BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

AUGUST, 1940.

Absorption spectra as an aid to research in organic and biological chemistry. A. E. GILLAM (J. Roy. Coll. Sci., 1940, **10**, 21—34).—A lecture. L. J. J.

Catalytic cyclisation of βζ-dimethyloctane in the presence of platinised charcoal. B. A. KAZANSKI, A. F. PLATE, and E. E. GOLDMAN (Compt. rend. Acad. Sci. U.R.S.S., 1939, **23**, 250—251).—Passage of βζ-dimethyloctane (I) over platinised charcoal at ~310° gave a condensate with increased n indicating the formation of an aromatic hydrocarbon (II). Since (II) is convertible into *p*-cymene-α-sulphonic acid (identified as Ba salt) it is concluded that (I) is partly hydrogenated to *p*-cymene. W. R. A.

Destructive hydrogenation of high mol. wt. polymerides. *iso*Butene polymeride, butadiene polymeride, and natural rubber. V. N. IPATIEV and R. E. SCHAAD (Ind. Eng. Chem., 1940, **32**, 762—764).—Destructive hydrogenation of rubber-like *iso*butene polymeride (prep. by treating *iso*butene in liquid C_3H_8 with $AlCl_3$ and HCl) at 250°/100 kg. per sq. cm. initial H_2 pressure, using NiO as catalyst, yields only paraffinic hydrocarbons, indicating that the polymerides probably have long aliphatic C chains. Similar treatment of polymerised butadiene (prep. by heating butadiene at 150°/40 atm. and freeing the product from oils of b.p. <300° by vac. distillation) and of rubber yields only naphthenic hydrocarbons, principally ethyl*cyclo*hexane and *p*-menthane, respectively. Hydrogenation of isoprene at 250°/100 atm. H_2 in presence of NiO yields $EtPr^{\beta}$ (32 wt.-%) and a polymeric compound, b.p. 155—190°. J. W. S.

Action of fluorine vapour on organic compounds. VIII. Influence of dilution on vapour-phase fluorination of ethane. DEW. S. YOUNG, N. FUKUHARA, and L. A. BIGELOW (J. Amer. Chem. Soc., 1940, **62**, 1171—1173; cf. A., 1940, II, 147).—In presence of Cu gauze, C_2H_6 and F_2–N_2 give $(CHF_2)_2$, $CHF_2{\cdot}CH_2F$, and *pentafluoroethane*, f.p. −103°, b.p. −38°/1200 mm., −48·5°/760 mm., the proportions varying according to those of the reactants. R. S. C.

Catalytic hydration of olefines. III. Sulphuric acid as a catalyst for continuous preparation of *tert.*-butyl alcohol from *iso*butylene. E. K. REMIZ and A. V. FROST (J. Appl. Chem. Russ., 1940, **13**, 210—214; cf. A., 1936, 819).—$CH_2{:}CMe_2$ is passed through 3% Ag_2SO_4 in 10% H_2SO_4 at 90—95°, the issuing gas is passed through a condenser and then back to the process, and $Bu^{\gamma}OH$ condensing is collected. H_2O is added continuously to the reaction vessel, to maintain const. $[H_2SO_4]$. R. T.

Synthesis of choline β-glycerophosphate. H. ARNOLD (Ber., 1940, **73**, [*B*], 87—90; cf. Contardi *et al.*, A., 1933, 863).—Na_2 β-glycerophosphate with AcOH (to neutrality) and $AgNO_3$ gives Ag_2 *β-glycerophosphate* (I), which with $Br{\cdot}[CH_2]_2{\cdot}NMe_3Br$ in boiling EtOH under N_2 yields *choline β-glycerophosphate* (II), b.p. 104—105°, strongly hygroscopic, decomposed by $CdCl_2$. With $Br{\cdot}[CH_2]_2{\cdot}NH_2,HBr$, (I) gives a resinous product, *colamine α-glycerophosphate* (?) (cf. Feulgen *et al.*, A., 1939, III, 915), m.p. 80—90° (sinters 60°). (II) has 0·001 of the activity of acetylcholine (III) on the frog's heart and on blood pressure in the cat. Its activity on intestinal and skeletal muscle is similar to but much weaker than that of (III). Its activity at 10^{-5} on the leech is equiv. to that of (III) at 10^{-8}. When heated at 100°, (II) is first activated (due to hydration?) and then deactivated. E. W. W.

Preparation of branched-chain aliphatic sulphonic acids. S. ZUFFANTI (J. Amer. Chem. Soc., 1940, **62**, 1044).—RBr and boiling, aq. Na_2SO_3 give 56·8—95·7% of RSO_3Na and thence by HCl–Et_2O *propane*-β-, m.p. −37° (109°), *β-methyl*-n-*propane*-α-, m.p. −61° (123°), *γ-methyl*-n-*butane*-α-, m.p. −5° (115°), and iso*butane*-β-, m.p. −76° (131°), *-sulphonic acid*, figures in parentheses being m.p. of the $m\text{-}C_6H_4Me{\cdot}NH_2$ salts. R. S. C.

Reaction of sulphur with mercuric acetate in glacial acetic acid. R. E. VALLRATH (J. Amer. Chem. Soc., 1940, **62**, 1310).—At 135° the reaction, $6Hg(OAc)_2 + S \rightarrow 6HgOAc + 6AcOH + H_2SO_4$, occurs in AcOH. Prolonged heating gives a little org. Hg compound. R. S. C.

Mechanism of esterification of strong organic acids. I. Esterification of neopentyl alcohol with the chloroacetic acids. O. R. QUAYLE and H. M. NORTON (J. Amer. Chem. Soc., 1940, **62**, 1170—1171).—$CH_2Bu^{\gamma}{\cdot}OH$ (I) (prep. from $MgBu^{\gamma}Cl$ and gaseous CH_2O) gives neopentyl acetate, b.p. 127°, *chloro*-, b.p. 180°, *dichloro*-, b.p. 194°, and *trichloro-acetate*, b.p. 202°, p-*nitro*-, m.p. 54—54·5°, and 3 : 5-*dinitro-benzoate*, m.p. 90—90·5°. Absence of unsaturation (Br) and hydrolysis to (I) prove that during esterification isomerisation does not occur and thus that the C·O linking remains intact. R. S. C.

Addition of hydrogen bromide to methyl methylacrylate. C. C. PRICE and E. C. COYNER (J. Amer. Chem. Soc., 1940, **62**, 1306—1307).—$CH_2{:}CMe{\cdot}CO_2Me$ and HBr give under all conditions $CH_2Br{\cdot}CHMe{\cdot}CO_2Me$. $CMe_2Br{\cdot}CO_2Me$ is prepared

for comparison from $Pr^{\beta}CO_2H$ by red P–Br etc. Physical consts. are recorded. R. S. C.

Carbonation of organoalkali compounds. H. Gilman and H. A. Pacevitz (J. Amer. Chem. Soc., 1940, **62**, 1301—1302).—Interaction of n-$C_5H_{11}Cl$ and Na in light petroleum and spraying the products on to solid CO_2 gives 36·4—51·5% of n-$C_5H_{11}\cdot CO_2H$ (I) and <2% of $CHBu^n(CO_2H)_2$ (II). Gaseous CO_2 gives 15·2—19·5% of (I) and 14·8—31·4% of (II). R. S. C.

Fatty acids. VI. Crystallisation methods in the isolation of arachidonic acid; comparison of the properties of this acid prepared by crystallisation and by debromination. Structure of arachidonic acid. G. Y. Shinowara and J. B. Brown (J. Biol. Chem., 1940, **134**, 331—340).—Crystallisation from $COMe_2$ of the esters of adrenal phosphatides yields 70—75% pure Me arachidonate, distillation of which yields the 95% pure ester (I). The properties of (I) are compared with those of the ester obtained by the bromination–debromination method. Comparison of the octabromide of (I), and of the arachidic acid obtained by reduction and its Me and Et esters, with synthetic specimens confirms their straight-chain structure. Ozonisation and oxidation ($KMnO_4$–$COMe_2$) of (I) yields MeCHO, succinic and adipic acids, but not malonic, oxalic, or azelaic acid. The $\Delta^{5,8,11,14}$ structure is suggested. A. Li.

Hydrolysis of fats and fatty acid esters. VIII. T. Ono (J. Agric. Chem. Soc. Japan, 1940, **16**, 439—453; cf. A., 1940, I, 260).—Selective hydrolysis of mixed glycerides is more readily carried out in heterogeneous than in homogeneous systems. More highly unsaturated acid radicals are more readily split off from fish oils by lipase or KOH at −10° than less saturated or saturated radicals. H. G. R.

Separation of hydroxy- from non-hydroxy-aliphatic acids by means of a dibasic acid anhydride. F. E. Kurtz and P. S. Schaffer (J. Amer. Chem. Soc., 1940, **62**, 1304—1305).—The mixed saturated esters are heated with $(CH\cdot CO)_2O$ (I) at 120°, and the product is dissolved in light petroleum and extracted with dil. KOH. For unsaturated esters $(CH_2\cdot CO)_2O$ in C_5H_5N at 130° (some tar formed) is preferable, as a side-reaction occurs with (I). R. S. C.

Increase in optical rotation of *d*-lactic acid. S. Fukuda (J. Biochem. Japan, 1939, **30**, 473—477).—With 23·4% aq. *d*-lactic acid (I), addition of H_3BO_3 up to a concn. of 2·5% increases $[\alpha]^{18}$ progressively from +2·14° to +5·12°; borax gives a max. increase at a concn. of 2·0%, higher concns. (up to 3·35%) decreasing $[\alpha]$. $UO_2(NO_3)_2$, especially in presence of KOH, and $NHPh\cdot NH_2$ increase $[\alpha]$, whilst $(NH_4)_2MoO_4$ gives a 50-fold increase [max. at 1 mol. per 5 mols. of (I)]. F. O. H.

Phosphorylated oxidation product of pyruvic acid. F. Lipmann (J. Biol. Chem., 1940, **134**, 463—464; cf. A., 1939, III, 1100).—$AcCO_2H$ is oxidised by enzyme solutions from *B. delbrückii* in presence of inorg. PO_4''' (with or without F′). The quantity of the latter (determined by deproteinisation with $CCl_3\cdot CO_2H$, neutralisation, and pptn. with $CaCl_2$) decreases by an amount nearly equiv. to the extra O used, an unstable org. phosphate being formed which behaves like acetyl phosphate. A. Li.

Synthesis of serine. J. L. Wood and V. du Vigneaud (J. Biol. Chem., 1940, **134**, 413—416).—Equimol. quantities of $CH_2Br\cdot CHBr\cdot CO_2Et$ and NaOEt at 0° give an 80—85% yield of $OEt\cdot CH_2\cdot CHBr\cdot CO_2Et$ (NaOMe gives poorer yields of the OMe-compound), for the synthesis of serine (A., 1937, II, 53). A. Li.

Extension of Reformatsky reaction. I. Ethyl bromomalonate and acetone. B. H. Iyer (J. Indian Chem. Soc., 1940, **17**, 215—218).—$CHBr(CO_2Et)_2$ with Zn and excess of $COMe_2$ yields $CH_2Ac\cdot CMe_2\cdot CH(CO_2Et)_2$ (I), also obtained from $CMe_2{:}CH\cdot COMe$ (II) and $CN\cdot CH_2\cdot CO\cdot NH_2$ (Qudrat-i-Khuda, A., 1929, 295), or by using (II) or diacetone alcohol instead of $COMe_2$. With only 1 mol. of $COMe_2$, (I) is obtained together with some (II) and unchanged reactants. The mechanism of the formation of (I) is discussed. A. Li.

Addition of αβ-unsaturated alcohols to the active methylene group. I. Action of ethyl acetoacetate on linalool and geraniol. M. F. Carroll (J.C.S., 1940, 704—706).—With $CH_2Ac\cdot CO_2Et$ (I) at 140—210°, linalool gives geranylacetone (II) (cf. Foster *et al.*, J.C.S., 1913, **103**, 1345) (55% yield), with an isomeric ketone, and the acetate, b.p. 84—86°/1 mm., of an alcohol, b.p. 82—85°/1·5 mm. With (I) at 200°, geraniol gives geranyl acetate, and (II) (19% yield). E. W. W.

Polyhydric alcohol–polybasic acid reaction. V. Glyceryl succinate and maleate polyesters. R. H. Kienle and F. E. Petke (J. Amer. Chem. Soc., 1940, **62**, 1053—1056; cf. A., 1939, II, 506).—Interaction of glycerol with $(CH_2\cdot CO_2H)_2$ and with $(CH_2\cdot CO)_2O$ is similar after 50% esterification. < the theoretical amount of H_2O is evolved, probably owing to retention of H_2O by the product. Interaction with $(CH\cdot CO)_2O$ leads to liberation of > the theoretical amount of H_2O, owing to anhydride formation and intra-esterification. Gelation of the products is associated with low mol. wt. (1100—1200). R. S. C.

Action of sodium alkoxides on ethyl *s*-diethoxysuccinate. II. Mechanism of formation of ethyl *as*-diethoxysuccinate from ethyl disodiotartrate. S. Fukunaga (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1940, **37**, 216—220; cf. A., 1940, II, 243).—Isomerisation of *d*-$[CH(OEt)\cdot CO_2Et]_2$ to $CO_2Et\cdot CH_2\cdot C(OEt)_2\cdot CO_2Et$ (I) is easily effected by NaOEt, less easily by $[CH(ONa)\cdot CO_2Et]_2$ (II), and scarcely by $CO_2Et\cdot CH(OH)\cdot CH(ONa)\cdot CO_2Et$. The change follows the course, (II) → $[CH(OEt)\cdot CO_2Et]_2$ → *trans*-$CO_2Et\cdot C(OEt){:}CH\cdot CO_2Et$ → (I). H. W.

Fully acetylated sugar acids and their derivatives. G. B. Robbins and F. W. Upson (J. Amer. Chem. Soc., 1940, **62**, 1074—1076).—Glucose and O_2 in 2N-KOH give K *d*-arabonate, which by way of the Ca and Na salt yields d-*arabonic acid*, m.p. 114—116°, $[\alpha]$ +10·5° in H_2O, or by way of the Ca salt and lactone d-*arabonamide*, m.p. 138—139°, $[\alpha]$ +38·6° in H_2O. The appropriate amide with $ZnCl_2$ in Ac_2O

at 0° gives d-*arabonamide tetra-acetate*, m.p. 123°, [α] +24·3°, d-*talonamide penta-acetate*, m.p. 104—106°, [α] +85·4°, and d-*galaheptonamide hexa-acetate*, m.p. 185—187°, [α] +2·1°. The crude or pure amide with N_2O_3 (A., 1938, II, 124) gives d-*arabonic acid tetra-* (I), m.p. 135—136°, [α] +32·5° (*phenylhydrazide*, m.p. 140—141°, [α] +8·4°; *Me* ester, m.p. 136°, [α] +42·3°), d-*mannonic acid penta-* (II), +H_2O, m.p. 75—76°, [α] +24·8° (*phenylhydrazide*, m.p. 173°, [α] +13·0°), d-*talonic acid penta-* (III), m.p. 142—144°, [α] +78·3° (*phenylhydrazide*, m.p. 162—163°, [α] +35·0°; *Me* ester, m.p. 78—79°, [α] +70·1°), d-*gulonic acid penta-* (IV), a syrup, [α] +1·8° (*phenylhydrazide*, a syrup, [α] +37·7°; *Me* ester, a syrup, [α] +4·4°), and d-α-*glucoheptonic acid hexa-* (V), +0·5H_2O, m.p. 94°, [α] +10·7° (*phenylhydrazide*, m.p. 154°, [α] +27·4°; *Me* ester, m.p. 93°, [α] +14·1°), *-acetate*. Direct acetylation of the acid yields (I), (III), *d*-galactonic acid penta-acetate (*phenylhydrazide*, m.p. 220°, [α] +23·6°; *Me* ester, m.p. 126—127°, [α] +2·5°), and d-α-*galaheptonic acid hexa-acetate*, m.p. 176—177°, [α] +15·3° (*phenylhydrazide*, m.p. 112—114°, [α] +25·0°; *Me* ester, m.p. 96—97°, [α] +18·8°). d-*Arabonolactone triacetate*, m.p. 68—69°, [α] +52·3°, and d-α-*galaheptonolactone penta-acetate*, m.p. 123—124°, [α] −16·9°, are prepared from the lactone by Ac_2O at 0°. Attempts to prepare (II), (IV), and (V) from the Na salts of the OH-acids by Ac_2O–AcOH give the acetylated lactones. *Me* d-*gluconate penta-acetate* has m.p. 124°, [α] +9·2°. Phenylhydrazides named above are prepared from the unacetylated phenylhydrazides by Ac_2O–$ZnCl_2$ at 0°. Me esters are prepared from the acetylated acids by CH_2N_2. Unless otherwise stated, [α] are $[\alpha]_D^{25}$ in $CHCl_3$.

R. S. C.

Mutarotation and rotatory dispersion of derivatives of *aldehydo-d*-galacturonic acid. R. J. Dimler and K. P. Link (J. Amer. Chem. Soc., 1940, **62**, 1216—1219).—The tetra-acetate of Me *d*-galacturonate Et mercaptal (modified prep.) gives (method : A., 1930, 1021) Me *aldehydo-d*-galacturonate tetra-acetate (I), m.p. 135—136°, $[\alpha]_{5893}^{25}$ −15·6° in $CHCl_3$, which yields, according to the method used, the α-, macro-m.p. 105—107°, micro-m.p. 135—136° after loss of EtOH at ~105°, $[\alpha]_{5893}^{25}$ +40·7° → +7·1° (no min.) in $CHCl_3$, or β-*Et semiacetal*, macro-m.p. 127—130°, micro-m.p. 135—136° after loss of EtOH at ~127°, $[\alpha]_{5893}^{25}$ −6·7° → +7·1° (min. −10·0°) in $CHCl_3$, the min. in [α] being due to rapid formation of (I) as intermediate in the mutarotation. *Et* d-*galacturonate Et mercaptal*, m.p. 128—129°, $[\alpha]_{5893}^{25}$ +15·7° in EtOH (*tetra-acetate*, m.p. 80—81°, $[\alpha]_{5893}^{25}$ +11·0° in $CHCl_3$), *Et* aldehydo-d-*galacturonate tetra-acetate* (II), m.p. 95—97°, $[\alpha]_{5893}^{25}$ −24·0° in $CHCl_3$, and *Et* d-*galacturonate tetra-acetate* β-*Et semiacetal*, m.p. 105—106°, $[\alpha]_{5893}^{25}$ −14·4° → −1·6° (no min.) in $CHCl_3$, are also prepared. The rotatory dispersion of (I) and (II) agrees with two-term Drude equations.

R. S. C.

Esters of alginic acid. H. J. Lucas and W. T. Stewart (J. Amer. Chem. Soc., 1940, **62**, 1070—1074).—HNO_3–H_2SO_4 introduces into alginic acid 0·49—1·2 NO_2 per mannuronic acid unit. The product lactonises when dried, but can be partly methylated without replacement of NO_2. Methylation of (I) is slow (CH_2N_2; affects CO_2H and OH) or accompanied by degradation (Me_2SO_4). R. S. C.

Rates of formation of sulphoaliphatic acids.—See A., 1940, I, 326.

Aldehyde complexes of copper salts. T. L. Davis and W. P. Green, jun. (J. Amer. Chem. Soc., 1940, **62**, 1272—1274).—Prep. and dissociation pressure of *compounds*, CuNCS,MeCHO, 2CuI,MeCHO, $Cu(OAc)_2$,MeCHO, 2CuNCS,PrCHO, and 3CuI,PrCHO, and the v.p. of PrCHO are recorded. R. S. C.

Chlorination and structure of acetylketen. C. D. Hurd and J. L. Abernethy (J. Amer. Chem. Soc., 1940, **62**, 1147—1148).—Keten dimeride (I) and Cl_2 in CCl_4 give *γ-chloroacetoacetyl chloride* (II), b.p. 93—96° (decomp.)/8 mm. (cf. Boese, A., 1940, II, 65), which with NH_2Ph in C_6H_6 gives *γ-chloroacetoacetanilide*, m.p. 140—141°. Crude (II) and EtOH at 0° give $CH_2Cl{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, b.p. 117—119°/17 mm. (I) is probably a mixture of COMe·CH:CO and crotono-β-lactone. R. S. C.

Keten acetals. V. Reaction of keten diethyl acetal with compounds containing an active hydrogen [atom]. H. M. Barnes, D. Kundiger, and S. M. McElvain (J. Amer. Chem. Soc., 1940, **62**, 1281—1287; cf. A., 1940, II, 202).—Most compounds containing active H attached to halogen, O, C, or N add to $CH_2{:}C(OEt)_2$ (I) by attachment of the H to CH_2, but $CH_2Ac{\cdot}CO_2Et$ and $CH_2(CO_2Et)_2$ add as H and $CHAc{\cdot}CO_2Et$ and $CH(CO_2Et)_2$, respectively. The latter additions are catalysed by NaOEt, the function of which is discussed. HBr and (I) in Bu^{α}_2O give EtBr (85%) and EtOAc (72%) by way of $CMeBr(OEt)_2$. 3 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}CO_2H$ and (I) in Et_2O give 3 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}CO_2Et$ (74%). PhOH and (I) give PhOEt (78%), EtOAc (59%), and PhOAc (17%). CH_2Bz_2 and (I) give *Ph* β-α′α′-*diethoxyethoxy*-β-*phenylvinyl ketone*, $CMe(OEt)_2{\cdot}O{\cdot}CPh{:}CH{\cdot}COPh$, m.p. 86—87°, hydrolysed by 5% H_2SO_4 to EtOH, AcOH, and CH_2Bz_2, and pyrolysed at 140°/38 mm. in N_2 to (I) (31%) and CH_2Bz_2 (61%). $CH_2Ac{\cdot}CO_2Et$ (1 mol.), (I) (2 mols.), and NaOEt (0·01 mol.) at 85° give $CMe(OEt)_3$ (78%) and much *Et* α-α′-*ethoxyethylideneacetoacetate*, b.p. 96—98°/1 mm. [hydrolysed by H_2O (2 mols.) in dioxan to AcOH (92%) or by H_2O (1 mol.) in dioxan to $CHAc_2{\cdot}CO_2Et$], with some EtOH and EtOAc. $CH_2(CO_2Et)_2$, (I), and a little NaOEt at 125° give *Et*$_2$ α-*ethoxyethylidenemalonate* (55%), m.p. 26—27° (lit. an oil), b.p. 100—102°/1 mm., hydrolysed by hot 2N-HCl to $CHAc(CO_2Et)_2$ and hydrogenated (Raney Ni; EtOH; 100°/2800 lb.) to *Et*$_2$ α-*ethoxyethylmalonate*, b.p. 66—67°/0·4 mm. $CHMe(CO_2Et)_2$ does not react with (I). $CH_2(SO_2Ph)_2$ and (I) in dioxan give tars. NH_3 and (I) at 110° give EtOH, MeCN, $NH{:}CMe{\cdot}NH_2$, and $CMe(OEt)_3$ (OEt·CHMe:NH is an intermediate). NH_2Ph and (I) give EtOH (86%), $NPh{:}CH{\cdot}CO_2Et$, and a little $NPh{:}CMe{\cdot}NHPh$. NHPhEt and (I) at 100° give $CMe(OEt)_3$ and N-*ethyl*-N-α-*ethoxyvinylaniline*, b.p. 129—130°/22 mm., hydrolysed to NHPhEt, EtOH, and AcOH. Boiling piperidine and (I) give 43% each of $CMe(OEt)_3$ and ααα-*tripiperidinoethane*, b.p. 113—115°/1 mm., hydro-

lysed by boiling 6N-H_2SO_4 to piperidine (83%) and AcOH (110%). R. S. C.

Crystalline phenylurethanes of sugar glucosides. M. L. Wolfrom and D. E. Fletcher (J. Amer. Chem. Soc., 1940, **62**, 1151—1153).—The appropriate methylglucoside and PhNCO in boiling, dry C_5H_5N give α-, m.p. 227° (decomp.), $[\alpha]_D^{23}$ +73° in $COMe_2$, and β-*methyl*-d-*glucoside tetra*-, m.p. 225° (decomp.), $[\alpha]_D^{23}$ +13° in C_5H_5N, β-*methyl*-d-*xyloside tri*-, m.p. 234° (decomp.), $[\alpha]_D^{22}$ −23° in $COMe_2$, and α-*methyl*-d-*mannoside tetra*-, m.p. 189—190° (decomp.), $[\alpha]_D^{20}$ −18° in $COMe_2$, -*phenylurethane*. R. S. C.

Action of phosphorus pentachloride on *aldehydo*-galactose penta-acetate. 1 : 1-Dichloride of *aldehydo*-galactose penta-acetate. M. L. Wolfrom and D. I. Weisblat (J. Amer. Chem. Soc., 1940, **62**, 1149—1151).—*aldehydo*-*d*-Galactose penta-acetate (I) and PCl_5 in boiling Et_2O give *di*-(1-*chloro*-aldehydo-d-*galactose penta-acetate*) *chlorophosphate*, $(OAc{\cdot}CH_2{\cdot}[CH(OAc)]_4{\cdot}CHCl{\cdot}O)_2POCl$ (II), m.p. 190° (decomp.), $[\alpha]_D^{26}$ −20° in $CHCl_3$, and a trace of 1 : 1-*dichloro*-aldehydo-d-*galactose penta-acetate*, $OAc{\cdot}CH_2{\cdot}[CH(OAc)]_4{\cdot}CHCl_2$ (III), m.p. 148—150°, $[\alpha]_D^{20}$ +11° in $CHCl_3$ (better obtained in boiling C_6H_6–$CaSO_4$ under defined conditions), which both reduce Fehling's solution only slowly. Hydrolysis of (II) by Ag_2O and a little H_2O in boiling PhMe gives (I). With boiling HCl–EtOH or –MeOH, (II) gives *Et* (IV), m.p. 156—158°, $[\alpha]_D^{21}$ −24° in $CHCl_3$, and *Me di*-(1-*chloro*-aldehydo-d-*galactose penta-acetate*) *phosphate*, $(OAc{\cdot}CH_2{\cdot}[CH(OAc)]_4{\cdot}CHCl{\cdot}O)_2{\cdot}PO_2R$, m.p. 187—188° (decomp.), $[\alpha]_D^{30}$ −19° in $CHCl_3$, respectively. With $ZnCl_2$–Ac_2O at 98°, (IV) gives *aldehydo*-*d*-galactose hepta-acetate (V). Boiling, aq. $Cu(OAc)_2$ is reduced by *d*-galactose, (I), *aldehydo*-*d*-galactose Pr^{β} semiacetal, (V), 1-chloro-*d*-galactose hexa-acetate, 1-methoxy-*d*-galactose hexa-acetate, 1-chloro-1-ethoxy-*d*-galactose penta-acetate, and *d*-galactopyranose tetra-acetate, but not by β- or α-*d*-galactopyranose penta-acetate, (II), or (III); the test has diagnostic val. R. S. C.

***aldehydo*-Maltose octa-acetate.** M. L. Wolfrom and M. Konigsberg (J. Amer. Chem. Soc., 1940, **62**, 1153—1154).—Maltose Et_2 mercaptal octa-acetate, $HgCl_2$, $CdCO_3$, and H_2O in $COMe_2$ give 78% of *aldehydo*-maltose octa-acetate, m.p. 116—117°, $[\alpha]_D^{22}$ +93·5° in $CHCl_3$, $[\alpha]_D^{25}$ +96° in EtOH, and (+EtOH) m.p. 66—67° (*oxime*, m.p. 93—94°, $[\alpha]_D^{24}$ +107° in $CHCl_3$, +100° in EtOH) (cf. A., 1939, II, 202). R. S. C.

Constitution of amylose and amylopectin of maize starch. K. H. Meyer (Arch. Sci. phys. nat., 1940, [v], **22**, Suppl., 19—23).—Extraction of maize starch with H_2O at 70° and cooling gives cryst. amylose (I). Fractionation of this yields an insol. variety which gives no reaction with I, and reverts to a sol. form when dissolved in aq. chloral and pptd. with $COMe_2$. The Ac derivative in $CHCl_3$ has η little < that of cellulose acetate; measurements of its osmotic pressure show that the amylose has mol. wt. 20,000—50,000. The Ac_3 and Me_3 derivatives give films resembling those of cellulose. Amylopectin has mol. wt. 400,000, and gives clear solutions (without scission) in aq. chloral at 80° or in aq. N_2H_4 or $(CH_2{\cdot}NH_2)_2$ at room temp. Pptn. of the aq. chloral solution with $COMe_2$ yields a temporarily sol. form which turns blue with I. The Me_3 and Ac derivatives give brittle films; η of the latter in $CHCl_3$ is <20%, and that of its acid hydrolysis products 25%, of the vals. for cellulose derivatives. (I) is hydrolysed completely by β-amylase to maltose, but (II) only partly, to a dextrin of mol. wt. 150,000. It is concluded that (I) has straight, and (II) branched, mols. A. Li.

Structure of the dextran synthesised from sucrose by *Betacoccus arabinosaceus*, Orla-Jensen. W. Z. Hassid and H. A. Barker (J. Biol. Chem., 1940, **134**, 163—170).—Sucrose with *B. arabinosaceus* yields a non-reducing dextran (I), $[\alpha]_D$ +184° in N-NaOH, mol. wt. 11,700 (Staudinger) or 2600 (sedimentation equilibrium method). Hydrolysis (dil. HCl) of (I) gives glucose, the downward mutarotation indicating that the units of (I) have the α configuration. Acetylation (AcOH containing Cl_2, then Ac_2O containing SO_2) of (I) followed by hydrolysis yields a H_2O-sol. form, $[\alpha]_D$ +180° in H_2O. Methylation (Me_2SO_4, followed by Na, MeI, and liquid NH_3 in PhOMe) of (I) yields a product, $[\alpha]_D$ +214° in $CHCl_3$, hydrolysed (aq. AcOH–HCl) to 2 : 3 : 4-trimethyl- and 2 : 3 : 4 : 6-tetramethyl-glucose in the mol. ratio 15 : 1. A. Li.

Degradation of long-chain molecules. H. Mark and R. Simha (Trans. Faraday Soc., 1940, **36**, 611—618).—Cellulose acetate (Ac 39·3%, mol. wt. ~93,000) was subjected to homogeneous acetolysis (Ac_2O + AcOH), and distribution curves for the degradation products were obtained at four different stages of the reaction. The results are in qual. agreement with the theory of Kuhn (A., 1932, 576) and Flory (A., 1936, 1452). F. L. U.

Similarity of cellulose to caoutchouc and the production of artificial cellulose threads as a macromolecular process. P. H. Hermans (Naturwiss., 1940, **28**, 223).—The very pronounced similarity of caoutchouc to cellulose shows that the latter does not occupy a unique position as a micellary substance under all conditions but must be regarded in the same manner as the other complex polymerides. Macromol. processes are mainly operative in the production of artificial fibres and in deformation processes. H. W.

Unusual hydrates of quaternary ammonium salts. D. L. Fowler, W. V. Loebenstein, D. B. Pall, and C. A. Kraus (J. Amer. Chem. Soc., 1940, **62**, 1140—1142).—The prep. and analysis of the following *compounds* are given (m.p. in parentheses): $NBu^a_4{\cdot}OH,xH_2O$ [x = 31 (30·2°), 4 (26°), 2]; $NBu^a_4F,18H_2O$ (37°); $N(iso\text{-}C_5H_{11})_4{\cdot}OH,xH_2O$ [x = 32 (31°), 4 (57·5°)]; $N(n\text{-}C_5H_{11})_4{\cdot}OH,4H_2O$; $(Bu^a_4N)_2C_2O_4,38H_2O$ (20—25°); $HCO_2NBu^a_4,33H_2O$ (12·5°); $NBu^a_4Br,26H_2O$ (14·5°); $HCO_2N(iso\text{-}C_5H_{11})_4,50H_2O$ (15—20°); $NBu^a_4{\cdot}OAc,60H_2O$ (10—15°); $EtCO_2NBu^a_4,50H_2O$ (17°); $NBu^a_4{\cdot}OBz,35H_2O$ (3·5°); $NBu^a_4{\cdot}NO_3,27H_2O$ (5·8°); $NBu^a_4Cl,30H_2O$ (15°). Several salts which do not yield hydrates are listed. $NMe_4{\cdot}OH,5H_2O$ was prepared and $NPr^a_4{\cdot}OH$, and $NEtPr^a_3{\cdot}OH$ were obtained. W. R. A.

Reaction of the esters of *dl*-leucine and *l*-leucine on Raney catalyst. G. Ovakimian, C. C. Christman, M. Kuna, and P. A. Levene (J. Biol. Chem., 1940, **134**, 151—161).—Hydrogenation (H_2 under pressure, Raney Ni) of *dl*-leucine Et ester in MeOH yields, at 135°, *dl*-leucinol, and at 185° or 200°, *NN*-dimethyl-leucinol, $CHMeBu^{\beta}\cdot NMe_2$ (I), and 2 : 5- and *NN'*-dimethyl-2 : 5-di*iso*butylpiperazine (II), in proportions varying according to time and temp. *l*-Leucine Et ester with excess of catalyst at 70° gives *l-leucinol*, b.p. 130°/18 mm., $[\alpha]_D^{25}$ +3·8° in MeOH (*picrate*, m.p. 120—121°, $[\alpha]_D^{25}$ +5·9° in MeOH). Hydrogenation of leucinol or *NN*-dimethyl-leucinol at 185° gives only (I). *dl*-Leucine Me ester when heated at 150° in MeOH under pressure, with or without H_2, gives 3 : 6-diketo-2 : 5-di-*n*-propylpiperazine, converted by H_2–catalyst under pressure at 200° into (II). Glycylglycine anhydride similarly yields *NN'*-dimethylpiperazine. The mechanism of these reactions is discussed. A. Li.

Determination of valine and leucine in presence of other amino-acids. C. Fromageot and P. Heitz (Enzymologia, 1939, **6**, 258—270).—Valine (I) is determined by converting, with HNO_2, into the corresponding α-OH-acid (Kendall and Friedemann, A., 1931, 246), which is heated at 100° under pressure with CrO_3 in AcOH for 3 hr. $COMe_2$ produced (65% of the theoretical yield) is distilled and colorimetrically determined by a modification of the method of Urbach (*ibid.*, 1082). Leucine (II) is determined in the same way but the period of heating is 4 hr. and the yield of $COMe_2$ is 58%. Other NH_2-acids, including *iso*leucine, do not interfere in either case. When (I) and (II) are present together one determination is made as for (II) alone and in a second determination, the conc. solution of OH-acids is oxidised at atm. pressure so that the $COMe_2$ produced is directly distilled. The yields of $COMe_2$ obtained when (I) and (II) are separately determined by the second method are 72 and 21%, respectively. The proportions of the acids are calc. according to a formula given. The amounts of each acid required for the determination are 2—20 mg. W. McC.

Racemisation of glutamic acid. J. M. Johnson (J. Biol. Chem., 1940, **134**, 459).—*l*(+)-Glutamic acid hydrochloride undergoes 4·6% racemisation when boiled with conc. HCl for 35 hr. The *d*(−)-acid in protein hydrolysates is presumably formed by similar racemisation. A. Li.

Pantothenic acid diphosphoric acid. D. W. Woolley (J. Biol. Chem., 1940, **134**, 461—462; cf. A., 1940, III, 537; II, 203).—$OAc\cdot CH_2\cdot CHMe_2\cdot CH(OAc)\cdot COCl$ with $NH_2\cdot[CH_2]_2\cdot CO_2Et$, followed by selective hydrolysis, yields pantothenic acid (*Ba* salt), which with $POCl_3$ in C_5H_5N gives the diphosphoric acid, which is biologically inactive, though the crude phosphorylated mixture has some activity. A. Li.

Action of 4-amino-2-methyl-1-naphthol on the oxidation of certain thiol groups. F. Bernheim and M. L. C. Bernheim (J. Biol. Chem., 1940, **134**, 457—458).—1 : 2 : 4-$OH\cdot C_{10}H_5Me\cdot NH_2$,HCl catalyses the oxidation (not inhibited by cyanide) to disulphide of cysteine or $SH\cdot CH_2\cdot CO_2H$ at p_H 7·8, rapidly oxidises SH groups in rat liver nucleoprotein, and causes a 50% inhibition in the action of cryst. papain hydrochloride on milk, but has little effect on the oxidation of reduced glutathione. The physiological significance of these effects is discussed. A. Li.

α-Bromo-α-sulphonamides. W. M. Ziegler and R. Connor (J. Amer. Chem. Soc., 1940, **62**, 1049—1053).—The products considered by Tröger *et al.* (A., 1905, i, 336) to be $RSO_2\cdot CHR'\cdot CO\cdot NHBr$ are $RSO_2\cdot CR'Br\cdot CO\cdot NH_2$ (*A*) and contain "positive" Br. *α-Bromo*-p-*toluene*- (I), m.p. 172—174°, and *α-bromo*-n-*butane*-*α'*-*sulphonylacetamide*, m.p. 130—131°, *α-bromo*-α-p-*toluene*- (II), m.p. 115—116°, and *α-bromo*-α-n-*butane*-*α'*-*sulphonyl*-n-*butyramide* (III), m.p. 57—58°, are best obtained by brominating $RSO_2\cdot CHR'\cdot CO\cdot NH_2$, usually in moist CCl_4; sometimes the reactions, $RSO_2\cdot CHR'\cdot CO_2H \rightarrow RSO_2\cdot CHR'\cdot COCl \rightarrow RSO_2\cdot CR'Br\cdot COCl \rightarrow (A)$, are feasible, although yields are smaller. NaOBr is less satisfactory, *e.g.*, yields p-$C_6H_4Me\cdot SO_2\cdot CHBr_2$ in place of (I). Under some conditions (*A*; R = H) is replaced by *αα-dibromo*-p-*toluene*-, m.p. 134—135°, and -n-*butane*-*α'*-*sulphonylacetamide*, m.p. 106—107°. Bu^aSNa and (II) in EtOH give p-$C_6H_4Me\cdot SO_2\cdot CHEt\cdot CO\cdot NH_2$ (60%); p-$C_6H_4Me\cdot SNa$ and (III) similarly give $(p\text{-}C_6H_4Me\cdot S)_2$ and $Bu^aSO_2\cdot CHEt\cdot CO\cdot NH_2$ (IV) (73%). All the Br-amides liberate 2 I from HI and with N_2H_4 give N_2 (Br_2-amides more rapidly than Br_1-amides). Piperidine and (I) in dioxan give the hydrobromide (60%) and p-$C_6H_4Me\cdot SO_2\cdot CH_2\cdot CO\cdot NH_2$ (45%). NaOEt–EtOH with (I) gives p-$C_6H_4Me\cdot SO_2\cdot CH_2Br$ (also obtained by boiling 5% NaOH) and with (III) gives 61% of (IV). M.p. are corr. R. S. C.

Rate of reaction of Grignard reagent with ethyl bromide.—See A., 1940, I, 326.

Redistribution reaction. V. PbR_4 compounds. G. Calingaert, H. A. Beatty, and H. Soroos. **VI. Lead alkyl halides.** G. Calingaert, H. Soroos, and H. Shapiro. **VII. Alkyl compounds of mercury, tin, silicon, and zinc.** G. Calingaert, H. Soroos, and V. Hnizda (J. Amer. Chem. Soc., 1940, **62**, 1099—1104, 1104—1107, 1107—1110; cf. A., 1940, II, 72).—V. The redistribution reaction leads to random distribution of products from $PbMe_4$–$PbEt_4$, $PbMe_3Et$–$PbMeEt_3$, $PbMe_2Et_2$, $PbMe_4$–$PbPr^a_4$, $PbMe_3Pr^{\beta}$–$PbMe_2Pr^{\beta}_2$, $PbEt_4$–$PbPr^a_4$, $PbEt_2Pr^a_2$, $PbMe_4$–$PbEt_4$–$PbPr^a_4$, $PbMe_2Bu^{\beta}_2$, and $PbMe_4$–$PbPh_4$ in presence of a little $AlCl_3$ at 80° alone or in hexane or decahydronaphthalene. $PhMe_3Bu^{\gamma}$ requires 100—130°, and $PbPh_4$–$Pb(C_6H_4\text{-}p)_4$ requires 200°. 21 other catalysts are listed, notably Al and Pb alkyl halides and metallic halides. Increase in temp. increases the rate of reaction but does not alter the proportions in which products are formed. Solvent may retard the reaction.

VI. Random distribution follows heating $PbMe_2EtCl$, $PbMe_3Cl$–$PbEt_3Cl$, $PbMe_4$–$PbEt_3Cl$, $PbMe_4$–$PbEt_3Br$, or $PbEt_4$–$PbMe_3Br$ in $COMe_2$ at 60° or hexane at 76° or 80°. Pb alkyl halides themselves act as catalysts.

VIII. In presence of a little $AlCl_3$, the redistribution

reaction leading to random distribution occurs with $HgMe_2$–$HgEt_2$ and HgMeEt at 25°, $SnMe_4$–$SnEt_4$ in pentane at 60°, and $SiEt_4$–$SiPr_4$ at 173—181°, but not with $ZnMe_2$–$ZnEt_2$ at ~60°. Pure HgMeEt is stable at room temp. or 127°. R. S. C.

Reactions of sulphur and vapours of organic compounds at different temperatures. G. D. Palmer, S. J. Lloyd, W. P. McLure, N. LeMaistre, W. S. Waring, and L. W. Bachman (J. Amer. Chem. Soc., 1940, **62**, 1005—1006).—Passage of C_6H_6, PhMe, NH_2Ph, PhOH, PhCl, etc. vapour into S at 240—260° gives resinous S-dyes, but at 260—300° lower yields of solids which are not dyes. At >300° other dyes are formed. High S content is necessary for deep colour. R. S. C.

Velocity of hydrogenation of aromatic and unsaturated hydrocarbons.—See A., 1940, I, 297.

Liquid-phase hydrogenation of *p*-cymene. K. A. Kobe and A. Vittone (Ind. Eng. Chem., 1940, **32**, 775—777).—*p*-Cymene is most efficiently hydrogenated to *p*-menthane (I), b.p. 171·0°, at 220°/initial H_2 pressure 1000 lb. per sq. in. in presence of Ni catalyst (1%). V.p., *d*, and *n* data for (I) for various temp. are also recorded. J. W. S.

Alkylation of benzene with alcohols, boron fluoride, and assistants. N. F. Toussaint and G. F. Hennion (J. Amer. Chem. Soc., 1940, **62**, 1145—1147).—C_6H_6 is alkylated by ROH (R = Pr^{α}, Pr^{β}, Bu^{α}, Bu^{β}, CHMeEt, Bu^{γ}, *n*-C_5H_{11}, *n*-C_8H_{17}, or *n*-$C_{12}H_{25}$) in presence of BF_3 and P_2O_5, H_2SO_4, or $PhSO_3H$. *n*- and *sec.*-Alcohols give *sec.*-alkylbenzenes. CHMeEt·OH and $Bu^{\gamma}OH$ give $PhBu^{\gamma}$. Dialkylation gives mainly *p*-compounds. R. S. C.

Trialkylated benzenes and their compounds with aluminium chloride and with aluminium bromide. J. F. Norris and J. N. Ingraham (J. Amer. Chem. Soc., 1940, **62**, 1298—1301).—Passing HBr into *s*-$C_6H_3Et_3$ and $AlBr_3$ gives a *compound* (I), $2AlBr_3$,2*s*-$C_6H_3Et_3$,HBr, m.p. 64—66° (cf. Gustavson, A., 1905, i, 336), stable at 12 mm., giving at 0·002 mm. a *compound*, $2AlBr_3$,*s*-$C_6H_3Et_3$. With AcCl, (I) gives 1 : 3 : 5 : 2-$C_6H_2Et_3$·COMe, and with EtBr gives *s*-$C_6H_3Et_3$ and EtBr. Passage of HCl into (I) causes introduction of >1 Cl. A *compound*, $2AlCl_3$,2*s*-$C_6H_3Et_3$,HCl, m.p. 48—49°, is similarly prepared. *s*-$C_6H_3Me_3$ gives the *compound*, $2AlBr_3$,3*s*-$C_6H_3Me_3$,HBr, m.p. 47—48°, stable at 12 mm., but at 0·002 mm. giving the *compound*, $2AlBr_3$,*s*-$C_6H_3Me_3$. *Compounds*, (i) $2AlBr_3$,3*ψ*-cumene,HBr, (ii) $2AlBr_3$,PhMe,HBr (stable at 12 mm.; loses PhMe at 0·002 mm.), and (iii) $2AlBr_3$,C_6H_6,HBr (loses C_6H_6 at12 mm.), are prepared. R. S. C.

Influence of organic radicals on para-hydrogen. II. Nature of diradicals. G. M. Schwab and N. Agliardi (Ber., 1940, **73**, [*B*], 95—98).—By the para-H_2 method (A., 1938, I, 625), tetraphenyl-*p*-xylylene and *pp'*-diphenylenebisdiphenylmethyl are found to contain <0·2% and 9·7%, respectively, of the free radical form. E. W. W.

Steric inhibition of resonance in aromatic nitro-compounds. G. W. Wheland and A. A. Danish (J. Amer. Chem. Soc., 1940, **62**, 1125—1127). —Substitution of 6 Me *o*- to the NO_2 depresses the acidity of $(p\text{-}NO_2\cdot C_6H_4)_3CH$ (cf. A., 1937, II, 92). 1 : 3 : 5-$C_6H_3Me_2$·MgBr and $ClCO_2Et$ give a crude carbinol, converted by HCl–Et_2O into *tri*-1 : 3 : 5-*xylylmethyl chloride*, m.p. 210°, which with Zn dust–AcOH–CO_2 gives *tri*-1 : 3 : 5-*xylylmethane*, m.p. 108°. Fuming HNO_3 in Ac_2O–AcOH then yields *tri*-4-*nitro*-3 : 5-*dimethylphenylmethane* (16%), m.p. 247°, and oily products, Zn dust in boiling AcOH gives the 4 : 4′ : 4″-$(NH_2)_3$-derivative, darkens at 190°, decomp. 275—280°, also obtained from 1 : 3 : 2-$C_6H_3Me_2$·NH_2 (I) by $CH(OEt)_3$ (gives the *trianilino*-compound, m.p. 179°), followed by (I) and its hydrochloride. R. S. C.

***pp'*-Diradical of diphenyl, of the triphenylmethyl type. I.** W. Theilacker and W. Ozegowski (Ber., 1940, **73**, [*B*], 33—43).—*m*-Tolidine sulphate gives (Sandmeyer) 4 : 4′-*dicyano*-2 : 2′-*dimethyldiphenyl*, m.p. 113°, b.p. 176°/2 mm., hydrolysed by dil. H_2SO_4 to 2 : 2′-*dimethyldiphenyl*-4 : 4′-*dicarboxylic acid*, m.p. 330—332°, the Et_2 ester, m.p. 70°, b.p. 220°/2 mm., of which with MgPhBr in Et_2O, followed by HCl, yields 2 : 2′-*dimethyl*-4 : 4′-*diphenylenebisdiphenylcarbinol* (I), m.p. 174° or (+1 AcOH) m.p. 121°; the Et_2 *ether*, m.p. 199—200° (obtained by use of EtOH–HCl) [which with dil. HCl in AcOH gives the *glycol acetate*, $2C_{40}H_{34}O_2$,$C_4H_8O_2$, m.p. 136° and 172° after re-solidification] with dry HCl in AcOH at 50—60° yields 2 : 2′-*dimethyl*-4 : 4′-*diphenylenebisdiphenylmethyl dichloride* (II), m.p. 207°, clearing at 210°, also obtained from (I). When shaken with Hg under CO_2, (II) in C_6H_6 gives 2 : 2′-*dimethyl*-4 : 4′-*diphenylenebisdiphenylmethyl* (III), m.p. 176—178° (to viscous drops, fluid at >200°). This free radical [which is contrasted with the Tschitschibabin hydrocarbon, 4 : 4′-diphenylenebisdiphenylmethyl (A., 1907, i, 503)] gives a bluish-green solution (0·01%) in C_6H_6, which at increasing concn. gives a dichroic solution, green by transmitted and red by reflected light. Air passed through a 4% C_6H_6 solution of (III) gives a *peroxide*, softens 152—153° (decomp.). The possibility of dimerism of (III) is discussed. E. W. W.

Formation of naphthalene-1 : 3-disulphonic acid under conditions of direct sulphonation of naphthalene. A. A. Tschuksanova (Compt. rend. Acad. Sci. U.R.S.S., 1940, **26**, 445).—$C_{10}H_8$ (16 g.) with conc. H_2SO_4 (65 g.) at 130° for 4 hr. yields the 1 : 3- (separated as the dichloride) as well as the 1 : 6-, 1 : 7-, 2 : 6-, 2 : 7-, and 1 : 5-disulphonic acids. A. Li.

Reactions of unsaturated and polynuclear aromatic hydrocarbons with sodium and calcium in liquid ammonia. W. Hückel and H. Bretschneider (Annalen, 1939, **540**, 157—189).—$C_{10}H_8$ and Na in Et_2O with liquid NH_3 at −75° to −65° give a green, then orange-red, and finally a red colour; decomp. with MeOH after ~20 min. affords 1 : 4-dihydronaphthalene (I) (cf. Schlenk *et al.*, A., 1928, 1031). At higher temp. a mixture of (I) and 1 : 2-dihydronaphthalene (II) results; at the b.p. of NH_3 some (II) is formed. In one experiment nearly pure (II) was obtained. Na in Et_2O–NH_3 at −60° converts (I) into (II), whilst (II) and Na in liquid NH_3 at −50° give tetrahydronaphthalene (cf. Wooster

et al., A., 1931, 340). Ca gives similar results. Ph_2 with Na or Ca in liquid NH_3 at −75° to −70° affords 3 : 4-dihydro-, b.p. 114°/12 mm. (nitrosochloride; nitrolpiperidide, m.p. 194°), converted by Na at −75° into 3 : 4 : 5 : 6-tetrahydro-diphenyl, b.p. 125—126°/14 mm. Terphenyl (prep. described) and Na in liquid NH_3 yield the 3 : 4-H_2-derivative (III), m.p. 70°, and a *hydrocarbon*, $C_{18}H_{14}$, m.p. 152—153° (does not contain a reactive double linking). Catalytic reduction of (III), which reacts readily with Na forming a red compound, gives 4-*cyclo*hexyldiphenyl. $(CHPh{:}CH\cdot)_2$ reacts fairly readily with Na or Ca affording apparently different products; liquid and solid hydrocarbons are isolated in each case. CH_2Ph_2 gives a blue colour with Ca and the product yields a little of an unsaturated hydrocarbon. 9 : 10-Diphenylanthracene (IV) and Na in liquid NH_3 give an orange or orange-red solution; decomp. with NH_4Cl or EtOH affords only (IV). Phenanthrene reacts partly with 2 Na or 1 Ca in liquid NH_3 at −75°; 1 : 2 : 3 : 4-tetrahydrophenanthrene, which is probably not the primary reaction product, is isolated. $(CH_2{:}CH\cdot)_2$ gives C_4H_8 and octadiene. CH. ABS. (*b*)

Structure of aromatic compounds. III. Action of acetyl chloride on magnesium α- and β-naphthylmethyl halides. N. CAMPBELL, W. ANDERSON, and J. GILMORE (J.C.S., 1940, 819—821). —1-$C_{10}H_7\cdot CH_2\cdot MgCl$ and AcCl give *αγ-di-1-naphthyl-β-methylpropene*, m.p. 174—176°, ozonised to 1-$C_{10}H_7\cdot CO_2H$ and 1-$C_{10}H_7\cdot CH_2\cdot COMe$ (2 : 4-*dinitrophenylhydrazone*, m.p. 174—176°). 2-$C_{10}H_7\cdot CH_2Br$ [improved prep. from 2-$C_{10}H_7Me$ and Br at 240—260° (Hg-vapour lamp)], or, better, 2-$C_{10}H_7\cdot CH_2Cl$ (I), forms with difficulty a Mg derivative which with AcCl in Et_2O gives *αγ-di-2-naphthyl-β-methylpropene* (?), m.p. 184—185°, non-reactive towards alkaline $KMnO_4$ or Br in CCl_4. $CO(CH_2Ph)_2$ and MgMeI give $CMe(CH_2Ph)_2\cdot OH$, which with *o*-$C_6H_4(CO)_2O$ and P_2O_5 at 160° gives $CH_2Ph\cdot CMe{:}CHPh$, b.p. 180°/15 mm. (cf. Sabatier *et al.*, A., 1913, i, 717), oxidised to $CH_2Ph\cdot COMe$. (I) is obtained from $SOCl_2$ and 2-$C_{10}H_7\cdot CH_2\cdot OH$ (II) [improved prep. by catalytic reduction (Adams Pt, $FeCl_3$) of the aldehyde]; attempted prep. of (II) from 2-$C_{10}H_7\cdot MgI$ and CH_2O gives 2 : 2′-$(C_{10}H_7)_2$. E. W. W.

Dehydrogenation. VI. S. C. SEN-GUPTA (J. Indian Chem. Soc., 1940, **17**, 183—188; cf. A., 1940, II, 254).—Hydrindene, *cyclo*pentane-1-acetic-1-carboxylic anhydride, and $AlCl_3$ in $PhNO_2$ give β-5-*hydrindoyl-αα-tetramethylenepropionic acid*, m.p. 140—141° (*Me* ester, m.p. 47—48°, b.p. 210—212°/5 mm.) [oxidised by $KMnO_4$ to 1 : 3 : 4-$C_6H_3(CO_2H)_3$], reduced by Zn–Hg–conc. HCl to 5-β-1′-*carboxy*-1′-*cyclopentylethylhydrindene*, m.p. 104—105°, b.p. 220°/6 mm. 85% H_2SO_4 at 100° then gives 1-*keto*-6 : 7-*trimethylene*-2 : 2-*tetramethylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 98—99°, oxidised by $KMnO_4$ to 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$ and reduced by Zn–Hg–HCl to 6 : 7-*trimethylene*-2 : 2-*tetramethylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 64—65°. With Se at 300—320°, later 340—350°, this spiran gives a product, m.p. 149—150° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 128—129°], which is probably 2 : 3-*trimethyleneanthracene* since it differs from 2 : 3-*trimethylenephenanthrene* (I) (synthesis below). Et *cyclo*pentanone-2-carboxylate, HCN, and a drop of aq. KCN at <0° give the cyanohydrin, converted by $SOCl_2$, first at <0° and then at the b.p., into Et 2-cyano-Δ¹-*cyclo*pentene-1-carboxylate, b.p. 133—135°/4 mm. Boiling, conc. HCl then yields Δ¹-*cyclo*pentene-1 : 2-dicarboxylic acid, m.p. 178°, the anhydride, b.p. 130°/5 mm., of which with $AlCl_3$ and $C_{10}H_8$ in $PhNO_2$ gives mixed keto-acids, m.p. 155—165°, and thence (Clemmensen) mixed 2-α- and 2-β-naphthylmethyl-Δ¹-*cyclo*pentene-1-carboxylic acids, b.p. 215—220°/5 mm. $ZnCl_2$ at 180° (85% H_2SO_4 at 100° causes sulphonation) followed by Clemmensen reduction then gives 2 : 3-*trimethylene*-1 : 4-*dihydrophenanthrene*, m.p. 101—102°, dehydrogenated by Se at 300—320° (sealed tube) to (I), m.p. 84° [*picrate*, m.p. 157°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 162—163°]. R. S. C.

Action of perbenzoic acid on aromatic hydrocarbons. H. J. ECKHARDT (Ber., 1940, **73**, [*B*], 13—15).—Carcinogenic hydrocarbons react more readily (cf. Fieser, A., 1938, III, 1022) with BzO_2H than do other hydrocarbons. The reaction is followed iodometrically over a 7—15-day period. Methylcholanthrene > 3 : 4-benzpyrene > pyrene > benzpyrene-5-aldehyde in reactivity. 5-Nitrobenzpyrene scarcely reacts. Fluorene, phenanthrene, chrysene, and $C_{10}H_8$ do not react. 6- > 4-Methyl-1 : 2-benzanthracene > 1 : 2-benzanthracene > anthracene > 1 : 2 : 5 : 6-dibenzanthracene in activity. E. W. W.

1-β-Styrylacenaphthene. E. B. HERSHBERG and L. M. JOSHEL (J. Amer. Chem. Soc., 1940, **62**, 1305—1306).—Acenaphthene-1-aldehyde and $CH_2Ph\cdot MgCl$ in boiling Et_2O–C_6H_6 give 1-*acenaphthylbenzylcarbinol* (88%), m.p. 109—110°, dehydrated by $KHSO_4$ at 200° to 1-*styrylacenaphthene* (71%), m.p. 93·2—94° [*dipicrate*, m.p. 141·5—143° (decomp.)]. M.p. are corr. R. S. C.

9- and 10-Methyl-1 : 2-benzanthracene. C. K. BRADSHER (J. Amer. Chem. Soc., 1940, **62**, 1077—1078).—Crude *o*-$C_6H_4Cl\cdot CH(OH)\cdot C_{10}H_7$-α (prep. from α-$C_{10}H_7\cdot MgBr$ and *o*-$C_6H_4Cl\cdot CHO$ in Et_2O) and red P–I–AcOH–H_2O give 1-o-*chlorobenzylnaphthalene*, b.p. 189—192°/2 mm., converted by CuCN in C_5H_5N at 250—260° into o-1-*naphthylmethylbenzonitrile*, m.p. 59—60°, b.p. 216—217°/3 mm. With MgMeI in C_6H_6, this gives an imine, hydrolysed to o-1-*naphthylmethylacetophenone* (69%), m.p. 39—40°, b.p. 216—217°/3 mm. Ring-closure by 34% HBr in AcOH gives 86% (29% over-all) of 10-methyl-1 : 2-benzanthracene. β-$C_{10}H_7\cdot MgX$ (X = Br or I) give similarly 2-o-*chlorobenzylnaphthalene*, b.p. 203—204°/3 mm., o-2-*naphthylmethyl-benzonitrile*, m.p. 84·5—85·5°, and -*acetophenone*, b.p. 221°/3 mm., and 9-methyl-1 : 2-benzanthracene. R. S. C.

Sulphonic acids of pyrene and their derivatives. E. TIETZE and O. BAYER (Annalen, 1939, **540**, 189—210; cf. Vollmann *et al.*, A., 1937, II, 450). —Pyrene (I) and $ClSO_3H$ (1 mol.) in C_2Cl_4, first at 0—5° and then at 10—20°/15—20 hr., give pyrene-3-sulphonic acid [Na salt (II), prep. by aq. Na_2SO_4]. 80% HNO_3 and (II) in AcOH at 15—25°/12 hr. afford a nitro-sulphonic acid, reduced (Fe, AcOH) to the NH_2-derivative (readily diazotised and couples

with R salt to a dull violet dye). 93·2% H_2SO_4 and (I) at 0° and then 15°/2 days, followed by NaCl, yield *Na_2 pyrene*-3 : 8-*disulphonate* (III) [also obtained from (II) and 93·2% H_2SO_4 at 5—10°/1 hr.], converted by ~25% (wt.) aq. KOH at 260°/40 atm. into 3 : 8-dihydroxypyrene (diacetate, m.p. 222—224°); a little pyrene-3 : 5-disulphonic acid [*Ca* salt is more sol. than that ≡ (III)] is isolable from the mother-liquors from (III). H_2SO_4,H_2O and (II) at 15°/1 day followed by $CaCO_3$ and K_2CO_3 give *Na K_2 pyrene*-3 : 5 : 8-*trisulphonate*. Treatment of (II) in H_2SO_4,H_2O with 65% oleum at 20°/15 hr., followed by $CaCO_3$ and 20% NaCl, affords *Na_4 pyrene*-3 : 5 : 8 : 10-*tetrasulphonate* (IV) [also from (I) and Na_2SO_4 in H_2SO_4,H_2O at 58° followed by 65% oleum at 50—55°], converted by aq. HCl–$NaClO_3$ into 3 : 5 : 8 : 10-tetrachloropyrene. The successive action of boiling ~20% NaOH, conc. HCl, HCO_2H (neutralisation), and 10% NaCl on (IV) gives *Na_3* 3-*hydroxypyrene*-5 : 8 : 10-*trisulphonate* (+H_2O); aq. 22% NH_3 at 200—210°/18 hr. affords *Na_3* 3-*aminopyrene*-5 : 8 : 10-*trisulphonate*. 3-Chloropyrene and Na_2SO_4 in H_2SO_4,H_2O with 65% oleum at 50—60° yield *Na_3* 3-*chloropyrene*-5 : 8 : 10-*trisulphonate* [unaffected by aq. NH_3 (autoclave)]. Fusion of (IV) with NaOH and some H_2O at 130—170° gives *Na_2* 3 : 5-*dihydroxypyrene*-8 : 10-*disulphonate* converted by 10% H_2SO_4 at 140—150°/12 hr. into 3 : 5-*dihydroxypyrene* (V), darkens in air, m.p. 220° (decomp.) (*diacetate*, m.p. 154—155°; Me_2 ether, m.p. 177—178°). Zn dust, (IV), and boiling dil. NaOH afford *Na_2 pyrene*-3 : 5-*disulphonate*, which with aq. NaOH at 210—220°/8 hr. yields *Na* 3-*hydroxypyrene*-5-*sulphonate*, with NaOH at 250—260°/15 hr. gives (V), and with HNO_3–H_2SO_4 at 18°/20 hr. affords 3 : 5-dinitropyrene-8 : 10-disulphonic acid [corresponding $(NH_2)_2$-compound]. (IV) and ~25% (wt.) NaOH at 240—250°/12 hr. give 3 : 5 : 8 : 10-*tetrahydroxypyrene*, m.p. 236—238° (*Me_4 ether*, m.p. 172—173°, not nitratable), which does not couple with diazo-solutions and is oxidised (CrO_3) to a black substance. Many of the above compounds show fluorescence; some are dyes and their behaviour with fabrics is given. Ch. Abs. (*b*)

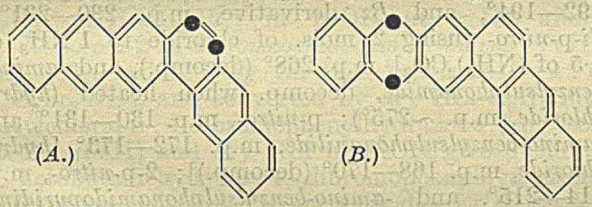
1-Methylchrysene. L. F. Fieser and L. M. Joshel (J. Amer. Chem. Soc., 1940, **62**, 1211—1214). —α-$C_{10}H_7$·CH_2·CO_2Na and *o*-C_6H_4Cl·CHO in Ac_2O at 135° give *o-chloro*-α-1-*naphthylcinnamic acid*, m.p. 171—172·5°, converted by KOH, first at 200—235° and later 245°, into the *lactone* (I) (4%), m.p. 244·5—245·5° (decomp.), of *o*-hydroxy-α-1-naphthylacetic acid. α-$C_{10}H_7$·CH_2·CO_2K and *o*-NO_2·C_6H_4·CHO in Ac_2O at 125—130° give *o*-NO_2·C_6H_4·CH:C($C_{10}H_7$-α)·CO_2H (68%), m.p. 181·8—182·8° (lit. 173—174°) (and a little *o*-NO_2·C_6H_4·CH:CH·CO_2H), reduced by $FeSO_4$ or, better, H_2–PtO_2 in EtOH to the NH_2-compound (II) (76%). Diazotisation ($C_5H_{11}O$·NO–H_2SO_4–EtOH) and subsequent treatment with Cu-bronze in aq. NaH_2PO_2 at 45—50° converts (II) into *chrysene*-1-*carboxylic acid* (III) (28%), m.p. 225—226° (decomp.) [and a little (I)], the *Me* ester (IV), m.p. 159—160°, of which with Na–EtOH–C_6H_6 gives 1-*hydroxymethylchrysene*, an oil, or with H_2–Cu chromite in dioxan at 250°/140 atm. gives 58·5% of 1-*methyl*-3—12 : 8*a* : 12*a*-*dodecahydrochrysene*, m.p. 98·8—99·8° [oxidised by 1 : 2 HNO_3–H_2O at 195—200° to $C_6H(CO_2H)_5$]. Hydrogenation of (IV) at 160° gives mostly an oily H_2-derivative. PCl_5 and (III) in boiling C_6H_6 give the acid chloride, which with NH_2Ph in $COMe_2$ gives the chloroanilide, converted by $SnCl_2$–HCl–Et_2O–$(CH_2Cl)_2$ at 0° into chrysene-1-aldehyde. The *semicarbazone*, m.p. 266—268° (decomp.), thereof with NaOEt–EtOH at 200° gives 17% of 1-*methylchrysene*, m.p. 116·8—117·6° (*picrate*, m.p. 141·6—142·4°). M.p. are corr. R. S. C.

Synthesis of 1 : 12-methylenechrysene and 9 : 1′-methylene-1 : 2-benzanthracene from 4 : 5-methylenephenanthrene. L. F. Fieser and J. Cason (J. Amer. Chem. Soc., 1940, **62**, 1293—1298).—4 : 5-Methylenephenanthrene (I), $(CH_2·CO)_2O$, and $AlCl_3$ in $PhNO_2$ at 0° (later 5°) give *γ-keto*-γ-4 : 5-*methylene*-1-*phenanthryl*-n-*butyric acid* (60%), m.p. 207—208° (decomp.) (*Me* ester, m.p. 124·8—125·5°; some isomeride also formed; HF gives a poor yield), reduced (best, crude) by Zn–Hg–HCl–PhMe (and a little AcOH) to γ-4 : 5-*methylene*-1-*phenanthryl*-n-*butyric acid* (55%), m.p. 176·6—177·6° [purified as *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 183·5—184·5°], which with HF gives 90% of 3-*keto*-1 : 12-*methylene*-3 : 4 : 5 : 6-*tetrahydrochrysene* (II), m.p. 167·5—168·5°. Treatment of (II) with $Al(OPr^{\beta})_3$ gives a crude carbinol, whence Pd–C at 300—320° gives a little impure 4 : 5-*methylenechrysene* (III). Clemmensen–Martin reduction of (II) gives 1 : 12-*methylene*-3 : 4 : 5 : 6-*tetrahydrochrysene* (IV) (59·5%), m.p. 129—129·4°. [With R. C. Clapp] Hydrogenation (Cu chromite; 160°) of (I) gives 4 : 5-*methylene*-9 : 10-*dihydrophenanthrene* (85%), m.p. 140·5—141·2°, whence are obtained as above *γ-keto*-γ-4 : 5-*methylene*- (99%), m.p. 224—224·5° (decomp.) (Na salt; *Me* ester, m.p. 137·1—137·4°), reduced (H_2–Cu chromite, very dil. aq. NaOH, 200°, 66%; or Clemmensen–Martin, 44%) to γ-4 : 5-*methylene*-, m.p. 154·5—155° (*Me* ester, m.p. 59·3—60°), -9 : 10-*dihydro*-2-*phenanthryl*-n-*butyric acid* (V) and thence (HF) 8-*keto*-9 : 1′-*methylene*- (49%), m.p. 201—203° (decomp.), hydrogenated (⩾1 atm.) to 9 : 1′-*methylene*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene* (94·5%), m.p. 83—83·5°. Dehydrogenation by Pd–C at 220° rising to 320° then gives 9 : 1′-methylene-1 : 2-benzanthracene. Dehydrogenation of (V) by Pd–C at 200° rising to 265° gives γ-4 : 5-*methylene*-2-*phenanthryl*-n-*butyric acid* (92%), m.p. 167·7—168·0° (purified as *Me* ester, m.p. 36·3—37·3°), which in HF gives 6-*keto*-1 : 12-*methylene*-3 : 4 : 5 : 6-*tetrahydrochrysene* (VI) (95%), m.p. 173—174°, and thence (H_2–Cu chromite; EtOH; 160°) 1 : 12-*methylene*-3 : 4 : 5 : 6 : 7 : 8-*hexahydrochrysene* (96·5%), m.p. 116·6—117·2°. Dehydrogenation (Pd–C; 220° rising to 270°) then gives (III) (64%), m.p. 172·4—172·9° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 194—195°; unstable picrate], also obtained (54·5%) similarly from (IV) or (19·5%) (VI). M.p. are corr. R. S. C.

[Nitration of] 3 : 4-benzpyrene. H. J. Eckhardt (Ber., 1940, **73**, [*B*], 15—18).—The conclusion of Fieser *et al.* (A., 1939, II, 364) that 3 : 4-benzpyrene is nitrated to 5-nitro-3 : 4-benzpyrene (I) is confirmed. The 9-position is excluded by its ready formation, and

the 10- by the non-identity of 10-amino-3 : 4-benzpyrene (Windaus *et al.*, A., 1939, II, 106) with the reduction product of (I). With excess of boiling CrO_3–AcOH, (I) gives 7-benzanthrone-3 : 4-dicarboxylic anhydride (showing 5- or 8-substitution); CrO_3–AcOH under milder conditions yields a mixture which by chromatographic analysis (C_6H_6, Al_2O_3) gives a dinitro-3 : 4-benzpyrene, m.p. 294°, probably identical with that obtained by Windaus *et al.* (A., 1937, II, 491), and a product reduced to 5 : 10- and 5 : 8-dihydroxy-3 : 4-benzpyrene diacetate (Vollmann *et al.*, A., 1937, II, 452). E. W. W.

Aromatic hydrocarbons. XXVIII. Hexaphene, a hydrocarbon of the phene series, and the analysis of its absorption spectrum by the anellation method. E. Clar (Ber., 1940, **73**, [*B*], 81—86).—By the anellation method (A., 1936, 599, 1102), which is reviewed, it is shown that the hydrocarbon (I) obtained by heating 2 : 7 : 1 : 8-$C_{10}H_4Me_2Bz_2$ is not 1′ : 2′-anthraceno-1 : 2-anthracene (II) (cf. A., 1929, 690) but *hexaphene* (cf. A., 1940, II, 124). The absorption spectrum of (II) would resemble that of 2′ : 1′-anthraceno-1 : 2-anthracene (cf. the spectrum resemblance between 1 : 2 : 5 : 6- and 1 : 2 : 7 : 8-dibenzanthracene). The spectrum of (I) contains three groups of bands, two (*o*α 467, *o*β 357, 339, and 324 mμ.) corresponding with the *o*-form (*A*), and one (443, 416, and 392 mμ.) with the *p*-form (*B*).



The diquinone from (I) is identified as *hexaphene*-5 : 16 : 9 : 14- (or, less probably, 5 : 16 : 8 : 15-)*diquinone*. E. W. W.

Synthesis of benzedrine. Q. Mingoia (Annali Chim. Appl., 1940, **30**, 187—198).—Methods of synthesis of benzedrine (I) are reviewed and the classification of sympathomimetic drugs is discussed. The following proposed methods give satisfactory yields of (I): (*a*) $CH_2Ph{\cdot}COMe$ (II) is converted into the oxime, which is reduced (Na–Hg–EtOH); (*b*) (II) is directly reduced in MeOH saturated with NH_3 by H_2 at room temp. and 1·5 atm., using Raney Ni (prep. according to Bougault *et al.*, A., 1939, II, 199) as catalyst; (*c*) condensation of (II) with $HCO{\cdot}NH_2$ or $HCO{\cdot}NHMe$, followed by hydrolysis (aq. HCl), washing with Et_2O, and fractional distillation of the basic product. The physico-chemical characteristics of, and analytical methods applied to, (I) are described. F. O. H.

Orientation problems. III. 4 : 6-Dinitro-*o*-toluidine. A. McGookin, S. R. Swift, and E. Tittensor (J.S.C.I., 1940, **59**, 92—94; cf. A., 1939, II, 255).—1 : 2 : 4-$C_6H_3Me(NO_2)_2$ could not be chlorinated or sulphonated; nitration by HNO_3 (*d* 1·5), 100% H_2SO_4, and some H_2O at 80—100° is almost quant. 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ is reduced by aq. NaHS or, less well, Zn dust and aq. NH_4Cl to 4 : 6 : 1 : 2-$(NO_2)_2C_6H_2Me{\cdot}NH{\cdot}OH$, m.p. 110°; NH_4HS in aq. dioxan (method: Voris *et al.*, A., 1938, II, 228) gives 30% of 2 : 6 : 1 : 4-$(NO_2)_2C_6H_2Me{\cdot}NH_2$, whilst $SnCl_2$–HCl in EtOH or dioxan affords (probably) di- and tri-amines. *o*-Toluic acid (I) and HNO_3 (*d* 1·52) at −10° give 4- and 6-NO_2-derivatives which are converted, as is (I), by 100% H_2SO_4–HNO_3 (*d* 1·52) at 20° into 4 : 6-*dinitro*-o-*toluic acid*, m.p. 206° (*Et* ester, b.p. 204°/750 mm., m.p. <15°; *chloride*, m.p. 68°, which with NaN_3 in $COMe_2$ affords the azide, m.p. 237—239°, not convertible into the amine); the *amide*, m.p. 181°, and cold aq. NaOCl give 4 : 6 : 1 : 2-$(NO_2)_2C_6H_2Me{\cdot}NH_2$ (II), m.p. 155° (cf. lit.). The (II), m.p. 135°, of Brand *et al.* (A., 1913, i, 717) is either a mixture or possibly a hydroxylamine. H. B.

Action of organo-magnesium compounds on araldoximes and their derivatives. Preparation of arylalkylamines of type $NHAr{\cdot}CHR_2$. P. Grammaticakis (Compt. rend., 1940, **210**, 716—718; cf. A., 1937, II, 421).—$CHPh{:}N{\cdot}OH$ (I) or $CHPh{:}NO{\cdot}CO{\cdot}NH_2$ (II) (1 mol.) with MgEtBr (6—10 mols.) in Et_2O gives mainly N-α-*ethyl*-n-*propylaniline* (III), b.p. 114°/14 mm. (*hydrochloride*, m.p. 161°; *oxalate*, m.p. 104°; *picrate*, m.p. 107°; *phenylcarbamyl* derivative, m.p. 78°), together with some $CPhEt{:}NH$ and NH_2Ph. Similarly, *p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OH$ (IV) or *p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}NO{\cdot}CO{\cdot}NH_2$ (V) with MgEtBr gives N-α-*ethyl*-n-*propyl*-p-*anisidine* (VI), b.p. 150°/14 mm. (*hydrochloride*, m.p. 190°; *oxalate*, m.p. 112°; *phenylcarbamyl* derivative, m.p. 96°), *p*-$OMe{\cdot}C_6H_4{\cdot}CEt{:}NH$, and *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2$ (VII). (I) or (II) with MgPhBr gives $NHPh{\cdot}CHPh_2$ (VIII), b.p. 225°/14 mm., m.p. 58° (*phenylcarbamyl* derivative, m.p. 125°), $CPh_2{:}NH$, and NH_2Ph. (IV) or (V) similarly yields N-*benzhydryl*-p-*anisidine* (IX), b.p. 243°/14 mm., m.p. 81° [*hydrochloride*, m.p. 194° (decomp.); *phenylcarbamyl* derivative, m.p. 132°], (VII), and *p*-$OMe{\cdot}C_6H_4{\cdot}CPh{:}NH$. (III), (VI), (VIII), and (IX) are formed in >80% yield, together with small amounts of NH_2Ar, by the action of MgEtBr or MgPhBr in Et_2O on $NHAr{\cdot}CHO$. J. L. D.

Molecular rearrangement of tertiary aralkylanilines. P. J. Drumm, W. F. O'Connor, and J. Reilly (J. Amer. Chem. Soc., 1940, **62**, 1241—1243).—$NPh(CH_2Ph)_2$,HCl at 200—220° (sealed tube) gives *p*-$NH_2{\cdot}C_6H_4{\cdot}CH_2Ph$, m.p. 36° (*hydrochloride*, m.p. 219°; *Bz* derivative, m.p. 165°; gives *diphenylmethane*-4-*azo*-β-*naphthol*, m.p. 141°), 2 : 4 : 1-$(CH_2Ph)_2C_6H_3{\cdot}NH_2$, m.p. 50° [*hydrochloride*, m.p. 171°; *Bz* derivative, m.p. 154°; gives 2 : 4-*dibenzylbenzene*-1-*azo*-β-*naphthol*, m.p. 154°, and 2 : 4 : 1-$(CH_2Ph)_2C_6H_3{\cdot}OH$, b.p. 252—254°/10 mm. (α-naphthylurethane, m.p. 143—144°)], and (probably) 2 : 4 : 6-*tribenzylaniline*, m.p. 61—62° (*hydrochloride*, m.p. 186°; *Bz* derivative, m.p. 149°; gives 2 : 4 : 6-*tribenzylbenzene*-1-*azo*-β-*naphthol*, m.p. 146°). Rearrangement, which occurs at <200°, cannot proceed by way of an olefine and probably not by way of a free radical since $(CH_2Ph)_2$ is not obtained, but probably proceeds by way of CH_2PhCl. In conformity with this view, heating $NPh(CH_2Ph)_2$,HBr in N_2 removes CH_2PhBr, identified as *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2CH_2Ph$. R. S. C.

M.p. of *p*-bromoanilides of solid aliphatic acids. D. F. Houston (J. Amer. Chem. Soc., 1940, **62**, 1303—1304).—The following m.p. are recorded for RCO·NH·C_6H_4Br-*p*: R = C_9H_{19} 101·9°, $C_{11}H_{23}$ 106·7°, $C_{13}H_{27}$ 110·2°, $C_{15}H_{31}$ 113·2°, and $C_{17}H_{35}$ 115·2°. R. S. C.

Organic phosphoric acid compounds. VII. Mono- and di-anilidophosphates. F. Zetzsche and W. Büttiker (Ber., 1940, **73**, [*B*], 47—49).—NH_2Ph,HCl (I) and $POCl_3$ at 120—140° give NHPh·$POCl_2$ (II), which with further (I) at 145—150° gives $(NHPh)_2POCl$ (III) (cf. Michaelis *et al.*, A., 1896, i, 344). Cholesterol (IV) and (II) in C_5H_5N at 40—45° yield *dicholesterylphosphoric acid monoanilide*, $C_{60}H_{96}O_3NP$, m.p. 196—197°. (IV) and (III) similarly give *monocholesterylphosphoric acid dianilide*, m.p. 182°. With (III), $(CH_2·OH)_2$ gives its *bisdianilidophosphate*, m.p. 180°, glycerol its *trisdianilidophosphate*, m.p. 206°, α-glyceryl *p*-nitrobenzoate its *α'(?)-dianilidophosphate*, m.p. 220°, and sucrose its *octadianilidophosphate*, m.p. 219—220°. Pyrocatechol gives a *bisdianilidophosphate*, m.p. 192°, which is stable to N-H_2SO_4 at 60—70° (3 hr.), but when heated with AcOH loses NH_2Ph. E. W. W.

Recognition of carboxylic acids as ureides [acyldiarylcarbamides] with aid of carbodiimides. VII. Detection of α-halogeno-fatty acids. F. Zetzsche and G. Röttger (Ber., 1940, **73**, [*B*], 50—56; cf. A., 1940, II, 129).—The following *N*-acyl-*NN'*-di-*p*-dimethylaminophenylcarbamides are prepared in which the acyl group is: *α-chloro-propionyl*, m.p. 140° (sinters at 138°), *-butyryl*, m.p. 146°, *-crotonyl*, m.p. 136—136·5°, and *-phenylacetyl*, m.p. 141° (sinters at 138°); *mono-**, m.p. 154°, *di-*, m.p. (impure) 145—146° (partly decomposed by cold $COMe_2$ or boiling MeOH into a white substance), and *tri-chloroacetyl*, m.p. 122° (with which di-*p*-dimethylaminophenylcarbamide is obtained) (decomposed by $COMe_2$ or MeOH); *α-bromo-propionyl*, m.p. 141°, *-n-butyryl*, m.p. 142°, *-isovaleryl*, m.p. 151°, *-n-hexoyl*, m.p. 137°, *-αβ-dimethylbutyryl*, m.p. 124°, *-palmityl*, m.p. 101°, *-tetracosanoyl*, m.p. 104°, and *-melissyl*, m.p. 97—98° (sinters at 94°) [obtained from α-bromomelissic acid (I), new m.p. 80·5°]; *αβ-dibromo-α-methylbutyryl*, decomp. 138° (sinters at 117°), and *-β-phenylpropionyl*, m.p. 156°; *mono-**, decomp. 165—170° (sinters at 153—155°), and *tri-bromoacetyl*, decomp. (impure) 122° (decomposed by $COMe_2$ or MeOH), *α-iodo-propionyl*, m.p. 143°, and *-melissyl*, m.p. 89° [from *α-iodomelissic acid*, m.p. 83—85°, obtained from (I) and KI in EtOH]; *iodoacetyl*, decomp. 165°; *β-chloro-propionyl**, m.p. 158°, and *-n-butyryl**, m.p. 151°; *β-bromo-propionyl**, m.p. 155° (decomp. 156°), *-n-butyryl**, m.p. 143°, and *-β-phenylpropionyl*, decomp. 152° [decomposed by $COMe_2$ first to a colourless substance, and then to a red substance, m.p. 172° (decomp.)]; *hexabromostearyl**, m.p. 153° (sinters at 147°); *bromofenchanecarboxyl**, m.p. 160°; *β-iodopropionyl* (II), m.p. 141°. All the above are yellow, except those marked *, which are colourless, and (II), which is yellowish-white. Colour is deepened by α-halogen; Br- and I- have a deeper colour than Cl-compounds. Carbamides of the above type are not obtained from αβ-dibromo-αβ-dimethylbutyric acid or from dibromo-α-*cyclo*geranic acid. E. W. W.

Preparation of sulphanilamides. M. C. Marquez (Bol. Soc. Quim. Peru, 1940, **6**, 17—20).—Preparative details are recorded for sulphanilamide, 2':4'-diaminoazobenzene-4-sulphonamide, and 2-sulphanilamidopyridine. F. R. G.

Sulphonamides and mechanism of their [physiological] action. G. Carrara and G. Monzini (Chim e l'Ind., 1940, **22**, 215—216).—The prep. and properties of sulphonamides (I) of therapeutic val. are briefly reviewed. The activity of (I) is related to production of azoxy-groups by oxidation in the organism. *Azoxybenzene-4:4'-disulphonamide*, m.p. 298—300°, and *-di(sulphon-2-pyridyl-amide)*, m.p. 280—283°, were prepared. F. O. H.

Derivatives of sulphanilamide.—See B., 1940, 566.

Chemotherapy of bacterial infections. I. Substances related to sulphanilamide. Synthesis of *p*-aminobenzylsulphonamide and its derivatives. P. L. N. Rao (J. Indian Chem. Soc., 1940, **17**, 227—232).—The following are prepared by condensing *p*-$NO_2·C_6H_4·CH_2·SO_2Cl$ with amines in C_5H_5N and reduction, usually with Sn + HCl: *p*-nitro- and *-amino-benzylsulphonamide*, m.p. 168° (*Ac*, m.p. 212°, *valeryl*, m.p. 188—189°, *hexoyl*, m.p. 192—194°, and *Bz* derivative, m.p. 230—231°); *di*-p-*nitro-* [using 2 mols. of chloride to 1 NH_3 or 0·5 of $(NH_4)_2CO_3$], m.p. 268° (decomp.), and *-amino-benzylsulphonamide*, decomp. when heated (*hydrochloride*, m.p. ~275°); p-*nitro-*, m.p. 130—131°, and *-amino-benzylsulphonanilide*, m.p. 172—173° [*hydrochloride*, m.p. 168—170° (decomp.)]; 2-p-*nitro-*, m.p. 214—215°, and *-amino-benzylsulphonamidopyridine*, m.p. 185—190° (?) (softens ~120°); p-*nitro-*, m.p. 199—200°, and *-amino-benzylsulphonylsulphanilamide*, m.p. 162—165° after softening [hydrochloride, m.p. 175—180° (decomp.)]. A. Li.

Oxidation of sulphanilamide and sulphapyridine by hydrogen peroxide.—See A., 1940, III, 598.

***p*-*N*-Acetylhydroxylaminobenzenesulphonamide and *p*-hydroxylaminobenzenesulphonic acid, both m.p. >300°.**—See A., 1940, III, 598.

Oxidation products of sulphanilamide. (Miss) M. K. Seikel (J. Amer. Chem. Soc., 1940, **62**, 1214—1216).—*p*-$NH_2·C_6H_4·SO_2·NH_2$ (I) with $K_3Fe(CN)_6$–KOH gives 20% of $(NH_2·C_6H_4·SO_2·NH_2-p)_2$ (II), m.p. 314° (decomp.). 30% H_2O_2 in AcOH converts (I) or (II) into *azoxybenzene-4:4'-disulphonamide* (III) (72%), m.p. 289—290° (decomp.), but in 6N-H_2SO_4 (I) gives both (II) and (III). $SnCl_2$–HCl reduces (II) or (III) to (I), but $Na_2S_2O_4$ in 0·2N-NaOH gives *hydrazobenzene-4:4'-disulphonamide* (IV), m.p. 224—224·5°. Oxidation (best, N-$FeCl_3$; 90—100% yield) of (IV) gives (II), which is best (46%) prepared by the reactions (I) → (III) → (IV) → (II). With 6N-HCl (32 mols.) and 30% H_2O_2 (8 mols.) at room temp., (I) gives 3:5-*dichlorosulphanilamide* ($SO_2·NH_2$ = 1), m.p. 205—205·5°, converted by 75% H_2SO_4 into 2:6:1-$C_6H_3Cl_2·NH_2$. R. S. C.

Reaction of formic acid [with aniline]. T. L. Davis and W. P. Green, jun. (J. Amer. Chem. Soc., 1940, **62**, 1274—1276).—When Br and anhyd. HCO_2H are allowed to react incompletely and treated with NH_2Ph at room temp., some $CO(NHPh)_2$ and its mixed 4 : 4′-Br_2- and 2 : 4 : 2′ : 4′-Br_4-derivatives are obtained. These products are not obtained if all the Br is first allowed to react with the HCO_2H and are probably formed from $CBr_2(OH)_2$, which is derived from a little $C(OH)_2$ in equilibrium with HCO_2H. R. S. C.

Interaction of arylhydrazines with halogenated aldehydes. H. Irving (J.C.S., 1940, 813—817; cf. A., 1933, 1036).—CHMeBr·CClBr·CHO (I) (1 mol.) or CHMeBr·CBr_2·CHO (II) with 2 : 4 : 1-$C_6H_3Hal_2$·NH·NH_2,HCl (1 mol.) in EtOH affords *β-bromo-α-ketobutaldehyde-2 : 4-dichloro-* (III), m.p. 135°, and *-dibromo-phenylhydrazone* (IV), m.p. 146° (decomp.). CHMeBr·CCl_2·$CH(OH)_2$ similarly affords the β-chloro-analogues. (I) or (II) (as hydrates) or CHMeCl·CClBr·$CH(OH)_2$ (1 mol.) and 2 : 4 : 1-$C_6H_3Cl_2$·NH·NH_2,HCl (V) (2 mols.) in boiling MeOH give α-keto-β-methoxybutaldehyde-2 : 4-dichlorophenylosazone, also obtained from (III) and (V) (1 mol.) in MeOH. (III) or (IV) and EtOH–NaOEt give the respective 4-hydroxy-1-(2′ : 4′-dihalogenophenyl)-5-methylpyrazole. Equimol. amounts of CHMeCl·CCl_2·$CH(OH)_2$ (VI) and 2 : 4 : 1-$C_6H_3Br_2$·NH·NH_2,HCl in EtOH at <15° afford *βγ-dichloro-α-2 : 4-dibromobenzeneazo-*Δ^{α}*-butene* (VII), m.p. 83°, reduced by Sn–HCl–AcOH to 2 : 4 : 1-$C_6H_3Br_2$·NH_2, and converted by dry HCl–C_6H_6 into butylchloral-2 : 4-dibromophenylhydrazone (not isolated). (VII) and dry HCl in EtOH give β-chloro-α-ketobutaldehyde-2 : 4-dibromophenylhydrazone. (VII) isomerises on refluxing with dry EtOH to *αβ-dichlorocrotonaldehyde-2 : 4-dibromophenylhydrazone* (VIII), m.p. 150° (N-*Ac* derivative, m.p. 166°); it isomerises when kept alone or, more rapidly, in C_6H_6, light petroleum, or $CHCl_3$, into the isomeride, m.p. 119° (Ac derivative, m.p. 141°), of (VIII). The two forms are regarded as *cis-* and *trans-*isomerides since either Ac derivative and dry Cl_2 in AcOH yield *ααββ-tetrachlorobutaldehyde-N-acetyl-2 : 4-dibromophenylhydrazone*, m.p. 108°. (VI) and (V) in dil. HCl–NaOAc, followed by Ac_2O–H_2SO_4, give *αβ-dichlorocrotonaldehyde-N-acetyl-2 : 4-dichlorophenylhydrazone* (IX), m.p. 153·5° [cf. isomeride, m.p. 122·5° (X) (crystal differences due to habit only)]. (IX) and Sn–HCl–AcOH give 2 : 4 : 1-$C_6H_3Cl_2$·NH_2. Both isomerides are unimol. in C_6H_6 (f.p.). Isomerism is due to differences in arrangement about the C:C linking since (IX) and (X) with Cl_2–AcOH give *ααββ-*tetrachlorobutaldehyde-*N*-acetyl-2 : 4-dichlorophenylhydrazone (cf. A., 1930, 324). (X) heated with AcCl (sealed tube) appears to be slowly converted into (IX). A. T. P.

Rate of dissociation of tetraphenylhydrazine.—See A., 1940, I, 325.

Preparation of stable diazo-compounds.—See B., 1940, 513.

Nitrosation of phenols. XVII. *o*-Fluorophenol, and a comparative study of the four *o*-halogenophenols. H. H. Hodgson and D. E. Nicholson (J.C.S., 1940, 810—812).—*o*-C_6H_4F·OH and aq. HNO_2 at 0° give 2-*fluoro*-4-*nitroso-* (I), m.p. 144° (decomp.), and some 2-*fluoro*-6-*nitro-phenol*, m.p. 87°. The quinoneoxime modification of (I) exists only in derivatives. (I) resembles other 4 : 2 : 1-NO·C_6H_3Hal·OH (*A*). The NO·HSO_4 method (A., 1940, II, 12) gives much improved yields of 2-chloro-, new m.p. 145°, -bromo-, new m.p. 156° (decomp.), and -iodo-4-nitrosophenol, new m.p. 162°. 2-*Fluoro-*, m.p. 89°, *-bromo-*, m.p. 105°, and *-iodo-benzoquinone-4-oxime Me ether*, m.p. 120°, are prepared from (*A*) and Me_2SO_4–moist K_2CO_3 or (*A*)–aq. NH_3–MeOH–$AgNO_3$ followed by MeI. (*A*) afford 2-*fluoro-*, m.p. 195° (decomp.), *-bromo-*, m.p. 191° (decomp.), and *-iodo-benzoquinone-4-oxime-1-p-nitrophenylhydrazone*, m.p. 187° (decomp.). Caro's acid and the respective 2-halogeno-4-aminoanisole at 0° yield 2-*fluoro-*, m.p. 69°, *-bromo-*, m.p. 85°, and *-iodo-4-nitrosoanisole*, m.p. 77°. The latter compounds or (*A*) and CH_2N_2 afford *glyoxime* NN′-*bis*-3-*fluoro-*, m.p. 211°, *-bromo-*, m.p. 211°, and *-iodo-4-methoxyphenyl ether*, m.p. 219°, together with some corresponding oxime Me ether (above). NO-compounds have a lower m.p. than the isomeric quinoneoxime. Results of Schiemann *et al.* (A., 1933, 1156) on nitration of *o*-C_6H_4F·OMe are confirmed. A. T. P.

Dealkylation of alkyl-substituted phenols.—See B., 1940, 515.

Organic molecular compounds. I. Influence of nitro-groups and second substituents on the formation of aromatic–nitroaromatic molecular compounds. I. C. Shinomiya (Bull. Chem. Soc. Japan, 1940, **15**, 92—103).—In ability to form mol. compounds, *s*-$(NO_2)_3$- > 2 : 4-$(NO_2)_2$- > NO_2-compounds. The effect of substituents is discussed. The following mol. *compounds* are described [*A* = α-, *B* = β-$C_{10}H_7$·OH; *C* = $C_{10}H_8$; *D* = 1 : 2 : 4 : 6-$C_6H_2(NO_2)_4$; *E* = tetryl; *F* = 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2$·OEt]: *AD*, m.p. 137°; *BD*, 130·5°; C_3D_2, m.p. 139·5°; A_3E_2, m.p. 80°; B_xE_y (of dissociation type); AF_2, m.p. 68°; BF_2, m.p. 75·5°; and CF_2, m.p. 73°. Eutectic points and series of melting and thawing points are also recorded, with phase diagrams. E. W. W.

Organic molecular compounds. II. Influence of nitro-groups and second substituents on the formation of aromatic–nitroaromatic molecular compounds. II. C. Shinomiya (Bull. Chem. Soc. Japan, 1940, **15**, 137—147; cf. preceding abstract).—*o*-$C_6H_4(NO_2)_2$ forms no mol. compounds with α- (I) or β-$C_{10}H_7$·OH (II). *as*-$C_6H_3(NO_2)_3$ forms *compounds* (1 : 1), m.p. 67°, with (I), (1 : 1), m.p. 63·5°, and (2 : 1), m.p. 73°, with (II), and (1 : 1), m.p. 52·5°, with $C_{10}H_8$ (III). 2 : 5 : 1-$(NO_2)_2C_6H_3$·OH forms (1 : 1) *compounds*, m.p. 101°, with α- (IV), and, m.p. 96·5°, with β-$C_{10}H_7$·NH_2 (V). 2 : 3 : 1-$(NO_2)_2C_6H_3$·OH forms (2 : 3) *compounds*, m.p. 105°, with (IV), and, m.p. 108°, with (V), but none with (I), (II), or (III). 3 : 4 : 1-$(NO_2)_2C_6H_3$·OH forms *compounds*, (1 : 1), m.p. 96°, with (IV), and, (2 : 3 ?), m.p. 83°, with (V), but none with (I), (II), or (III). 3 : 5 : 1-$(NO_2)_2C_6H_3$·OH forms (1 : 1) *compounds*, m.p. 110·5°, with (IV); m.p. 97°, with (V); m.p. 107°, with (I); m.p. 93°, with (II); and, m.p. uncertain,

with (III). Eutectic points etc. and phase-rule diagrams are given. E. W. W.

Preparation of *o*-nitrophenetole from *o*-chloronitrobenzene.—See B., 1940, 513.

Migration of the carbamyl radical in *o*-aminophenol derivatives. L. C. Raiford and K. Alexander (J. Org. Chem., 1940, **5**, 300—311).—Reduction of *o*-$NPh_2{\cdot}CO_2C_6H_4{\cdot}NO_2$-*o* and its substitution products causes migration of $NPh_2{\cdot}CO$ from O to N to give the corresponding *o*-carbamidophenol (*A*). The structures of these compounds are established by preparing them by the direct action of the acid chloride on the required *o*-aminophenol and by showing that the Me ethers obtained from (*A*) and CH_2N_2 are identical with the products obtained by treatment of the related anisidines with the required carbamyl chloride. Reduction of the related *o*-nitrophenyl phenylmethylcarbamate gives the *o*-aminophenyl derivative. This is also obtained by treatment of *o*-$NH_2{\cdot}C_6H_4{\cdot}OH$ with NPhMe·COCl but in this reaction the isomeride is also obtained. Partial hydrolysis of mixed diacyl derivatives containing either of these carbamyl radicals attached to O and another acyl R(Ph)·CO bound to N causes loss of the latter acyl and migration of the former to N. As in many other examples, the heavier acyl is ultimately found attached to N. Migration is not observed when the second radical is $ArSO_2$. The following are described: o-*diphenylcarbamidoanisole*, m.p. 106—107°; 4-bromo-2-nitrophenyl diphenylcarbamate, new m.p. 137—138°; 4-*bromo*-2-*diphenylcarbamidoanisole*, m.p. 155—156°; *o*-nitrophenyl phenylmethylcarbamate, m.p. 111—112°; o-*phenylmethylcarbamidoanisole*, m.p. 77—78°; diacyl derivatives of *o*-$NH_2{\cdot}C_6H_4{\cdot}OH$, N-*acetyl*-O-*diphenylcarbamyl*-, m.p. 150—153°; O-*acetyl*-N-*diphenylcarbamyl*-, m.p. 119—121°; ON-*di*(*diphenylcarbamyl*)-, m.p. 184—185°; N-*diphenylcarbamyl*-, m.p. 190—191°; N-*benzoyl*-O-*diphenylcarbamyl*-, m.p. 153—154°; O-*benzoyl*-N-*diphenylcarbamyl*-, m.p. 210—212°; diacyl derivatives of 2 : 4 : 1-$NH_2{\cdot}C_6H_3Br{\cdot}OH$, N-*acetyl*-O-*diphenylcarbamyl*-, m.p. 176—178°; O-*acetyl*-N-*diphenylcarbamyl*-, m.p. 117—118°; N-*diphenylcarbamyl*-, m.p. 198°; ON-*di*(*diphenylcarbamyl*)-, m.p. 198°; diacyl derivatives of *o*-$NH_2{\cdot}C_6H_4{\cdot}OH$, O-*phenylmethylcarbamyl*-N-p-*toluenesulphonyl*-, m.p. 125—126°; N-*phenylmethylcarbamyl*-O-p-*toluenesulphonyl*-, m.p. 111—112°; o-*aminophenyl phenylmethylcarbamate*, m.p. 105—106°; o-*phenylmethylcarbamidophenol*, m.p. 171—172°. H. W.

Phenyl*iso*amyl [γ-phenyl-αα-dimethylpropyl] acetate. K. N. Kinzerskaja (J. Appl. Chem. Russ., 1940, **13**, 222—226).—$Ph{\cdot}[CH_2]_2{\cdot}CMe_2{\cdot}OAc$ (I) is prepared as follows (yields in parentheses): $Ph{\cdot}[CH_2]_2{\cdot}OH$ (+ HBr) → $Ph{\cdot}[CH_2]_2{\cdot}Br$ (92%) (+ Mg) → $Ph{\cdot}[CH_2]_2{\cdot}MgBr$ (+ $COMe_2$) → $Ph{\cdot}[CH_2]_2{\cdot}CMe_2{\cdot}OH$ (71%) (+ Ac_2O) → (I) (88·5%). R. T.

Dehydration of *cis*- and *trans*-2-phenyl*cyclo*hexanols. C. C. Price and J. V. Karabinos (J. Amer. Chem. Soc., 1940, **62**, 1159—1161).—*o*-$C_6H_4Ph{\cdot}OH$ and H_2–Raney Ni in EtOH at 140—150°/135 atm. (not PtO_2 at 70°/3—4 atm.) give cis-2-*phenyl*cyclo*hexanol* (I) (75%), m.p. 41—42°, b.p. 140—141°/16 mm. (*phenylurethane*, m.p. 127·5—128°), oxidised by CrO_3–AcOH to 2-phenyl*cyclo*hexanone, which is reduced by Na–Hg–EtOH to *trans*-2-phenyl-*cyclo*hexanol (II), m.p. 56—57°. Dehydration of (I) and (II) by boiling H_3PO_4 involves *trans*-elimination. Thus, (I) gives mainly 1-phenyl-Δ¹-*cyclo*hexene, b.p. 126—128°/16 mm. (oxidised by $KMnO_4$ to $COPh{\cdot}[CH_2]_4{\cdot}CO_2H$), and (II) gives mainly 3-*phenyl*-Δ¹-cyclo*hexene* (III), b.p. 115—117°/16 mm. (cf. Uspenski, A., 1923, i, 669) [with boiling 5% HNO_3 gives $CO_2H{\cdot}CH_2{\cdot}CHPh{\cdot}[CH_2]_2{\cdot}CO_2H$, and with $KMnO_4$ gives BzOH and (?) $BzCO_2H$]; small amounts of the other olefine are also formed, probably owing to isomerisation prior to dehydration since (III) is stable to H_3PO_4. M.p. are corr. R. S. C.

Formation of sulphonium compounds from benzyl iodide and organic disulphides. O. Haas and G. Dougherty (J. Amer. Chem. Soc., 1940, **62**, 1004—1005).—R_2S_2 and CH_2PhI with HgI_2 or $FeCl_3$ in $COMe_2$ at room temp. give *tribenzyl*-, m.p. 136—137°, dibenzylethyl-, and dibenzyl-*n*-butyl-sulphonium iodide, all + HgI_2, and *tribenzylsulphonium iodide*, + $FeCl_3$, m.p. 142°. A reaction mechanism is postulated, one step of which, $(CH_2Ph)_2SI_2$ + HgI_2 (in $COMe_2$) → $(CH_2Ph)_2S,HgI_2$ + I_2, is realised experimentally. R. S. C.

Alkanolamines. IX. Reducing and hydrolysing action of ethanolamines on dichloronitrobenzenes. C. B. Kremer and A. Bendich (J. Amer. Chem. Soc., 1940, **62**, 1279—1281).—Ability of $NH_2{\cdot}[CH_2]_2{\cdot}OH$ (I) and $C_6H_3Cl_2{\cdot}NO_2$ to condense is less in absence than in presence of a solvent, reduction, hydrolysis, formation of additive compounds, and reduction of end-products increasing. The latter reactions occur to a greater extent with $NH([CH_2]_2{\cdot}OH)_2$ (II) and $N([CH_2]_2{\cdot}OH)_3$ (III). 2 : 5 : 1-$C_6H_3Cl_2{\cdot}NO_2$ (IV) (1 mol.) with (I) (1—2 mols.) alone or with Na_2CO_3 or NaOAc gives 2 : 4 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}NH{\cdot}[CH_2]_2{\cdot}OH$ (usually the main product), 2 : 5 : 1-$C_6H_3Cl_2{\cdot}NH_2$ (V), 2 : 4 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}OH$ (VI), 2 : 4 : 1-$NH_2{\cdot}C_6H_3Cl{\cdot}NH{\cdot}[CH_2]_2{\cdot}OH$, and $(2 : 5 : 1\text{-}C_6H_3Cl_2{\cdot}N{:})_2$, the amounts varying according to the conditions. (II) or (III) with (IV) gives (V), but (VI) is the main product in presence of Na_2CO_3. 3 : 4 : 1-$C_6H_3Cl_2{\cdot}NO_2$ with (I) (alone or with Na_2CO_3) gives 4 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}NH{\cdot}[CH_2]_2{\cdot}OH$, but with (II) or (III) gives 4 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}OH$, 3 : 4 : 1-$C_6H_3Cl_2{\cdot}NH_2$, and 3 : 4 : 3′ : 4′-*tetrachloroazobenzene*, m.p. 195·5° (corr.), the quantities varying according to the conditions. 2 : 4 : 1-$C_6H_3Cl_2{\cdot}NO_2$ with (I) gives mainly tar, but with (II) 2 : 4 : 1-$C_6H_3Cl_2{\cdot}NH_2$ (1%) is isolated. 3 : 5 : 1-$C_6H_3Cl_2{\cdot}NO_2$ with (I) and Na_2CO_3 gives 3 : 5 : 3′ : 5′-*tetrachloroazobenzene* (VII) (60%), m.p. 158·5° (corr.), and 3 : 5 : 1-$C_6H_3Cl_2{\cdot}NH_2$ (20%), and with (II) gives (VII). R. S. C.

Relative reactivities of organo-metallic compounds. XXX. Co-ordinate compounds in the colour test for organo-metallic compounds. H. Gilman and R. G. Jones (J. Amer. Chem. Soc., 1940, **62**, 1243—1247; cf. A., 1940, II, 239).—$CO(C_6H_4{\cdot}NMe_2\text{-}p)_2$ (I) and MgPhBr in Et_2O–N_2 give a 1 : 1 additive compound, which regenerates 88% of (I) when hydrolysed but is sufficiently unstable to give enough $(p\text{-}NMe_2{\cdot}C_6H_4)_2CPh{\cdot}O{\cdot}MgBr$ to yield after hydrolysis the I–AcOH colour test. A similar com-

pound is formed in C_6H_6–N_2, but is less stable therein, giving in aq. NH_4Cl only 45% of (I) with 42% of $(p\text{-}NMe_2\cdot C_6H_4)_2CPh\cdot OH$ (II). Excess of MgPhBr and use of C_6H_6 increase the sensitivity of the colour test. LiPh and (I) give no stable complex in Et_2O or C_6H_6, but yield 78 and 92·5%, respectively, of (II) without any regenerated (I). The order of decreasing reactivity and increasing tendency to form co-ordinate compounds with ketones is LiPh, MgPhBr, $GaPh_3$; the relation between these two properties and the responsibility of the latter for effects previously ascribed to steric hindrance are discussed. The forms, m.p. 107—107·5° and 121—122° (cf. lit.), of (II) are obtained. R. S. C.

Chaulmoogra phosphatides. H. Arnold (Ber., 1940, **73**, [*B*], 90—94; cf. A., 1939, II, 132).—The Na salt of monohydnocarpoyl-β-glycerophosphoric acid with AcOH and $AgNO_3$ forms the *silver* (Ag + Ag_2) salt, which with $Br\cdot[CH_2]_2\cdot NMe_3Br$ (I) gives *choline monohydnocarpoyl-β-glycerophosphate*, $C_{24}H_{46}O_7NP$. Dihydnocarpoylglycerol gives in the usual way Ag_2 *dihydnocarpoyl-β-glycerophosphate*. Ag_2 *chaulmoogryl-hydnocarpoyl-β-glycerophosphate* with (I) gives the *choline* ester, m.p. 170—175° (softens at 70°). The corresponding *choline* salt has m.p. 160—165°. The new compounds appear to have no curative action in leprosy. E. W. W.

Ring-closure of acyclic ureides resulting from elimination of alcohol. Esters of β-phenylalanine-*N*-acetic acid and related compounds. (Misses) D. A. Hahn, M. J. McLean, and M. M. Endicott (J. Amer. Chem. Soc., 1940, **62**, 1087—1091).—$CO_2H\cdot CH_2\cdot NH\cdot CH(CH_2Ph)\cdot CO_2H$ (I) and HCl–MeOH or –EtOH give according to the conditions the Me_2 ester *hydrochloride*, decomp. 144—145°, *N-carbomethoxy-* (II), m.p. 185—186° (decomp.), stable in H_2O, and *N-carbethoxy-methyl-β-phenylalanine hydrochloride* (III), m.p. 170—172° (decomp.), hydrolysed in H_2O. With 1 equiv. of NaOMe–MeOH or of aq. $KHCO_3$, (II) gives *N-carbomethoxymethyl-β-phenylalanine* (IV), m.p. 208—210° (decomp.). In boiling H_2O, (III) gives *N-carbethoxymethyl-β-phenylalanine* (V), m.p. 206—208° (decomp.). NH_3–EtOH converts (IV) or (V) into *β-phenylalanine-N-acetamide* (VI), m.p. 196—197° (decomp.), hydrolysed by dil. HCl to (I). (II) and (III) are sol. in EtOH and H_2O, but (IV) and (V) are insol. *K* of (IV), (V), and (VI) are similar. With KCNO under various conditions, (II), (III), (IV), and (V) give mixtures (cf. A., 1938, II, 279) containing 26—70% of 1-*α-carboxy-β-phenylethylhydantoin*, m.p. 157—158° (*Na* salt, "anhyd.," decomp. 188—300°, and +EtOH, m.p. 60—70°, resolidifies at 91°; *Me* ester, m.p. 105—106·5°), the absorption spectrum of which closely resembles that of 5-benzyl-1-carboxymethylhydantoin. R. S. C.

Optical constants of benzamide, its homologues, and aliphatic amides. M. L. Willard and C. Maresh (J. Amer. Chem. Soc., 1940, **62**, 1253—1257).—Optical properties of NH_2Bz and 11 Ph-substituted derivatives thereof and of $RCO\cdot NH_2$ (R = Me, Et, Pr, Bu^{α}, and Bu^{β}) are recorded and may be used for identification. *p*-Ethyl-, m.p. 164·2±0·5°, p-*propyl-*, m.p. 128·4±0·5°, p-n-, m.p. 121·5±0·4°, p-iso-, m.p. 151·2±0·2°, and p-sec.-*butyl-*, m.p. 117·2±0·5°, *-benzamide* are reported. R. S. C.

Synthesis of iodohippuric acids. I. 2 : 5-, 3 : 5-, and 3 : 4-Di-iodohippuric acids. C. J. Klemme and J. H. Hunter (J. Org. Chem., 1940, **5**, 227—234).—Addition of AcOH to an aq. solution of $o\text{-}NH_2\cdot C_6H_4\cdot CO_2K$ and KI–KOI gives 2 : 5 : 1-$NH_2\cdot C_6H_3I\cdot CO_2H$, m.p. 210—211·5° (yield 72·2%), converted into 2 : 5 : 1-$C_6H_3I_2\cdot CO_2H$. This with $SOCl_2$ affords 2 : 5-*di-iodobenzoyl chloride*, m.p. 93—94·5°, which condenses with aq. $NH_2\cdot CH_2\cdot CO_2Na$ to 2 : 5-*di-iodohippuric acid*, m.p. 210·5—211°. 3-*Iodo*-4-*aminobenzoic acid*, m.p. 203—204°, is obtained by treatment of $p\text{-}NH_2\cdot C_6H_4\cdot CO_2H$ with ICl in AcOH or (with 2 : 4 : 1-$C_6H_3I_2\cdot NH_2$) with KI–KOI and AcOH, and is converted into 3 : 4 : 1-$C_6H_3I_2\cdot CO_2H$, the *chloride*, m.p. 74—76°, of which is condensed to 3 : 4-*di-iodohippuric acid*, m.p. 150—154°, softens at 148°. $o\text{-}NH_2\cdot C_6H_4\cdot CO_2H$ and ICl in 25% HCl at 80° afford 2 : 3 : 5 : 1-$NH_2\cdot C_6H_2I_2\cdot CO_2H$, m.p. 230—232°, whence successively 3 : 5 : 1-$C_6H_3I_2\cdot CO_2H$ (chloride, m.p. 67—68°) and 3 : 5-di-iodohippuric acid, m.p. 208—209°. H. W.

Halogenation of salicylic acid. L. H. Farinholt, A. P. Stuart, and D. Twiss (J. Amer. Chem. Soc., 1940, **62**, 1237—1241).—2 : 3 : 5 : 1-$OH\cdot C_6H_2Br_2\cdot CO_2H$ and Br in 60% oleum at ~30° give *tetra-* (I), decomp. ~235—240° (*Ac* derivative, m.p. 162·5°), or, if less Br is used, 3 : 5 : 6-*tri-bromosalicylic acid* (II), m.p. 210·5° (*Ac* derivative, m.p. 145°). 2 : 3 : 5 : 1-$OH\cdot C_6H_2Cl_2\cdot CO_2H$ and Cl_2 in 60% oleum at 80—90° give 3 : 5 : 6-*trichlorosalicylic acid* (III), m.p. 207° (*Ac* derivative, m.p. 129·5°), converted by Br–60% oleum at ~30° into 3 : 5 : 6-*trichloro-4-bromosalicylic acid* (IV), m.p. 213° (*Ac* derivative, m.p. 144°). Attempts to prepare tri-iodo- and other tetrahalogeno-derivatives failed. Structures are proved by decarboxylating with soda–lime; 2 : 3 : 4 : 5-*tetrabromo-*, m.p. 123° (*acetate*, m.p. 110·5°; *benzoate*, m.p. 133°), and 2 : 4 : 5-*trichloro-3-bromo-phenol*, m.p. 126° (*benzoate*, m.p. 125°), are thus obtained. With Br–AcOH–H_2O at 60°, (I), (II), (III), and (IV) give $C_6Br_5\cdot OH$, 2 : 3 : 4 : 6 : 1-$C_6HBr_4\cdot OH$, 3 : 4 : 6 : 2 : 1-$C_6HCl_3Br\cdot OH$, and 3 : 4 : 6 : 2 : 5 : 1-$C_6Cl_3Br_2\cdot OH$, respectively. Cl_2 and (III) in 30% AcOH give 2 : 3 : 4 : 6 : 1-$C_6HCl_4\cdot OH$. R. S. C.

Oxidation of salicylates in alkaline solution. E. A. Brecht and C. H. Rogers (J. Amer. Pharm. Assoc., 1940, **29**, 178—183).—The formation of brown-coloured oxidation products from salicylic acid (I) and related compounds was studied. Na salicylate (and other phenolic compounds) in 25% NaOH with H_2O_2 slowly forms the Na_2 salt of 2 : 5-dihydroxy-*p*-benzoquinone; on keeping, this gives a dark brown, amorphous ppt. (I) oxidised by air in slightly alkaline solution or by H_2O_2 gives a brown *product* ("acid salicylate-brown"), $C_{12}H_8O_6$, containing 3 OH and yielding metallic (*e.g.*, Na_3) salts. F. O. H.

Preparation of depsides by means of azides. III. Action of trimethylgallazide on diphenols. R. O. Pepe (Anal. Asoc. Quím. Argentina, 1940, **28**,

34—50; cf. A., 1938, II, 491).—3 : 4 : 5 : 1-$(OMe)_3C_6H_2\cdot CO\cdot N_3$ (I) (2 mols.) in $COMe_2$ with the appropriate diphenol in N-NaOH gives o-, m.p. 155°, m-, m.p. 147°, and p-*phenylene di*-(3 : 4 : 5-*trimethoxybenzoate*), m.p. 218°. 0·5 mol. of (I) yields similarly o-, m.p. 172°, m-, m.p. 125°, and p-*hydroxyphenyl* 3 : 4 : 5-*trimethoxybenzoate*, m.p. 154°. With 1 mol. of (I) mixtures are formed; *m*-$C_6H_4(OH)_2$ affords the highest yield of di-, and *o*-$C_6H_4(OH)_2$ affords predominately mono-ester. F. R. G.

Synthesis of carbalkoxystilbenes. R. C. Fuson and H. G. Cooke, jun. (J. Amer. Chem. Soc., 1940, **62**, 1180—1183).—Condensation of ArCHO and *p*-$CO_2Me\cdot C_6H_4\cdot CH_2Br$ by Zn dust in C_6H_6 and dehydration of the product by Ac_2O–C_6H_6 gives *Me stilbene*- (I) (21%), m.p. 158—159° (*dibromide*, m.p. 192—193°), 4′-*chlorostilbene*- (II) (22%), m.p. 161—162° [*dibromide*, m.p. 202—203° (decomp.)], and 4′-*bromostilbene*- (20%), m.p. 179—180° (*dibromide*, m.p. 211—213°), -4-*carboxylate*. *Me* ω-*bromo*-m-*toluate* (prep. from *m*-$C_6H_4Me\cdot COCl$ by Br at ~180° and later MeOH), m.p. 46—47°, with *p*-$C_6H_4Cl\cdot CHO$ gives similarly *Me* 4′-*chlorostilbene*-3-*carboxylate* (18%), m.p. 110—111° (*dibromide*, m.p. 175—176°). CH_2PhCl and PhCHO give *trans*-$(CHPh)_2$ and CH_2Ph_2. *p*-$CHO\cdot C_6H_4\cdot CO_2Me$ and *p*-$C_6H_4Cl\cdot CH_2Br$ give (II) and *di*-p-*chlorobenzyl*, m.p. 100°. Meerwein's method (A., 1939, II, 262) gives 52% of (I) or 36% of *Et stilbene*-4-*carboxylate*, m.p. 105—106° (*dibromide*, m.p. 180—181°), but gives poor yields of Cl-derivatives. *Me* ω-*iodo*-p-, m.p. 76—77°, and -m-*toluate*, m.p. 52—53°, are prepared from the corresponding Br-esters by NaI in $COMe_2$. R. S. C.

Diarylphthalides derived from dialkylanilines. B. Hoï (Compt. rend., 1940, **210**, 701—703).—4′-Methoxy-2′-methyl-5′-*iso*propylbenzophenone-2-carboxyl chloride with $NPhMe_2$ and $AlCl_3$ in cold C_6H_6, followed by treatment with dil. H_2SO_4 and steam-distillation, gives α-p-*dimethylaminophenyl*-α-(2′-*methyl*-5′-iso*propyl*-p-*anisyl*)*phthalide*, m.p. 207—208° (decomp.). *o*-$C_6H_4Bz\cdot CO_2H$, *o*-4-anisoyl- and *o*-2 : 5-dimethoxybenzoyl-benzoic acid similarly yield α-p-*dimethylaminophenyl*-α-*phenyl*-, m.p. ~160° (decomp.), -p-*anisyl*-, m.p. ~76—77°, and -2 : 5-*dimethoxyphenylphthalide*, m.p. 235° (decomp.), respectively. These phthalides give coloured solutions in conc. H_2SO_4 but not with alkalis unless a phenolic group exists as in α-p-*diethylaminophenyl*-α-p-*hydroxyphenylphthalide*, m.p. 105—106° (decomp.), prepared from *p*-$NEt_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot COCl$-*o*, PhOH, and $AlCl_3$. J. L. D.

Disproportionation in the synthesis of aryloxymalonic acids. J. B. Niederl and R. T. Roth (J. Amer. Chem. Soc., 1940, **62**, 1154—1156).—1 mol. each of NaOAr and $CHBr(CO_2Et)_2$ in abs. EtOH give $OAr\cdot CH(CO_2Et)_2$ (I) by condensation, and $(OAr)_2C(CO_2Et)_2$ and $CH_2(CO_2Et)_2$ by disproportionation. Use of $CHCl(CO_2Et)_2$ gives (I). *Phenoxy*-, m.p. 124° (decomp.) (*Et*$_2$ ester, m.p. 52—53°; *amide*, m.p. 214—215°), m-*tolyloxy*-, m.p. 138° (decomp.) (*Et*$_2$ ester, b.p. 154—156°/4 mm.; *diamide*, m.p. 216—217°), *di*-m-*tolyloxy*-, m.p. (anhyd.) 148° (decomp.), (+$3H_2O$) 87° (*Et*$_2$ ester, b.p. 202—205°/3 mm.), and p-*nitrophenoxymethyl*-, m.p. 142° (decomp.) (*Et*$_2$ ester, m.p. 50—51°), -*malonic acid* are described. Rearrangement of the esters cannot be effected. R. S. C.

Dinitriles of dicarboxylic acids.—See B., 1940, 515.

Methylenedisalicylic acid and its hexamethylenetetramine salt. B. Oddo (Annali Chim. Appl., 1940, **30**, 180—187).—Salicylic acid, 34% CH_2O, and 25% H_2SO_4 are autoclaved for 100 min. at 90—95°; the solid product, when washed with warm H_2O and with C_6H_6, affords methylenedisalicylic acid, m.p. 243° (decomp.) (cf. Clemmensen *et al.*, A., 1911, i, 542), which, directly mixed with $(CH_2)_6N_4$ or pptd. from $COMe_2$ solution by C_6H_6, yields $(CH_2)_6N_4$ *methylenedisalicylate* (I), softens ~60°, decomp. 120°. (I), the colour reactions of which are given, inhibits potato-oxidase, has bacteriostatic activity, is lethal in rabbits in intravenous doses of 0·85 g. per kg., and, in sufficiently high concns., depresses blood pressure, respiration, and cardiac movement. F. O. H.

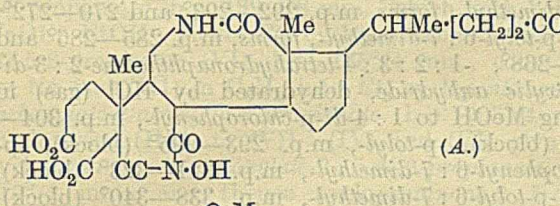
New alkaline fusion procedure. 3-Chloro-4-hydroxy-5-sulphobenzoic acid and its conversion into 3 : 4-dihydroxy-5-sulphobenzoic acid. G. V. Medox and N. K. Dobrovolskaja (J. Appl. Chem. Russ., 1940, **13**, 191—194).—4 : 3 : 1-$OH\cdot C_6H_3Cl\cdot CO_2H$ and 10% oleum (30 min. at 84°, then 3 hr. at 145—150°) yield 3-*chloro*-4-*hydroxy*-5-*sulphobenzoic acid* (*K* and K_2, +1·5H_2O, salts). This, when heated for 4 hr. at 180° with KOH and paraffin wax, in presence of KI and Cu, yields 3 : 4-*dihydroxy*-5-*sulphobenzoic acid* (*K* salt). The paraffin isolates the reaction mass from atm. O_2. R. T.

Dicyclic structures prohibiting Walden inversion. ***dicyclo*[2, 2, 2]Octane derivatives with substituents at the bridgehead.** P. D. Bartlett and S. G. Cohen (J. Amer. Chem. Soc., 1940, **62**, 1183—1189).—The Br of 9-bromoanthracene-9 : 10-*endo*-αβ-succinic anhydride (I) (Barnett *et al.*, A., 1934, 1102) is unaffected by 30% KOH in 1 : 1 H_2O–EtOH because Walden inversion is impossible; only the *trans*-acid, m.p. 238—240° (barely affected by Ac_2O), is obtained; 10% KOH gives the *cis*-acid, converted at the m.p. or in warm Ac_2O into (I). 9-Bromo-9-methylfluorene (prep. described) reacts readily with EtOH at 25° (half-life period ~5 min.) to give 9-*ethoxy*-9-*methylfluorene*, m.p. 82—83°. Na with (I) in EtOH gives ~10% of *trans*-anthracene-9 : 10-*endo*-αβ-succinic acid (II), but Ag or $AgNO_3$ reacts little if at all. The isomerides of (II) are equilibrated by conc. alkali. 9-Aminoanthracene, softens at 120°, m.p. ~135—140° (cf. lit.), when kept, gives a compound, m.p. 216—217°. 9-Nitro- and 9-acetamido-anthracene with $(CH\cdot CO)_2O$ in boiling xylene give 9-*nitro*-, m.p. 244—245°, and 9-*acetamido*-*anthracene*-9 : 10-endo-αβ-*succinic anhydride* (III), sinters at 257°, m.p. ~268°, respectively, which could not be converted into the 9-NH_2-derivative (IV). With NaOH, (III) gives the trans-*acid*, sinters at 250°, m.p. 253°. *Et* 9-*anthrylcarbamate*, m.p. 224—225°, gives the 9 : 10-endo-αβ-*succinic anhydride*, m.p. 252—254° (decomp.), hydrolysed by NaOH to (IV), m.p. 260—262° (decomp.). With HNO_2, (IV) gives the 9-*OH*-compound (yield erratic, up to 65%), m.p. 174—175°, unstable in alkali. R. S. C.

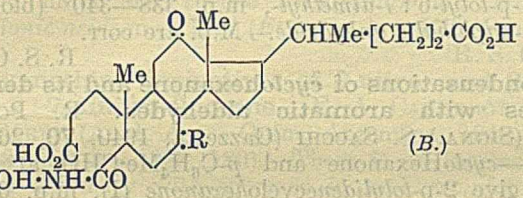
Tannin, m.p. 165—166° (decomp.), $[\alpha]_D^{27}$ +17·5° in acetone (hexamethyl derivative, m.p. 172—174°), from bark of *Acer spicatum*.—See A., 1940, III, 618.

Steroid-like derivatives [lactams].—See B., 1940, 567.

Reaction of hydroxamic acids. M. Schenck and L. Wolf (Ber., 1940, **73**, [*B*], 25—28).—The evolution of gas on treatment with $KMnO_4$ in 10% NaOH is apparently a general reaction of hydroxamic acids. Acet- and benz-hydroxamic acid give largely N_2O, with some N_2. The β-acid (*A*) (cf. A., 1938, II, 99) gives N_2 with 1·5% of O_2 (cf. Schenck, Z. physiol. Chem., 1939, **262**, 47). The oximinoketohydroxamic acid, $C_{24}H_{36}O_8N_2$ (*B*; R = N·OH), gives N_2 and a substantial proportion of N_2O. The diketohydroxamic acid, $C_{24}H_{35}O_8N$ (*B*; R = O), gives N_2 with only a trace of N_2O. Other N-containing bile acid derivatives studied give either no gas or only traces. E. W. W.



(*A.*)



(*B.*)

Hydrogenation of benzaldehyde under pressure. G. I. Deschalit (J. Appl. Chem. Russ., 1940, **13**, 195—197).—PhMe is obtained in 64% yield by hydrogenation of PhCHO (2 hr. at 300—350°/90 atm.). R. T.

Molecular rearrangements involving optically active radicals. VIII. Wolff rearrangement of optically active diazoketones. J. F. Lane, J. Willenz, A. Weissberger, and E. S. Wallis (J. Org. Chem., 1940, **5**, 276—285).—*d*-CH_2Ph·CHMe·COCl is converted by CH_2N_2 in anhyd. Et_2O at 0°—room temp. into *d*-β-phenyl-α-methylethyl CHN_2 ketone (I), α_D^{20} +67·2° (*l* = 0·5); the (impure) l-*isomeride*, α_D^{20} −27·9° (*l* = 0·5), is hydrolysed by 50% HCO_2H at room temp. to δ-phenyl-γ-methylbutan-α-ol-β-one, α_D^{20} −14·03° (*l* = 0·5), identified as the p-*nitrobenzoate*, m.p. 73°. When treated with acids in the absence of a catalyst (I) gives an optically active CO-alcohol without appreciable racemisation. With NH_3 in MeOH–$AgNO_3$ it undergoes a Wolff rearrangement giving a partly racemised (−)-β-*benzylbutyramide*, m.p. 80—81°, whilst with Ag_2O and $Na_2S_2O_3$ in aq. 25% dioxan it yields optically inactive β-benzylbutyric acid (*amide*, m.p. 83°). *d*-CPhMeEt·CO·CHN_2 (impure) under the last conditions gives an optically inactive acid. H. W.

Action of phosphorus pentachloride on β-phenylbenzylideneacetophenone. C. R. Conard (J. Amer. Chem. Soc., 1940, **62**, 1002—1003).—CPh_2:CH·COPh and PCl_5 in boiling C_6H_6 give oily 1 : 2-dichloro-1 : 3-diphenylindene (I) (cf. A., 1912, i, 989; for mechanism and analogous reaction with Br, cf. Barré *et al.*, A., 1928, 1009). O_3 converts (I) in CCl_4 into *o*-$C_6H_4Bz_2$ (II). With boiling EtOH–C_6H_6, (I) gives 2-*chloro*-1-*ethoxy*-1 : 3-*diphenylindene*, m.p. 135·5—136°, ozonised to (II). R. S. C.

Activation of aluminium chloride in the Friedel–Crafts reaction.—See A., 1940, I, 326.

Condensation of paraformaldehyde with acetomesitylene. R. C. Fuson and C. H. McKeever (J. Amer. Chem. Soc., 1940, **62**, 999—1001).—2 : 4 : 6 : 1-$C_6H_2Me_3$·C(:CH_2)·O·MgBr and gaseous CH_2O in Et_2O at 0° give β-*hydroxypropiomesitylene* (I), b.p. 135—138°/4 mm., which with conc. HCl at room temp. gives β-chloropropiomesitylene, m.p. 46—46·5°, obtained also from 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CH:CH_2 (II) by HCl. Contrary to previous work (A., 1939, II, 162), 2 : 4 : 6 : 1-$C_6H_2Me_3$·COMe, paraformaldehyde (III), and K_2CO_3 in MeOH at room temp. give mainly β-*methoxy*-α-*methylenepropiomesitylene* (IV), b.p. 110·5—111°/1·5 mm. (*dibromide*, m.p. 50·5—51·2°), reduced (H_2–Raney Ni; MeOH; 2 atm.) to 2 : 4 : 6 : 1-$C_6H_2Me_3$·$COPr^\beta$. The reaction mechanism is proved by realisation of the following steps: (I) ⟶ (distillation) (II) ⟶ (MeOH–K_2CO_3 or MeOH–conc. HCl) β-*methoxypropiomesitylene*, b.p. 117—117·5°/2·5 mm. (with Br–CCl_4 gives 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CHBr·CHMeBr) ⟶ [(III)–MeOH–K_2CO_3] (IV). K_2CO_3 and (III) in MeOH convert (II) into (IV) and a little βδ-dimesityl-$\Delta^{\beta\delta}$-pentadiene. R. S. C.

Acetylretene and reten-6-ol. W. P. Campbell and D. Todd (J. Amer. Chem. Soc., 1940, **62**, 1287—1292).—Acetylretene (I) and β-retenol are shown to be $C_{(3)}$-derivatives. The retenol (II) obtained from ferruginol and hinokiol (A., 1939, II, 382, 438) is the 6-OH-compound. Retene, AcCl, and $AlCl_3$ in $PhNO_2$, first at −5° and then at 5°, give (I) (45%; mother-liquor yields a product, m.p. 85—89°, and a picrate, m.p. 127—132°), which with 1 : 2 HNO_3–H_2O (later more HNO_3) at 190—200° gives 1 : 2 : 3 : 5-$C_6H_2(CO_2H)_4$ (III). 6-Methoxy-1-methylphenanthrene gives similarly the 3-*Ac* derivative (21%), m.p. 126·5—127° (picrate, m.p. 146—148·5°), oxidised by KI_3 in NaOH–dioxan to the 3-*carboxylic acid*, m.p. 233—235°, which with HNO_3 gives (III). Me 6-hydroxydehydroabietate (IV) and Se at 280—285° (later 335°) in N_2 give 68% of *reten*-6-*ol*, m.p. 179—180°, identical with (II). Me *O*-methylpodocarpate, AcCl, and $AlCl_3$ in $PhNO_2$, first at 0° and then at 5°, give 80% of the 7-*Ac* derivative, m.p. 119—119·5°, $[\alpha]_D^{25}$ +142° in EtOH (oxime, m.p. 190—193°), and thence ($MgMeCl$–Et_2O) *Me* O-*methyl*-7-α-*hydroxy*iso*propylpodocarpate*, m.p. 148—150°, $[\alpha]_D^{25}$ +119° in EtOH. In boiling AcOH this affords *Me* O-*methyl*-7-iso*propenyl*-, m.p. 120·5—121·5°, $[\alpha]_D^{25}$ +136° in EtOH, and thence (H_2–PtO_2–95% EtOH) -7-iso*propyl*-*podocarpate* (V), m.p. 109—109·5°, $[\alpha]_D^{25}$ +124° in EtOH. *Me* 6-*methoxydehydroabietate* [prep. from (IV) by $MgMeCl$–Et_2O, followed by Me_2SO_4; other methods fail or are erratic], m.p. 65·5—66·5°, $[\alpha]_D^{25}$ +87° in EtOH, differs from (V). Se converts (V) into 6-

methoxyretene, of which 22% is isolated as such and 30% by hydrolysis to (II). R. S. C.

Properties of benzoylmesitoylmethane. R. P. Barnes, C. I. Pierce, and C. C. Cochrane (J. Amer. Chem. Soc., 1940, **62**, 1084—1087).—Mesitaldehyde is obtained in 80% yield by hydrogenating (Pd–$BaSO_4$) mesitoyl chloride in boiling xylene and in 50% yield [with 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO_2H and -$C_6H_2Me_3$·CH(OH)·CO_2H] by oxidising ($KMnO_4$–KOH) 2 : 4 : 6 : 1-$C_6H_2Me_3$·COMe to 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CO_2H and warming the anil thereof with conc. H_2SO_4. 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CHBr·CHPhBr and KOAc in boiling AcOH give 91—92% of *mesityl α-bromostyryl ketone*, m.p. 86°, which reduces $KMnO_4$, absorbs Br, with MgPhBr gives 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CHBr·$CHPh_2$, and with hot, conc. KOH–MeOH gives 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CH:CPh·OH (I), m.p. 76—77°, also obtained from (V) (below) by hot HCl–MeOH. (I) is 100% enolic in MeOH, but <1% in CCl_4, gives a *Cu* derivative, m.p. 221° (decomp.), and with Br in $CHCl_3$ + $CaCO_3$ gives *β-bromo-α-phenyl-γ-mesitylpropane-αγ-dione* (II), m.p. 64—66°, which is 24% enolic and with hot KOAc–AcOH gives mainly (I) with some 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·COPh (III). Addition of (I) and then of Br–AcOH to C_5H_5N–H_2SO_4–AcOH gives the ββ-*Br*$_2$-derivative, m.p. 107—108°, analogous to (II), converted by KOAc–AcOH into (III). With boiling AcCl, (II) gives *mesityl α-bromo-β-acetoxystyryl ketone*, m.p. 96°, and with boiling KOAc–Ac_2O gives also some 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·C(OAc):CPh·OAc. 2 : 4 : 6 : 1-$C_6H_2Me_3$·[CHBr]$_2$·COPh (IV) and KOAc–AcOH give *Ph α-bromo*-2 : 4 : 6-*trimethylstyryl ketone*, m.p. 95°, and thence by hot NaOMe–MeOH 2 : 4 : 6 : 1-$C_6H_2Me_3$·C(OMe):CH·COPh (V), obtained similarly also from (IV). R. S. C.

Diene addition products to diaroylethylenes and their transformation products. R. Adams and R. B. Wearn (J. Amer. Chem. Soc., 1940, **62**, 1233—1237; cf. A., 1940, II, 103).—Addition of *trans*-(:CH·COAr)$_2$ (*A*) (Ar = *p*-C_6H_4Cl, *p*-tolyl, or mesityl) to (CH:CH_2)$_2$, (CMe:CH_2)$_2$ (I), or *cyclo*pentadiene in boiling C_6H_6 gives 4 : 5-*di*-p-*chlorobenzoyl*-, m.p. 125°, -p-*toluoyl*-, m.p. 127°, and -*mesitoyl*- (II), m.p. 204°, -Δ^1-cyclo*hexene*, 4 : 5-*di*-p-*chlorobenzoyl*-, m.p. 151°, and -p-*toluoyl*-, m.p. 129°, -1 : 2-*dimethyl*-Δ^1-cyclo*hexene*, 4 : 5-*di*-p-*chlorobenzoyl*-, m.p. 139°, -p-*toluoyl*-, m.p. 106°, and -*mesitoyl*-, m.p. 117°, -3 : 6-endo*methylene*-Δ^1-cyclo*hexene*. (*A*) (Ar = mesityl) does not add to (I). The *endo*methylene products and (II) do not give furans, but with boiling Ac_2O–syrupy H_3PO_4 the other *cyclo*hexenes give 1 : 2-*di*-p-*chlorophenyl*-, m.p. 215°, 1 : 2-*di*-p-*tolyl*-, m.p. 210°, 1 : 2-*di*-p-*chlorophenyl*-4 : 5-*dimethyl*-, m.p. 236°, and 1 : 2-*di*-p-*tolyl*-4 : 5-*dimethyl*-, m.p. 237°, -3 : 6-*dihydro*iso*benzfuran*. By Br–$CHCl_3$ are obtained 1 : 2-*dibromo*-4 : 5-*di*-p-*chlorobenzoyl*-, m.p. 181°, -p-*toluoyl*-, m.p. 177°, -*mesitoyl*-, m.p. 202°, -p-*chlorobenzoyl*-1 : 2-*dimethyl*-, m.p. 173°, and -p-*toluoyl*-1 : 2-*dimethyl*-, m.p. 184°, -cyclo*hexane*. The Br_2-compounds and a little H_2SO_4 in boiling AcCl (not Ac_2O–H_3PO_4) or, less well, the dihydro*iso*benzfurans and Br–$CHCl_3$ at 0° give 4 : 5-*dibromo*-1 : 2-*di*-p-*chlorophenyl*-, m.p. 179°, and -p-*tolyl*-3 : 4 : 5 : 6-*tetrahydro*iso*benzfuran*, m.p. 166°; the corresponding 1 : 2-Me_2 compounds are unstable. Addition of Br to the appropriate dihydro*iso*benzfurans and anhyd. NaOAc in boiling AcOH gives *o*-$C_6H_4(COR)_2$ (R = *p*-C_6H_4Cl or *p*-tolyl), 4 : 5-*di*-p-*chlorobenzoyl*-, m.p. 168—169°, and 4 : 5-*di*-p-*toluoyl*-, m.p. 164°, -o-*xylene*, which with boiling NaOH–EtOH, later activated Zn dust in NaOH–EtOH, and finally AcOH–EtOH–Zn dust give 1 : 2-di-*p*-chlorophenyl-, m.p. 199—200°, -p-*tolyl*-, m.p. 125°, -p-*chlorophenyl*-4 : 5-*dimethyl*-, m.p. 213°, and -p-*tolyl*-4 : 5-*dimethyl*-, m.p. 186°, -iso*benzfuran*. With (:CH·CO)$_2$O in C_6H_6 at room temp. (5 min.) these products give 1 : 4-*epoxy*-1 : 4-*di*-p-*chlorophenyl*-, m.p. 264—266°, -p-*tolyl*-, m.p. 256—258°, -p-*chlorophenyl*-6 : 7-*dimethyl*-, *forms*, m.p. 292—293° and 270—272°, and -p-*tolyl*-6 : 7-*dimethyl*-, *forms*, m.p. 285—286° and 267—268°, -1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride*, dehydrated by HCl (gas) in boiling MeOH to 1 : 4-*di*-p-*chlorophenyl*-, m.p. 304—305° (block), -p-*tolyl*-, m.p. 293—295° (block), -p-*chlorophenyl*-6 : 7-*dimethyl*-, m.p. 321—323° (block), and -p-*tolyl*-6 : 7-*dimethyl*-, m.p. 338—340° (block), -2 : 3-*naphthalic anhydride*. M.p. are corr. R. S. C.

Condensations of *cyclo*hexanone and its derivatives with aromatic aldehydes. R. Poggi and (Signa.) S. Sacchi (Gazzetta, 1940, **70**, 269—273).—*cyclo*Hexanone and *p*-C_6H_4Me·CHO at the b.p. give 2-p-*tolylidene*cyclo*hexanone* (I), m.p. 61—62° {*semicarbazone*, m.p. 210° (decomp.); *oxime*, m.p. 129·5—130° (softens 125°) [*Bz*, m.p. 105° (softens 102°), and Ac derivative, m.p. 116—117·5° (softens 110°)]}, with 2 : 6-di-*p*-tolylidene*cyclo*hexanone, m.p. 169—170° (softens 164°), also obtained from (I), which also yields 6-*benzylidene*-, m.p. 119° (softens 115°), and 6-*anisylidene*-2-p-*tolylidene*-cyclo*hexanone*, m.p. 149° (softens 147°). E. W. W.

Synthesis of keto-acids. Synthesis of 2-*p*-anisyl*cyclo*pentanone-3-carboxylic acid. N. N. Chatterjee and G. N. Barpujari (J. Indian Chem. Soc., 1940, **17**, 157—160).—*p*-OMe·C_6H_4·CH(OH)·CN, m.p. 67°, and CN·CHNa·CO_2Et in EtOH give *Et αβ-dicyano-β-p-anisylpropionate*, m.p. 81°, b.p. 225°/5 mm. (and a small amount of an acid, m.p. 226°), which without isolation condenses with Cl·[CH_2]$_2$·CO_2Et to give *Et*$_2$ αβ-*dicyano*-α-p-*anisyl*-n-*butane*-βδ-*dicarboxylate*, b.p. 233—236°/4 mm. This is hydrolysed by boiling 20% H_2SO_4 to α-p-*anisyl*-n-*butane*-αβδ-*tricarboxylic acid*, m.p. 183° (rapid heating), the *Et*$_3$ ester, b.p. 205—215°/3 mm., of which with "mol." Na in boiling C_6H_6 yields *Et*$_2$ 2-p-*anisyl*-cyclo*pentanone*-3 : 5-*dicarboxylate*, b.p. 200—212° (decomp.)/4 mm., converted by boiling 20% H_2SO_4 into 2-p-*anisyl*cyclo*pentanone*-3-*carboxylic acid*, m.p. 135° [*semicarbazone*, m.p. 233° (decomp.)]. R. S. C.

Synthesis of keto-acids. Action of sodium ethoxide on diethyl *cyclo*pentanone-2-carboxylate-2-acetate. N. N. Chatterjee, B. K. Das, and G. N. Barpujari (J. Indian Chem. Soc., 1940, **17**, 161—166).—*Et*$_2$ cyclo*pentanone*-2-*carboxylate*-5-*acetate* (I), b.p. 160—165°/16 mm., is obtained from Et$_2$ *cyclo*pentanone-2-carboxylate-2-acetate [prep. from Et *cyclo*pentanone-2-carboxylate (II) by $CH_2Cl·CO_2Et$ (III) and "mol." Na in C_6H_6], b.p. 142—

144°/4 mm., by boiling NaOEt–EtOH, probably by way of the open-chain acid (cf. Perkin *et al.*, J.C.S., 1909, **95**, 2010). With boiling HCl it gives *cyclo*pentanone-2-carboxylic acid, isolated as *semicarbazone*, m.p. 198°. With " mol." Na and (III) in C_6H_6 it gives *Et*$_3$ cyclo*pentanone*-2-*carboxylate*-2 : 5-*diacetate*, b.p. 199—200°/8 mm., converted by boiling, conc. HCl into cyclo*pentanone*-2 : 5-*diacetic acid*, m.p. 177° (*Et*$_2$ ester, b.p. 168—170°/6 mm.). (I) with $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ (IV) gives similarly *Et*$_3$ cyclo*pentanone*-2-*carboxylate*-5-*acetate*-2-β-*propionate*, b.p. 200°/4 mm., and thence cyclo*pentanone*-2-*acetic*-5-β-*propionic acid* (V), m.p. 126° (*Et*$_2$ ester, b.p. 170°/4 mm.). (II) gives similarly Et$_3$ *cyclo*pentanone-2-carboxylate-2-β-propionate, b.p. 189°/18 mm., which with boiling NaOEt–EtOH yields *Et*$_2$ cyclo*pentanone*-2-*carboxylate*-5-β-*propionate* (VI), b.p. 175°/4 mm., converted by Na and (III) in C_6H_6 into *Et*$_3$ cyclo*pentanone*-2-*carboxylate*-2-*acetate*-5-β-*propionate*, b.p. 205°/4 mm. [hydrolysed (HCl) to (V)]. (IV) and (VI) give *Et*$_3$ cyclo*pentanone*-2-*carboxylate*-2 : 5-*di*-β-*propionate*, b.p. 215°/4 mm., and thence cyclo*pentanone*-2 : 5-*di*-β-*propionic acid*, m.p. 122° (*Et*$_2$ ester, b.p. 172°/4 mm.).

R. S. C.

Azomethine derivatives of 2-nitro- and 2 : 5- and 2 : 7-dinitro-fluorene. E. A. Calderón and H. Pérez (Anal. Asoc. Quím. Argentina, 1940, **28**, 5—33; cf. A., 1928, 180).—There is an increase in colour intensity with increase in mol. wt. for the following azomethines which were prepared from the nitrofluorenes with the appropriate NO-compounds in EtOH–KCN: 2-*nitro*-, m.p. 214°, 2 : 5-*dinitro*-, m.p. 200°, and 2 : 7-*dinitro-fluorenone*-p-*dimethylaminoanil*, m.p. 225°, and the *azomethines*, m.p. 153°, 280·5°, and 280°, of 4-aminoantipyrine and 2-nitro-, 2 : 5-dinitro-, and 2 : 7-dinitro-fluorenone, respectively. Fluorene did not yield an azomethine under similar conditions.

F. R. G.

Fused carbon rings. XVIII. Further investigations of model substances of the sexual hormone type. V. C. E. Burnop and R. P. Linstead (J.C.S., 1940, 720—727; cf. A., 1938, II, 269).—1-Methyl-2-Δ$^\gamma$-butenyl*cyclo*hexanol and AcOH (excess)–Ac_2O–H_2SO_4 followed by hydrolysis (20% MeOH–KOH) afford 9-methyldecahydro-β-naphthol (I), epimeric mixture, b.p. 135—138°/19 mm., oxidised by CrO_3–AcOH to *cis*-2-keto-9-methyldecahydronaphthalene (cf. A., 1937, II, 412). (I) [improved prep. from 2-methyl-1-Δ$^\gamma$-butenyl*cyclo*hexanol; some (II) is formed] is dehydrated by $KHSO_4$ to *cis*-9-methyloctahydronaphthalene (II), which is oxidised by aq. K_2CO_3–$KMnO_4$ to *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (III), converted by $Ba(OH)_2$ at 320° into *cis*-8-methyl-2-hydrindanone (IV). Thus (II) behaves as the Δ^2-isomeride (*loc. cit.*). Ozonolysis of (II) in $CHCl_3$ at 0° or EtOAc at −73° to −76° indicates the presence of some Δ^1-isomeride; hydrolysis (H_2O) of the ozonide, followed by hot aq. NaOH–H_2O_2, affords (III) (40%) and impure (V) (below) (12%) (separable through the Me esters), converted by $Ba(OH)_2$ at 320° into *cis*-8-methyl-2- [semicarbazone (formed in cold), m.p. 218—219°] and -1-hydrindanone [semicarbazone (in hot), m.p. 223—224°], respectively. *cis*-1-Methyl*cyclo*hexane-1-carboxylic-2-β-propionic acid (V) has m.p. 108—109° (cf. A., 1938, II, 269). (II) and $Pb(OAc)_4$–AcOH at 70° afford an acetate, hydrolysed by KOH–MeOH to cis-9-*methyl*-Δ^1-*octahydro*-3-*naphthol*, b.p. 125—130°/12 mm., hydrogenated (PtO_2, EtOH) to the -*decahydronaphthol*, b.p. 130—132°/12 mm., which is oxidised (CrO_3–AcOH) to *cis*-3-keto-9-methyldecahydronaphthalene (VI), m.p. 47° (cf. du Feu *et al.*, A., 1937, II, 196). (II) and O_2 + Fe^{II} phthalocyanine at 70° yield *cis*-3-keto-9-methyl-Δ^1-octahydronaphthalene (VII), b.p. 130°/16 mm. (*semicarbazone*, m.p. 202—203°), hydrogenated (Pd–EtOH) to (VI). (II) and SeO_2–Ac_2O at 60°, then 100°, afford a compound, b.p. 110—115°/13 mm., hydrolysed by KOH–EtOH to an alcohol, b.p. 120—130°/16 mm., which is oxidised (CrO_3) to (VII). The above oxidations of (II) involve attack at $C_{(3)}$; the Δ^2-form present does not react. $Al(OPr^\beta)_3$–$Pr^\beta OH$ and (IV) afford cis-8-*methyl*-2-*hydrindanol*, probably an epimeric mixture, b.p. 120—122°/21 mm., dehydrated ($KHSO_4$) to *cis*-8-methylhexahydroindene (VIII), b.p. 61—62°/19 mm.; aq. $KMnO_4$ then gives *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid. (VIII) and H_2O_2–AcOH at room temp., followed by hydrolysis of the diacetate with KOH–MeOH, afford cis-8-*methylhydrindane*-1 : 2-*diol*, b.p. 170—172°/18 mm., dehydrated by $KHSO_4$ at 200° to the -1-hydrindanone. *trans*-Δ^2-Octahydronaphthalene and $Pb(OAc)_4$–AcOH at 70° give (mainly) trans-Δ^2-*octahydro*-α-*naphthyl acetate*, b.p. 131°/12 mm. [hydrolysed by KOH–EtOH to trans-Δ^2-*octahydro*-α-*naphthol* (IX), b.p. 133—134°/16 mm.], and some diacetate of trans-*decahydronaphthalene*-2 : 3-*diol*, m.p. 140°. (IX) and H_2 (PtO_2, EtOH) give the decahydronaphthol, oxidised to not quite pure *trans*-1-ketodecahydronaphthalene. (IX) and $KHSO_4$ (or HCl–EtOH) give a *hexahydronaphthalene*, b.p. 82°/17 mm. (double linkings probably at 2 : 3 and 1 : 9) [maleic anhydride adduct, m.p. 275° (decomp.)], reduced (H_2–PtO_2–EtOH) to (mainly) *cis*-decahydronaphthalene, and converted by Pd–C at 160°, then 100% H_2SO_4 at 100°, into Na tetrahydronaphthalene-2-sulphonate + *cis*- and *trans*-decahydronaphthalene.

A. T. P.

Direct introduction of the angular methyl group. R. B. Woodward (J. Amer. Chem. Soc., 1940, **62**, 1208—1211).—5 : 6 : 7 : 8-Tetrahydro-2-naphthol (3·5 g.) and $CHCl_3$ in 10% aq. NaOH at 75° give 3-aldehydo-5 : 6 : 7 : 8-tetrahydro-2-naphthol (1·8 g.) and 2-*keto*-10-*dichloromethyl*-2 : 5 : 6 : 7 : 8 : 10-*hexahydronaphthalene* (0·8 g.), m.p. 167·5—168·5° [absorption max. 235 (log ε 4·14) and 329 mμ. (log ε 1·38)], hydrogenated (PtO_2) in MeOH to 2-*hydroxy*-10-*dichloromethyldecahydronaphthalene*, m.p. 92·5—93°, sublimes at 64°/high vac. (α-*naphthylurethane*, m.p. 152·5—153°), which with H_2–Pd–$BaSO_4$ in 10% KOH–MeOH followed by AcOH–CrO_3 gives 2-keto-10-methyldecahydronaphthalene.

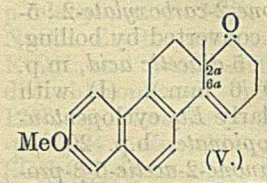
R. S. C.

Naphthalene series. I. Synthesis of 5-bromo- and -chloro-1-keto-7 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene. R. H. Siddiqui. **II. Reactions of the $CH_2{\cdot}CO$ group.** R. H. Siddiqui and Salah-ud-din (J. Indian Chem. Soc., 1940, **17**, 145—147, 148—151).—I. 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 160—161°, is re-

duced (Clemmensen) to 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}[CH_2]_3{\cdot}CO_2H$, m.p. 60—61° (lit. 57—59°), which with Br–air in AcOH gives the 6-Br-derivative (I), m.p. 139—140° (lit. 135—136°), and thence by P_2O_5 in boiling moist C_6H_6 5-*bromo*-1-*keto*-7 : 8-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (II) (10—15%), m.p. 91—92° [2 : 4-*dinitrophenylhydrazone*, m.p. 220—225° (decomp.); *semicarbazone*, m.p. 215°, hydrolysed by aq. $H_2C_2O_4$ to (I) (m.p. 142—143°) or by $H_2C_2O_4$–$COMe_2$ to (II)]. γ-6-*Chloro*-3 : 4-*dimethoxyphenylbutyric acid*, m.p. 111—112°, and 5-*chloro*-1-*keto*-7 : 8-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 75° (*oxime*, m.p. 187°; 2 : 4-*dinitrophenylhydrazone*, m.p. 239—240°), are similarly prepared.

II. 1-Keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene does not give an oximino-derivative, gives oily CHMe:, CH_2:, and $CH_2{\cdot}CH{\cdot}CH$: derivatives, 2-*CHPh*:, m.p. 131° (with $KMnO_4$ gives a little *m*-hemipinic acid), -o-, m.p. 152°, -m-, m.p. 131°, and -p-*OMe*·$C_6H_4{\cdot}CH$:, m.p. 159°, -3′ : 4′-$(OMe)_2C_6H_3{\cdot}CH$:, m.p. 148°, -2′-furfurylidene-, m.p. 151°, -3′ : 4′-CH_2O_2:$C_6H_3{\cdot}CH$:, m.p. 182°, -*CHPh*:*CH*·*CH*:, m.p. 160°, -m-, m.p. 190°, -o-, amorphous, m.p. 152°, and -p-$NO_2{\cdot}C_6H_4{\cdot}CH$:, amorphous, m.p. 270°, derivatives. R. S. C.

Fused carbon rings. XIX. Synthesis of tetracyclic compounds of the sexual hormone type. V. C. E. Burnop, G. H. Elliott, and R. P. Linstead (J.C.S., 1940, 727—735; cf. A., 1938, II, 269; Bachmann *et al.*, A., 1940, II, 225).—Na 1 : 2 : 3 : 4-tetrahydronaphthalene-6-sulphonate and KOH at 200—280° afford 6-hydroxy- and thence (Me_2SO_4–aq. NaOH) 6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (+ some 2-$C_{10}H_7{\cdot}OMe$), oxidised by CrO_3–AcOH at 5—10° to 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (I), m.p. 77·5°. (I) and $CH_2Br{\cdot}CO_2Et$–Zn wool–C_6H_6 afford a OH-ester, dehydrated by P_2O_5–C_6H_6 to Et 6-methoxy-3 : 4-dihydro-1-naphthylacetate, b.p. 164—168°/1·5 mm., whence (Bouveault–Blanc) β-6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylethyl alcohol, b.p. 158—162°/1 mm. (some 6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid is formed), and, by PBr_3–C_6H_6–C_5H_5N, the bromide, b.p. 150—155°/0·7 mm. The latter and $CKMe(CO_2Et)_2$ in xylene give an ester, hydrolysed by KOH–MeOH to β-6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylethylmethylmalonic acid, converted at 165°/40 mm. into γ-6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthyl-α-methyl-*n*-butyric acid, which is dehydrogenated by Pd–asbestos (or Pt–C) at 270—280°/40 mm. to γ-6-methoxy-1-naphthyl-α-methyl-*n*-butyric acid, m.p. 87°. P_2O_5–C_6H_6 (or $SnCl_4$ on the chloride) then gives 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (II), m.p. 107°. γ-1-Naphthyl-α-methylbutyric acid and $SOCl_2$–C_5H_5N give the chloride, converted by $SnCl_4$–CS_2 at −15°, then at room temp., into 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (III). Mg Δ^5-pentenyl bromide (IV) and (I) afford 6-*methoxy*-1-Δ^5-*pentenyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthol*, b.p. 168—172°/1·5 mm., which with aq. $KMnO_4$–Na_2CO_3 gives an acid product, and this when distilled with $H_2C_2O_4$ yields γ-6-methoxy-3 : 4-dihydro-1-naphthylbutyric acid, m.p. 133—134° (softens at 127°) (may be partially dehydrogenated) (cf. Robinson *et al.*, A., 1937, II, 196). (II) and (IV) yield an alcohol, converted by $KMnO_4$–$COMe_2$–Na_2CO_3 into an unstable acid (formula given), which with P_2O_5–C_6H_6 gives the 3-*keto*-10-*methoxy*-2a-*methyl*-*hexahydrochrysene* (V), m.p. 187° (semicarbazone, m.p. 260°), hydrogenated (H_2–PtO_2–AcOH) by addition at C_6 and C_{6a} to the -*octahydrochrysene*, m.p. 212—213° (semicarbazone, m.p. 245°), and thence to the 3-hydroxy-10-methoxy-2*a*-methyloctahydrochrysene [*s*-$C_6H_3(NO_2)_3$ *compound*, +MeOH, m.p. 155°]. Mg Δ^γ-butenyl bromide and (III) afford a product, dehydrated on distillation (dehydration of higher boiling material can be completed by heating with SiO_2 gel at 180°/10 mm.); chromatographic separation gives mainly 2-*methyl*-1-Δ^γ-*butenyl*-3 : 4-*dihydrophenanthrene* (VI), b.p. 162°/0·3 mm. [purified through the *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 65—66°, which on exposure to air and light has m.p. 60—62°, and then (8 days) 80—85°; picrate, m.p. 72—73° (cf. Cohen *et al.*, A., 1936, 62)], and some of the corresponding *tert.*-alcohol, $C_{19}H_{22}O$. Pd–C at 260—265° and then 280—285° converts (VI) into 2-*methyl*-1-n-*butylphenanthrene* (VII), m.p. 73° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 147—148°; *picrate*, m.p. 128°]. (VI) and Ac_2O–H_2SO_4–AcOH at 0°, then at room temp., afford a product, b.p. ~152°/0·5 mm. 2-Methyl-1-Δ^γ-butenyl*cyclo*hexanol and H_3PO_4 (dehydrated at 235°) in AcOH at room temp., then at 85°, give the acetate, b.p. 125—131°/9 mm., of *cis*-9-methyldecahydro-2-naphthol. (VI) similarly yields 16-methylhexahydrochrysene (VIII) (double linking probably at $C_{(4)}$: $C_{(5)}$) [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 123°], best obtained with (VII), from (VI) and P_2O_5 at 140°. (VIII) and Se at 310—330° afford chrysene. (VIII) is not oxidised satisfactorily by $KMnO_4$, $Pb(OAc)_4$–AcOH, or SeO_2–Ac_2O; ozonisation and oxidation (alkaline H_2O_2) give an acidic compound, m.p. 165—167° (previous softening). A. T. P.



(V.)

Carbonyl compounds of *cyclo*pentanopolyhydrophenanthrene series.—See B., 1940, 566.

Reagent for determining œstrone.—See A., 1940, III, 581.

Steroids. II. 6(α)-Hydroxyprogesterone. M. Ehrenstein and T. O. Stevens (J. Org. Chem., 1940, 5, 318—328).—*Pregnane*-3(β) : 5 : 6(trans)-*triol*-20-*one* 3 : 6-*diacetate*, m.p. 215·5—216·5°, $[\alpha]_D^{18}$ −2·0° in $COMe_2$, obtained from the triol (A., 1939, II, 554) and boiling Ac_2O, is hydrolysed under defined conditions to the 6-*monoacetate*, m.p. 222—226°, which is oxidised (CrO_3 in 80% AcOH at room temp.) to *pregnane*-5 : 6(trans)-*diol*-3 : 20-*dione* 6-*acetate*, m.p. 215—217·5°. This is transformed by HCl in $CHCl_3$ at <4° into Δ^4-*pregnen*-6(α)-*ol*-3 : 20-*dione acetate* [6(α)-*hydroxyprogesterone acetate*] (I), m.p. 145—146°, $[\alpha]_D^{17.5}$ +89·7° in abs. EtOH, which does not give a yellow colour with $C(NO_2)_4$ in $CHCl_3$; its ultra-violet absorption spectrum has a max. at 232 mμ. The corresponding OH-compound appears very unstable and hydrolysis (KOH–MeOH) of (I) seems to yield *pregnane*-3 : 6 : 20-*trione*, m.p. 226·5—230° (impure *trioxime*, m.p. 165—170°), which is indifferent towards Ac_2O and C_5H_5N

at 100°. (I) has distinct progestational and possibly slight adrenal cortical activity. *Pregnane*-3(β) : 5 : 6(cis)-*triol*-20-*one* 3 : 6-*diacetate*, m.p. 251·5—252°, $[\alpha]_D^{17·5}$ +56·6° in $COMe_2$, is obtained from boiling Ac_2O and the triol (*loc. cit.*). H. W.

Reactions of *o*-benzoquinone.—See B., 1940, 513.

Substituted *p*-quinones and quinols.—See B., 1940, 515.

Hydrogenation of benzoquinone with palladium and platinum catalysts. E. F. Rosenblatt (J. Amer. Chem. Soc., 1940, **62**, 1092—1094).—H_2–Pt–C reduces *p*-O:C_6H_4:O in 5% HCl to *cyclo*hexanol, but H_2–Pd–C is similarly ineffective. Hydrogenation occurs only to quinol in neutral solution (EtOH, MeOH) or AcOH, and in MeOH or EtOH Pd–C causes faster reaction than does Pt–C. R. S. C.

Peroxidase action. II. Oxidation of *p*-toluidine. B. C. Saunders and P. J. G. Mann (J.C.S., 1940, 769—772; cf. A., 1936, 462).—The peroxidase, derived from horseradish or turnips, readily oxidises *p*-$C_6H_4Me·NH_2$ in presence of dil. H_2O_2–AcOH at p_H 4·5 at room temp. to give 4-amino-, m.p. 236°, and 4-*p*-toluidino-2 : 5-toluquinonebis-*p*-tolylimine, m.p. 183° [H_2SO_4–EtOH at room temp. give (II) (below)], $NH(C_6H_4Me$-*p*$)_2$, a little (*p*-$C_6H_4Me·N:)_2$ (I), traces (produced by hydrolysis) of 4-amino- and 4-*p*-toluidino-2 : 5-toluquinone-2-*p*-tolylimine (II), and a substance, m.p. 167°. *p*-$C_6H_4Me·NO_2$ is not formed. H_2O_2–$FeSO_4$–AcOH cause a different reaction; (I) + (II) are among the products formed. Adaptation of Irvine's filter (A., 1915, ii, 832) for continuous elution of a chromatogram is described. A. T. P.

Quinones by the peroxide oxidation of aromatic compounds. R. T. Arnold and R. Larson (J. Org. Chem., 1940, **5**, 250—252).—Many aromatic hydrocarbons and their simple derivatives can be oxidised to quinones by 30% H_2O_2 in glacial AcOH, the yields being comparable with those obtained by dichromate oxidation. The greatest val. of the reaction appears to lie in the selective oxidation of alkyl polycyclic derivatives. The following are cited: 1-$C_{10}H_7$·CHO to 1 : 4-O:$C_{10}H_6$:O, also obtained from $C_{10}H_8$ at 80°; durene to duroquinone at 100°; *o*-xylene to *o*-xyloquinone (trace) at 120°; 2-$C_{10}H_7Me$ to 2-methyl-1 : 4-naphthaquinone (yield 30%) at 80°; 2 : 3-$C_{10}H_6Me_2$ to 2 : 3-dimethyl-1 : 4-naphthaquinone (yield 78%) under similar conditions; 1 : 2-benzanthracene in boiling solution to 1 : 2-benzanthra-9 : 10-quinone (yield 46%); pyrene in boiling solution to a mixture of pyrenequinones. H. W.

Constitution of vitamin-K_2. S. B. Binkley, R. W. McKee, S. A. Thayer, and E. A. Doisy (J. Biol. Chem., 1940, **133**, 721—729).—Previous work (A., 1939, III, 853; 1940, III, 146) and that now described indicate that vitamin-K_2 (I) is probably 2-*methyl*-3-*γηλοτψ*-*hexamethyl*-$\Delta^{\beta\xi\kappa\sigma\chi}$-*tetracosahexaenyl*-1 : 4-*naphthaquinone*. Decomp. of the ozonides from dihydrovitamin-K_1 and -K_2 diacetate (II) with Zn dust in Et_2O–AcOH gives 1 : 4-*diacetoxy*-2-*methyl*-3-*naphthylacetaldehyde*, m.p. 115—115·5° (*semicarbazone*, m.p. 206—206·5°), oxidised (AcOH–CrO_3) to the -3-naphthylacetic acid, m.p. 209—210° (cf. A., 1939, II, 513). The ozonide from (II) (1 mol.) also affords $COMe_2$ (1 mol.) and lævulaldehyde (5 mols.; similarly obtained in 75% yield from farnesol). The absence of substituents in the benzenoid ring of (I) is shown by oxidation ($COMe_2$–$KMnO_4$) of (II) to *o*-$C_6H_4(CO_2H)_2$. (I) does not respond to Craven's colour test (A., 1931, 972). H. B.

Carbonyl constituents of eucalyptus oils. III. Constitution of phellandral. *d*-, *l*-, and *dl*- (synthetic) -Phellandric acids. R. G. Cooke, A. K. Macbeth, and T. B. Swanson (J.C.S., 1940, 808—810).—Oxidation of *d*-phellandral with $AgNO_3$–NaOH gives d-*phellandric acid*, m.p. 144—145°, $[\alpha]_D^{20}$ +112·8° in MeOH (p-*chloro*-, m.p. 78—78·5°, $[\alpha]_D^{20}$ +71° in $CHCl_3$, and p-*bromo-phenacyl* esters, m.p. 86°, $[\alpha]_D^{20}$ +68·1° in $CHCl_3$); the *l*-acid is similarly obtained (p-*chloro*-, m.p. 78—78·5°, $[\alpha]_D^{20}$ −57° in $CHCl_3$, p-*bromo-phenacyl*, m.p. 86°, $[\alpha]_D^{20}$ −52·2° in $CHCl_3$, and p-*nitrobenzyl* esters, m.p. 56—57°). The *l*-acid in AcOH with PtO_2–H_2 affords *cis*-hexahydrocuminic acid and in NaOH with Ni–H_2 yields the corresponding *trans*-acid. Bromination of the chloride of the *trans*-acid gives *α-bromohexahydrocuminic acid*, m.p. 91°, the Et ester of which is debrominated and hydrolysed by Na–MeOH to dl-*phellandric acid*, m.p. 143—144° (p-*bromophenacyl* ester, m.p. 86—86·5°). These results afford additional support for the structure of phellandral as 4-*iso*propyl-Δ^1-*cyclo*hexene-1-aldehyde (Δ^1-tetrahydrocuminal). F. R. S.

Chloro- and bromo-derivatives of pinane. A. Gandini (Gazzetta, 1940, **70**, 254—265).—Pinane (I) (prep. from *l*-pinene and Pt–H_2 at room temp.) reacts more readily than menthane, camphor, or cineole with halogens. In $CHCl_3$ with Cl_2 (1 mol.) in H_2O (sunlight) (I) gives 2-*chloropinane* (II), b.p. 82°/30 mm., $[\alpha]_D^{20}$ −5·74°, with ??-*dichloropinane*, b.p. 106—108°/30 mm., less stable chlorination products, and unchanged (I). With Br (1 mol.), (I) similarly gives 2-*bromopinane* (III), m.p. 70—72°, b.p. 75—85°/5 mm., and other products. With aq. $KMnO_4$, (II) or (III) gives terebinic acid (IV). With KOPh at 150°, (II) or (III) yields mixed pinenes, b.p. 160—165°, hydrogenated to (I). With AgOAc–AcOH at 100°, (III) [or (II)] gives the acetate, b.p. 40—50°/0·1 mm., of an alcohol, $C_{10}H_{18}O$, b.p. 83°/14 mm., which is oxidised (Beckmann) to a ketone [probably 2-ketopinane (pinocamphone)] (V), b.p. 72—73°/14 mm. (oxime, b.p. 108—112°/3 mm.; semicarbazone, m.p. 222—230°). With H_2O over activated C at 400°, (V) gives thymol and carvacrol. 5% $KMnO_4$ oxidises (V) to (IV). E. W. W.

Sesquiterpene alcohol, torreyol. I. K. Nishida and H. Uota (J. Soc. Chem. Ind. Japan, 1940, **43**, 64—65B).—The oil (1060 g.), $[\alpha]_D$ +38·7°, from the leaves (528 kg.) of *Torreya mucifera*, S. et Z., contains 0·57% of torreyol, $C_{15}H_{26}O$, m.p. 139—140°, which is probably CH_2–CHMe—CH·CH_2·CH_2 / CH_2·C(CMe_2)·CH·CH_2·CMe·OH. It gives colour reactions for C:C, a cryst., hygroscopic acetate, contains a *tert.* OH, with H_2–Pd-black in EtOH gives a H_2-derivative (I), m.p. 106—107°, $[\alpha]_D$ −10·79°, with Se gives cadalene, with boiling HCO_2H gives *torreyene*, $C_{15}H_{24}$, b.p. 89—90°/1 mm., $[\alpha]_D$ +46·67°

(hydrogenated to cadinene), and with HCl–Et_2O gives a *compound*, $C_{15}H_{26}Cl_2$, m.p. 118—119°. Boiling HCO_2H dehydrates (I) to *dihydrotorreyene*, b.p. 90—91°/1 mm., $[\alpha]_D$ +13·05°. R. S. C.

Constitution of calameon. H. Böhme (Arch. Pharm., 1940, **278**, 1—7).—Calameon (I) is a singly unsaturated, di*tert*., dicyclic sesquiterpene alcohol of the cadalene (II) series. The presence of a double linking in (I) is established by oxidation with *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ and of 2 OH by Zerevitinov's method. (I) is hydrogenated (Pd–C–MgO in 96% EtOH) to *dihydrocalameon*, m.p. 133°, and converted by boiling 50% H_2SO_4 into calamene, b.p. 137—139°/12 mm., α_D^{17} −6·60° (l = 0·5), which is dehydrogenated by S at 200—260° to (II). H. W.

Triterpene group. VII. Minor triterpenoid constituents of *Manila elemi* resin. (Miss) I. M. Morice and J. C. E. Simpson (J.C.S., 1940, 795—799).—A new and standardised method is described for the prep. of breïn (I) from the resin, depending on fractional elution from activated Al_2O_3, followed by formylation. The *diformate* of (I) has m.p. 220—221°, $[\alpha]_D^{21}$ +67°, hydrolysed to (I), m.p. 221—222°, $[\alpha]_D^{26}$ +63·5° (diacetate, m.p. 197—198°, $[\alpha]_D^{17}$ +70°; dibenzoate, m.p. 209—210°, $[\alpha]_D^{17}$ +58°). From the mixed alcohols, there have been isolated *maniladiol*, $C_{30}H_{50}O_2$, m.p. 220—221°, $[\alpha]_D^{19}$ +68° (*diformate*, m.p. 186—187°, $[\alpha]_D^{17}$ +84°; *diacetate*, m.p. 193—194°, $[\alpha]_D^{20}$ +80°; *dibenzoate*, m.p. 233—234°, $[\alpha]_D^{17}$ +63·5°), and ψ-taraxasterol (*formate*, m.p. 219—221°, $[\alpha]_D^{17}$ +51°); it is probable that the latter is produced during the working up of the resin by cyclisation of a tetracyclic isomeride. All $[\alpha]$ are in $CHCl_3$. F. R. S.

Essential oil of *Evodia littoralis*.—See B., 1940, 494.

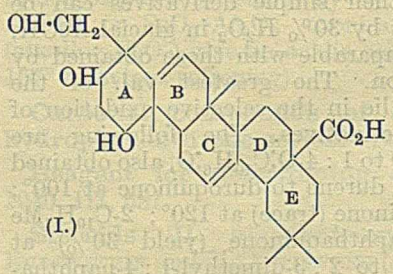
Oleo margosa from *Melia azadirachta*, neem oil. I. Isolation of the constituents of the oil. M. Qudrat-i-Khuda, S. K. Ghosh, and A. Mukherjee (J. Indian Chem. Soc., 1940, **17**, 189—194).—Distillation of the commercial oil, $d_4^{22\cdot9}$ 0·9108, $n_4^{22\cdot9}$ 1·46185, I val. 69·56, sap. val. 198·8, in steam gives *neemola*, $C_{15}H_{30}O_3S$, b.p. 156—158°/118 mm. (nauseous odour; decolorises Br; sol. in aq. Na_2CO_3). The non-volatile portion yields to hot H_2O a bitter glucoside, *margosin*, $C_{28}H_{48}O_{10}$, m.p. 193—195°, and after hydrolysis (KOH–aq. EtOH) *neem acid*-A, $C_{14}H_{28}O_2$, m.p. 67°, -B, $C_{16}H_{32}O_2$, m.p. 55° (also present in the volatile portion), -C, $C_{15}H_{28}O_2$, m.p. 47—48°, b.p. 189—190°/4 mm. {*Me* ester, b.p. 177°/3 mm. [*dibromide*, b.p. 230° (decomp.)/4 mm.]; olefinic}, and -D, $C_{18}H_{32}O_2$, m.p. 31—33°, b.p. 194—195°/4 mm. {*Me* ester, b.p. 183°/3 mm. [*dibromide*, b.p. 223° (decomp.)/4 mm.]; *cyclo*paraffinoid}. R. S. C.

Identity of obaculactone, evodin, and dictamnolactone with limonin. M. S. Schechter and H. L. Haller (J. Amer. Chem. Soc., 1940, **62**, 1307—1309).—These substances are identical, have m.p. (from $COMe_2$–EtOH) 299—300° (corr.), (from AcOH) 297—298° (corr.), $[\alpha]_D^{20\cdot5}$ −129° in $COMe_2$, +32·6° in N-KOH–EtOH, have the composition, $C_{26}H_{30}O_8$, contain no OAlk, CO, or OH, and are hydrogenated to a mixture. R. S. C.

Alcohol, $C_{30}H_{49}{\cdot}OH$, m.p. 110—112° (decomp.) (dibromide, m.p. 135—140°; acetate, m.p. 165—167°; benzoate, m.p. 205—206°), from cotton plant latex.—See A., 1940, III, 618.

Sterols. XCVIII. Conversion of *iso*sarsasapogenin (smilagenin) into tigogenin. R. E. Marker, E. Rohrmann, and E. M. Jones (J. Amer. Chem. Soc., 1940, **62**, 1162—1163).—The "*iso*"-configuration of the side-chain of tigogenin (I) (cf. A., 1940, II, 184) is confirmed. *iso*Sarsasapogenone and Br–HBr–AcOH give the Br_2-derivative, m.p. 184—188° (decomp.), which in boiling C_5H_5N yields *bromo*-$\Delta^{4:5}$-*dehydroisosarsapogenone*, m.p. 200—205° (decomp.) [? *pyridinium* salt, m.p. 245—246° (decomp.)]. Na–EtOH then gives (I). Neotigogenin is isomerised to (I) by boiling HCl–EtOH. R. S. C.

Sapogenins. IX. Occurrence and constitution of bassic acid. B. J. Heywood and G. A. R. Kon (J.C.S., 1940, 713—720).—Bassic acid (I) (cf. Heywood *et al.*, A., 1939, II, 436) has been isolated from the seeds of all except two of the Sapotaceæ examined, and appears to be the characteristic sapogenin of the order. Me bassate occurs in two forms, α, m.p. 214—215°, $[\alpha]_D$ +64°, and β, m.p. 220°, $[\alpha]_D$ +55·5°, both of which give the same acetonyl derivative (cf. van der Haar, A., 1930, 92). This compound is oxidised (AcOH–H_2CrO_4) to an *acetonyl* compound, m.p. 181—183°, hydrolysed to *Me dehydrobassate*, m.p. 202—203·5° (*semicarbazone*, m.p. 210—213°), and possessing no reducing properties; the OH having undergone oxidation must be secondary. The Br-lactone (*acetonyl* compound, m.p. 205—206°) with Zn–AcOH gives a hydroxy-lactone, m.p. 236°, and is oxidised (AcOH–H_2CrO_4) to a *triketone*, $C_{29}H_{39}O_5Br$, m.p. 245° (decomp.) [*mono*-2 : 4-*dinitrophenylhydrazone*, m.p. 286—288° (decomp.); 2 : 4-*dinitrophenylhydrazone* of Me ether, m.p. 294—295° (decomp.)]; the absorption spectra indicate two conjugated double bonds. With Br in AcOH, the triketone affords a *dibromo-triketone*, $C_{29}H_{36}O_5Br_2$, m.p. 229° (decomp.). Oxidation of the β-ester with Cu-bronze yields a *diketone*, $C_{30}H_{42}O_4$, b.p. 130—140°/0·00064 mm., which is oxidised to a neutral product [2 : 4-*dinitrophenylhydrazone*, m.p. 274—276° (decomp.)] and reduced (PtO_2–H_2) to a H_4-compound, $C_{30}H_{46}O_4$, m.p. 218—219°. From the evidence it is deduced that the third OH of (I) is placed on $C_{(4)}$ in ring A and one of the double bonds is in ring B between $C_{(6)}$ and $C_{(7)}$. The complete formula for (I) is suggested. F. R. S.



(I.)

Resin acids. III. Primary resin acids isolated from Russian pine resin. V. N. Krestinski, S. S. Malevskaja, N. F. Komschilov, and E. V. Kazeeva (J. Appl. Chem. Russ., 1939, **12**, 1840—1847).—*Pinus sylvestris* resin is a mixture of isomeric acids, $C_{19}H_{29}{\cdot}CO_2H$, three of which have been identified as *d*- (I) and *l*-pimaric acid (II) and α-sapinic

acid (III); the presence of β-pimaric acid is uncertain. (I) and (II) are present in the resin of *P. maritima* and *palustris* and *Picea excelsa*. (II) and (III) are converted into abietic acid by heating at 200—210° (1—1·5 hr.); under these conditions (I) is recovered unchanged. (I) and (II) have very similar absorption spectra. R. T.

Pharmacologically valuable components of Indian hemp. II. "Cannabinum tannicum" and modified determination of tannin. K. W. Merz and K. G. Bergner (Arch. Pharm., 1940, **278**, 97—109).—"Cannabinum tannicum," formerly used as a hypnotic, is not the tannate of an alkaloid and does not contain appreciable amounts of other substances of pharmacological interest. Two samples consisted eseentially of mixtures of K and Mg tannate with lactose. Traces of chlorophyll, choline, and an odoriferous glucoside containing coumarin were also present with hemp resin in pharmacologically significant amount. Attempts to prepare a "cannabinum purum" by decomp. of cannabine tannate with ZnO were unsuccessful. H. W.

Vitamin-B_1. XIX. Derivatives of γ-acetopropyl alcohol. J. R. Stevens and G. A. Stein (J. Amer. Chem. Soc., 1940, **62**, 1045—1048; cf. A., 1939, II, 289).—α-Chloro-α-acetobutyrolactone (I) and HCl (12 c.c. in 410 c.c. of H_2O) at 100° give 3-*chloro*-2-γ-*chloro*-δ-*keto*-n-*amyloxy*-2-*methyltetrahydrofuran* (II) (62%), b.p. 111—112°/1 mm. [previously (A., 1936, 1394) reported as (III)], and some γ-*chloro*-δ-*keto*-n-*pentan*-α-*ol* (III), b.p. 20—24°/0·003 mm. Distillation at 1 mm. dehydrates (III) to (II). Hydrolysis of (II) to (III) is easy; *e.g.*, it occurs in dil., aq. solution at 60° as shown by crysoscopy and by isolation of (III); with HCS·NH_2,H_2O, (II) gives 4-methyl-5-β-hydroxyethylthiazole. COMe·$[CH_2]_3$·OH (IV) and Br–H_2O at 24—30° give mainly COMe·CHBr·$[CH_2]_2$·OH, but after distillation only 3-*bromo*-2-γ-*bromo*-δ-*keto*-n-*amyloxy*-2-*methyltetrahydrofuran*, b.p. 40° (bath)/0·008 mm., is obtained. This is readily hydrolysed by H_2O but the alcohol formed cannot be isolated. (IV) is more stable; when repeatedly distilled at 10 mm., it gives 2-δ-*keto*-n-*amyloxy*-2-*methyltetrahydrofuran* (V), b.p. 110—112°/12 mm. [gives the semicarbazone of (IV)], the reaction being catalysed by a trace of HCl. The structure of the ethers is proved as follows. With MgMeI, (V) gives (1 mol. consumed; no active H) (IV) and OH·CMe_2·$[CH_2]_3$·OH, indicating addition at the CO. With NHPh·NH_2 (excess) in Et_2O, (III) gives NHPh·NH_2,HCl and 3-*chloro*-2-δ-*benzeneazo*-Δ$^{\gamma}$-*pentenyl*-2-*methyltetrahydrofuran*, m.p. ~85° (decomp.). (III) gives ~ twice as much I after as before hydrolysis. 3-Chloro-2-ethoxy-2-methyltetrahydrofuran (does not react with NHPh·NH_2 or NaOI) is prepared from (I) by H_2SO_4–80% EtOH at 40—50° or similarly from (III) and with aq. HCl (p_H 3) gives (III). R. S. C.

Velocity of transformation of acetonedioxalic ester into chelidonic ester.—See A., 1940, I, 297.

Chalkones. Reactions of *o*-hydroxyphenyl 6-methoxy-2 : 3-benzostyryl ketone and of some derivatives. B. G. Acharya, R. C. Shah, and T. S. Wheeler (J.C.S., 1940, 817—819).—2 : 1-OMe·$C_{10}H_6$·CHO (I) (modified prep.), *o*-C_6H_4Ac·OH (II), and aq. NaOH–EtOH at 60° afford o-*hydroxyphenyl* 6-*methoxy*-2 : 3-*benzostyryl ketone* (III), m.p. 142° (*Ac* derivative, m.p. 107°). 2 : 1-OH·$C_{10}H_6$·CHO (IV) and *o*-C_6H_4Ac·OMe (V) similarly yield o-*anisyl* 6-*hydroxy*-2 : 3-*benzostyryl ketone*, m.p. 153°. (II) and (IV), or (I) and (V), give o-*hydroxyphenyl* 6-*hydroxy*-, m.p. 140° [also from (III)–$AlCl_3$ at 125°], or o-*anisyl* 6-*methoxy*-2 : 3-*benzostyryl ketone*, m.p. 103°, respectively. (II), (IV), and HCl–EtOAc for 4 days yield 2′-*hydroxy*-5 : 6-*benzoflavylium chloride*, m.p. 215—220° (decomp.). (III) and H_2O_2 in aq. KOH–EtOH afford 2-(2′-*methoxy*-1′-*naphthyl*)-3-*chromonol* (VI), m.p. 239° (*Ac* derivative, m.p. 173°). (III), CH_2Ac·CO_2Et, and NaOEt–EtOH give *Et* 5-o-*hydroxyphenyl*-3-(2′-*methoxy*-1′-*naphthyl*)-Δ^5-cyclo*hexenone*-2-*carboxylate*, m.p. 187° (*semicarbazone*, m.p. 172°; *oxime*, m.p. 212°). (III), *cyclo*hexanone, and Na–Et_2O give 2-β-o-*hydroxybenzoyl*-α-2′-*methoxy*-1′-*naphthylethyl*cyclo*hexanone*, m.p. 178°. (III) and Br–$CHCl_3$ yield o-*hydroxyphenyl* αβ-*dibromo*-β-2-*methoxy*-1-*naphthylethyl ketone*, m.p. 152° (decomp.), converted by EtOH into the α-*bromo*-β-*ethoxy*-analogue (VII), m.p. 179°, or by aq. KCN into 2-(2′-*methoxy*-1′-*naphthyl*)*chromone*, m.p. 178° (cf. Nadkarni *et al.*, A., 1938, II, 18). (VII) and aq. NaOH–EtOH at 60° give 1-(2′-*methoxy*-1′-*naphthylidene*)*coumaran*-2-*one* (VIII), m.p. 178° (2 : 4-*dinitrophenylhydrazone*, m.p. 238°) (characteristic reactions of keto-ethylenic group not affected by cyclic linking), converted by Br–$CHCl_3$ into the *dibromide*, m.p. 158° [aq. KOH–EtOH gives (VI)], and thence by EtOH into 1-*bromo*-1-(*ethoxy*-2′-*methoxy*-1′-*naphthylmethyl*)*coumaran*-2-*one*, m.p. 165°. (VIII), CH_2Ac·CO_2Et, and NaOEt–EtOH afford *Et* 2-(2′-*methoxy*-1′-*naphthyl*)-3 : 4-1″ : 2″-*coumarano*-Δ^4-cyclo*hexen*-6-*one*-1-*carboxylate*, m.p. 174° (*oxime*, m.p. 188°). (VIII) and *cyclo*hexanone give 1-(2′-*keto*-1′-cyclo*hexyl*-2″-*methoxy*-1″-*naphthylmethyl*)*coumaran*-2-*one*, m.p. 184°. A. T. P.

Pechmann condensation of *p*-orsellinic acid with ethyl acetoacetate. Synthesis of 7-hydroxy-4 : 5-dimethylcoumarin. S. M. Sethna and R. C. Shah (J. Indian Chem. Soc., 1940, **17**, 211—214).—*p*-Orsellinic acid with CH_2Ac·CO_2Et and conc. H_2SO_4 yields, at 100°, 5-hydroxy-4 : 7-dimethylcoumarin, and at 60—70°, an 8-*carboxylic acid*, m.p. 225° (efferv.), which when heated gives 7-*hydroxy*-4 : 5-*dimethylcoumarin* (I), m.p. 248—250° (*Ac*, m.p. 119—121°, and *Bz* derivative, m.p. 130—131°; *Me ether*, m.p. 117—119°; does not give a CHPh:CH·CO_2H derivative), hydrolysed (aq. NaOH) to orcacetophenone. The Me_2 ether of the latter condenses (Na) with EtOAc giving 2 : 4-*dimethoxy*-6-*methylbenzoylacetylmethane*, m.p. 74—76° (*Cu* derivative, m.p. 198—200°), cyclised (Ac_2O–HBr at room temp.) to the *Me ether*, m.p. 150—152° (unaffected by boiling with 50% EtOH–KOH), of 7-*hydroxy*-2 : 5-*dimethylchromone*, m.p. 253—255° (*Ac* derivative, m.p. 195—197°), differing from (I). A. Li.

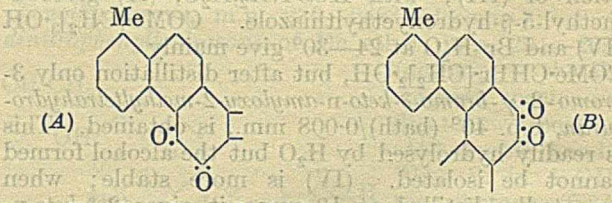
Kostanecki–Robinson reaction. I. Acetylation of orcacetophenone and its monomethyl ether. S. M. Sethna and R. C. Shah (J. Indian Chem. Soc., 1940, **17**, 239—243).—Orcacetophenone

(I) with NaOAc in Ac_2O yields 7-*acetoxy*-, m.p. 125—126° (2 : 4-*dinitrophenylhydrazone*, m.p. 238—239°), hydrolysed by cold conc. H_2SO_4 to 7-*hydroxy*-5-*methyl*-4-*acetomethylcoumarin*, m.p. 214° {2 : 4-*dinitrophenylhydrazone*, m.p. 250—260° (decomp.); *Me ether* [also prepared from the Me_1 ether of (I), NaOAc, and Ac_2O], m.p. 123—124°}, further hydrolysed by cold dil. NaOH to 7-hydroxy-4 : 5-dimethylcoumarin [identical with that prepared from *p*-orsellinic acid (preceding abstract)]. With NaOAc and Ac_2O this gives only the *O*-Ac derivative. The mechanism of the first reaction is discussed. A. Li.

Constituents of red sandalwood. I. Constitution of homopterocarpin. E. Späth and J. Schläger (Ber., 1940, **73**, [*B*], 1—12).—Homopterocarpin (I) (cf. Raudnitz *et al.*, A., 1935, 1372) (prep. from red sandalwood improved by removal of colouring matters from Et_2O extract with 1% KOH) is identified as 4 : 2′-*oxido*-7 : 4′-*dimethoxy*isoflavan. (I) is not recovered after dissolution in conc. H_2SO_4; when distilled with Pd or Se it gives no recognisable products. In AcOH with Pd–H_2 at 50—60° it gives *l*-dihydrohomopterocarpin (2′-*hydroxy*-7 : 4′-*dimethoxy*-isoflavan) (II), new m.p. 156—157°, with opening of the ·O· bridge. Alkali fusion of (II) gives *m*-$C_6H_4(OH)_2$. (II) is sol. in dil. alkali, and with Me_2SO_4 it gives 7 : 2′ : 4′-*trimethoxy*isoflavan (III), m.p. 61—62°, b.p. 170—180° (bath)/0·01 mm. The conclusion of Leonhardt *et al.* (A., 1936, 81) that (I) contains a CO group is incorrect; their dinitrophenylhydrazone is obtained from (II) only after long heating and (presumably) oxidation. (II) is resistant to Na–EtOH or Zn–HCl reduction, and with MgMeI gives no carbinol. PCl_5 gives only an amorphous product. With 0·5% hot aq. KOH, followed by $KMnO_4$ and CH_2N_2, (II) gives the Me_2 ester of 2 : 5 : 1-CO_2H·C_6H_3(OMe)·O·CH_2·CO_2H (Perkin *et al.*, J.C.S., 1908, **93**, 504), also obtained from 2 : 5 : 1-CO_2Me·C_6H_3(OMe)·ONa and CH_2Cl·CO_2Me at 170°, followed by hydrolysis. With hot aq. $KMnO_4$, (III) gives 2 : 4 : 1-$(OMe)_2C_6H_3$·CO_2H. Synthetically, 2 : 4 : 1-$(OMe)_2C_6H_3$·CH_2·CN with *m*-$C_6H_4(OH)_2$ and $ZnCl_2$ in Et_2O, followed by saturation with HCl and boiling, gives 2 : 4-*dihydroxyphenyl* 2′ : 4′-*dimethoxybenzyl ketone*, m.p. 155—156°, b.p. 200—210° (bath)/0·02 mm., which with CH_2N_2 gives the corresponding 2-*hydroxy*-4-*methoxyphenyl* compound, m.p. 114—115°. This with HCO_2Et and Na at 20°, followed by ice and HCl, gives 7 : 2′ : 4′-*trimethoxy*isoflavone, m.p. 148—149°, b.p. 190—200° (bath)/0·02 mm., reduced (Pd–C–H_2) to dl-7 : 2′ : 4′-*trimethoxy*isoflavan (IV), m.p. 88—89°, b.p. 170—180° (bath)/0·01 mm. The difference in m.p. between (III) and (IV) is ascribed to the optical activity of (III), (IV) being racemic. (III) is not racemised at 240° in vac. (24 hr.), but either (III) or (IV) with AcOH–CrO_3 gives 7 : 2′ : 4′-*trimethoxy*-2 : 3-*dihydro*isoflavone, m.p. 111—112°, b.p. 180—210°/0·02 mm., converted (H_2–Pd–C) into (IV). Possible alternative formulæ for (I) and (II) are rejected. Presence of an ·O· bridge in (I) shows that (II) cannot be a 4′-OH-compound. The bridge in (I) cannot be in the 2 : 2′-position, as this would imply acetal properties; a 3 : 2′-bridge would involve a 4-membered ring. E. W. W.

Flavans. J. B. Niederl and A. Ziering (J. Amer. Chem. Soc., 1940, **62**, 1157—1158).—*m*-C_6H_4Et·OH (I), *cyclo*hexanone, and HCl (no solvent; cf. A., 1939, II, 416), first at 50° and then at room temp., or 2-*cyclo*hexylidene*cyclo*hexanone, (I), and HCl at room temp. give 2-2′-*hydroxy*-4′-*ethylphenyl*-7-*ethyl*-2 : 3-*tetramethylene*-4 : 4-*pentamethyleneflavan*, m.p. 195—196° (*Br*$_2$-derivative, m.p. 180—181°; *benzoate*, m.p. 169—170°; 3 : 5-*dinitrobenzoate*, m.p. 176°; *acetate*, m.p. 118—119°). R. S. C.

New type of natural quinone colouring matter of the phenanthrofuran class. F. von Wessely and S. Wang (Ber., 1940, **73**, [*B*], 19—24).—Tanshinone I (I) (cf. Nakao *et al.*, A., 1935, 754), new m.p. 232—234°, with Ac_2O–NaOAc–Zn gives a reduced and acetylated *compound*, $C_{22}H_{18}O_5$, m.p. 209° (sinters 207°). With Zn–NaOH under N_2, followed by Me_2SO_4, (I) in EtOH yields a reduced *Me*$_2$ *ether*, $C_{20}H_{18}O_3$, m.p. 93—94·5°. The quinoxaline from (I) (cf. *loc. cit.*) has new m.p. 221—222° (from Et_2O), or 196° (from melt) (dimorphous). With AcOH–CrO_3 and some H_2SO_4, (I) gives the *anhydride* (II), m.p. 196° (sinters 194°), of 1 : 5 : 6-$C_{10}H_5Me(CO_2H)_2$ (III), m.p. 192° (decomp.) (cf. *loc. cit.*), which when heated with $NaHCO_3$ is decarboxylated to 1-$C_{10}H_7Me$. (III) very easily gives (II), which is synthesised as follows. *o*-C_6H_4Me·$[CH_2]_2$·Cl with $CHNa(CO_2Et)_2$ gives the *Et*$_2$ ester, b.p. 185—187°/9 mm., of α-*carboxy*-γ-*o*-*tolyl*-n-*butyric acid*, m.p. 139° (sinters 136°), which at 160° yields γ-*o*-*tolyl*-n-*butyric acid*, m.p. 70·5° (sinters 67°), b.p. 140° (bath)/10 mm., of which the *Et* ester, b.p. 140—150° (bath)/9 mm., with KOEt and $Et_2C_2O_4$ gives *Et* α-*oxalyl*-γ-*o*-*tolyl*-n-*butyric acid* (decomp. on distillation at reduced pressure). This (crude) with conc. H_2SO_4 gives 1-*methyl*-7 : 8-*dihydronaphthalene*-

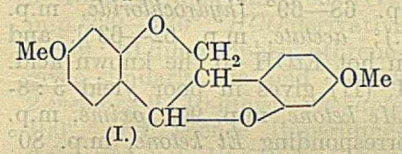


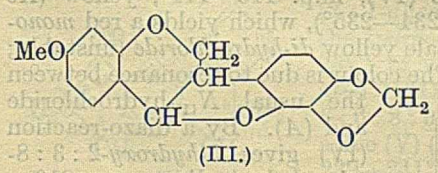
5 : 6-*dicarboxylic anhydride*, m.p. 161° (sinters 159°), dehydrogenated by S at 150—170° to (II). This (from either source) gives an *ethylimide*, m.p. 181·5° (sinters 178°). (I) is regarded as the *o*-quinone of a phenanthrofuran, in which (*A*) or (*B*) is linked to the residue ·O·CH:CMe· or ·O·CMe:CH·. E. W. W.

Synthetic experiments in the benzpyrone series. II. Synthesis and derivatives of flavono- and coumarino-7′ : 8′-5 : 4-furan-3-ones. L. R. Row and T. R. Seshadri (Proc. Indian Acad. Sci., 1940, **11**, A, 206—211; cf. A., 1939, II, 278).—7-*Chloroacetoxy*-4-*methylcoumarin* (prep. by CH_2Cl·COCl from the 7-OH-compound at 120° or, less well, from 4-methylumbelliferone in C_5H_5N), m.p. 181—182°, and $AlCl_3$ at 175° give 4-*methylcoumarino*-7′ : 8′-5 : 4-*furan*-3-*one* (30%), m.p. 254—256° (*CHPh*:, m.p. 194—196°, and *Ac* derivatives, m.p. 172—173°). 7-*Chloroacetoxyumbelliferone* (similarly prepared), m.p. 163—164°, and $AlCl_3$ at 160° give *coumarino*-7′ : 8′-5 : 4-*furan*-3-*one*, m.p. 252—253° (*CHPh*:, m.p. 284—286°, and *Ac* derivative, m.p. 152—

153°). Similarly are prepared 7-*chloroacetoxy-flavone*, m.p. 138—139°, and -3-*methoxyflavone*, m.p. 169°, *flavono*-, $+0{\cdot}5H_2O$, m.p. 206—207° (*CHPh*:, $+2H_2O$, m.p. 224—225°, and *Ac* derivative, m.p. 260—261°), and 3′-*hydroxyflavono*-7′ : 8′-5 : 4-*furan*-3-*one*, $+H_2O$, m.p. 284—286° (*CHPh*:, m.p. 274°, and *Ac* derivative, m.p. 192°). R. S. C.

Chemistry of the "insoluble red" woods. I. Pterocarpin and homopterocarpin. A. McGookin, A. Robertson, and W. B. Whalley (J.C.S., 1940, 787—795).—Homopterocarpin (I), m.p. 87°, $[\alpha]_{5461}^{20{\cdot}5}$ −236·6° in $CHCl_3$, contains two OMe and no OH or CO. It is oxidised ($KMnO_4$–$COMe_2$–H_2O) to 5-methoxy-2-carboxyphenoxyacetic acid and 2-hydroxy-4-methoxybenzoic acid. With Pd–C–H_2 or Zn–Hg–HCl, (I) affords *l*-dihydrohomopterocarpin, oxidised ($KMnO_4$–$COMe_2$–H_2O) to 7-*methoxychroman*-3-*carboxylic acid* (II), m.p. 149°. *O*-Methyldihydrohomopterocarpin is oxidised ($KMnO_4$–$COMe_2$–H_2O) to a *ketone*, $C_{15}H_9O_2(OMe)_3$, probably an *iso*flavanone, m.p. 127° (2 : 4-*dinitrophenylhydrazone*, m.p. 184°; *oxime*, m.p. 185·5°), which is further oxidised ($KMnO_4$–NaOH) to a *product*, $C_{15}H_9O_3(OMe)_3$, m.p. 178°. The constitution (I) is suggested. Pterocarpin (III), m.p. 164·5°, $[\alpha]_{5461}^{20{\cdot}5}$ −207·5° in $CHCl_3$, is similarly oxidised to the products obtained from (I), together with a neutral substance, m.p. 272°. Oxidation of dihydropterocarpin gives (II) but with CrO_3 a substance [2 : 4-*dinitrophenylhydrazone*, m.p. 202—203° (decomp.)] is obtained. *O*-Methyldihydropterocarpin is oxidised to a *ketone*, $C_{16}H_{10}O_4(OMe)_2$, m.p. 118—119° (2 : 4-*dinitrophenylhydrazone*, m.p. 248°). The constitution (III) is suggested. 4-*O*-Methyl-β-resorcylaldehyde, KOH, and $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$ give 5-*methoxy*-2-*formyl*-p-*phenoxypropionic acid*, m.p. 159° [2 : 4-*dinitrophenylhydrazone*, m.p. 241·5°; *semicarbazone*, m.p. 218° (decomp.)], which is oxidised ($KMnO_4$) to the *-carboxy-acid*, m.p. 143°. The formyl-acid is cyclised (NaOAc–Ac_2O) to 7-*methoxy*-Δ^3-*chromen*-3-*carboxylic acid*, m.p. 201°, hydrogenated (Pd–C) to (II). Et 2-aldehydo-5-methoxyphenoxyacetate (2 : 4-*dinitrophenylhydrazone*, m.p. 176·5°) is cyclised (NaOEt) to *Et* 6-*methoxycoumarone*-2-*carboxylate*, m.p. 87° [acid (IV), m.p. 206°], and 2-aldehydo-5-methoxyphenoxyacetic acid (2 : 4-*dinitrophenylhydrazone*, m.p. 273°). The acid chloride from (IV) with HCN gives the *nitrile*, m.p. 101°, which could not be converted into the corresponding pyruvic acid. The acid chloride with CH_2N_2 affords the *diazo-ketone*, m.p. 90—91° (slight decomp.), which is converted through the *amide*, m.p. 148°, into 6-*methoxycoumarone*-2-*acetic acid*, m.p. 104°. F. R. S.


(I.)


(III.)

5-Chloro-6-methoxy-2 : 1-naphththioindoxyl.—See B., 1940, 517.

Glutamic acid series. C. R. Harington and R. C. G. Moggridge (J.C.S., 1940, 706—712).—The acid chloride of α-benzyl *N*-carbobenzyloxyglutamate with CH_2N_2 followed by HCl gives *benzyl* ε-*chloro*-α-*carbobenzyloxyamido*-δ-*ketohexoate*, m.p. 125°, in which the Cl could not be replaced by H. N-p-*Toluenesulphonylglutamic acid*, m.p. 131°, $[\alpha]_D$ +22° in EtOAc, prepared from glutamic acid, p-$C_6H_4Me{\cdot}SO_2Cl$, and 2N-NaOH, with AcCl or Ac_2O affords the mixed *anhydride* of AcOH and 5-keto-1-*p*-toluenesulphonylpyrrolidine-2-carboxylic acid, m.p. 148°, from which the latter *acid* (I), m.p. 130°, $[\alpha]_D$ −28° in EtOAc, is obtained by heating in 70% aq. dioxan. "*p*-Toluenesulphonation" of 5-ketopyrrolidine-2-carboxylic acid does not give (I) and the structure is proved as follows. The chloride of (I) with CH_2N_2–HCl yields 5-*keto*-1-p-*toluenesulphonyl*-2-*chloroacetylpyrrolidine*, m.p. 141°, $[\alpha]_{5461}$ −18·5° in dioxan, from which the Cl is removed by H_2–Pd–$CaCO_3$ to form the -2-*acetylpyrrolidine*, m.p. 135·5°, $[\alpha]_{5461}$ −4·5° in dioxan (*Br*-derivative, 153·5°). This compound and NaOH afford α-*toluenesulphonamido*-δ-*ketohexoic acid*, m.p. 138° [*Br*-derivative, m.p. 148·5° (decomp.)], which reduces Fehling's solution, is reduced by Zn–Hg–HCl to p-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$, and is oxidised (NaOBr) to dl-N-p-*toluenesulphonylglutamic acid*, m.p. 172·5°, also obtained by synthesis from glutamic acid. α′-*Chloro*-α-p-*toluenesulphonamidoacetone*, m.p. 142°, from *p*-toluenesulphonylglycyl chloride and CH_2N_2, and ω-p-*toluenesulphonamidoacetophenone*, m.p. 116°, from the *K* salt of p-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ and $COPh{\cdot}CH_2Br$, both reduce Fehling's solution and are reduced to p-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$. The chloride of (I) and NH_3 give 5-*keto*-1-p-*toluenesulphonylpyrrolidine*-2-*carboxylamide* (II), m.p. 196°, which with NaOH affords N-p-*toluenesulphonyl*iso*glutamine* (III), m.p. 158—170°. Oxidation of (II) occurs with KOH–Br with formation of $CHBr_3$, (III), and increasing quantities of p-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ with increased Br. Reduction of (III) with Na in liquid NH_3 gives *N*-carbobenzyloxy*iso*glutamine. N-p-*Toluenesulphonylaspartic anhydride*, m.p. 148°, prepared from the corresponding acid and AcCl, with NaOMe in MeOH affords α(?)-*Me* N-p-*toluenesulphonylaspartate*, m.p. 96°. F. R. S.

Metal pyridine complex salts. VI. Cobaltous and nickelous dipyridine salts of fatty acids. T. L. Davis and A. V. Logan (J. Amer. Chem. Soc., 1940, **62**, 1276—1279; cf. A., 1937, II, 31).—Prep., dissociation pressure from 15° (or more) to 70—88°, and d^{25} (and thence the shrinkage on formation) of Co^{II} and Ni^{II} $(C_5H_5N)_2$ *acetate*, *propionate*, *butryate*, iso*butyrate*, and *valerate* are recorded. The Ni compounds are the more stable. Ni compounds have max. stability at ~60°, but Co compounds are less stable at higher temp. Increase in mol. wt. decreases the stability. C_2- and C_4-compounds are more stable than C_3- or C_5-compounds. Chain-branching has little effect. R. S. C.

Complex compounds of platinum with complex amines.—See A., 1940, I, 299.

Some β-substituted α-picolines. A. Dornow (Ber., 1940, **73**, [*B*], 78—80).—Et 2-methylnicotinate shaken with 25% aq. NH_3 gives 2-*methylnicotinamide*

(I), m.p. 158° [*picrate*, m.p. 180—181° (decomp.)]. With NaOCl in 10% KOH (water-bath), (I) gives 3-*amino*-2-*methylpyridine*, m.p. 115—116° [*picrate*, m.p. 234° (decomp.); *Bz* derivative, m.p. 114—115°], converted into 3-*iodo*-, m.p. 36—37° [*picrate*, m.p. 168° (decomp.)], and 3-*hydroxy*-2-*methylpyridine* (II), m.p. 167—168° [*picrate*, m.p. 204° (decomp.)]. (I) has no antipellagra activity. (II) has not the physiological activity of adermin [lacking the 4 : 5-$(OMe)_2$ groups of the latter]. E. W. W.

M.p. of nicotinic acid. R. Gording and L. A. Flexser (J. Amer. Pharm. Assoc., 1940, **29**, 230—231).—Slow heating (>0·5° per min.) gives 235·5—236·6° (corr.). F. O. H.

2-Alkylmercurithiolpyridine-5-carboxylic acids. Preparation and stability of their solutions. L. A. Walter and R. J. Fosbinder (J. Amer. Pharm. Assoc., 1940, **29**, 211—213).—The following were prepared by treating the alkylmercuric chloride (Grignard prep.) with an alkali–EtOH solution of 2-thiolpyridine-5-carboxylic acid: 2-*ethyl*-, m.p. 250° (decomp.), 2-n-*propyl*-, m.p. 210° (decomp.), and 2-n-*butyl-mercurithiolpyridine-5-carboxylic acid*, m.p. 190° (decomp.). These acids (as Na salts at p_H 8·8 or 11·0) are resistant to oxidation even in presence of catalytic metals (Cu, Mn, Fe). F. O. H.

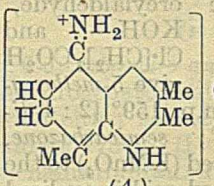
Reaction between a highly substituted bromopyridine and lithium. C. F. H. Allen and G. F. Frame (J. Amer. Chem. Soc., 1940, **62**, 1301).—2-Bromo-3 : 4 : 6-triphenylpyridine and Li (not Mg) in Et_2O–N_2 give a compound, unaffected by CO_2, aldehydes, or ketones, but with cold acid giving 20—25% of 2 : 4 : 5-*triphenylpyridine*, m.p. 112°. 4-Bromo-2 : 3 : 5-triphenylfuran does not react with Mg or Li. R. S. C.

Ultra-violet absorption spectra and the formation of indole and indolenine derivatives. P. Grammaticakis (Compt. rend., 1940, **210**, 569—571; cf. A., 1939, II, 487).—The absorption spectra in EtOH of (type I) indole, *N*-ethyl- and 2 : 3-dimethyl-indole (I), 1 : 2 : 3 : 4-tetrahydrocarbazole, *N*-ethyl- and 1-methyl-1 : 2 : 3 : 4-tetrahydrocarbazole (II) are similar, as are those (type II) of 3 : 3-dimethyl-, its trimeride, and 2 : 3 : 3-trimethylindolenine, and 11(?)-methyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine (III). *N* : 3 : 3-Trimethyl-2-methyleneindolenine shows marked absorption. The first band of type II is less marked and is nearer the ultra-violet than that of type I. 2-Methyl*cyclo*hexanonephenylhydrazone with MgRX or cold 2N-H_2SO_4–EtOH gives (III), b.p. 146°/12 mm., m.p. 68° (*picrate*, m.p. 170°), and (II), b.p. 185°/12 mm., m.p. 72° (*picrate*, m.p. 152°). $CMePr^{\beta}$:N·NHPh similarly yields 2 : 3 : 3-trimethylindolenine and (I). *iso*Butylidenephenylhydrazine similarly gives 3-methylindole and 3 : 3-*dimethylindolenine*, b.p. 95°/12 mm., m.p. 40°. J. L. D.

Reduced *iso*quinolines.—See B., 1940, 495.

Synthetic drugs. I. Partial reduction of some alkyl quaternary salts of pyridine- and quinoline-carboxylamides. T. S. Ma (Dissert., Chicago Univ., 1940, 1—16).—1-Propyl-1 : 6-dihydronicotinamide (cf. Karrer *et al.*, A., 1937, II, 260) with PtO_2–H_2 in EtOH or Et_2O gives only a gummy product; neither substance has oxytocic activity. Cinchoninamide gives an *ethiodide*, m.p. 218—219°. The methiodide is reduced ($Na_2S_2O_4$) to a gummy product. Quinaldinamide does not react with $Pr^{\alpha}I$ at 120—140°, but with Me_2SO_4 at 110°, followed by KI, gives its *methiodide* (I), m.p. 209—210°, also obtained by action of aq. NH_3 on Me quinaldinate methiodide (Mills *et al.*, J.C.S., 1922, **121**, 2008). $Na_2S_2O_4$ reduces (I) to products, m.p. 153—154°, and 225° (darkens 160°, sinters 180°), both regarded as impure 1-*methyldihydroquinaldinamide*, and both possessing oxytocic activity. E. W. W.

Petroleum bases. I. Reactions of 2 : 3 : 8-trimethylquinoline. A. Burger and L. R. Modlin, jun. (J. Amer. Chem. Soc., 1940, **62**, 1079—1083).—2 : 3 : 8-Trimethylquinoline (I) and SeO_2 in boiling EtOH give 82% of 3 : 8-*dimethylquinoline*-2-*aldehyde* (II), m.p. 107—108° [*oxime*, m.p. 172—174° (many metallic derivatives); *semicarbazone*, sinters at 185°, m.p. 190—192° (decomp.)], which is hydrogenated (PtO_2; EtOH) to 3 : 8-*dimethyl*-2-*hydroxymethylquinoline*, m.p. 68—69° [*hydrochloride*, m.p. 176—185° (decomp.); *acetate*, m.p. 62—63°], and oxidised by Ag_2O in hot EtOH to the known acid. With CH_2N_2–MeOH, (II) gives in poor yield 3 : 8-*dimethyl*-2-*quinolyl Me ketone*, m.p. 90° (*oxime*, m.p. 153—154°); the corresponding *Et ketone*, m.p. 80° (*oxime*, m.p. 146—148°), is similarly but readily prepared. HNO_3 (*d* 1·49) converts (I) at 100° into the 5-NO_2-derivative (III), m.p. 124°, oxidised by SeO_2 to 5-*nitro*-3 : 8-*dimethylquinoline*-2-*aldehyde*, m.p. (+EtOH) 165° or (anhyd.) 167° [*oxime*, m.p. 180—181° (many metallic derivatives)], which is also obtained from (II) by boiling HNO_3 (*d* 1·49). $SnCl_2$–17% HCl at 100° reduces (III) to 5-*amino*-2 : 3 : 8-*trimethylquinoline* (IV), m.p. 110—111°, yellow (*Ac* derivative, m.p. 234—235°), which yields a red *mono*- (sublimes) and pale yellow *di-hydrochloride* (unstable; becomes red). The colour is due to resonance between



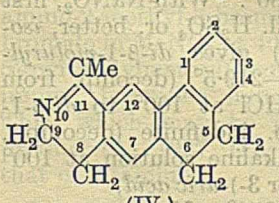
(*A*.)

the usual $N_{(1)}$-hydrochloride and (*A*). By a diazo-reaction (IV) gives 5-*hydroxy*-2 : 3 : 8-*trimethylquinoline*, m.p. 219—219·5°, sublimes at 125°/0·1 mm. [*Me ether*, m.p. 80° (*picrate*, m.p. 198—199°), also obtained from 4 : 1 : 2-OMe·C_6H_3Me·NH_2 and tiglaldehyde]. Hydrogenation (PtO_2; AcOH) of (I) gives mixed 2 : 3 : 8-*trimethyldecahydroquinoline*, b.p. 89—91°/10 mm. [*hydrochloride*, m.p. 251—275° (decomp.)]. R. S. C.

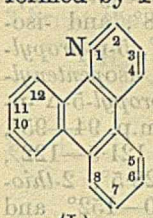
Phenanthridines.—See B., 1940, 516.

Phenanthrene series. XXIV. Phenolic amino-alcohols and naphth*iso*quinolines derived from 9 : 10-dihydrophenanthrene. A. H. Stuart and E. Mosettig (J. Amer. Chem. Soc., 1940, **62**, 1110—1116; cf. A., 1939, II, 115, 343).—2-Acetoxy-7-acetyl-9 : 10-dihydrophenanthrene (I) and Br in Et_2O–EtOH and Hg-light give 7-*bromoacetyl*-, m.p. 123—124°, converted by $NHEt_2$–C_6H_6 into 2-*acetoxy*-7-β-*diethylaminoacetyl*-9 : 10-*dihydrophenanthrene*, m.p. 89—90°, the *perchlorate*, m.p. 165—166°, of which

with H_2–PtO_2 in EtOH gives 2-acetoxy-, an oil (*hydrochloride*, m.p. 154—155°), hydrolysed to 2-hydroxy-7-β-diethylamino-α-hydroxyethyl-9 : 10-dihydrophenanthrene, an oil (*hydrochloride*, m.p. 202—203°). With $NHEt_2$ and aq. CH_2O in N_2 at 100° or $NHEt_2$,HCl and paraformaldehyde in boiling *iso*-C_5H_{11}·OH, (I) gives 2-acetoxy-7-β-diethylaminopropionyl- (*hydrochloride*, m.p. 132—134°) and thence 2-*hydroxy*-7-*γ-diethylamino*-α-*hydroxypropyl*-9 : 10-*dihydrophenanthrene*, m.p. (+2EtOAc) 129—130°, (solvent-free) 185—186° (*hydrochloride*, m.p. 180—181°; *Bz*$_2$ derivative *hydrochloride*, m.p. ~157—159°). 9 : 10-Dihydrophenanthrene-2-carboxylic acid (prep. from the 2-Ac derivative by 1·5% aq. NaOCl) and $SOCl_2$ give the acid *chloride*, m.p. 50—51°, hydrogenated (Rosenmund) to 9 : 10-dihydrophenanthrene-2-aldehyde (70%) (obtainable with difficulty directly), which with $MeNO_2$–NaOH–EtOH gives 2-β-*nitrovinyl*-9 : 10-*dihydrophenanthrene*, m.p. 77° (electrolytic reduction gives only 16% of amine). Me β-9 : 10-dihydro-2-phenanthrylpropionate, an oil, gives the *hydrazide*, m.p. 134—135°, and thence (Curtius) 2-β-aminoethyl-9 : 10-dihydrophenanthrene (II), an oil (*hydrochloride*, m.p. 229—230°; *HCO* derivative, m.p. 91°). 2-Methoxy-9 : 10-dihydrophenanthrene-7-carboxylic acid gives similarly the acid *chloride*, m.p. 87—88°, and 2-*methoxy*-9 : 10-*dihydrophenanthrene*-7-*aldehyde*, m.p. 100°, and thence [piperidine–$CH_2(CO_2H)_2$–C_5H_5N] β-2-*methoxy*-9 : 10-*dihydro*-7-*phenanthryl-acrylic*, m.p. 192—193°, and (H_2–PtO_2–EtOH) *-propionic acid*, m.p. 177° (*Me* ester, m.p. 61—62°; *hydrazide*, m.p. 155—156°), and 2-methoxy-7-β-aminoethyl-9 : 10-dihydrophenanthrene (III) (*hydrochloride*, sinters from 240°, m.p. indefinite). Most attempts at ring-closure of (II) and (III) failed. The *Ac* derivative, m.p. 112°, of (II) with $POCl_3$ in boiling PhMe gives 11-methyl-5 : 6 : 8 : 9-tetrahydronaphth-[2 : 1-*g*]*iso*quinoline (IV), the *hydrochloride*, m.p. 230—232°, of which is hydrogenated (PtO_2; EtOH) to the 5 : 6 : 8 : 9 : 10 : 11-H_6-derivative (V) (*hydrochloride*, m.p. 239—241°). With MeI–KOH–$COMe_2$, (V) gives 10 : 10 : 11-*trimethyl*-5 : 6 : 8 : 9 : 10 : 11-*hexahydronaphth*[2 : 1-*g*]*iso*quinolinium *iodide* (VI), m.p. 231°, decomposed at 200° to 10 : 11-dimethyl-5 : 6 : 8 : 9 : 10 : 11-hexahydronaphth[2 : 1-*g*]*iso*quinoline, an oil [*hydrochloride*, m.p. 234—236°; methiodide = (VI); also obtained by hydrogenating (PtO_2; EtOH) the *methiodide*, m.p. 267—268°, of (IV)]. The *Ac* derivative, m.p. 125—126°, of (III) gives similarly 3-methoxy-11-methyl-5 : 6 : 8 : 9-tetra- (28%) (*hydrochloride*, m.p. 249—250°; *methiodide*, m.p. 287—288°), 3-methoxy-11-methyl-5 : 6 : 8 : 9 : 10 : 11-hexa- (*hydrochloride*, m.p. 261—263°; *methiodide*, m.p. 256—258°), and 3-*methoxy*-10 : 11-*dimethyl*-5 : 6 : 8 : 9 : 10 : 11-*hexa-hydronaphth*[2 : 1-*g*]*iso*quinoline, m.p. 97—98° (*hydriodide*, m.p. 236—238°; *hydrochloride*, m.p. 200—202°). Alternative structures are possible for the tetracyclic bases. R. S. C.


(IV.)

Phenanthrene series. XXV. Dibenzo-[*f*, *h*]-quinoline and 7-methoxydibenzo-[*f*, *h*]quinoline. J. Krueger and E. Mosettig (J. Org. Chem., 1940, **5**, 313—317; cf. A., 1939, II, 86).—9-Acetylphenanthrene is treated with NH_2OH,HCl in C_5H_5N–EtOH followed by HCl in boiling Ac_2O–AcOH; the product is hydrolysed and then converted by NH_3 into 9-aminophenanthrene, m.p. 128—130°, which is transformed by $PhNO_2$, glycerol, and H_2SO_4 at 145° into dibenzo-[*f*, *h*]quinoline (I), m.p. 167—169° (*hydrochloride*). This is hydrogenated (PtO_2 in glacial AcOH) to 1 : 2 : 3 : 4-*tetrahydrodibenzo*-[f, h]*quinoline* (II), m.p. 117—118° (corr.) (*hydrochloride*, m.p. 245—247° after softening at 230°). MeI and KOH in aq. $COMe_2$ convert (II) into 1-*methyl*-1 : 2 : 3 : 4-*tetrahydrodibenzo*-[f, h]*quinoline*, m.p. 81—83° (corr.) [*hydrochloride*, decomp. (indef.), 230—275° (corr.) after incipient melting at ~200°]. 9-Amino-3-hydroxyphenanthrene is converted by $PhNO_2$, $FeSO_4$, glycerol, and H_2SO_4 at 145° into 7-*hydroxydibenzo*-[f, h]*quinoline*, m.p. 270—273° (vac.) (*hydrochloride*, m.p. indef.). This is reduced (H_2 at 150°/140 atm.; chromite catalyst in abs. EtOH) to 7-*hydroxy*-1 : 2 : 3 : 4-*tetrahydrodibenzo*-[f, h]*quinoline*, m.p. 230—232° (corr.) (*hydrochloride*, m.p. 279—281°), which with MeI and KOH in aq. $COMe_2$ at 100° gives 7-*methoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydrodibenzo*-[f, h]-*quinoline*, m.p. 131·5—133° (corr.) [*hydrochloride*, m.p. 204—206° (corr.; decomp.); *methiodide*, m.p. (indef.) 200° after softening at 145° and evolving gas at 175°]. H. W.


(I.)

Benz-acridones and -thioxanthones.—See B., 1940, 433.

5 : 5-Disubstituted hydantoins. D. Marsh and C. L. Lazzell (J. Amer. Chem. Soc., 1940, **62**, 1306).—Bucherer's method gives 3—48% of 5-cyclo*hexyl*-5-*methyl*-, m.p. 204—205°, 5-*styryl*-5-*methyl*-, m.p. 217° (decomp.), 5-*methyl*-5-β-*methylpropenyl*-, m.p. 209—210°, 5-p-*aminophenyl*-5-*methyl*-, m.p. 100—101°, 5-*methyl*-5-β-*hydroxyisobutyl*-, m.p. 180—181°, and 5 : 5-*di*-p-*dimethylaminophenyl*-, m.p. 136—137°, *-hydantoin*. R. S. C.

[Condensation products of 2-thiohydantoin.]—See A., 1940, I, 300.

1-Phenyl-3-methyl-5-pyrazolone-4-aldehyde. G. Losco (Gazzetta, 1940, **70**, 284—286; cf. A., 1940, II, 55).—1-Phenyl-3-methyl-5-pyrazolone (II) and its -4-aldehyde (II) in boiling EtOH give methenylbis-4-(1-phenyl-3-methyl-5-pyrazolone) (III), which with boiling 5% NaOH regenerates (I) and (II). With KOH–EtOH–$CHCl_3$, (I) gives (II) and (III). E. W. W.

Synthesis of monoketopiperazines. S. R. Aspinall (J. Amer. Chem. Soc., 1940, **62**, 1202—1204).—Gradual addition of $CH_2Cl·CO_2Et$, $CHEtBr·CO_2Et$, or $CMe_2Br·CO_2Et$ to an excess of $(CH_2·NH_2)_2$ in EtOH gives 2-*keto*-, m.p. 136° (*PhSO*$_2$, m.p. 188°, *phenylcarbamido*-, m.p. 171°, and *phenylthiocarbamido*-derivative, m.p. 199°; *picrate*, m.p. 180°; *hydrochloride*, m.p. 208°), 2-*keto*-3-*ethyl*-, m.p. 60° (*PhSO*$_2$ derivative, m.p. 148°), and 2-*keto*-3 : 3-*dimethyl*-, m.p. 134° (*PhSO*$_2$ derivative, m.p. 206°), *-piperazine*, respectively. M.p. are corr. R. S. C.

Substituted vinylbarbituric acids. IV. Derivatives containing a primary Δ^1-alkenyl group. A. C. Cope, W. H. Hartung, (Miss) E. M. Hancock, and F. S. Crossley (J. Amer. Chem. Soc., 1940, **62**, 1199—1201; cf. A., 1939, II, 284).—$CHR{:}CH{\cdot}CR'(CO_2Et)_2$ and $CO(NH_2)_2$ with NaOEt–EtOH give 12—70% of 5-*ethyl*-5-iso*butenyl*-, m.p. 161·5—162°, -n-*pentenyl*-, m.p. 96·5—98°, and -iso*pentenyl-barbituric acid*, m.p. 126·5—127°, 5-n-*propyl*-5-Δ^α-n-*propenyl*-, m.p. 150·5—151°, and -iso*pentenyl-barbituric acid*, m.p. 101—102°, 5-iso*propyl*-5-Δ^α-n-*propenyl*-, m.p. 140—141°, -n-*pentenyl*-, m.p. 94—95°, and -iso*pentenyl-barbituric acid*, m.p. 121·5—122°, 5-n-*butyl*-5-Δ^α-*propenyl*-, m.p. 127·5—128·5°, 2-*thio*-5-*ethyl*-5-Δ^α-α-*methyl*-n-*butenyl*-, m.p. 150—152°, and 1-*methyl*-5-n-*propyl*-5-Δ^α-α-*methyl*-n-*butenyl-barbituric acid*, m.p. 50·5—52·5°, 5-*ethyl*- (I), m.p. 109—110°, 5-n-, m.p. 83—84°, and 5-iso-*propyl*- (II), m.p. 107—108°, 5-n-*butyl*-, m.p. 111—112°, 1-*methyl*-5-iso*propyl*-, an oil, and 2-*thio*-5-iso*propyl*-, m.p. 109—110°, -5-Δ^α-n-*butenylbarbituric acid*. Much alcoholysis also occurs. Structures are proved by hydrogenation of (I) and (II) and by ozonisation. β-iso*Propyl*-Δ^β-*hexenoamide*, m.p. 123—124°, is also obtained. The acids produce powerful but very fleeting narcosis. R. S. C.

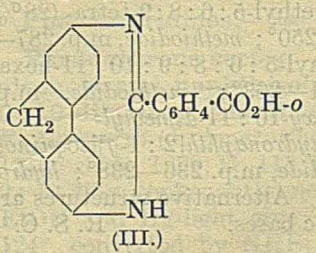
Thiobarbiturates. III. *N*-Substituted derivatives. F. S. Crossley, E. Miller, W. H. Hartung, and M. L. Moore (J. Org. Chem., 1940, **5**, 238—243; cf. A., 1936, 1125).—$CEt_2(CO_2Et)_2$, allylthiocarbamide, and NaOEt (mol. ratio, 1 : 1·6 : 3) condense smoothly to 5 : 5-*diethyl*-1-*allyl*-2-*thiobarbituric acid*, m.p. 97·5—98°; 5-*ethyl*-1-*allyl*-5-iso*amyl*-2-*thiobarbituric acid*, b.p. 175—180°/1 mm., is obtained similarly. With methyl-, ethyl-, or phenyl-thiocarbamide under these conditions the main products appear to be *dialkyl*-N-*methylthiocarbamylmalonamic acids* of which the *Me Pr*^{a}, m.p. 109—109·5° (decomp.), *Et*$_2$, m.p. 132·5—133°, *Et Pr*^{a}, m.p. 120·5—121° (decomp.), *phenylethyl*, m.p. 131—132° (decomp.), and *Pr*^{a} *allyl*, m.p. 97—98° (decomp.), derivatives are described. If the mol. reactant ratio is altered to 1·1 : 1 : 1·1 the following -2-*thiobarbituric acids* are obtained: 1 : 5-*dimethyl*-5-iso*propyl*-, m.p. 107—107·5°; 1 : 5-*dimethyl*-5-α-*methylbutyl*-, b.p. 148—150°/1 mm.; 1 : 5-*dimethyl*-5-Δ^1-cyclo*hexenyl*-, m.p. 140—141°; 1-*methyl*-5 : 5-*diethyl*-, m.p. 123—124°; 1-*methyl*-5-*ethyl*-5-n-*propyl*-, m.p. 79—80°; 1-*methyl*-5-*ethyl*-5-iso*propyl*-, m.p. 104—104·5°; 1-*methyl*-5-*ethyl*-5-iso*propenyl*-, m.p. 94·5—95°; 1-*methyl*-5-*ethyl*-5-iso*amyl*-, m.p. 84·5—85°; 5-*phenyl*-1-*methyl*-5-*ethyl*-, m.p. 120—121°; 5-*benzyl*-1-*methyl*-5-*ethyl*-, m.p. 119—119·5°; 5-*benzyl*-1 : 5-*diethyl*-, b.p. 170—175°/1 mm. *Phenylethylacetylmethylthiocarbamide* has m.p. 107—107·5°. H. W.

Synthetic drugs. II. Attempted synthesis of 4-methyl-5 : 5-dialkyluracils. T. S. Ma (Dissert., Chicago Univ., 1940, 17—31).—$CEt_2Ac{\cdot}CO_2Et$ (I) does not condense with $CO(NH_2)_2$ or its analogues at 150—180°. With $CS(NH_2)_2$ and NaOEt at 120°, (I) gives a product, m.p. 210—211°. $CMe_2Ac{\cdot}CO_2Et$, which does not react with $CO(NH_2)_2$, with $NH_2{\cdot}C(NH){\cdot}OEt$ at room temp. gives a product, m.p. 295° (decomp.), or at 50° or 63—65°, products, m.p. <300°. These products have high N content and are not uracils. With large excess of $SOCl_2$, (I) gives a partly chlorinated product. $NH{:}CMe{\cdot}CHEt{\cdot}CN$ with Na followed by EtI gives β-*imino*-$\alpha\alpha$-*diethylbutyronitrile* (impure?), b.p. 118—120°/1 mm., which with PhNCO gives at room temp. (60 days) a very small yield of β-*phenylcarbimido*-$\alpha\alpha$-*diethyl*- (impure), m.p. 233—234°, with -α-*ethyl-butyronitrile*, m.p. 144—145°. E. W. W.

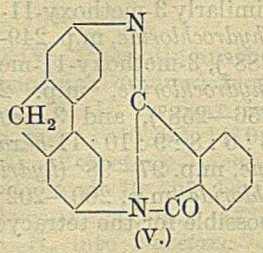
Synthesis of pyrimidines and uric acids from cystamine. E. J. Mills, jun. and M. T. Bogert (J. Amer. Chem. Soc., 1940, **62**, 1173—1180).—$(CH_2)_2NH$ (which is caustic) and H_2S in much EtOH give $SH{\cdot}[CH_2]_2{\cdot}NH_2$ (I), m.p. 97—98·5° (hydrochloride, m.p. 70·2—70·7°, obtained also from 2-thiolthiazoline), but in conc. solution give $(NH_2{\cdot}[CH_2]_2)_2S$, an oil, converted by $NH_2{\cdot}CO{\cdot}NH{\cdot}NO_2$ (I) in H_2O at 100° into *di*-β-*carbamidoethyl sulphide*, m.p. 221—222°. O_2 converts (I) in H_2O or 95% EtOH into cystamine (dihydrochloride, sinters at ~206°, m.p. 212—212·5°), which with (II) gives *di*-β-*carbamidoethyl disulphide* (III), m.p. 166—167°. With $CH_2(CO_2H)_2$ in AcOH–Ac_2O at 65—70°, rising to 80—90°, (III) gives $\beta\beta'$-*di*(*carboxyacetylcarbamidoethyl*) *disulphide*, $(\cdot S{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO_2H)_2$ (IV) (25—30%), m.p. 141—142° (gas), and a little *di*-β-1-*barbiturylethyl disulphide* (V), m.p. 216·8—218·8°. At the m.p. (IV) gives CO_2 and β-*acetylcarbamidoethyl* β'-*carboxyacetylcarbamidoethyl disulphide*, m.p. 197·5—199° (corr.), which in boiling H_2O gives *di*-β-*acetylcarbamidoethyl disulphide*, sinters at 206°, m.p. 209—210° [obtained also from (IV) by Ac_2O and a little H_2SO_4 at 100°]. With $CH_2(CO_2H)_2$ in Ac_2O (slight excess) at 70°, (III) gives the 3-*Ac*$_2$ derivative, sinters at 214—217°, m.p. 219—223°, of (V), hydrolysed to (V) by boiling conc. HCl. (V) is also obtained from (IV) by Ac_2O–AcOH at 80°. With $NaNO_2$, first in boiling H_2O and then in dil. H_2SO_4 or, better, *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$–HCl–EtOH, (V) gives *di*-β-1-*violurylethyl disulphide*, m.p. 218·5—219·5° (decomp. from ~200°), reduced by $SnCl_2$–HCl at 100° to *di*-β-1-*uramilylethyl disulphide*, m.p. indefinite (decomp.), which with (II) in faintly alkaline solution at 100° gives *Et*$_2$ *disulphide* $\beta\beta'$-*di*-1-(or 3-)-*uric acid*, $(S{\cdot}[CH_2]_2{\cdot}C_5H_3O_3N_2)_2$, m.p. >350°. M.p. are corr. R. S. C.

Bis*iso*indolenylidenes.—See B., 1940, 434.

Fluorene. I. Condensation of 2 : 7-diaminofluorene with phthalic anhydride. B. A. Porai-Koschitz and A. M. Efros (Bull. Acad. Sci. U.R.S.S., 1938, Cl. Sci. Tech., No. 3, 43—60).—2 : 7-Diaminofluorene (I) and *o*-$C_6H_4(CO)_2O$ (II) in H_2O (8 hr. at the b.p.) yield a *substance* said to be (III), m.p. 280°



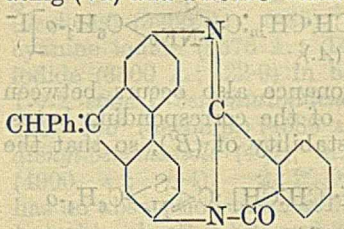
(III.)



(V.)

(decomp.), together with 2 : 7-*diphthalimidofluorene* (IV), m.p. 292°. (III) is converted into the *substance*

(V), m.p. 340°, by heating in Ac_2O or C_5H_5N (at the b.p.), or by heating alone at 120°; (V) is also prepared from (I) and (II) in $NPhMe_2$, at the b.p. 2-Aminofluorene and (II) in $NPhMe_2$ (2·5 hr. at the b.p.) yield 2-*phthalimidofluorene*, m.p. 276°, the 7-NO_2-derivative, m.p. 308°, of which is reduced (Zn in EtOH–$CaCl_2$) to 7-*amino*-2-*phthalimidofluorene* (VI), m.p. 262°, from which (V) is obtained by boiling for 5 hr. with $NPhMe_2$. (VI) and PhCHO (25 min. at the b.p.) yield 2-*benzylideneamino*-7-*phthalimidofluorene*, m.p. 246°, regenerating (VI) and PhCHO when hydrolysed (10% HCl).



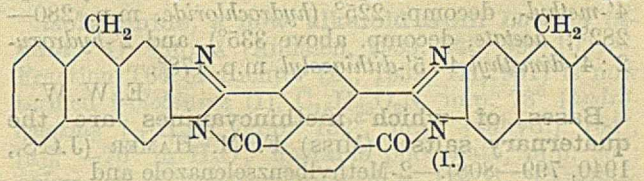
(VII.)

(VI) and (II) in $NPhMe_2$ (5 hr. at the b.p.) afford (IV), whilst in EtOH (2 hr. at the b.p.) the product is 2-*phthalimido*-7-*fluorenylphthalamic acid*. (V) and PhCHO (35 min. at the b.p.) give the *substance* (VII), m.p. 367°. 2-Aminofluorene and PhCHO (30 min. at the b.p.) yield 2-*benzylideneaminofluorene*, m.p. 152°, readily hydrolysed by acids. R. T.

1-(4′-Amino-2′-methyl-5′-pyrimidylmethyl)-2-methyl-3-β-hydroxyethylpyridinium bromide, heterovitamin-B_1. P. Baumgarten and A. Dornow (Ber., 1940, **73**, [*B*], 44—46).—2-Methylpyridine-3-carboxylic acid hydrochloride with $SOCl_2$ gives the -3-carboxyl chloride hydrochloride, which with CH_2N_2 gives 3-*diazoacetyl*-2-*methylpyridine*, m.p. 58—59° (*picrate*, m.p. 147°), and this when heated in AcOH and treated with Zn in boiling conc. HCl yields 2-methyl-3-β-hydroxyethylpyridine (cf. Schmelkes *et al.*, A., 1939, II, 522) [*methiodide*, m.p. 135°; *benzoate picrate*, m.p. 199—200° (decomp.)], which with 4-amino-2-methyl-5-bromomethylpyrimidine dihydrobromide in $MeNO_2$ at 40° gives 1-(4′-amino-2′-methyl-5′-pyrimidylmethyl)-2-methyl-3-β-hydroxyethylpyridinium bromide hydrobromide (cf. Schmelkes). This, which may be identical with Funk's S-free product (A., 1937, III, 493), has an activity 1/26 of that of vitamin-B_1. E. W. W.

Constitution of yeast ribonucleic acid. IV. Syntheses of uridylic and guanylic acids, uridine 5-phosphate, and guanosine 5-phosphate. J. M. Gulland and G. I. Hobday (J.C.S., 1940, 746—752).—Phosphorylation of uridine by $POCl_3$ in C_5H_5N gives uridine 5-phosphate, identified as the brucine salt, and with $POCl_3$ and $Ba(OH)_2$ yields a mixture of 3- and 5-phosphate, fractionated as the brucine salts; the constitutions assigned have been confirmed by comparison of the rates of liberation of free phosphate from them and from uridylic acid in hot 0·1N-H_2SO_4. Phosphorylation of guanosine in C_5H_5N with $POCl_3$ or $PhPOCl_2$ affords *guanosine* 5-*phosphate* in small yield. The 3-phosphate is obtained with $Ba(OH)_2$ and $POCl_3$ or $PhPOCl_2$; its identity with guanylic acid from yeast ribonucleic acid is proved by comparison of [α] and of rates of dephosphorylation in acid solution, and by a method of mixed m.p. of the brucine salts. $PhPOCl_2$ has been investigated as a phosphorylating agent; Ba α-glycerophosphate has been prepared. F. R. S.

Fluorene series. II. Preparation of vat diiminazole dyes of the fluorene series. B. A. Porai-Koschitz and O. K. Nikiforova (J. Appl. Chem. Russ., 1940, **13**, 215—221; cf. B., 1938, 40).—2 : 3-Diaminofluorene condenses with 1 : 4 : 5 : 8-$C_{10}H_4(CO_2H)_4$ (12 hr. at 170—180°) giving a mixture of isomerides of (I), oxidised ($Na_2Cr_2O_7$ in AcOH; 3 hr. at the b.p.) to a mixture [(I) with CO for CH_2)]



(I.)

of a violet and a yellow dye, or a brown dye for cotton. The H sulphate of its leuco-derivative dyes wool a bright yellow colour. R. T.

Transformation of *iso*oxazole-3-carboxylic acids into pyrazole derivatives. IV—VI. S. Cusmano (Gazzetta, 1940, **70**, 227—235, 235—240, 240—246).—IV. 5-Phenyl- (I) and 5-methyl-*iso*oxazole-3-carboxylic acid (II) with $NHPh·NH_2$ (III) and Cu in EtOH (or C_6H_6 etc.) give respectively 1 : 5-diphenyl- and 1-phenyl-5-methyl-pyrazole-3-carboxylic acid, which above their m.p. give the corresponding pyrazoles. If NH_2Ph is substituted for (III) there is no reaction.

V. With N_2H_4,H_2O (IV) and Cu in EtOH, (I) and (II) give respectively 5-phenyl- and 5-methyl-pyrazole-3-carboxylic acid, which yield 5-phenyl- and 5-methyl-pyrazole.

VI. 5-*p*-Nitrophenyl*iso*oxazole-3-carboxylic acid with (III) and (IV) gives respectively 1-*phenyl*-5-p-*nitrophenyl*- (V), m.p. 255° (*Et* ester, m.p. 168°), and 5-p-*nitrophenyl*-*pyrazole*-3-*carboxylic acid* (VI), m.p. 275° (*Et* ester, m.p. 215°). Above the m.p., (V) gives 1-*phenyl*-5-p-*nitrophenyl*-, m.p. 93°, reduced (Zn–AcOH) to -5-p-*aminophenyl*-, m.p. 130° (*Ac* derivative, m.p. 167°), oxidised by $KMnO_4$–H_2SO_4 to 1-phenylpyrazole-5-carboxylic acid; (VI) gives 5-p-*nitrophenylpyrazole*, m.p. 195°. E. W. W.

Morpholines.—See B., 1940, 431.

Sulphathiazole. J. Laudon and B. Sjögren (Svensk Kem. Tidskr., 1940, **52**, 64—67).—2-Sulphanilamidothiazole (I), m.p. 200° (corr.), solubility in H_2O 0·5 g. per l. at 20° (cf. B.P. 517,272; B., 1940, 326; also Fosbinder and Walter, A., 1939, II, 525), is pharmacologically similar to the C_5H_5N analogue, but is the more active against pneumococcus type V and less so against type III. M. H. M. A.

Synthesis of derivatives of 4 : 5′-dithiazolyl and 4 : 5′-glyoxalinylthiazole. E. Ochiai, Y. Tamamushi, and F. Nagasawa (Ber., 1940, **73**, [*B*], 28—32).—CAc_2:N·OH with Pd–C–H_2 in N-HCl, followed by heating with conc. aq. KCNS, gives the 2-*SH* derivative (I), decomp. 308°, of 5-*acetyl*-4-*methylglyoxaline* (II), m.p. 151° (*semicarbazone*, m.p. 151°), into the *nitrate*, m.p. 200°, of which (I) is converted by boiling 10% HNO_3. With Br–AcOH, (II) gives the *hydrobromide*, decomp. 223°, of 5-*bromoacetyl*-4-*methylglyoxaline*. This with $NH_2·CHS,H_2O$, $CS(NH_2)_2$, and $CSMe·NH_2$ in MeOH or EtOH gives respectively

4-(4′-*methyl*-5′-*glyoxalinyl*)*thiazole* (*picrate*, m.p. 178°), and its 2-NH_2-, decomp. 210° (*hydrochloride*, decomp. 253°; *acetate*, decomp. 315°), and 2-*Me* derivative, m.p. 183° (*hydrochloride*, m.p. 225°; *picrate*, m.p. 205°). 2-Hydroxy-5-acetyl- with Br–$CHCl_3$ gives 2-*hydroxy*-5-*bromoacetyl*-4-*methylthiazole*, m.p. 167°, which with the above reagents yields respectively 2′-*hydroxy*-4′-*methyl*-, m.p. 184·5°, 2-*amino*-2′-*hydroxy*-4′-*methyl*-, decomp. 225° (*hydrochloride*, m.p. 280—282°; *acetate*, decomp. above 335°), and 2′-*hydroxy*-2 : 4′-*dimethyl*-4 : 5′-*dithiazolyl*, m.p. 178°.

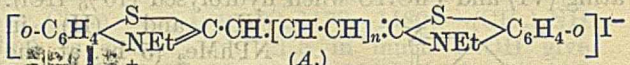
E. W. W.

Bases of which methincyanines are the quaternary salts. (Miss) F. M. Hamer (J.C.S., 1940, 799—808).—2-Methylbenzselenazole and *p*-$C_6H_4Me{\cdot}SO_3Et$ fused together give a substance which with 2-methylthiobenzthiazole followed by KI affords *methin*-[2-*benzthiazole*][3-(2-*ethyldihydrobenzselenazole*)] *hydriodide*, m.p. 243° (decomp.), converted into the *base*, m.p. 134—135°. 3 : 3′-Diethylthiacarbocyanine iodide and $NPhEt_2$ yield *trimethin*-[2-*benzthiazole*][2-(3-*ethyldihydrobenzthiazole*)], m.p. 136—137°. Methin-[2-quinoline][2-(3-methyldihydrobenzthiazole)] forms a *hydrochloride*. 2-Methylthioquinoline and *p*-$C_6H_4Me{\cdot}SO_3Me$ give *methin*-[2-(1-*methyldihydroquinoline*)][2-*benzthiazole*], m.p. 140° [*hydriodide*, m.p. 185° (decomp.)]. *Methin*-[2-*quinoline*][2-(3-*ethyldihydrobenzthiazole*], m.p. 151° [*hydriodide*, m.p. 264° (decomp.)], is obtained from 2-methylthioquinoline and 2-methylbenzthiazole etho-*p*-toluenesulphonate. 2-Ethylthioquinoline etho-*p*-toluenesulphonate and 2-methylbenzthiazole afford *methin*-[2-(1-*ethyldihydroquinoline*)][2-*benzthiazole*], m.p. 160° [*hydriodide*, m.p. 223° (decomp.)]. 3 : 1′-Dimethyl-4 : 5-benzthia-2′-cyanine iodide and $NPhEt_2$ afford *methin*-[2-(1-*methyldihydroquinoline*)]-[2-(4 : 5-*benzbenzthiazole*)], m.p. 172°; the corresponding 1-*Et* compound, m.p. 133°, is similarly obtained. 3 : 1′-Diethyl-6 : 7-benzthia-2′-cyanine iodide and $NPhEt_2$ give *methin*-[2-*quinoline*][2-(3-*ethyldihydro*-6 : 7-*benzbenzthiazole*)], m.p. 204°. *Methin*-[2-(1-*ethyldihydroquinoline*)][2-(6 : 7-*benzbenzthiazole*)], m.p. 228°, is obtained from 2-ethylthioquinoline etho-*p*-toluenesulphonate and 2-methyl-6 : 7-benzbenzthiazole. 2-Ethylthiobenzthiazole and *p*-$C_6H_4Me{\cdot}SO_3Et$ followed by KI yield *methin*-[4-*quinoline*][2-(3-*ethyldihydrobenzthiazole*)] *hydriodide*, m.p. 288° (decomp.), from which the *base*, m.p. 131°, can be obtained. 2-Ethylthioquinoline etho-*p*-toluenesulphonate and quinaldine afford *methin*-[2-*quinoline*][2-(1-*ethyldihydroquinoline*)], m.p. 140°; the corresponding 1-*Me* compound has m.p. 154°.

On passing from a base to the thiacyanine or selenathiacyanine which is its alkiodide, the shift of absorption max. towards the red is about the same as on passing to the corresponding acid salt. There is a greater shift on passing from trimethin base to thiacarbocyanine (1020 A.) or to acid salt (950 A.). On passing from a thia-2′-cyanine base, having the alkyldihydro-structure in the benzthiazole nucleus, to the thia-2′-cyanine, the absorption max. shifts further towards the red (~600 A.) than on passing to an acid salt (~450 A.). The hitherto unknown isomeric bases with the alkyldihydro-structure in the quinoline nucleus have about the same absorption max. as the thia-2′-cyanines themselves; it does not shift on addition of acid but shifts towards the blue on exposure to light.

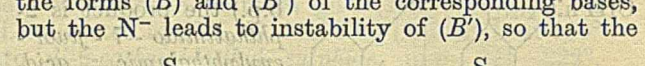
F. R. S.

Colour and constitution. I. Halochromism of anhydronium bases related to cyanine dyes. L. G. S. Brooker, R. H. Sprague, C. P. Smyth, and G. L. Lewis (J. Amer. Chem. Soc., 1940, **62**, 1116—1125).—Cyanine dyes (*A*; $n = 0$, 1, or 2) owe their colour to resonance; the two extreme states are identical and resonance is thus complete, leading to

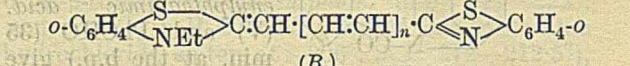


(*A*.)

very high colour. Resonance also occurs between the forms (*B*) and (*B*′) of the corresponding bases, but the N^- leads to instability of (*B*′), so that the

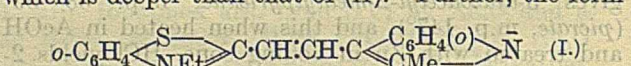


(*B*.)



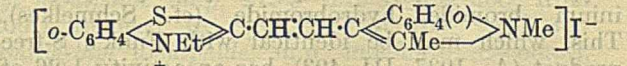
(*B*′.)

hybrid tends much more towards (*B*) and the bases are lighter in colour than the methiodides. In the mixed base, the ionic form of which is (I), the negative charge on the pyrrole N conforms to the nature of the pyrrole ring, thus stabilising (I), aiding resonance with its non-ionic form and leading to a colour which is deeper than that of (*A*). Further, the form

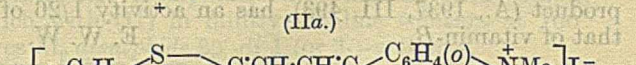


(I.)

(II*a*) of the methiodide of (I) is so much more favoured than (II*b*) that resonance is incomplete and the colour of (II) is lighter than that of (I) (reversed halochromy). This also leads to (II) being lighter



(II*a*.)

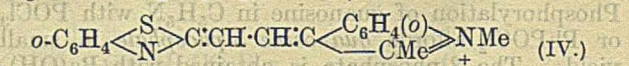


(II*b*.)

than (*A*) or the "symmetrical" (III), the two forms of which, being identical, lead to more complete

(III.)

resonance. Similarly, the ionic form (IV), with the negative charge lying on the benzthiazole N, is less

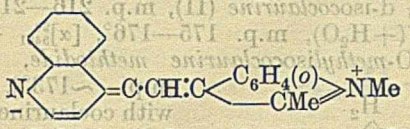


(IV.)

(V.)

stable than (I) and this base is, therefore, much less coloured. For the same reason, the base (V) is much

more deeply coloured than (VI). Dipole moments support some of the above arguments. Figures in

(VI.) 

parentheses below are absorption max. and $\varepsilon \times 10^{-4}$, unless otherwise stated in MeOH. 3 : 3′-Diethylthiacyanine iodide (4230 A.; 8·45) in boiling $NPhMe_2$ gives the base (*B*; $n = 0$) (46%), m.p. 163—164° (darkens) (3960 A.; 5·85). 2 : 2′-Diethylthia-carbocyanine iodide (5575 A.; 14·8) and -dicarbocyanine iodide (6500 A.; 22·9) in boiling $NPhMe_2$–CO_2 give 1-*γ*-2′-*ethyl*-1′-*benzthiazolidene*-*propenyl*- (65%), m.p. 138—140° (decomp.) (4580 A.; 5·65), and -$\Delta^{\alpha\gamma}$-*pentadienyl*-*benzthiazole* (4%), m.p. 161—162° (decomp.) (4900 A.; 6·4). 2 : 2′-Diethylthiatricarbocyanine has an absorption max. at 7580 A. (24·6). 1-Methylbenzthiazole ethiodide and 2-methylindole-3-aldehyde (VII) in boiling Ac_2O give the *hydriodide* (93%), m.p. 283—284° (decomp.), whence 3-β-2′-*ethyl*-1′-*benzthiazolidene*-2-*methylindolenine* (I), m.p. 286—288° (5060 A.; C_5H_5N), is obtained by NaOH–$COMe_2$–H_2O, which in boiling MeI–$PhNO_2$ gives the *methiodide* [2′-*ethylbenzthiazole*-1′-1 : 2-*dimethylindole*-3-*dimethincyanine iodide*] (II), m.p. 269—271° (decomp.) (4970 A.; C_5H_5N), also obtained (86%) from 1-methylbenzthiazole etho-*p*-toluenesulphonate and 1 : 2-dimethylindole-3-aldehyde (VIII) in boiling Ac_2O (product treated with NaI). 1-Methylbenzthiazole (2 mols.) and (VIII) (1 mol.) in conc. HCl at 100° give 3-β-1′-*benzthiazolylvinyl*-1 : 2-*dimethylindole* (IV) (50%), m.p. 150—151° (decomp.) (3920 A.; C_5H_5N) [ethiodide = (II)]. 1 : 2-Dimethylindole and (VIII) (1 mol. each) in conc. HCl give a salt, which with NaI gives *bis*-(1 : 2-*dimethylindole*-3-)*methincyanine iodide* (III) (35%), m.p. 221—222° (decomp.) (4950 A.; 5·3; $MeNO_2$). Lepidine methiodide (IX) and (VII) in boiling Ac_2O give the base (V) (72%), m.p. 249—251° (decomp.) (lit., +2$CHCl_3$, m.p. 240°) (5710, 6160 A.; C_5H_5N) [*hydriodide*, m.p. 319—320° (decomp.)]. Lepidine and (VIII) in boiling HCl give 3-β-4′-*quinolylvinyl*-1 : 2-*dimethylindole* (VI) (43%), m.p. 192—193° (decomp.) (3940 A.; C_5H_5N). With MeI, (V) or (VI) gives 1 : 2-*dimethylindole*-3-1′-*methylquinoline*-4′-*dimethincyanine iodide*, m.p. 297—298° (decomp.) (5390 A.; C_5H_5N), obtained also from (IX) and (VIII) in boiling Ac_2O. R. S. C.

Cyanine dyes.—See B., 1940, 568.

Lupin alkaloids. XIX. Synthesis of racemic lupinine. K. Winterfeld and H. von Cosel (Arch. Pharm., 1940, **278**, 70—81).—Picolinic acid is converted by short, successive treatments with $SOCl_2$ at 60° into the chloride, transformed by CH_2N_2 in C_6H_6 into 2-*pyridyl diazomethyl ketone* (*aurichloride*, m.p. 118—120°; *phenylhydrazone*, m.p. 220°), which slowly decomposes on exposure to air. It is converted by 50% AcOH at 60—70° into 2-*pyridyl* CH_2·*OH ketone* (I), decomp. 160° [*aurichloride* (+1H_2O), m.p. 161°; *platinichloride*, m.p. 214—215° (decomp.); *reineckate*, decomp. 180—185°; p-*nitrophenylhydrazone*, m.p. 208—210°], which is resistant to acetylation. (I) is transformed by activated Mg and OEt·[CH_2]$_3$·Br in Et_2O into 2-*pyridylhydroxymethyl*-*γ*-*ethoxypropylcarbinol* (*reineckate*, decomp. 205°), which gives OH·[CH_2]$_3$·OEt when heated at 35—45°/0·01 mm. and is hydrogenated (PtO_2 in AcOH) to 2-*piperidylhydroxymethyl*-*γ*-*ethoxypropylcarbinol*. This is hydrolysed and cyclised by HI (*d* 1·7) (2-α*δ*-*di*-*iodobutylpiperidine*) to *r*-lupinine, analysed as the *picrolonate*, m.p. 179° (decomp.). H. W.

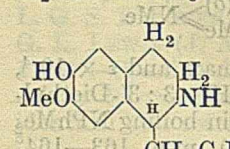
***iso*Lobinine, a new alkaloid from *Lobelia inflata*.** O. Thomä (Annalen, 1939, **540**, 99—103).—Fraction T64 of Richter (A., 1939, III, 931) is now termed iso*lobinine* (I), $C_{18}H_{25}O_2N$, m.p. 78° [*hydrochloride* (+H_2O), m.p. 132°, m.p. (anhyd.) 154°, $[\alpha]_D^{20}$ −76° in H_2O; unstable phosphate, m.p. 80°; *oxime*, an oil (*hydrochloride*, m.p. 186°)]. Catalytic reduction of (I) gives a H_2-derivative (II), b.p. 175°/4 mm., whilst thermal decomp. at 170—215°/10 mm. affords ?COMeEt (*p*-nitrophenylhydrazone, m.p. 180°). Oxidation (CrO_3) of (I) yields BzOH and AcOH; (II) gives BzOH and scopolic acid. Ch. Abs. (*b*)

***Lobelia* alkaloids. VII. Accessory alkaloids of *Lobelia inflata*.** H. Wieland, W. Koschara, E. Dane, J. Renz, W. Schwarze, and W. Linde (Annalen, 1939, **540**, 103—156; cf. A., 1932, 68).—Methods of fractionation are described. *dl*-Lelobanidine (I), $C_{18}H_{29}O_2N$, m.p. 68° (*hydrochloride*, m.p. 78—79°; *hydriodide*, m.p. 159°; *platinichloride*; *methiodide*, m.p. 162—164°), contains 2 OH since it gives a Bz_2 derivative, m.p. 178°. Oxidation (CrO_3, AcOH) of (I) affords dl-*lelobanine* (II), $C_{18}H_{25}O_2N$, oil (*perchlorate*, m.p. 136°; *hydrochloride*, m.p. 142°), oxidised (CrO_3, H_2SO_4) to AcOH, $EtCO_2H$, BzOH, and scopolic and methylgranatic acid (III). Successive treatment of (II) with MeI and Ag_2O ($NHMe_2$ evolved) gives a neutral oil, which is catalytically reduced to a glycol, $C_{17}H_{28}O_2$, b.p. 117—118°/0·03 mm., m.p. ~8°; this with CrO_3–dil. H_2SO_4 affords α*ι*-*diketo*-α-*phenylundecane* (IV), m.p. 51° [*semicarbazone*, m.p. 186° (decomp.)]. CO_2Et·[CH_2]$_7$·COCl, b.p. 168—169°/20 mm. (prep. by partial hydrolysis of the Et_2 ester and subsequent treatment with $SOCl_2$), and ZnEtI give 65% of the *Et* ester, b.p. 186°/21 mm., of θ-*ketoundecoic acid*, m.p. 56° [chloride and C_6H_6 yield (IV)]. Resolution of (I) can be effected with *d*-camphorsulphonic acid; (I) is 2-β-hydroxy-β-phenylethyl-1-methyl-6-β-hydroxy-*n*-butylpiperidine. *l*-Lelobanidine I (V) [*hydrochloride* (+2H_2O), m.p. 86°, $[\alpha]_D$ −41·5° in EtOH; *hydriodide*, m.p. 171°; *perchlorate*, m.p. 176°; *Ac*$_2$ derivative *hydrochloride*, m.p. 195—196°; *PhSO*$_2$ derivative *hydrochloride*, m.p. 110—115°] is oxidised (CrO_3, AcOH, room temp./5 days) to l-*lelobanine* (VI) (*hydrochloride*, m.p. 186°, $[\alpha]_D$ +19·5° in EtOH) and also to AcOH, $EtCO_2H$, BzOH, and *l*-(III). *l*-Lelobanidine II [hydrochloride (+1·5H_2O), m.p. 102—105°, $[\alpha]_D$ −41·7° in EtOH; hydriodide, m.p. 165°] is also oxidised to (VI). d-*Norlelobanidine*, $C_{17}H_{27}O_2N$, m.p. 90°, $[\alpha]_D$ +62·8° in EtOH [*hydrochloride*, m.p, 193°; hydrobromide, m.p. 202°; hydriodide, m.p. 190°; (m-NO_2·C_6H_4·*CO*)$_2$, m.p. 212°, and *PhSO*$_2$ derivative, m.p. 150°], is methylated (*p*-C_6H_4Me·SO_3Me) to (V). Hofmann degradation of *d*-norlelobanine, m.p. 174°, $[\alpha]_D$ −11·5° in EtOH (as its methiodide), gives (III). Lobinine is oxidised

(CrO_3, 15% H_2SO_4) to BzOH (1 mol.) and a *base*, $C_9H_{13}O_4N$, m.p. 207—208° [unsaturated ($KMnO_4$); absorbs 2 H but does not afford a homogeneous product], and is reduced (H_2, PtO_2) to 25—30% of β-lelobanidine (*hydriodide*, m.p. 181°, $[\alpha]_D$ −39·2± 0·5° in EtOH; *perchlorate*, m.p. 152°). *iso*Lobinine (VII) (Thomä, preceding abstract) similarly absorbs >4 H; after absorption of 4 H, (V), m.p. 83°, appears to be formed. Reduction of (VII) with 2% Na–Hg in AcOH gives a base (*hydrochloride*, m.p. 161°), differing from (X) (below) and lobinol. Oxidation (CrO_3, AcOH) of (VII) affords 50% of *iso*lobinanine (*hydrochloride*, m.p. 151°, $[\alpha]_D$ −11±0·3° in EtOH); the hygroscopic methiodide with $NaHCO_3$ yields an unsaturated diketone (VIII), m.p. 82—83°, also obtained from (VI). Lobinanidine (IX), $C_{18}H_{27}O_2N$, m.p. 95°, $[\alpha]_D$ −120° in EtOH [*hydrochloride*, m.p. 169°; *hydriodide*, m.p. 200°; *PhSO*$_2$ derivative, m.p. 125° (turbid; clears 135°)], is oxidised (CrO_3, AcOH, 70—80°) to lobinanine (perchlorate, m.p. 130°) and also to lobinic acid. Catalytic reduction of (IX) gives 60% of α-lelobanidine (*hydriodide*, m.p. 174°, $[\alpha]_D$ −37° in EtOH) and degradation of lobinanine methiodide affords (VIII). *iso*Lobinanidine (X) [*hydrochloride* (+2H_2O), m.p. 111°, $[\alpha]_D^{20}$ −28·3° in H_2O; *hydriodide*, m.p. 164°] is reduced catalytically to (V). The following are also described: *base*, $C_{19}H_{26}O_3N_2$, m.p. 232° (decomp.) [*hydrochloride*, m.p. 299—300° (decomp.); *hydriodide*, m.p. 279°; *perchlorate*, m.p. 254—255°; *methiodide*, m.p. 244° (decomp.); *Bz*, m.p. 280° (decomp.), and *Br*-derivative, m.p. 288° (decomp.)]; *bases*, $C_9H_{19}ON$, b.p. 118—120°/1—2 mm., m.p. 85—87°, and $C_{14}H_{21}ON$, m.p. 103°, b.p. 135—137°/1—2 mm., separated by distillation; *base*, $C_{14}H_{21}ON$, m.p. 81° (*aurichloride*, m.p. 182°; *Bz* derivative, m.p. 118°), oxidised to a *ketone*, $C_{14}H_{19}ON$ [hydrochloride (+H_2O), m.p. 109°] or to a compound, $C_7H_{13}O_2N$, m.p. 235°. $OH{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, m.p. 116°, $[\alpha]_D$ −18·4±0·5°, was isolated.

$CHNaAc{\cdot}CO_2Et$ and $(CH_2)_5Br_2$ give $CO_2Et{\cdot}CHAc{\cdot}[CH_2]_5{\cdot}Br$, converted by 48% HBr into η-keto-octyl bromide, b.p. 202—203°/30 mm., which with $CHNaBz{\cdot}CO_2Et$ affords *Et* θ-*keto*-α-*benzoyldecoate*. MeOH–KOH converts this into αι-*diketo*-α-*phenyldecane*, m.p. 64·5° (*semicarbazone*, m.p. 194°). $CO_2Et{\cdot}[CH_2]_6{\cdot}COCl$, b.p. 146°/12 mm., gives $CO_2Et{\cdot}[CH_2]_6{\cdot}COEt$ and thence α*θ-diketo*-α-*phenyldecane*, m.p. 44—45°. CH. ABS. (*b*)

Curare alkaloids. V. Alkaloids of some *Chondrodendron* species and the origin of radix pareiræ bravæ. H. KING (J.C.S., 1940, 737—746).—When radix pareiræ bravæ yields *l*-bebeerine it comes from *C. platyphyllum* and when it yields *d*-bebeerine from *C. microphyllum*; *C. candicans* contains the *d*-compound. All these species contain bebeerine (*d*- or *l*-) and d-*iso*chondrodendrine (I) in widely varying proportions. From the leaves of *C. platyphyllum*, there has been isolated l-*chondrofoline*, $C_{35}H_{36}O_6N_2$, m.p. ~135° (slow efferv.) [*nitrate*, m.p. 225° (decomp.)], which is phenolic and contains three OMe; on degradation by a one-stage Hofmann reaction it gives *O*-methylchondrofolinemethine methiodide, identical with inactive *O*-methylbebeerinemethine methiodide *B*. A probable structure is assigned. From a large amount of radix pareiræ bravæ a new alkaloid, d-iso*coclaurine* (II), m.p. 216—217° [*hydrochloride* (+H_2O), m.p. 175—176°, $[\alpha]_{5461}^{20}$ +23·9° in H_2O; O-*methyl*iso*coclaurine methiodide*, (+2H_2O), m.p. ~173°], isomeric with coclaurine, has been isolated; its constitution is as shown.



(II.)

(I) forms a sulphate (+15H_2O), m.p. anhyd. 291—292° (efferv.), $[\alpha]_{5461}$ +115·6° in H_2O; a methiodide (+8H_2O), m.p. 287° (decomp.), $[\alpha]_{5461}^{20}$ +64·3° in H_2O; *O*-methyl*iso*chondrodendrine methiodide, m.p. 312° (decomp.), $[\alpha]_{5461}^{20}$ +1·5° in H_2O; and α-O-*methyl*iso*chondrodendrinemethine hydrochloride* (+2H_2O), m.p. 299° (decomp.). Probable structures are assigned to (I), and protocuridine and neoprotocuridine, isomeric phenolic alkaloids of pot-curare. A classification of certain bisbenzyl*iso*quinoline alkaloids is given. F. R. S.

Two-dimensional chromatography. C. LAPP and K. ERALI (Bull. Sci. pharmacol., 1940, **42**, 49—58).—In a rapid micro-chromatographic method for the separation and determination of very small amounts of org. substances, these are adsorbed on a thin layer of MgO, $MgCO_3$, or kaolin, and after washing with an org. solvent, the layer of adsorbent is dried, and the type and degree of fluorescence in Wood's light are determined. J. N. A.

Determination of arsenic in organic arsenic compounds. R. TIOLLAIS and H. PERDREAU (Bull. Sci. pharmacol., 1940, **42**, 58—64).—The substance is boiled with conc. H_2SO_4 until decolorised and, after dilution and neutralisation with NaOH, the As_2O_3 is titrated with 0·1N-I in presence of $KHCO_3$. The method is rapid and accurate, and applicable to arsenicals in general if Cl is absent. J. N. A.

Determination of glycerol. H. KA (J. Agric. Chem. Soc. Japan, 1940, **16**, 461—475).—A method utilising the Lovibond Tintometer, based on Denigès' colour reaction with codeine after removal of impurities with CaO, is described. H. G. R.

Colorimetric micro-determination of formaldehyde. D. MATSUKAWA (J. Biochem. Japan, 1939, **30**, 385—394).—The sample (2 c.c. of 0·02—1·0 mg.-% solution of CH_2O) is treated with 0·5% $NHPh{\cdot}NH_2$ at 40°, 2·5% $K_3Fe(CN)_6$ is added followed by conc. HCl, and the red colour that develops is evaluated in a step-photometer. The method is exemplified by change in concn. of CH_2O in toxin preps. during incubation. F. O. H.

Detection and determination of picrolonic acid. S. FUKUDA (J. Biochem. Japan, 1939, **30**, 465—471).—Picrolonic acid (I) (2 mols.) rapidly heated to 124° condenses (with liberation of NO and H_2O) to give a *substance*, $C_{20}H_{14}O_7N_6$, which with NaOH produces a deep red colour. This reaction is used for the detection and (approx.) determination of (I). With arginine, lysine, and spermidine picrolonates, the method gives vals. ~85% of those calc. for the (I) content. F. O. H.