ-*iso*hexolactone by hydrogenation (Raney Ni; 25°/6·5 atm.) and conversion into $OH·CMe_2·[CH_2]_2·CO·NH_2$, m.p. 98·5—99·5°, and γ-hydroxy-β-(? α-)methyl*iso*hexoamide, m.p. 104—106°. Very little (**I**) is obtained at 25°. 30% of (**II**), m.p. 9—9·5°, b.p. 87°/14 mm., 207°/750 mm., is obtained from $COMe·[CH_2]_2·CO_2Bu^a$ by MgMeBr–Et_2O at −35°, hydrolysis by boiling 15% KOH–EtOH, and finally acidification. Me_2 fumarate and MgMeBr give only the mixed lactones. *trans*-$(OH·CMe_2·CH{:})_2$ (**III**), m.p. 101·5—102·5° (cf. Bourguel *et al.*, *loc. cit.*), is obtained (65%) by condensing $COMe_2$ with $(:C·MgBr)_2$ and reducing the product. As anticipated, the dielectric const. of (**III**) is < that of (**I**). (**I**) is dehydrated by boiling 15% H_2SO_4 or by conc. HCl at −10°, followed by C_5H_5N, to 2 : 2 : 5 : 5-tetramethyl-2 : 5-dihydrofuran, b.p. 100—102°/747 mm. (cf. Zalkind, A., 1923, i, 176), hydrogenated (Raney Ni; 25°/6·5 atm.) to the H_4-derivative (**IV**), b.p. 125—128°, which with HBr in light petroleum gives $(CMe_2Br·CH_2)_2$ (**V**), m.p. 67·5—68·5°). $(CH_2·CO_2Et)_2$ (0·7 mol.) and MgMeBr (2·9 mols.) at −20° give $(OH·CMe_2·CH_2)_2$, dehydrated by 85% H_3PO_4 at 140° to (**IV**), whence (**V**) is obtained. Conc. HCl and (**III**) at −10° give slowly *βε-dichloro-βε-dimethyl-Δ$^{\gamma}$*-n-*hexene*, b.p. 175—180°/745 mm., 75—80°/21 mm. Boiling H_2SO_4–AcOH–H_2O (15 : 42·5 : 42·5 parts. by wt.) converts (**III**) into $(CH_2{:}CMe·CH{:})_2$ (**VI**), b.p. 128°/746 mm., 34—35°/18 mm. (maleic anhydride adduct, m.p. 135—136°), and its (?) *dimeride*, b.p. 145—147°/18 mm. (maleic anhydride adduct, sublimes at ~225°), but at room temp. gives (**VI**) and (?) $CH_2{:}CMe·CH{:}CH·CMe_2·OH$, b.p. 145—165°. R. S. C.

Reactions relating to carbohydrates and polysaccharides. LXI. Mechanism of polymerisation of ethylene oxide. S. Perry and H. Hibbert (*J. Amer. Chem. Soc.*, 1940, 62, 2599—2604).—Reactions are described favouring step-wise formation of linear polymerides from $(CH_2)_2O$ (cf. Whitby *et al.*, A., 1928, 627). The degree of polymerisation of the products formed by KOH decreases regularly as the amount of H_2O present is changed from 10 to 0·01 mol. A similar gradual decrease occurs as $(CH_2)_2O$ reacts with increasing amounts of $(CH_2·OH)_2$ in presence of a little KOH. Similar results are obtained with $H·(O·[CH_2]_2)_n·OH$ (*n* = 2—6 or 18) in presence of NaOH or Na in absence of O_2 and H_2O. The degree of polymerisation increases regularly with time as $(CH_2)_2O$ is polymerised by aq. KOH. The product obtained after completion of the reaction of $(CH_2)_2O$ with $H·(O·[CH_2]_2)_2·OH$ reacts further with more $(CH_2)_2O$ to produce products of yet higher mol. wt. and this process may be repeated several times. Polymerides are also formed from $(CH_2)_2O$ with MeOH, EtOH, NH_2Ph, or $OH·[CH_2]_2·OMe$ in presence of a little catalyst, but not with $(CH_2·OMe)_2$. Dioxan is never formed. R. S. C.

Syntheses of di-β-hydroxyethyl sulphide from ethylene oxide and hydrogen sulphide. H. F. Tseou and T. L. Pan (*J. Chinese Chem. Soc.*, 1939, **7**, 29—32).—$2(CH_2)_2O$ and H_2S with Fe or Al_2S_3 at 340° afford good yields of $(OH·CH_2·CH_2)_2S$ (cf. Tschitschibabin *et al.*, A., 1935, 606). Apparatus is described. A. T. P.

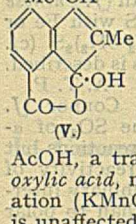
α-Bromo-sulphones. W. M. Ziegler and R. Connor (*J. Amer. Chem. Soc.*, 1940, **62**, 2596—2599).—The SO_2 of α-bromo-sulphones activates the Br for oxidation reactions but deactivates it for metathesis. The increased reactivity of Br in most α-Br-ketones etc. is thus due to preliminary interaction of the CO etc. with the reagent rather than to polar effects. General syntheses of bromo-sulphones are described. *p*-$C_6H_4Me·SO_2Me$ (**I**) with MgEtBr in Et_2O–C_6H_6 gives C_2H_6 and *p*-$C_6H_4Me·SO_2·CH_2·MgBr$, which with Br in C_6H_6 gives 50% of *p*-$C_6H_4Me·SO_2·CH_2Br$ (**II**), m.p. 89—90°. This method is the most convenient but is not applicable to dialkyl sulphones owing to formation of isomerides. (**II**) is also obtained (33%) from *p*-$C_6H_4Me·SO_2Na$ and CH_2Br_2 in boiling EtOH, but not from (**I**) by Br or NaOBr–$Bu^{\gamma}OCl$. Bu^aSNa and CH_2Br_2 in boiling, abs. EtOH give $(CH_2·SBu^a)_2$, an oil, oxidised by 30% H_2O_2–AcOH–Ac_2O at 20—40° to $(CH_2·SO_2Bu^a)_2$, m.p. 180—181°, which with boiling KCN–H_2O–EtOH gives 72% of Bu^aSO_2Na. With CH_2Br_2 in boiling EtOH this gives 41% of *CH_2Br Bu^a sulphone* (**III**), m.p. 47—48°. Crude oily $Bu^aSO_2·CHEt·CO_2Na$, obtained from $CHEtBr·CO_2Na$ and Bu^aSO_2Na in boiling H_2O, with NaOBr at 0° gives 25% of *α-bromo*-n-*propyl Bu^a sulphone*, b.p. 133—136°/5 mm. However, *p*-$C_6H_4Me·SO_2·CH_2·CO_2Na$ and NaOBr at 0° give only (70%) *p*-$C_6H_4Me·SO_2·CHBr_2$ (**IV**), m.p.

116—117°. $Bu^{\alpha}SNa$ and (II) give 76% of (I) and $Bu^{\alpha}_2S_2$ (not isolated); p-C_6H_4Me·SNa and (III) give 90% of (p-C_6H_4Me·S)$_2$ and an oil. MgPhBr and (II) in boiling Et_2O give (I) (59%) and PhBr (77%). C_5H_5N reacts very slowly with (II) or (III) in boiling, abs. EtOH, giving 8% of (p-C_6H_4Me·SO_2·CH_2)$_2$ and 2% of ($Bu^{\alpha}SO_2$·CH_2)$_2$, respectively. NaOEt and (II) in boiling EtOH give 74% of (I) and MeCHO (not identified). (II) and (III) do not react with HI or N_2H_4. (II) does not react with $NHMe_2$ at room temp. or 40—50° or with KCN in boiling 75% EtOH. (III) does not react with boiling NaOAc–EtOH. N_2H_4 and (IV) slowly generate a little N_2. R. S. C.

Syntheses of acetic acid at high pressures.—See B., 1940, 777.

Structure of vinyl polymerides. IX. Catalysts. C. S. Marvel and E. H. Riddle (*J. Amer. Chem. Soc.*, 1940, **62**, 2666—2670; cf. A., 1940, II, 23).—Polymerisation of CH_2:CH·OAc by ultra-violet light gives polymerides, (I) mol. wt. (η) 23,700 and (II) mol. wt. 28,050. KOH–MeOH at room temp. hydrolyses (I) to a glycol, indifferent to HIO_4. Polymerisation by $CdCl_2$ gives a polymeride, mol. wt. 19,400, the glycol from which is also unaffected by HIO_4. These polymerides are both head-to-tail, cross-linked types. BF_3,Et_2O or C_6H_4Me·N_2BF_4 gives black polymerides containing many conjugated ethylenic linkings. CH_2:CHBr·CO_2Me in dioxan in ultra-violet light or with BF_3–Et_2O–PhMe gives polymerides, mol. wt. 11,200 and 6700, respectively, whence Zn removes 85—95% of the Br; they are thus similar. CH_2:CHBr in ultra-violet light or with BF_3,Et_2O gives polymerides, differing physically but both losing Br and HBr to Zn and losing HBr to KI. Polyvinyl chloride loses only 72% of its Cl to Zn and no HCl to KI. R. S. C.

Mechanism of polymerisation. VI. Heat-polymerisation of methyl sorbate, and constitution of the dimeric products. E. H. Farmer and C. R. Morrison-Jones (*J.C.S.*, 1940, 1339—1346; cf. Kuhn *et al.*, A., 1932, 258).—Distillation of the products of heating Me sorbate in CO_2 at 185—235° gives monomeric (6%, chiefly Me sorbate), dimeric (I) (81%), and higher polymeric fractions. Prolonged fractionation and hydrolysis of (I) yields chiefly a semi-resinous acid, with 1-*methyl*-2-*propenyl*-Δ^4-cyclo*hexene*-3 : 4- (II), m.p. 216°, 1-*methyl*-3-*propenyl*-Δ^4-cyclo*hexene*-2 : 4- (III), m.p. 191°, 1-*methyl*-3-*propenyl*-Δ^3-cyclo*hexene*-2 : 4-*dicarboxylic acid* (IV), m.p. 200°, and an (impure ?) acid, m.p. 164—169°. One ester fraction with NH_2·C_6H_4·MgBr gives a *dianilide*, $C_{24}H_{26}O_2N_2$, m.p. 288—290° (decomp.), unaffected by prolonged boiling with MeOH–KOH. AcCl converts (II) into its *anhydride*, m.p. 84°, hydrolysed by boiling H_2O to (II). Hydrogenation (PtO_2) of (II) gives 1-*methyl*-2-n-*propyl*cyclo*hexane*-3 : 4-*dicarboxylic acid*, m.p. 188°, and an acid, m.p. (crude) 154—159°, whilst dehydrogenation (Se) affords 2-n-*propyltoluene*-3 : 4-*dicarboxylic acid*, m.p. 178° (also obtained by Pd–C dehydrogenation), and (V) (?), m.p. (crude) 167—169°, oxidised to 3-oxalylbenzene-1 : 2 : 4-tricarboxylic acid, m.p. 212—216° (decomp.) (*Me*$_4$ ester, m.p. 102°). The ozonide (prepared in EtOAc) of (II) with H_2O, Na_2CO_3, and then $KMnO_4$ at 0° yields AcOH, $H_2C_2O_4$, and CO_2H·CH_2·CMe(CO_2H)·CHMe·CO_2H (VI). The ozonide prepared in $CHCl_3$ similarly yields AcOH, a trace of $H_2C_2O_4$, and *β-methylbutane-αγδδ-tetracarboxylic acid*, m.p. 169°, which when heated yields (VI). Oxidation ($KMnO_4$) of (II) gives only AcOH and $H_2C_2O_4$. (III) is unaffected by AcCl. Hydrogenation (PtO_2) of (III) yields 4-*methyl*-2-n-*propyl*isophthalic *acid* (VII), m.p. 164°, together with an acid, m.p. (crude) 145—150°, whilst dehydrogenation (Se) gives m-$C_6H_4(CO_2H)_2$. Oxidation ($KMnO_4$ or O_3 in $CHCl_3$) of (III) proceeds as with (II). (IV) is hydrogenated (PtO_2) to (VII), and undergoes no isomerisation with MeOH–KOH or conc. HCl. The mechanism of the formation of the dimerides is discussed. A. Li.



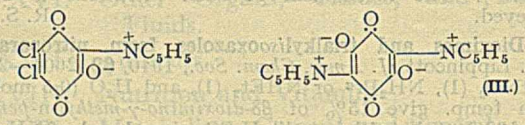
(V.)

Esters of fatty acids. D. Price and R. Griffith (*J. Amer. Chem. Soc.*, 1940, **62**, 2884).—The following are prepared. Phenacyl nonoate and undecoate, oils, *tridecoate*, m.p. 45—45·5°, *pentadecoate*, m.p. 53·6° (rapid heating), and *heptadecoate*, m.p. 60—60·5°. p-*Phenylphenacyl nonoate*, m.p. 70·8—71·3°, *undecoate*, m.p. 79·5—80°, *tridecoate*, m.p. 86·5—87°, *pentadecoate*, m.p. 91·3—91·8°, and *heptadecoate*, m.p. 95·3—95·8°. *p*-Nitrobenzyl heptoate, nonoate, undecoate, and tridecoate, oils, *pentadecoate*, m.p. 39·5—40°, and *heptadecoate*, m.p. 48·5—49°. R. S. C.

Constitution of arachidonic acid. D. E. Dolby, L. C. A. Nunn, and I. Smedley-Maclean (*Biochem. J.*, 1940, **34**, 1422—1426).—Oxidation of arachidonic acid with alkaline $KMnO_4$ gives $H_2C_2O_4$, AcOH, $BuCO_2H$, and succinic acid, with some HCO_2H, hexoic and glutaric acids. $H_2C_2O_4$ accounts for $\leqslant$50% of the CH_2 groups. Adipic acid is not obtained. The formula Me·$[CH_2]_4$·$[CH$:$CH·CH_2]_4$·$[CH_2]_2$·CO_2H is suggested. P. G. M.

Condensations. XIV. Alkylation of ethyl acetoacetate by *iso*propyl acetate in presence of boron trifluoride. D. S. Breslow and C. R. Hauser (*J. Amer. Chem. Soc.*, 1940, **62**, 2611—2612; cf. A., 1940, II, 363).—$CH_2Ac·CO_2Et$, $Pr^{\beta}OAc$, and BF_3 give 42·1% of $CHPr^{\beta}Ac·CO_2Et$. The mechanism of such reactions of esters is discussed. R. S. C.

Colour reaction of maleic anhydride, *p*-benzoquinone, their partially substituted derivatives, and citric acid. Some zwitterions. A. Schönberg and A. F. A. Ismail (*J.C.S.*, 1940, 1374—1378; cf. A., 1940, II, 35).—Colour reactions with PPh_3 are recorded for 5 maleic anhydride (I) and 12 *p*-benzoquinone derivatives, some of them requiring heating. Thymoquinone and (I) give colours in absence of solvent. Itaconic anhydride reacts (owing to isomerisation) only in solution. With PPh_3 in C_6H_6, (I) gives a cryst. *betaine*, m.p. ~160°, and an amorphous substance (responsible for the colour) which when heated in CO_2 gives PPh_3. Chloranil with


(II.)

(III.)

C_5H_5N and AcOH or HCO_2H in boiling $CHCl_3$ gives a betaine (II), m.p. >330°. Chlor- or brom-anil or (II) with C_6H_5N in H_2O yields the *dibetaine* (III), m.p. >300°, which with boiling Ac_2O gives a *compound*, $C_{16}H_{10}O_4N_2$, m.p. >300° (*hydrate*). (II) or (III) with boiling aq. Na_2CO_3 or $KMnO_4$ yields C_5H_5N. A. Li.

***sec.*-Alkyl α-bromo-ketones. I. Reaction with sodium alkoxides. Synthesis of *tert.* acids by rearrangement.** J. G. Aston and R. B. Greenburg (*J. Amer. Chem. Soc.*, 1940, **62**, 2590—2595).—COMe·CMe_2Br (I) and NaOR yield $\beta\gamma$-epoxy-γ-alkoxy-β-methyl-*n*-butane (cf. Ward, A., 1929, 1072), which either rearranges spontaneously to $Bu^{\gamma}CO_2R$ or, if ROH is present, yields OH·CMe_2·CMe(OR)$_2$. NaOMe and (I) in abs. MeOH at room temp. give OH·CMe_2·CMe(OMe)$_2$ (II) (76·5%), b.p. 159—161°/730 mm. (cf. Froning *et al.*, A., 1940, II, 187), hydrolysed by boiling 2% HCl to OH·CMe_2·COMe (III). With 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH·NH_2 in 2N-HCl, (II) gives the 2 : 4-*dinitrophenylhydrazone* (IV), m.p. 139—140°, of (III), but in abs. MeOH gives γ-*methoxy*-γ-*methyl*-n-*butan*-β-*one*-2 : 4-*dinitrophenylhydrazone* (V), m.p. 138—139°. NaOEt and (I) in abs. EtOH give 32% of γγ-*diethoxy*-β-*methyl*-n-*butan*-β-*ol* (VI), b.p. 110—112°/98 mm., and 17·6% of $Bu^{\gamma}CO_2Et$. (VI) gives, as above, (III), (IV), and γ-*ethoxy*-γ-*methyl*-n-*butan*-β-*one*-2 : 4-*dinitrophenylhydrazone*, m.p. 110·5—111°. NaOPr$^{\beta}$–Pr$^{\beta}$OH and (I) give 20% of $Bu^{\gamma}CO_2Pr^{\beta}$ and 8% of (?) OH·CMe_2·CMe(OPr$^{\beta}$)$_2$, b.p. 67—95°/46 mm. Addition of Na (1 atom) and then of (I) (1 mol.) to MeOH (1·5 mol.) in abs. Et_2O gives 39% of $Bu^{\gamma}CO_2Me$ and 12% of (II). NaOEt in Et_2O gives similarly 61·3% of $Bu^{\gamma}CO_2Et$, and NaOPr$^{\beta}$ in Et_2O gives 64% of $Bu^{\gamma}CO_2Pr^{\beta}$. COEt·$CMe_2Br$ (VII) and NaOMe–MeOH give γγ-*dimethoxy*-β-*methyl*-n-*pentan*-β-*ol* (65·5%), b.p. 82·5°/100 mm., which yields in 2N-HCl, MeOH, or EtOH the 2 : 4-*dinitrophenylhydrazones*, m.p. 125—126°, 139—139·5°, and 128—129°, of OH·CMe_2·COEt, OMe·CMe_2·COEt, and OEt·CMe_2·COEt, respectively. NaOMe and (VII) in Et_2O give 57% of $CMe_2Et·CO_2Me$. Boiling aq. KOH and (I) give 76% of (III), which in 2N-aq. HCl gives (IV) and in HCl–MeOH gives (V). γ-*Bromo*-γ-*methyl*-n-*pentan*-β-*one*, b.p. 57°/19 mm. (prep. from COMe·CHMeEt), yields similarly γ-*hydroxy*-γ-*methyl*-n-*pentan*-β-*one*, b.p. 148—150°/730 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°). (II) is recovered after treatment with $MgPr^{\beta}Br$–Et_2O, Me_2SO_4–NaOH, or HCl–MeOH, although with the two first-named reagents reaction occurs. R. S. C.

Esters of diacetone alcohol. R. C. Huston and H. E. Ungnade (*J. Amer. Chem. Soc.*, 1940, **62**, 2885).—OH·CMe_2·CH_2·COMe and boiling $(RCO)_2O$ give 70% of CMe_2:CH·COMe and 10—15% of δ-*keto*-α-*methyl*-n-*amyl*

acetate, b.p. 171—173°/742 mm., 72—73°/10 mm. (*semicarbazone*, m.p. 137·5—138°), *propionate*, b.p. 182—184°/742 mm., 80—81°/8 mm. (*semicarbazone*, m.p. 144·5—145°), and *butyrate*, b.p. 192—193°/742 mm., 97—98°/12 mm. (*semicarbazone*, m.p. 110·4—110·8°). R. S. C.

Synthesis of a new dimethyl-β-methylglucoside. R. E. Reeves, M. H. Adams, and W. F. Goebel (*J. Amer. Chem. Soc.*, 1940, **62**, 2881—2882).—β-Methylglucoside 3-*p*-toluenesulphonate triacetate is converted successively into (by HCl–MeOH at 37°) β-methylglucoside 3-*p*-toluenesulphonate, the CPh_3 ether (*diacetate*, m.p. 145—147°, $[\alpha]_D$ +14·5° in $CHCl_3$) thereof, (Purdie method) 2 : 4-dimethyl-β-methylglucoside 6-CPh_3 ether 3-*p*-toluenesulphonate, and (Na–Hg–EtOH) 2 : 4-*dimethyl-β-methylglucoside*, m.p. 122—123°, $[\alpha]_D^{29}$ −18·6° in $COMe_2$, in 2·5% yield, the intermediates being oils. R. S. C.

Oxidation of aldoses with hypoiodite. VIII. Oxidation of digitoxose with hypoiodite. K. Myrbäck (*Svensk Kem. Tidskr.*, 1940, **52**, 200—203).—Digitoxose is shown to have the glucose-galactose configuration by its rate of oxidation with NaOI. M. H. M. A.

Tetra-acetylaldehydophenylglucosides. R. T. Williams (*J.C.S.*, 1940, 1402—1403).—*p*-OH·C_6H_4·CHO with β-glucose penta-acetate and 10% of anhyd. $ZnCl_2$ or 1% of *p*-$C_6H_4Me{\cdot}SO_3H$ (Helferich *et al.*, A., 1933, 379) gives poor yields of *p*-aldehydophenyl-β-*d*-glucoside tetra-acetate, $[\alpha]_D^{19}$ −27·9° to −28° in $CHCl_3$ (2 : 4-*dinitrophenylhydrazone*, m.p. 216—218°). *m*-OH·C_6H_4·CHO similarly yields m-*aldehydophenyl-α-d-glucoside tetra-acetate*, m.p. 123—124°, $[\alpha]_D^{22}$ +153·9° in $CHCl_3$ (2 : 4-*dinitrophenylhydrazone*, m.p. 170°), which gives a hard resin when deacetylated (NaOMe in MeOH), whilst *o*-OH·C_6H_4·CHO gives only 3 : 4 : 7 : 8-dibenz-2 : 6 : 9-bis-dioxan. A. Li.

Cardiac glycoside, m.p. 130°, from *Asclepias curassavica*.—See A., 1940, III, 862.

Nature of the glucosidic linkings in starch. K. Myrbäck (*Svensk Kem. Tidskr.*, 1940, **52**, 126—133).—β-Glucosidic linkings are not present in starch, but vals. of $[\alpha]$ for limit dextrins suggest that a few 1 : 6-α-glucosidic linkings are present. M. H. M. A.

Arylsuphonyl derivatives of ethylenediamine. L. H. Amundsen and R. I. Longley, jun. (*J. Amer. Chem. Soc.*, 1940, **62**, 2811—2812).—$NH_2{\cdot}[CH_2]_2{\cdot}NHAc$ and $ArSO_2Cl$ in aq. $NaHCO_3$ at room temp. give N-*benzene-*, m.p. 104·9—105·2°, and N-*p-toluene-sulphonyl-N′-acetylethylenediamide*, m.p. 109·5—109·9°, hydrolysed by boiling aq. HCl to N-*benzene-*, m.p. 172·1—173·6°, and *N-p*-toluene-sulphonylethylenediamine, m.p. 123—124°. Boiling $(CH_2{\cdot}NH_2)_2$ with $ArSO_2Cl$ in C_6H_6 or by Schneider's method (A., 1896, i, 200) gives *NN′*-di-benzene-, m.p. 168·6—169·3°, and *-p*-toluene-sulphonethylenediamide, m.p. 162·6—163·6°, converted by $ArSO_2Cl$ in $PhNO_2$ at the b.p. (Ar = Ph) or, better for Ar = *p*-C_6H_4Me, 100° into *tetrabenzene-*, m.p. 209—209·7°, and -p-*toluene-sulphonethylenediamide*, m.p. 248·5—249·7°. $N(ArSO_2)_2{\cdot}[CH_2]_2{\cdot}NH{\cdot}SO_2Ar$ could not be obtained. R. S. C.

Action of diazobenzene on alkylacetoacetic ester as method of preparing α-amino-acids and phenylhydrazones of α-keto-acids. I. Synthesis of *iso*leucine and leucine. V. V. Feofilaktov [with L. A. Bogdanova and A. S. Onischtschenko]. **III. Synthesis of alanine.** V. V. Feofilaktov and V. Zajtzeva (*J. Gen. Chem. Russ.*, 1940, **10**, 247—254, 255—259).—An account of work already noted (A., 1940, II, 70).

Action of Grignard reagents on heavy metal salts. V. Formation of olefines in the reaction with silver bromide. J. H. Gardner and C. J. Snyder (*J. Amer. Chem. Soc.*, 1940, **62**, 2879—2880; cf. A., 1939, II, 496; 1940, II, 198).—*n*-$C_6H_{13}{\cdot}MgBr$ and AgBr in Et_2O at, successively, 0°, room temp., and the b.p. give *n*-$C_{12}H_{26}$ and a little *n*-C_6H_{12} and $CHBu^a{:}CH_2$ (identified as dibromide). R. S. C.

II.—HOMOCYCLIC.

***p*-Bromophenylcyclopentane.** R. D. Kleene (*J. Amer. Chem. Soc.*, 1940, **62**, 2883).—Addition of Br to phenylcyclopentane and I gives p-*bromophenylcyclopentane* (55%), b.p. 115—118°/20 mm., oxidised by $Na_2Cr_2O_7$ to *p*-$C_6H_4Br{\cdot}CO_2H$. R. S. C.

Continuous sulphonation of benzene.—See B., 1940, 777.

Nitration mixtures. I. M. Usanovitsch. **II. Nitration of toluene in presence of acetic acid and nitrobenzene.** M. Usanovitsch and S. Abidov. **III. Nitration of toluene in presence of sulphuric and trichloroacetic acid.** M. Usanovitsch and I. Gluchov. **IV. Nitration of toluene in presence of monochloroacetic acid and ethyl nitrate.** M. Usanovitsch and T. Suschkevitsch (*J. Gen. Chem. Russ.*, 1940, **10**, 219—222, 223—226, 227—229, 230—232).—I. Nitration of aromatic hydrocarbons is effected by $[NO(OH)_2]^+$ or $N(OH)_3^{\cdot\cdot}$, but of aliphatic hydrocarbons by NO_3'.

II. In the systems PhMe–HNO_3–AcOH or –$PhNO_2$, the yield of $C_6H_4Me{\cdot}NO_2$ falls, and of $CH_2Ph{\cdot}NO_2$ and BzOH rises, with increasing [AcOH] or $[PhNO_2]$. It is concluded that these solvents favour the reactions $N(OH)_3^{\cdot\cdot} + O'' \rightleftharpoons HNO_3 + H_2O \rightleftharpoons [NO(OH)_2]^+ + OH'$.

III. Max. yields of $C_6H_4Me{\cdot}NO_2$ are obtained with 1 : 1 HNO_3–H_2SO_4 or 1 : 3 HNO_3–$CCl_3{\cdot}CO_2H$, and of $C_6H_3Me(NO_2)_2$ with 15 : 85 HNO_3–H_2SO_4. $CH_2Ph{\cdot}NO_2$ is not formed.

IV. Production of $C_6H_4Me{\cdot}NO_2$ and $CH_2Ph{\cdot}NO_2$ falls steadily with rising concn. of the indifferent solvents $CH_2Cl{\cdot}CO_2H$ or $EtNO_3$. Undissociated HNO_3 is not a nitrating agent. R. T.

Polyalkylbenzenes. XXVII. Preparation of pure ethylbenzenes. XXVIII. Physical properties of tetraethylbenzenes. XXIX. Jacobsen reaction. VII. L. I. Smith and C. O. Guss. **XXXI. Preparation and physical properties of 1 : 2 : 3-trimethylbenzene (hemimellithene).** L. I. Smith and L. J. Spillane (*J. Amer. Chem. Soc.*, 1940, **62**, 2625—2629, 2630—2631, 2631—2635, 2639—2642; cf. A., 1940, II, 301; 1939, II, 306).—XXVII. Controlled passage of EtCl into C_6H_6 (11·27 mols.) and $AlCl_3$ (1·5 mols.) at 70—75° gives readily separable mixtures of 1 : 3 : 5- and less 1 : 2 : 4-$C_6H_3Et_3$, 1 : 2 : 3 : 5- and 1 : 2 : 4 : 5-$C_6H_2Et_4$, C_6HEt_5, or C_6Et_6, the proportions of the products formed being varied at will according to the amount of EtCl used. *vic.* Compounds are not formed. Separation of isomerides depends mainly on smooth sulphonation by $ClSO_3H$ (not H_2SO_4 or SO_3–dioxan) at 0—10° and hydrolysis of the purified Na salts or acids by steam-distillation from 50% H_2SO_4. 1 : 2 : 4 : 5-*Tetraethylbenzene*-3-, $+H_2O$, m.p. 105—107° (amide, new m.p. 123—125°; *anilide*, m.p. 107—108°), and 1 : 2 : 3 : 5-*tetraethylbenzene*-4-*sulphonic acid*, $+H_2O$, m.p. 97—99° (*amide*, m.p. 56—57°; *anilide*, m.p. 78—79°), are described.

XXVIII. The following data, d^{20}, n_D^{20}, and v.p. are recorded. 1 : 2 : 4 : 5-, f.p. 10°, b.p. 246°/734 mm., 1 : 2 : 3 : 5-, f.p. −21°, b.p. 247·4°/734 mm., and 1 : 2 : 3 : 4-$C_6H_2Et_4$, f.p. < −50°, b.p. 251·1°/734 mm.

XXIX. Jacobsen rearrangement of 1 : 2 : 4 : 5- and 1 : 2 : 3 : 5-$C_6H_2Et_4$ or 1 : 2 : 4 : 5 : 3-$C_6HEt_5{\cdot}SO_3H$ in conc. H_2SO_4 at 100° is very facile. That of C_6HEt_5 is slow and gives poor yields. 1 : 2 : 3 : 4-*Tetraethylbenzene*-5-*sulphonic acid*, $+H_2O$, m.p. 118—120° (amide, m.p. 103—105°; *anilide*, m.p. 120—121°), is formed in all cases and by distillation in steam from 50% H_2SO_4 at 140° gives ≮90% of 1 : 2 : 3 : 4-$C_6H_2Et_4$. *Pentaethylbenzenesulphonic acid*, $+H_2O$, m.p. 113—115° (*chloride*, m.p. 137—138°; *anilide*, m.p. 140—141°; *Et* ester, m.p. 70—71°), is obtained in 89% yield by $ClSO_3H$ and is readily hydrolysed to C_6HEt_5 by conc. H_2SO_4 at room temp.

XXXI. Prep. of 1 : 2 : 3-$C_6H_3Me_3$, f.p. −25·41±0·05° (corr.), b.p. 176·2±0·1° (*n*, *d*, and v.p. also given), from $CH_2Ph{\cdot}MgCl$ and paraformaldehyde by way of *o*-$C_6H_4Me{\cdot}CH_2{\cdot}OH$ (**I**), *o*-$C_6H_4Me{\cdot}CH_2Cl$, and 2 : 3 : 1-$C_6H_3Me_2{\cdot}CH_2{\cdot}OH$ (**II**) in 26% over-all yield is described. (**I**) is accompanied by large amounts of the formal, and (**II**) by *o*-$C_6H_4Me{\cdot}[CH_2]_2{\cdot}OH$. Chlorides are prepared (83—91%) by HCl in light petroleum. Reduction of (**II**) is smoothly (92%) effected by H_2–Cu–Cr_2O_3 at 225°/100—190 atm., but not by other methods. R. S. C.

Polyalkylbenzenes. XXX. Nitration of tetra-, penta-, and hexa-ethylbenzenes. Bromination of the tetraethylbenzenes. L. I. Smith and C. O. Guss (*J. Amer. Chem. Soc.*, 1940, **62**, 2635—2638; cf. A., 1935, 1114).—Addition of HNO_3 (*d* 1·5) to C_6Et_6, C_6HEt_5, or 1 : 2 : 4 : 5-$C_6H_2Et_4$ gives 17%, 69·7%, and 61%, respectively, of 1 : 2 : 4 : 5 : 3 : 6-$C_6Et_4(NO_2)_2$, m.p. 145—147°, converted by $SnCl_2$, followed by $FeCl_3$, into 3 : 1 : 2 : 4 : 5 : 6-O:C_6Et_4:O (73%), m.p. 58—59°. 1 : 2 : 3 : 4- and 1 : 2 : 3 : 5-$C_6H_2Et_4$ give 5 : 6-dinitro-1 : 2 : 3 : 4- (**I**) (68%), new m.p. 117—118°, and 4 : 6-*dinitro*-1 : 2 : 3 : 5-*tetraethylbenzene* (35%), m.p. 93·5—94·5°, respectively. Reduction of (**I**) affords 5 : 6-*diamino*-1 : 2 : 3 : 4-

tetraethylbenzene, m.p. 69—70°, which yields 10 : 11 : 12 : 13-*tetraethylphenanthrophenazine*, m.p. 169—170°, and 2-*methyl*-4 : 5 : 6 : 7-*tetraethylbenziminazole*, m.p. 241—242°. Bromination in $CHCl_3$ or AcOH gives 3-*bromo*-1 : 2 : 4 : 5-, m.p. 9°, b.p. 149°/9 mm., 4-*bromo*-1 : 2 : 3 : 5-, b.p. 150°/9 mm., and 5-bromo-1 : 2 : 3 : 4-tetraethylbenzene, b.p. 152°/9 mm., and in $CHCl_3$ 3 : 6-dibromo-1 : 2 : 4 : 5- (**II**), m.p. 112—113°, 4 : 6-*dibromo*-1 : 2 : 3 : 5-, m.p. 48·5—49·5°, and 5 : 6-dibromo-1 : 2 : 3 : 4-tetraethylbenzene, m.p. 76—77°. Nitration of (**II**) gives a small amount of a (?) dibromotrimethylbenzyl nitrate, m.p. 120—122°. R. S. C.

Reaction of polystyrenes with bromine [and with benzoyl hydrogen peroxide]. L. Marion (*Canad. J. Res.*, 1940, **18, B**, 309—317).—Attempts to detect a double linking in polystyrenes by BzO_2H gave low results. The reaction with Br depends greatly on concn., but in the more dil. solutions some Br is added. F. J. G.

Dehydrogenation. II. Elimination and migration of methyl groups from quaternary carbon atoms during catalytic dehydrogenation. R. P. Linstead, S. L. S. Thomas, and (in part) K. A. O. Michaelis (*J.C.S.*, 1940, 1127—1134).—The dehydrogenation of *cis*-9-methyl-deca- (**I**) or -octa-hydronaphthalene (**II**) vapour at 300—330° (cf. A., 1937, II, 406) is further examined, with that of other hydronaphthalenes. Catalysts of increased activity are obtained when the method of Willstätter *et al.* (A., 1921, ii, 186) is modified by pptg. the metal at a higher dilution, with stirring. Pt and Pd catalysts give similar results, although Pd apparently has a greater tendency to cause side reactions. In activity, metal–C > metal–asbestos > metal as "black." The course of dehydrogenation of substances containing quaternary C varies with the carrier. Catalysts on asbestos produce greatest migration of angular Me, and approx. equal elimination; the latter strongly predominates with catalysts on C. Thus (**I**) and (**II**) give, with Pt–C, $C_{10}H_8$ and CH_4, and, with Pt– or Pd–asbestos, these and 1-$C_{10}H_7$Me (**III**). Of possible mechanisms of migration of Me from $C_{(9)}$ to $C_{(1)}$, that of ring-opening between $C_{(1)}$ and $C_{(9)}$, with re-formation at $C_{(5)}$, is excluded by dehydrogenating *cis*-4 : 9-dimethyloctahydronaphthalene (**IV**) to 1 : 5-$C_{10}H_6Me_2$ (**V**) (cf. *loc. cit.*). Initial purity of (**IV**) is now established by cyclising 2 : 6-dimethyl-1-Δ$^{\gamma}$-butenyl*cyclo*hexanol by AcOH–Ac_2O–H_2SO_4 to cis-4 : 9-*dimethyldecahydro-α-naphthol*, m.p. 93°, b.p. (crude) 132—142°/13 mm., which with $KHSO_4$ at 194° gives (**IV**), dehydrogenated by Pt–C and Pt–asbestos to (**III**) and to (cryst.) (**V**), as main products respectively. A second possible mechanism, intermediate formation of a C_3-ring involving $C_{(1)}$ or $C_{(9)}$, would with cis-1 : 9-*dimethyloctahydronaphthalene* (VI), b.p. 87°/8—9 mm., imply formation either of a *cyclo*butane ring at $C_{(1)\text{ and }(9)}$ or of a *cyclo*propane ring at $C_{(8)\text{ and }(9)}$, and thus of 1-$C_{10}H_7$Et or of 1 : 8-$C_{10}H_6Me_2$, respectively. Actually (**VI**), prepared by $H_2C_2O_4$-dehydration of cis-1 : 9-*dimethyldecahydro-α-naphthol* [from *cis*-1-keto-9-methyldecahydronaphthalene (Grignard)], is unaffected by Pt–asbestos at 335°, and with Pt–C gives (**III**), with no higher homologue. A third possible mechanism is migration of a hydrocarbon fragment.

Of *gem*-Me_2 compounds, 1 : 1-dimethyltetrahydronaphthalene (**VII**) over Pt–C at 305° gives (**I**) as main product, but over Pd–C at 315° in a continuous circulation apparatus gives also some 1 : 2-$C_{10}H_6Me_2$. 1 : 1 : 6-Trimethyltetrahydronaphthalene (ionene) over Pt–asbestos or Pd–C at 305—330° gives 1 : 6-$C_{10}H_6Me_2$ (synthesised by Clemmensen reduction of 1-keto-4 : 7-dimethyltetrahydronaphthalene, prepared from γ-*p*-tolylvaleryl chloride and $SnCl_4$), no $C_{10}H_5Me_3$ being detected. There is thus much less tendency for Me to migrate from a *gem* than from an angular group. Resistant hydrocarbons with catalysts on C at ≮325° evolve gas copiously and apparently in part give smaller fragments, the yield of liquid products falling to ~70%. In two experiments, (**VII**) and Pt–C at ~320° gave, during early stages, some $C_{10}H_8$ [due to transitory presence in the catalyst of abnormally active centres (?)], as did (**VI**). E. W. W.

Ozonisation of hydrindene. L. Long, jun. and L. F. Fieser (*J. Amer. Chem. Soc.*, 1940, **62**, 2670—2673).—Ozonisation of hydrindene (**I**) in EtCl at −30° or AcOH at room temp. and subsequent hydrogenation (Pd–$CaCO_3$) gives up to 60% of 1-hydrindone with $(CHO)_2$ (up to 1·4% isolated as *p*-nitrophenylosazone or glyoxime) and $(CH_2{\cdot}CO_2H)_2$ (up to 11·4%). Reaction in other solvents is less satisfactory. 62·5% of $(CH_2{\cdot}CO_2H)_2$ is obtained by ozonisation of *cyclo*pentane-1 : 2-dione (modified prep.), f.p. 0° [dioxime, m.p. ~190° (decomp.)], and probably originates therefrom in the decomp. of (**I**). Thus, the Mills–Nixon orientation of ethylenic linkings (A., 1931, 83) in (**I**) is preferred. R. S. C.

Determination of acenaphthene.—See B., 1940, 778.

Abnormal acetoacetic ester synthesis. II. Reaction of sodium with fluorene and benzyl benzoate. H. F. Tseou and T. S. Chow (*J. Chinese Chem. Soc.*, 1939, **7**, 27—28).—Fluorene, $CH_2Ph{\cdot}OBz$ and Na at 170—190° (13 hr.) afford 9-benzylfluorene, m.p. 131°, and BzOH; no 9-benzoylfluorene is obtained. A. T. P.

Aromatic cyclodehydration. VII. Phenanthrene. C. K. Bradsher and R. W. Wert (*J. Amer. Chem. Soc.*, 1940, **62**, 2806—2807; cf. A., 1940, II, 271).—*o*-$C_6H_4Ph{\cdot}MgI$ and MeCHO in Et_2O give 56% of *α-o-diphenylylethyl alcohol*, m.p. 110·5—111·5°, dehydrated by $KHSO_4$ at 160° to *o*-$C_6H_4Ph{\cdot}CH{:}CH_2$ (24%), b.p. 127—130°/5 mm. *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in Et_2O then gives an oxide (not isolated), which in boiling HBr–AcOH affords a little phenanthrene (**I**). Crude *o*-$C_6H_4Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}OMe$, obtained from *o*-$C_6H_4Ph{\cdot}CO{\cdot}CH_2{\cdot}OMe$ by $Al(OPr^{\beta})_3$, with boiling HBr–AcOH gives 46% of (**I**). R. S. C.

Determination of phenanthrene.—See B., 1940, 778.

Polycyclic aromatic hydrocarbons. XXVI. C. L. Hewett and R. H. Martin (*J.C.S.*, 1940, 1396—1398).—Paraformaldehyde with HCl in glacial AcOH, followed by 1 : 2 : 3 : 4-$C_6H_2Me_4$, yields 2 : 3 : 4 : 5 : 2′ : 3′ : 4′ : 5′-*octamethyldiphenylmethane*, m.p. 146—147°, and 2 : 3 : 4 : 5 : 1-$C_6HMe_4{\cdot}CH_2Cl$, which is converted via the nitrile and acid into $C_6HMe_4{\cdot}CH_2{\cdot}CO_2Na$. This with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ and Ac_2O yields *o-nitro-*, m.p. 214—215°, reduced ($FeSO_4$) to *o-amino-α*-2′ : 3′ : 4′ : 5′-*tetramethylphenylcinnamic acid*, m.p. 235—236°, which when diazotised and treated with Cu powder yields *Me o-hydroxy-α*-2′ : 3′ : 4′ : 5′-*tetramethylphenylcinnamate*, m.p. 172—173°, and 1 : 2 : 3 : 4-*tetramethyl*-10-*phenanthroic acid*, m.p. 226—227°, decarboxylated (Cu-bronze in quinoline) to 1 : 2 : 3 : 4-*tetramethylphenanthrene*, m.p. 92—93° [picrate (unstable); *s*-$C_6H_3(NO_2)_3$ *complex*, m.p. 161—162°]. A. Li.

Fluorescence of hydrocarbons and of their mixtures with naphthacene. F. Weigert (*Trans. Faraday Soc.*, 1940, **36**, 1033—1035).—Experiments illustrating the influence of a minute proportion of naphthacene on the fluorescence of 1 : 2 : 5 : 6-dibenzacridine and a no. of condensed hydrocarbons in $COMe_2$ solution and in microcryst. suspensions are described. F. L. U.

Hydrogenation of aniline.—See B., 1940, 842.

Nitro-derivative of 2-bromo-*m*-4-xylidine. W. C. Spitzer (*J. Amer. Chem. Soc.*, 1940, **62**, 2884).—1 : 3 : 2 : 4-$C_6H_2Me_2Br{\cdot}NHAc$ and H_2SO_4–HNO_3 at <15° give the *Ac* derivative, m.p. 171—172° (hydrolysed by boiling 50% H_2SO_4), of 2-*bromo*-6-*nitro*-4-m-*xylidine*, m.p. 129—130° (sublimes), which gives (diazo-reaction) 1 : 3 : 2 : 4-$C_6H_2Me_2Br{\cdot}NO_2$. R. S. C.

Sulphonation of ethylaniline. G. V. Shirolkar, I. S. Uppal, and K. Venkataraman (*J. Indian Chem. Soc.*, 1940 **17**, 443—448; cf. A., 1939, II, 150).—NHPhEt yields with 20% oleum at 185—190°, *p*-, and with 20% oleum at 50—60° followed by more conc. oleum at <40°, a mixture (proportions depending on concn. of oleum) of *p*- and *m*-$NHEt{\cdot}C_6H_4{\cdot}SO_3H$. *N*-Ethylaniline-*o*-, m.p. 212—213° (decomp.) (from *o*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$, Et_2SO_4, and Na_2CO_3), -*m*-, and -*p*-sulphonic acids with *p*-$C_6H_4Me{\cdot}SO_2Cl$ and C_5H_5N yield the *p*-toluenesulphonyl-*N*-ethylanilinesulphonic acids (*p*-$C_6H_4Cl{\cdot}NH_2$ salts, m.p. 181—183°, 111°, and 217—218°, respectively), also prepared by ethylating (Et_2SO_4) the *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$. A. Li.

[Sodium *p*-α-sulphoethylaminobenzenesulphonamide] therapeutic product of sulphanilamide class.—See A., 1941, III, 33.

Soluble aromatic sulphonamide compounds.—See B., 1940, 897.

Nitrogenous compounds of mercury as promoters of the chemical activity of selenium, and their rôle in the preparation of azo-compounds, azines, and dyes from arylamines by the action of sulphur or selenium. P. S. Pischtschimuka (*J. Gen.*

Chem. Russ., 1940, **10**, 305—318).—Dehydrogenation of aromatic amines by S or Se, with production of hydrazo- and azo-compounds, azines, thiazines (selenazines), and their coloured derivatives is catalysed by Hg compounds in which Hg is attached directly to N. For NH_2Ph and $Hg(NHAc)_2$ the yield of NPh:NPh rises in the series: no solvent, C_5H_5N, EtOH, PhMe, $C_6H_4Me_2$, CCl_4, ligroin (b.p. 90—110°), light petroleum (b.p. 45—65°), $CHCl_3$, *cyclo*hexane, C_6H_6; in C_6H_6 the yield rises in the order: HgO, $Hg(NHPh)_2$, $HgNH_2Cl$, Hg phthalimide, Hg succinamide, $CO(NH)_2Hg$, $HgCN_2$, Hg succinimide, $Hg(NHAc)_2$, $Hg(NHBz)_2$. With $Hg(NHAc)_2$ in C_6H_6, the yield of azo-compound rises in the order: *o*-$C_6H_4Me{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}N{:}NPh$, *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$, *m*-xylidine, *m*-$C_6H_4Me{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}OMe$, *m*-$NH_2{\cdot}C_6H_4{\cdot}NO_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}NO_2$, NH_2Ph, *p*-$C_6H_4Me{\cdot}NH_2$, *o*-tolueneazotoluidine (I), *p*-$C_6H_4Cl{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$; no reaction occurs with *o*-nitroarylamines. *p*-Nitrophenol yields coloured products, α-$C_{10}H_7{\cdot}NH_2$ gives iminonaphthathiazine dyes, and β-$C_{10}H_7{\cdot}NH_2$ gives ββ′-dinaphthazine; azo-compounds are not obtained in these cases. In addition to azo-compound the *substance*, (*o*-$C_6H_4Me{\cdot}N_2{\cdot}C_6H_3Me{\cdot}N{:})_2$, m.p. 201°, is obtained from (I). Compounds of the type $Hg(NH{\cdot}COR)_2$ are supposed to tautomerise as follows: $Hg(NH{\cdot}COR)_2 \rightleftharpoons R{\cdot}CO{\cdot}NH{\cdot}Hg{\cdot}O{\cdot}CR{:}NH \rightleftharpoons Hg(O{\cdot}CR{:}NH)_2$. R. T.

Effect of substituents on the germicidal activity of phenols. II. Alkyl derivatives of 2 : 4-dichlorophenol. S. L. Chien and L. Y. Yun. **III. Chlorinated hydroxyphenyl alkyl sulphides.** S. L. Chien and K. T. Chow (*J. Chinese Chem. Soc.*, 1939, **7**, 40—45, 46—51; cf. A., 1937, II, 239).—II. 2 : 4 : 1-$C_6H_3Cl_2{\cdot}OH$ (at just above m.p.) and Alk·COCl at 100° afford 2 : 4-dichlorophenyl acetate, b.p. 167—168°/80 mm., propionate, b.p. 148°/14 mm., n-*butyrate*, b.p. 161—163°/20 mm., and n-*valerate*, b.p. 172°/16 mm., which are rearranged by $AlCl_3$ at 170° to 3 : 5-*dichloro*-2-*hydroxy*-*acetophenone*, m.p. 95—96°, -*propiophenone*, m.p. 115—116°, -*butyrophenone*, m.p. 49—50°, and -*valerophenone*, m.p. 46—47°, respectively, reduced (Clemmensen) to 2 : 4-*dichloro*-6-*ethyl*-, b.p. 202—203°/22 mm., -n-*propyl*-, b.p. 136—137°/14 mm., -n-*butyl*-, b.p. 161—163°/11 mm., and -n-*amyl*-*phenol*, b.p. 165—167°/24 mm., respectively.

III. 4 : 2 : 1-$NH_2{\cdot}C_6H_3Cl{\cdot}OH$ (modified prep.) is converted (diazo-reaction and decomp. of xanthate ester by NaOH) into 3-*chloro*-4-*hydroxythiophenol*, m.p. 39—40°, which with RI in ROH–NaOH affords 3-*chloro*-4-*hydroxyphenyl Me*, b.p. 130—131°/10 mm., *Et*, b.p. 128—129°/8—9 mm., *Pr*$^{\alpha}$, b.p. 140—142°/10 mm., and *Bu*$^{\alpha}$ *sulphide*, b.p. 145—148°/8—10 mm. A. T. P.

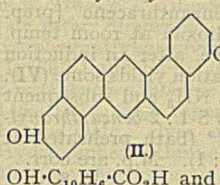
Organic molecular compounds. V. Formation of crystalline organic molecular compounds. C. Shinomiya (*Bull. Chem. Soc. Japan*, 1940, **15**, 309—314; cf. A., 1940, I, 412).—Data relating to the formation of cryst. mol. compounds having as one constituent α- or β-$C_{10}H_7{\cdot}OH$, α- or β-$C_{10}H_7{\cdot}NH_2$, or a derivative of *s*-$C_6H_3(NO_2)_3$ are tabulated and discussed with reference to the influence of configuration on compound formation. F. L. U.

Action of tyrosinase on quinol.—See A., 1941, III, 47.

Preparation of synthetic sex hormones. I. Hexœstrol. S. Bernstein and E. S. Wallis (*J. Amer. Chem. Soc.*, 1940, **62**, 2871—2873).—*p*-OMe·$C_6H_4{\cdot}COEt$ (prep. from the OH-ketone by Me_2SO_4–NaOH at 80°), b.p. 151—152°/19 mm., and Na–EtOH give *p*-OMe·$C_6H_4{\cdot}CHEt{\cdot}OH$ (60%), b.p. 137—140°/11·5 mm. (N_2), converted by gaseous HBr at 0° into the bromide, which (crude) with Na wire in Et_2O gives (*p*-OMe·$C_6H_4{\cdot}CHEt)_2$ (15%), m.p. 142—143·5°. Demethylation by AcOH–HI (*d* 1·7) at 135—140° gives 87% of (*p*-OH·$C_6H_4{\cdot}CHEt)_2$, m.p. 184—185°. R. S. C.

4 : 4′-Dihydroxy-αβ-diethylstilbene.—See B., 1940, 844.

Synthesis of 4′ : 8′-dihydroxy-1 : 2 : 5 : 6-dibenzanthracene. Its relation to products of metabolism of the hydrocarbon. J. Cason and L. F. Fieser (*J. Amer. Chem. Soc.*, 1940, **62**, 2681—2687).—1 : 2-Benzanthraquinone with 30% oleum at ~35° gives the 4′-sulphonic acid, best (94%) isolated as *p*-$C_6H_4Me{\cdot}NH_2$ salt, decomp. >300°, which affords (method of Sempronj, A., 1939, II, 514) 4′-hydroxy-1 : 2-benzanthracene, m.p. 231·5—232·5° (*loc. cit.*, 230°) [acetate, m.p. 195—195·5° (*loc. cit.*, 193—194°)]. Pyrolysis of crude 2 : 1-$C_{10}H_6Me{\cdot}CO{\cdot}C_{10}H_7$-2 at 430±5° gives 31% of 1 : 2 : 5 : 6-dibenzanthracene (I), m.p. 260—262°, oxidised by $Na_2Cr_2O_7$ (less well, CrO_3) in boiling AcOH to the quinone (79·5%), m.p. 244—249°. With 30% oleum at >35° this gives 1 : 2 : 5 : 6-dibenzanthraquinone-4′ : 8′-disulphonic acid (K_2 salt), isolated as (*p*-$C_6H_4Me{\cdot}NH_2)_2$ salt, which with Zn dust in aq. NH_3 at 85—90° gives Zn 1 : 2 : 5 : 6-dibenzanthracene-4′ : 8′-disulphonate, converted by KOH at 300—310° into 4′ : 8′-*dihydroxy*-1 : 2 : 5 : 6-*dibenzanthracene* (II), m.p. 415—418° (vac.), resolidifies, and then unmelted at >460° (vac.). $Na_2Cr_2O_7$ oxidises the *diacetate*, m.p. 360—362° (decomp.; vac.), thereof in boiling AcOH to the *quinone diacetate*, m.p. 340—345° (decomp.; vac.), which with KOH at 260° (later 280°) gives 5 : 2-OH·$C_{10}H_6{\cdot}CO_2H$ and with boiling KOH–EtOH gives 4′ : 8′-*dihydroxy*-1 : 2 : 5 : 6-*dibenzanthraquinone*, decomp. 370—375° (vac.). The rabbit-metabolism product from (I) (Levi *et al.*, *Chem. and Ind.*, 1937, 446) differs from (II), but the rat- and mice-metabolism product (Dobriner *et al.*, *Proc. Soc. Exp. Biol. Med.*, 1939, **41**, 67) is identical with (I). Metabolism and chemical substitution may thus occur at different points. M.p. are corr. R. S. C.



(II.)

Rearrangement of *o*-tolyl triphenylmethyl ether. Direct synthesis of 4-methoxy-3-methyltetraphenylmethane. H. A. Iddles and H. L. Minckler (*J. Amer. Chem. Soc.*, 1940, **62**, 2757—2759).—Rearrangement of *o*-$C_6H_4Me{\cdot}O{\cdot}CPh_3$ to 2 : 1 : 5-OH·$C_6H_3Me{\cdot}CPh_3$ is confirmed (cf. A., 1940, II, 12, 78). 2 : 1 : 5-OMe·$C_6H_3Me{\cdot}COPh$ (prep. from *o*-$C_6H_4Me{\cdot}OMe$ by BzCl and $SnCl_4$ in C_6H_6), m.p. 78°, with MgPhBr gives 80% of 4-*methoxy*-3-*methyltriphenylcarbinol* (I), m.p. 76·5°. 1 : 5 : 2-$C_6H_3MeBr{\cdot}OMe$ (prep. from the phenol by Me_2SO_4 and 33% NaOH at 40°), m.p. 66·5—67°, gives a Grignard reagent, which with $COPh_2$ in Et_2O gives 50% of (I). AcBr and (I) in light petroleum give the *bromide*, m.p. 106°, which with MgPhBr gives 4 : 3 : 1-OMe·$C_6H_3Me{\cdot}CPh_3$, m.p. 162° (Br-derivative, m.p. 185°) (cf. *locc. cit.*). R. S. C.

Trimethylquinol monophytyl ether.—See B., 1940, 897.

Derivatives of thymol. T. H. Tang and C. H. Chao (*J. Chem. Eng. China*, 1939, **6**, 23—26).—Aminothymol (I) heated with the acid chloride gives the *Bz*$_1$, m.p. 119—120°, and *cinnamoyl*, m.p. 231°, derivatives; BzCl and 10% NaOH at <25° afford the *Bz*$_2$ derivative, m.p. 164—165°. *Piperidylaminothymol*, m.p. 164—165° (previous darkening), is formed when (I) is heated with piperidine. *Salicylidene*- and *vanillylidene-aminothymol* have m.p. 170—171° and 197°, respectively. Contrary to Gilfillan *et al.* (cf. A., 1937, II, 14), nitrosothymol dissolves in saturated HCl to a colourless solution which turns red with alkali; a green colour is due to admixed, unknown, oily impurity. H. B.

Thiol and cysteine derivatives of 1 : 2-benzanthracene, 10-methyl-1 : 2-benzanthracene, and 3 : 4-benzpyrene. J. L. Wood and L. F. Fieser (*J. Amer. Chem. Soc.*, 1940, **62**, 2674—2681).—The cysteine derivatives described below are unstable and may not persist as such during tests for carcinogenic activity. S_2Cl_2 and 1 : 2-benzanthracene (after an induction period, if pure), best in light petroleum, give a product converted by molten Na_2S,H_2O at 130° into 10-*thiol*-1 : 2-*benzanthracene* (I), dimorphic, m.p. 115° (instantaneous), resolidifying with m.p. 138°, and 139·9—140·7°, sublimes at 130°/1 mm. (S-CH_2Ph derivative, m.p. 128·2—129·4°), also obtained from the Grignard reagent of 10-bromo-1 : 2-benzanthracene (II) by S in C_6H_6. Oxidation of (I) by $Na_2Cr_2O_7$–AcOH at 60° gives 1 : 2-benzanthraquinone and by O_2 in NaOH–aq. dioxan containing a trace of $FeCl_3$ gives *di*-1 : 2-*benz*-10-*anthranyl disulphide* (III), m.p. 208·2—209·7° (decomp.; vac.). (II) is converted into 1 : 2-benzanthracene by KSH in 95% EtOH at 180°. Gradual addition of equiv. amounts of aq. NaOH and *dl*-$CH_2Cl{\cdot}CH(CO_2H){\cdot}NH_2,HCl$ to the Na salt of (I) in aq. dioxan–N_2 gives 25% of S-1 : 2-*benz*-10-*anthranylcysteine*, decomp. 192—194° (yellow at 187°) [converted into (III) in boiling dioxan], and (III). 3 : 4-Benzpyrene and S_2Cl_2 in light petroleum (as above) or 5-chloro-3 : 4-benzpyrene and KSH in 95% EtOH at 150° give 5-*thiol*-3 : 4-*benzpyrene*, decomp. 205—206° (197—198·5°) [S-CH_2Ph derivative, decomp. 170·2—172·2°; derived *disulphide* (IV), m.p. 271—272° (decomp.; vac.)], and thence as above S-3 : 4-*benz*-5-*pyrenylcysteine*, decomp. 146·7—147·5° (varies with rate of heating), and (IV). 10-Chloromethyl-1 : 2-benzanthracene (V), m.p. 190—190·6°, and $CS(NH_2)_2$ in boiling abs. EtOH give 86% of S-1 : 2-

benz-10-*anthranylmethylisothiocarbamide*, m.p. 160° (instantaneous), resolidifies, m.p. >235° [*hydrochloride*, m.p. 213—214° (decomp.)], which with Na_2CO_3 and a trace of $Na_2S_2O_4$ in boiling H_2O–MeOH gives 10-*thiolmethyl*-1 : 2-*benzanthracene*, m.p. 172·7—174·7° (S-CH_2Ph derivative, m.p. 150·2—150·6°). The derived *disulphide* (**VI**) has m.p. 244·5—245° (decomp.; vac.). 10-Methyl-1 : 2-benzanthracene [prep. from (**V**) by $SnCl_2$ and conc. HCl in dioxan at room temp. and later 100°] and S_2Cl_2 in hexane give, after an induction period, a crude mercaptan, whence oxidation yields some (**VI**). Reduction of *l*-cystine by Na in liquid NH_3 and subsequent addition of NH_4Cl, PhMe, and (**V**) gives S-1 : 2-*benzanthranylmethyl*-l-*cysteine*, decomp. 205·7—206·7° (bath preheated at 205°), $[\alpha]_D^{23}$ −7·5° in dioxan–2N-HCl (2 : 1). M.p. are corr. R. S. C.

Retropinacolin rearrangement of 10 : 10-diaryl-9 : 10-dihydro-9-phenanthrols. (Miss) E. J. H. Chu and F. Wei (*J. Chinese Chem. Soc.*, 1939, **7**, 20—23; cf. A., 1935, 973; Bachmann, A., 1933, 1159).—10 : 10-Di-*p*-phenetyl- or -*p*-chlorophenyl-9-phenanthrone and Zn dust–NaOH–EtOH or (better) $MgPr^{\beta}Br$–Et_2O–C_6H_6 give 10 : 10-*di*-p-*phenetyl*- (**I**), m.p. 146·2°, or -p-*chlorophenyl*-9 : 10-*dihydro*-9-*phenanthrol* (**II**), m.p. 159·3°, respectively, reoxidised by CrO_3–AcOH to the corresponding phenanthrone. (**I**) and (**II**) are converted quantitatively by I–AcOH into 9 : 10-*di*-p-*phenetyl*-, m.p. 207°, and -p-*chlorophenyl*-*phenanthrene*, m.p. 244°, respectively, oxidised by CrO_3–AcOH to the corresponding 2 : 2′-diaroyldiphenyl. A. T. P.

Reactions of 2 : 2′-diacyldiphenyls. I. Reaction between 2 : 2′-diacyldiphenyls and magnesium ethyl bromide. (Miss) E. J. H. Chu (*J. Chinese Chem. Soc.*, 1939, **7**, 24—26).—2 : 2′-Dibenzoyldiphenyl and MgEtBr afford 2 : 2′-*di*-(α-*hydroxy*-α-*phenylpropyl*)*diphenyl*, m.p. 221·7—222·7°. Similarly prepared are 2 : 2′-*di*-(α-*hydroxy*-α-p-*diphenylyl*-, m.p. 183·6—184·6°, -p-*phenetyl*-, m.p. 135—136°, -m-*tolyl*-, m.p. 156·3—157·3°, and -p-*chlorophenyl*-*propyl*)*diphenyl*, m.p. 228·5—229·5°. A. T. P.

Sterols. CVIII. Preparation of dihydroandrosterone and related compounds from diosgenin and tigogenin. R. E. Marker (*J. Amer. Chem. Soc.*, 1940, **62**, 2621—2625).—Tigogenone (**I**) [prep. from diosgenin by way of tigogenin (**II**)] and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give (**II**) (separated as digitonide) and epi*tigogenin* (**III**), m.p. 242—245° [*acetate*, m.p. 199—202°; oxidised to (**I**)], which with Ac_2O at 200° gives ψ-epi*tigogenin* (**IV**), m.p. 148—150°, reconverted into (**III**) by conc. HCl–EtOH and oxidised by CrO_3–AcOH at 25° to Δ^{16}-*allo*pregnene-3 : 20-dione (**V**). Oxidation of the crude acetate of (**IV**) and subsequent hydrolysis gives Δ^{16}-allo*pregnen*-3(α)-*ol*-20-*one* (**VI**), m.p. 219—222° [*acetate* (**VII**), m.p. 156—158°], reduced (H_2–Pd–$BaSO_4$; EtOH–Et_2O; 1·5 atm.) to *allo*-pregnan-3(α)-ol-20-one, m.p. 172—174° [acetate (**VIII**), m.p. 138—140°, obtained also by hydrogenation of (**VII**)]. With Caro's acid in AcOH, (**VIII**) gives a mixture, whence removal of ketones by Girard's reagent and hydrolysis yields androstane-3(α) : 17(α)-diol, m.p. 219—222° (diacetate, m.p. 160—162°). H_2–PtO_2 at 3 atm. converts (**IV**) in AcOH into *dihydro*-ψ-epi*tigogenin*, m.p. 193—196° [oxidised to (**V**)], the *diacetate*, m.p. 118—121°, of which with CrO_3–AcOH gives (**VI**). R. S. C.

Photodehydrogenation of sterols. I. $\Delta^{2:4}$-Cholestadiene. R. P. Jacobsen and C. Z. Nawrocki (*J. Amer. Chem. Soc.*, 1940, **62**, 2612—2614).—Irradiation (W) of ergosterol in C_6H_6 containing a little EtOH and mixed halogenofluoresceins gives 61—64% of diergostatrienol, m.p. 198—199° (decomp.) [general absorption at <2900 A.; *diacetate*, m.p. 201—202° (decomp.)]. Dehydroergosterol in presence of rose-Bengal in EtOH gives 50% of diergostatetraenol (50%), m.p. 194—195° (decomp.), absorption max. at 2650 A. (log ε 3·95). $\Delta^{2:4}$-Cholestadiene gives similarly a very small yield of a *dicholestadiene*, m.p. 203—204° (decomp.) (general absorption at <2600 A.). M.p. are corr. R. S. C.

Alkylation of cyanophenylpyruvic ester. G. S. Skinner and A. J. Green (*J. Amer. Chem. Soc.*, 1940, **62**, 2882).—CN·CHPh·CO·CO_2Me with CH_2:CH·CH_2Br or CH_2PhCl and NaOEt–EtOH at 0° and then 70° gives α-*phenyl*-Δ^{γ}-*pentenonitrile*, b.p. 134—135°/16 mm., and αβ-*diphenylpropionitrile*, m.p. 52—53°, b.p. 159—160°/6 mm., respectively, but with Me_2SO_4 or Et_2SO_4 and NaOEt–EtOH gives *Me* α-*keto*-β-*cyano*-β-*phenyl*-n-*butyrate*, b.p. 148—150°/2 mm., and -n-*valerate*, b.p. 161—162°/5 mm., respectively. R. S. C.

γγ′-Di-*p*-tolyl-γγ′-suberodilactone. C. C. Price (*J. Amer. Chem. Soc.*, 1940, **62**, 2884—2885).—*p*-C_6H_4Me·CO·$[CH_2]_2$·CO_2H and Zn dust in boiling 80% AcOH give γ-*p*-tolyl-γ-butyrolactone, m.p. 67—68° (lit. 69°), and a little γγ′-*di*-*p*-*tolyl*-γγ′-*suberodilactone*, m.p. 275—276°. R. S. C.

Action of diazobenzene on alkylacetoacetic ester as method of preparing α-amino-acids and phenylhydrazones of α-keto-acids. II. Synthesis of phenylalanine. IV. Synthesis of the phenylhydrazone of phenylpyruvic acid. V. V. Feofilaktov and E. Vinogradova (*J. Gen. Chem. Russ.*, 1940, **10**, 255—257, 260—262).—An account of work already noted (A., 1940, II, 70, 85).

Synthesis of 2-, 4-, and 9-fluorenylacetic acid. W. E. Bachmann and J. C. Sheehan (*J. Amer. Chem. Soc.*, 1940, **62**, 2687—2690).—2-Acetylfluorene (prep. from fluorene, Ac_2O, and $AlCl_3$ in $PhNO_2$ at, successively, −5°, 0°, and room temp.), m.p. 128—129° (lit., 132°), and NH_4 polysulphide in dioxan at 160° give 2-*fluorenylacetamide* (70%), m.p. 264—266° (slight decomp.), hydrolysed by boiling, HCl–AcOH to 2-fluorenylacetic acid, m.p. 186—187° (lit. 178°), sublimes at 170°/0·01 mm., also obtained (32%) by the Arndt–Eistert reaction from fluorene-2-carboxylic acid. Fluorenone-4-carboxylic acid and Zn dust in aq. NaOH–PhMe give 9-hydroxyfluorene-4-carboxylic acid (85%), reduced (92%) by red P–I–AcOH–H_2O to fluorene-4-carboxylic acid, which gives (Arndt–Eistert) 4-*fluorenylacetic acid* (**I**) (89%), m.p. 178·5—179°. 4-*Fluorenonylacetic acid*, m.p. 206—207° after softening, sublimes at 180°/0·01 mm. (*Me* ester, m.p. 135·5—136°, sublimes at 0·01 mm.), is obtained from the 4-carboxylic acid by the Arndt–Eistert reaction and is reduced to (**I**) by Zn–NaOH, followed by HI. 9-Bromofluorene (prep. from fluorenol by AcBr), m.p. 102—103°, gives by $CH_2(CO_2Et)_2$ etc. 9-fluorenylacetic acid (89%), m.p. 131·5—132·5° (lit., 128—129°, 137°, 138—139°), b.p. 170°/0·01 mm. R. S. C.

Tertiary naphthenic acids. I. Synthesis of 1 : 2 : 3 : 3-tetramethyl*cyclo*pentane-1-carboxylic acid from camphor. B. Shive, J. T. Horeczy, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1940, **62**, 2744—2746).—*iso*Lauronolic acid (modified prep.) and H_2–Raney Ni in dioxan at 175°/4500 lb. or (slowly) H_2–PtO_2–AcOH at 1·5 atm. give the H_2-acid (amide, new m.p. 164°; *anilide*, m.p. 156—157°), the chloride, b.p. 201°/746 mm., of which with C_6H_6 and $AlCl_3$ gives 3-*benzoyl*-1 : 1 : 2-*trimethyl*cyclo*pentane*, b.p. 299°/751 mm. (*oxime*, m.p. 105—106°). $NaNH_2$–C_6H_6 and then MeI in PhMe give 3-*benzoyl*-1 : 1 : 2 : 3-*tetramethyl*cyclo*pentane*, b.p. 307—308°/750 mm. (*oxime*, m.p. 154—155°), oxidised by O_3 in CCl_4 followed by alkaline H_2O_2 to 1 : 2 : 3 : 3-*tetramethyl*-cyclo*pentane*-1-*carboxylic acid* (**I**), m.p. 125—126°, and converted by $NaNH_2$ into (**I**) and its *amide*, m.p. 85—86°. (**I**) is not identical with the acid obtained from Californian petroleum by Horeczy *et al.* (cf. Roberts *et al.*) (both unpublished). R. S. C.

Esters of brominated aminobenzoic acids. M. B. Moore and E. H. Volwiler (*J. Amer. Chem. Soc.*, 1940, **62**, 2799—2801).—3 : 2 : 1-NO_2·C_6H_3Br·CO_2K, Br·$[CH_2]_2$·Br, and a trace of $NHEt_2$ at ~140° give γ-*bromo*-n-*propyl* 2-*bromo*-3-*nitrobenzoate*, an oil, which with $NHBu^{\alpha}_2$ gives the γ-di-n-butylamino-n-propyl ester, the hygroscopic hydrochloride of which is reduced by Fe to γ-di-n-butylamino-n-propyl 2-bromo-3-aminobenzoate (*hydriodide*, m.p. 160—161°). 4 : 2 : 1-NO_2·C_6H_3Br·CO_2H leads by similar reactions to γ-*di*-n-*butylamino*-n-*propyl* 2-*bromo*-4-*aminobenzoate hydriodide*, m.p. 149—150°. Passage of Br vapour into procaine hydrochloride in H_2O or, better, interaction of procaine with Br–$CHCl_3$ gives β-diethylaminoethyl 3-bromo-4-aminobenzoate {hydrochloride, m.p. 154—155° [lit. (+H_2O) 157—158°]; *hydrobromide*, m.p. 165—166°}. *p*-NH_2·C_6H_4·CO_2·$[CH_2]_3$·NBu^{α}_2 (**I**) and Br–AcOH at room temp. give γ-di-n-butylamino-n-propyl 3-bromo-4-aminobenzoate (*acetate*, m.p. 71—72°; hydrobromide, m.p. 129—130°), which with $Pr^{\alpha}Br$ in boiling $Pr^{\alpha}OH$ gives the 3-bromo-4-n-propylaminobenzoate (*hydrochloride*, m.p. 146—148°). (**I**) and Br–$CHCl_3$ at room temp. give γ-*di*-n-*butylamino*-n-*propyl* 3 : 5-*dibromo*-4-*aminobenzoate hydrobromide*, m.p. 162·5—163°. Alkylation (as above) leads to γ-*di*-n-*butylamino*-n-*propyl* 3-*bromo*-4-n-*butyl*-, m.p. 116—117°, 2-*bromo*-3-n-*butyl*-, m.p. 169—171°, and 3 : 5-*dibromo*-4-n-*propyl*-, m.p. 117—118°, -*aminobenzoate hydrochloride*. The monobromoamino-esters are anæsthetics, the salts of which are inconveniently insol. The dibromoamino-esters are mainly convulsant. R. S. C.

Chloralamides. II. Chloral-nitro- and -bromo-salicylamide. N. W. Hirwe, (Miss) K. D. Gavankar, and B. V. Patil (*Proc. Indian Acad. Sci.*, 1940, **11**, **A**, 512—516).—Chloralsalicylamide (**I**) with HNO_3 (*d* 1·2) at room temp. for 4 days gives *chloral-3-nitrosalicylamide* (**II**), m.p. 154° [*Na*$_2$, *K*$_2$, and *Ca* salt (+5H_2O)], with some 5-nitrosalicylamide, m.p. 224—225°. (**II**) is also obtained from 3-nitrosalicylamide and chloral (**III**), which with 5-bromo-3-nitrosalicylamide (**IV**) gives *chloral-5-bromo-3-nitrosalicylamide*, m.p. 155° (decomp.). Bromination of (**II**) in AcOH gives (**IV**). In conc. H_2SO_4–HNO_3 (*d* 1·45), (**I**) gives *chloral-3 : 5-dinitrosalicylamide*, m.p. 154° (decomp.), whilst chloral-2-methoxybenzamide (**V**) gives *chloral-5-nitro-*, m.p. 155° (decomp.), or -3 : 5-*dinitro-2-methoxybenzamide*, m.p. 142—143° (decomp.), according to the conditions used. In AcOH with Br vapour, (**I**) gives *chloral-5-bromo-* (**VI**), m.p. 150—152°, and, in presence of I, -3 : 5-*dibromo-salicylamide*, m.p. 158—160°, whilst (**V**) gives *chloral-5-bromo-2-methoxybenzamide*, m.p. 147—148°. These compounds [except (**VI**)] are also synthesised from (**III**), which also yields *chloral-3-bromosalicylamide*, m.p. 161°, and -3-*bromo-*, m.p. 129°, -3 : 5-*dibromo-*, m.p. 156°, and -3-*nitro-2-methoxybenzamide*, m.p. 106° (decomp.). E. W. W.

Chloralamides. Action of potassium cyanide on α-chloro-chloral-chloro- and -bromo-2-methoxybenzamides and hydrolysis of the resulting α-cyano-compounds. N. W. Hirwe and K. N. Rana (*J. Indian Chem. Soc.*, 1940, **17**, 481—484; cf. A., 1940, II, 220).—α-Chlorochloral-5-chloro-2-methoxybenzamide [5-chloro-2-methoxybenz-αβββ-tetrachloroethylamide] and KCN–$COMe_2$ afford N-ββ-*dichloro-α-cyano-*, m.p. 171—172° (yield, ~39%), and thence [conc. HCl at 100° (bath)] N-ββ-*dichloro-α-carboxy-vinyl-5-chloro-2-methoxybenzamide*, m.p. 199—200° (decomp.) [*Na* and *Ba* (+2H_2O) salts] (high yield). Similarly prepared are N-ββ-*dichloro-α-cyanovinyl-3 : 5-dichloro-*, m.p. 172—173°, -5-*bromo-*, m.p. 177—178°, and -3 : 5-*dibromo-2-methoxybenzamide*, m.p. 220—221° (decomp.), and N-ββ-*dichloro-α-carboxyvinyl-3 : 5-dichloro-*, m.p. 202—203° (decomp.) [*Na* (+H_2O) and *Ba* (+4H_2O) salts], -5-*bromo-*, m.p. 203—204° (decomp.) [*Na* and *Ca* (+2H_2O) salts], and -3 : 5-*dibromo-2-methoxybenzamide*, m.p. 217—218° (decomp.) [*Na* (+2H_2O) and *Ba* (+3H_2O) salts]. A. T. P.

Phenylthiocarbamides. The triad –N·C·S–. IX. Thiobenzamide. H. Krall and V. Sagar (*J. Indian Chem. Soc.*, 1940, **17**, 475—479; cf. A., 1938, II, 358).—Thiobenzamide (**I**) yields with N-KOH (1 equiv.), H_2S (67%), PhCN, and a trace of NH_3, and with N-HCl (1 equiv.), H_2S (9·5%), NH_3 (10%), and BzOH. The latter reaction occurs to 2% in neutral solution. HNO_2 with (**I**) yields, in presence of HCl, NO (79%) and dibenzenylazosulphime (von Hofmann *et al.*, A., 1892, 1109), and in presence of AcOH, N_2 (38%) and NO (62%). It is concluded that in neutral solution (**I**) contains 40% of the form CSPh·NH_2; acids and alkalis effect almost complete rearrangement to the form NH:CPh·SH. A. Li.

Colour in relation to chemical constitution of the phthalein dyes. Phthaleins of mixed type. S. Dutt (*Proc. Indian Acad. Sci.*, 1940, **11**, **A**, 483—490).—Unsymmetrical phthaleins obtained from *o*-C_6H_4Bz·CO_2H and phenols and aminophenols have much less intense colour in alkaline solution than have the symmetrical phthaleins from *o*-$C_6H_4(CO_2H)_2$; this is ascribed to less intense (because unidirectional) tautomerism in the former between lactonoid and quinonoid forms. In some compounds, hot alkali is needed to develop colour. The *p*-hydroxydiphenylphthalein (phenylphenolphthalein) obtained by Pechmann (A., 1881, 96) was heavily contaminated with phenolphthalein; the pure compound has new m.p. 92·5° and gives a light yellow solution (max. absorption at 4450 A.) in dil. NaOH. The following are prepared (colours in dil. NaOH and absorption max.): *phenyl-o-*, m.p. 133° (light yellow; 4510 A.), and -m-*cresol-*, m.p. 146° (light yellow in hot NaOH; 4450 A.); *phenyl-carvacrol-*, m.p. 236°, and -*thymol-*, m.p. 253° (both deep yellow in hot NaOH; 4480 A.); -*resorcinol-*, m.p. 169° (orange yellow; 4710 A.); -*pyrocatechol-*, m.p. 86° (red; 5330 A.); -*quinol-*, m.p. 241° (deep yellow; 4565 A.); -α-*naphthol-*, m.p. 229° (deep yellow; 4900 A.); -*phloroglucinol-*, m.p. 117° (deep yellow; 4650 A.); -*pyrogallol-*, m.p. 126° (deep yellow; 4725 A.); and -m-*dimethylaminophenol-phthalein*, m.p. 124°, and its *hydrochloride*, m.p. 102° (pink in EtOH and H_2O respectively; 5550 A.). E. W. W.

8-Amino-1-naphthoic acid.—See B., 1940, 845.

Reaction of substituted phenanthrenes with lithium *n*-butyl. H. Gilman and T. H. Cook (*J. Amer. Chem. Soc.*, 1940, **62**, 2813—2817).—2-, 3-, and 9-Bromophenanthrene with LiBu^n in Et_2O–N_2, followed by CO_2, give the 2- (37%), 3- (32%), and 9-carboxylic acid (51%), respectively. 2-Hydroxyphenanthrene gives 2-*hydroxyphenanthrene-3-carboxylic acid* (1·5%), m.p. 276—277° after sintering [*Me ether* (**I**), m.p. 211—213° (Me ester, dimorphic, m.p. 77—78° and 94—95°)]. 2-Methoxyphenanthrene gives a Li derivative, converted by CO_2 into (**I**) (39%) and by air in presence of MgBu^{n}Br into 3-*hydroxy-2-methoxyphenanthrene* (18·5%), m.p. 145—146° (*acetate*, m.p. 146—147°) (and other products), which with Me_2SO_4–50% KOH–$COMe_2$ gives 2 : 3-dimethoxyphenanthrene (**II**). 3-Hydroxyphenanthrene is metalated with difficulty. 3-Methoxyphenanthrene gives the 2-Li derivative, converted as above into 3-*methoxyphenanthrene-2-carboxylic acid* (33%), m.p. 185° (Me ester, m.p. 134—134·5°), and 2-*hydroxy-3-methoxyphenanthrene* (30%), m.p. 171—172° [Me ether = (**II**); *acetate*, m.p. 142—144°]. 9-Hydroxyphenanthrene gives a Li derivative, converted by CO_2 into 9-*hydroxyphenanthrene-x-carboxylic acid*, m.p. 158—160° (decomp.) [*Me ether* (**III**), m.p. 197—199°], and by Br into a little of a compound, m.p. 124—124·5°, which with CrO_3–AcOH gives phenanthraquinone. 9-Methoxyphenanthrene gives a Li derivative, converted by CO_2 into the 10-carboxylic acid and (**III**), and by O_2–MgBu^{n}Br into (?) 10-*hydroxy-9-methoxyphenanthrene*, m.p. 94—95·5°. R. S. C.

Cyclic *o*-dinitriles.—See B., 1940, 845.

Influence of substitution on the formation of derivatives of α-hydrindone and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. Synthesis of 1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 2-dicarboxylic acid. N. N. Chatterjee and G. N. Barpujari (*J. Indian Chem. Soc.*, 1940, **17**, 292—296).—Successive treatments of CN·CHNa·CO_2Et in EtOH with OH·CHPh·CN and $CH_2Cl·CO_2Et$ give *Et*$_2$ αβ-*dicyano-α-phenyl-n-propane-βγ-dicarboxylate*, b.p. 205—207°/4 mm., hydrolysed by boiling 70% H_2SO_4 to α-phenyl-*n*-propane-αβγ-tricarboxylic acid, m.p. 204° (*Et*$_3$ ester, b.p. 185—190°/5 mm.), which with H_2SO_4 (*d* 1·84) at 100° affords 1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene-3 : 4-dicarboxylic acid* (**I**), m.p. 179—182°, oxidised by alkaline $KMnO_4$ to *o*-$C_6H_4(CO_2H)_2$. Clemmensen reduction of (**I**) gives 1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 2-dicarboxylic acid, m.p. 193° when rapidly heated. Similarly *p*-OMe·C_6H_4·CH(OH)·CN (**II**) affords *Et*$_2$ αβ-*dicyano-α-p-anisyl-n-propane-βγ-dicarboxylate*, b.p. 232—237°/3 mm., which gives α-p-*anisyl-n-propane-αβγ-tricarboxylic acid*, m.p. 190° when rapidly heated (*Et*$_3$ ester, b.p. 210—215°/5 mm.), which is sulphonated and not cyclised by H_2SO_4. Condensation of (**II**) with CN·CHNa·CO_2Et gives *Et* αβ-*dicyano-β-p-anisylpropionate*, b.p. 225°/5 mm., m.p. 81°, hydrolysed by boiling dil. H_2SO_4 to *p*-anisylsuccinic acid, m.p. 205° (anhydride, m.p. 91°; *Et*$_2$ ester, b.p. 185°/4 mm.). H. W.

Reactions of keten with salicylaldehyde and *p*-hydroxybenzaldehyde. J. W. Williams and A. Sadle (*J. Amer. Chem. Soc.*, 1940, **62**, 2801—2803).—Pure *o*-OH·C_6H_4·CHO (**I**) and keten at room temp. give 84% of *o*-OAc·C_6H_4·CHO (**II**) and 9% of coumarin (**III**). In presence of a drop of H_2SO_4 31% of (**III**) is obtained. With anhyd. NaOAc in $COMe_2$ 1—2% of *o*-OAc·C_6H_4·CH:CH·CO_2H (**IV**) is formed. In presence of H_2SO_4, keten and (**II**) give only 2—5% of (**III**). Possible reaction mechanisms are discussed. When boiled alone, (**II**) gives slowly a little (**III**), the amount being slightly increased by presence of a drop of H_2SO_4; presence of anhyd. NaOAc leads to (**III**) and (**I**); in all cases AcOH and Ac_2O are formed from liberated keten. *p*-OH·C_6H_4·CHO and keten in $COMe_2$ at room temp. give 91% of *p*-OAc·C_6H_4·CHO (**V**) (oxidised by air), but presence of anhyd. NaOAc leads to 5% of *p*-OAc·C_6H_4·CH:CH·CO_2H, also obtained in 6% yield similarly from (**V**). The *p*-OAc-compounds are hydrolysed by cold 10% aq. NaOH. R. S. C.

Acenaphthene series. I. 3-Benzoylacenaphthene and related compounds. (Miss) E. J. H. Chu (*J. Chinese Chem. Soc.*, 1939, **7**, 14—19).—3-Benzoylacenaphthene (**I**) (improved prep.) affords a mixture, m.p. 175—183°, of oximes [one has m.p. 184° (decomp.); cf. Graebe *et al.*, A., 1903, i, 409], converted by $PhSO_2Cl$–C_5H_5N or by PCl_5–C_6H_6 into a mixture of 3-acenaphthanilide and 3-benzamidoacenaphthene [one has m.p. 178·5—179·5° (decomp.), the other m.p. 213—213·5° (decomp.)], hydrolysed (boiling KOH–EtOH for 3 days) to the respective acids. (**I**) and MgPhBr afford *diphenyl-*

3-*acenaphthylcarbinol*, m.p. 200·8° (decomp.). (I) is reduced (modified Clemmensen) to 3-benzylacenaphthene or (by Zn dust–NaOH–EtOH) to phenyl-3-acenaphthylcarbinol.

A. T. P.

Cyclisation of dieninenes. IX. Synthesis of a new perhydrophenanthr-9-one. C. S. Marvel and R. V. White. **X. Dodecahydrophenanthrone obtained from di*cyclo*hexenylacetylene.** C. S. Marvel, D. E. Pearson, and R. V. White (*J. Amer. Chem. Soc.*, 1940, **62**, 2739—2740, 2741—2743; cf. below).—IX. 9-Hydroxyphenanthrene and H_2–Raney Ni–EtOH at 150°/267 atm. give 9-*hydroxytetradecahydrophenanthrene* (44%), m.p. 66·5—67·5°, b.p. 115—120°/3·5 mm., oxidised by CrO_3–AcOH at room temp. to 9-*ketotetradecahydrophenanthrene*, m.p. 56—57°, b.p. 110—115°/3·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 232—233°; *oxime*, m.p. 210—212°). HNO_3 then gives *dodecahydrodiphenic acid*, m.p. 174—175° (*anhydride*, m.p. 103—104°, not cyclised at 250—350°).

X. Crude 9-keto-$\Delta^{13:14}$-dodecahydrophenanthrene (I) (Linstead *et al.*, A., 1939, II, 307), purified by boiling with Zn dust in AcOH, then has m.p. 37° (*loc. cit.*, 39°), b.p. 113—115°/1·5 mm., and gives an oxime, m.p. 186° (lit. 183—184°); the non-cryst. portion, b.p. 117—118°/1·5 mm., gives an oxime, m.p. 124·5—126·5°. Crude (I) is hydrogenated (Pd) to 9-ketotetradecahydrophenanthrene (II), m.p. 47—48° (lit. 51°), which with Br–$CHCl_3$ gives the (? 14-)Br-derivative, b.p. 125—126°/1·5 mm., reconverted into (I) by boiling C_5H_5N. Dibromination of (II) and subsequent treatment with C_5H_5N gives a *compound*, $C_{14}H_{15}OBr$, m.p. 186—188°, containing an aromatic ring. Bromination of liquid 9-ketotetradecahydrophenanthrene, b.p. 116—118°/1·5 mm. (oxime, m.p. 137—142°), and then treatment with C_5H_5N gives (I), identified as oxime. MgMeBr and MgEtBr convert (I) into impure 9-hydroxy-9-methyl-, b.p. 94—96°/1 mm., and -ethyl-$\Delta^{13:14}$-dodecahydrophenanthrene, dehydrated by $KHSO_4$ at 150°/16 mm. to *hydrocarbons*, $C_{15}H_{22}$, b.p. 78—80°/1 mm., and $C_{16}H_{24}$, b.p. 117—118°/2 mm., which with Pd–C at 320° give 9-methyl-, m.p. 91—92° (picrate, new m.p. 154—155°), and nearly pure 9-ethyl-phenanthrene, respectively. MgPhBr and (I) give a *hydrocarbon*, $C_{20}H_{24}$, b.p. 138—140°/1 mm., dehydrogenated (Pt–C, CO_2, 320°) to (?) 9-*phenyloctahydrophenanthrene*, m.p. 95·5—96°. The structure of (I) is thus confirmed.

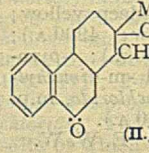
R. S. C.

Cyclisation of dieninenes. VIII. Ring-closures with α- and β-*cyclo*hexenylacetylene derivatives of octahydronaphthalene. C. S. Marvel, D. E. Pearson, and L. A. Patterson (*J. Amer. Chem. Soc.*, 1940, **62**, 2659—2665; cf. A., 1939, II, 499).—Mixed *cis*- and *trans*-1-ketodecahydronaphthalene, C_2H_2, and $CMe_2Et{\cdot}OK$–$CMe_2Et{\cdot}OH$–Et_2O give mixed cis- and trans-1-*hydroxy*-1-*acetylenyldecahydronaphthalene* (J), b.p. 74—76°/1·5 mm., which with first MgEtBr and then *cyclo*hexanone gives mixed α-1-*hydroxy*cyclo*hexyl*-β-1′-*hydroxydecahydro*-1′-*naphthylacetylene*, b.p. 186—194°/3 mm., dehydrated by $KHSO_4$ to α-Δ^1-cyclo*hexenyl*-β-$\Delta^{1'}$-*octahydro*-1′-*naphthylacetylene*, b.p. 156—162°/3 mm. Cyclisation by H_2SO_4–AcOH at 0° then gives 2-*keto*-$\Delta^{2a:6a}$-*hexadecahydrochrysene* (II), m.p. 103·5—104° (2 : 4-*dinitrophenylhydrazone*, m.p. 200°), and (?) 1-$\Delta^{1'}$-*octahydro*-1′-*naphthyl*-Δ^1-*hexahydrocoumarone* (III), b.p. 144—150°/3 mm. Zn–Hg–HCl–AcOH–PhMe reduces (II) to $\Delta^{2a:6a}$-*hexadecahydrochrysene*, b.p. 141—143°/3 mm., which with Pt–C in CO_2, first at 315° and then at 340°, gives chrysene, similarly obtained from (II) by Pt–C in CO_2 but only impure by S. H_2–Raney Ni in EtOH at 150°/200 atm. reduces (II) to the saturated alcohol, which with CrO_3–AcOH gives 2-keto-octadecahydrochrysene, m.p. 109·5—110°, b.p. 150—156°/1·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 197—198°). With MgMeI in Et_2O–C_6H_6, this gives a carbinol, b.p. 142—147°/1·5 mm., dehydrogenated and dehydrated by Pt-black on asbestos in CO_2 at 320° to 2-methylchrysene, m.p. 160—161° [picrate, m.p. 171—172° (lit. 170°)]. In presence of Raney Ni at 160°/267 atm. (III) absorbs ~2 H_2 to give a compound, b.p. 123—130°/1·5 mm., whence Pt-black yields chrysene. With HBr in boiling AcOH, (III) gives a substance, $C_{18}H_{28}O$, b.p. 166—170°/2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 198°). *trans*- and *cis*-2-Ketodecahydronaphthalene, respectively, give *trans*-, m.p. 94—94·5° (lit. 91·5°), b.p. 85—89°/15 mm., and cis-2-*hydroxy*-2-*acetylenyldecahydronaphthalene*, b.p. 90—94°/2 mm., trans-, m.p. 133°, and cis-α-1-*hydroxy*cyclo*hexyl*-β-2′-*hydroxydecahydro*-2′-*naphthylacetylene*, b.p. 178—184°/3 mm., and α-Δ^1-cyclo*hexenyl*-β-trans- (IV), b.p. 152—156°/3 mm., and -cis-(? $\Delta^{2'}$)-*octahydro*-2′-*naphthylacetylene* (V), b.p. 132—140°/3 mm. Cyclisation of (IV) gives an oil, converted by Zn–AcOH into $\Delta^{1:2}$-*hexadecahydro*-1 : 2-*benzanthr*-3-*one* (VI), m.p. 59—60° (2 : 4-*dinitrophenylhydrazone*, m.p 252—253°), and a *by-product*, b.p. 151—152°/1·5 mm. [with HBr–AcOH gives a product, $C_{18}H_{28}O$, b.p. 151—156°/1·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 225°)]. (V) gives similarly a $\Delta^{1:2}$-*hexadecahydro*-1 : 2-*benzanthr*-3-*one* (VII), b.p. 158—165°/3 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 150—153°), and a by-product, b.p. 155—158°/3 mm. Clemmensen–Martin reduction and then Pt-black dehydrogenation of (VI) and (VII) gives 1 : 2-benzanthracene. Attempts to prepare a methylcarbinol etc. failed. The MgBr derivative of (I) and 1-ketodecahydronaphthalene give αβ-di-1-hydroxydecahydro-1-naphthylacetylene, an oil, and thence ($KHSO_4$) αβ-*di*-Δ^{1}-*octahydro*-1-*naphthylacetylene*, b.p. 176—180°/? 3 mm., which with H_2SO_4–AcOH–C_6H_6 gives a non-ketonic substance, b.p. 178—181°/1 mm., whence Pd-black–asbestos–CO_2 affords a little picene and HBr–AcOH gives a *substance*, $C_{22}H_{32}O$, b.p. 180—183°/1 mm. αβ-*Di*-2-*hydroxy*-cis-*decahydro*-2-*naphthylacetylene* (similarly prepared), m.p. 125—126°, gives *di*-(? Δ^2)-cis-*octahydro*-2-*naphthylacetylene*, b.p. 215—220°/3 mm., whence H_2SO_4–AcOH at 5—8° gives a *substance*, (?) $C_{22}H_{32}O$, b.p. 215—222°/3 mm., dehydrogenated to a *substance*, m.p. 182—183° (not the expected 2 : 3 : 6 : 7-dibenzphenanthrene).

R. S. C.

Synthetic investigations on the degradation products of bile acids, sex hormones, etc. I. Synthesis of 7-methyldi*cyclo*-[0 : 3 : 3]-octan-1-one. II. Synthesis of ketodeoxyœstric acid. D. K. Banerjee (*J. Indian Chem. Soc.*, 1940, **17**, 423—428, 453—462).—I. Distillation of $COMe{\cdot}[CH_2]_2{\cdot}CO_2Et$ and $CN{\cdot}CH_2{\cdot}CO_2Et$ with NH_2Ac and glacial AcOH (vapours at 105—110°) yields a residue of *Et* α-*cyano*-β-*methyl*-Δ^{α}-*butene*-αδ-*dicarboxylate*, b.p. 154—160°/5·5 mm., which with aq. KCN followed by cold aq. HCl yields *Et*$_2$ αβ-*dicyano*-β-*methyladipate*, b.p. 190—192°/6 mm., hydrolysed to *Et*$_3$ β-*methylbutane*-αβδ-*tricarboxylate*, b.p. 169—170°/10 mm., cyclised (Na in C_6H_6) to *Et*$_2$ 3-*methyl*cyclo*pentanone*-2 : 3-*dicarboxylate*, b.p. 153°/8·5 mm. The Na derivative of this with $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ in C_6H_6 affords *Et*$_3$ 3-*methyl*cyclo*pentanone*-2 : 3-*dicarboxylate*-2-β-*propionate*, b.p. 194—197°/7 mm. [also obtained (poor yield) from the K derivative], hydrolysed to 3-*methyl*cyclo*pentanone*-3-*carboxylic*-2-β-*propionic acid*, m.p. 116° (*semicarbazone*, m.p. 228°), reduced (Clemmensen) and esterified to *Et*$_2$ 1-*methyl*cyclo*pentane*-1-*carboxylate*-2-β-*propionate*, b.p. 140—142°/4·5—5 mm. This is cyclised (Na in C_6H_6) to 30% of *Et* 7-*methyldi*cyclo-[0 : 3 : 3]-*octan*-1-*one*-2-*carboxylate*, b.p. 119—120°/6 mm., hydrolysed to 7-*methyldi*cyclo-[0 : 3 : 3]-*octdn*-1-*one*, b.p. 70°/6 mm. (*semicarbazone*, m.p. 210°) (cf. Errington *et al.*, A., 1938, II, 269), oxidised (HNO_3) to 1-methylcyclopentane-1-carboxylic-2-acetic acid, m.p. 126—127° (mainly the *trans*-form).

II. $COMe{\cdot}[CH_2]_3{\cdot}CO_2Et$, $CN{\cdot}CH_2{\cdot}CO_2Et$, NH_2Ac, and glacial AcOH yield (as above) *Et* α-*cyano*-β-*methyl*-Δ^{α}-*pentene*-αε-*dicarboxylate*, b.p. 175—178°/7·5 mm., and thence *Et*$_2$ αβ-*dicyano*-β-*methylpimelate*, b.p. 192—193°/4 mm., hydrolysed and esterified to *Et*$_2$ β-*carbethoxy*-β-*methylpimelate*, b.p. 168°/6 mm. Cyclisation (Na in C_6H_6) of this yields a *compound*, $C_{13}H_{20}O_5$, b.p. 156°/7 mm. $CN{\cdot}CNaPh{\cdot}CO_2Et$ with $Cl{\cdot}[CH_2]_2{\cdot}COMe$ in C_6H_6 yields *Et* α-*cyano*-γ-*acetyl*-α-*phenylbutyrate*, b.p. 172—175°/5 mm. (*semicarbazone*, m.p. 154—155°), hydrolysed to γ-*acetyl*-α-*phenylbutyric acid*, b.p. 195—197°/6 mm., the *Et* ester, b.p. 143—145°/4·5 mm. (*semicarbazone*, m.p. 119—120°), of which with $CN{\cdot}CH_2{\cdot}CO_2Et$, NH_2Ac, and AcOH affords *Et* α-*cyano*-ε-*phenyl*-β-*methyl*-Δ^{α}-*pentene*-αε-*dicarboxylate*, b.p. 200—208°/4 mm. Addition of HCN and hydrolysis of the product converts this into δ-*carboxy*-α-*phenyl*-δ-*methylpimelic acid*, m.p. 169—171°, the *Et*$_4$ ester, b.p. 202—204°/5 mm., of which is cyclised (Na in C_6H_6) to *Et*$_2$ 6-*phenyl*-3-*methyl*cyclo*hexanone*-2 : 3-*dicarboxylate*, b.p. 195—197° (some decomp.)/5 mm. The Na derivative of this with $CH_2Br{\cdot}CO_2Et$ in C_6H_6 and the K derivative with $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ in xylene yield (after hydrolysis and esterification) respectively *Et*$_2$ 6-*phenyl*-3-*methyl*cyclo*hexanone*-3-*carboxylate*-2-*acetate* (I), b.p. 180—186°/2·5 mm., and -β-*propionate*, b.p. 185—190°/1·6 mm. [together with *Et* 6-*phenyl*-3-*methyl*cyclo*hexanone*-3-*carboxylate*, b.p. 182—187°/6 mm. (*semicarbazone*, m.p. 175·5—176·5°) in each case]. (I) with Zn wool, $CH_2Br{\cdot}CO_2Et$, and a trace of I in PhMe affords *Et*$_3$ 2-*phenyl*-5-*methyl*-Δ^1-cyclo*hexene*-5-*carboxylate*-1 : 6-*diacetate*, b.p.



(II.)

186—200°/1·8 mm., which on prolonged boiling with excess of red P and HI (*d* 1·7) followed by treatment of the product with conc. H_2SO_4 at 100° (bath) yields ketodeoxyœstric acid (**II**) (*semicarbazone*, m.p. 165—175°). A. Li.

Synthesis of 6-hydroxy-17-equilenone (an isomeride of equilenin) and two of its homologues. W. E. Bachmann and D. W. Holmes (*J. Amer. Chem. Soc.*, 1940, **62**, 2750—2757; cf. A., 1939, II, 261; 1940, II, 225).—1-Keto-9-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (modified prep. starting from 4 : 1-OMe·$C_{10}H_6$·CO·$[CH_2]_2$·CO_2H), m.p. 99—100° (lit. 98°), gives (methods ; *loc. cit.*) *Me* 1-*keto*-9-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*glyoxylate*, m.p. 124—124·5°, *Me* 1-*keto*-9-*methoxy*- (**I**), m.p. 120·5—121°, and 1-*keto*-9-*methoxy*-2-*methyl*- (**II**), m.p. 137—137·5°, -1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*. Hydrolysis of (**II**) by KOH–aq. MeOH and then sublimation at 200°/0·4 mm. gives 1-*keto*-9-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 82—83°. With $CH_2Br·CO_2Me$ and Zn, (**II**) gives Me_2 1-*hydroxy*-9-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*-1-*acetate* (**III**), m.p. 130—131°, and thence anti-9-*methoxy*-2-*carboxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylideneacetic acid* (**IV**), m.p. 224·5—226° (decomp.; bath preheated at 215°), and the *anhydride*, m.p. 239—240·5°, sublimes at 220°/0·4 mm., of the *syn*-isomeride. Partial hydrolysis of the Me_2 ester, m.p. 104·5—105°, of (**IV**) gives the 2-Me_1 ester, m.p. 197·5—199° (decomp.), the K salt of which is oxidised by $KMnO_4$ to (**II**), thus proving survival of the C-skeleton. Treatment of (**III**) with, successively, $SOCl_2$–C_5H_5N–C_6H_6, boiling KOH–MeOH, 45% aq. KOH at 100°, and 2% Na–Hg in warm H_2O gives α- (~28%), m.p. 233—235° (bath preheated at 220°), and β-9-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylic*-1-*acetic acid* (~51%), m.p. 228·5—230° (decomp.), also obtained similarly from the K salts of the unsaturated acids or (1 part of α- and 6 parts of β-acid) by hydrogenating (PtO_2) (**IV**) in AcOH. CH_2N_2 then gives the α-, m.p. 107—108°, and β-Me_2 ester, m.p. 96—97°, which by partial hydrolysis give the 2-Me_1 esters, α-, m.p. 198·5—200°, and β-*form*, dimorphic, m.p. 190—192° and 202·5—204°, converted by the Arndt–Eistert process into *Me* β-9-*methoxy*-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionate*, α-, m.p. 152·5—153·5°, sublimes at 200°/0·4 mm., and β-*form*, m.p. 75·5—76·5°. Cyclisation by NaOMe then gives *Me* 6-*methoxy*-17-*equilenone*-16-*carboxylate* (nomenclature: A., 1940, II, 349), α-, m.p. 151—152° (vac.), and β-*form*, m.p. 140—141° (vac.), which, when hydrolysed by HCl–AcOH–H_2O and then sublimed at 200°/0·01 mm., give 6-*methoxy*-17-*equilenone* (**V**), α-, m.p. 147·5—149° (vac.), and β-*form*, m.p. 112—113° (vac.), with small amounts of 6-*hydroxy*-17-*equilenone* (**VI**), α-, m.p. 240—242° (vac.; bath preheated at 220°), and β-*form*, m.p. (+ solvent) 101—102° (gas) and (solvent-free) 171·5—172·5° (vac.), also obtained from (**V**) by HCl–AcOH–H_2O–N_2. The Na derivative of (**I**) with EtBr gives *Me* 1-*keto*-9-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*, dimorphic, m.p. 95·5—97° and 113—114°, and thence (as above) Me_2 1-*hydroxy*-9-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*-1-*acetate*, m.p. 103·5—104·5°, anti-9-*methoxy*-2-*carboxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylideneacetic acid*, m.p. 203·5—205° (decomp.), and the *anhydride*, m.p. 228·5—229·5°, of the *syn*-acid, 9-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylic*-1-*acetic acid*, α-, m.p. 230·5—232·5°, and β-*form*, m.p. (+xC_6H_6) 155° (gas) and (solvent-free) 223—225° (Me_2 ester, α-, m.p. 133·5—134·5°, and β-*form*, m.p. 99·5—100·5°; 2-Me_1 ester, α-, m.p. 198·5—199·5°, and β-*form*, m.p. 160—161°), *Me* β-9-*methoxy*-2-*carbomethoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionate*, α-, m.p. 129—130°, and β-*form*, m.p. 73—74°, *Me* 6-*methoxy*-19-*methyl*-17-*equilenone*-16-*carboxylate*, α-, m.p. 161—162° (vac.), and β-*form*, 118—120° (vac.), 6-*methoxy*-, α-, m.p. 142—142·5°, and β-*form*, m.p. 75—76°, and 6-*hydroxy*-19-*methyl*-17-*equilenone* (**VII**), α-, m.p. 206—208° (vac.), and β-*form*, m.p. (+solvent) 109—110° (gas) and (solvent-free) 121·5—123°. By hydrolysis, the Arndt–Eistert and other reactions as above, β-9-*methoxy*-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionic acid*, α-, m.p. 167·5—168·5°, and β-*form*, m.p. 135·5—137° (prep. from the Me_2 esters), gives *Me* γ-9-*methoxy*-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthryl*-n-*butyrate*, α-, m.p. 94·5—95·5°, and β-form, an oil, "*Me* 6-*methoxy*-D-*homo*-17a-*equilenone*-17-*carboxylate*" [*Me* 3-*keto*-8-*methoxy*-2a-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 2a : 6a-*octahydrochrysene*-4-*carboxylate*], α-, m.p. 152—154° (vac.), and β-*form*, m.p. 150—151° (vac.), 6-*methoxy*-, α-, m.p. 131—132·5° (vac.), and β-*form*, m.p. 142—143°, and 6-*hydroxy*-D-*homo*-17a-*equilenone* (**VIII**), α-, m.p. 227—229° (vac.), and β-*form*, m.p. 223—225° (vac.). (**VI**) has no œstrogenic activity in 0·5-mg., (**VII**) and (**VIII**) have none in 1-mg., doses (both forms in all cases). R. S. C.

Ketonic bile acids.—See B., 1940, 898.

Constitution of pedicinin. P. K. Bose and P. Dutt (*J. Indian Chem. Soc.*, 1940, **17**, 499—507).—Pedicinin (**I**) (Na_2 salt), isolation (from *Didymorcarpus pedicellata*) described, is probably 2 : 5-*dihydroxy*-3-*methoxy*-6-*cinnamoyl*-1 : 4-*benzoquinone*; it is sol. in aq. $KHCO_3$. The constitution assigned by Sharma *et al.* (A., 1939, II, 274) is incorrect. (**I**) and Zn dust–Ac_2O at 100° (bath) afford *tetra-acetyldihydropedicinin* (2 : 3 : 5 : 6-*tetra-acetoxy*-4-*methoxyphenyl styryl ketone*), m.p. 207—208°, whilst (**I**) and H_2 (Pd–C; EtOH) at 30°/760 mm. afford a H_4-derivative (**II**) (probably 2 : 3 : 5 : 6-tetrahydroxy-4-methoxyphenyl β-phenylethyl ketone) (yellow), converted rapidly by air-oxidation into *dihydropedicinin* (2 : 5-*dihydroxy*-3-*methoxy*-6-β-*phenylpropionyl*-1 : 4-*benzoquinone*) (**III**), m.p. 134° (Na_2 salt), similarly reduced to (**II**). Similar hydrogenation of pedicellin (**IV**) affords dihydropedicellin, b.p. 135—145°/0·1 mm., converted by HNO_3 (*d* 1·4)–AcOH into a semi-solid product, hydrolysed by warm 5% aq. NaOH to (**III**). (**IV**) and HNO_3 (*d* 1·4)–AcOH (40—50 sec.) give mainly *methylpedicinin* (5-*hydroxy*-2 : 3-*dimethoxy*-6-*cinnamoyl*-1 : 4-*benzoquinone*); reaction for 1·5 min. affords much (**I**) also. A. T. P.

Extensions of the vitamin-K_1 synthesis. L. F. Fieser, M. Tishler, and N. L. Wendler (*J. Amer. Chem. Soc.*, 1940, **62**, 2861—2866).—Mainly a detailed account of work already reported (A., 1940, II, 226). The following appears new. The adduct of toluquinone and $(CH_2{:}CH)_2$ has m.p. 80—81°. 2-Methyl-5 : 8-dihydro-1 : 4-naphthaquinol has m.p. 173—174° (darkens at 170°). 2 : 3 : 5-Trimethyl-6-phytylquinol has m.p. 92°; the corresponding quinone with H_2–$PdCl_2$–MeOH, followed by Ag_2O–Et_2O, gives 2 : 3 : 5-*trimethyl*-6-*dihydrophytyl*-1 : 4-*benzoquinone*, an oil (*quinol diacetate*, m.p. 54—55°). α-Tocopherol allophanate has m.p. 175—176° (lit. 172°). R. S. C.

Hydro-, oxido-, and other derivatives of vitamin-K_1 and related compounds. M. Tishler, L. F. Fieser, and N. L. Wendler (*J. Amer. Chem. Soc.*, 1940, **62**, 2866—2871).—Partly a detailed account of work already reported (A., 1940, II, 226, 311; 1940, III, 820). Pt- or Pd-hydrogenation of vitamin-K_1 followed by oxidation (Ag_2O) of the resulting quinol gives always the H_6-compound, but partial hydrogenation in MeOH in presence of Raney Ni similarly affords the βγ-H_2-derivative. 2-*Dihydrophytyl*-1 : 4-*naphthaquinone*, an oil, is similarly obtained, but 3-γ-*phenyl*-n-*propyl*-2-*methyl*-1 : 4-*naphthaquinone*, m.p. 42°, is obtained by oxidation of the quinol from the $CHPh{:}CH·CH_2$ compound and H_2–$PdCl_2$ in MeOH. 2-Methyl-1 : 4-naphthaquinone and H_2–$PdCl_2$ in AcOH give 2-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 4-*naphthaquinol*, m.p. 165—167° (diacetate, m.p. 100—101°). Commercial 1 : 6-$C_{10}H_6Me_2$ is a mixture and affords 2 : 8- (**I**), m.p. 135—135·5°, and 2 : 5-*dimethyl*-1 : 4-*naphthaquinone* (**II**), m.p. 93·5—94·5°. Toluquinone and piperylene in dioxan at 60—70° give 1 : 4-*diketo*-2 : 8-*dimethyl*-5 : 8 : 9 : 10-*tetrahydronaphthalene* (**III**), softens at ~96°, m.p. (final) 101·5°, isomerised by $SnCl_2$–HCl–EtOH to 2 : 8-*dimethyl*-5 : 8-*dihydro*-1 : 4-*naphthaquinol*, m.p. 91—91·5°, which with CrO_3–AcOH–H_2O at 60° gives (**I**). The oily product formed with (**III**) affords (**II**) by a similar series of reactions. 4 : 1-, m.p. 83·5—84·5°, and 3 : 2-$C_{10}H_6Me·OH$, m.p. 160·9—161·5° (corr.), and 9-methylperinaphthen-7-one, m.p. 156·5—157·2° (corr.), are prepared by known methods. 1-Keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 140°/13 mm. (*semicarbazone*, m.p. 195—196°), best obtained from $CH_2Ph·CHMe·CH_2·CO_2H$ by 80% H_2SO_4 at 100°, with Se at 310—330° (25%) or S at 250° (30%) gives 3 : 1-$C_{10}H_6Me·OH$, m.p. 91—93·5°, solidifies, remelts at 93·5—94° (*benzoate*, m.p. 75—76°). 1-Keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 136—137°/16 mm. (oxime, m.p. 98—99°; *semicarbazone*, m.p. 205—206°), with Br gives 41% of 2 : 1-$C_{10}H_6Me·OH$, m.p. 63—64° (*benzoate*, m.p. 94—95°; *acetate*, m.p. 81—82°), also obtained in 55% yield from 2 : 1-$C_{10}H_6Me·NH_2$. R. S. C.

Constitution of celastrol. III. O. Gisvold (*J. Amer. Pharm. Assoc.*, 1940, **29**, 432—434; cf. A., 1940, II, 138).—Celastrol (**I**) is probably a mono- or 3 : 4(or 2 : 3)-di-alkyl-8-hydroxy-

1 : 2(or -1 : 4)-naphthaquinone (total alkyl = $C_{12}H_{26}$), and has no significant antihæmorrhagic activity. Oxidation (aq. alkaline $KMnO_4$) of (I) gives a little ? 3 : 1 : 2-$OH{\cdot}C_6H_3(CO_2H)_2$, m.p. 242—244° (lit. 161—163°, 244°). Cryst. substances could not be obtained from (I) or methylcelastrol (II) by AcOH–CrO_3. Reductive acetylation of (II) affords the corresponding *quinol diacetate*, m.p. 210°.

F. O. H.

III.—TERPENES.

Cyanocamphoranilic acids and their rotatory powers. M. Singh and A. Singh (*J. Indian Chem. Soc.*, 1940, **17**, 485—486).—Camphoric anhydride and *p*- or *m*-$CN{\cdot}C_6H_4{\cdot}NH_2$ with a little fused NaOAc at 120—130° (bath) afford 4'-, m.p. 140°, $[\alpha]_D$ +58·0° in MeOH, +51·5° in EtOH, or 3'-*cyanocamphoranilic acid*, m.p. 108—110°, $[\alpha]_D$ +48·7° in MeOH, +38·8° in EtOH, respectively. Vals. of $[\alpha]$ are anomalous, resembling those for the Cl-derivatives (cf. A., 1928, 1377). A. T. P.

Enol-acetate in the triterpene series. E. R. H. Jones and K. J. Verrill (*J.C.S.*, 1940, 1512).—β-Amyranonyl acetate with KOAc and Ac_2O gives an *enol-acetate*, m.p. 225—227°, $[\alpha]_D^{20}$ +44° in $CHCl_3$. F. R. S.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Sapogenins. X. Carbon skeleton and the position of the second hydroxyl group of quillaic acid. P. Bilham and G. A. R. Kon (*J.C.S.*, 1940, 1469—1474).—Quillaic acid (I) with Na–EtOH and N_2H_4 in a sealed tube at 200° gives deoxyquillaic acid (II) and with $CH_2Ph{\cdot}OH$ instead of EtOH, *quillaol*, $C_{29}H_{46}O_3$, m.p. 147—150°, is obtained. Oxidation of Me deoxyquillaate to the diketo-ester followed by reduction gives *Me* 16-*keto-oleanolate*, m.p. 204—205°, which is hydrolysed (KOH) to a mixture of 16-*keto*-$\Delta^{12:13(?)}$-*oleanene* (III), m.p. 220—222°, $[\alpha]_D$ −146·9° in $CHCl_3$, and an isomeric *ketone*, m.p. 160—161°, $[\alpha]_D$ +13° in $CHCl_3$. Reduction of (III) with Na–EtOH yields 16-*hydroxy*-$\Delta^{12:13(?)}$-*oleanene*, m.p. 179°, surface-film measurements of which show that the second OH of (I), $OH^{(2)}$, is situated on $C_{(16)}$ in ring D and it can be inferred that the CO_2H must be attached to $C_{(17)}$ at the junction of rings D and E. Reduction (Na–EtOH) of (II) and of (III) gives a *hydrocarbon*, $C_{29}H_{48}$, m.p. 193—193·5°, $[\alpha]_D$ +23° in $CHCl_3$, which is evidently a stereoisomeride of Winterstein and Stein's oleanene II (A., 1932, 856), from which it differs by the *trans*-locking of rings D and E. This has been converted into oleanene III (cf. Winterstein *et al.*, A., 1933, 718), proving that the C skeleton of (I) must be identical with that of oleanolic acid and gypsogenin. F. R. S.

Sarcostin. I. Preliminary study of its behaviour with reagents. J. W. Cornforth and J. C. Earl (*J.C.S.*, 1940, 1443—1447).—Sarcostin (I) with cold conc. HCl gives an amorphous product, $C_{21}H_{28}O_3$. Oxidation of (I) with $Pb(OAc)_4$ results in the use of 3—4 mol. proportions, the first very rapidly, with the formation of MeCHO, a neutral *product*, $C_{21}H_{32}O_6$, m.p. 186—187°, succinic acid, 2-*methyl*-1 : 3-cyclo*pentanedione* (II) (?), $C_6H_8O_2$, m.p. 210°, and non-cryst. material. The $(OAc)_3$-derivative of (I) with $Pb(OAc)_4$ yields a ketonic *substance*, $C_{27}H_{40}O_{10}$, m.p. 90—110°, solidifying and m.p. 164—165° [*semicarbazone*, m.p. 150—170° (decomp.)], which is oxidised ($KMnO_4$) to a *substance*, $C_{23}H_{36}O_6$ or $C_{19}H_{30}O_5$, m.p. 161—162°. Hydrogenation of (I) with PtO_2–H_2 affords *dihydrosarcostin*, $C_{21}H_{36}O_6$, m.p. 245—246°, oxidised [$Pb(OAc)_4$; 2 mols.] to MeCHO, a neutral *product*, $C_{19}H_{28}O_5$, m.p. 194—195°, and (II); the H_2-compound forms a $(OAc)_3$-derivative, m.p. 246—247°. Dehydrogenation of (I) with Se appears to give Diels' hydrocarbon and condensation with $COMe_2$ affords a *product*, m.p. 225—226°, containing 1 mol. of (I) to 2 mols. of $COMe_2$. (I) must contain a double bond, a $CHMe{\cdot}OH$ side-chain, and two glycol groups.

F. R. S.

Constituents of the higher fungi. II. Unsaturated system of polyporenic acid *A*. L. C. Cross and E. R. H. Jones (*J.C.S.*, 1940, 1491—1493).—Hydrogenation (H_2–PtO_2) of polyporenic acid *A* (I) gives the *H*$_2$-*acid* A, m.p. 216°, $[\alpha]_D^{20}$ +66° in C_5H_5N, which forms a *Me* ester, m.p. 142°, $[\alpha]_D^{20}$ +76° in $CHCl_3$, and *Me ester-acetate* (II), m.p. 142°, $[\alpha]_D^{20}$ +36° in $CHCl_3$. Ozonolysis of the Me ester-acetate of (I) yields a 50% amount of CH_2O and a small quantity of *Me ester keto-acetate* (?), m.p. 194°, $[\alpha]_D^{20}$ +121° in $CHCl_3$, whilst (II) similarly affords < 4% of CH_2O, indicating that the reactive double bond of (I) must be present in an exocyclic CH_2 group. The Me ester of (I) with HCO_2H gives the *Me ester-formate* (+0·5MeOH), m.p. 148°, $[\alpha]_D^{20}$ +84° in $CHCl_3$, and it is not cyclised.

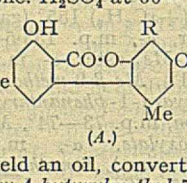
F. R. S.

Chemical investigation of Indian fruits. I. Bitter principles of pamparapanas (Indian shaddock). T. R. Seshadri and J. Veeraraghaviah (*Proc. Indian Acad. Sci.*, 1940, **11**, A, 505—511).—Methods are described for isolating the bitter principles of the peels (best dried), rags, and seeds of this plant. The first two contain 0·13% and 1% of naringin (I), respectively, whilst the seeds contain 0·15% of (I), ~0·6% of limonin (II), with ~0·03% of *iso*limonin (III). (I) has not been observed before in citrus seeds. The properties of (III) observed by Higby (A., 1939, III, 343) (contrary to those previously described) are confirmed. Attempted methylation of (II) is unsuccessful. Shaddock peels have advantages as cattle fodder. E. W. W.

Soil and peat humic acids. I. Isolation and purification of the acids. G. C. Esh and S. S. Guha-Sircar (*J. Indian Chem. Soc.*, 1940, **17**, 326—331).—Fats, waxes, and resinous matters are removed from the soil by extraction with C_6H_6–EtOH (1 : 1) and the residue is treated with 2% HCl at 100° for 1·5 hr. After treatment with H_2O at 100° the product is stirred with cold 4% KOH in a closed vessel for 8—10 hr. After three such treatments, the dark humate solutions are acidified with dil. HCl and the pptd. humic acid is thoroughly washed with H_2O. After repetition of the alkali–acid treatment, the dried material is separated into EtOH-sol. hymatomelanic acid (I) and EtOH-insol. humic acid (II); the latter is extracted with AcBr, washed with Et_2O, and dried at 80—85°. The ash in peat humic acids is greyish-white in colour and contains Fe, Si, Al, Mg, and traces of Cu whereas that of (II) is reddish-brown showing is high % of Fe. (I) has a relatively low ash content. OMe is not high in any humic acid and Ac is absent. The acids do not evolve appreciable amounts of furfuraldehyde when boiled with 12% HCl. CH_2O_2 appears to be absent. H. W.

V.—HETEROCYCLIC.

Kostanecki–Robinson reaction. II. Propionylation and butyrylation of orcacetophenone and its monomethyl ether. S. M. Sethna and R. C. Shah (*J. Indian Chem. Soc.*, 1940, **17**, 487—494; cf. A., 1940, II, 285).—Orcacetophenone (I) and $EtCO_2Na$–$(EtCO)_2O$ at 180—190° afford an oil, converted by conc. H_2SO_4 at room temp. into 7-*hydroxy*-4-*propionylmethyl*-3 : 5-*dimethylcoumarin*, m.p. 207—209° [*acetate*, m.p. 111—113°; *Me ether* (II), m.p. 75—77°; 2 : 4-*dinitrophenylhydrazone*, m.p. 255—256° (decomp.)], which with 60% aq. NaOH at room temp. gives 7-*hydroxy*-3 : 4 : 5-*trimethylcoumarin*, m.p. 195—197° (*Me ether*, m.p. 90—92°). Orcacetophenone 4-Me ether (III), as above, affords (II), whilst the Me_2 ether (IV) and $EtCO_2Et$–Na, with cooling, and then at 115—120°, give 2' : 4'-*dimethoxy*-6'-*methylbenzoylpropionylmethane*, b.p. 185—190°/2—4 mm., converted by HBr (*d* 1·78) into 7-*methoxy*-5-*methyl*-2-*ethylchromone*, m.p. 130—132°, demethylated by HI (*d* 1·7)–Ac_2O at 130—140° to the 7-*OH*-compound, m.p. 195—197°. *p*-Orsellinic acid (V), $CHAcMe{\cdot}CO_2Et$, and conc. H_2SO_4 at 60—70° for 16 hr. [4 hr. gives (V) only] give a small amount of a *substance*, m.p. 235—237° (decomp.) [probably (*A*), R = CO_2H], obtained similarly from (V)–H_2SO_4; at 240—250° it affords a *substance*, m.p. 265—267° [probably (*A*), R = H]. (I) and Pr^aCO_2Na–$(Pr^aCO)_2O$ at 180—190° yield an oil, converted by H_2SO_4 at room temp. into 7-*hydroxy*-4-*butyrylmethyl*-5-*methyl*-3-*ethylcoumarin*, m.p. 155—156° [*acetate*, m.p. 79—80°; *Me ether*, m.p. 51—54°; 2 : 4-*dinitrophenylhydrazone*, m.p. 253—254° (decomp.)], and thence by 10% aq. NaOH at room temp. into 7-*hydroxy*-4 : 5-*dimethyl*-3-*ethylcoumarin*, m.p. 170—172° (*Me ether*, m.p. 79—81°). (III) and Pr^aCO_2Na–$(Pr^aCO)_2O$ at 180—190° give an impure oil, but (IV) similarly, at 115—120°, affords 2 : 4-*dimethoxy*-6-*methylbenzoylbutyrylmethane*, b.p. 220—225°/20—25 mm. (*Cu* salt, m.p. 175—177°), converted by HBr (*d* 1·78) into 7-*methoxy*-, m.p. 97—98°, and thence [HI (*d* 1·7)–Ac_2O at 145—155°] -*hydroxy*-5-*methyl*-2-n-*propylchromone*, m.p. 163—165°.



(*A*.)

A. T. P.

Chromones of the naphthalene series. III. Rapid quantitative transformation at room temperature of *o*-aroyloxyacetoarones into *o*-hydroxydiaroylmethanes. V. V. Ullal, R. C. Shah, and T. S. Wheeler (*J.C.S.*, 1940, 1499—1500).—NaOEt–EtOH is an effective reagent for the rapid quant. transformation at room temp. of *o*-aroyloxyacetoarones into the corresponding *o*-hydroxydiaroylmethanes, which can be readily cyclised at room temp. to the corresponding chromones. The following are described: 2-p-*anisoyloxy*-, m.p. 122°, 2-(1′-*naphthoyloxy*)-, m.p. 113°, 2-(2′-*naphthoyloxy*)-, m.p. 103°, 2-(3′-*methoxy*-2′-*naphthoyloxy*)-, m.p. 116°, 2-(1′-*methoxy*-2′-*naphthoyloxy*)-, m.p. 122°, and 2-*palmityloxy*-1-*acetonaphthone*, m.p. 40°, and 2-*cinnamoyloxy*-4-*methoxyacetophenone*, m.p. 99°; *benzoyl*-2-*hydroxy*-, m.p. 137°, p-*anisoyl*-2-*hydroxy*-, m.p. 102°, and 2-*hydroxydi*-1-*naphthoyl*-, m.p. 163°; 2-*hydroxy*-, m.p. 136°, 2-*hydroxy*-3′-*methoxy*-, m.p. 175°, and 2-*hydroxy*-1′-*methoxy*-1 : 2′-*dinaphthoyl*-*methane*, m.p. 165°; 2-*hydroxy*-1-*naphthoylpalmitylmethane*, m.p. 112°; and 2-*hydroxy*-4-*methoxybenzoylcinnamoylmethane*, m.p. 140°; 2-(1′-*naphthyl*)-, m.p. 159°, 2-(2′-*naphthyl*)-, m.p. 198°, 2-(3′-*methoxy*-2′-*naphthyl*)-, m.p. 168°, 2-(1′-*methoxy*-2′-*naphthyl*)-, m.p. 144°, 2-*pentadecyl*-, m.p. 89°, 2-(3′-*hydroxy*-2′-*naphthyl*)-, m.p. >300° (*acetate*, m.p. 153°), and 2-(1′-*hydroxy*-2′-*naphthyl*)-5 : 6-*benzochromone*, m.p. >300° (*acetate*, m.p. 189°).

F. R. S.

***N*-Vinylethinylmethylpiperidine.**—See B., 1940, 780.

Cyanine dyes of the pyridine series. M. Q. Doja (*J. Indian Chem. Soc.*, 1940, **17**, 347—350).—2-p-*Dimethylaminostyrylpyridine methochloride*, m.p. 117°, *methobromide*, m.p. 262°, and methiodide and the p-*dimethylaminoanils* of 2-*methylpyridine methochloride* and *methobromide*, m.p. 235° and 237°, respectively, have been prepared. The absorption spectra and fluorescence of these substances are described. H. W.

α-Pyridinium compounds of higher fatty acids and amides.—See B., 1940, 778.

Tetrahydro*iso*quinolino-alcohols derived from tetrahydronaphthalene. E. Mosettig and E. L. May (*J. Org. Chem.*, 1940, **5**, 528—543).—1-*Keto*-6-*acetoxy*-, m.p. 61—62°, 1-*keto*-7-*hydroxy*-, m.p. 162—164°, and 1-*keto*-7-*acetoxy*-, m.p. 79—80°, -1 : 2 : 3 : 4-*tetrahydronaphthalene* are described. 2-*Bromo*-1-*keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 78—80°, could not be caused to react with tetrahydro*iso*quinoline or piperidine. 1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene, CH_2O, and tetrahydro*iso*quinoline hydrochloride at 100° afford 1-*keto*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 90—91° (*picrate*, m.p. 118—120° after softening at 86°). Attempts to hydrogenate the ketone (PtO_2 in EtOH) lead to fission into base and 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, whereas the hydrochloride is hydrogenated to 1-*hydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 94·5—95° [*hydrochloride*, m.p. 202—203° (decomp.)]. 1-*Keto*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 95°, gives a *hydrochloride*, m.p. 219—221° (decomp.) after softening at 146°, which is reduced to the 1-*hydroxy*-base, m.p. 95·5—96° (*hydrochloride*, m.p. 182·5—184°). 1-*Keto*-6-*methoxy*-2-1′ : 2′ : 3′ : 4-*tetrahydro*-2-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 146—147°, is reduced to the 1-*OH*-base, m.p. 125·5—126° (corr.) [*hydrochloride*, m.p. 178—179° (decomp.)]. The non-cryst. 1-*keto*-6-*methoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* gives a *hydrochloride*, m.p. 127—128° and 218° (decomp.) after evolution of gas and resolidification at 160°. This is hydrogenated (PtO_2 in 95% EtOH) to the 1-*OH*-base, m.p. 124·5—125° (corr.), which is converted by HCl–EtOH or Ac_2O–C_5H_5N into (?) 6-*methoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-3 : 4-*dihydronaphthalene*, m.p. 135·5—136°; the *hydrochloride*, m.p. 201—202·5°, appears to be reduced (H–PtO_2–EtOH) to 6-methoxytetrahydro*iso*quinoline and 6-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene. 1-*Keto*-6-*acetoxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 151—152°, is hydrolysed to the 1-*OH*-base, m.p. 156—157° (decomp.) [*hydrochloride*, m.p. 158—160° (decomp.)], and reduced (PtO_2 in 95% EtOH) to 1-*hydroxy*-6-*acetoxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride* (I), m.p. 189—192·5° (decomp.). Reduction of the appropriate ketone leads to 1 : 6-*dihydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. (indef.) 111—121° (decomp.) [*hydrochloride*, m.p. 105—107° (decomp.) and 190—196° (decomp.) after resolidification]. Hydrolysis (KOH–MeOH) of (I) yields 6-*hydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-3 : 4-*dihydronaphthalene*, m.p. 136—137° (corr.) [*hydrochloride*, m.p. 187—188° (decomp.) or, +MeOH, m.p. 126—128·5° (decomp.); *hydrochloride* of Ac derivative, m.p. 204—206·5° (decomp.)], hydrogenated to tetrahydro*iso*quinoline and 6-*hydroxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 88—88·5° (corr.). 1-*Keto*-6-*acetoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 200—202° (decomp.) after softening at 162°, is reduced to the 1-*OH*-compound (*hydrochloride*, m.p. 181·5—183°) and hydrolysed to the 1 : 6-$(OH)_2$-base, m.p. 145·5—146·5° (corr.) [*hydrochloride*, m.p. 207—208°, acetylated to a *substance*, $C_{23}H_{26}O_3NCl$, m.p. 203—204·5° (decomp.)]. 1-*Keto*-7-*methoxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 104—105° (corr.) [*hydrochloride*, m.p. 119—120° (corr.)], is formed with a *by-product*, $C_{24}H_{24}O_4$, m.p. 138—139° (corr.), by the customary method. It is reduced to the 1-*OH*-compound, m.p. 111·5—112° (corr.) [*hydrochloride*, m.p. 207·5—209° (decomp.); *Ac* derivative *hydrochloride*, m.p. 167·5—169·5°]. 1-*Keto*-7-*methoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 220—221° (decomp.) after softening at 156°, is reduced to the 1-*OH*-base, m.p. 135—135·5° (corr.) [amorphous *hydrochloride*, m.p. 154—163°; *picrate*, m.p. 150—151·5°; *Ac* derivative *hydrochloride*, m.p. 182·5—183·5°]. 1-*Keto*-7-*acetoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 209—211° (decomp.) after softening at 158°, gives the 1-*OH*-compound (*hydrochloride*, m.p. 149—160°). 1 : 7-*Dihydroxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 173—174·5° (corr.), gives a *hydrochloride*, m.p. 209°. 1-*Hydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-iso*quinolylmethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 133·5—134° (corr.), did not yield a cryst. hydrochloride or picrate.

H. W.

Sulphonamides. I. G. L. Juneja, K. S. Narang, and J. N. Ray (*J. Indian Chem. Soc.*, 1940, **17**, 495—498).—*p*-NHAc·C_6H_4·SO_2Cl and the respective aminoquinoline in dry $CHCl_3$ give 5-, m.p. 254° (decomp.), 6-, m.p. 283°, or 8-*p*-acetamido-, m.p. 194°, and thence [HCl (*d* 1·15) at 100° (bath)] 5-, m.p. 226—228°, 6-, m.p. 200°, or 8-*p*-amino-benzenesulphonamidoquinoline, m.p. 188° (cf. Bobrański, A., 1939, II, 179). 6-Aminoquinoline and CH_2Cl·COCl in dioxan at 70° (2 min.) afford 6-p-*chloro*-, m.p. 166—168° (decomp.), converted by $NHEt_2$ or piperidine in EtOH into 6-p-*diethylamino*-, m.p. 137°, or 6-p-*piperidino*-*acetamidobenzenesulphonamidoquinoline*, m.p. 131°, respectively. Similarly prepared are: 6-p-*chloro*- (*hydrochloride*), -*diethylamino*-, m.p. 147—149°, and -*piperidino*-*propionamido*-, m.p. 198—201°; 8-p-*chloro*- [*hydrochloride*, m.p. 220° (decomp.)], -*diethylamino*-, m.p. 115—116°, and -*piperidino*-*acetamido*-, m.p. 172—173°; 8-p-*chloro*- [*hydrochloride*, m.p. 228° (decomp.)], -*diethylamino*-, m.p. 95—96°, and -*piperidino*-*propionamido*-, m.p. 178°; 5-p-*chloro*- (*hydrochloride*, m.p. 226°) and -*piperidino*-*acetamidobenzenesulphonamidoquinoline*, m.p. 217—218°. Encouraging results are reported when some of the above compounds are tested on mice infected with pneumococci. A. T. P.

Phthalocyanines.—See B., 1940, 784.

Chemotherapy of malaria. 6-Methoxyquinolyl-8-hydrazine and synthesis of some heterocyclic compounds from it. B. K. Nandi (*J. Indian Chem. Soc.*, 1940, **17**, 449—452).—6-*Methoxyquinolyl*-8-*hydrazine* (I), m.p. 67° (from 6-methoxy-8-aminoquinoline, HNO_2, and $SnCl_2$), with dil. HCl and KCNS yields 1-(6′-*methoxyquinolyl*-8′)-*thiosemicarbazide*, m.p. 259—261°, which with COPh·CH_2Br in boiling EtOH gives 2-(8′-*hydrazino*-6′-*methoxyquinolyl*)-4-*phenylthiazole*, m.p. 121—124°. *cyclo*Hexanone in EtOH with (I) in dil. AcOH gives the 6-*methoxyquinolyl*-8-*hydrazone*, m.p. 91°, converted by warm dil. H_2SO_4 into the sulphate of 6′-*methoxyquinolino*-(7′ : 8′ : 3 : 2)-4 : 5 : 6 : 7-*tetrahydroindole*, m.p. 181—182° (*hydrochloride*, m.p. 256—259°). With CH_2Ac·CO_2Et at 100° (I) yields a product, m.p. 72°, which when heated gives 1-(6′-*methoxyquinolyl*-8′-)3-*methylpyrazol*-5-*one*, m.p. 135°. The hydrochloride of (I) with $AcCO_2H$ yields a product converted by boiling conc. HCl into 6′-*methoxyquinolino*-(7′ : 8′ : 3 : 2)-*pyrrole*-5-*carboxylic acid*, m.p. 197—198°. With

KCNO (I) yields 1-(6′-*methoxyquinolyl*-8′)-*semicarbazide*, m.p. 236—239° (softening at 225°), and with *dl*-arabinose in dil. AcOH, the 6-*methoxyquinolyl*-8-*hydrazone*, m.p. 140°. A. Li.

Chemotherapy of bacterial infections. III. Synthesis of (N^4)-amino-substituted heterocyclic derivatives of sulphanilamide. K. Ganapathi (*Proc. Indian Acad. Sci.*, 1940, **12, A**, 274—283).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, HCl, and KCNS give p-*sulphonamidophenylthiocarbamide* (I), m. p. 197°, converted by $CH_2Cl{\cdot}CHCl{\cdot}OEt$ in boiling H_2O into 2-p-*sulphonamidoanilinothiazole* or 2-p-*sulphonamidoanilothiazoline*, m.p. 240° (decomp.). Similar reactions lead to 2-p-*sulphonamidoanilo*-3-*allyl*-, m.p. 139·5—141°, and -3-*phenyl*-, m.p. 193°, -*thiazoline*. 2-p-*Sulphonamidoanilo*-4-*phenyl*-3-*allylthiazoline*, m.p. 209—210°, and 2-p-*sulphonamidoanilino*-4-*phenylthiazole* (or 2-p-*sulphonamidoanilo*-4-*phenylthiazoline*), m.p. 228—230°, are described. Condensation of (I) with $CHAcBr{\cdot}CO_2Et$ or $CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ in H_2O at 100° yields *Et* 2-p-*sulphonamidoanilino*-4-*methylthiazole*-5-*carboxylate*, m.p. 243—245°, and *Et* 2-p-*sulphonamidoanilinothiazolyl*-4-*acetate* (or *Et* 2-p-*sulphonamidoanilothiazolinyl*-4-*acetate*), m.p. 219—220° (slight decomp.). $CHAcBr{\cdot}CH_2{\cdot}CO_2Et$ similarly gives *Et* 2-p-*sulphonamidoanilino*-4-*methylthiazolyl*-5-*acetate* (or *Et* 2-p-*sulphonamidoanilo*-4-*methylthiazolinyl*-5-*acetate*), m.p. 163° after softening at 154°. (I) and $CH_2Cl{\cdot}CO_2Et$ or $CH_2Cl{\cdot}CO_2H$ in boiling abs. EtOH or $CH_2Cl{\cdot}COCl$ in $COMe_2$ afford N-p-*sulphonamidophenyl*-ψ-*thiohydantoin*, m.p. (indef.) 240—255°, accompanied by $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ if reaction is prolonged or effected in dil. EtOH or H_2O. N^1-*p*-Sulphonamidophenyl-*N*-allylthiocarbamide and I in boiling EtOH followed by NH_3 give 2-p-*sulphonanilino*-5-*iodomethylthiazoline* (or 2-p-*sulphonamidoanilo*-5-*iodomethylthiazolidone*), m.p. 115—119°. Diazotisation of 2-N'-sulphanilamidothiazole and coupling with 4-aminothiouracil leads to 4-*amino*-5-[4′-(2)-*thiazolylsulphonamidophenylazo*]*thiouracil*. 2-(4-N′-*Sulphanilamidobenzenesulphonamido*)*thiouracil* has m.p. 163—168°. 5-Chloroacridine (improved prep. described) is dissolved in 5—8 times its wt. of PhOH at 100° and the solution is heated with the powdered amine, $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR$, thereby giving N⁴-5-*acridylsulphanilamide*, m.p. 245—246°, 2-N⁴-5-*acridylsulphanilamidopyridine*, m.p. 268—269° (decomp.), and 4-N⁴-5-*acridylsulphanilamido*-*aniline*, m.p. 278—282°, -*nitrobenzene*, m.p. >285°, and -*benzenesulphonamide*, m.p. >280°. None of the thiazole and related derivatives shows any activity in streptococcal or pneumococcal infections in mice. Some of the acridine compounds exhibit considerable activity in streptococcal infections; they are inactive in pneumococcal infections. For pronounced antibacterial action the heterocyclic ring should be substituted in the sulphonamide radical leaving a free NH_2-group which appears to play some significant but imperfectly understood rôle in the mechanism of therapeutic action. H. W.

Cyanine dyes.—See B., 1940, 846, 847.

Alkaloid of *Berberis umbellata*, Wall. I. Isolation and examination of umbellatine. R. Chatterjee (*J. Indian Chem. Soc.*, 1940, **17**, 289—291).—The stem bark yields optically inactive *umbellatine* (I), $C_{21}H_{21}O_8N$, m.p. 206—207° (decomp.), which when crystallised from H_2O contains 5·5H_2O; 0·5H_2O is retained at 110°/vac. whilst at 120° slight decomp. commences. (I) contains 2 OMe and appears to be a *sec.* amine since it gives a cryst. *methiodide* and *nitrosoumbellatine*, m.p. 265—267° (decomp.). The presence of 1 CH_2O_2 group is confirmed. *Umbellatine hydrochloride* and *platinichloride*, which char without melting, are described. H. W.

Synthesis of benzonicotine. B. K. Nandi (*J. Indian Chem. Soc.*, 1940, **17**, 285—288).—Addition of Et quinoline-3-carboxylate and 1-methylpyrrolid-2-one to EtOH-free NaOEt in C_6H_6 gives 3′-1′-*methylpyrrolid*-2′-*onyl* 3-*quinolyl ketone*, m.p. 120° (*monopicrate*, m.p. 178°), converted by fuming HCl at 140—145° into 3-*quinolyl* γ-*methylamino*-n-*propyl ketone*, b.p. 165—175°/0·01 mm. (*platinichloride*, m.p. 215—220°). This is reduced (H_2–Pd–C–"extra norite" in HCl–EtOH) to 3-*quinolyl*-γ-*methylamino*-n-*propylcarbinol*, b.p. 200—204°/0·5 mm. (*platinichloride*, m.p. 286—288°; *dipicrate*, m.p. 199—201°), in poor yield, which with HI (*d* 1·94) and red P at 100—110° affords α-3-quinolyl-δ-methylamino-*n*-butyl iodide, converted into r-*benzonicotine* (I), b.p. 172—175°/0·1 mm. [*dipicrate*, m.p. 224—225°; *platinichloride*, m.p. 232—234°; *aurichloride*, m.p. 239—240° (decomp.)]. Physiologically natural *l*-nicotine is three times as active as (I). H. W.

Alkaloids of fumariaceous plants. XXVIII. *Corydalis nobilis*, **Pers.** R. H. F. Manske (*Canad. J. Res.*, 1940, **B, 18**, 288—292).—This plant contains protopine, cryptopine, *d*- and *dl*-tetrahydropalmatine, stylopine, *d*-*iso*corypalmine (I), corytuberine (II), biculline (III), and corlumine, with three unidentified bases, one non-phenolic, *alkaloid F* 53, $C_{17}H_{17}O_4N$ (?), m.p. 183°, and two phenolic, *alkaloid F* 54, $C_{17}H_{19}O_3N(OMe)_2$, m.p. 143°, and *alkaloid F* 55, m.p. 209°. Taxonomically, the plant is unique in forming both (II) and (III); its roots do not contain acetylornithine. Alkaloid F 34, m.p. 218°, from *C. caseana* (A., 1938, II, 383) is identical with the *dl*-form of (I). E. W. W.

VI.—ORGANO-METALLIC COMPOUNDS.

Alkyl esters of mono- and di-arylarsenious acids. G. Kamai and V. M. Zoroastrova (*J. Gen. Chem. Russ.*, 1940, **10**, 921—926).—The following esters were prepared by the reaction $AsPhCl_2 + NaOR \rightarrow AsPh(OR)_2$: R = Me, Et, Pr^{α}, b.p. 128—129°/8 mm., Pr^{β}, b.p. 118—119°/11 mm., Bu^{α}, b.p. 147—148°/10 mm., Bu^{β}, b.p. 144—144·5°/12 mm., iso*amyl*, b.p. 153—154·5°/11 mm. The esters AsRR′·OR″ were obtained analogously: R = R′ = Ph, R″ = Et [*compound*, m.p. 160—162° (decomp.), with CuI], R″ = Pr^{α}, b.p. 174—175°/10 mm. (*compound*, m.p. 140—142°, with CuI); R = Ph, R′ = *p*-C_6H_4Me, R″ = Pr^{α}, b.p. 188—189°/11 mm. Isomerisation of these esters does not occur when they are heated with alkyl halides. R. T.

VIII.—ANALYSIS.

Manometric carbon determination. D. D. Van Slyke and J. Folch (*J. Biol. Chem.*, 1940, **136**, 509—541).—A combustion mixture of furming H_2SO_4, H_3PO_4, CrO_3, and HIO_3 effects complete oxidation in 1—3 min., giving theoretical yields of CO_2 with compounds hitherto resistant to wet combustion (cholesterol, palmitic acid, etc. The CO_2 is collected and measured in the Van Slyke–Neill manometric apparatus, a solution of NaOH and N_2H_4 being used for absorption (cf. A., 1933, 1314). Factors for calculation are derived. No modifications are required for substances containing N, S, halogen, or alkali metal. A. Li.

Calorimetric determination of small amounts of acetylene. T. F. Tschernakovskaja (*Sintet. Kautschuk*, 1936, No. 2, 29—31).—A measured vol. of C_2H_2 in $(CH_2{:}CH)_2$ and N_2 is passed through ammoniacal Cu solution containing gelatin (three preps. described) (Ilosvay–Schultze reagent; cf. A., 1916, ii, 649) and the pink coloration due to Cu_2C_2 is matched against a titration in an exactly similar flask with standardised C_2H_2 solution (0·02—0·03 c.c. of C_2H_2 per c.c. of H_2O) (accuracy, 4%). Ch. Abs. (*c*)

(A) **Reduction of nitro-compounds with liquid zinc amalgam, for analytical purposes.** (B) **Liquid zinc amalgam method as applied to analysis of nitrobenzaldehydes.** M. M. Lobunetz (*Bull. Sci. Univ. Kiev*, 1939, No. 4, 23—36, 41—44).—(A) *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ and *m*- and *p*- but not *o*-nitrocinnamic acid may be determined (error ≯0·5%) by reduction to amines by means of liquid Zn–Hg in dil. H_2SO_4, followed by titration with $KBrO_3$–KBr.

(B) The method is applicable to *m*- but not to *o*- or *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$. R. T.

Iodometric determination of nitrosobenzene. M. M. Lobunetz and E. N. Gortinskaja (*Bull. Sci. Univ. Kiev*, 1939, No. 4, 37—39).—1 g. of PhNO is dissolved in 150 c.c. of EtOH, and H_2O is added to 250 c.c. 30 c.c. of 6N-HCl and 20 c.c. of 20% KI are added to 25 c.c. of solution, and I liberated by the reaction $PhNO + 2HI \rightarrow NHPh{\cdot}OH + 2I$ is titrated. R. T.

Simple method for determination of 2-methyl-1 : 4-naphthaquinol diacetate, a substance exhibiting vitamin-*K* activity. H. Berlin (*Svensk Kem. Tidskr.*, 1940, **52**, 233—238).—The diacetate (I), 15—35 mg., or an Et_2O extract of substances containing ~25 mg. of (I), is dissolved in 20 c.c. of NHAcMe, the temp. adjusted to 18°, 10 c.c. of 2N-NaOH are added, and the time, *t*, required for the development of a red colour is measured. The content of (I) is read from a curve ([A] is approx. $\propto 1/t$). F. J. G.

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