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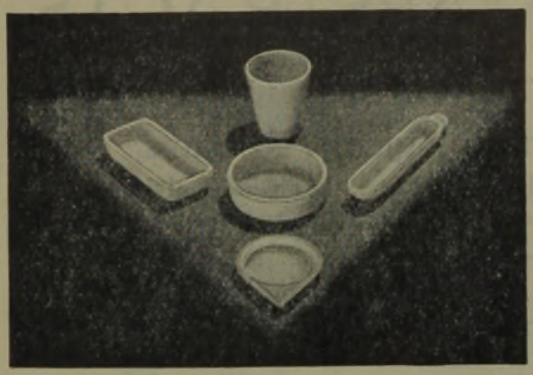

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BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1943.

I.—ALIPHATIC.

Products from the Wurtz reaction. Mechanism of their formation. A. Saffer and T. W. Davis (*J. Amer. Chem. Soc.*, 1942, **64**, 2039—2043).—At 320°/200 mm., MeI, EtI, or MeI–EtI with Na gives complex mixtures containing H_2, C, saturated and unsaturated hydrocarbons (much CH_4 from MeI or C_2H_6 from EtI). The results are explained as due to formation of alkyl radicals, which react mainly with excess of halide. Secondary radicals disappear by interaction with each other or Na. R. S. C.

Tracer studies with radioactive hydrogen. (A) Synthesis of labelled methyl iodide. (B) Menschutkin reaction.—See A., 1943, I, 39.

Photo-oxidation of methyl iodide.—See A., 1943, I, 40.

Common basis of intramolecular rearrangements. IX. Formation of *cyclo*propanes from monohalides. III. Action of sodium alkyls on aliphatic chlorides. Relation to the Wurtz reaction. F. C. Whitmore and H. D. Zook (*J. Amer. Chem. Soc.*, 1942, **64**, 1783—1785; cf. A., 1942, II, 83).—$HgEt_2$ (excess) and Na in *n*-C_5H_{12}–N_2 at 25° give NaEt (80%) and 5—8% Na–Hg. NaEt and *n*-$C_6H_{13}Cl$ at −10° to 0° give (*a*) by coupling *n*-C_8H_{18} (40%) and (*b*) $CH_2{:}CHBu^{\alpha}$ (46%) + C_2H_6 (52%). $NaPr^{\alpha}$ (prep. from $HgPr^{\alpha}{}_2$ in *n*-C_8H_{18}–N_2) and $CH_2Bu^{\gamma}Cl$ do not react at <50° but at 50—60° give 1 : 1-dimethyl*cyclo*propane (75%), C_3H_8 (70%), $Bu^{\alpha}Bu^{\gamma}$ (4%), and C_3H_6 (5%; probably formed by decomp. of $NaPr^{\alpha}$). $CH_2Bu^{\gamma}Cl$ does not react with 6% Na–Hg. NaAlk thus reacts partly as a base, removing HHal from the halide, and this is their effect when they are formed in the Wurtz reaction. The olefine is derived solely from the halide and the simple paraffin from the NaAlk. R. S. C.

Higher hydrocarbons. II. Five λ-substituted heneicosanes. F. C. Whitmore, J. N. Cosby, W. S. Sloatman, and D. G. Clarke (*J. Amer. Chem. Soc.*, 1942, **64**, 1801—1803; cf. A., 1942, II, 341).—*n*-$C_{12}H_{25}$·MgBr (**I**) and *n*-C_5H_{11}·CO_2Et (1·07 mols.) give *n*-C_5H_{11}·$C(C_{12}H_{25}$-*n*$)_2$·OH (**II**), b.p. 225—229°/1 mm., and some *n*-$C_{10}H_{22}$ and hexadecan-η-one. Dehydration of (**II**) by $CuSO_4$–N_2 at 160—180°, purification of the olefine by SiO_2 gel, and then hydrogenation over Ni at 120°/1100 lb. gives λ-n-*amyl*-n-*heneicosane*, m.p. −9·1°, b.p. 192°/1 mm. λ-*α-Ethyl*-n-*propyl*-, b.p. 187°/1 mm., and λ-cyclo*pentyl*-n-*heneicosane*, m.p. −12·7°, b.p. 186°/1 mm., are similarly prepared using ~2 mols. of the appropriate ester. MeOBz (3 mols.) and (**I**) in Et_2O give, after dehydration of the carbinol, λ-*phenyl*-Δ^{κ}-n-*heneicosene*, b.p. 203°/1 mm., hydrogenated in presence of very active Ni at room temp./1800 lb. to λ-*phenyl*-, m.p. 20·8°, b.p. 204°/1 mm., or in presence of Ni at 150°/1500—1800 lb. to λ-cyclo*hexyl*-n-*heneicosane*, m.p. −7·2°, b.p. 209°/1 mm. Et *cyclo*pentanecarboxylate, b.p. 171·9°/737 mm., is prepared (48·5%) from Mg *cyclo*pentyl bromide and Et_2CO_3 in Et_2O at 0°. *n*, *d*, and η are recorded for the hydrocarbons. Purities are >95%. R. S. C.

Allylic rearrangements. XIII. Kinetics and mechanisms of the conversion of crotyl and methylvinylcarbinyl chlorides into acetates and ethyl ethers. J. D. Roberts, W. G. Young, and S. Winstein (*J. Amer. Chem. Soc.*, 1942, **64**, 2157—2164; cf. A., 1942, II, 293).—Bimol. interaction of $CHMe{:}CH{\cdot}CH_2Cl$ (**I**) or $CH_2{:}CH{\cdot}CHMeCl$ (**II**) with OEt′ or OAc′ gives only the normal product and solvolytic (S_N1) reaction gives mixtures. The first type can be induced without the latter. Interaction of (**I**) with NaOEt in EtOH is of the second order, little changed by adding a little H_2O. Solvolysis of (**I**) with EtOH at 25° is of the first order, k_1 ($1{\cdot}84 \times 10^{-4}$) of which is much increased by H_2O ($12{\cdot}3 \times 10^{-4}$ in presence of 5·35 mols. of H_2O per l.). 99% pure Et ether is obtained from 0·7M-(**I**) and 0·9M-NaOEt, and >96%-pure Et ether from 1·3M-(**II**) and 1·8M-NaOEt. With KOAc or diphenylguanidinium acetate in AcOH, (**I**) or (**II**) gives mixed acetates, the kinetics being those of mixed-order reactions, but KOAc–Ac_2O at 100° reacts homogeneously with (**I**) and NEt_4·OAc–$COMe_2$ at 58° similarly with (**II**). R. S. C.

Dehydration $\Delta^{\alpha\epsilon}$-hexadien-γ-ol to $\Delta^{\alpha\gamma\epsilon}$-hexatriene and $\Delta^{1:3}$-*cyclo*hexadiene. L. W. Butz (*J. Amer. Chem. Soc.*, 1942, **64**, 1978—1979).—Dehydration (conditions: A., 1940, II, 182) of $CH_2{:}CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH{:}CH_2$ gives some $\Delta^{1:3}$-*cyclo*hexadiene (**I**), since with $(CH{\cdot}CO)_2O$ at 30° the product gives the *endo*ethylene-

tetrahydrophthalic anhydride, m.p. 147°, also obtained from pure (**I**). However, the amount of (**I**) formed varies uncontrollably. R. S. C.

Synthesis of higher alcohols from water-gas under pressure.—See B., 1942, II, 393.

Preparation and properties of polyethoxyethanes and their bromo-derivatives. S. M. McElvain and P. M. Walters (*J. Amer. Chem. Soc.*, 1942, **64**, 1963—1965).—$CMe(OEt)_3$ and Br (1 mol.) in C_5H_5N at ~30°, later 60—70°, give 53% of $CHBr_2{\cdot}C(OEt)_3$, b.p. 102—104°/8 mm., converted by boiling KOEt–EtOH into $CH_2Br{\cdot}C(OEt)_3$ and thence (excess of alkali or separate experiment) $CMe(OEt)_3$. $CHMe(OEt)_2$ and Br in C_5H_5N at 10—15° give $CH_2Br{\cdot}CH(OEt)_2$ (23%) and $CHBr_2{\cdot}CH(OEt)_2$ (29%). $OEt{\cdot}CH_2{\cdot}CH(OEt)_2$ with Br in C_5H_5N at 65° gives a mixture, including 15% of $(OEt)_2CH{\cdot}CHO$, b.p. 79°/12 mm., but in absence of a solvent suffers fission to EtBr (0·85), H_2O (0·97), EtOH (0·75), and $CHBr_2{\cdot}CH(OEt)_2$ (0·25 mol.). $(CH_2{\cdot}OEt)_2$ and Br at 80° or in C_5H_5N at 65° give mixtures. $CHBr_2{\cdot}CH(OEt)_2$ and boiling KOH–EtOH give $CHBr{:}C(OEt)_2$ (62·5%), b.p. 72—73°/11 mm.; $CHCl_2{\cdot}CH(OEt)_2$ gives $CHCl{:}C(OEt)_2$ (60%), b.p. 57—58°/10 mm. $OEt{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, m.p. 82—83°, b.p. 225—230°, and P_2O_5 at 150—180° give $OEt{\cdot}CH_2{\cdot}CN$ (60%), b.p. 133—134°. Et_3 *ethoxyorthoacetate* (prep. from $CH_2Cl{\cdot}CN$), b.p. 69—70°/10 mm., 180—181°/740 mm., is largely decomposed by Br in C_5H_5N at 80°. $OEt{\cdot}CHBr{\cdot}CH(OEt)_2$ and KOEt–EtOH give $CHBr{:}C(OEt)_2$ (cf. A., 1938, II, 4). R. S. C.

Tracer studies with radioactive carbon. Synthesis and oxidation of three-carbon acids.—See A., 1943, I, 39.

Fats from fatty acids having an odd number of carbon atoms. W. Keil (*Z. physiol. Chem.*, 1942, **274**, 175—185).—See A., 1943, III, 131. $CHEtBu^{\alpha}{\cdot}CH_2{\cdot}OH$ and HBr at 100—130° give the bromide, b.p. 72—75°/10 mm., converted by, successively, $CHNa(CO_2Et)_2$–EtOH, boiling KOH–EtOH, and heat at 180° into *γ-ethyl*-n-*octoic acid*, b.p. 142—143°/10 mm. The derived Et ester, b.p. 108—110°/10 mm., with H_2–Cu chromite at 270° gives $CHEtBu^{\alpha}{\cdot}[CH_2]_2{\cdot}OH$, b.p. 108—110°/10 mm., and thence, as above, the bromide (**I**), b.p. 104—106°/10 mm., and ε-*ethyl*-n-*decoic acid*, a liquid. With boiling KCN–KI–EtOH, (**I**) gives the nitrile, b.p. 126—128°/14 mm., which with HCl–EtOH and then NaOH gives δ-*ethyl*-n-*nonoic acid*, b.p. 163—166°/17 mm. (Et ester, b.p. 126—130°/17 mm.). *n*-Decaldehyde and MgMeBr–Et_2O give *n*-undecan-β-ol and thence the bromide, b.p. 128°/15 mm., *n*-$C_9H_{19}{\cdot}CHMe{\cdot}CH(CO_2Et)_2$, b.p. 150—152°/2 mm., and, by aq. NaOH at 130—150° and then decarboxylation at 180°, β-*methyl*-n-*dodecoic acid*, b.p. 125—130°/16 mm. *n*-Octaldehyde gives similarly *n*-nonan-β-ol, the *bromide*, b.p. 116—118°/38 mm., Me β-methyl-*n*-decoate, b.p. 110—113°/18 mm. (by H_2–Cu chromite at 280°/180 atm.; then HBr), γ-methyl-*n*-decyl bromide, b.p. 120—124°/20 mm., and δ-*methyl*-n-*dodecoic acid*, b.p. 132°/10·6 mm. R. S. C.

Action of fatty acids on copper.—See A., 1943, I, 40.

Preparation of orthoesters. S. M. McElvain and J. W. Nelson (*J. Amer. Chem. Soc.*, 1942, **64**, 1825—1827).—MgRX and $C(OEt)_4$ give $CR_2(OEt)_2$ and $CR_3{\cdot}OEt$ with very little $CR(OEt)_3$. Prep. of $CR(OEt)_3$ is best (59—78%) effected by treating $OEt{\cdot}CR{:}NH,HCl$ (*A*) with EtOH (15 mols.) in presence of Et_2O (1—3 vols.; optimum stated for Me—Bu) at the b.p. (39—46°). If R is branched, the yield is lower (Pr^{β} 27—30, Bu^{β} 21—23%). However, $CH_2Cl{\cdot}C(OEt)_3$ is best prepared by EtOH alone at ~40°. The decomp., $(A) \rightarrow RCO{\cdot}NH_2 + EtCl$, becomes appreciable only at higher temp. (60—80°). Prep. of (*A*) from RCN and HCl–EtOH is described. Et_3 ortho-acetate, b.p. 144—146°/740 mm., -propionate, b.p. 70—72°/32 mm., -n-, b.p. 58—59°/7 mm., and -iso-*butyrate*, b.p. 50—51°/7 mm., -n-, b.p. 49—50°/3 mm., and -iso-*valerate*, b.p. 57—59°/7 mm., and -chloroacetate, b.p. 68—70°/10 mm., are prepared. R. S. C.

Preparation of high-molecular derivatives of aliphatic hydroxy-monocarboxylic acids.—See B., 1942, II, 394.

Production of purified sodium lactate.—See B., 1942, II, 394.

Purification of ethyl lactate.—See B., 1942, II, 394.

Loco weeds. V. Constituents of *Astragalus earlei*. A. Stempel and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 432—443; cf. A., 1940, II, 185; III, 462).—The substances previously called "α-

and β-earleine" are identified as betaine and choline respectively. The reported pptn. of the active constituent of *A. earlei* by phosphotungstic acid is probably due to adsorption on the ppt. Reinecke salt ppts. a highly active fraction from which a cryst. substance has been isolated and also ppts. bases with a strong ninhydrin reaction. A *dihydroxyvalerolactone*, m.p. 52—53°, $[\alpha]_D^{25}$ −64·7° in H_2O (*di-acetate*, m.p. 86—87°, $[\alpha]_D^{25}$ −7·09° in $CHCl_3$; *phenylhydrazide* of the OH-acid corresponding to the lactone, m.p. 114—115°, $[\alpha]_D^{28}$ +42°±2° in MeOH, +45° in H_2O), has been isolated from extracts of the weed together with glycerol. Possible structures for the lactone are discussed. Enzymic action of yeast, takadiastrase, or emulsin affects the carbohydrate constituents of the weed without apparently affecting the activity. d-*Xylomethylonic acid phenylhydrazide*, m.p. 132—133°, $[\alpha]_D^{28}$ +33° in MeOH, +21° in H_2O, is incidentally described. M.p. are corr. H. W.

Preparation of lævulic acid.—See B., 1942, II, 394.

Formation of complex tungsto-tartrates.—See A., 1943, I, 40.

Long-chain acids. V. Aleuritic acid. P. C. Mitter and S. Mukherjee (*J. Indian Chem. Soc.*, 1942, **19**, 303—307).—*Et* ε-*bromo*-, b.p. 128—130°/16 mm. (from the OH-compound and PBr_3 in C_6H_6–C_5H_5N), with NaOMe yields *Et* ε-*methoxy-hexoate*, b.p. 94—95°/15 mm., reduced (Na + EtOH) to ε-*methoxyhexyl alcohol*, b.p. 112°/18 mm., the *bromide*, b.p. 98—99°/19 mm., from which with Mg followed by OMe·$[CHBr]_2$·$[CH_2]_7$·Cl (Noller *et al.*, A., 1934, 991) in Et_2O yields a product converted by Zn dust in BuOH into *o-methoxy*-Δ^9-*pentadecenyl chloride*, b.p. 198—204°/5 mm. This yields a nitrile, hydrolysed (EtOH–KOH) to *o-methoxy*-Δ^9-*hexadecenoic acid*, b.p. 194°/2 mm. Et aleuritate is reduced (Na + BuOH) to *aleurityl alcohol*, m.p. 56°, oxidised [$Pb(OAc)_4$ in AcOH] to OH·$[CH_2]_8$·CHO (small yield). A. Li.

Production of per-acids.—See B., 1942, II, 394.

***O*-Penta-acetyl-*d*-gluconates of polyhydric alcohols and cellulose.** M. L. Wolfrom and P. W. Morgan (*J. Amer. Chem. Soc.*, 1942, **64**, 2026—2028).—The appropriate alcohol with gluconyl chloride penta-acetate in C_5H_5N gives *ethylene glycol di-*, m.p. 94—95°, $[\alpha]$ +15°, *propane-αγ-diol di-*, m.p. 88—89°, $[\alpha]$ +18·5°, *di-β-hydroxyethyl ether di-*, m.p. 111—112°, $[\alpha]$ +12°, *glyceryl tri-*, amorphous, softens at 58—65°, $[\alpha]$ +20°, d-*sorbitol hexa-*, amorphous, softens at 65—78°, $[\alpha]$ +30°, *d-mannitol hexa-*, amorphous, softens at 65—78°, $[\alpha]$ +37°, and α-*methyl*-d-*glucopyranoside tetra-*, amorphous, softens at 68—72°, $[\alpha]$ +57°, -O-*penta-acetyl*-d-*gluconate*. In C_5H_5N, mercerised cotton linters gives a coloured, but in NEt_3–$PhNO_2$ at 80° gives a cream-coloured, *product*, containing 0·45 penta-acetyl-*d*-gluconyl (*A*) unit per anhydroglucose (*B*) unit. Modified cellulose acetate [1·72 Ac^{21} per (*B*) unit], $[\alpha]_D^{24}$ −13° in C_5H_5N, in C_5H_5N gives a *product*, $[\alpha]_D^{21}$ −10° in C_5H_5N, $[\alpha]_D^{24}$ +2·5° in $CHCl_3$ (gives dark, brittle films), containing 0·75 (*A*) per (*B*) unit, but in NEt_3–$CHCl_3$ at 60° gives a *product*, $[\alpha]_D^{23}$ −9° in C_5H_5N, $[\alpha]_D^{24}$ +1° in $CHCl_3$ (gives colourless, flexible films), containing 0·37 (*A*) per (*B*) unit. Unless otherwise stated, $[\alpha]$ are $[\alpha]_D^{25}$ in $CHCl_3$. R. S. C.

Production of isomeric trioxymethylene.—See B., 1942, II, 394.

Keten acetals. X. Elimination of hydrogen bromide from acetals of α-bromo-aldehydes. *iso*Propyl- and *n*-propyl-keten diethyl acetal. S. M. McElvain, R. L. Clarke, and G. D. Jones (*J. Amer. Chem. Soc.*, 1942, **64**, 1966—1969; cf. A., 1942, II, 296).—$CHR(OEt)_2$ (R = Pr^β, b.p. 133—136°, Pr^α, b.p. 143—144°, or Bu^β, b.p. 156—158°) [modified prep. from $CH(OEt)_3$ and MgRX] with Br give $CMe_2Br{\cdot}CH(OEt)_2$, b.p. 63—64°/7 mm., $CHEtBr{\cdot}CH(OEt)_2$, b.p. 82—84°/12 mm., and $CHPr^\beta Br{\cdot}CH(OEt)_2$ (**I**), b.p. 55—56°/3 mm. (20—40%), which with 1·4N-$KOBu^\gamma$–$Bu^\gamma OH$ give $CH_2{:}CMe{\cdot}CH(OEt)_2$ (64%), b.p. 136—137°, $CHMe{:}CH{\cdot}CH(OEt)_2$ (41%), b.p. 48—49°/21 mm., and $CMe_2{:}CH{\cdot}CH(OEt)_2$ (62%), b.p. 59—60°/16 mm., respectively. Interaction of (**I**) with 0·75N- or 2N-NaOEt–EtOH or 0·75N-$KOBu^\gamma$–$Bu^\gamma OH$ at 80° is of the second order, faster with $KOBu^\gamma$. $Bu^\beta CN$ (prep. from $Bu^\beta CO{\cdot}NH_2$ by P_2O_5 at 90°, later 130°), b.p. 127—129°, gives $CBu^\beta(OEt)_3$ and thence (Br–C_5H_5N) *Et*$_3$ *α-bromo-ortho*isovalerate (67%), b.p. 63—64°/1·3 mm., which with Na gives iso*propylketen Et*$_2$ *acetal* [*αα-diethoxy-γ-methyl*-Δ^α-*butene*] (80%), b.p. 96—97°/100 m., 156—157°/745 mm. (structure proved by exothermic hydrolysis by very dil. HCl to $Bu^\beta CO_2Et$). *Et*$_3$ *α-bromo-ortho*-n-*valerate*, b.p. 69—70°/2 mm., and n-*propylketen Et*$_2$ *acetal* [*αα-diethoxy*-Δ^α-n-*pentene*], b.p. 107—108°/100 mm., 167—168°/737 mm. (hydrolysed to $Bu^\alpha CO_2Et$), are similarly prepared. $CHR_2{\cdot}CH{:}C(OEt)_2$ are not rearranged to $CR_2{:}CH{\cdot}CH(OEt)_2$ by boiling $KOBu^\gamma$–$Bu^\gamma OH$. The mode of elimination of HBr from (**I**) is inconclusively discussed. R. S. C.

Manufacture of ketens and olefines.—See B., 1942, II, 395.

Condensation products of keten with ketones. B. H. Gwynn with E. F. Degering (*J. Amer. Chem. Soc.*, 1942, **64**, 2216—2218).—Keten reacts with ketones having ≮3 α-H in presence of a little H_2SO_4 (not H_3PO_4 or *p*-$C_6H_4Me{\cdot}SO_3H$), giving enol acetates (properties described). $COMe_2$, COMeEt, mesityl oxide, etc. react rapidly; COPhMe, $COMeBu^\gamma$, and $CMe_2{:}CH{\cdot}COMe$ react slowly, and $COPr^\beta_2$ not at all. R. S. C.

Photo-enolisation of ketones.—See A., 1943, I, 40.

Manufacture of (A) quaternary ammonium compounds, (B) carboxyl chlorides, and (C) carboxyl esters, of quaternary ammonium compounds.—See B., 1942, II, 395.

Nature and constitution of shellac. XVI. Preparation of *θιο*-trihydroxypentadecylamine from aleuritic acid by the Naegeli–Curtius series of reactions. A. L. Davis and W. H. Gardner (*J. Amer. Chem. Soc.*, 1942, **64**, 1902—1905; cf. A., 1941, II, 265).—Aleuritic [*θιο*-trihydroxypalmitic] acid, m.p. 101—101·5°, and 5% HCl–MeOH give the *Me* ester, m.p. 73°, and thence the *hydrazide*, m.p. 139—139·5°, which with aq. $NaNO_2$ and then 25% AcOH at 0° gives the azide (**I**), decomp. 52°. In boiling C_6H_6, (**I**) gives *θιο-trihydroxypentadecylcarbimide*, m.p. 103·5—104·5°, hydrolysed by boiling 50% aq. NaOH to the *-amine*, m.p. 146—147° [*picrate*, m.p. 118—119° (decomp.)]. In boiling H_2O, (**I**) gives *NN'*-di-*θιο*-trihydroxypentadecylcarbamide, m.p. 122·5—123°, and in boiling EtOH *θιο*-trihydroxypentadecylurethane, m.p. 78—79° (cf. Nagel, A., 1927, 447; 1931, 960), neither of which products could be hydrolysed. R. S. C.

***NN*-Dimethylethylenediamine and [its] derivatives.** R. Baltzly, J. S. Buck, and W. S. Ide (*J. Amer. Chem. Soc.*, 1942, **64**, 2232—2233).—$NMe_2{\cdot}[CH_2]_2{\cdot}NH_2$, b.p. 107° (hygroscopic dihydrochloride, m.p. ~160°), gives the p-*nitrobenzoate hydrochloride* (**I**), m.p. 182·5—183·5°, hydrogenated (PtO_2–EtOH–HCl here and below) to the p-*aminobenzoate dihydrochloride*, m.p. 190—191° [the derived *methochloride hydrochloride*, decomp. >230°, is obtained from the methochloride derived from (**I**)]. The *p*-nitrobenzoate hydrochloride, m.p. 247—248·5°, gives *β-p*-aminophenylureidoethyldimethylamine [*dihydrochloride*, m.p. 182—184° (decomp.); *methochloride hydrochloride*, m.p. 186°]. *β-p*-Aminophenylacetamido- [*dihydrochloride*, m.p. 209·5—210·5°; *methochloride hydrochloride*, m.p. 155—156° (decomp.)], *β-phenylthioureido-*, m.p. 83—83·5°, and β-sulphanilamido-ethyldimethylamine [*dihydrochloride*, m.p. 211·5—213·5° (decomp.)] are also described. R. S. C.

Optical configuration of glutamic acid isolated from casein hydrolysates by six procedures. (Miss) J. C. Opsahl and L. E. Arnow (*J. Amer. Chem. Soc.*, 1942, **64**, 2035—2039).—After hydrolysis of casein by boiling 20% HCl the glutamic acid (**I**) isolated by six different methods contains 2·5—6·2% of the *d*-form. Recoveries are recorded for hydrolysates containing added *dl*-(**I**); for the two best methods these are 76—89 and 82—96%. The methods used are detailed. R. S. C.

***r*-β-Hydroxyglutamic acid.** E. Abderhalden and G. Pitschak (*Z. physiol. Chem.*, 1940, **265**, 31—38).—An improved method is given for the prep. of *r*-β-hydroxyglutamic acid (**I**) from casein. Acetyl-*l*-glutamic acid, m.p. 186—187°, is converted by CH_2N_2 and subsequent distillation into the corresponding optically inactive Me_2 ester, b.p. 158—162°/0·1 mm., m.p. 80° (also obtained from the *dl*-acid, m.p. 176—180°), and Me_2 glutamate. *r*-β-Hydroxyglutamic acid hydrochloride, NaOAc, AcOH, and Ac_2O yield a product which when treated with CH_2N_2 and then distilled affords the compound $\begin{matrix}CH_2{\cdot}CH\\ \\ CO{-}NH\end{matrix}\!\!>\!C{\cdot}CO_2Me$. Methylation of (**I**) with CH_2N_2 or MeOH–HCl is accompanied by ring-closure. *Me*$_2$ *carbobenzyloxyglutamate*, b.p. 211—214°/0·6—0·8 mm., and *β-hydroxyglutamate*, b.p. 208—210°/0·5 mm., *carbobenzyloxy*-l-*aspartic acid*, m.p. 112—115°, $[\alpha]_D^{10}$ +13·85° in aq. NaOH (*Me*$_2$ ester, b.p. 204°/0·25 mm.), and *Me*$_2$ 2 : 5-*diketopiperazine*-3 : 6-*diacetate* are incidentally described. H. W.

Manufacture of organic amides.—See B., 1942, II, 395.

Preparation of [linear] polyamides.—See B., 1942, II, 395.

Mono- and di-substituted guanidines. J. S. Buck, R. Baltzly, and C. W. Ferry (*J. Amer. Chem. Soc.*, 1942, **64**, 2231—2232).—$NH{:}C(SMe){\cdot}NH_2,H_2SO_4$ and the appropriate amine give *β-morpholinoethyl-*, m.p. 197°, *ββ-diethoxyethyl-*, m.p. 154°, NN-*dicyclohexyl-*, m.p. 195°, N-*benzyl*-N-*methyl-*, m.p. 252° (decomp.), and *δ-phenoxybutyl-*, m.p. 199—199·5°, *-guanidine sulphate*, $2B,H_2SO_4$. α-$C_{10}H_7{\cdot}NH{\cdot}CH_2Ph$, $CN{\cdot}NH_2$, and HCl in $C_5H_{11}{\cdot}OH$ give N-*α-naphthyl*-N-*benzylguanidine hydrochloride*, m.p. 223—224°. *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2$ (2 mols.) and CNBr (1 mol.) at 150° give *NN'-di*-p-*methoxybenzylguanidine hydrochloride*, m.p. 125·5—126·5°. α-$C_{10}H_7{\cdot}NH{\cdot}CS{\cdot}NHMe$ (from α-$C_{10}H_7{\cdot}NCS$ and NH_2Me) with Me_2SO_4 and then PbO–NH_3 gives N-*α-naphthyl*-N'-*methylguanidine hydrochloride*, m.p. 220—220·5° (decomp.). R. S. C.

II.—SUGARS AND GLUCOSIDES.

Synthesis of *epi*lactose and lactose. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1852—1856).—Total synthesis of *epi*lactose and lactose is detailed (cf. A., 1942, II, 351). Condensation of acetobromo-*d*-galactose (prep. from β-*D*-galactopyranose penta-acetate by HBr–AcOH at 0° and later 5°), m.p. 84—85° (lit. 82—83°, 85°), $[\alpha]$ +242° in C_6H_6 (cf. A., 1924, i, 371), and 2 : 3-*iso*propylidene-*D*-mannosan <1,5>β<1,6> by

Ag_2O–$CaSO_4$–I in $CHCl_3$ at 24° 7 days), hydrolysis of the product by 80% AcOH at 100°, and heating with NaOAc–Ac_2O at 100° gives 4-β-D-*galactopyranosido*-D-*mannosan*<1,5>β<1,6> 2 : 3 : 2′ : 3′ : 4′ : 6′-*hexa-acetate* (30%), m.p. 193—194°, $[\alpha]_D^{20}$ −62·7° in $CHCl_3$. With H_2SO_4–Ac_2O–AcOH at 0° this gives α-epi*lactose octa-acetate* (**I**) (99%), m.p. 96—97°, $[\alpha]_D^{20}$ +41·2° in $CHCl_3$, hydrolysed by $Ba(OMe)_2$–MeOH at 5° to β-*epi*lactose, m.p. 195—196°, $[\alpha]_D^{20}$ +~17° → +27·2° in H_2O (*k* 0·0151). HBr–AcOH–Ac_2O at 5° and then Zn dust–H_2PtCl_6 in 50% AcOH at 0° converts (**I**) into lactal hexa-acetate, m.p. 114°, $[\alpha]_D^{20}$ −18·0° in $CHCl_3$, which with BzO_2H in Et_2O–EtOAc–H_2O at 25° gives β-lactose hexa-acetate, m.p. 89—90°, $[\alpha]_D^{20}$ −4·5° in $CHCl_3$, and thence $[Ba(OMe)_2]$ α-lactose, $+H_2O$, m.p. 202° (decomp.), $[\alpha]$ +81° → +52·7° in H_2O (*k* 0·0042). M.p. are corr. R. S. C.

Reactions relating to carbohydrates and polysaccharides. LXV. Improved technique for fractionation of partly methylated glucosides. I. Levi, W. L. Hawkins, and H. Hibbert (*J. Amer. Chem. Soc.*, 1942, **64**, 1957—1959).—Small quantities of glucosides are fractionated (Podbielniak; apparatus described) with 95—97% recovery and formation of <1% of non-volatile residue. In an example, 2·957 g. of 2 : 3-di-, 2 : 3 : 4-tri-, and 2 : 3 : 4 : 6-tetra-methylmethylglucosides are thus separated. R. S. C.

Reactions relating to carbohydrates and polysaccharides. LXVI. Structure of the dextran synthesised by the action of *Leuconostoc mesenteroides* on sucrose. I. Levi, W. L. Hawkins, and H. Hibbert (*J. Amer. Chem. Soc.*, 1942, **64**, 1959—1962).—The semi-micro-distillation technique (see above) is used to confirm the finding (A., 1938, II, 44; cf. Brauns, A., 1938, II, 220) that the dextran named yields, by complete methylation and hydrolysis, a 1 : 3 : 1 mixture of 2 : 3-di- (**I**), 2 : 3 : 4-tri-, and 2 : 3 : 4 : 6-tetra-methylmethylglucoside. (**I**) is identified as 2 : 3-dimethylglucophenylhydrazide. Possible structures for the dextran are indicated. R. S. C.

Lichenin. E. G. V. Percival and H. Granichstädten (*Nature*, 1942, **150**, 549).—Lichenin (**I**) with 1 mol. of KOH for each anhydroglucose unit forms an unstable additive compound, but both 2- and 6-methylglucose are present in the products of hydrolysis after methylation under anhyd. conditions. This indicates that the primary alcohol groups in (**I**) are not shielded as in cellulose. A. A. E.

Molecular constitution of enzymically synthesised starch. W. Z. Hassid and R. M. McCready (*J. Amer. Chem. Soc.*, 1941, **63**, 2171—2173).—Starch (**I**), $[\alpha]_D$ +170° in N-NaOH, synthesised from the Cori ester by potato phosphorylase, with Ac_2O–C_5H_5N at 60° gives a "triacetate," $[\alpha]_D$ +170° in $CHCl_3$, mol. wt. (η) 84,000, hydrolysed by 0·5N-KOH at room temp. to (**I**), $[\alpha]_D$ +168°, and converted by Me_4SO_4–30% NaOH at 55° into a "Me_3" ether, $[\alpha]_D$ +216° in $CHCl_3$, mol. wt. (η) 54,000. This, by hydrolysis, gives 2 : 3 : 6-tri- but no tetra- or di-methylglucose, showing that the glucose units form long chains or loops and that natural synthesis of starch involves enzymes more complicated than phosphorylase. R. S. C.

Estimation of the dialdehyde type of oxidation in hydroxystarches and hydroxycelluloses. D. H. Grangaard, E. K. Gladding, and C. B. Purves (*Paper Trade J.*, 1942, **115**, *TAPPI Sect.*, 75—80).—Oxidation of starch and cellulose by HIO_4 changes the glucose residues of which they consist into chains of semi-acetals of $(CHO)_2$ with 2 erythrose units. Boiling 10% HCl–MeOH converts periodate-hydroxystarch (**I**) into ~50% of the expected amount of $[CH(OMe)_2]_2$, isolated by means of its volatility with steam and determined as $(CHO)_2$ either colorimetrically or by pptn. with 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH·NH_2. The other half of the $(CHO)_2$ residues in (**I**) condenses with the erythrose residues present during methanolysis to a cyclic acetal which probably contains a 1 : 4-dioxan ring. Control experiments show that this substance is only slightly volatile with steam and interferes in a reproducible way with the determination of $[CH(OMe)_2]_2$. When the analytical method is extended to include both acetals it recovers ≮90% of the $(CHO)_2$ units present in (**I**) or periodate-hydroxycellulose (**II**). Oxidation of starch by aq. IO_4' is selective only below 20° and within the limits pH 2—5 and in these conditions is 90—95% efficient. Properly prepared (**II**) gives analyses corresponding to ~90% of dialdehydic oxidation and possibly a trace of the same type of oxidation is present in a MnO_4'-hydroxycellulose. Entirely negative results are obtained with products formed by means of S_2O_8'', OBr', OCl', Cr_2O_7'', and HNO_3. It is probable that the no. of different Cu-reducing structures initially produced from cellulose by any oxidising agent is ≯4. H. W.

Determination of the mol. wt. of cellulose by an end-group method. —See A., 1943, I, 8.

***O*-Penta-acetyl-*d*-gluconates of cellulose.**—See A., 1943, II, 23.

III.—HOMOCYCLIC.

Formation of *cyclo*propanes.—See A., 1943, II, 21.

Isomerisation of β-carotene. Isolation of a stereoisomeride having increased adsorption affinity. A. Polgár and L. Zechmeister (*J. Amer. Chem. Soc.*, 1942, **64**, 1856—1861).—β-Carotene (**I**) is converted by heat (boiling light petroleum, b.p. 60—70°; 190°) (CO_2) or catalysts (I– or conc. HCl–light petroleum) into a mixture of pigments, of which 9—10 are stereoisomerides of (**I**). The products are separated by chromatography [$Ca(OH)_2$]. The isolated products are isomerised by I to similar mixtures containing much (**I**). Some of the products are adsorbed more strongly than is (**I**). Of these, *neo-β-carotene* U (**II**) (17%) is obtained having m.p. 122—123° (corr.; block; CO_2), α 0 in C_6H_6, absorption max. 4—8 mμ. < those of (**I**). The stereochemistry is discussed. (**I**) probably has 1, Gillam's ψ-α-carotene 2, and a labile isomeride (shift of absorption max. 20 mμ.) 4—5 *cis*-linkings. R. S. C.

Methylation of aromatic nitro-compounds with lead tetra-acetate. L. F. Fieser, R. C. Clapp, and W. H. Daudt (*J. Amer. Chem. Soc.*, 1942, **64**, 2052—2060).—1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ (**I**) is methylated by $Pb(OAc)_4$ in AcOH to 1 : 3 : 2 : 4 : 6-$C_6HMe_2(NO_2)_3$ (**II**), interaction being induced by long heating at 100°, boiling for a short time, local superheating, or adding $CH_2(CO_2H)_2$. Yields are the same by all methods, but optimum (28—32%) if 2·5—3 equivs. of $Pb(OAc)_4$ are used. Methylation is also effected by warm Pb_2O_3–AcOH or by prolonged boiling with PbO_2–AcOH. *s*-$C_6H_3(NO_2)_3$ gives similarly (**I**) + some (**II**), but (**II**) is unaffected by further treatment. *m*-$C_6H_4(NO_2)_2$ gives ~30% of 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ + 1 : 3 : 4 : 6- or 1 : 3 : 2 : 4-$C_6H_2Me_2(NO_2)_2$; for identification the products are nitrated, the (**II**) formed is separated, and (**I**) then isolated as complex with β-$C_{10}H_7$·NH_2. $PhNO_2$ with $Pb(OAc)_4$ (3 mols.) gives 4·9% of *o*- + some *p*-C_6H_4Me·NO_2, isolated by nitration etc. as above and converted by fractionation and subsequent oxidation into *o*- + *p*-NO_2·C_6H_4·CO_2H. After a long induction period, 2·4 equivs. of $Pb(OAc)_4$ are consumed by boiling C_6H_6–AcOH, but the product (18%) is CH_2Ph·OAc; methylation is the first reaction, since PhMe and $Pb(OAc)_4$ give CH_2Ph·OAc (11%). PhCl similarly gives (? mixed) C_6H_4Cl·CH_2·OAc, whence alkali yields *p*-C_6H_4Cl·CH_2·OH. $C_{10}H_8$ is oxidised, yielding α-$C_{10}H_7$·OAc (26%). Trials with α-$C_{10}H_7$·NO_2, 1 : 5- and 1 : 8-$C_{10}H_6(NO_2)_2$, 1 : 3 : 8- and 1 : 4 : 5-$C_{10}H_5(NO_2)_3$, and 1 : 3 : 6 : 8-$C_{10}H_4(NO_2)_4$ are unpromising, but a trace of 2 : 1 : 8-$C_{10}H_5Me(NO_2)_2$ is obtained. (**II**) is obtained from (**I**) by Ac_2O_2 in boiling C_6H_6 (10·6%) or by anodic oxidation in NaOAc–AcOH (9% yield), which reactions suggest possible mechanisms. R. S. C.

Kinetics of the oxidation by permanganate of side-chains to the benzene nucleus. I. Oxidation of monochlorotoluenes.—See A., 1943, I, 38.

Preparation of benzene derivatives [diphenyls].—See B., 1942, II, 395.

Further nitration of dinitrodiphenyls. F. H. Case (*J. Amer. Chem. Soc.*, 1942, **64**, 2225).—Hot HNO_3 (*d* 1·5) converts 2 : 3′-dinto 2 : 4 : 3′-*tri-nitrodiphenyl*, m.p. 137—138° (cf. Blakey *et al.*, A., 1928, 165), also obtained similarly with the 3 : 4 : 4′-$(NO_2)_3$-derivative, m.p. 205—206°, from the 3 : 4′-$(NO_2)_2$-compound (proof of structure). (*m*-NO_2·$C_6H_4)_2$ gives 3 : 4 : 3′-*trinitrodiphenyl*, m.p. 179—180°, which yields the known 3 : 3 : 3′ : 4′-$(NO_2)_4$-derivative, m.p. 203—204° (lit. 186°). R. S. C.

Nitration of halogenodiphenyls. I. Nitro-derivatives of 4-bromodiphenyl. F. H. Case (*J. Amer. Chem. Soc.*, 1942, **64**, 1848—1852).—Nitration of *p*-C_6H_4PhBr gives 4-bromo-3 : 4′- (**I**), m.p. 210—211° (lit. 205—206°), and -3 : 2′-dinitrodiphenyl (**II**), m.p. 154—155° (lit. 147—148°) (cf. A., 1927, 1062; 1934, 62; 1938, II, 225), structures being proved thus. (**I**) is obtained from 3 : 4-NO_2·$C_6H_3(NH_2)$·C_6H_4·NO_2-4′ by, successively, $NaNO_2$–conc. H_2SO_4 at 0°, H_3PO_4, Br–NaBr–H_2O at 0°, and Cu, and by nitration of 4-NO_2·C_6H_4·C_6H_4Br-4′ (**III**). (**II**) is obtained from 2-NO_2·C_6H_4·C_6H_4Br-4′ (**IV**) by conc. HNO_3–H_2SO_4 at <30° and with CrO_3 gives 3 : 4 : 1-NO_2·C_6H_3Br·CO_2H (**V**). 4-Bromo-3 : 2′ : 4′-trinitrodiphenyl, m.p. 180—181°, is obtained from (**I**), (**II**), (**III**), or (**IV**) by HNO_3 (*d* 1·59) at 100° (cf. Le Fèvre *et al.*, A., 1926, 1027). Nitration of 3-NO_2·C_6H_4·C_6H_4Br-4′ gives, according to the conditions, (*a*) a mixture (**VI**), $C_{12}H_6O_6N_3Br$, m.p. 181—182° [oxidised to (**V**)], and a little 4-*bromo*-2 : 3′-*dinitrodiphenyl* (**VII**), m.p. 143—144°, (*b*) (**VII**) and 4-*bromo*-3 : 3′-*dinitrodiphenyl* (**VIII**), m.p. 189—190° [oxidised to (**V**)], or (*c*), by HNO_3 (*d* 1·59) at 100°, 4-*bromo*-2 : 3′ : 4′- (**IX**), m.p. 170—171°, and a little 4-*bromo*-3 : 3′ : 4′-*trinitrodiphenyl*, m.p. 192—193° [obtained similarly from (**VI**)]. 3-NO_2·C_6H_4·C_6H_4·NH_2-4′ and KNO_3–oleum at <6° give 2 : 3′-*dinitro*-4-*aminodiphenyl*, m.p. 157—158° (*Ac* derivatives, m.p. 215—216°), and thence 2-NO_2·C_6H_4·C_6H_4·NO_2-3′ and (**VII**). 3-NO_2·C_6H_4·C_6H_4·NHAc-4′ and HNO_3 (*d* 1·5) in Ac_2O–AcOH give 3 : 3′-*dinitro*-4-*aminodiphenyl*, m.p. 206—207°, by way of the *Ac* derivative (**X**), m.p. 241—242°, and thence (3-NO_2·$C_6H_4)_2$ and (**VIII**). With NH_3–EtOH at 150° (**IX**) gives 4-*bromo*-2 : 3′-*dinitro*-4′-*aminodiphenyl*, m.p. 223—224°, and thence (**VII**) and 2 : 4-NO_2·C_6H_3Br·C_6H_3Br·NO_2-4′ : 3′. 3 : 4-*Dinitrodiphenyl* [prep. from 1 : 3 : 4-$C_6H_3I(NO_2)_2$, PhI, and Cu powder at 280°], m.p. 87—88°, with NH_3–EtOH at 150° gives 3 : 1 : 4-NO_2·C_6H_3Ph·NH_2 and with Br–AcOH–$FeCl_3$ (trace) at 90° gives 4-*bromo*-3′ : 4′-*dinitrodiphenyl* (**XI**), m.p. 167—168°, converted by HNO_3 (*d* 1·59) into 4-*bromo*-

3 : 3′ : 4′-*trinitrodiphenyl*, m.p. 192—193°, which is also obtained from (**VI**) or (**XI**). HNO_3 (*d* 1·5) at <8° converts 3 : 4 : 1-NO_2·C_6H_3(NHAc)·C_6H_4·NO_2-3′ into 3 : 5 : 3′-*trinitro*-4-*acetamido*-, m.p. 242—243° (also obtained from 3-NO_2·C_6H_4·C_6H_4·NHAc-4′), and thence -4-*amino-diphenyl*, m.p. 233°. With, successively, $NaNO_2$–H_2SO_4 at 0°, H_3PO_4 at 2°, oleum at 15—20°, and boiling EtOH, (**X**) gives 3 : 5 : 3′-*trinitrodiphenyl*, m.p. 177—178° [also obtained from *m*-C_6H_4I·NO_2, 1 : 3 : 5-$C_6H_3I(NO_2)_2$ (**XII**), and Cu powder at 270°], and by Schoutissen's method 4-*bromo*-3 : 5 : 3′-*trinitrodiphenyl*, m.p. 222—223°. 3 : 5 : 3′ : 5′-*Tetranitrodiphenyl*, m.p. 228—229°, is obtained from (**XII**) by Cu powder at 270°.

R. S. C.

Preparation of poly*cyclo*hexyldiphenyls.—See B., 1942, II, 396.

Separation of *cis*- and *trans*-stilbenes by application of the chromatographic brush method. L. Zechmeister and W. H. McNeely (*J. Amer. Chem. Soc.*, 1942, **64**, 1919—1921).—*cis*- and *trans*-(CHPh·)$_2$, -*p*-OMe·C_6H_4·CH:CHPh, and -*p*-C_6H_4Me·CH:CHPh are separated by adsorption on Al_2O_3, extruding the column, and painting a streak with 1% $KMnO_4$ down the column; the two zones are indicated by brown stains. 1—2% of one form can be detected in the other.

R. S. C.

" Tervalent " carbon. XXI. Tetra*cyclo*hexyldiphenylethane. K. Ziegler and P. Herte (*Annalen*, 1942, **551**, 222—234; cf. Marvel *et al.*, A., 1930, 1279; Neunhoeffer, A., 1937, II, 16).—Di*cyclo*hexylphenylcarbinol is converted by AcOH saturated with HBr in Et_2O into the bromide, m.p. 126—127°, which with dry Ag_2O and powdered $AgNO_3$ in MeOH affords di*cyclo*hexylphenylmethyl Me ether, m.p. 75—76°. This is transformed by K–Na into the corresponding K compound (**I**), converted by EtOH into di*cyclo*hexylphenylmethane, b.p. 201—202°/12 mm. (*p*-NO_2-derivative, m.p. 112—113°), also obtained by hydrogenation of *cyclo*hexyl*cyclo*hexylidenephenylmethane, and by CO_2 into di*cyclo*hexylphenylacetic acid (**II**), m.p. 250—252° (lit. 242—244°) (*Ag* salt). (**I**) and $(CMe_2Br)_2$ in Et_2O at −15° to −20° afford *tetra*cyclo*hexyldiphenylethane*, m.p. 157—158° (under N_2), transformed by K–Na followed by CO_2 into (**II**). The mol. wt. in freezing C_6H_6 is 470. It is autoxidised in boiling Et_2O to di*cyclo*hexylphenylmethyl peroxide, m.p. 182—184°; in presence of pyrogallol (**III**) it appears to yield the H peroxide which has not been definitely characterised. Its rate of autoxidation resembles that of any other labile ethane and in particular the rate of absorption of O_2 is independent of the O_2 pressure if (**III**) is present. In C_6H_6 it decolorises I but the reaction cannot be regarded as an identification of radicals since the rate of decomp. at room temp. is too small to permit a sufficiently rapid addition of I, which obviously attacks directly the very weak, central C–C linking. It greatly accelerates the autoxidation of $\Delta^{1:3}$-*cyclo*hexadiene and styrene. Solutions of the substance in C_6H_6, prepared with exclusion of air, lose their ability as O_2-carriers after prolonged heating, the ethane being irreversibly decomposed after primary dissociation followed by disproportionation.

H. W.

Dissociation of hexa-arylethanes. XIV. Ethanes derived from mixtures of triaryl halides. C. S. Marvel and C. M. Himel (*J. Amer. Chem. Soc.*, 1942, **64**, 2227).—Treating mixed triarylmethyl halides (6 pairs) with Ag gives products, the degree of dissociation of which (determined by magnetic susceptibility) is ≪ the mean of the dissociation of the pairs of radicals.

R. S. C.

Dissociation of hexa-arylethanes. XII. Effect of naphthyl and diphenyl groups. C. S. Marvel, J. W. Shackleton, C. M. Himel, and J. Whitson (*J. Amer. Chem. Soc.*, 1942, **64**, 1824—1825; cf. A., 1941, II, 284).—The following % dissociation in 0·1M. solution in C_6H_6 are determined by means of magnetic susceptibilities: $[(p\text{-}C_6H_4Ph)_2CPh]_2$ 18±2; $(p\text{-}C_6H_4Ph)_6C_2$ 26±5, $(\beta\text{-}C_{10}H_7\text{·}CPh_2)_2$ 6±2, $[(\beta\text{-}C_{10}H_7)_2CPh]_2$ 13±2, $(\beta\text{-}C_{10}H_7)_6C_2$ 21±10, 24±5, $(\alpha\text{-}C_{10}H_7\text{·}CPh\text{·}C_6H_4Ph\text{-}p)_2$ 54±2. The relatively low results of Bachmann *et al.* (A., 1937, II, 90) are thus confirmed. Calculation for 0·1M. solution by the law of mass action from measurements at other concns. is proved permissible (26±2 to 29±5) for 0·839—7·0% solutions of $(\alpha\text{-}C_{10}H_7\text{·}CPh_2)_2$ in C_6H_6 at 25°. β-$C_{10}H_7$ are much less dissociated than are α-$C_{10}H_7$ derivatives. *Phenyldi-β-naphthyl-*, m.p. 168—169°, and -p-*diphenylyl-methyl peroxide*, m.p. 151—152°, and *phenyldi-β-naphthylmethyl chloride*, m.p. 159—160°, are described.

R. S. C.

Quaternary salts. R. Baltzly, C. W. Ferry, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2231).—*n*-$C_{18}H_{37}$·NPhMe, b.p. 234°/3 mm. (*methiodide*, m.p. 93—94°), β-cyclo*hexylethylbenzyldimethylammonium chloride*, m.p. 206° (decomp.), *benzyldimethyl-β-bromoethylammonium bromide*, m.p. 174°, and *α-naphthylmethyltriethylammonium chloride*, m.p. 197° (decomp.), are prepared.

R. S. C.

Acylacetarylamides.—See B., 1943, II, 5.

Influence of the 5-nitro-group on halogenation and nitration of 5-nitro-1-naphthylamine and related naphthalides. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1942, 723—725).—5 : 1-NO_2·$C_{10}H_6$·NH_2 (**I**) yields with Br in $CHCl_3$ at 50° 2-*bromo*-, m.p. 121·5° (*Ac* derivative, m.p. 139°) [deaminated by diazotisation ($NaNO_2$–H_2SO_4 in AcOH) and treatment with Cu_2O in EtOH to 2 : 5-$C_{10}H_6Br$·NO_2], or 2 : 4-*dibromo*-5-*nitro*-1-*naphthylamine*, m.p. 159·5° [*Ac* derivative, m.p. 230·5° (decomp.)], and with $Hg(OAc)_2$ in AcOH at 100°, 5-*nitro*-1-*naphthylamine*-2-*mercuriacetate*, m.p. >400°. This with I in aq. KI at 100° gives 2-*iodo*-5-*nitro*-1-*naphthylamine*, m.p. 121·5—122·5° (*Ac* derivative, m.p. 169·5°), converted (diazo-methods) into 2 : 5-$C_{10}H_6I$·NO_2, new m.p. 91·5°, and 1 : 2-*di-iodo*-5-*nitronaphthalene*, m.p. 132·5°. 5 : 1-NO_2·$C_{10}H_6$·NHAc (**II**) with Cl_2 in AcOH at 100° yields only the *Ac* derivative, m.p. 235·5°, of 2 : 4-*dichloro*-5-*nitro*-1-*naphthylamine*, m.p. 116·5°, deaminated (as above) to 2 : 4-*dichloro*-5-*nitronaphthalene*, m.p. 116·5°. Nitration of (**II**) gives 4 : 5 : 1-$(NO_2)_2C_{10}H_5$·NHAc, hydrolysed and deaminated to 1 : 8-$C_{10}H_6(NO_2)_2$. 5-*Nitro*-p-*toluenesulphon*-1-*naphthalide*, m.p. 171° [from (**I**) and *p*-C_6H_4Me·SO_2Cl in C_5H_5N], and AcOH–HNO_3 (*d* 1·5) yield the p-C_6H_4Me·SO_2 derivative, m.p. 206°, of 2 : 4 : 5 : 1-$(NO_2)_3C_{10}H_4$·NH_2, m.p. 310° (lit. 305°, 310°). 2-*Chloro*-5-*nitronaphthalene* (from 5 : 2-NO_2·$C_{10}H_6$·NH_2) has m.p. 100·5°.

A. Li.

Phenylthiocarbamides. The triad –N·C·S–. XII. Phenylcyanamide, its properties and derivatives. Phenylhydrazine-α-carboxylic acid. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1942, **19**, 343—348).—NHPh·$CS·NH_2$ with $Cu(OAc)_2$ in an alkaline medium gives NHPh·CN [separates from H_2O as (mainly) a monohydrate at 30° and trihydrate at 0—15°; hydrochloride, m.p. 118°; H sulphate; *NO*-derivative, m.p. 155—156°, which with NaOH affords NO·NPh·CO_2Na (corresponding *Ag* salt), reduced (Sn, dil. HCl) to CO_2H·NPh·NH_2,HCl]. NHPh·CN polymerises to triphenyl*iso*melamine.

F. R. S.

Preparation of sulphanilylcarbamide. E. H. Cox (*J. Amer. Chem. Soc.*, 1942, **64**, 2225—2226).—NH_2·C(OEt):NH,HCl, *p*-NHAc·C_6H_4·SO_2Cl, and K_2CO_3 in $COMe_2$–H_2O at 0° give p-*acetamidobenzenesulphonyl*-O-*ethyl*iso*carbamide* (87%), m.p. 223—224°, hydrolysed by conc. HCl at 100° to sulphanilylcarbamide (80%), m.p. 140—146° (gas) (*NH_4*, *K*, and *Na* salts).

R. S. C.

***p*-Aminobenzenesulphon-ββ-dimethylacrylamide.**—See B., 1943, III, 21.

Acylation experiments with sulphanilamide and heterocyclic amines. II, III. F. Bergmann and D. Schapiro (*J. Org. Chem.*, 1942, **7**, 419—423).—Sulphanilamide (**I**) and (:CH·CO)$_2$O in $COMe_2$, dioxan, or xylene give N^4-sulphanilamidomaleic acid, m.p. 209—210°, converted by boiling 2% H_2SO_4–EtOH into the *Et* ester, m.p. 204—205°, with some N-*phenylmaleimide*-p-*sulphonamide*, softens at 220°, decomp. 285°. *trans*-CO_2Et·CH:CH·COCl (**II**) and (**I**) in $COMe_2$–C_5H_5N yield *Et* N^4-*sulphanilamidofumarate*, m.p. 219° (corresponding *acid*, m.p. 295°). (**I**) and citraconic anhydride in dioxan at 5° and then at room temp. afford the *acid*, $C_{11}H_{12}O_5N_2S$, m.p. 175° and ~210° after re-solidification, easily transformed into the *imide*, m.p. 217—218°. 8-Amino-6-methoxyquinoline (**III**) and (:CH·CO)$_2$O in boiling $COMe_2$ yield 6-methoxyquinoline-8-*N*-maleamic acid, m.p. 225° [*Et* ester, m.p. 177°, and its *hydrochloride* (+0·5H_2O), m.p. 212° (decomp.)]. *Et* 6-*methoxyquinoline*-8-N-*fumaramate*, m.p. 105° [*hydrochloride*, m.p. 195° (decomp.)], results from (**II**) and (**III**) in $COMe_2$. 6-*Methoxyquinoline*-8-*citraconimide* has m.p. 179°.

III. Gradual addition of Cl·$[CH_2]_2$·COCl in C_6H_6 to (**III**) in C_6H_6 leads to 8-*β-chloropropionamido*-6-*methoxyquinoline*, m.p. 104°, which with boiling MeOH–$NHEt_2$ gives *γ-acrylamido*-6-*methoxyquinoline*, b.p. 210°/0·4 mm., m.p. 119—120° (hydrochloride, m.p. 208°; *dibromide*, m.p. 171—172°).

H. W.

Interpretation of the Sandmeyer reaction. III. Further evidence in favour of a mechanism involving anionoid halogen. H. H. Hodgson, S. Birtwell, and J. Walker (*J.C.S.*, 1942, 720—723).—PhN_2HSO_4 with $CuSO_4$ and NaBr gives 38% of PhBr. The yield (63%) of *p*-C_6H_4Br·NO_2 (**I**) from *p*-NO_2·C_6H_4·N_2HSO_4, $CuSO_4$, and NaBr is unaffected by added $(NH_4)_2S_2O_8$, but $FeCl_3$ gives 74% of a 1 : 1 mixture of (**I**) and *p*-C_6H_4Cl·NO_2 (**II**); with H_2O_2 the yield of (**I**) is reduced. Conversion of *p*-NO_2·C_6H_4·N_2Cl into (**II**) is catalysed by $FeCl_3$ or $CuCl_2$ in H_2O or in HCl but not by $ZnCl_2$; $SnCl_4$ and $AlCl_3$ have little effect. Production of ArCl from ArN_2Cl and $CuCl_2$ (or $CuSO_4$ and NaCl) increases with increasing positivity of the diazonium cation. The reactions studied can be interpreted by the mechanism previously proposed (A., 1942, II, 52, 254). Cu^I salts do not possess the almost unique character claimed by Sandmeyer and by Waters (A., 1942, II, 222).

A. Li.

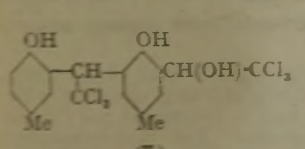
Halogenation of esters in the diphenyl series. I. Chlorination of *p*-diphenylyl acetate. C. M. S. Savoy and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1942, **64**, 2219—2221).—*p*-C_6H_4Ph·OAc with Cl_2 and a little I in CCl_4 and then KOH–aq. EtOH gives 4-*chloro*-4′-*hydroxydiphenyl*, m.p. 145—146° (*acetate*, m.p. 113°), also obtained (4%) by treating benzidine with, successively, $NaNO_2$–aq. HCl, CuCl–HCl at room temp. and later 60°, and $NaNO_2$–aq. HCl at room temp. and later 60°. 2-*Chloro*-, m.p. 68°, 2 : 6-*dichloro*-, m.p. 64°, and 2 : 6 : 4′-*trichloro*-4-*diphenylyl acetate*, m.p. 79·5°, are prepared from the corresponding phenols by boiling NaOAc–Ac_2O.

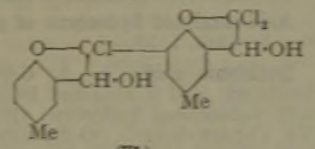
R. S. C.

Nuclear methylation of phenols by means of methanolic sodium methoxide. J. W. Cornforth, (Mrs.) R. H. Cornforth, and (Sir) R. Robinson (*J.C.S.*, 1942, 682—684).—The *C*-methylation method

used in the pyrrole series is extended. Although PhOH, *o*- and *p*-$C_6H_4(OH)_2$, and α-$C_{10}H_7$·OH are unaffected by NaOMe–MeOH at 220° (autoclave) for ~10 hr., β-$C_{10}H_7$·OH (**I**) is partly methylated to 1 : 2-$C_{10}H_6Me$·OH (**II**). Resorcinol (**III**) and *s*-$C_6H_3(OH)_3$ similarly yield 2 : 4 : 6 : 1 : 3-$C_6HMe_3(OH)_2$; with (**III**), some HCO_2H and (probably) a *C*-methyl- or -dimethyl-β-resorcylic acid are also formed. 2 : 2′-Dihydroxy-di-α-naphthylmethane gives an improved yield (75%) of (**II**), showing that nascent (**I**) is more readily methylated than ordinary (**I**). Benzylidenedi-β-naphthol gives 2 : 1-OH·$C_{10}H_5$·CH_2Ph (**I**), and (**II**), whilst 1-piperidino-2- and 4-piperidino-1-naphthol yield (**II**) [(**I**) is not formed] and 4 : 1-$C_{10}H_4Me$·OH, respectively. 2 : 7-*Dihydroxy*-1 : 8-*bispiperidinomethylphenanthrene*, m.p. 219—220° (from 2 : 7-dihydroxyphenanthrene, piperidine, and aq. CH_2O in EtOH), is reduced by NaOMe–MeOH at 200° for 6 hr., and the product methylated to (probably) 2 : 7-*dimethoxy*-1 : 8-*dimethylphenanthrene*, m.p. 256—257°. Mechanisms of reaction are discussed. A. T. P.

Interaction of *p*-cresol and other phenols with chloral and its hydrate. M. P. Balfe and W. C. Webber (*J.C.S.*, 1942, 718—720).—In $CHCl_3$ at room temp. in presence of K_2CO_3, CCl_3·CHO yields with PhOH, *Ph* (7·5%), m.p. 15—18°, and with *p*-cresol, *p-tolyl 333-trichloro-α-hydroxyethyl ether* (35%) (**I**), m.p. 46—47°, but does not react with *o*- or *m*-cresol, *p*-NO_2·C_6H_4·OH, or *p*-OH·C_6H_4·CO_2H. Repeated saturation of molten *p*-cresol + CCl_3·$CH(OH)_2$ with HCl yields 3-*333*-trichloro-α-hydroxyethyl-*p*-cresol (35%) (**II**), also obtained when (**I**) is kept for several months in HCl gas or in solution containing K_2CO_3. (**II**) in AcOH saturated with HCl gives the 4-*monoacetate* (**III**), m.p. 168° [colour (fugitive when heated) with $FeCl_3$], which with *p*-cresol and 99% H_2SO_4 in AcOH yields the *monoacetate* (**IV**), m.p. 198°, of *aaa*-trichloro-*33*-di-4-hydroxy-*m*-tolylethane [*diacetate* (Ac_2O–NaOAc), m.p. 162°]. (**II**), *p*-cresol, and 99% H_2SO_4 in AcOH at 50—60° yield (**III**), (**IV**), and a *diacetate*, m.p. 200° (slight decomp.) [also obtained from (**II**) and 99% H_2SO_4 in $PhNO_2$ at 15°, with or without *p*-cresol: acetylated ($NaOAc$–Ac_2O) to the *triacetate*, m.p. 178°, of (**V**). (**II**) with aq. KOH yields the *compound* (? **VI**), m.p. 184° (*diacetate*, m.p. 133°).


(V.)


(VI.)

CCl_3·CHO or its hydrate with (best) 79·8% H_2SO_4 yields a complex of composition CCl_3·CH(OH)·O·SO_2·OH,1·5H_2O + 21·2% of H_2SO_4,1·5H_2O. A. Lr.

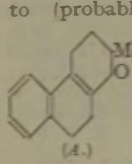
Oxidation of *p*-cresol by peroxidase. W. W. Westerfeld and C. Lowe (*J. Biol. Chem.*, 1942, **145**, 463—470).—Horseradish peroxidase, H_2O_2, and *p*-cresol at pH 6·5 (PO_4''' buffer) give the keto-dimethyltetrahydrodiphenylene oxide (**I**) of Pummerer *et al.* (A., 1925, i, 1262). 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenyl (*diacetate*, m.p. 88°), and (probably) 2 : 2′-*dihydroxy*-3-(6′-*hydroxy*-m-*tolyl*)-5 : 5′-*dimethyldiphenyl*, m.p. 196·5° (*triacetate*, m.p. 107°) (cf. *loc. cit.*). 2 : 3′-Dihydroxy-5 : 6′-dimethyldiphenyl [from (**I**) and 48% HBr at 100° (bath)] (*dibenzoate*, m.p. 131·5—132°), is methylated (Me_2SO_4, 10% NaOH) and then oxidised ($KMnO_4$, 1% NaOH) to 2 : 3′-*dimethoxydiphenyl*-5 : 6′-*dicarboxylic acid*, m.p. 263—264°. Oxidation ($KMnO_4$, $COMe_2$) of (**I**) gives 1 : 4-*dimethyl*-1 : 2-*dihydrocoumarone*-1-*carboxylic*-2-*acetic acid* (**II**), m.p. 149—150° (anhydride, m.p. 125—126°), oxidised ($KMnO_4$, dil. NaOH) to 1-*methyl*-1 : 2-*dihydrocoumarone*-1 : 4-*dicarboxylic*-2-*acetic acid*, m.p. 238—240°. KOH-fusion of (**II**) at 250°, followed by methylation (Me_2SO_4) and oxidation ($KMnO_4$, 2% NaOH), gives 4 : 1 : 3-OMe-$C_6H_2(CO_2H)_3$. P. G. M.

α-Decylresorcinol.—See B., 1943, II, 5.

Alkylquinols and related compounds. A. H. Cook, I. M. Heilbron, and F. B. Lewis (*J.C.S.*, 1942, 659—661).—Neither p-*anisyl stearate*, m.p. 50°, nor *palmitate*, m.p. 51·5°, obtained from the acyl chloride and *p*-OH·C_6H_4·OMe–Et_2O–C_5H_5N (cold), would undergo the Fries reaction. The following are prepared from quinol Me_2 or Et_2 ether, the acid chloride, and $AlCl_3$ in $C_2H_2Cl_4$ at 0° : 2 : 5-*dimethoxystearophenone*, m.p. 46°, *-palmitophenone* (**I**), b.p. 205°/0·18 mm., m.p. 51·5°, *-myristophenone*, b.p. 209°/0·5 mm., m.p. 43°, and *-laurophenone*, b.p. 175—178°/0·2 mm., m.p. 27·5°; 2 : 5-*diethoxymyristophenone*, b.p. 204°/0·29 mm., m.p. 44·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 78°), and *-laurophenone*, b.p. 180—190°/0·34 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 77·5°). 2 : 5-*Diethoxypalmitophenone*-2 : 4-*dinitrophenylhydrazone* has m.p. 75°. 2 : 4 : 5-*Trimethoxylaurophenone* melts at 53°. Clemmensen reduction affords 2 : 5-*dimethoxy*-, b.p. 188°/0·2 mm., and *-diethoxy-octadecyl*-, b.p. 210°/0·06 mm., 2 : 5-*dimethoxy*-, b.p. 210°/0·5 mm., and *-diethoxyhexadecyl*-, b.p. 219°/0·1 mm., 2 : 5-*dimethoxy*-, b.p. 165°/0·5 mm., and *-diethoxy-tetradecyl*-, b.p. 183°/0·1 mm., and 2 : 5-*dimethoxy*-, b.p. 154°/0·5 mm., and *-diethoxy-dodecyl-benzene*, b.p. 176°/0·7 mm., dealkylated by 50% HBr–AcOH (4—6 hr.) to *octadecyl*-, m.p. 100·5°, *hexadecyl*-, m.p. 112°, *tetradecyl*-, m.p. 110°, and *dodecyl-quinol*, m.p. 105°, which are oxidised by Ag_2O–Et_2O to the respective *benzoquinones*, m.p. 76°, 83°, 77·5°, and 72°. Octadecylbenzoquinone and Ac_2O (+H_2SO_4) yield 2 : 4 : 5-*triacetoxyoctadecylbenzene*, m.p. 73°. (**I**) and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give *α-hydroxy-α*-2 : 5-*dimethoxyphenylhexadecane*, m.p. 34°, dehydrated ($NaHSO_4$ at 200°) to *α*-2 : 5-*dimethoxyphenyl*-Δ^{α}-*hexadecene*, m.p. 43°. The 2 : 5 : 1-$(OMe)_2C_6H_3$·COAlk and MgMeI afford, not *tert.*-alcohols, but olefines, viz., *α*-2 : 5-*dimethoxyphenyl*-α-*methyl*-Δ^{α}-*octadecene*, b.p. 202°/0·5 mm., -Δ^{α}-*hexadecene*, m.p. 35°, and -Δ^{α}-*tetradecene*, b.p. 175°/0·2 mm., and *α*-2 : 4 : 5-*trimethoxyphenyl*-α-*methyl*-Δ^{α}-*dodecene*, b.p. 203°/0·5 mm.; demethylation by HBr–AcOH gives 5-*methoxy*-2-*tetradecylcoumaran* (or 6-*methoxy*-2-*tridecylchroman*), b.p. 196°/0·2 mm., 5-*hydroxy*-3-*methyl*-2-*hexadecylcoumaran* (or 6-*hydroxy*-4-*methyl*-2-*pentadecylchroman*), b.p. 192—194°/0·2 mm., 5-*hydroxy*-3-*methyl*-2-*tetradecylcoumaran* (or 6-*hydroxy*-4-*methyl*-2-*tridecylchroman*), b.p. 200°/0·2 mm., and 5-*hydroxy*-3-*methyl*-2-*decylcoumaran* (or 6-*hydroxy*-4-*methyl*-2-*nonylchroman*), b.p. 178—183°/0·2 mm. Palmityl-ψ-cumoquinol Me_2 ether could not be prepared. A. T. P.

Synthesis of substances related to the sterols. XL. (A) **Preparation of 2 : 7-dihydroxyphenanthrene and derivatives.** (B) **Reduction of 1-γ-ketobutyl-2-naphthol.** J. W. Cornforth and (Sir) R. Robinson (*J.C.S.*, 1942, 684—689; cf. A., 1941, II, 365).—(A) Clemmensen reduction of 3 : 3′-dimethoxybenzoin (**I**), followed by hydrogenation of the crude product (contains 3 : 3′-dimethoxystilbene) in EtOH (Raney Ni) at normal temp. and pressure, gives 3 : 3′-dimethoxydibenzyl (**II**), also obtained from (**I**) and aq. C_5H_5N–$CuSO_4$ at 90—100°, followed by reduction and hydrogenation of the dimethoxybenzil. (**II**) is best prepared from *m*-OMe·C_6H_4·CH_2Cl (improved prep.), by reaction of its Grignard reagent with anhyd. $FeCl_3$. 3 : 3′-*Dihydroxydibenzyl*, m.p. 139—140°, is oxidised by $FeCl_3$ to yellow resins. (**II**) and $Hg(OAc)_2$–AcOH–I at 50° afford 6 : 6′-*di-iodo*-3 : 3′-*dimethoxydibenzyl*, m.p. 113—114°, cyclised by Cu-bronze at ~260° to 2 : 7-*dimethoxy*-9 : 10-*dihydrophenanthrene*, m.p. 108—109°, which is dehydrogenated by S at 220—230° to 2 : 7-dimethoxyphenanthrene (**III**), m.p. 169—170°, converted by boiling HI–AcOH into the $(OH)_2$-compound (**IV**) (*dibenzoate*, m.p. 252—253°) (not transformed into its Me ethers by HCl–MeOH). (**IV**) and Me_2SO_4–10% aq. NaOH–$COMe_2$ yield (**III**) and 2-*hydroxy*-7-*methoxyphenanthrene* (**V**), m.p. 173—174°, less readily prepared from the monobenzoate of (**III**) by methylation and hydrolysis. Hydrogenation (Cu chromite in EtOH) of (**V**) at 170—175°/100 atm. gives 2-*hydroxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 123—124°, with (probably) some 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-H_8-derivative. 2 : 7-*Dihydroxy*-9 : 10-*dihydrophenanthrene* (**VI**), m.p. 206—208° (from the Me_2 ether and HI–AcOH), with BzCl at 210—220° gives the *dibenzoate*, m.p. 208—210°, and some monobenzoate; methylation of the latter with aq. $COMe_2$–Me_2SO_4–NaOH, followed by alkaline hydrolysis, gives 2-*hydroxy*-7-*methoxy*-9 : 10-*dihydrophenanthrene* (**VII**), m.p. 118—120°. The Na derivative of (**VII**) and CO_2 at 210—220°/20 atm. yield 2-*hydroxy*-7-*methoxy*-9 : 10-*dihydrophenanthrene*-3-*carboxylic acid*, m.p. 225—226° (decomp.); 2 : 7-*dihydroxy*-9 : 10-*dihydrophenanthrene*-3 : 8-*dicarboxylic acid*, m.p. 305° (decomp.), is obtained from (**VI**) and CO_2 at 200°/5 atm. *m*-OMe·C_6H_4·CH_2·COCl (**VIII**), *p*-$C_6H_4(OMe)_2$, and $AlCl_3$–CS_2, followed by Clemmensen reduction of the product and subsequent methylation, give 2 : 5 : 3′-*trimethoxydibenzyl*, b.p. 177—180°/0·4 mm. (demethylation gives tars). *Me* 2-*hydroxy*-4-*phenylacetoxybenzoate*, m.p. 53—54°, is obtained from 2 : 4 : 1-$(OH)_2C_6H_3$·CO_2Me (**IX**) and CH_2Ph·COCl–$AlCl_3$–CS_2, whereas condensation in $PhNO_2$ at 50—60° affords *Me* 2 : 4-*dihydroxy*-5-*phenylacetylbenzoate*, m.p. 150—151°, reduced (Clemmensen) to *Me* 2 : 4-*dihydroxy*-5-β-*phenylethylbenzoate*, m.p. 114—115° (aq. NaOH–EtOH give 4-β-phenylethylresorcinol). (**VIII**), (**IX**), and $AlCl_3$–$PhNO_2$ at 30° afford a product, m.p. 165° (softens at 150°), hydrolysed by aq. NaOH–EtOH to an acid, m.p. 237—240°, which loses CO_2 at 240° to give 4-m-*methoxyphenylacetylresorcinol*, m.p. 109—110°. $AlCl_3$ or $ZnCl_2$, (**VIII**), and methylumbelliferone at 140°, and then 170°, give no new product.

(B) Hydrogenation (Cu chromite–EtOH) of 1-γ-ketobutyl-2-naphthol (**X**) at 135°/75 atm. yields 2-*hydroxy*-1-γ-*hydroxybutyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**XI**), forms, m.p. 111—112°, and b.p. 215—220°/10 mm., but the corresponding diketone could not be obtained. (**XI**) is oxidised by $K_2Cr_2O_7$–H_2SO_4–aq. AcOH–C_6H_6 to (probably) 1-*hydroxy*-2-*keto*-1-γ-*ketobutyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 79—80°. (**XI**) and $Al(OBu^{\gamma})_3$–C_6H_6–$COMe_2$ give a *substance*, b.p. 156—158°/9 mm., probably (*A*). (**XI**) and $Al(OBu^{\gamma})_3$–$COMeEt$–C_6H_6 give a compound, b.p. 175—200°/15 mm., which affords a 2 : 4-*dinitrophenylhydrazone*, m.p. 212—213° (decomp.), probably derived from the diketone. (**XI**) and Raney Ni (N_2) at 150—160° give α-methyltetrahydro-5 : 6-benzochroman, new m.p. 72—73°, also obtained from (**X**) by benzylation, followed by $CH(OEt)_3$–HCl–EtOH, and hydrogenation (Raney Ni) of the 2-benzyloxy-1-γ-ketobutylnaphthalene Et_2 acetal at 100°/100 atm. (**X**) and H_2–Raney Ni–EtOH at 180°/125 atm. afford *perhydro*-2-*methyl*-5 : 6-*benzochroman*, b.p. 132—133°/9 mm., partly converted by an equal wt. of Ac_2O


(A.)

(+1% $ZnCl_2$) at 200° into an unsaturated *monoacetate*, b.p. 167—172°/9 mm. A. T. P.

Halogenation of phenolic ethers and anilides. XIII. Arrhenius activation energies for di- and poly-substituted aromatic ethers.—See A., 1943, I, 38.

Formation and rearrangement of *o*-tolyl benzhydryl ether. H. A. Iddles, D. H. Chadwick, J. W. Clapp, and R. T. Hart (*J. Amer. Chem. Soc.*, 1942, **64**, 2154—2157).—Contrary to Schorigin (A., 1929, 183), the compound, m.p. 139—141°, obtained from *o*-cresol and $CHPh_2$·OH in AcOH–H_2SO_4 at 100°, is 3 : 5-*dibenzhydryl*-o-*tolyl acetate* (**I**); at room temp. 5-*benzhydryl*-o-*cresol* (**II**), m.p. 101°, b.p. 180—185°/2 mm., is obtained. *o*-C_6H_4Me·O·$CHPh_2$ (prep. from $CHPh_2Cl$ and *o*-C_6H_4Me·ONa in Et_2O), b.p. 175—178°/4 mm., with $ZnCl_2$ at 150° also gives (**II**). Br in CCl_4 converts (**II**) into the 3-*Br*-compound, m.p. 117—118°, which is also obtained (70%) from 1 : 3 : 2-C_6H_3MeBr·OH and $CHPh_2$·OH in AcOH–H_2SO_4 at room temp. With Me_2SO_4–NaOH at 40°, (**II**) gives the *Me ether* (67%), m.p. 74—76°, also obtained (43%) from 2 : 1 : 5-OMe·C_6H_3Me·MgBr by $CHPh_2Cl$ or (75%) from 2 : 1 : 5-OMe·C_6H_3Me·CPh_2·OH by Zn dust in AcOH. 2 : 1 : 3-OH·C_6H_3Me·CPh_2·OH and Zn–AcOH give 3-*benzhydryl*-o-*cresol* (70%), m.p. 76—78°, which with Br–CCl_4 gives the 5-*Br*-derivative (45%), m.p. 97—100° (acetate, m.p. 157—158°), also obtained (m.p. 100—103°) from 1 : 5 : 3-C_6H_3MeBr·OH and $CHPh_2$·OH in AcOH–H_2SO_4 at 100°. 2 : 1 : 3 : 5-OH·$C_6H_2Me(CO_2Me)_2$ (modified prep.) and MgPhBr in boiling Et_2O give an orange *substance* (75%), 5 : 1 : 3 : 2-CPh_2:$C_6H_2Me(CPh_2$·OH):O, m.p. 206—208°, reduced by Zn dust in boiling AcOH to 3 : 5-*dibenzhydryl*-o-*cresol*, amorphous, m.p. 50—60° [3 : 5-*dinitrobenzoate*, m.p. 206—207°; acetate = (**I**)]. R. S. C.

Quaternary salts from β′-dimethylamino-β-thymoxydiethyl ether. C. W. Ferry, A. E. Ardis, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2232).—Na thymoxide or 6-chlorothymoxide with boiling (Cl·$[CH_2]_2)_2O$ and then 33% $NHMe_2$–MeOH at 145°/~150 lb. give oily bases, which with RHal yield *benzyl*-, m.p. 122—123°, and p-*chlorobenzyl*-, m.p. 166—166·5°, *-β-β′-thymoxyethoxyethyldimethylammonium chloride*, *β-β′-6-chlorothymoxyethoxyethyltrimethylammonium iodide*, m.p. 152°, p-*chloro*-, m.p. 160°, and p-*bromo*-, m.p. 156·5—157°, *-benzyl-β-β′-6-chlorothymoxyethoxyethyldimethylammonium chloride*. R. S. C.

Quaternary salts containing aryloxy-ethyl and -propyl groups. W. S. Ide, R. Baltzly, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2234).—Na thymoxide and 6-chlorothymoxide with OH·$[CH_2]_n$·Br give OH·$[CH_2]_n$·X and thence (PBr_3) Br·$[CH_2]_n$·X and ($NHMe_2$–MeOH; 120—125°) NMe_2·$[CH_2]_n$·X, which with AlkHal yield *β-thymoxy*-, m.p. 176°, and *β-6-chlorothymoxy-ethyltrimethylammonium iodide*, m.p. 228°, *benzyl*-, m.p. 194°, p-, m.p. 216°, and o-*chlorobenzyl*-, m.p. 175°, *-β-6-chlorothymoxyethyldimethylammonium chloride*, *γ-6-chlorothymoxy*-n-*propyltrimethylammonium iodide*, m.p. 229°, p-*chlorobenzyl*-, m.p. 204°, and p-*bromobenzyl*-, m.p. 191°, *-γ-6-chlorothymoxy*-n-*propyldimethylammonium chloride*, and *di-γ-6-chlorothymoxy*-n-*propyldimethylammonium chloride*, m.p. 184—187°. *β-6-Chlorothymoxyethyl-pyridinium*, m.p. 119—120°, and -2 : 4-*dimethylthiazolinium bromide*, m.p. 214°, are prepared. R. S. C.

Unsymmetrical disubstituted carbamides. J. S. Buck, W. S. Ide, and R. Baltzly (*J. Amer. Chem. Soc.*, 1942, **64**, 2233).—NHRR′ and NH_2·CO·NH·NO_2 give N-*methyl*-N-n-*hexyl*-, m.p. 75°, N-p-*anisyl*-N-sec.-*butyl*-, m.p. 140°, *-β-methyl*-n-*butyl*-, m.p. 130°, *-ββ-dimethyl*-n-*propyl*-, m.p. 155°, and *-αγ-dimethyl*-n-*butyl*-, m.p. 110°, *-carbamide*. R. S. C.

5-Amino-2-hydroxybenzenesulphonamide and related compounds. R. T. Williams (*J.C.S.*, 1942, 708—709).—5 : 2 : 1-NH_2·C_6H_3(OH)·SO_3H and C_5H_5N–Ac_2O at room temp. afford C_5H_5N 5-*acetamido*-2-*acetoxybenzenesulphonate*, m.p. 143—144°, converted by PCl_5 into 5-*acetamido*-2-*acetoxybenzenesulphonyl chloride* (**I**), m.p. 148—149°. (**I**) and 50% aq. NH_3, followed by cold 2N-HCl, yield 5-*acetamido*-2-*hydroxybenzenesulphonamide*, m.p. 215°, hydrolysed by boiling aq. HCl to the 5-NH_2-compound, m.p. 202° (decomp.). 5-*Acetamido*-2-*acetoxybenzenesulphonanilide*, m.p. 150° (decomp.), obtained from (**I**) and NH_2Ph–AcOEt, is hydrolysed by boiling 2N-HCl to 5-*amino*-2-*hydroxybenzenesulphonanilide*, m.p. 159°. 3 : 4 : 1-NH_2·C_6H_3(OH)·SO_3H gives C_5H_5N 3-*acetamido*-4-*acetoxybenzenesulphonate*, m.p. 162°, and thence the corresponding *sulphonyl chloride* (**II**), m.p. 143°, and 3-*acetamido*-4-*acetoxy*-, m.p. 205°, and 3-*amino*-4-*hydroxy-benzenesulphonanilide*, m.p. 172° (poor yield). (**II**) and aq. NH_3, followed by hydrolysis with 2N-HCl, give a non-cryst. product. 4 : 2 : 1-NHAc·C_6H_3(OAc)·SO_2Cl gives 4-*acetamido*-2-*acetoxy*-, m.p. 213—214°, whence 4-*amino*-2-*hydroxybenzenesulphonanilide*, m.p. 184°. A. T. P.

Vital stains. I. A. A. Goldberg (*J.C.S.*, 1942, 713—716).—Vital stains of the trypan-blue type, containing I or As, are synthesised. 5 : 1 : 2-C_6H_3IMe·N_2Cl and 8 : 3 : 6 : 1-OH·$C_{10}H_4(SO_3Na)_2$·NH_2 (**I**) in aq. NaOH at 0—5°, then at 40°, give Na_2 1-*amino*-2-(5′-*iodo*-o-*tolueneazo*)-8-*naphthol*-3 : 6-*disulphonate*, which with tetrazotised *o*-tolidine in NaOH affords Na_4 3 : 3′-*dimethyldiphenyl*-4 : 4′-*bis*-[2″-*azo*-8″-*amino*-1″-*hydroxy*-3″ : 6″-*disulphonaphthalene*-7″-(5‴-*iodo*-o-*azotoluene*)]; the benzidine and dianisidine analogues are prepared. 1 : 2 : 6 : 4-N_2Cl·$C_6H_2I_2$·AsO_3H_2 and (**I**) afford Na_4 1-*amino*-2-(2′ : 6′-*di*-*iodo*-4′-*arsonobenzeneazo*)-8-*naphthol*-3 : 6-*disulphonate*, converted into Na_8 3 : 3′-*dimethyldiphenyl*-4 : 4′-*bis*-[2″-*azo*-8″-*amino*-1″-*hydroxy*-3″ : 6″-*disulphonaphthalene*-7″-(*azo*-2‴ : 6‴-*di*-*iodobenzene*-4‴-*arsonate*)]. $CH_2(C_6H_4$·NH_2-*p*$)_2$ and 1–$CaCO_3$–H_2O–Et_2O give 3 : 3′-*di*-*iodo*-4 : 4′-*diaminodiphenylmethane*, m.p. 80—85°, which is tetrazotised and coupled with K_4 2-*amino*-1-(4′-*arsonobenzeneazo*)-8-*naphthol*-3 : 6-*disulphonate* to give K_8 3 : 3′-*di*-*iododiphenylmethane*-4 : 4′-*bis*-(2″-*azo*-7″-*amino*-1″-*hydroxy*-3″ : 6″-*disulphonaphthalene*-8″-*azobenzene*-4‴-*arsonate*). 4 : 2 : 6 : 1-SO_3H·$C_6H_2I_2$·N_2Cl and (**I**) afford Na_3 1-*amino*-2-(2′ : 6′-*di*-*iodo*-4′-*sulphobenzeneazo*)-8-*naphthol*-3 : 6-*disulphonate* (**II**). Benzidine-2 : 2′-disulphonic acid in aq. NaOH at 80°, added to ICl–aq. HCl at 80°, affords Na_2 5 : 5′-*di*-*iodobenzidine*-2 : 2′-*disulphonate* (**III**), which (tetrazotised) with (**II**) gives Na_8 5 : 5′-*di*-*iodo*-2 : 2′-*disulphodiphenyl*-4 : 4′-*bis*-[2″-*azo*-8″-*amino*-1″-*hydroxy*-3″ : 6″-*disulphonaphthalene*-7″-(*azo*-2‴ : 6‴-*di*-*iodobenzene*-4‴-*sulphonate*)]. 1 : 4 : 6 : 2-NH_2·$C_6H_2I_2$·CO_2H, m.p. 228—230° (from *o*-NH_2·C_6H_4·CO_2Na and ICl–aq. HCl, at 70—80°), gives Na_3 1-*amino*-2-(2′ : 4′-*di*-*iodo*-6′-*carboxybenzeneazo*)-8-*naphthol*-3 : 6-*disulphonate*, and thence, with tetrazotised (**III**), Na_8 5 : 5′-*di*-*iodo*-2 : 2′-*disulphodiphenyl*-4 : 4′-*bis*-[2″-*azo*-8″-*amino*-1″-*hydroxy*-3″ : 6″-*disulphonaphthalene*-7″-(*azo*-2‴ : 4‴-*di*-*iodobenzene*-6‴-*carboxylate*)]. A. T. P.

Condensation of *o*-, *m*-, and *p*-thiocresols with *o*-bromonitrobenzene, 2 : 5-dichloro- and 2 : 5-dibromo-nitrobenzene. P. S. Varma, K. S. V. Raman, and N. H. Malani (*J. Indian Chem. Soc.*, 1942, **19**, 354—356).—C_6H_4Me·SNa (or K) and the halogen compounds (with Cu-bronze for *o*-C_6H_4Br·NO_2) at ~180—200° give 2′-*nitro*-2-, b.p. 210—215°/16 mm., m.p. 86°, -3-, b.p. 222°/18 mm., m.p. 86·5°, and -4-*methyl*-, m.p. 87·5°, 4-*chloro*-, m.p. 121°, and 4-*bromo*-2-*nitro*-4′-*methyl*-, m.p. 124°, and 4-*chloro*-2-*nitro*-2′-*methyldiphenyl sulphide*, b.p. 200—205°/18 mm., m.p. 82·5°. 4-*Bromo*-2-*nitro*-4′-*methyldiphenyl sulphone* has m.p. 132°. F. R. S.

Energy-level treatment of reaction data.—See A., 1943, I, 38.

Acid-catalysed hydrolysis of phenyl-substituted aliphatic esters.—See A., 1943, I, 39.

Isethionic acid. A. A. Goldberg (*J.C.S.*, 1942, 716—718).—Isethionic acid is obtained from Et_2SO_4 and 60% oleum at ≯10°, with subsequent hydrolysis (H_2O) and is isolated as the Ca salt. *Na* O-*phenylacetyl*-, O-*β-phenylpropionyl*-, and O-*acetylmandelyl-isethionate* [from Na isethionate and the acid chloride at 140° (alone in the first case) or in xylene] are hydrolysed slowly in neutral, more rapidly in acid, and very rapidly in strongly alkaline solution. Pharmacological applications of these are discussed, and lethal dosages for mice are given. A. Li.

Manufacture of hydroxylamine and mandelic acid.—See B., 1943, II, 5.

Preparation of substituted mandelic acids and their bacteriological effects. III. J. L. Riebsomer, D. Stauffer, F. Glick, and F. Lambert (*J. Amer. Chem. Soc.*, 1942, **64**, 2080—2081; cf. A., 1939, II, 62).—Figures in parentheses below are bacteriological activities relative to OH·CHPh·CO_2H. $CO(CO_2Et)_2$, the appropriate hydrocarbon, and $SnCl_4$ give OH·CAr$(CO_2Et)_2$, in which Ar = 2 : 4 : 1-, b.p. 150—155°/4—5 mm., 3 : 4 : 1-, b.p. 157—160°/4—5 mm., and 2 : 5 : 1-$C_6H_3Me_2$, b.p. 154—156°/4—5 mm., *p*-CH_2Ph·C_6H_4, b.p. 225—230°/4—5 mm., and *p*-C_6H_4Ph, converted by 20% KOH and then aq. HCl into 2 : 4- (3·5), m.p. 113—115° [*acetate* (0·5), m.p. 92°], 3 : 4- (3·5), m.p. 135°, and 2 : 5-*dimethyl*- (3·5), m.p. 116·5—117° [*acetate* (<1), m.p. 112—113°; *propionate* (<1), m.p. 86°], p-*benzyl*- (<1), m.p. 133·5—134·5°, and p-*phenyl-mandelic acid* (0), m.p. 192° [*acetate* (0), m.p. 133°; *propionate* (0), m.p. 107°]. Structures are proved by oxidation to the expected benzoic acid. 2-$C_{10}H_7Me$ gives a very poor yield of an acid, m.p. 146·5—147·5°; $CHPh_3$ gives an impure acid, m.p. 90—95°; 1-$C_{10}H_7Me$, fluorene, acenaphthene, and anthracene do not give the expected acids. Crude xylene gives a product as active as the isomerides but too toxic. Mandelic acid acetate (1), m.p. 76—76·5°, and *propionate* (2), m.p. 58°, and p-*methylmandelic acid acetate* (0·5), m.p. 104—105°, are also reported. R. S. C.

Condensations of γ-bromocrotonic esters with zinc. K. Ziegler, W. Schumann, and E. Winkelmann (*Annalen*, 1942, **551**, 120—126; cf. Fuson *et al.*, A., 1938, II, 442).—CH_2Br·CH:CH·CO_2Me, PhCHO, and Zn wool in boiling C_6H_6 readily give *Me δ-hydroxy-δ-phenyl-Δ^{α}-pentenoate*, b.p. 175—179°/11 mm., which absorbs 1 H_2 (Pd–$BaSO_4$ in EtOAc) giving a product dehydrated (KHSO$_4$ at 150—170°) to CHPh:CH·$[CH_2]_2$·CO_2Me, b.p. 158—162°/10 mm., m.p. 75°, which is hydrogenated and then hydrolysed to Ph·$[CH_2]_4$·CO_2H. CHPh:CH·CHO similarly gives a little Ph·$[CH:CH]_3$·CO_2Me. CH_2Br·CMe:CH·CO_2Me (**I**) and PhCHO readily afford essentially Me δ-hydroxy-δ-phenyl-β-methyl-Δ^{α}-pentenoate, b.p. 192—203°/14 mm. (64%), hydrolysed to the *acid*, m.p. 154°, and hydrogenated (Pd–$BaSO_4$ in abs. EtOH) to OH·CHPh·CH_2·CHMe·CH_2·CO_2Me, m.p. 65°; it is converted by PBr_3 in C_6H_6 at room temp. into *Me*

δ-bromo-δ-phenyl-β-methyl-Δ$^{\alpha}$-pentenoate, which with collidine under N_2 at 110° gives the Me ester, b.p. 173—181°/12 mm., of *δ-phenyl-β-methyl-Δ$^{\alpha\gamma}$-pentadienoic acid*, m.p. 157°, hydrogenated to *δ-phenyl-β-methyl*-n-*valeric acid*. *ε-Phenyl-β-methyl-Δ$^{\alpha\beta\delta}$-hexatrienoic acid*, m.p. 192°, is obtained by hydrolysing the distilled product from (**I**) and CHPh:CH·CHO. H. W.

Lactones related to the cardiac aglycones. X. Synthesis of simple, hydroxylated β-substituted Δ$^{\alpha\beta}$-butenolides. E. R. Marshall, J. A. Kuck, and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 444—456). —Dropwise addition of $CH_2Br·CO_2Et$ in C_6H_6 to a boiling mixture of *p*-OMe·C_6H_4·CO·CH_2·OMe, C_6H_6, and Zn gives *Et β-hydroxy-γ-methoxy-β-p-anisylbutyrate* (**I**), b.p. 152—160°/0·6 mm., which does not absorb H_2 in EtOH containing PtO_2. The corresponding *acid*, m.p. 102·5—103·5°, is transformed by HBr–AcOH at 110—120° into *β-p-anisyl-Δ$^{\alpha\beta}$-butenolide* [*β-p-anisyl-Δ$^{\alpha}$-butenolactone*] (**II**), m.p. 120°, demethylated by AcOH–HBr at 120—140° to (slightly impure) *β-p-hydroxyphenyl-Δ$^{\alpha\beta}$-butenolide* (**III**), m.p. 262·5—263·5° (sealed capillary) (*acetate*, m.p. 138·6—140·7°), also obtained directly from (**I**). *p*-OAc·C_6H_4·COCl is transformed by successive treatments with CH_2N_2 and AcOH into *p*-OAc·C_6H_4·CO·CH_2·OAc, m.p. 94·6—95·6°, which is converted by Zn and $CH_2Br·CO_2Et$ followed by hydrolysis into (**III**), which gives a strong Legal test and with CH_2N_2 gives (**II**). *m*-OAc·C_6H_4·CO_2H is transformed through the chloride, CHN_2 ketone, and *m*-OAc·C_6H_4·CO·CH_2·OAc into *β-m-hydroxyphenyl-Δ$^{\alpha\beta}$-butenolide*, m.p. 187·5—188·5° (sealed capillary), which gives a positive Legal test, a colour with $FeCl_3$, and decolorises Br–H_2O; the *Me ether*, m.p. 86·3—87·3°, gives a positive Legal but negative $FeCl_3$ test. *o*-OAc·C_6H_4·CO·CHN_2 is converted by glacial AcOH into coumaranone (**IV**), also formed with an orange *compound*, m.p. 204—205°, using AcOH at room temp. and subsequently at 100°. *o*-OMe·C_6H_4·CO·CHN_2 reacts violently with AcOH in absence of a solvent but smoothly in presence of Et_2O to give (**IV**). *o*-OMe·C_6H_4·MgBr and OMe·CH_2·CN afford *o*-OMe·C_6H_4·CO·CH_2·OMe, b.p. 149—152°/10 mm. (semicarbazone, m.p. 138·1—139·1°), converted into Et *β*-hydroxy-*γ*-methoxy-*β-o*-anisylbutyrate (**V**), b.p. 127—128°/0·2 mm., and thence into *β-o-anisyl-Δ$^{\alpha\beta}$-butenolide*, m.p. 95·1—95·6°; this is transformed by HBr, HBr–AcOH, or AcOH under varied conditions into coumaronyl-3-acetic acid, m.p. 89·2—91·2°, mixed with unchanged material. Reduction (PtO_2 in AcOH) of (**V**) yields *Et β-hydroxy-γ-methoxy-β-2-methoxy*cyclo*hexylbutyrate*, b.p. 122—123°/1 mm., with some hexahydrocoumaronyl derivatives; the ester does not react satisfactorily with HCl or HBr. *o*-OMe·C_6H_4·CO_2Me is hydrogenated (Raney Ni) at 200°/2000—2700 lb. per sq. in. to *Me 2-methoxy*cyclo*hexanecarboxylate*, b.p. 96·5—97°/15 mm. (but mainly to Me *cyclo*hexanecarboxylate), converted into the *acid*, b.p. 122—123°/5 mm. (*p-toluidide*, m.p. 130·2—132·4°), the acid chloride, *ω*-diazo-*o*-methoxyhexahydroacetophenone, and thence into a mixture of hexahydrocoumaranone and *ω*-acetoxy-*o*-methoxyhexahydroacetophenone. High-pressure hydrogenation of *o*-OH·C_6H_4·CO_2Me in EtOH gives Et hexahydrosalicylate, b.p. 110—115°/13 mm., hydrolysed to a mixture of acids, m.p. 76—78° and 109—110°, and transformed by NH_3 into the *amide*, m.p. 113·7—114·7°. The crude acid is transformed by AcCl in boiling Et_2O followed by distillation into *2-acetoxy*cyclo*hexanecarboxylic acid*, m.p. 66·1—66·6° (*p-toluidides*, m.p. 154—155·9° and 124—143°). The crude acid is transformed into the chloride and thence into the CHN_2 ketone, which could not be satisfactorily converted into *ω* : *o*-diacetoxyhexahydroacetophenone. None of the lactones described above shows cardiac activity when tested in frogs. M.p. are corr. H. W.

Preparation of hexahydro-*p*-toluamides. M. Delépine and M. Badoche (*Ann. Chim.*, 1942, [xi], **17**, 179—182).—*p*-Toluic acid is hydrogenated (PtO_2–AcOH) to the H_6-derivative (**I**), b.p. 128—130°/13 mm., partly converted by HCl at 235—240° for 2 hr. into the *trans*-acid, m.p. 111° (60% yield) [amide, m.p. 226° (block)]. (**I**) is a mixture, consisting mainly of *cis*-hexahydro-*p*-toluic acid [amide, m.p. 163° (block) or 160—160·5° (tube)]. Other m.p. (lit.) of the amides are those of mixtures. A. T. P.

Basic indium salicylates. T. Moeller (*J. Amer. Chem. Soc.*, 1942, **64**, 2234).—Anhyd. $In_2(SO_4)_3$ (1 mol.) and *o*-OH·C_6H_4·CO_2Na (3 mols.) in H_2O gives *basic In salicylate*, $In(C_7H_5O_3)_2·OH, +3H_2O$, converted at 110° or in boiling MeOH into the anhyd. *salt*. R. S. C.

Chloralamides. Chloral-5-acetamidosalicylamide and related compounds. K. N. Rana (*J. Indian Chem. Soc.*, 1942, **19**, 299—302).—*5-Acetamidosalicylamide* (+H_2O), m.p. 204—206° (loses H_2O at 110°) [from 5 : 2 : 1-NHAc·C_6H_3(OH)·CO_2Me and aq. NH_3], heated with chloral yields *5-acetamidosalicyl-βββ-trichloro-α-hydroxyethylamide*, m.p. 176—177° (decomp.) [violet colour with $FeCl_3$]; *Me$_2$ ether* (Me_2SO_4), m.p. 166—167°; *Bz$_2$* m.p. 187—188°, and *Ac$_2$* derivative (Ac_2O), m.p. 212—214°], dehydrated (cold conc. H_2SO_4) to *6-acetamido-2-trichloromethylbenzometoxazone*, m.p. 218—219° (*Ac* derivative, m.p. 197—198°). Formation and stability of 5-substituted chloralsalicylamides are promoted by positive substituents. A. Li.

Diamino-peptides. R. Baltzly, W. S. Ide, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2231).—Hydrogenation of $NMe_2·[CH_2]_2·CO·NH·C_6H_4·NO_2$-*p* (prep. from $Br·[CH_2]_2·CO·NH·C_6H_4·NO_2$-*p* and $NHMe_2$) (hydrochloride, m.p. 200—201°) and its methochloride in HCl–EtOH gives *β-dimethylaminopropion*-p-*aminoanilide dihydrochloride*, m.p. 218—219°, and the corresponding *methochloride hydrochloride*, m.p. 211—212°, respectively. $NEt_2·[CH_2]_2·NH_2$ (prep. from $NEt_2·CH_2·CN$ by Na–EtOH) gives the *p*-$NO_2·C_6H_4$·CO derivative hydrochloride, m.p. 164—165°; this and its ethochloride yield (hydrogenation) N-p-*aminobenzoyl-N′N′-diethylethylenediamine dihydrochloride*, m.p. 176·5—178°, and the corresponding *ethochloride hydrochloride*, m.p. 228°, respectively. $NMe_2·[CH_2]_2·CN$ gives similarly $NMe_2·[CH_2]_3·NH_2$ (dihydrochloride, m.p. 182—184°; *p*-$NO_2·C_6H_4$·CO derivative hydrochloride, m.p. 190—192°), and N-p-*aminobenzoyl-N′N′-dimethyltrimethylenediamine dihydrochloride*, m.p. 184—185°. The *p*-nitrophenylcarbamate of OH·$[CH_2]_2$·NEt_3Cl is reduced to the *p*-aminophenylcarbamate (*hydrochloride*, m.p. 138—139°). R. S. C.

Action of thionyl chloride on 2 : 3-hydroxynaphthoic acid. J. W. Airan and S. V. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 333—334).—2 : 3-OH·$C_{10}H_6·CO_2H$ (**I**) with $SOCl_2$ at 110° yields the lactone, m.p. 240°, hydrolysed (dil. NaOH) to (**I**). A. Li.

Reaction of furoic acid with aromatic compounds. II. Reaction of methyl furoate with benzene and chlorobenzene. C. C. Price and C. F. Huber. **III.** C. C. Price, E. C. Chapin, and M. Rieger (*J. Amer. Chem. Soc.*, 1942, **64**, 2136—2139, 2227—2228; cf. A., 1941, II, 291).—II. Me furoate, C_6H_6, and $AlCl_3$ at 0° and later 70° give 1-$C_{10}H_7·CO_2$Me (32—46%) (cf. McCorkle *et al.*, *Proc. Iowa Acad. Sci.*, 1936, **43**, 205) and a tar, containing *Me 9-ethyl-9* : *10-dihydro-9-anthroate* (**I**) (11—20%), m.p. 52—54°, b.p. 144—145°/0·04 mm., but with PhCl at 0° and later 90—100° gives 6 : 1-$C_{10}H_6Cl·CO_2H$ (~40%) and its Me ester (15%). Formation of (**I**) involves reductive fission of the *endo*-$[CH_2]_2$ bridge. The structure of (**I**) is proved by conversion into anthracene (**II**) (61%) by soda-lime at slightly >360° and by oxidation by CrO_3–AcOH–H_2O to anthraquinone (**III**) (80%) or by less CrO_3 to Me 9-ethyl-10-anthrone-9-carboxylate (35%) (2 : 4-*dinitrophenylhydrazone*, m.p. 215°; isolated by Girard's reagent T), and by resistance to hydrolysis.

III. The crude acids obtained from furoic acid (**IV**) and C_6H_6 by $AlCl_3$ (*loc. cit.*) probably contain 9-ethyl-9 : 10-dihydro-9-anthroic acid, since by oxidation they give (**III**) and by distillation with soda-lime give (**II**) (10%) with an oil, which with S gives 1 : 4-$C_{10}H_6Ph_2$. The acids from (**IV**) and PhMe give, by soda-lime, 2 : 7-dimethylanthracene (from 3 : 6-dimethyl-9-ethyl-9 : 10-dihydro-9-anthroic acid), but only tars by other methods. R. S. C.

Synthesis of phthalides from 3 : 4 : 5-trimethoxybenzoic acid. F. E. King and T. J. King (*J.C.S.*, 1942, 726—727).—3 : 4 : 5 : 1-$(OMe)_3C_6H_2·CO_2H$, aq. 40% CH_2O, and conc. HCl at 140° yield 3 : 4 : 5-trimethoxyphthalide (**I**) or (more HCl) its 6-CH_2Cl derivative (**II**), m.p. 85° [also obtained from (**I**), CH_2O, and conc. HCl]; in each case ~5% of 6 : 6′-*methylenebis*-3 : 4 : 5-*trimethoxyphthalide* (**III**), m.p. 199°, is isolable. (**I**) with NaOEt and $Et_2C_2O_4$ in PhMe and N_2 at 100° (bath) affords *Et* 3 : 4 : 5-*trimethoxyphthalidylglyoxylate*, m.p. 188—189°. With CH_2O and HCl, syringic acid yields 4-*hydroxy*-3 : 5-*dimethoxy*-6-*chloromethylphthalide*, m.p. 185°, and 6 : 6′-*methylenebis*-4-*hydroxy*-3 : 5-*dimethoxyphthalide*, m.p. 223—224° [methylated to (**III**)], whilst 2 : 3 : 4 : 1-OH·$C_6H_2(OMe)_2·CO_2H$ gives only 5 : 5′-*methylenebis*-2-*hydroxy*-3 : 4-*dimethoxybenzoic acid*, m.p. 252° (efferv.). A. Li.

Kinetics and equilibria of the carbinol formation of phenolphthalein. —See A., 1943, I, 39.

Monoperphthalic acid.—See B., 1943, II, 5.

Synthesis of 3-hydroxyphthalic acid. O. Gisvold (*J. Amer. Pharm. Assoc.*, 1942, **31**, 202—203).—3 : 1 : 2-$NO_2·C_6H_3(CO_2H)_2$ is hydrogenated (Pt-black or Raney Ni in EtOH) to the NH_2-acid, converted (diazo-method) into 3 : 1 : 2-OH·$C_6H_3(CO_2H)_2$, m.p. 154° (lit. 151°, 244°) [anhydride, m.p. 195° (lit. 198—199°)]. J. E. P.

Inhibition of oxidation of aldehydes.—See A., 1943, III, 36.

Kinetics of oxidation of aldehydes by chromic acid. III. Oxidation of tolualdehydes. IV. Oxidation of bromobenzaldehydes.—See A., 1943, I, 38.

Behaviour of pyrogallol trimethyl ether and 3 : 4 : 5-trimethoxybenzonitrile with Grignard reagents. C. D. Hurd and H. E. Winberg (*J. Amer. Chem. Soc.*, 1942, **64**, 2085—2086).—3 : 4 : 5 : 1-$(OMe)_3C_6H_2·CN$ (prep. outlined) and $MgBu^{\beta}Br$ in boiling PhMe give mainly 4 : 3 : 5 : 1-OH·$C_6H_2(OMe)_2·COBu^{\beta}$ (**I**) (cf. Haller *et al.*, A., 1939, II, 508), but in Et_2O–PhMe at 40° give only 3 : 4 : 5 : 1-$(OMe)_3C_6H_2·COBu^{\beta}$ (**II**), b.p. 164—166°/6 mm., m.p. 37—39°. The structure of (**I**) is shown by prep. from (**II**) by H_2SO_4 at 35—40° and by oxidation (CrO_3–AcOH) to 1 : 2 : 6 : 4-O:$C_6H_2(OMe)_2$:O. 1 : 2 : 3-$C_6H_3(OMe)_3$ and MgMeI in boiling PhMe give 2 : 6 : 1-$(OMe)_2C_6H_3·OH$. R. S. C.

Synthesis of 2-substituted phenanthrenes. B. Riegel, M. H. Gold, and M. A. Kubico (*J. Amer. Chem. Soc.*, 1942, **64**, 2221—2222).—2-Substituted phenanthrenes are best (2-Ac 53, -EtCO 45, -Pr$^{\beta}$CO 48, -$CO_2Me·[CH_2]_2·CO$ 70, and -NH_2 25%) prepared by dehydro-

genating the corresponding readily available 9 : 10-H_2-derivatives by S at, *e.g.*, 250—280°. 2-iso*Butyryl*-9 : 10-*dihydrophenanthrene*, m.p. 71·6—72·6°, and *-phenanthrene*, m.p. 116·8—117·6°, and *Me γ-keto-γ-2-phenanthryl*-n-*butyrate*, m.p. 112·2—112·6°, are described. M.p. are corr. R. S. C.

Photochemical reactions of ketones. II. Benzpinacol and benzpinacolin. A. Banchetti (*Gazzetta*, 1941, **71**, 685—693).—The reduction of $COPh_2$ in $Pr^{\beta}OH$–HCl in sunlight gives $(CPh_2{\cdot}OH)_2$ (**I**), tetraphenylethylene oxide (**II**), and CPh_3Bz (**III**), in proportions depending on acidity and temp. In Et_2O–HCl in sunlight, (**II**) is formed. Mechanisms are discussed. With P_2O_5 in boiling C_6H_6, (**I**) gives (**III**). In boiling EtOH containing some dil. HCl, (**I**) is unchanged. E. W. W.

Synthesis of *o-o'*-anisoylbenzoic acid. B. P. Geyer (*J. Amer. Chem. Soc.*, 1942, **64**, 2226—2227).—Adding *o*-OMe·C_6H_4·MgBr (prep. from Mg activated by EtBr) in Et_2O to *o*-$C_6H_4(CO)_2O$ in C_6H_6 gives *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}$OMe-*o* (54%), m.p. 143—143·5°, and *αα*-di-*o*-anisylphthalide (18%), m.p. 148—149°. R. S. C.

Amino-alcohols. XI. Arylglyoxylohydroxamyl chlorides. N. Levin and W. H. Hartung (*J. Org. Chem.*, 1942, **7**, 408—415).—COAr·CCl:N·OH (**I**) are obtained by gradual addition of alkyl nitrite to a solution of COAr·CH_2Cl in Et_2O through which HCl is slowly passing. (**I**) are converted into OH·N:CAr·CCl:N·OH by NH_3OH,HCl in aq. EtOH at room temp. Thus are obtained phenylglyoxylohydroxamyl chloride (**II**), m.p. 132—133°, and the corresponding chloroglyoxime, decomp. 186—187°. The following derivation of (**II**) have been obtained; the m.p. of the corresponding *chloroglyoximes* are placed in parentheses: p-*methyl-*, m.p. 126—128° (decomp. 185—186°); p-*phenyl-*, m.p. 157—158° (decomp. 177°); p-*chloro-*, m.p. 120—121° (decomp. 181—182°); p-*methoxy-*, m.p. 137—139°; p-*hydroxy-*, decomp. 158—159° (decomp. 183—184°); 3 : 4-*dihydroxy-*, decomp. 184—185°. Alkaline decomp. of (**I**) gives the corresponding benzoic acids in excellent yield. (**I**) and NH_2Ph in anhyd. Et_2O at room temp. give the corresponding anilides; phenylglyoxylohydroxamanilide, m.p. 145—146° (decomp.), and its p-*methyl-*, m.p. 163—164° (decomp.), p-*phenyl-*, m.p. 135—136° (decomp.), p-*chloro-*, m.p. 145—146° (decomp.), p-*methoxy-*, m.p. 148—150° (decomp.), p-*hydroxy-*, m.p. 164—165° (decomp.), and 3 : 4-*dihydroxy-*, m.p. 155°, -derivatives are described. (**I**) appear to be catalytically hydrogenated to phenylethanolamine and its derivatives. H. W.

Dioximes. CXXV. G. Ponzio (*Gazzetta*, 1941, **71**, 693—695).—The compound, m.p. 108°, regarded by Avogadro (A., 1924, i, 294) as *oximino*-p-*tolylacetonitrile oxide* (**I**), is α-p-*tolylglyoxime peroxide* [3-p-*tolyl*-1 : 2 : 5-*oxadiazole* 5-*oxide*] (**II**); this in Et_2O with aq. Na_2CO_3 gives (**I**), m.p. 112°, which, unlike (**II**), with conc. HCl readily gives *p*-tolylchloroglyoxime, *p*-$C_6H_4Me{\cdot}C(:N{\cdot}OH){\cdot}CCl:N{\cdot}OH$. With HCl–$Et_2O$, benzoyloximino-*p*-tolylacetonitrile oxide gives *p*-$C_6H_4Me{\cdot}C(:N{\cdot}OBz){\cdot}CCl:N{\cdot}OH$. E. W. W.

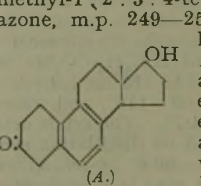
Enediols. X. An aminostilbenediol. R. C. Fuson and S. L. Scott (*J. Amer. Chem. Soc.*, 1942, **64**, 2152—2153; cf. A., 1942, II, 91).—(2 : 6 : 1-$C_6H_3Me_2{\cdot}CO)_2$ and HNO_3 (*d* 1·59) at 0° give the 3 : 3'-(NO_2)$_2$- (**I**) (92%), m.p. 211—212° (corr.), and 3 : 5 : 3' : 5'-(NO_3)$_4$-derivative (1%), m.p. 273—275° (decomp.), and a substance, m.p. 241—243° (decomp.; corr.). (**I**) does not form an oxime or react with NHPh·NH_2. H_2–PtO_2 reduces (**I**) in EtOH slowly to colourless [3 : 2 : 6 : 1-$NH_2{\cdot}C_6H_2Me_2{\cdot}C(OH):]_2$ (**II**), which is oxidised with great ease to 3 : 3'-*diamino*-vic.-*xylil*, m.p. 201—202° (corr.) (*Ac_2* derivative, m.p. 296—297°). (**II**) yields a hydrochloride (**III**), which with aq. NaOH gives an orange substance, m.p. 229—230° (decomp.; corr.). (**III**) with Ac_2O–C_5H_5N, or (**II**) with boiling Ac_2O, gives *αβ-diacetoxy-αβ-di*-3-*diacetamido*-vic.-*xylylethylene*, m.p. 241—242° (corr.). 3-NH_2 thus does not affect the stability of the enediol. R. S. C.

Absorption spectra and structures of pyrethrins I and II.—See A., 1943, I, 31.

Structures of highly arylated indenones. Their behaviour with bromine. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2127—2130).—2 : 3 : 5 : 6-Tetraphenylindanone (**I**) and Br in $CHCl_3$ give (probably) 2-*bromo-* (**II**) (84%), m.p. 241° (decomp.), and then 2 : 7a-*dibromo*-2 : 3 : 5 : 6-*tetraphenyl*-2 : 7a-*dihydroindenone* (**III**), m.p. 270° (decomp.), which is also obtained (75%) from (**I**) by 2 mols. of Br. KI–AcOH, KOH–EtOH, or MgRX reduces (**III**) to (**II**), but Zn–AcOH yields (**I**). HBr has no effect on (**II**) or (**III**); (**II**) may be formed by allylic rearrangement. $(CH{\cdot}CO)_2O$ does not add to (**II**) or (**III**). With MgPhBr and then aq. NH_4Cl, (**II**) gives 2 : 3 : 5 : 6-*tetraphenyl*-2 : 7a-*dihydroindenone* (50%), m.p. 125° (instantaneous) or 95°, resolidifies, remelts at 164—166°, rearranged at the m.p. or in boiling AcOH to (**I**). 2 : 3 : 5 : 6-Tetraphenyl-3*a* : 4- or -3*a* : 7*a*-dihydroindenone with Br–$CHCl_3$ gives 4-*bromo*-2 : 3 : 5 : 6-*tetraphenyl*-3a : 4-*dihydroindenone* (**IV**) (84%), m.p. 196° (0·5 active H; adds 1·5 MgMeI), dehydrogenated by Br–$CHCl_3$ to 4-*bromo*-2 : 3 : 5 : 6-*tetraphenylindenone* (**V**) (90%), m.p. 234—235°. (**V**) is reduced by Zn–AcOH to 4-*bromo*-2 : 3 : 5 : 6-*tetraphenylindanone* (57%), m.p. 175°, and with MgPhBr gives 4-*bromo*-1-*hydroxy*-1 : 2 : 3 : 5 : 6-*pentaphenylindene* (52%), m.p. 249°. MgPhBr and (**IV**) give (mechanism discussed) 2 : 3 : 5 : 6 : 7-*pentaphenyl*-3a : 7a-*dihydroindenone* (27%), m.p. 246° [and a *product* (20%), $C_{75}H_{57}O_2Br$, m.p. 229° (decomp.) (consumes 2·7 MgMeI; 2 active H)], which with MgPhBr gives 1-*hydroxy*-1 : 2 : 3 : 5 : 6 : 7-*hexaphenyl*-3a : 7a-*dihydroindene* (69%), m.p. 240° (not dehydrated by 2% H_2SO_4–AcOH), and with HBr gives a *substance*, $C_{39}H_{27}Br$, m.p. 194°. MgMeI and (**IV**) give 2 : 3 : 5 : 6-*tetraphenyl*-7-*methyl*-3a : 7a-*dihydroindenone* (**VI**) (33%), m.p. 170°, and, in one experiment, 10% of a *ketone*, $C_{34}H_{26}O$, m.p. 217°. (**VI**) consumes 1 MgMeI, showing 0·3 active H, is unaffected by HBr or $(CH{\cdot}CO)_2O$, and with Br gives the 7a-*Br*-derivative (80%), m.p. 239°, whence it is regenerated by MgMeI. R. S. C.

Enolisation in the Reformatsky reaction. M. S. Newman (*J. Amer. Chem. Soc.*, 1942, **64**, 2131—2133).—Recovery of ketone after a Reformatsky reaction is due to enolisation and formation of $CR_2{:}CR'{\cdot}OZnBr$ and AlkOAc. Thus, acetomesitylene (**I**) consumes 1 mol. of $CH_2Br{\cdot}CO_2Me$ (**II**) in presence of Zn and C_6H_6 but, after hydrolysis, yields 50% of MeOAc and 90% of (**I**); MeOAc is also obtained by distillation prior to hydrolysis, but in ≯ traces by prolonged boiling of (**II**) and Zn in C_6H_6. Experiments with 1-keto-2-*o*-tolyl-3-methyl- and 1-keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene and 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (modified prep.) show that (i) for different Br-esters enolisation of the ketone increases in the order $CH_2Br{\cdot}CO_2Et$ < $CHMeBr{\cdot}CO_2Et$ < $CHEtBr{\cdot}CO_2Et$; (ii) use of I to initiate reaction decreases enolisation; (iii) use of dioxan as a solvent promotes enolisation. R. S. C.

Preparation of 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene from β-naphthol and analogous transformations. J. W. Cornforth, (Mrs.) R. H. Cornforth, and (Sir) R. Robinson (*J.C.S.*, 1942, 689—691).—2-$C_{10}H_7{\cdot}$OMe with Na–EtOH at 115° (bath), followed by immediate hydrolysis (aq. HCl), gives 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (**I**) (56%). 1 : 2-$C_{10}H_6$Me·OMe similarly affords 2-*keto*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**II**) (10%), b.p. 137—138°/18 mm. [*semicarbazone*, m.p. 200—202° (decomp.)], and some 2-methoxy-1-methyl-5 : 6 : 7 : 8-tetrahydronaphthalene, m.p. 51°. 2-*Keto*-5-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**III**) (63%), b.p. 120—122°/0·4 mm., is similarly prepared from 1 : 6-$C_{10}H_6(OMe)_2$; the 6-OMe-isomeride is formed by hydrolysis (aq. EtOH–HCl) of 2 : 6-dimethoxy-3 : 4-dihydronaphthalene (A., 1941, II, 295). Dehydrogenation (S at 220—225°) of 1-keto-6-methoxy-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene and methylation (Me_2SO_4–aq. NaOH) of the phenol gives 2 : 5-*dimethoxy*-1-*methylnaphthalene*, m.p. 85°; reduction and hydrolysis then yields 2-keto-5-methoxy-1-methyl-(*semicarbazone*, m.p. 188—190°) and some 1-keto-6-methoxy-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (2 : 4-dinitrophenylhydrazone, m.p. 249—250°). Equilenin Me ether when reduced and hydrolysed affords the *keto-alcohol* (*A*), m.p. 152—153°, $[\alpha]_D^{22}$ +33·6° in EtOH. The reaction is general only for 2-methoxynaphthalenes; reduction of 2 : 7-dimethoxyphenanthrene gives only the 9 : 10-H_2-derivative. (**I**) and MeI–NaOPr$^{\beta}$–Pr$^{\beta}$OH (in N_2) give (**II**), whereas (**III**) similarly yields 2-*keto*-5-*methoxy*-1 : 1-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 83—85° (*semicarbazone*, m.p. 192—194°; 2 : 4-*dinitrophenylhydrazone*, m.p. 184°).



(*A.*)

A. T. P.

Structure of the bimolecular product formed by the action of acidic dehydrating agents on anhydroacetonebenzil. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2123—2127).—The substance previously (A., 1933, 1164) believed to be 4 : 7-*endo*-keto-3 : 3a : 5 : 6- is now considered to be 4 : 7-endo*keto*-2 : 3 : 5 : 6-*tetraphenyl*-3a : 4 : 7 : 7a-*tetrahydroindenone* (**I**), the rearrangement, $>CPh{\cdot}CPh{:}CH \rightarrow >CH{\cdot}CPh{:}CPh$, occurring during the formation of (**I**) from anhydroacetonebenzil [4-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone]. (**I**) consumes 2 MgMeI, adding 1 mol. and giving 1 CH_4; with MgRHal it gives only (75—85%) monocarbinols; addition occurs at $C_{(1)}$; the *endo*-CO enolises, reacts with MgMeI, and, after decomp., ketonises. With Br–AcOH at 100°, (**I**) gives the 4 : 7 : 7a-*Br*$_3$-derivative, m.p. 229—230°, converted by MgMeI into 4 : 7 : 7*a*-*tribromo*-1-*hydroxy*-2 : 3 : 5 : 6-*tetraphenyl*-1-*methyl*-4 : 7-endo-α-*hydroxyethylidene*-3a : 4 : 7 : 7a-*tetrahydroindene* (**II**), m.p. 278° [consumes 2·7 MgMeI, then regenerates (**II**)]. PCl_5 converts (**I**) in boiling C_6H_6 into a *Cl*$_1$-derivative, m.p. 215°. By MgRHal and then standard reactions, (**I**) gives 1-*hydroxy*-4 : 7-endo-*keto*-2 : 3 : 5 : 6-*tetraphenyl*-1-*methyl*-, m.p. 262° [*acetates*, *forms* (prep. by AcCl), m.p. 202° and (prep. by Ac_2O–H_2SO_4) m.p. 180°; derived 1-*chloride*, m.p. 219°, and 1-*bromide*, m.p. 191°)], -2 : 3 : 5 : 6-*tetraphenyl*-1-α-*naphthyl*- (**III**), m.p. 295° (derived 1-*bromide*, m.p. 233°), and -1 : 2 : 3 : 5 : 6-*pentaphenyl*- (**IV**), m.p. 226° [*acetate* (prep. by Ac_2O–H_2SO_4), m.p. 235°; derived 1-*chloride*, m.p. 216°], -3a : 4 : 7 : 7a-*tetrahydroindene*. 2 : 3 : 5 : 6-Tetraphenylindenone and MgPhBr give 1-*hydroxy*-1 : 2 : 3 : 5 : 6-*pentaphenylindene* (87%), m.p. 220°, converted by warm HBr–AcOH into the 1-*bromide* (89%), m.p. 203°. With Zn dust in boiling AcOH this gives a *hydrocarbon*, $C_{39}H_{28}$, m.p. 280°, which is also obtained (with evolution of CO and H_2O) from (**IV**) at 290—310°, a rearrangement

occurring in one or other reaction. (**III**) gives similarly a *hydrocarbon*, $C_{43}H_{30}$, m.p. 298°. Both oximes (*loc. cit.*) of (**I**) with boiling EtOH–conc. HCl regenerate (**I**). Formation of 2-phenylquinoline from CHPh:CH·CH:NPh (unimol. in boiling EtOH) (Peine, A., 1884, i, 1344) involves a rearrangement analogous to that during the prep. of (**I**). R. S. C.

Action of organomagnesium compounds on dianils of αβ-diketones. Cyclisation of the α-anilinoketones obtained. (Mlle.) M. Garry (*Ann. Chim.*, 1942, [xi], **17**, 5—99).—Partly an account of work previously reviewed (A., 1939, II, 376). γ-Anilino-β-anilo-γ-methylbutane [Me α-anilino*iso*propyl ketone anil] (**I**), m.p. 66° [picrate, m.p. 150° (decomp.); *Ac* derivative, m.p. 242°], is hydrolysed to the ketone (**II**) [oxime, m.p. 142°, also obtained from (**I**) and NH_2OH, or from NO·CHMe·CMe_2·O·NO_2 and NH_2Ph (cf. Klingstedt, A., 1926, 44); *semicarbazone*, m.p. 182°; picrate, m.p. 112°; Ac derivative, m.p. 74°; *methiodide* (**III**), m.p. 175° (decomp.)], which is reduced by Na–EtOH to *γ-anilino-γ-methylbutan-β-ol*, b.p. 149°/17 mm. (*N-phenylcarbamyl* derivative *phenylcarbamate*, m.p. 191°; unstable picrate, m.p. 110°). (·CMe:NPh)$_2$ (**IV**) with MgMeI in boiling C_6H_6 gives *βγ-dianilino-βγ-dimethylbutane* (**V**), m.p. 37°, b.p. 216—217°/12 mm. [*sulphate*, m.p. 190° (decomp.); *dihydrochloride*, m.p. ~190° (decomp.); *picrate*, m.p. 163°]. The anil, m.p. 95° (softens from 82°), b.p. 218—219°/20 mm. (picrate, m.p. 143—144°), of γ-anilino-γ-methylpentan-β-one (picrate, m.p. 95°) and *γδ-dianilino-γδ-dimethylhexane*, forms, m.p. 89° and 65° (probably stereoisomerides) [the mixture gives a *dihydrochloride*, m.p. ~170° (decomp.), and a *monopicrate*, m.p. 138° (decomp. from 125°)], are prepared from (**IV**) and MgEtBr. γ-Anilino-β-anilo-γ-methylheptane (**VI**), m.p. 74°, b.p. 225—230°/18 mm. [from (**IV**) and $MgBu^aBr$–Et_2O], is hydrolysed (aq. HCl) to the ketone (**VII**), m.p. 86° [picrate, m.p. 130°, also obtained from (**VI**) and picric acid]. Hydrolysis of the crude reaction product also affords some NHPhBu and (probably) 2 : 3-dimethyl-1-butylindole, b.p. 155—160°/17 mm. (*picrate*, m.p. 97°). $MgBu^aBr$ and (**IV**) in C_6H_6 give εζ-dianilino-εζ-dimethyldecane [*dihydrochloride*, m.p. 135° (decomp.)]. (**IV**) and CH_2Ph·MgCl afford *γ-anilino-β-anilo-δ-phenyl-γ-methylbutane*, m.p. 100°, and thence the *ketone* (**VIII**), m.p. 74°, b.p. 208—210°/16 mm. (*picrate*, m.p. 125°; *oxime*, m.p. 178°), reduced to *γ-anilino-δ-phenyl-γ-methylbutan-β-ol*, b.p. 213°/14 mm. Ph α-anilino-α-phenylethyl ketone (**IX**), m.p. 142° (*hydrochloride*, m.p. 138—142°; *picrate*, m.p. 168°), is not obtained (cf. Cameron, A., 1930, 345) from *Ph α-chloro-α-phenylethyl ketone*, m.p. 57—58° (from COPh·CPhMe·OH and $SOCl_2$), and NH_2Ph, whereby (probably) *Ph α-phenylvinyl ketone*, m.p. 52—57°, results. (·CPh:NPh)$_2$ and MgEtI give *β-anilino-α-anilo-αβ-diphenylbutane*, m.p. 183·5° (free *ketone*, m.p. 143°), with (mainly) COPh·CPh:NPh, NH_2Ph, NHPhEt, Bz_2, NHPhBz, and BzOH. Absorption spectra of many of the compounds are shown. (**II**) with NH_2Ph (excess) and NH_2Ph,HCl at 180°, with a little NH_2Ph,HCl at 180°, or with $ZnCl_2$ at 140°, gives 2 : 3 : 3-trimethylindolenine, b.p. 110°/10 mm. [picrate, m.p. 155°; methiodide, also obtained by heating (**III**)], also prepared from (**II**) by heating with a little Na_2SO_4 or NH_2Ph,HCl. NHPh·CMeEt·COMe similarly yields 2 : 3-dimethyl-3-ethylindolenine, b.p. 128°/22 mm., and (**VII**) with a little NH_2Ph,HCl at 180° affords 2 : 3-*dimethyl-3-butylindolenine*, b.p. 142—143°/17 mm. (*picrate*, m.p. 137°; *methiodide*, m.p. 211°). (**VIII**) with NH_2Ph + NH_2Ph,HCl at 175—180° gives 2 : 3-dimethylindole and a little CH_2Ph·NHPh, but with $ZnCl_2$ at 180° affords 3-*benzyl*-2 : 3-*dimethylindolenine*, b.p. 188—190°/18 mm. (*picrate*, m.p. 139°). (**IX**) and NH_2Ph + NH_2Ph,HCl at 160—165° yield one or other of the isomerides, 2 : 3-*diphenyl*-3- (**X**), m.p. 108° (no reaction with Ac_2O; *picrate*, m.p. 155°), or 3 : 3-*diphenyl*-2-*methylindolenine* (**XI**), m.p. 145° (*picrate*, m.p. 210°); (**XI**) is usually formed and conditions for preparing (**X**) are not established. The *methiodide*, m.p. 188°, of (**X**) is converted by NaOH–EtOH into (probably) 2-hydroxy-2 : 3-diphenyl-1 : 3-dimethylindoline, m.p. 110°, whereas the *methiodide*, m.p. 230°, of (**XI**) and aq. NaOH in Et_2O give 3 : 3-*diphenyl*-1-*methyl*-2-*methyleneindoline*, m.p. 101° (*picrate*, m.p. 178°). With Ac_2O–NaOAc, (**XI**) affords 1-*acetyl*-3 : 3-*diphenyl*-2-*methyleneindoline*, m.p. 138°. Cyclisation of (**IX**) to (**XI**) is effected by a little NH_2Ph,HCl at 170—180°, or by heating its hydrochloride to 190°. (**X**) is synthesised from Mg 2 : 3-diphenylindolyl iodide and MeI in PhMe at 90°, or from the *phenylhydrazone*, m.p. 129—131°, of COPh·CHPhMe and aq. HCl. A. T. P.

Action of alkaline reagents on the bimolecular product formed by the action of acidic dehydrating agents on anhydroacetonebenzil. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2120—2123).—4 : 7-*endo*Keto-2 : 3 : 5 : 6-tetraphenyl-3*a* : 4 : 7 : 7*a*-tetrahydroindenone (modified prep.; 90% yield) with boiling KOH–EtOH gives 2 : 3 : 5 : 6-*tetraphenyl*-3*a* : 4 : 7 : 7*a*-*tetrahydroindenone-7-carboxylic acid* (**I**) (76%), m.p. 275—276° (no CO evolved) (*anilide*, m.p. 269°) (cf. A., 1933, 1164; 1937, II, 457). NaOMe or NaOEt gives similarly the *Me*, m.p. 193° [also obtained from (**I**) by CH_2N_2], and *Et* ester, m.p. 159—160° (with some acid), respectively, of (**I**). The esters are stable to $KMnO_4$–$COMe_2$, but (**I**) with $KMnO_4$–aq. K_2CO_3 at 85—95° gives, by loss of HCO_2H, 2 : 3 : 5 : 6-*tetraphenyl*-3*a* : 4-*dihydroindenone* (**II**) (56%), m.p. 239—240°, which is also obtained from 2 : 3 : 5 : 6-tetraphenyl-3*a* : 7*a*-dihydroindenone (**III**) (modified prep.; 70—75% yield; cf. *loc. cit.*) by HBr–AcOH at 100° or H_2SO_4–AcOH. (**II**) does not add (:CH·CO)$_2$O, adds 1 MgMeI (no gas), and at 300° is isomerised to 2 : 3 : 5 : 6-tetraphenylindanone (**IV**). With MgPhBr–Et_2O at room temp., followed by aq. NH_4Cl, (**II**) gives, by 1 : 2- and 1 : 4-addition, respectively, 1-*hydroxy*-1 : 2 : 3 : 5 : 6-*pentaphenyl*-3*a* : 4-*dihydroindene* (**V**) (25%), m.p. 233°, and 2 : 3 : 5 : 6 : 7-*pentaphenyl*-3*a* : 4 : 7 : 7*a*-*tetrahydroindenone* (**VI**) (60%), *forms*, m.p. 178—179° and 145—146°; when dil. acid replaces the NH_4Cl, a *hydrocarbon*, $C_{39}H_{28}$ (**VII**), m.p. 222°, which does not add (:CH·CO)$_2$O, is isolated instead of (**V**). These results prove the structure of (**I**). With MgPhBr and then aq. NH_4Cl, (**IV**) gives 1-*hydroxy*-1 : 2 : 3 : 5 : 6-*pentaphenylindane*, m.p. 228—229° (decomp.), and thence (H_2SO_4–AcOH) (**VII**); (**III**) gives similarly a glassy carbinol and then (**VII**). (**VI**) exists partly as the enol, since with AcCl it gives an *acetate* (70%), m.p. 115° [consumes 2 MgMeI without evolution of gas; subsequent hydrolysis regenerates (**VI**)], and with MgMeI gives 0·67 CH_4; it gives no oxime, does not react with (:CH·CO)$_2$O, and with Br–$CHCl_3$ affords the 7a-*Br*-derivative, anhyd., m.p. 218—219°, and +C_6H_6, softens at ~144°, m.p. 234° [whence (**VI**) is regenerated by MgMeI (1 mol. consumed; no CH_4 evolved)], which is unaffected by C_5H_5N, KOAc, HBr, AcCl, or Br. Some of the above reactions necessitate allylic rearrangements. R. S. C.

Decahydronaphthalene-1 : 5-dione and 2 : 2′-diketodi*cyclo*pentyl. B. J. F. Hudson and (Sir) R. Robinson (*J.C.S.*, 1942, 691—693).—Et α-bromoadipate and Ag powder at 140—160° give *Et$_4$ octane-αδεθ-tetracarboxylate*, b.p. 192—195°/0·2—0·3 mm., converted by K (not Na) in PhMe at room temp., followed by hydrolysis with aq. EtOH–HCl, into 2 : 2′-*diketodi*cyclo*pentyl* (**I**), m.p. 67—69° [*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 230—240° (decomp.)], contaminated with (probably) (**III**) (below). Methylation ($NaNH_2$–MeI–Et_2O) of (**I**) gives a *Me*$_1$ derivative, b.p. 175—185°/14 mm. [*dioxime*, m.p. 207—211° (decomp.)]. (**I**) is prepared (2—4% yield) in a purer form by hydrolysis (aq. NaOH–EtOH) of the product from Et sodio*cyclo*pentanone-2-carboxylate and I in Et_2O. Hydrogenation (Raney Ni in EtOH) of 1 : 5-$C_{10}H_6(OH)_2$ at 150—200°/120 atm. gives mixed decahydro-α-naphthols (*cis*-form, m.p. 92—94°, isolated) and 5—8% of x-*decahydronaphthalene*-1 : 5-*diol* (**II**), m.p. 130—150° [a form, m.p. 159—161°, probably a stereoisomeride of that described by Campbell *et al.* (A., 1942, II, 90), is described]. Use of Cu chromite as catalyst gives mainly phenolic products; 5 : 6 : 7 : 8-tetrahydro-1-naphthol, m.p. 65°, and a *substance*, m.p. 165—170° (*acetate*, m.p. 129—131°), are isolated. (**II**) and CrO_3–aq. AcOH at 0° to room temp. yield 10% of *decahydronaphthalene*-1 : 5-*dione* (**III**) (probably *trans*), m.p. 165—167° [*bisphenylhydrazone* (**IV**), m.p. 230°], or a mixture of (**III**) and the cis-*form*, m.p. 68—72° [*bisphenylhydrazone* (**V**), m.p. 172—173° to a gum, becoming clear at 208—210°]; mixtures are converted into (**III**) by AcOH at 100° (6 hr.). (**V**) and aq. HCl or EtOH–HCl yield 3 : 4 : 7 : 8 : 9 : 10-*hexahydronaphtha*(1 : 2 : 5 : 6)-*bis*-(2 : 3)-*indole*, m.p. 312—316° (decomp.); (**IV**) similarly yields a *substance*, m.p. 292—296° (decomp.). A. T. P.

Homogeneous catalysis and solvent effects in or diene synthesis. —See A., 1943, I, 21.

Alkylation of 1 : 4-naphthaquinones with esters of quadrivalent lead. L. F. Fieser and F. C. Chang (*J. Amer. Chem. Soc.*, 1942, **64**, 2043—2052).—$Pb(OAc)_4$ in boiling AcOH introduces Me adjacent to a CO of 1 : 4-naphthaquinone or its alkyl derivatives, the reaction being much accelerated by presence of a promoter, *e.g.*, $CH_2(CO_2H)_2$, MeOH, etc. (cf. below). 2-Methyl-5 : 8-dihydro-1 : 4-naphthaquinol (**I**) etc. promotes its own methylation. Use of RCO_2H, a promoter, and an excess of Pb_3O_4 leads to introduction of R. (**I**) (improved prep.) or the derived H_2-quinone with $Pb(OAc)_4$ in boiling AcOH gives 2 : 3-dimethyl-1 : 4-naphthaquinone (**II**) (up to 28%) (*quinol diacetate*, m.p. 190—190·5°). 2-Methyl-1 : 4-naphthaquinone (**III**) is slowly affected by this treatment, but is rapidly converted into (**II**) if interaction occurs in presence of $CH_2(CO_2H)_2$ (49% yield), $CHMe(CO_2H)_2$, $CH_2Ac·CO_2Et$, $CHEtAc·CO_2Et$ (46% yield), MeOH, or tartronic acid, but $CMe_2(CO_2H)_2$, $CH_2(CO_2Et)_2$, $CHPh_3$, *cyclo*pentadiene, and acenaphthene are ineffective. *o*-Xyloquinone and $(CH_2{:}CMe)_2$ in boiling EtOH give 2 : 3 : 6 : 7-*tetramethyl*-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone*, m.p. 105—106·5°, isomerising to 2 : 3 : 6 : 7-tetramethyl-5 : 8-dihydro-1 : 4-naphthaquinol, m.p. 269—270·5° (lit. 232°), oxidised by CrO_3 or $Pb(OAc)_4$ to 2 : 3 : 6 : 7-tetramethyl-1 : 4-naphthaquinone, m.p. 169·5—170° (lit. 167—168°) (*quinol diacetate*, m.p. 216—217°), which is also obtained from 2 : 6 : 7-trimethyl-5 : 8-dihydro-1 : 4-naphthaquinol by $Pb(OAc)_4$ in boiling AcOH. 2-Methyl-3-ethyl-1 : 4-naphthaquinone, m.p. 72—72·6° (*quinol diacetate*, m.p. 106—108°, resolidifies, remelts at 116—117°), is obtained from (**III**) by $EtCO_2H$, Pb_3O_4, and $CH_2Ac·CO_2Et$ at 100° or from 1 : 2 : 4-O:$C_{10}H_5Et$:O by $Pb(OAc)_4$–AcOH–$CH_2(CO_2H)_2$. With RCO_2H, Pb_3O_4, and a promoter at 100° to 120—130° (**III**) gives similarly 2-*methyl*-3-n- (**IV**) (47%), m.p. 65—65·4°, sublimes at 53—58°/1 mm. (*quinol diacetate*, m.p. 93·5—95°), and -3-iso-*propyl*- (**V**) (59%), m.p. 110—111·2° (*quinol diacetate*, m.p. 115—116°), -3-n-*heptyl*- (34%), m.p. 80·4—80·8°, sublimes at 70—76°/1 mm. (*quinol diacetate*, m.p. 64—65°), -3-*benzyl*- (65% crude), m.p. 108—108·5°, sublimes at 80°/1 mm. (*quinol diacetate*, m.p. 163—164·5°), and -3-β-*phenylethyl*- (14·5%), m.p. 73—73·5°

(quinol diacetate, m.p. 140·5—141·2°), -1 : 4-*naphthaquinone*. 1 : 2 : 4-O:$C_{10}H_5Pr^{\alpha}$:O, m.p. 40·5—41° (lit. 39—39·5°), with $Pb(OAc)_4$ and $CH_2(CO_2H)_2$ in boiling AcOH (not at 100°) gives (**IV**). *β-Naphthyldimethylcarbinol* (prep. from 2-$C_{10}H_7$·COMe by MgMeI), m.p. 65—65·5°, could not be reduced. 2-$C_{10}H_7Pr^{\beta}$ (prep. by a Friedel-Crafts reaction; 14% yield) with CrO_3 gives 1 : 2 : 4-O:$C_{10}H_5Pr^{\beta}$:O, an oil, which with $Pb(OAc)_4$–$CH_2(CO_2H)_2$–AcOH gives (**V**). M.p. are corr. R. S. C.

Alkylation of *p*-quinones by acyl peroxides. L. F. Fieser and A. E. Oxford (*J. Amer. Chem. Soc.*, 1942, **64**, 2060—2065).—Interaction of 1 : 2 : 4-O:$C_{10}H_5Me$:O (**I**) with $Pb(OAc)_4$ (excess) in AcOH at 90—100° is promoted by MeOH, H_2O, $Pr^{\beta}OH$, $Bu^{\gamma}OH$ (induction period), Pr^{β}_2O, C_6H_6, PhMe, *cyclo*hexane (**II**), and *n*-C_8H_{18}, the products being 1 : 2 : 3 : 4-O:$C_{10}H_4Me_2$:O, CO_2, and (?) C_2H_6. In absence of (**I**), all the promoters except $Bu^{\gamma}OH$ cause decomp. of $Pb(OAc)_4$ in AcOH, relative efficiencies being C_6H_6 > (**II**) > C_8H_{18} > PhMe. The (**II**) is largely unchanged; the decomp. of $Pb(OAc)_4$ eventually ceases but is restarted by adding more (**II**); $Pb(OAc)_4$ is unchanged in (**II**) alone and then does not methylate (**I**); $Pb(OAc)_2$ formed may be partly responsible, since it retards the reaction of (**I**) with $Pb(OAc)_4$ in AcOH–PhMe–(**II**). Diacyl peroxides (best, 1 mol.) in AcOH at 90° alkylate many quinones, no promoter being required; the acyl may be unsaturated; the reacting quinone may be substituted by a lower alkyl, Br, or OH, but not by OMe or higher alkyl; aroyl and aracyl peroxides are consumed but give no or indefinite products. Thus are prepared: from (**I**), 2-*methyl*-3-*pentadecyl*- (60%), m.p. 95—97°, -3-*heptadecyl*- (60%), m.p. 96°, -3-Δ^{μ}-*heneicosenyl*- (? mixed isomerides) (small yield), m.p. 39—81°, -3-*norchaulmoogryl*- (40%), softens at 57°, m.p. 65—68°, -3-Δ^{ι}-*decenyl*- (40%), m.p. 68°, and -3-Δ^{α}-*hexadecenyl*- (25%), m.p. 72—73°, -1 : 4-*naphthaquinone*; phthiocol (50%) from 1 : 2 : 4-O:$C_{10}H_5(OH)$:O; 2-*pentadecyl*-1 : 4-*naphthaquinone* (small yield), m.p. 71—72°, from 1 : 4-O:$C_{10}H_6$:O; duroquinone (small yield) and 2 : 3 : 5-*trimethyl*-6-*pentadecyl*-1 : 4-*benzoquinone* (25%), m.p. 74°, from 1 : 2 : 3 : 5 : 4-O:C_6HMe_3:O; 1 : 2 : 3 : 5 : 4-O:$C_6HMe(OMe)_2$:O from 1 : 2 : 6 : 4-O:$C_6H_2(OMe)_2$:O; 1 : 3 : 6 : 2 : 5 : 4-O:$C_6Ph_2(OH)_2$:O (very little) and 2 : 5-*dihydroxy*-3-*pentadecyl*-1 : 4-*benzoquinone* (small yield), m.p. 136—138°, from 1 : 2 : 5 : 4-O:$C_6H_2(OH)_2$:O; 1 : 2 : 3 : 5 : 6 : 4-O:C_6MeBr_3:O (with H_2–Pd–$BaSO_4$–NaOAc gives toluquinol) (68%) from 1 : 2 : 3 : 5 : 4-O:C_6HBr_3:O. R. S. C.

Celastrol. Spectrographic characterisation and colour tests. L. F. Fieser and R. N. Jones (*J. Amer. Pharm. Assoc.*, 1942, **31**, 315—317).—The ultra-violet absorption spectra of celastrol (**I**) and methylcelastrol indicate β-naphthaquinonoid structures. Colour reactions with aq. EtOH–$NaHSO_3$, boroacetic anhydride, and CN·CH_2·CO_2Et–NH_3–EtOH indicate that (**I**) is an 8-hydroxy-3 : 4-dialkyl-1 : 2-naphthaquinone and may be the 2-methyl-3-hydrogeranyl (or homohydrogeranyl) derivative. F. O. H.

" Naphthylidenesulphanilamide " derivatives. F. Irreverre and M. X. Sullivan (*J. Amer. Chem. Soc.*, 1942, **64**, 2230—2231).—Treating *p*-NH_2·C_6H_4·SO_2·NH_2 (**I**) in H_2O with 1 : 4 : 2-O:$C_{10}H_5(SO_3Na)$:O at ~50—60° (later 0°) gives 3-*hydroxy*-1 : 4-*naphthaquinone*-1-p-*sulphamylanil*, m.p. 271—273°; (**I**) with, successively, 1 : 4 : 6 : 2-O:$C_{10}H_4(SO_3Na)_2$:O, H_2O_2, and NaCl at room temp. (later 0°) gives *Na* 3-*hydroxy*-1 : 4-*naphthaquinone*-1-p-*sulphamylanil*-7-*sulphonate*, and with 1 : 2 : 4-O:$C_{10}H_5(SO_3K)$:O at ~70° and then HCl at 30° (later cooling at 0°) gives 3-p-*sulphamylanilino*-2-*sulpho*-1 : 4-*naphthaquinone*-1-p-*sulphamylanil*, m.p. 276—278°. R. S. C.

Naphtol AS series. VII. Synthetic experiments. IV. 2-Hydroxy-3-naphthoyl derivatives of aminoanthraquinones. R. V. Bhat, (Miss) K. D. Gavankar, and K. Venkataraman (*J. Indian Chem. Soc., Ind. Ed.*, 1942, **5**, 171—177; cf. A., 1942, II, 405).—1-2′-*Hydroxy*-3′-*naphthoylaminoanthraquinone*, m.p. 240—241° (*acetate*, m.p. 261—262°; *benzoate*, m.p. 225—226°; p-*toluenesulphonate*, m.p. 288—289°), is prepared from 1-aminoanthraquinone (**I**) and 2 : 3-OH·$C_{10}H_6$·COCl in boiling $PhNO_2$. 1 : 4-Diaminoanthraquinone similarly affords 1 : 4-*di*-(2′-*hydroxy*-3′-*naphthoylamino*)*anthraquinone*, m.p. 290—291° [*diacetate*, m.p. 285—286° (decomp.); *dibenzoate*, m.p. 249—250°; *di*-p-*toluenesulphonate*, m.p. 225—226°], but 1 : 5-diaminoanthraquinone similarly yields 1-*amino*-5-(2′-*hydroxy*-3′-*naphthoylamino*)*anthraquinone*, m.p. 278—279° [Ac_2 derivative, m.p. 325° (decomp.)], insol. in NaOH–EtOH at 60°. 1-p-*Nitrobenzamidoanthraquinone*, m.p. 280—281° [from (**I**) and *p*-NO_2·C_6H_4·COCl in PhCl at 150°], is reduced by Fe and a little AcOH to the NH_2-derivative, m.p. 336—337°, converted into 1-p-2′-*hydroxy*-3′-*naphthoylaminobenzamidoanthraquinone*, m.p. 349—350°. Clear solutions are not obtained with the compounds and aq. alkali. Dyeing trials (as vat dyes; also after development) are recorded. A. T. P.

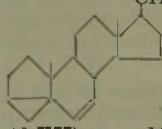
IV.—STEROLS AND STEROID SAPOGENINS.

Recovery of sterols.—See B., 1943, III, 21.

Beech bark (*Fagus silvatica*). **III.** E. Clotofski and W. Herr (*Ber.*, 1942, **75**, [*B*], 237—243).—Extraction with light petroleum and concn. of the extract causes the separation of a mixture of isomeric fatty alcohols and paraffins, a *compound* (**I**), m.p. 290—292°, $[\alpha]_D^{18}$ +56·3° in $CHCl_3$, and a sterol (**II**) isolated by pptn. with digitonin and also obtained with arachidic and resin acid from the light petroleum mother-liquors. (**I**) gives the Salkowski and Liebermann–Burchard reactions. It could not be recovered unchanged by hydrolysis of the *acetate*, m.p. 271°, *formate*, m.p. 181°, or *benzoate*, m.p. 118—122°. It is hydrolysed by C_5H_{11}·OH–HCl to a *compound*, $C_{29}H_{48}O_2$, m.p. 232° (*diacetate*, m.p. 273°), which is neutral and does not contain :CO; a sugar residue is not removed by hydrolysis. (**II**), $C_{24}H_{40}O$ (+EtOH), m.p. 134°, $[\alpha]_D^{18}$ −31·25° in $CHCl_3$, is identical with the sterol isolated by Zellner (A., 1926, 1281) but not with stigmasterol. The *acetate* (**III**), m.p. 121—122°, $[\alpha]_D^{18}$ −32·4° in $CHCl_3$, *dibromoacetate*, m.p. 123—124°, *benzoate*, m.p. 141·5°, p-*nitrobenzoate*, m.p. 187°, and *allophanate*, m.p. 258°, are described. Oxidation of (**II**) by $Al(OBu^{\gamma})_3$ in $COMe_2$–C_6H_6 affords the *ketone*, $C_{24}H_{38}O$, m.p. 103°; the corresponding *semicarbazone*, m.p. 248° (decomp.), is reduced (Wolff–Kishner) to the *hydrocarbon*, $C_{24}H_{40}$, m.p. 77—78°. Hydrogenation [Pd–C in Et_2O–AcOH (1 : 1)] yields the dihydrosteryl acetate, m.p. 130·5°, hydrolysed to the dihydrosterol, m.p. 138°. The presence of one double linking is confirmed by titration with Br. H. W.

Chemical behaviour of cafesterol. P. N. Chakravorty and M. M. Wesner (*J. Amer. Chem. Soc.*, 1942, **64**, 2235).—Data in the literature (Wettstein, A., 1942, II, 198, 371; Slotta *et al.*, A., 1939, II, 18) are corr. Cafesterol (**I**) does not contain an aromatic ring, since with HNO_3 it gives only a non-acidic NO_2-compound, m.p. 220—230°. It contains reactive, conjugated ethylenic linkings: with (:CH·CO)$_2$O in C_6H_6 at room temp. or slightly warm it gives an adduct, m.p. 185—192°, but decomp. occurs in boiling C_6H_6. In EtOH it absorbs 2 H_2 (20% Pd–C), giving a H_4-derivative, m.p. 153—155°; this and its acetate, m.p. 150—152°, give no colour with conc. HCl in EtOH. Na–EtOH or –C_5H_{11}·OH reduces (**I**) to a product, m.p. 153—156° (with conc. HCl–EtOH gives a stable purple colour) [acetate, m.p. 162—165° (yellow-orange colour with HCl), which with (:CH·CO)$_2$O gives an adduct, m.p. 185° (no colour with HCl)]. No details are given. R. S. C.

Preparation and dehydration of diphenyl-6-methoxy-*i*-norcholenylcarbinol. B. Riegel, M. F. W. Dunker, and McC. J. Thomas (*J. Amer. Chem. Soc.*, 1942, **64**, 2115—2120).—*Me* 6(α)-*methoxy*-i-*cholenate* (prep. from Me 3-*p*-toluenesulphonyloxy-Δ^5-cholenate and KOAc–MeOH), a syrup, $[\alpha]_D^{21}$ +44·1° in $CHCl_3$, with MgPhBr–Et_2O and then aq. NH_4Cl gives *diphenyl*-6(α)-*methoxy*-i-*norcholenylcarbinol* (**I**), m.p. 139—140·2°, $[\alpha]_D^{27}$ +43·9° in $CHCl_3$. Me 3-hydroxy-Δ^5-cholenate with an excess of MgPhBr gives *diphenyl*-3-*hydroxy*-Δ^5-*norcholenylcarbinol* (**II**), softens at 95°, melts (effervescence; ? dehydration), resolidifies at 108°, remelts at 169·4—172·2° [3-p-*toluenesulphonate* (**III**), m.p. 143·2—144° or (? loss of H_2O) m.p. 62°, resolidifies, remelts at 136—137°]. KOAc–MeOH converts (**III**) into (**I**). (**II**) or its 3-acetate (prep. by Ac_2O–C_5H_5N), m.p. 163·2—165·5° (lit. 172—172·5°), in boiling Ac_2O–AcOH or AcOH gives 3-*acetoxy*-24 : 24-*diphenyl*-$\Delta^{5:23}$-*choladiene* (**IV**), m.p. 166·6—167·4°, also obtained from (**I**) by boiling AcOH. Hydrolysis of (**IV**) by boiling NaOPr$^{\alpha}$–Pr$^{\alpha}$OH (later addition of H_2O) or by activated Al_2O_3 in boiling xylene gives 3-*hydroxy*-24 : 24-*diphenyl*-$\Delta^{5:23}$-*choladiene*, m.p. 173—174°, the 3-p-*toluenesulphonate*, m.p. 130·6—131·5°, of which with KOAc–MeOH gives αα-*diphenyl*-β-6(α)-*methoxy*-i-*bisnorcholenylethylene* (**V**), m.p. 109·1—110·1°, $[\alpha]_D^{25}$ +67·8° in $CHCl_3$ [with Ac_2O–AcOH gives (**IV**)]. With I in boiling xylene, (**I**) gives (?) *diphenyl*-3-*iodo*-Δ^5-*norcholenylcarbinol*, m.p. 168·2—169·4°. Activated Al_2O_3 and (**I**) in boiling xylene give (?) αα-*diphenyl*-β-6(β)-*methoxy*-i-*bisnorcholenylethylene* (**VI**), m.p. 161·8—163°, $[\alpha]_D^{25}$ −38·6 ± 2° in $CHCl_3$ [with Ac_2O–AcOH gives (**IV**)]. *Me* 3-*methoxy*-Δ^5-*cholenate* (prep. from the 3-*p*-toluenesulphonate by boiling MeOH), m.p. 109·2—109·6°, $[\alpha]_D^{23}$ —44·6° in $CHCl_3$, with MgPhBr (excess) gives *diphenyl*-3-*methoxy*-Δ^5-*norcholenylcarbinol*, m.p. 164·8—165·9°, dehydrated by boiling AcOH to 3-*methoxy*-24 : 24-*diphenyl*-$\Delta^{5:23}$-*choladiene*, m.p. 114·5—115·3°, $[\alpha]_D^{24}$ −11·55 ± 0·66° in $CHCl_3$, which is also obtained from (**V**) or (**VI**) by boiling H_2SO_4–MeOH. With activated Al_2O_3 in boiling xylene, (**V**) gives a *hydrocarbon* (? **VII**), m.p. 162—163°, $[\alpha]_D^{25}$ −18·5° in $CHCl_3$, converted into (**IV**) by boiling AcOH. M.p. are corr. R. S. C.


CHMe·CH_2·CH:CPh_2

(**VII.**)

Marine products. XII. Oxidation of poriferasterol. A. M. Lyon and W. Bergmann (*J. Org. Chem.*, 1942, **7**, 428—431).—Poriferasterol is oxidised by $Al(OPr^{\beta})_3$ in boiling PhMe–*cyclo*hexanone to *poriferastenone*, m.p. 111—112·5°, $[\alpha]_D^{25}$ +56·7° (2 : 4-*dinitrophenylhydrazone*, m.p. 231·8—234·5°; *semicarbazone*, m.p. 229—230°). Treatment of poriferasteryl acetate (**I**) with 1 mol. proportion of Br and then with O_3 gives 3(β)-hydroxybisnorcholenic acid, m.p. 291—292° (decomp.) [*Me* ester, m.p. 140—141° (acetate, m.p. 137·5°)]. Ozonisation of (**I**) gives a C_7 fragment isolated as the 2 : 4-*dinitrophenylhydrazone*, $C_{13}H_{18}O_4N_4$, m.p. 113—114°, $[\alpha]_D^{25}$ ±0°.

Clionasterol is shown to be 22 : 23-dihydroporiferasterol. M.p. are corr. H. W.

Derivatives of œstrone containing oxygen at $C_{(16)}$. M. N. Huffman (*J. Amer. Chem. Soc.*, 1942, **64**, 2235—2236).—16-Oximino-œstrone (**I**) and Zn in AcOH give mixed α-ketols (*A*), including a 16-hydroxy-œstrone, m.p. 234—237°, $[\alpha]_D^{29.5}$ −102° in EtOH [benzoate, m.p. 241·5—243·5°; oxime, m.p. 222·5—223°; Me ether, m.p. 174—177° (oxime, m.p. 175—177°)]; H_2–PtO_2 reduces (*A*) to mixed triols, including an œstriol, m.p. 267—269°, $[\alpha]_D^{29.5}$ +88° in EtOH (Me ether, m.p. 141—142°; triacetate, m.p. 152°). Œstrone Me ether gives mixed α-ketols, oxidised by $Cu(OAc)_2$ to 16-keto-œstrone Me ether, m.p. 176—178°, the dioxime, m.p. 230°, of which is also obtained from the Me ether of (**I**) and NH_2OH. 16-Keto-œstrone-dioxime, m.p. 230—231°, with $Cu(OAc)_2$–EtOH gives a highly coloured Cu complex, sol. in $CHCl_3$, but no coloured Ni or Co complex. No details are given. R. S. C.

Sterols. CLI. Rearrangement of 17 : 21-dibromo*allo*pregnan-3(β)-ol-20-one acetate. R. E. Marker, H. M. Crooks, jun., R. B. Wagner, and E. L. Wittbecker. **CLII. Rearrangement of 16 : 17-dibromopregnan-3(β)-ol-20-one.** R. E. Marker, R. B. Wagner, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 2089—2092, 2093—2097).—CLI. *allo*Pregnan-3(β)-ol-20-one (**I**) and Br (1 mol.) in AcOH at room temp. give the 17-*Br*-derivative (**II**), m.p. 93—96°, which with Fe dust in AcOH at 100° or H_2–Pd–$BaSO_4$ in C_5H_5N–dioxan at 40 lb. regenerates (**I**) and with boiling C_5H_5N gives Δ^{16}-*allo*pregnen-3(β)-ol-20-one. 3(β)-Acetoxy*allo*pregnan-20-one (**III**) gives similarly 17-*bromo*-3(β)-*acetoxy*allo*pregnan*-20-*one* (**IV**), m.p. 155°, converted into (**III**) by H_2–Pd–$BaSO_4$ in MeOH–dioxan–C_5H_5N at 40 lb. and by boiling C_5H_5N into 3(β)-acetoxy-Δ^{16}-*allo*pregnen-20-one [with Zn dust in AcOH gives (**III**)]. CrO_3–AcOH at room temp. oxidises (**II**) to a mixture, which with boiling C_5H_5N or KOAc–AcOH gives Δ^{16}-*allo*pregnene-3 : 20-dione (**V**) and with Fe dust in AcOH at 100° gives *allo*pregnane-3 : 20-dione [obtained from (**V**) by Zn dust in AcOH at 100°]. 2 mols. of Br with (**III**) or 1 mol. with (**IV**) in AcOH at 40° gives 17 : 21-*dibromo*-3(β)-*acetoxy*-allo*pregnan*-20-*one*, m.p. 174°, converted by boiling KOH–MeOH into 3(β)-*hydroxy*-$\Delta^{17(20)}$-allo*pregnen*-21-*oic acid* (**VI**), m.p. 249°. The derived OAc-acid with O_3–$CHCl_3$ and then hot KOH–MeOH gives *iso*androsterone (isolated as semicarbazone). Oxidation of (**VI**) by $Al(OBu^{\gamma})_3$–$COMe_2$–C_6H_6 and then reduction by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ gives 3(α)-*hydroxy*-$\Delta^{17(20)}$-allo*pregnen*-21-*oic acid*, m.p. 232—235°, converted by O_3–$CHCl_3$ etc. into androsterone. *cyclo*Hexyl Me ketone with Br at 0° and then KOH–EtOH at room temp. gives *cyclo*hexylideneacetic acid.

CLII. 3(β)-Acetoxy-Δ^{16}-pregnen-20-one with Br–AcOH gives the *dibromide*, m.p. 137—140°, whence it is regenerated by H_2–Pd–$BaSO_4$ in C_5H_5N–dioxan at 3 atm., boiling C_5H_5N, NaI–MeOH, or KOAc–AcOH, and which with boiling KOH–MeOH gives 3(β)-*hydroxy*-$\Delta^{17(20)}$-*pregnen*-21-*oic acid* (**VII**), m.p. 254—256° (decomp.) (*acetate*, m.p. 161—163°), and its *Me* ester (**VIII**), m.p. 153—156° [*acetate* (**IX**), m.p. 103—105°; also prepared from (**VII**) by CH_2N_2]. H_2–PtO_2 at 3 atm. reduces (**VII**) to 3(β)-hydroxypregnan-21-oic acid (**X**) {acetate; *Me* ester (**XI**), m.p. 141—143° [*acetate* (**XII**), m.p. 105—106°]} and (**IX**) to (**XII**). With O_3–$CHCl_3$ or $KMnO_4$–KOH at 0°, (**VII**) gives ætiocholan-3(β)-ol-20-one. With, successively, $Al(OPr^{\beta})_3$–$COMe_2$–PhMe, $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$, removal of precipitable material by digitonin, and O_3–$CHCl_3$, (**VIII**) gives ætiocholan-3(α)-ol-17-one. Na–n-C_5H_{11}·OH and then KOH–MeOH converts (**VII**) or (**X**) into 3(α)-*hydroxypregnan*-21-*oic acid*, m.p. 224—226° [*Me* ester, m.p. 118—119° (*acetate*, m.p. 85—87°)], oxidised by CrO_3–AcOH to 3-*ketopregnan*-21-*oic acid*, m.p. 170—172° (*Me* ester, m.p. 121—123°), whence it is regenerated by H_2–PtO_2 in dioxan at 3 atm. Na–EtOH reduces (**XI**) to *pregnane*-3(β) : 21-*diol*, m.p. 164—166° (*diacetate*, m.p. 76—79°; *pregnane*-3(α) : 17-*diol*, m.p. 205—206°, is similarly prepared. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Reactions of β-pinene. II. With selenium dioxide in acetic acid W. D. Stallcup and J. E. Hawkins (*J. Amer. Chem. Soc.*, 1942, **64** 1807—1809; cf. A., 1942, II, 178).—β-Pinene and SeO_2 in Ac_2O (less good, AcOH) give pinocarvyl acetate (**I**) with some carvopinone (**II**), pinocarvone (**III**), and, in AcOH, pinocarveol (**IV**); the amount of SeO_2 used is of minor importance. SeO_2 in boiling EtOH converts (**IV**) mainly into (**II**). Hydrogenation (Pd–C; *cyclo*hexane; 100°/1200 lb.) of (**IV**) gives *d-cis*-pinocampheol, m.p. 55·5—56°, $[\alpha]_D^{25}$ +39° in Et_2O, of (**I**) gives *d-cis*-pinocamphyl acetate, b.p. 80—82°/2—3 mm., 227—228° (corr.)/760 mm., $[\alpha]_D^{25}$ +23°, of (**II**) gives *l-trans*-pinocamphone (**V**), b.p. 212° (corr.), $[\alpha]_D^{25}$ −13·5° [semicarbazone, m.p. 227·5—228° (corr.)], and of (**III**) gives a pinocamphone, b.p. 75°/2—3 mm., α_D −29° (β-semicarbazone, m.p. 185°). The method of formation and structure of the ketones are discussed. R. S. C.

Preparation and properties of camphormonoamides. M. Delépine (*Ann. Chim.*, 1942, [xi], **17**, 171—178).—*d*-α- (combines with EtOH, $COMe_2$, but not with H_2O) and *d*-β-camphoramide have vals. of $[\alpha]_D$ of +25° and +73·2°, respectively, in EtOH. *iso*Camphoric acid and $SOCl_2$ at room temp., followed by NH_3–Et_2O, give l-α-iso*camphoramide*, m.p. 193°, $[\alpha]_D$ −46·4° in EtOH, *l-iso*camphordiamide monohydrate, m.p. 132°, $[\alpha]_D$ −37·8° in H_2O (anhyd., $[\alpha]_D$ −41·25° in H_2O), and a neutral *substance*, $C_{10}H_{16}ON_2$, m.p. 187°, $[\alpha]_D$ −82·8° in EtOH. *l*-β-*iso*Camphoramide (modified prep.), new m.p. 171° (block), has $[\alpha]_D$ −51·4° in EtOH. *l-iso*Camphoric acid is converted into the *l*-α-Et ester, and thence by $SOCl_2$ into its β-acid chloride, which with NH_3–Et_2O, followed by aq. NH_4Cl, yields *Et* α-iso*camphorate* β-*amide*, m.p. 121°, $[\alpha]_D$ −51·5° in EtOH (corresponding Me ester, $[\alpha]_D$ −63·2° in EtOH). *d*-Camphoric acid and $SOCl_2$, followed by NH_3–Et_2O, yield (mainly) camphoric anhydride and *d*-α-camphoramic acid. *d*-α-, m.p. 248° (block), $[\alpha]_D$ +37·3° in EtOH, and *d*-β-camphormethylamide, m.p. 178° (block), $[\alpha]_D$ +65·9° in EtOH, are prepared. A. T. P.

Hydrolysis of amides. M. Delépine and M. Badoche (*Compt. rend.*, 1942, **214**, 588, 591, and *Ann. Chim.*, 1942, [xi], **17**, 183—212).—*d*-CHPhEt·CO·NH_2, m.p. 81°, $[\alpha]_D$ +52·6° in EtOH, and 2N-HCl at 100° (bath) give the *d*-acid, whereas boiling 2N-NaOH affords almost entirely the *r*-acid owing to racemisation of the amide prior to hydrolysis. Although *d*-CHPhEt·CO·NHPh, m.p. 81·5°, $[\alpha]_D$ +102° in EtOH, is stable to boiling 2N-HCl, boiling 2N-NaOH (4 hr.) causes partial racemisation; EtOH–NaOH (21 hr.), gives inactive acid + anilide. *r*-NH_2·CHPh·CH(OH)·CO·NH_2 and aq. $Ba(OH)_2$ yield two *r*-acids, m.p. 240° (block) and 290° (block) (10%), but 2N-HCl causes little isomerisation, giving mainly the former. *d*-α-Camphoramide (**I**) and boiling H_2O give *d*-camphoric acid (**II**), $[\alpha]_D$ +48·8° in EtOH, and camphoric anhydride (62·5% conversion); the β-amide (**III**) similarly gives some anhydride and probably some α-amide. Camphoric acid and boiling H_2O yield no anhydride; the latter reacts slowly with boiling H_2O. A mixture of $(NH_4)_2$ camphorate, anhydride, and H_2O in a sealed tube at 100° affords some α-amide. (**I**) and boiling 2N-HCl give (**II**) and 10% of camphorimide (**IV**); 61% of (**II**) and 39% of (**IV**) are obtained similarly from (**III**), and (**III**)–20% HCl give 50—70% of (**IV**). (**I**) is slowly hydrolysed by 5N-NaOH (8 hr.) to give camphoric acid containing 20% of *l-iso*-acid (**V**), separable by AcCl at room temp.; similarly after boiling (**III**) for 15 hr., 50% of (**III**), 25% of (**II**), and 3·5% of *iso*-acid, probably formed through (**IV**) (which can be isolated), are obtained. *l*-α- (**VI**) and -β-*iso*camphoramide (**VII**) are unaltered by boiling H_2O, but are hydrolysed (α- more readily) by 2N-HCl to (**V**); no imide nor anhydride is formed. Alkaline hydrolysis of (**VI**) gives (**V**) and some (**II**). (**VII**) is difficult to hydrolyse; after boiling with 4N-NaOH for 4 hr., a trace of *d*-acid is formed. *l-iso*Camphordiamide (**VIII**) and boiling 2N-HCl (8 hr.) give (**V**) and (**VI**), whereas (**VIII**) and N-NaOH (10 hr.) yield *d*-β-*cis*-camphoramide, rotation becoming positive. (**V**) shows only 1·3% conversion into *d*-acid on boiling with 5N-NaOH for 8·5 hr. *d*-α-Camphormethylamide (**IX**) reacts slowly with boiling H_2O, giving probably some *d*-β-methylamide (**X**); (**X**) similarly yields 21% of anhydride and (**IX**). (**IX**) can be isolated from a mixture of camphoric acid neutralised with NH_2Me, anhydride, and H_2O, heated in a sealed tube at 100° for 3 hr. (**IX**) and, more readily, (**X**) are converted by 2N-HCl into the methylimide, m.p. 42—43°, $[\alpha]_D$ +11·4° in EtOH. *cis*-Hexahydro-*p*-toluamide (**XI**), refluxed with 2N-HCl for 7 hr., is partly transformed (15%) into the *trans*-amide (**XII**); (**XI**) and aq. NaOH–EtOH yield 35% of (**XII**), and excess of alkali affords 50% of the *trans*-acid (**XIII**), m.p. 111°. (**XII**) is not isomerised, and yields only (**XIII**). In general, acids saponify the amides with liberation of the corresponding acid, whereas alkalis often cause racemisation or isomerisation, probably owing to keto–enol change $CR_2{:}C(OH)\cdot NH_2$. A. T. P.

Configuration of nickel bisformylcamphor-ethylenediamine.—See A., 1943, I, 5.

Reactivity of terpene nuclei. Halogenation of dihydroterpenes. A. Gandini (*Gazzetta*, 1941, **71**, 722—729).—A review (cf. Gandini, A., 1936, 1257; 1939, II, 220; 1940, II, 283; *Gazzetta*, 1940, **70**, 604). In the halogenation of dihydroterpenes, Me and Pr^{β} groups are unaffected, the nucleus being attacked. In dicyclic terpenes, halogenation is first in the β-position to $C_{(7)}$, in contrast to menthane, first halogenated at $C_{(4)}$. E. W. W.

VI.—HETEROCYCLIC.

Reaction of furoic acid with aromatic compounds.—See A., 1943, II, 34.

Alkylquinols and related compounds.—See A., 1943, II, 29.

Nitration of 5-hydroxy-4-methylcoumarin and 5-hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester. N. B. Parekh and R. C. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 335—338).—5-Hydroxy-4-methylcoumarin with HNO_3–H_2SO_4 at 0° gives the 8-NO_2-derivative (**I**), m.p. 174—176° (efferv.), and at room temp., the 6 : 8-$(NO_2)_2$-compound, m.p. 181—182°. Me 5-hydroxy-4-methylcoumarin-6-carboxylate with AcOH–HNO_3 affords the 8-NO_2-derivative, m.p. 201—202°, hydrolysed to the corresponding *acid*, m.p. 220—221°, also obtained by nitration of 5-hydroxy-4-methyl-

coumarin-6-carboxylic acid, and decarboxylated (AcOH–HCl) to (**I**). F. R. S.

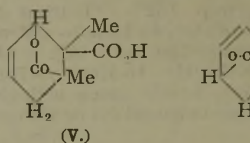
Aluminium chloride—reagent for the condensation of β-ketonic esters with phenols. VII. Condensation of 4-nitroresorcinol with ethyl acetoacetate. N. B. Parekh and R. C. Shah (*J. Indian Chem. Soc.*, 1942, **19**, 339—342).—4 : 1 : 3-NO_2·$C_6H_3(OH)_2$ and $CH_2Ac·CO_2Et$ in $PhNO_2$ with $AlCl_3$ give, in poor yield, 6-*nitro*-5-*hydroxy*-4-*methylcoumarin* (**I**), m.p. 209—210° (*Me* ester, m.p. 132—133°), which is converted by Me_2SO_4–NaOH successively into 5-*nitro*-6-*hydroxy*-2-*methoxy*- (+0·5H_2O), m.p. 162—163° (efferv.), and 5-*nitro*-2 : 6-*dimethoxy*-β-*methylcinnamic acid*, m.p. 206—208°. The formation of (**I**) in the condensation indicates chelation between NO_2 and OH in the resorcinol. F. R. S.

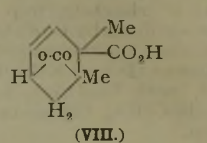
Dibenzfurans.—See B., 1943, II, 6.

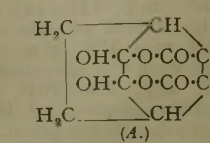
Synthesis of cantharidin. K. Ziegler, G. Schenck, and E. W. Krockow [with A. Siebert, A. Wenz, and H. Weber] (*Annalen*, 1942, **551**, 1—79).—Me_2 3 : 6-*endo*methylenehexahydrophthalate is converted by CPh_3Na at room temp. followed by MeI (better Me_2SO_4) and hydrolysis into *cis*-1 : 2-dimethyl-3 : 6-*endo*methylenehexahydrophthalic anhydride (" methylenecantharidin "), m.p. 206° (Me_2 ester of the corresponding acid, m.p. 57°), with a small proportion of trans-1 : 2-*dimethyl*-3 : 6-endo*methylenehexahydrophthalic acid*, m.p. 320—323° (Me_2 ester, m.p. 44°); the *exo*-anhydride does not appear to be formed. Attempts to methylate Me_2 norcantharidate similarly were unsuccessful.

trans-Δ⁴-*Tetrahydrophthalodinitrile*, m.p. 125°, is obtained in small yield from fumaronitrile (prep. from the diamide, *p*-$C_6H_4Me·SO_2Cl$, and anhyd. C_5H_5N described), $(CH_2{:}CH)_2$, and PhMe at 100° but the change is accompanied by the formation of much rubber-like polymeride. This is avoided by passing the gas into the dinitrile and PhMe at 170—180°, when a 76% yield is very slowly obtained. It does not appear to be methylated smoothly. 1 : 2-*Dimethyl*-Δ⁴-*tetrahydrophthalic anhydride* (**I**), m.p. 101°, is obtained with much polymeride when $(CMe{:}CO)_2O$ and $(CH_2{:}CH)_2$ are heated in a sealed tube; the yield attains 50% when the gas is passed into a solution of the anhydride in decahydronaphthalene at 192° in 720 hr. and 60% when the reactants without solvent are heated at 170—180° in an autoclave of such size that the bulk of the $(CH_2{:}CH)_2$ remains in the gaseous phase. (**I**) is stable at 400° and is hydrolysed by alkali to the *acid*, m.p. 200° with re-formation of (**I**), which also slowly results when a solution of the acid in H_2O is boiled. It is hydrogenated to 1 : 2-dimethylhexahydrophthalic anhydride (**II**), m.p. 129°, identical with the deoxycantharidin of Gadamer (A., 1917, i, 659, 704); the corresponding acid, m.p. 180°, passes partly into the anhydride in boiling H_2O. The characteristic instability of the cantharidindicarboxylic acids is therefore due to the presence of the bridge. (**I**) and Br in CCl_4 (small quantities should be used or, better in AcOH) afford 4 : 5-*dibromo*-1 : 2-*dimethylhexahydrophthalic anhydride*, m.p. 181°, which is rapidly converted by boiling aq. NaOH into an *anhydride*, $C_{10}H_{12}O_4$, m.p. 182° (vac.), and the corresponding dicarboxylic *acid*, $C_{10}H_{14}O_5$, m.p. 178°. Other reagents for the elimination of HBr give uninviting products but NMe_3 at 100° gives large amounts of non-volatile products and ~10% of 1 : 2-*dimethyl*-1 : 2-*dihydrophthalic anhydride* (**III**), b.p. 112°/2 mm., m.p. 70°. (**III**) is quantitatively hydrogenated to (**II**), is converted by alkali and cold acid into the corresponding *acid*, m.p. 158° with re-formation of (**III**), and with Br in AcOH yields at least two *dibromides*, the most sparingly sol. of which has m.p. 126°. This loses only 1 Br when treated with different reagents, *e.g.*, $AgNO_3$ in EtOH or aq. $COMe_2$. (**III**) and NH_3 at 250° yield 1 : 2-dimethyl-1 : 2-dihydrophthalimide, m.p. 136°, the dehydrocantharidinimide of Gadamer (*loc. cit.*). (**I**) and $(CH_2·CO)_2NBr$ in boiling CCl_4 give a mixture (**IV**) of 6-bromo-1 : 2-dimethyl-Δ⁴-tetrahydrophthalic anhydrides, separated by crystallisation into a small proportion of a stable monobromide, m.p. 106°, and a large proportion of an *isomeride*, m.p. 72°, which tends to lose HBr spontaneously. When heated at 150° and then at 180° (**IV**) gives (**III**) in variable yield dependent on experimental conditions. Boiling 20% NaOH hydrolyses (**IV**) to iso*cantharic acid B* (**V**), m.p. 204—206° [Me ester (**VI**), m.p. 72°], converted by boiling AcCl into 6-*acetoxy*-1 : 2-*dimethyl*-Δ⁴-*tetrahydrophthalic anhydride*, b.p. 310°, m.p. 101·5—102°, identical with the substance obtained by oxidising (**I**) with SeO_2–Ac_2O. (**V**) is reduced (Pd–$BaSO_4$ in abs. EtOH) to dihydrocantharic acid, m.p. 263° [Me_2 ester (**VII**), m.p. 58—60°]. (**VI**) and $(CH_2·CO)_2NBr$ at 130—135° afford *Me bromo*iso*cantharate*, m.p. 166°, converted by H_2–Pd–$BaSO_4$ into (**VII**), m.p. 65°. Treatment of the non-volatile products of the prep. of (**III**) with boiling aq. NaOH followed by acid gives *ψ-cantharic acid* (**VIII**), m.p. 187° (Me ester, m.p. 100°; H_2-derivative, m.p. 270—273°).

$(CMe·CO)_2O$ and *cyclo*hexadiene, best in presence of C_6H_6, at 170—180° afford 1 : 2-*dimethyl*-3 : 6-endo*vinylenehexahydrophthalic anhydride* (**IX**), m.p. 263·5°, oxidised by NaOBr to the *bromolactonic acid*, $C_{12}H_{15}O_4Br$, m.p. 231—232° (discoloration, decomp.) (*Me* ester, m.p. 164—165°), and further to the mutually interconvertible *dilactone*, $C_{12}H_{14}O_4$, m.p. ~375°, or *hydroxylactonic acid*, $C_{12}H_{16}O_5,H_2O$, m.p. ~375° (*Me* ester, m.p. 177—178°). (**IX**) is converted by dissolution in NaOH and oxidation with $KMnO_4$ into 1 : 2-*dimethyl*-3 : 6-endo*dihydroxyethylenehexahydrophthalic anhydride* [3 : 6-endo*dihydroxyethylenedeoxycantharidin*] (**X**), m.p. 303°, transformed by $COMe_2$ containing a few drops of conc. H_2SO_4 into the *:CMe₂ ether*, m.p. 214—215°. (**X**) is converted by HNO_3 (*d* 1·5) at 100° into the *dinitrate*, m.p. 157—158°. HNO_3 (*d* 1·2) oxidises (**X**) at 100° to 4 : 5-*diketo*-1 : 2-*dimethyl*-3 : 6-endo*ethylenehexahydrophthalic acid* (+H_2O); the colourless form is probably (*A*). It becomes yellow at >260° (diketonic form) and has m.p. 315—320° when slowly heated, 338—340° (decomp.) in bath preheated to 330°.

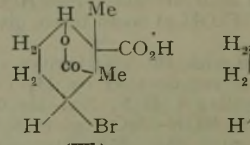

(V.)

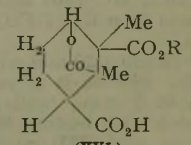

(VIII.)

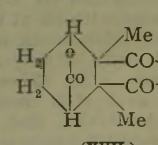

(A.)

It is converted by CH_2N_2 into the yellow *Me*$_2$ ester, m.p. 173—174°, and by boiling Ac_2O into the yellow *anhydride* (m.p. as for acid), which spontaneously absorbs H_2O and becomes colourless when exposed to air. The acid is transformed by evaporation with fuming HNO_3 into cis-1 : 2-*dimethyl*cyclo*hexane*-1 : 2 : 3 : 6-*tetracarboxylic dianhydride* (**XI**), m.p. 245—246°, converted by boiling H_2O into the tetracarboxylic acid. (**XI**) is transformed by prolonged action of CH_2N_2 in aq. Et_2O into the corresponding cis-*Me*$_4$ ester (**XII**), m.p. 108—109°, whereas in aq. $COMe_2$ a cis-*Me*$_2$ ester, m.p. 156°, results, converted by further methylation (CH_2N_2) into (**XII**). Neutralisation (phenolphthalein) of (**XI**) with NaOMe–MeOH, addition of HCl (Congo-red), and treatment of the product with CH_2N_2 leads to (**XII**), whereas evaporation of the solution to dryness and treatment of the residue with Me_2SO_4–NaOMe under strictly defined conditions gives *Me*$_4$ 1 : 2-*dimethyl*cyclo*hexane*-cis-1 : 2-trans-3 : 6-*tetracarboxylate* (**XIII**), m.p. 111—112°. This is partly hydrolysed by alkali to the 1 : 2-*Me*$_2$ 3 : 6-*H*$_2$ ester (+H_2O) (lost at 120°), m.p. 208°, also obtained by acid hydrolysis (20·2% HCl) of (**XIII**). 20·2% HCl and (**XII**) yield essentially the 1 : 2-Me_2 3 : 6-H_2 ester.

(**XIII**) is neutralised with 2N-NaOH and transformed under strictly defined conditions into the Ag_2 salt, which is converted by Br in CCl_4 into acidic products (**XIV**) and a " neutral oil " from which *Me* epi*hydrobromocantharate*, m.p. 115—116°, is isolated. It is hydrolysed by boiling 48% HBr to the *acid* (**XV**), anhyd. or +1H_2O, m.p. 185—186°, which, when heated, affords cantharic acid and


(XV.)


(XVI.)


(XVII.)

cantharidin. (**XIV**) contain 4-*bromo*-2 : 3-*dicarbomethoxy*-2 : 3-*dimethyl*cyclo*hexane*-1-*carboxylic acid*, m.p. 119°, and the *ester lactone* (**XVI**) (R = Me), m.p. 184—185°, hydrolysed by 48% HBr to the *lactonedicarboxylic acid* (**XVI**) (R = H), m.p. 296—297° (change at 205—220°), also obtained as a by-product of the prep. of (**XV**); it is transformed by boiling Ac_2O into the *anhydride* (**XVII**), m.p. 296—297°. The configuration of cantharidin is discussed. H. W.

Cleavage of ethylene linkage by thionyl chloride. A. Schönberg and W. Asker (*J.C.S.*, 1942, 725).—Dixanthylene (**I**), dithioxanthylene, *NN'*-dimethyldiacridine, diflavylene, and dithioflavylene undergo cleavage when boiled with $SOCl_2$ and the product dissolved in C_6H_6 and shaken with H_2O at 30°, yielding the ketones. The product from (**I**) and $SOCl_2$ with NH_2Ph yields xanthoneanil. A. Li.

Synthesis of a 3 : 4-diaminotetrahydrothiophen and a comparison of its stability with the diaminocarboxylic acid derived from biotin. G. W. Kilmer, M. D. Armstrong, G. B. Brown, and V. du Vigneaud (*J. Biol. Chem.*, 1942, **145**, 495—501; cf. A., 1942, II, 387).—*dl*-[$CH_2Br·CH(OH)·]_2$ and aq. Na_2S at 50—60°, then at 100°, followed by treatment of the product with HCl in a sealed tube at 150° or with HBr (reflux) give 3 : 4-*dichloro*-, m.p. 60—61°, or *-dibromotetrahydrothiophen*, m.p. 83—89°; attempted replacement of halogen by the use of NH_3, *o*-$C_6H_4(CO)_2NK$, and other reagents was unsuccessful, as also were attempts to replace Br in the derived sulphone. αδ-*Dichlorobutane*-β*γ-diol*, m.p. 62—63°, b.p. 113—118°/4 mm., obtained by $KMnO_4$ oxidation of αδ-dibromo-Δ$^{\beta}$-butene, is converted by aq. Na_2S into 3 : 4-*dihydroxytetrahydrothiophen*, m.p. 54—58° (HI at 210° gives much H_2S). Et_4 tetrahydrothiophen-3 : 3 : 4 : 4-tetracarboxylate (**I**) (modified prep.), b.p. 200—208°/8 mm., and N-NaOH at 80°, followed by heating the residue at 140—160°, esterification to the di-ester with HCl–EtOH at room temp., and heating with N_2H_4,H_2O (water-bath), afford *tetrahydrothiophen*-3 : 4-*dicarboxylic dihydrazide* (**II**), m.p. 226—227° (previous softening), also obtained in lower yield by partial hydrolysis of (**I**) with 0·1N-NaOH at room temp., followed by decarboxylation and treatment with N_2H_4. (**II**) and $NaNO_2$ in N-HCl–Et_2O followed by interaction of the azide with EtOH give 3 : 4-*diurethanotetrahydrothiophen*,

m.p. 176—178°, converted by HCl (sealed tube; 100—105°) into 3 : 4-*diaminotetrahydrothiophen dihydrochloride*, incipient decomp. ~250° [aq. NaOH gives the free diamine (**III**), m.p. ~40°; *dipicrate*, incipient decomp. ~250°; Ac_2, sublimes at 260—265°, and Bz_2 derivative, m.p. 295—300° (previous softening)]. A cyclic urea derivative could not be obtained by treating (**III**) with $COCl_2$–NaOH, and Et_2CO_3 did not yield a CO: derivative. (**III**) is unchanged with fuming HI at 210°, but at 250° ~5—10% of its S is liberated as H_2S, and 10—15% of its N as volatile base; it is thus more stable than the diaminocarboxylic acid derived from biotin. A. T. P.

1-*p*-Aminobenzenesulphonamido-2 : 5-dimethylpyrrole. E. O'F. Walsh (*J.C.S.*, 1942, 726).—*p*-Acetamidobenzenesulphonhydrazide and acetonylacetone in AcOH give 1-p-*aminobenzenesulphonamido*-2 : 5-*dimethylpyrrole*, m.p. 202° (decomp.), after hydrolysis (NaOH). 1-p-*Toluenesulphonamido*-2 : 5-*dimethylpyrrole*, m.p. 144°, is similarly prepared. F. R. S.

Synthesis of vitamin B_6.—See B., 1943, III, 21.

Some anilinopyridine derivatives. W. O. Kermack and (Miss) A. P. Weatherhead (*J.C.S.*, 1942, 726).—From the appropriate Cl-derivative and NH_2-compound, the following have been prepared: 2-*anilino*-, m.p. 263°, and 2-p-*anisidinonicotinic acid*, m.p. 295°, 4-*anilinopyridine*, m.p. 173°, N-(4′-*pyridyl*)*anthranilic acid hydrochloride*, m.p. 185°, and N-(3′-*pyridyl*)*anthranilic acid*, m.p. 238°. These acids could not be cyclised with either H_2SO_4 or $POCl_3$. F. R. S.

Preparation of certain 3-substituted indoles. (Mrs.) R. H. Cornforth and (Sir) R. Robinson (*J.C.S.*, 1942, 680—682).—Indole and indole-2-carboxylic acid (**I**) are converted by MeOH–NaOMe at 210—220° into skatole, which may be conveniently prepared in this way. Treatment of (**I**) with the appropriate alcohol gives the following: 3-ethyl- (picrate, m.p. 121°), 3-n-*propyl*-, b.p. 162—164°/20 mm., 3-n-*butyl*- (picrate, m.p. 114°), 3-n-*heptyl*-, m.p. 60°, 3-*benzyl*-, m.p. 103°, 3-*γ*-*phenylpropyl*-, m.p. 73°, 3 : 7-*dimethyl*-, m.p. 56°, and 3-cyclo*hexyl*-7-*methyl-indole*, m.p. 115°. (**I**) could not be alkylated by means of *sec.* alcohols and their Na derivatives. A mechanism for the reaction is suggested. F. R. S.

Reaction with hydrazoic acid in sulphuric acid. IV. Behaviour of substances containing the system –CO·CO·NH–. G. Caronna (*Gazzetta*, 1941, **71**, 585—589).—Isatin (or acetylisatin) with NaN_3 in H_2SO_4 gives anthranilamide; *N*-ethylisatin gives *o*-ethylaminobenzamide. COPh·CO·NHPh gives the same products as benzil (cf. Spielman *et al.*, A., 1938, II, 64). E. W. W.

Synthesis of 4 : 5-dihydroxyquinoline. L. Musajo and (Signa.) M. Minchilli (*Gazzetta*, 1941, **71**, 762—765).—3 : 4 : 1-NH_2·C_6H_3Cl·OH and CO_2Me·CH_2·CO·CO_2Me in boiling Et_2O give *Me*$_2$ 2-*chloro*-5-*hydroxyanilosuccinate*, m.p. 101—102°, which in petroleum jelly at 220° gives *Me* 8-*chloro*-4 : 5-*dihydroxyquinoline*-2-*carboxylate*, m.p. 143°, reduced in aq. MeOH–NaOAc by H_2 (Pd–C) to the *Me* ester, m.p. 253°, of 4 : 5-*dihydroxyquinoline*-2-*carboxylic acid*, m.p. 305° (decomp.). Above its m.p. this yields 4 : 5-*dihydroxyquinoline*, m.p. 231—232°. E. W. W.

Utilisation of alkoxy-ketones in the synthesis of quinolines by the Pfitzinger reaction. II. S. D. Lesesne [with H. R. Henze] (*J. Amer. Chem. Soc.*, 1942, **64**, 1897—1900; cf. A., 1939, II, 388; 1940, II, 24).—Isatin and COEt·CHMe·OMe, b.p. 154—155°/746 mm. (semicarbazone [Wallace], m.p. 120·5°), in 33% aq. KOH at 100° give 3-*methyl*-2-*α*-*methoxyethylcinchonic acid* (**I**) (74%), m.p. 234° (decomp.) [*Me* ester, m.p. 57° (picrate, m.p. 179°)]. At 250° (**I**) gives CO_2 and, by fission and reduction, 3-methyl-2-ethylquinoline (14%) [picrate, m.p. 191° (corr.) (lit. 193°)], with conc. HCl at 100° gives 3-*methyl*-2-*α*-*hydroxyethylcinchonic acid* (55%), +H_2O, m.p. 265° (picrate, explodes at >310°), with boiling HI–red P gives, after 6 hr., 3-*methyl*-2-*ethylcinchonic acid* (**II**) (78%), m.p. 279° (picrate, m.p. 198°), or, after 7 days, 3-*methyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (**III**) (70%), b.p. 253°/716 mm. (picrate, m.p. 188°), and with H_2–PtO_2 in EtOH gives 3-*methyl*-2-*α*-*methoxyethyl*-1 : 2 : 3 : 4-*tetrahydrocinchonic acid*, m.p. 232° (decomp.). (**III**) suffers fission by Sn–HCl at 100°, giving 3-methyl-1 : 2 : 3 : 4-tetrahydroquinoline, b.p. 117°/15 mm. [picrate, m.p. 159° (corr.) (lit. 155°)]. With $SOCl_2$ at 0° and then the appropriate amine, (**I**) gives 3-*methyl*-2-*α*-*methoxyethylcinchondi-ethyl*- (**IV**), m.p. 94°, -iso*amyl*-, m.p. 190°, and -*allyl*-*amide*, m.p. 112°, and, by NH($[CH_2]_2$·OH), the *diester-amide*, (RCO_2·$[CH_2]_2$)$_2$NH, m.p. 200°. (**II**) gives similarly 3-*methyl*-2-*ethylcinchondi-ethyl*- (**V**), m.p. 100°, -iso*amyl*-, m.p. 132°, and -*allyl*-*amide*, an oil, and the *diester-amide*, (RCO_2·$[CH_2]_2$)$_2$NH, m.p. 295°. Isatin and COMe·CHMe·OMe, b.p. 115—116°/739 mm. (semicarbazone [Wallace], m.p. 141°), lead similarly to 2-*α*-*methoxyethylcinchonic acid*, m.p. 186° (decomp.), 2-*ethylcinchonic acid*, m.p. 180°, and 2-ethylquinoline [picrate, m.p. 148° (lit. 147°)]. With isatin in KOH, acetoin and COPh*α* give *bis*-2-*cinchonic acid* [*di*-4-*carboxy*-2-*quinolyl*] (**VI**) (58%), m.p. 367° [*diethylamide* (**VII**), m.p. 257°], and 2-*phenyl*-3-*ethylcinchonic acid* (**VIII**), m.p. 286° [picrate, m.p. 147°; *diethylamide* (**IX**), m.p. 244°], respectively. M.p. are corr. Inactivity is recorded as follows: (**I**), (**II**), (**VI**), (**VIII**), and (**IX**) against *Plasmodium cathemerium* in canaries; (**IV**), (**V**), and (**VIII**) against avian malaria; (**VII**) orally against *Streptococcus viridans* in mice. R. S. C.

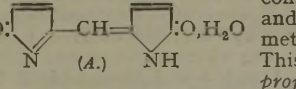
Acylation experiments with sulphanilamide and heterocyclic amines.—See A., 1943, II, 28.

Quinolines and acridines.—See B., 1943, II, 6.

α-Alkoxyvinyl- and α-alkoxyethyl-barbituric acids. S. M. McElvain and H. Burkett (*J. Amer. Chem. Soc.*, 1942, **64**, 1831—1836). —CH_2:$C(OR)_2$, $CH_2(CO_2Et)_2$, and NaOR at 125—130° give a mixture, separated for R = Et, of OR·CMe:$C(CO_2Et)_2$ (*A*) and CH_2:$C(OR)$·$CH(CO_2Et)_2$ (*B*), which with AlkBr or AlkI in, best (usually 55—85% yield), $Pr^{\beta}OH$ gives CH_2:$C(OR)$·$CR'(CO_2Et)_2$, converted by $CO(NH_2)_2$ and $NaOPr^{\beta}$–$Pr^{\beta}OH$ in poor yield into 5-alkyl-5-α-alkoxyvinylbarbituric acids or by H_2–Raney Ni in EtOH at 120°/1850 lb. into OR·CHMe·$CR'(CO_2Et)_2$, which in EtOH give good yields of 5-alkyl-5-α-alkoxyethylbarbituric acids. Alkylation of OR·CHMe·$CH(CO_2Et)_2$ is impossible. The pharmacological properties, sometimes pronounced, are briefly discussed. The following are obtained: *Et*$_2$ *α-ethoxyethylidene-* (**I**) (66%), m.p. 26—27°, b.p. 79—83°/0·03 mm. (with O_3 gives no CH_2O), and *α-ethoxyvinyl-malonate* (**II**) (11%), b.p. 69—70°/0·03 mm. [with O_3 in AcOH–Ac_2O gives CH_2O; with NaOEt at 125° slowly gives (**I**)]; mixtures of (*A*) and (*B*), in which R = Pr, b.p. 110—112°/3 mm., Bu$^{\alpha}$, b.p. 135—140°/2·5 mm., and *iso*amyl, b.p. 120—130°/0·05 mm.; *Et*$_2$ *ethyl-α-ethoxy-*, b.p. 87—91°/0·1 mm. [prep. from (**I**) or (**II**); also obtained from CEtNa$(CO_2Et)_2$ by CHMeCl·OEt in C_6H_6], -n-*propoxy*-, b.p. 121—130°/2·3 mm., -n-*butoxy*-, b.p. 110—120°/0·5 mm., and -iso*amyloxy*-, b.p. 104—110°/0·04 mm., *-vinylmalonate*; *Et*$_2$ *allyl*-, b.p. 92—96°/0·1 mm., n-*propyl*-, b.p. 97—98°/1 mm., n-*butyl*-, b.p. 88—91°/0·04 mm., and iso*amyl*-, b.p. 84—90°/0·01 mm., *-α-ethoxyvinylmalonate*; *Et*$_2$ *ethyl-α-ethoxy-*, b.p. 71—72°/0·03 mm., -n-*propoxy*-, b.p. 77—78°/0·03 mm., -n-*butoxy*-, b.p. 83—84°/0·03 mm., -iso*amyloxy*-, b.p. 89—90°/0·03 mm., *-ethylmalonate*; *Et*$_2$ *α-ethoxyethyl*-n-*propyl*-, b.p. 81—82°/0·03 mm., -n-*butyl*-, b.p. 85—86°/0·04 mm., -iso*amyl*-, b.p. 88—89°/0·03 mm., *-allyl*-, b.p. 78—79°/0·04 mm., and -sec.-*amyl*-, b.p. 83—84°/0·03 mm., *-malonate*; *Et*$_2$ *α-propoxyethyl-allyl*-, b.p. 97—98°/0·18 mm., and -sec.-*amyl-malonate*, b.p. 101—102°/0·06 mm.; *5-ethyl-5-α-ethoxy-*, m.p. 189·5—190°, -n-*propoxy*-, m.p. 177—179°, and -iso*amyloxy*-, m.p. 153—154°, *-vinylbarbituric acid*; *5-α-ethoxyvinyl-5-allylbarbituric acid*, m.p. 158—160°; *5-n-butyl*-, m.p. 169—170°, and *5-iso*amyl-5-*α-ethoxyvinylbarbituric acid*, m.p. 165·5—166°; *5-ethyl-5-α-ethoxy*-, m.p. 181—181·5°, -n-*propoxy*-, m.p. 177·5—178°, -n-*butoxy*-, m.p. 132·5—133°, and -iso*amyloxy*-, m.p. 129·2—130°, *-ethylbarbituric acid*; *5-α-ethoxyethyl-5-n-propyl*-, m.p. 168·5—169°, -n-*butyl*-, m.p. 138—139°, -iso*amyl*-, m.p. 136—137°, *-allyl*-, m.p. 127—128°, and -sec.-*amyl*-, m.p. 169—169·5°, *-barbituric acid*; *5-α-n-propoxyethyl-5-allyl*-, m.p. 160—160·5°, and -sec.-*amyl-barbituric acid*, *forms*, m.p. 210·5—212° and 153·5—154·5°. R. S. C.

2-Sulphanilamidopyrimidine.—See B., 1942, III, 21.

Pentduopent reaction. V. H. von Dobeneck (*Z. physiol. Chem.*, 1942, **275**, 1—15).—Prep. of propentduopent (*A*) solutions, essentially by alkaline H_2O_2, from hæmin, bilirubin (**I**), biliverdin, urobilin, stercobilin, and blood is described and absorption max. of the products are recorded. Animal organs, urine, pneumococci, and icterus serum do not give the pentduopent (*B*) reaction, *i.e.*, a red colour on treatment of solutions of (*A*) with alkaline $Na_2S_2O_4$. A positive reaction by urine indicates presence of hæmin. (*A*) are considered to include the structure shown and (*B*) to be 5 : 5′-dihydroxypyrromethenes (or the derived CO-form). This is supported by analysis of the *propentduopent* from (**I**), the *Zn* salt of that from the Me_2 ester of opsic acid-methene, the *Cu* salt of that from ætiohæmin-I, and the Me_2 ester of 5 : 5′-dihydroxy-3 : 3′-dimethylpyrromethene-4 : 4′-dipropionic acid, and by the following results. Et 3-formyl-2 : 4-dimethyl- with H_2–Raney Ni in EtOH at 160°/150 atm. gives Et 2 : 3 : 4-trimethylpyrrole-5-carboxylate (60%), m.p. 127° (and, sometimes, a dimeride, m.p. 228°, of Et 2 : 4-dimethylpyrrole-5-carboxylate). 2 : 2′-Dibromo-3 : 4 : 3′ : 4′-tetramethylpyrromethene with boiling KOAc–AcOH–H_2O gives 5 : 5′-*dihydroxy*-3 : 4 : 3′ : 4′-*tetramethylpyrromethene* (>5%), m.p. 211°, which with H_2O_2–NaOH gives the 3 : 4 : 3′ : 4′-*Me*$_4$ derivative, m.p. 223°, of (*A*) and with H_2–PtO_2 in MeOH gives the derived *pyrromethane*, m.p. 214°. 5 : 5′-*Dihydroxy*-4 : 4′-*dicarbomethoxy*-3 : 3′-*dimethylpyrromethane*, m.p. 147°, is obtained from the corresponding (*A*) or (*B*). R. S. C.



Bile pigments. XXXV. Synthesis of biliverdin (uteroverdin), bilirubin, biliverdins XIII*α* and III*α*, and of vinylneoxanthic acid. H. Fischer and H. Plieninger (*Z. physiol. Chem.*, 1942, **274**, 231—260).—Opsopyrrolecarboxylic acid is converted by H_2O_2 in C_5H_5N at 55° into β-5- (**I**), m.p. 183°, with a smaller amount of -2- (**II**), m.p. 140—145°, -hydroxy-4-methylpyrrole-3-propionic acid. (**I**) is converted (MeOH–HCl, not CH_2N_2) into the *Me* ester, m.p. 85—87°, and thence by N_2H_4,H_2O in boiling MeOH into the *hydrazide*,

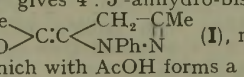
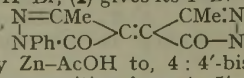
m.p. 148°. This is converted by HNO_2 at −5° into the unstable *azide*, transformed by boiling EtOH into 5-*hydroxy*-4-*methyl*-3-β-*carbethoxyaminoethylpyrrole* (**III**), m.p. 80—85°, which could not be hydrolysed to the amine by acid or alkali by reason of the instability of the pyrrole ring. (**III**) is condensed with opsopyrrolealdehyde (**IV**) in alkaline medium to 5-*hydroxy*-4 : 3′-*dimethyl*-3-β-*carbethoxyaminoethylpyrromethene*-4-*propionic acid* (**V**), m.p. 205°, which with CH_3O–HCl affords *Me*$_2$ 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 8-*tetramethyl*-2 : 7-β-*carbethoxyaminoethyl*-2α : 7′γ-*bilidiene*-4 : 5-*dipropionate*, m.p. 250°. This is dehydrogenated by *p*-O:C_6H_4:O in AcOH at 100° to the *glaucobilinurethane*, m.p. 248°, also obtained from (**V**), Ac_2O, and HCO_2H at 100° and hydrolysed by 18% HCl at 135—140° to 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 8-*tetramethyl*-2 : 7-β-*aminoethyl*-2′α : 7′γ-*bilidiene*-4 : 5-*dipropionic acid dihydrochloride* (**VI**), which when benzoylated and esterified (MeOH–HCl) gives an unidentified *compound*, $C_{49}H_{52}O_8N_6$, m.p. 145°. Prolongation of the reaction between (**III**) and (**IV**) (see above) leads to the unstable 5′-*hydroxy*-3 : 4′-*dimethyl*-3′-β-*aminoethylpyrromethene*-4-*propionic acid*, m.p. 230—240° [*Me* ester (**VII**), m.p. (indef.), 90—120° (decomp.)], benzoylated and esterified (MeOH–HCl) to *Me* 5′-*hydroxy*-3 : 4′-*dimethyl*-3′-β-*benzamidoethylpyrromethene*-4-*propionate*, m.p. 235°, which condenses with Ac_2O–HCO_2H to *Me*$_2$ 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 8-*tetramethyl*-2 : 7-*di*-β-*benzamidoethylbilitriene*-4 : 5-*dipropionate*, m.p. 195—220°. The corresponding -2 : 7-*di*-β-*acetamidoethyl acid* (*Me*$_2$ ester, m.p. 220°) is hydrolysed by boiling 18% HCl to (**VI**). Methylation (NaOH–Me_2SO_4) of (**VI**) followed by elimination of NMe_3 and esterification (MeOH–HCl) leads to biliverdin XIIIα Me_2 ester, m.p. 245° (Kofler), also obtained by the action of KOH–MeOH containing $Zn(OAc)_2$ and MeI on (**VI**) and converted by fusion with *m*-$C_6H_4(OH)_2$ into Me vinylneoxanthobilirubate, m.p. 187°, also obtained from (**VII**). (**II**) and 5-formyl-3-acetyl-2 : 4-dimethylpyrrole after esterification yield Me 5-hydroxy-4′-acetyl-3 : 3′ : 5′-trimethylpyrromethene-3-propionate, m.p. 250°. (**II**) is transformed by HCl–MeOH into the *Me* ester, m.p. (indef.) 45°, and thence successively into the hydrazide, m.p. 162°, *azide*, and *carbethoxyamino*-derivative and 5′-*hydroxy*-3 : 3′-*dimethyl*-4′-β-*carbethoxyaminoethylpyrromethene*-4-*propionic acid* (*Me* ester, m.p. 227°); this is converted by Ac_2O–HCO_2H followed by esterification into *Me*$_2$ 1′ : 8′-*dihydroxy*-2 : 3 : 6 : 7-*tetramethyl*-1 : 8-*di*-β-*carbethoxyaminoethylbilitriene*-4 : 5-*dipropionic acid* (**VIII**) and 1′ : 8′-*dihydroxy*-2 : 3 : 6 : 7-*tetramethyl*-1 : 8-*di*-β-*acetamidoethylbilitriene*-4 : 5-*dipropionic acid* are obtained as described for the isomerides. The latter substance is hydrolysed to the non-cryst. amine hydrochloride, which is transformed into biliverdin IIIα, m.p. 230° (Kofler). (**VIII**) and Me formylvinylneoxanthate in boiling MeOH–48% HBr afford *Me*$_2$ 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 7-*tetramethyl*-2-*vinyl*-8-β-*aminoethylbilitriene*-4 : 5-*dipropionate hydrobromide*, hydrolysed and then transformed by $Zn(OAc)_2$ and Me_2SO_4 into biliverdin IXα, m.p. 206—209°. (**V**) is converted by treatment with HCN–HCl in $CHCl_3$ and then with H_2O into 5-*hydroxy*-5′-*aldehydo*-3′ : 4-*dimethyl*-3-β-*carbethoxyaminoethylpyrromethene*-4′-*propionic acid*, m.p. 233°, which is condensed to *Me*$_2$ 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 7-*tetramethyl*-2 : 8-*di*-β-*carbethoxyaminoethylbilitriene*-4 : 5-*dipropionate*, m.p. 210° (Kofler), transformed by conc. HCl at 100° into biliverdin IXα [Me ester, m.p. 199—200°, hydrolysed (KOH–MeOH) and reduced ($Na_2S_2O_4$) to bilirubin].

H. W.

Action of sodium amalgam on position-isomeric, monoalkyl derivatives of 5-keto-3-thion-6-benzyl-1 : 2 : 4-triazine. E. Cattelain (*Compt. rend.*, 1942, **214**, 429—431).—2-Monoalkyl derivatives are not affected by Na–Hg, which cyclises β-alkylthiosemicarbazones of $CH_2Ph{\cdot}CO{\cdot}CO_2H$, the liberated alkali acting as a dehydrating agent. 3-Monoalkyl compounds give the 3 : 4-H_2-derivatives without opening of the heterocyclic ring. 4-Monoalkyl derivatives give 1 : 6-H_2-derivatives without rupture of the ring whereas the parent compound suffers ring opening between 4 and 5 and then adds 2 H at 1 and 6 yielding $CH_2Ph{\cdot}CH(CO_2H){\cdot}[NH]_2{\cdot}CS{\cdot}NH_2$.

H. W.

Diacylamino-1 : 3 : 5-triazines.—See B., 1943, II, 7.

Pyrazole nucleus. Transposition of bis-4 : 5′- into bis-4 : 4′-pyrazolene. G. B. Crippa and R. Caracci (*Gazzetta*, 1941, **71**, 574—580).—1-Phenyl-3-methyl-5-pyrazolone with BzOH at 100° (8—10 hr.) or NH_2Ph at 180° gives 4 : 5′-anhydro-bis-(1-phenyl-3-methyl-5-pyrazolone),  (**I**), m.p. 258° (cf. Ionescu *et al.*, A., 1928, 74), which with AcOH forms a *compound*, M_2,AcOH, m.p. 244°. With AcOH–Br, (**I**) gives its 4′-*Br*-derivative, m.p. 214°, with "pyrazole-blue,"  (**II**), also obtained from, and reduced by Zn–AcOH to, 4 : 4′-bis-(1-phenyl-3-methyl-5-pyrazolone). The transposition from 4 : 5′- to 4 : 4′-structure on formation of (**II**) is attributed to enolisation of (**I**), which in fact gives (Me_2SO_4) a *Me ether*, 5-*methoxy*-1-*phenyl*-4-(1′-*phenyl*-3′-*methylpyrazolyl*)-3-*methylpyrazole*, m.p. 130°, which with Br–AcOH gives only a 4′-*Br*-derivative, m.p. 93°, with no 4 : 4′-product of "pyrazole-blue" type.

E. W. W.

Quinoxaline cyanines. I. A. H. Cook, J. Garner, and C. A. Perry (*J.C.S.*, 1942, 710—713).—Dimethylquinoxaline methiodide (**I**) in C_5H_5N with *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ in Ac_2O gives 2-(1 : 3-*dimethylquinoxaline*)-1-(4-*dimethylaminobenzene*)*dimethincyanine*, m.p. 244° (*methosulphate*, m.p. 182—183°), which may also be prepared without the isolation of the methiodide; the corresponding -3-*methyl*-1-*ethyl* compound (*ethosulphate*, m.p. 170—171°) may also be similarly obtained. 1 : 3 : 3-Trimethyl-2-methyleneindoline-ω-aldehyde and (**I**) yield 2-(1 : 3-*dimethylquinoxaline*)-2-(1 : 3 : 3-*trimethylindoline*)*trimethincyanine*, m.p. 188°. Quinaldine methiodide and diphenylformamidine afford 2-*anilinovinylquinoline methiodide* (**II**), m.p. 256° (decomp.); with the appropriate reagents, 2-*methylanilinovinyl-benzoxazole ethiodide*, -*benzthiazole methiodide* (**III**), m.p. 244°, and -*quinoline methiodide*, m.p. 271°, are similarly obtained. Of these three compounds, only (**III**) can be hydrolysed (NaOH) to 1-*methyl*-2-*methylenebenzthiazoline*-ω-*aldehyde*, m.p. 99°. With Ac_2O–NaOAc, (**I**) and (**II**) give 2-(1 : 3-*dimethylquinoxaline*)-2-(1-*methylquinoline*)*trimethincyanine*, m.p. >360°. 2-(1 : 3-*Dimethylquinoxaline*)-2-(1-*methylbenzoxazole*)*trimethincyanine iodide*, decomp. >300°, may be obtained similarly without the isolation of the intermediate derivatives. HCO_2Na and (**I**) in Ac_2O when kept below 20—25° yield *bis*-2-(1 : 3-*dimethylquinoxaline*)*trimethincyanine iodide*, m.p. 204—205°, after treatment with KI. *o*-$NH_2{\cdot}C_6H_4{\cdot}NHPh$ with Ac_2 followed by Ac_2O and *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ in C_5H_5N and treated with NaCl gives 2-(1-*phenyl*-3-*methylquinoxaline*)-1-(4-*dimethylaminobenzene*)*dimethincyanine chloride*, decomp. ~320°. By using the same amine with the appropriate aldehyde under specified conditions the following are obtained: 2-(1-*phenyl*-3-*methylquinoxaline*)- (*acetate*, m.p. 154°) and 2-(1-*phenylquinoxaline*)-2-(1 : 3 : 3-*trimethylindoline*)-*trimethincyanine* (*iodide*, m.p. 177°); *bis*-2-(1-*phenyl*-3-*methylquinoxaline*)*trimethincyanine acetate*, m.p. 161° (*chloride*, decomp. >300°); and 2-(1-*phenylquinoxaline*)-1-(4-*dimethylaminobenzene*)*dimethincyanine iodide*, decomp. >300°. A strong bathochromic influence of the quinoxaline system is evident from the deep blue colour of the cyanines described.

F. R. S.

Exchange experiments with radioactive tracers.—See A., 1943, I, 38.

Condensations between methoxyacetonitrile and ketones. *iso*-Oxazole group. C. Musante (*Gazzetta*, 1941, **71**, 553—565).—$OMe{\cdot}CH_2{\cdot}CN$ (**I**) and COMeEt with Na in Et_2O, followed by dil. H_2SO_4, gives a mixture, b.p. 92—97°/21—22 mm., probably of $OMe{\cdot}CH_2{\cdot}C(:NH){\cdot}CH_2{\cdot}COEt$ (**II**) and $OMe{\cdot}CH_2{\cdot}C(:NH){\cdot}CHMeAc$, converted by hydrolysis or on keeping into a mixture of diketones, which with N_2H_4–EtOH, followed by aq. $KMnO_4$ and conc. HCl gives pyrazole-3 : 5-dicarboxylic acid, showing the presence of the diketone corresponding to (**II**). Similarly (**I**) and COPhMe (**III**) give β-*imino*-γ-*methoxy*-n-*butyrophenone* (**IV**), m.p. 27—30°, b.p. 180°/6—7 mm. (*Cu* salt, m.p. 188—190°), which with $FeCl_3$–EtOH gives a *product*, m.p. 156—157°. When heated with 20% NaOH, (**IV**) evolves NH_3, giving (**III**). With NaOEt–NH_2OH,HCl in EtOH, (**IV**) gives 5-*phenyl*-3-*methoxymethyl*iso*oxazole*, b.p. 180°/28—29° (oxidised by AcO_2H to the 3-carboxylic acid), formed by initial replacement of :NH by :N·OH. With conc. HCl at 160—170°, (**IV**) yields 5-*phenyl*-3-*chloromethyl*iso*oxazole*, m.p. 47·5—48·5°, hydrolysed by 10% KOH to give (**III**). *p*-$OMe{\cdot}C_6H_4{\cdot}COMe$ and (**I**) give β-*imino*-γ-*methoxy*-n-*butyro*-p-*methoxyphenone*, m.p. 96—98° (*Cu* salt, m.p. 210°), which with NH_2OH gives 5(or 3)-p-*anisyl*-3(or 5)-*methoxymethyl*iso*oxazole*, m.p. 55°, oxidised by AcO_2H to *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$. *p*-$C_6H_4Br{\cdot}COMe$ and (**I**) give β-*imino*-γ-*methoxy*-n-*butyro*-p-*bromophenone* [*Cu* salt, m.p. 221° (decomp.)].

E. W. W.

Sulphonamide derivatives of *iso*oxazole. C. Musante (*Gazzetta*, 1941, **71**, 565—573).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and 4-amino-3 : 5-dimethyl-, -5- and -3-methyl-, and -3-phenyl-*iso*oxazole (obtained by $SnCl_2$ reduction of the 4-NO_2-compound) at 100° give products which with aq. HCl yield respectively 4-p-*anilinesulphonamido*-3 : 5-*dimethyl*-, m.p. 193—194° (*Ac* derivative, m.p. 245—246°), -5-*methyl*-, m.p. 136—137° [*Ac*, m.p. 222—224° (darkening), and *Ac*$_2$, m.p. 189—190°, derivatives], -3-*methyl*-, m.p. 146—148° (*Ac* derivatives, m.p. 192°) (which with $NaNO_2$ gives a product, darkening at 200°), and -3-*phenyl*-iso*oxazole*, m.p. 170—171°. *p*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$ and 3 : 5-dimethyliso*oxazole*-4-sulphonyl chloride give 3 : 5-*dimethyl*iso*oxazole*-4-*sulphon*-p-*aminoanilide*, m.p. 167°.

E. W. W.

2-Thiolthiazolines.—See B., 1943, II, 7.

Raman spectra of thiazole and its mono- and di-substituted derivatives.—See A., 1943, I, 31.

Vapour pressure of hydrates of sulphathiazole sodium. J. Crusellas (*J. Amer. Pharm. Assoc.*, 1942, **31**, 157—158).—Data for commercial preps. of the mono- (**I**), sesqui- (**II**), and hexa-hydrate indicate that there are two structural modifications of (**I**) and that (**II**) is the most stable hydrate under average conditions.

F. O. H.

Action of phenylhydrazine on saccharin and thiosaccharin. (Signa.) A. Mannessier-Mameli (*Gazzetta*, 1941, **71**, 596—614).—Saccharin (**I**) and thiosaccharin (**II**) with $NHPh{\cdot}NH_2$ (**III**) at room temp. give respectively the *saccharinate*, m.p. 130°, sweet, and *thiosaccharinate* (**IV**), m.p. 109—110°, bitter, of (**III**). In AcOH, or

at 140—145°, (**II**) and (**III**) give *saccharinphenylhydrazone* (**V**), m.p. 225° (decomp. 230°) (*Bz* derivative, m.p. 330—335°), not obtained under similar conditions from (**I**) and (**III**), which, however, give (**V**) at 160—180°, with saccharinphenylimine and *o*-amidosulphonylbenzanilide. When heated above its m.p., (**IV**) gives (**V**). H_2O_2 oxidises (**V**) to (**I**) and an amorphous product. At 235—240°, (**V**) gives saccharinimine, (**I**), and NH_2Ph. Its reducing properties suggest that (**V**) is tautomeric with 3-*phenylhydrazino-ψ-saccharin*. E. W. W.

Condensation of phenanthrenequinone with the diaminocarboxylic acid derived from biotin. K. Hofmann, G. W. Kilmer. D. B. Melville, and V. du Vigneaud (*J. Biol. Chem.*, 1942, **145**, 503—509; cf. A., 1942, II, 387).—The diaminocarboxylic acid derived from biotin gives the *dibenzoquinoxaline* (**I**), $C_{23}H_{20}O_2N_2S$, m.p. 202—204°, and not the dihydroquinoxaline, suggesting that biotin possesses a 5-membered ring, and is probably *A*. The ultraviolet absorption spectra of the *dibenzodihydroquinoxaline* (**II**), m.p. 183—185°, derived from 3 : 4-diaminotetrahydrothiophen differs from that given by (**I**). (**II**) heated at 200° and then sublimed at 200°/2 mm. gives the *dibenzoquinoxaline* derivative, m.p. 228—233°, the absorption spectrum of which is similar to that of (**I**). A. T. P.

(*A.*)

VII.—ALKALOIDS.

Erythrina alkaloids. XII. Chromatographic analyses of erysodine, erysovine, and "erysocine." Technique for preparative isolation. K. Folkers and J. Shavel, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1892—1896; cf. A., 1942, II, 120).—These alkaloids are best separated by chromatography (Al_2O_3; $CHCl_3$; sometimes development by EtOH; technique described). Erysodine (**I**) and erysovine (**II**) are homogeneous, but "erysocine" (A., 1940, II, 332; cf. Gentile *et al.*, A., 1942, II, 275) is thus resolved into (**I**) and (**II**). Erysopine, (**I**), and (**II**) are isolated from *E. cubensis*, Wright, *E. pallida*, Britton and Rose, and *E. arborescens*, Roxb., (**I**) and (**II**) from *E. Folkersii*, Kruk. and Mold., *E. velutina*, Willd., and *E. excelsa*, Baker, and (**I**) from *E. Berteroana*, Urb. R. S. C.

Quinine sulphamate. K. H. Stahl and R. A. Kuever (*J. Amer. Pharm. Assoc.*, 1942, **31**, 154—156).—Quinine (1 mol.) with $NH_2{\cdot}SO_3H$ (1 or 2 mols.) in EtOH gives *quinine sulphamate*, m.p. 171—173° (decomp.), and *disulphamate*, m.p. 173—175° (decomp.). Photomicrographs of the crystals of the salts are given. F. O. H.

Cinchona alkaloidal salts of sulphanilamide.—See B., 1943, III, 21.

Ergot alkaloids. XIX. Transformation of *dl*- and *d*-lysergic acid into 6 : 8-dimethylergolines. R. G. Gould, jun., L. C. Craig, and W. A. Jacobs (*J. Biol. Chem.*, 1942, **145**, 487—494; cf. A., 1939, II, 525).—*dl*-Lysergic acid, m.p. 251° (decomp.), and Na–BuOH give dl-*dihydrolysergic acid*, m.p. 290—300°; sublimation at 350°/25 mm. then yields the unsaturated dl-*lactam*, $C_{16}H_{16}ON_2$, m.p. 313—316° (cf. A., 1938, II, 384), hydrogenated (PtO_2–AcOH at room temp.) to the saturated dl-*lactam*, $C_{16}H_{18}ON_2$, m.p. 332—336° and 310—315° (possibly racemic modifications); the two forms are combined and reduced by Na–BuOH possibly to (mainly) 7-hydroxy-6 : 8-dimethylergoline, and sublimation of the product at 200°/0·2 mm. affords dl-*dehydro*-6 : 8-*dimethylergoline*, m.p. 182—186°, hydrogenated (PtO_2–AcOH) to dl-6 : 8-*dimethylergoline*, m.p. 227—229° (two cryst. forms), identical with the synthetic product. The structure of lysergic acid is thus confirmed. Optically active α-dihydrolysergic acid is similarly converted into the unsaturated lactam, and thence (H_2; PtO_2–EtOH) into the saturated *lactam*, m.p. 332—336° [some stereoisomeride (**I**), m.p. 300—308°, is also isolated], a dehydro-6 : 8-dimethylergoline, m.p. 155—157°, and 6 : 8-dimethylergoline, m.p. 246—248° (apparent change of cryst. form at 170°), $[\alpha]_D^{20}$ −49° in $CHCl_3$. (**I**) similarly affords a little 6 : 8-dimethylergoline, m.p. 234—238°. The unsaturated *lactam*, $C_{16}H_{16}ON_2$, obtained from γ-dihydrolysergic acid at 350°/25 mm. has m.p. 239—240°, $[\alpha]_D^{20}$ −197° in C_5H_5N. A. T. P.

VIII.—ORGANO-METALLIC COMPOUNDS.

New heterocyclic systems. F. G. Mann, F. G. Holliman, and D. R. Lyon (*Nature*, 1942, **150**, 603).—*o*-Br·$[CH_2]_2$·C_6H_4·CH_2Br condenses readily with alkyl- or aryl-dichloroarsines in presence of metals to give stable 2-alkyl(aryl)-1 : 2 : 3 : 4-tetrahydro*iso*arsinolines. Less good yields of 2-aryldihydro*iso*arsindoles are obtainable by the use of *o*-xylylene dibromide. A. A. E.

Vital stains.—See A., 1943, II, 31.

Electrolysis of Grignard reagents. Short-lived free radicals in ethyl ether. R. Pearson and W. V. Evans (*Trans. Electrochem. Soc.*, 1942, **82**, *Preprint* 23, 257—264).—Hydrocarbons have been prepared by electrolysing ethereal Grignard reagents and the tendencies of the liberated free radicals to combine or to disproportionate have been determined. Me, if in sufficiently high concn., forms C_2H_6, but if the concn. is low Me attacks the solvent forming CH_4, C_2H_4, C_2H_6, EtOH, and Pr$^\beta$OH. Et disproportionates whereas Pr$^\alpha$ both combines and disproportionates. Branching of the C chain decreases the combining tendency, probably by steric effect, whereas increase in C chain length increases this tendency. Bz, CH_2Ph, and *cyclo*hexyl combine. The current efficiency is ~100%. Possible reaction mechanisms are discussed. Mg aryl compounds have similarly been examined. The results support previous theories of the formation of free radicals by electrolysis. C. R. H

Tetra-aryl-phosphonium, -arsonium, and -stibonium salts. II. Mechanism of their formation by the aluminium chloride reaction. D. R. Lyon and F. G. Mann (*J.C.S.*, 1942, 666—671).—$AlCl_3$ and $AsPh_3$ combine in CS_2 to give *trichlorotriphenylarsinealuminium* (**I**), [$AsPh_3$→$AlCl_3$], oxidised in PhBr by air to $AsPh_3O$. *Tetraphenylarsonium picrate* has m.p. 201—202°, and the *thiocyanate*, m.p. 268—270°. At 200° (**I**) and PhBr give the $AsPh_4$ salt, without formation of by-products. The formation of (**I**) is confirmed by the prep. of mixed salts: *triphenyl*-p-*tolylarsonium iodide* (+H_2O, m.p. 186—187°), *thiocyanate* (+H_2O, m.p. 147—148°); *diphenyldi*-p-*tolylarsonium iodide* (+1·5H_2O, m.p. 194—195°); and *phenyltri*-p-*tolylarsonium iodide*, m.p. 205—206°, and *thiocyanate*, m.p. 143—144°. (**I**) is thermally stable to ~250°. When (**I**) is prepared with impure $AlCl_3$, C_6H_6 is evolved and $AsPh_4$ salt is produced. $AlCl_3$ and $AsPh_2Cl$ in CS_2 give the unstable additive product, *trichlorodiphenylchloroarsinealuminium* (**II**), which, at 200°, gives $AsPh_4Cl$ and As. When impure $AlCl_3$ is used, C_6H_6 is produced and less $AsPh_4$. $AsPh_4$ is not produced by heating PhBr and (**II**). With $AlCl_3$ and $AsPhCl_2$, *trichlorotris*(*phenyldichloroarsine*)*aluminium* is formed, a non-ionic compound containing 6-covalent Al; on heating $AsCl_3$ and $AsPh_2Cl$ are formed. C_6H_6 and $AsCl_3$ with $AlCl_3$ give $AsPhCl_2$, which reacts as described. Thus the As ion can arise in only two ways: by the interaction of (**I**) and PhBr, and by the thermal decomp. of [$AsClPh_2$→$AlCl_3$]. The following are also described: *tri*-o-*tolylarsine hydroxyoxybromide*, m.p. 148—152°, *oxydibromide*, m.p. 232°, *oxydipicrate*, m.p. 169—171°, and *hydroxyoxyiodide*; *tetra*-p-*tolylarsonium iodide*, m.p. 253—255°, and *thiocyanate* (+H_2O), m.p. 207—209°; *tetra*-m-*tolylarsonium iodide*, m.p. 155—156°; *tetra*-p-*tolylphosphonium iodide*, m.p. 260—264°, and the *m*-compound, m.p. 175—176°; and *tetraphenylphosphonium thiocyanate*. F. R. S.

IX.—PROTEINS.

Analysis and minimum mol. wt. of β-lactoglobulin. E. Brand and B. Kassell (*J. Biol. Chem.*, 1942, **145**, 365—378).—The min. mol. wt. of β-lactoglobulin (**I**) (42,000) obtained from the distribution of the S-containing NH_2-acids and from the arginine content agrees with the mol. wt. in solution (41,600). (**I**) contains 364(±3) NH_2-acid residues + 1 to 6 terminal NH_2-acids. 1 mol. contains the following residues: cysteine 4, half-cystine 8 (*i.e.*, 4 S·S linkings), methionine 9, tryptophan 4, tyrosine 9, arginine 7, threonine 21, serine ~15, amide groups 22, histidine 4—6, and lysine 31—36. The side-chains of (**I**) contain >45 OH and it is suggested that these contribute to the cohesion of the mol. by H bridges through H_2O mols. J. E. P.

***X*-Ray diffraction studies of iodinated amino-acids and proteins.**—See A., 1943, I, 8.

Phosphopeptones of caseinogen (lactotyrins).—See A., 1942, III, 902.

Ultracentrifugal isolation from lung tissue of a macromolecular protein component with thromboplastic properties.—See A., 1943, III, 84.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Purification and chemistry of penicillin. J. R. Catch, A. H. Cook, and I. M. Heilbron (*Nature*, 1942, **150**, 633—634).—By chromatography from an org. solvent on a column consisting of a H_2O-retentive support associated with an inorg. base, penicillin (**I**) is recovered quantitatively and manifold concn. is easily accomplished. The yellow Sr salt, $C_{24}H_{34}O_{11}NSr$, has no measurable optical activity. Dil. acid, alkali, or moist org. bases afford by fission a H_2O-sol. acid, an insol. *pigment* ($C_{16}H_{20}O_6$ or possibly $C_{16}H_{18}O_5{,}H_2O$), MeCHO, and a little αβ-unsaturated aldehyde, $C_7H_{12}O$) but no CO_2. Reduction of (**I**) with Al–Hg affords as hydrolysis product an insol. *compound*, $C_{16}H_{20}O_5$. Ozonolysis of the pigment affords MeCHO, whilst degradation with alkaline permanganate affords <3 mols. of $H_2C_2O_4$. A. A. E.

Beech bark (*Fagus silvatica*).—See A., 1943, II, 39.

XI.—ANALYSIS.

Standardisation of chromatographic analysis. A. L. LeRosen (*J. Amer. Chem. Soc.*, 1942, **64**, 1905—1907).—Chromatography may be put on a quant. basis by use of the terms, S = length of absorbent column containing a unit vol. of solvent/length of empty tube required to contain the same vol. of solvent, V_0 = the const. rate of flow of the solution (the initial rate is abnormally fast), and R = rate of movement of an adsorbate zone relative to that of the developing solvent. This is illustrated for various carotenoids on $Ca(OH)_2$ developed by C_6H_6 and is used successfully to predict the behaviour of some mixtures. R. S. C.

Determination of ammonia by a diffusion method.—See A., 1943, I, 41.

Kjeldahl distillation without absorbing acid.—See A., 1943, I, 41.

Sulphur in organic compounds containing nitrogen and halogen. Acidimetric micro-determination. E. L. Brewster and W. Riemann (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 820—821).—The H_2SO_4 resulting from the combustion in O_2 is evaporated in a stream of purified air, HNO_3 and HCl being removed by evaporation. Apparatus and procedure are detailed. J. D. R.

Qualitative and quantitative analysis of hydrocarbon mixtures by means of their Raman spectra. D. H. Rank, R. W. Scott, and M. R. Fenske (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 816—819).—A linear relation between the relative intensity of the Raman lines compared with an internal standard and the vol. concn. is shown for six binary mixtures of hydrocarbons, one of which is an azeotropic mixture of min. b.p. This linear relationship is general for mixtures of nearly all hydrocarbons within the limits set for the determination of intensities of Raman lines by means of photographic plates. Scattering coeffs. are described and vals. for this const. are given for a series of hydrocarbons. Qual. and quant. analysis of hydrocarbon mixtures by means of Raman spectra could be substituted for infra-red analysis in cases where components of the mixtures contain appreciable % of the constituents to be determined. J. D. R.

Identification of alcohols and alkyl hydrogen sulphates with *S*-benzylthiuronium chloride. R. K. Bair and C. M. Suter (*J. Amer. Chem. Soc.*, 1942, **64**, 1978).—Alcohols are converted by $ClSO_3H$–dioxan and then *S*-benzylthiuronium chloride in H_2O or aq. EtOH into *Pr*$^{\alpha}$, m.p. 111·5—112·5°, *Pr*$^{\beta}$, m.p. 142—143°, *Bu*$^{\alpha}$, m.p. 100—101°, *CHMeEt*, m.p. 117—119°, *Bu*$^{\beta}$, m.p. 136—137°, n-*amyl*, m.p. 85—86°, n-*hexyl*, m.p. 85—86°, n-*heptyl*, m.p. 77—79°, n-*octyl*, m.p. 42—70°, n-*decyl*, m.p. 73—75°, n-*dodecyl*, m.p. 74—76°, *myristyl*, m.p. 87—88°, cyclo*hexyl*, m.p. 163—164°, *bornyl*, m.p. 174—175°, and *menthyl*, m.p. 149—150°, S-*benzylthiuronium sulphate* and *ethylene di*-S-*benzylthiuronium disulphate*, m.p. 180—181°. $NaAlkSO_4$ are similarly identified. MeOH and EtOH do not give cryst. salts. *S*-*p*-Chlorobenzylthiuronium chloride gives waxy salts. M.p. are corr. R. S. C.

Effect of formaldehyde on the volatilisations of ammonia, mono-, di-, and tri-methylamine. G. J. Benoit, jun., and E. R. Norris (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 823—825).—CH_2O renders NH_3 almost completely non-volatile at room temp., but has no effect on the recovery of NMe_3. It does not completely prevent the volatilisation of NH_2Me and $NHMe_2$. When $NHMe_2$ and NH_2Me are distilled in presence of CH_2O anomalies are observed which in the case of $NHMe_2$ are probably due to MeOH present in the aq. CH_2O. J. D. R.

Micro-determination of urea-nitrogen. J. C. Bock [with F. A. Kordecki] (*J. Biol. Chem.*, 1941, **140**, 519—523).—A very simple but accurate micro-method is described. 0·5 c.c. of blood is treated with urease in presence of Na_2CO_3, and the liberated NH_3 is absorbed in 0·1N-HCl and determined by nesslerisation. The method is applicable to determination of urea-N in urine provided that NH_3-N is determined by the same method. J. N. A.

Derivatives in the indane group as reagents for amines. IV. Methylbindone. G. Wanag (*Z. anal. Chem.*, 1942, **123**, 292—305).—In glacial AcOH a green coloration is given by aromatic primary mono-, di- (not *o*-), tri-, and tetra-amines (≥ 2 NH_2 in one ring). ·NO_2 and ·SO_3H, but not ·Hal, ·OH, :CO, or ·CO_2H, interfere. The reaction is also given by NHPhR (R ≠ Me, Et), *o*-C_6H_4Me·NHR, $NPhR_2$ (not C_6H_4Me·NR_2), $C_{10}H_7$·NHR, $C_{10}H_7$·NMe_2, *sec.*, purely aromatic amines with Ph, C_6H_4Me, and α-$C_{10}H_7$ radicals, NPh_2Et, and NPh_2·CH_2Ph. A. A. E.

Photometric determination of arginine. E. Brand and B. Kassell (*J. Biol. Chem.*, 1942, **145**, 359—364).—The intensity of the colour developed by arginine (**I**) in the Sakaguchi reaction (Weber, A., 1930, 755) decreases linearly with increasing amounts of (**I**), and the inhibition of colour development by NH_3 and by histidine likewise follows a linear course. Extrapolation to zero concn. yields the same colour value per unit wt. of (**I**). The (**I**) content of a protein is determined by estimating the apparent (**I**) contents of different amounts of a hydrolysate and then extrapolating to zero protein concn. The (**I**) content of cryst. proteins is: swine pepsin (0·96%, 2 residues per mol.), trypsinogen (1·61%), chymotrypsinogen (2·83%, 6 residues per mol.), β-lactoglobulin (2·87%, 7 residues per mol.), trypsin (3·27%), ribonuclease (5·16%), horse serum-albumin *A* (5·49%, 22 residues per mol.), horse serum-albumin *B* (5·52%, 22 residues per mol.), human serum-albumin (6·30%, 25 residues per mol.). J. E. P.

Determination of both cystine and cysteine in mixtures. M. X. Sullivan, W. C. Hess, and H. W. Howard (*J. Biol. Chem.*, 1942, **145**, 621—624).—Cystine (**I**) and cysteine (**II**) when determined by the CN′–(**I**) method are equiv., mol., for mol., in chromogenic val., deviations being due to impurity in (**II**), irregular H_2O content, or to oxidation. When determined by the amalgam–cyanide procedure, (**I**) and (**II**) are equiv. in chromogenic val. mg. for mg., since 1 mol. of (**I**) gives 2 mols. of (**II**). (**I**) and (**II**) can be determined, either singly or in mixtures. A. T. P.

Colorimetric micro-method for determination of cystine and cysteine. B. Vassel (*J. Biol. Chem.*, 1941, **140**, 323—336).—The method is based on formation of a blue colour by heating cystine (**I**) or cysteine (**II**) or both in acid solution with *p*-NH_2·C_6H_4·NMe_2 in presence of $FeNH_4(SO_4)_2$, and determination of the % absorption at 580 mμ. by a spectrophotometer. The method is applicable to 0·01—0·20 mg. of (**I**) or (**II**) per c.c. of solution (error ±3%). The formation of the blue colour depends on a SH and a primary NH_2 which are separated by two CH_2. Reduced glutathione and homocystine do not give the blue colour but they interfere with determination of (**I**) by causing reduction of the blue to a leuco-compound. Ascorbic acid and tyrosine have no effect on the determination, but when the former is added after formation of the blue colour, it causes reduction to the leuco-compound. J. N. A.

Colour reactions of phenols. A. Steigmann (*J.S.C.I.*, 1942, **61**, 180).—Monohydric phenols and resorcinol give blue or bluish-green colorations with Na β-naphthaquinonesulphonate in presence of NH_3 in aq. solution. *p*-Substituted phenols give a very weak reaction or none. Blue and violet colours are also given by certain phenols when oxidised together with *p*-NH_2·C_6H_4·NHPh or other *p*-phenylenediamines, preferably by chloramine-*T*; here again *o*- and *m*-phenols give the strongest reactions. The characteristic yellow Ag and red-brown Cu salt of C_6Cl_5·OH are described.

Determination of purines. G. H. Hitchings and C. H. Fiske (*J. Biol. Chem.*, 1941, **140**, 491—499; cf. A., 1941, II, 276).—The protein-free tissue filtrate containing 3—4 mg. of purine-N is diluted to ~30 c.c. in a 50 c.c. conical-tip centrifuge tube and neutralised to phenolphthalein. After heating to 100° the purine bases are pptd. by addition of 0·8 c.c. of saturated aq. $NaHSO_3$ and 1 c.c. of 10% aq. $CuSO_4$. The ppt. is centrifuged after 3 min., and washed twice with 10-c.c. portions of hot H_2O. The ppt. is suspended in 3 c.c. of 3N-HCl and boiled cautiously. After addition of 15 c.c. of H_2O the mixture is heated on the steam-bath while H_2S is passed in for ~3 min. The mixture is then cooled, diluted to 25 c.c., filtered, and N determined in an aliquot by the micro-Kjeldahl method. J. N. A.

Determination of sodium phenylethylbarbiturate. E. A. Kocsis and E. Kovács (*Z. anal. Chem.*, 1942, **124**, 40—42).—The aq. Na phenylethylbarbiturate (**I**) is pptd. by an excess of 0·1N-$AgNO_3$. The ppt. is collected on a No. 1 G4 Jena crucible (not paper), and the excess of $Ag^{\cdot}$ in the filtrate determined by Volhard's method using 0·1N-KCNS. $Ag^{\cdot}$ can be determined by adding excess of (**I**), followed by excess of 0·1N-$AgNO_3$, and then titration of excess $Ag^{\cdot}$ with 0·1N-KCNS. L. S. T.

Capillary analysis of some important opium alkaloids in filtered ultra-violet light. E. A. Kocsis and Z. Holló (*Z. anal. Chem.*, 1942, **124**, 35—40).—The colours given by 1% aq. solutions of morphine, codeine, thebaine, papaverine, narcotine, and narceine on Schleicher & Schüll No. 602 filter-paper in daylight and in ultra-violet light are tabulated and discussed. L. S. T.

Relation of alkaloidal to inorganic chemistry.—See A., 1943, I, 42.

Determination of arsenic in organic arsenical compounds. F. B. Rodman and H. N. Wright (*J. Amer. Pharm. Assoc.*, 1942, **31**, 200—202).—The Lehmann volumetric method (U.S.P. X) gives significantly lower results than the Treadwell–Hall gravimetric method. J. E. P.

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396 In formula (*A*) the ring on the extreme right should be shown attached to the apex of the adjacent *cyclo*pentane ring, not to the side.

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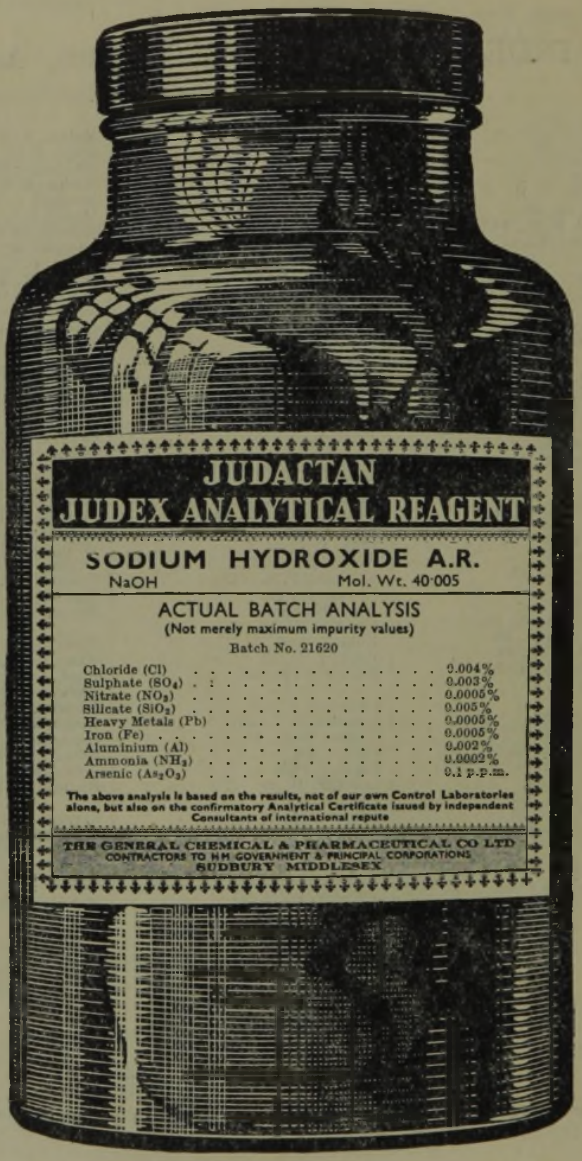

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