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A II—ORGANIC CHEMISTRY

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A II—Organic Chemistry

NOVEMBER, 1944.

I.—ALIPHATIC.

Rearrangement of alkyl halides.—See A., 1944, I, 252.

Preparation of *aaa*-trichloropropane.—See B., 1944, II, 269.

Oxidations [of dienes] by hydrogen peroxide in presence of selenious anhydride. P. Seguin (*Compt. rend.*, 1943, **216**, 667—668).—SeO_2 is more convenient than OsO_4 or V_2O_5 for oxidations by means of H_2O_2. To limit the oxidation to one of two double linkings, the best solvent is $Bu^{\gamma}OH$. Second to this is $COMe_2$, although this is itself partly oxidised. The reaction should be carried out with conc. solutions, as otherwise it is liable to be lengthy. Experiments on *cyclo*hexene (I) show that 4 g. of SeO_2 are required per g.-mol. of the substance being oxidised. The oxidation is complete in about a week, but may be regarded as practically complete after 48 hr. In the oxidation of (I) a 45% yield of *trans-cyclo*hexanediol was obtained with no trace of the *cis*-compound, whereas when OsO_4 is used, a mixture of *cis*- and *trans*-compound is obtained. In the oxidation of dienes, 2 OH add on across 1 : 2 rather than 1 : 4. *cyclo*Pentene-1 : 2-diol was obtained from *cyclo*pentadiene. Piperylene gave a mixture of $CHMe{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ and a little $CH_2{:}CH{\cdot}CH(OH){\cdot}CHMe{\cdot}OH$. $(CHPh{:}CH)_2$ was very resistant to oxidation. A. J. M.

Solubilities of high mol. wt. normal aliphatic primary alcohols.—See A., 1944, I, 221.

Manufacture of unsaturated alcohols.—See B., 1944, II, 246.

Properties of Δ^{δ}-penten-α-ol. Preparation of divinylmethane. R. Paul and H. Normant (*Compt. rend.*, 1943, **216**, 689—691).—2-Methyltetrahydrofuran (I) is obtained from $CH_2{:}CH{\cdot}[CH_2]_3{\cdot}OH$ (II) by distilling with conc. H_2SO_4 (88% yield) or, less well, by $NaHSO_3$–pumice at 170°. Al_2O_3 at 390° converts (I) into $CHMe{:}CH{\cdot}CH{:}CH_2$ (15%) and (**II**) (11%). Passing $CH_2{:}CH{\cdot}[CH_2]_3{\cdot}OAc$ over glass wool at 560° gives $CH_2(CH{:}CH_2)_2$ (60%), b.p. 26—27° (tetrabromide, m.p. 85·5—86°). R. S. C.

Manufacture of acylated secondary alcohols.—See B., 1944, II, 246.

Manufacture of ethers from olefines.—See B., 1944, II, 271.

Glyceryl α-*n*-dodecyl ether. O. Grummitt and R. F. Hall (*J. Amer. Chem. Soc.*, 1944, **66**, 1229—1230).—*n*-$C_{12}H_{25}{\cdot}OH$ (2 mols.), epichlorohydrin (1 mol.), and a little anhyd. $FeCl_3$ at 160° give $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}C_{12}H_{25}$-*n* (39%; less in absence of $FeCl_3$ or with other proportions of reagents), b.p. 157°/1 mm., converted by NaOH in boiling $Bu^{\alpha}{}_2O$ into *βγ-epoxy-n-propyl* n-*dodecyl ether* (74%), b.p. 132—135°/1—2 mm., whence 5% H_2SO_4 at 160° (not boiling dil. HCl) (apparatus: C, 1944, Part 4) gives *glyceryl α-n-dodecyl ether* (78%), m.p. ~20° [oxidised quantitatively, but slowly, by $Pb(OAc)_4$ in AcOH]. R. S. C.

Preparation and catalytic reduction of γ-nitro-β-butyl *p*-nitrobenzoate. J. R. Reasenberg and G. B. L. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 991—994).—MeCHO and $EtNO_2$ with NaOH–EtOH–H_2O (a little) at room temp. give $NO_2{\cdot}[CHMe]_2{\cdot}OH$ (I), b.p. 90°/11 mm., reduced (H_2–Raney Ni; EtOH; 3—4 atm.) to $NH_2{\cdot}[CHMe]_2{\cdot}OH$ (**II**), b.p. 159° [H oxalate, m.p. 164° (decomp.); oxalate, m.p. 206° (decomp.)], there being no evidence of formation of stereoisomerides (cf. Vanderbilt *et al.*, A., 1940, II, 62). With *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ in C_5H_5N at <25°, (I) gives a mixture, m.p. 85—90°, of stereoisomerides, whence repeated crystallisations or, better, two treatments with 0·1 mol. of NaOH in hot aq. EtOH give a pure *γ-nitro-β-*p-*nitrobenzoyloxy*-n-*butane* (III), m.p. 107—108°; the other isomeride is more readily hydrolysed or converted into $NO_2{\cdot}CMe{:}CHMe$ and is thus lost. With 3 H_2 in presence of Raney Ni and a little $PtCl_4$ in dioxan or in presence of PtO_2 as catalyst, (III) gives *α-nitro-β-*p-*aminobenzoyloxy*-n-*butane* (**IV**), m.p. 101—102° [*hydrochloride* (**V**), m.p. 182—183° (decomp.; rapid heating); nitrate, m.p. 167—169° (decomp.; rapid heating); *Ac* derivative, m.p. 110°]. With PtO_2 (not Ni) in EtOH, (**V**) is hydrogenated to *γ-nitro-β-4-amino*cyclo*hexanecarboxyloxy*-n-*butane hydrochloride*, decomp. 177° (slow heating) or 184° (rapid heating) (derived *platinichloride*, $+2H_2O$). With 6 H_2 in presence of Raney Ni–$PtCl_4$ or PtO_2 in EtOH, (I) gives by reduction and spontaneous rearrangement *β-*p-*aminobenzamido-γ-hydroxy*-n-*butane* (**VI**), m.p. 145—146° (hydrochloride; acetate, m.p. 145—146°). (**II**) yields *p*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}[CHMe]_2{\cdot}OH$, m.p. 158°, whence (**VI**) is obtained by H_2–Raney Ni in EtOH. (**VI**) is also obtained from (**IV**) by H_2–Raney Ni. All reductions to (**VI**) give also small amounts of a *substance*, $C_{15}H_{24}N_2O_2$, an anæsthetic oil (*Ac*$_2$ derivative, m.p. 151°; *picrate*, m.p. 171·5—172°). R. S. C.

Alkyl sulphites. *cyclo*Hexyl sulphite. L. P. Kyrides (*J. Amer. Chem. Soc.*, 1944, **66**, 1006—1007).—Adding $SOCl_2$ to *cyclo*hexanol at 25°/vac., falling to 5°/vac., and then slowly raising the temp. to 55° gives 93·5% of di*cyclo*hexyl sulphite, b.p. 165°/4 mm., which is stable although it smells of SO_2 and *cyclo*hexene (cf. Voss *et al.*, A., 1935, 1492; Carré *et al.*, *ibid.*, 480). Me_2, b.p. 124—127°, Et_2, b.p. 154—157°, $Pr^{\beta}{}_2$, b.p. 73—74°/25 mm., $Bu^{\alpha}{}_2$, b.p. 124—126°/29 mm., and di-β-octyl sulphite, b.p. 147—149°/5—6 mm., are similarly prepared in excellent yields. R. S. C.

Unsaturated synthetic glycerides. VII. Preparation and properties of synthetic α-monoglycerides and simple triglycerides of linoleic and linolenic acids. B. F. Daubert and A. R. Baldwin (*J. Amer. Chem. Soc.*, 1944, **66**, 997—1000; cf. A., 1944, II, 287).—*iso*Propylideneglycerol with linolenyl or linoleyl chloride (1 mol.) in quinoline–$CHCl_3$ at room temp. and then aq. HCl–Et_2O at ~0° gives *α-monolinolenin*, *forms*, m.p. −13·5° and 15·7° (*hexabromide*, m.p. 172°), and α-monolinolein, *forms*, m.p. −22·8° and 12·3° (hexabromide, m.p. 101·5°), respectively. Trilinolenin, *forms*, m.p. −44·6° and −24·2°, and trilinolein, *forms*, m.p. −45·6° and −12·9° (cf. Wheeler *et al.*, A., 1940, II, 116), are prepared at 100°. R. S. C.

Preparation of cyanomethyl chloroformate. See B., 1944, II, 246.

***tert.*-Butyl trichloroacetate.** W. E. Scovill, R. E. Burk, and H. P. Lankelma (*J. Amer. Chem. Soc.*, 1944, **66**, 1039).—*Bu^{γ} trichloroacetate*, m.p. 25·5°, b.p. 37°/1 mm., is obtained (95%) from $CCl_3{\cdot}COCl$ and $Bu^{\gamma}OH$ in C_5H_5N or (80%) from $CCl_3{\cdot}CO_2H$ and $CH_2{:}CMe_2$. R. S. C.

Preparation and properties of *n*-alkyl acrylates. C. E. Rehberg and C. H. Fisher (*J. Amer. Chem. Soc.*, 1944, **66**, 1203—1207).—Good yields of Et, b.p. 43°/103 mm., Pr^{α}, b.p. 44°/40 mm., Bu^{α}, b.p. 35°/8 mm., *n*-amyl, b.p. 48°/7 mm., *n*-hexyl, b.p. 40°/1·1 mm., *n*-heptyl, b.p. 57°/1 mm., *n*-octyl (**I**), b.p. 57°/0·05 mm., *n*-nonyl, b.p. 76°/0·2 mm., *n*-decyl, b.p. 120°/5 mm., *n*-dodecyl, m.p. ~4°, b.p. 120°/0·8 mm., *n*-tetradecyl, m.p. ~14°, b.p. 138°/4 mm., and *n*-hexadecyl acrylate (**II**), m.p. ~24°, b.p. 148°/0·04 mm., are obtained by heating $CH_2{:}CH{\cdot}CO_2Me$ (**III**), b.p. 80°, ROH, a little H_2SO_4 [or, less well, *p*-$C_6H_4Me{\cdot}SO_3H$, $Al(OBu^{\gamma})_3$, or Al–Hg], and quinol or *p*-$C_6H_4(NH_2)_2$ with continuous removal of the MeOH–(**III**) azeotrope. Compositions of various azeotropes of ROH with (**III**) are given. Polymerisation in emulsion gives products which increase in stickiness from (**III**) (not sticky) to (**II**); the brittle point is a min. (−65°) with (**II**). Physical data of the esters are recorded. R. S. C.

Isolation and properties of naturally occurring octadecenoic (oleic) acids. R. C. Millican and J. B. Brown (*J. Biol. Chem.*, 1944, **154**, 437—450).—Octadecenoic acids isolated by low-temp. crystallisation of the Me esters of C_{18}-acids from a no. of fats and oils have been compared with oleic acid (**I**) similarly obtained from olive oil. The acids of chicken fat and of peanut, cottonseed, corn, and linseed oils appear to be identical with (**I**). Those of lard, beef tallow, beef adrenal phosphatides, pork liver lipins, human fat, and, to a somewhat smaller extent, soya-bean and rape-seed oils appear to be mixtures of (**I**) with other isomeric acids, (**I**) being the principal component. The results appear to confirm the previously reported presence of vaccenic acids in beef fat and lard. F. R. S.

Secondary reactions of ozonolysis of the ethylenic linking. M. Stoll and A. Rouve (*Helv. Chim. Acta*, 1944, **27**, 950—961).—The observations of Rieche *et al.* (A., 1944, II, 287) are extended and confirmed. Catalytic hydrogenation of Et oleate ozonide ceases after ~70% of the theoretical quantity of gas has been absorbed. The yield of aldehydes is generally ⩾55—65% and 10—15% of acids are produced by spontaneous scission of the ozonide due to the heat of the hydrogenation or to H_2O formed in the reaction. Saturated non-aldehydic compounds are formed in 15—25% yield and include fatty acid esters. It appears that scission does not occur

exclusively between the two C atoms united by the ethylenic linking but that in small proportion the terminal C of the products may be removed. Ozonisation of brassidyl or erucyl acetate in EtOAc and hydrogenation of the ozonide followed by removal of acids and distillation, heating, or treatment of the product with boiling $NaHSO_3$ causes the development of fresh acidity and evolution of gas. The monomeric, easily reduced ozonide must therefore be accompanied by one or more peroxides not reduced by H_2. These can be the polymeric ozonides of Rieche which decompose thus: ·O·CHR·O·O·CHR′·O·CHR·O·O·CHR′·O· (R = ·$[CH_2]_7$·Me; R′ = ·$[CH_2]_{12}$·O_2Ac] → Me·$[CH_2]_{11}$·OAc + CO (CO_2) + Me·$[CH_2]_7$·CO_2H(CHO) + Me·$[CH_2]_6$·Me + CO_2(CO) + OAc·$[CH_2]_{12}$·CHO(CO_2H). Lauryl acetate has been isolated in 2—5% yield. The scheme does not explain other secondary products. The wt. of the ozonide is always > that calc. for one ethylenic linking and the sap. val. of the crude product is always > that of the original material. After hydrogenation the sap. val. remains unchanged and is unaltered by separation of the aldehydes. The sap. val. of the neutral, non-aldehydic portions has therefore been raised and from them Et *n*-nonoate and Et *ω*-acetoxytridecoate have been isolated. If the EtOAc used is free from EtOH it must itself have participated in the change, which may be expressed; 2Me·$[CH_2]_7$·CH·O·O·CH·$[CH_2]_{12}$·OAc + 2EtOAc → (—O—) Me·$[CH_2]_7$·CHO + CO_2Et·$[CH_2]_{12}$·OAc + Me·$[CH_2]_7$·CO_2Et + CHO·$[CH_2]_{12}$·OAc + 2AcOH. Scission occurs after the introduction of O_3, during either evaporation of the solution or hydrogenation. The use of ozonolysis for determining the position of a double linking may thus give rise to error. H. W.

Ricinoleic acid derivatives.—See B., 1944, II, 271.

Physiological antioxidants. P. Györgv and R. M. Tomarelli (*J. Biol. Chem.*, 1944, **154**, 317—324).—($NHMe·C_6H_4·N:)_2$ retards the autoxidation of linoleic acid (**I**) and synergistically enhances the antioxidant activity of rice bran extract or quinol but is ineffective with *α*-tocopherol (**II**). (**II**) is the only antioxidant tested which inhibits the oxidation of (**I**) and carotene catalysed by soya-bean lipoxidase but $NHPh_2$ has a slight activity. H. G. R.

Lipins of tubercle bacilli. LXVI. Structure of tuberculostearic acid. S. F. Velick (*J. Biol. Chem.*, 1944, **154**, 497—502).—*X*-Ray examination of the crystal structure of the amides of tuberculostearic acid (**I**) and of *dl*-*ι*-methylstearic acid (**II**) gives results that are consistent with the hypothesis that (**I**), although showing no detectable optical rotation, is optically active, and support the structure of the *d*- or *l*-form of (**II**) for (**I**). F. R. S.

Preparation and pyrolysis of lactic acid derivatives. Production of β-alkoxyethyl and tetrahydrofurfuryl acrylates. M. L. Fein, W. P. Ratchford, and C. H. Fisher (*J. Amer. Chem. Soc.*, 1944, **66**, 1201—1203).—Heating 81·8% lactic acid with OR·$[CH_2]_2$·OH or tetrahydrofurfuryl alcohol and a little H_2SO_4 in C_6H_6 with continuous removal of H_2O gives *β-methoxyethyl* (56%), b.p. 81—82°/6 mm., *β-ethoxyethyl* (60%), b.p. 86—87°/5 mm., *β-butoxyethyl* (81%), b.p. 109—110°/6 mm., and *β-tetrahydrofurfuryl lactate* (79%), b.p. 114—115°/5 mm., which are also obtained in 70, 72, 71, and 84% yield, respectively, by heating Et lactate with the appropriate alcohol and Al–Hg with continuous removal of EtOH. 1·1 mols. of Ac_2O then yield 90—95% of the corresponding *α*-acetoxypropionates, (**I**) b.p. 100—101°/7 mm., (**II**) b.p. 105—106°/6 mm., b.p. 120—121°/5 mm., and b.p. 132—133°/7 mm., respectively. When passed as vapour through a Pyrex glass tube at 475—525°, these give OMe·$[CH_2]_2$ (47·5%; yields in this reaction are quoted per mol. of reacted ester and are max.), b.p. 56°/12 mm., OEt·$[CH_2]_2$ (40%), b.p. 77°/19 mm., OBu·$[CH_2]_2$ (34%), b.p. 80°/6 mm., and tetrahydrofurfuryl acrylate (**III**) (70%), b.p. 87°/9 mm. (all obtained also by trans-esterification), with larger amounts of AcOH; (**II**) yields also 20—50% of MeCHO; (**I**) yields also 20% of MeCHO and 30% of MeOH. Thus, *β*-OR does not stabilise Et acrylate. The stability of (**III**) may be due to only one *β*-H being present in the alcohol component (cf. Claborn, U.S.P. 2,229,997; B., 1942, II, 55). Physical consts. of the esters are recorded. R. S. C.

Preparation, tautomerism, and reactions of γ-chlorinated acetoacetic ester. F. Arndt, L. Loewe, and L. Capuano (*Rev. Fac. Sci. Istanbul*, 1943, **8**, **A**, 122—152).—CCl_3·CHO is condensed with $CH_2(CO_2H)_2$ in boiling AcOH to CCl_3·CH(OH)·CH_2·CO_2H, the Et ester, m.p. 55—56°, of which is partly oxidised by CrO_3 in AcOH containing $KHSO_4$ or $K_2S_2O_7$ at room temp. The product is extracted with Et_2O and the extract is shaken with 20% NH_3, which is immediately acidified, thus giving crude *Et γγγ-trichloroacetoacetate* (**I**), b.p. 91·5°/2·5 mm., which is purified through the *Cu* salt, m.p. 88·5 with darkening and then 92—93°. The b.p. does not remain const. when (**I**) is kept. (**I**) gives a dark red colour with $FeCl_3$ and is decomposed by NaOH with formation of $CHCl_3$. *Me γγγ-trichloroacetoacetate* (**II**), b.p. 77°/2·5 mm., 89—90°/4 mm. [*Cu* derivative, m.p. 156—157° (decomp.), softens at 110—112°], is obtained similarly, CH_2Cl·CO·CH_2·CO_2Et (**III**), b.p. 81—82°/3·5 mm., 103°/12 mm. (Cu derivative, m.p. 160°, decomp. 169°), and the corresponding Me ester (**IV**), b.p. 85°/4 mm., are described. (**I**) is stable to steam and hence can be kept when pure whereas (**II**) is hygroscopic and readily yields a cryst. *hydrate* (**V**), m.p. 65—67° (indef.), softens at 58°, and loses H_2O at ~115°, whereby the difference between ketonic and enolic form is destroyed. Hydrates are not formed by (**I**) or (**II**). (**I**), (**II**), (**III**), and (**IV**) are sol. in dil. alkali and dil. NH_3 whilst (**I**) and (**II**) dissolve also in Na_2CO_3; all the alkaline solutions are unstable. The indirect Br titration method of Meyer is not applicable to chlorinated acetoacetic esters, which liberate I from acidified KI without intermediate use of Br. The direct titration method shows that the proportion of enol is greater in (**III**) than in (**IV**) and greater in either than in $CH_2Ac·CO_2Et$. (**III**) does not give a sharp end-point but the proportion of enol in the undiluted material is > that in (**III**). Br is very slowly decolorised by (**V**). In EtOH (**IV**) appears to exist as an equilibrium mixture of ketone, enol, and their common acetal. (**III**) and (**IV**) react more vigorously than $CH_2Ac·CO_2Et$ with CH_2N_2; (**I**) and (**II**) when nearly anhyd. react violently and hence are pronouncedly acidic. With (**III**) and (**IV**) the products contain about equal proportions of the enol Me ether and ethylene oxide, the acidifying action of CH_2Cl being balanced by the electromeric action of the *A* effect. With (**I**) and (**II**) the acidifying action of CCl_3 dominates to such an extent that the product is almost exclusively enol ether practically free from the ethylene oxide. CCl_3·$CH(OH)_2$ and CHN_2·CO_2Et at 100° give (**I**) and Et *γγγ*-trichloroglycidate (**VI**), b.p. 115—116°/11 mm., in the ratio 1 : 10. (**VI**) is unchanged by fuming, aq. HCl but is transformed by HCl–EtOH into the *chlorohydrin*, b.p. 122°/6 mm. H. W.

Condensations. Carboxylation and carbethoxylation of (XXIV) ketones, (XXV) esters, using sodium triphenylmethide reagent. (XXIV) β-Keto-ester synthesis. (**XXIV**) E. Baumgarten, R. Levine, and C. R. Hauser. (**XXV**) E. Baumgarten and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 862—865, 1037—1038; cf. A., 1944, II, 213).—XXIV. $COBu^{\beta}_2$ with CPh_3Na at 0° and then Et_2CO_3 at room temp. gives $COBu^{\beta}$·$CHPr^{\beta}$·CO_2Et (50%), but COMeEt with CPh_3Na and then *p*-$C_6H_4Ph·O·CO·OEt$ (**I**) gives only COEt·CH:CMeEt. Carboxylation of CORR′ is effected by interaction with CPh_3Na and then solid CO_2 in N_2, followed by esterification by CH_2N_2. Thus, COMeEt gives *Me β-keto*-n-*valerate* (37%), b.p. 73—76°/16 mm. (Cu salt, m.p. 160·3—160·9°), which with $NHPh·NH_2$ in AcOH gives 1-phenyl-3-ethyl-5-pyrazolone and with NaOMe–Bu^{α}Br–MeOH at 60° gives *Me α-propionyl*-n-*hexoate* (47%), b.p. 108—112°/16 mm., whence H_2SO_4–AcOH yields *n*-C_5H_{11}·COEt. Pinacolone gives similarly *Me β-keto-γγ-dimethyl*-n-*valerate* (57%), b.p. 82—84°/17 mm., $COPr^{\beta}_2$ gives *Me β-keto-aaγ-trimethyl*-n-*valerate* (55%), b.p. 94—96°/26 mm., and $COBu^{\beta}_2$ gives *Me β-keto-δ-methyl-α*-iso*propyl*-n-*hexoate* (42%), b.p. 114—116·5°/19 mm. In general, when using CPh_3Na, the latter method is preferable to direct carbethoxylation.

XXV. By carboxylation in presence of CPh_3Na and then hydrolysis, $Pr^{\beta}CO_2$Et gives $CMe_2(CO_2H)_2$ (**II**) (73%), m.p. 193—194° (decomp.) (lit. 192—193°), and EtOAc gives $CH_2(CO_2H)_2$ (**III**) (34%); without hydrolysis, $Pr^{\beta}CO_2Bu^{\gamma}$ gives *Bu$^{\gamma}$ H dimethylmalonate* (**IV**) (81%), m.p. 80·0—80·9°, and Bu^{γ}OAc gives *Bu$^{\gamma}$ H malonate* (**V**) (57%), decomp. when distilled. At 140—150°, (**IV**) gives CMe_2:CH_2, (**II**), and some $Pr^{\beta}CO_2H$; at 120° (**V**) gives (**III**). In presence of CPh_3Na, EtOAc and Et_2CO_3 give $CH_2(CO_2Et)_2$ (41%) and $CH_2Ac·CO_2Et$ (12%); $Pr^{\beta}CO_2$Et and (**I**) give $CMe_2(CO_2Et)_2$ (83%); Bu^{γ}OAc and (**I**) give $CO_2Et·CH_2·CO_2Bu^{\gamma}$ (25%). R. S. C.

Induced oxidation of oxalic acid by dichromate with ferrous sulphate as indicator.—See A., 1944, I, 253.

Emetic [antimony] derivatives of oxalic and glyoxylic acids. Y. Volmar and G. Gœttelmann (*Compt. rend.*, 1943, **216**, 828—828).—$H_2C_2O_4$ and CHO·CO_2H unite with Sb_2O_3 to form antimonyl derivatives; those from $H_2C_2O_4$ are difficult to purify and exhibit a tendency to crystallise with one or more mols. of $H_2C_2O_4$ or normal oxalate. The products from $AcCO_2H$ and CHO·CO_2H are less easy to prepare and are more hydrolysable. The following are described: $SbHC_2O_5$; $SbK_2H(C_2O_4)_3,2H_2O$; $SbK(C_2O_4)_2,H_2O$; $SbK_3H_2(C_2O_4)_3,4H_2O$. H. G. R.

Purification of maleic anhydride.—See B., 1944, II, 246.

New type of active (partial) racemates. A. Fredga (*Arkiv Kemi, Min., Geol.*, 1944, **18**, **B**, No. 4, 7 pp.).—The possibility is indicated that, in some circumstances, an optically active compound may form a racemic-like mol. compound with an inactive compound of similar structure but without centres of asymmetry. An example is found in the system (+)-dimethylglutaric–glutaric acid (**I**). The m.p. curve of (**I**) with *r*- or *meso*-dimethylglutaric acid is of the ordinary eutectic type. H. W.

Formation of ketobutyrolactone carboxylic esters (ketoparaconic esters) and the mechanism of reaction of ketolisation of oxalacetic ester. H. Gault and R. Durand (*Compt. rend.*, 1943, **216**, 848—850).—*Et α-keto-γ-butyrolactone-β-carboxylate* (**I**), m.p. 108° (*phenylhydrazone*, m.p. 142·5°; *semicarbazone*, m.p. 209°), is obtained from $CO_2Et·C(OK)$:CH·CO_2Et (**II**) and excess of 35% CH_2O at −1°. Similarly prepared from MeCHO is the *γ-Me* derivative of (**I**), an

oil (*phenylhydrazone*, m.p. 130°). A mechanism is suggested whereby RCHO [as $CHR(OH)_2$] yields an adduct with (**II**), followed by loss of H_2O + EtOH. The above results show that AlkCHO react similarly to ArCHO. A. T. P.

Trihydroxy*iso*butyric acid and its derivatives. H. M. Coleman [with J. W. E. Glattfeld] (*J. Amer. Chem. Soc.*, 1944, **66**, 1183—1188).—97% conversion of glycerol into $CO(CH_2{\cdot}OH)_2$ (**I**) (crystallo-optical properties described) by *Acetobacter suboxydans* at pH 6·0—6·8 is detailed, the reaction being followed by treatment of samples with HIO_4 and back-titration thereof. Gradually adding NaCN to (**I**) in HF, concn. to a syrup, and then hydrolysing by aq. HCl at 0° gives $(OH{\cdot}CH_2)_2C(OH){\cdot}CO_2H$ (**II**) (84%), m.p. 117° (*NHPh·NH*$_2$, m.p. 121—122°, and *p-toluidine* salt, m.p. 126·5—127°), isolated by way of the basic Ba, BaX·OH, and then the Ca, $+4H_2O$, salts. With BzCl–C_5H_5N at 0°, (**II**) gives the *ββ′-dibenzoate*, m.p. 137° [*NHPh·NH*$_2$ (?) salt, m.p. 110°], but at 130—135° gives the tribenzoate [*NHPh·NH*$_2$ (?) salt, m.p. 137—137·5° (red)], and with AcCl at 65° gives the *triacetate*, a resin [*NHPh·NH*$_2$ (?) salt, $2(OAc{\cdot}CH_2)_2C(OAc){\cdot}CO_2H,3NHPh{\cdot}NH_2$, m.p. 94° (red)], but by heating in Ac_2O at 100° and distilling at 200—240° (bath)/1 mm. yields a *dimer*, m.p. 86—86·5°, of (?) tetra-acetoxymethylglycolide. R. S. C.

Autoxidation of ascorbic acid in presence of copper.—See A., 1944, I, 253.

Autoxidation of ascorbic acid in presence of vanadic acid, molybdic acid, and tungstic acid sols.—See A., 1944, I, 253.

Preparation of fully acetylated aldonic acids and nitriles. K. Ladenburg, M. Tishler, J. W. Wellman, and R. D. Babson (*J. Amer. Chem. Soc.*, 1944, **66**, 1217—1218).—d-*Ribonic acid tetra-acetate* (**I**), m.p. 139—140°, $[\alpha]_D^{25}$ −27·5° in AcOH, is obtained by HCl–Ac_2O in the stated yields from Cd (85%), NH_4 (46%), K (25%), Ca (22%), and Ba (4%) *d*-ribonate. Cd arabonate similarly gives 86% of *d*-arabonic acid tetra-acetate. K ribonate and AcOH at 60° give d-*ribonic acid*, m.p. 112—113°, $[\alpha]_D^{25}$ −17·3° in MeOH, unstable at room temp., which by the method of Robbins *et al.* (A., 1940, II, 266) gives (**I**) (15%), d-*ribolactone triacetate* (**II**) (10%), m.p. 54—56°, $[\alpha]_D^{25}$ +27° in $CHCl_3$, and an oil. With HCl–Ac_2O at 50° *d*-ribolactone gives (**II**) (88%). *d*-Ribonamide tetra-acetate and $POCl_3$ in boiling $CHCl_3$ give d-*ribononitrile tetra-acetate*, m.p. 71—72°, $[\alpha]_D^{25}$ +34·45° in $CHCl_3$. d-*Arabononitrile tetra-acetate*, m.p. 120—121°, $[\alpha]_D^{25}$ −3·5° in $CHCl_3$, and *d*-gluconononitrile penta-acetate are similarly prepared. R. S. C.

Salts of galacturonic acid and their application to the preparation of galacturonic acid from pectic substances. H. S. Isbell and H. L. Frush (*J. Res. Nat. Bur. Stand.*, 1944, **32**, 77—94).—Neutralisation of galacturonic acid (**I**) with the corresponding carbonate or hydroxide gives *Na*, $[\alpha]_D^{20}$ +36·0°, *K* (+0·5H_2O), $[\alpha]_D^{20}$ +31·6°, NH_4 (+0·5H_2O), $[\alpha]_D^{20}$ +35·5°, *Cd* (+2H_2O), $[\alpha]_D^{20}$ +28·4°, and *Ag* (+0·5H_2O), $[\alpha]_D^{20}$ +25·1°, *β-galacturonates* and *Ca* (+H_2O) (**II**), $[\alpha]_D^{20}$ +36·8°, and *Sr* (+5H_2O), $[\alpha]_D^{20}$ +29·1°, *α-galacturonates*. Neutralisation of (**I**) with the correct proportions of the carbonates and/or hydroxides affords *Na Ca* (+6H_2O) (**III**), $[\alpha]_D^{20}$ +32·4°, *Na Sr* (+6H_2O), $[\alpha]_D^{20}$ +30·2°, and *K Ca* (+6H_2O), $[\alpha]_D^{20}$ +31·4°, *α-galacturonates*. (**III**) treated with enough $H_2C_2O_4$ to ppt. Ca followed by the corresponding carbonate gives *Na Ba* (+6H_2O), $[\alpha]_D^{20}$ +27·8°, *Na Cd* (+6H_2O), $[\alpha]_D^{20}$ +27·3°, and *Na Pb* (+6H_2O), $[\alpha]_D^{20}$ +29·0°, *α-galacturonates*. All $[\alpha]_D$ vals. are at equilibrium in H_2O. Mutarotation studies are used to assign the configurations. (**II**) and (**III**) are recommended for the isolation of (**I**) from pectic substances. D. G.

Dimethyl dimethylene-*l*-idosaccharate. W. G. M. Jones and L. F. Wiggins (*J.C.S.*, 1944, 363).—*l*-Iditol (from *l*-sorbose with H_2–Raney Ni) oxidises (HNO_3) to *l*-idosaccharic acid, isolated as Ca salt. This, with paraformaldehyde and H_2SO_4 followed by MeOH, yields Me_2, dimethylene-*l*-idosaccharate, m.p. 296°, identical with that from epimerisation of Me_2 dimethylene-*d*-gluco- and -*d*-manno-saccharate. D. G.

Structure of monomethylene-*d*-glucosaccharolactone. W. G. M. Jones and L. F. Wiggins (*J.C.S.*, 1944, 364—366).—αγ-Monomethyleneglucosaccharo-βε-lactone on oxidation (CrO_3 in AcOH) and esterification yields *Me*$_2$ *αγ-monomethylenexylotrihydroxyglutarate* (**I**), m.p. 204°, identical with that obtained from *d*-xylose by oxidation (HNO_3) to Ca xylotrihydroxyglutarate, condensation with paraformaldehyde, and esterification. (**I**) yields the free *i*-acid, m.p. 253—254°, and the diamide, m.p. 286° (negative Weerman test for α-OH), and on methylation (MeI and Ag_2O) affords *Me*$_2$ *β-methyl-αγ-monomethylenexylotrihydroxyglutarate*, m.p. 157°, giving the *diamide*, m.p. 295° (decomp.), with NH_3 in MeOH. Me_2 monomethyleneglucosaccharate gives (MeI and Ag_2O) *Me δ-methyl-αγ-monomethyleneglucosaccharo-βε-lactone*, m.p. 149° and *Me*$_2$ *βδ-dimethyl-αγ-monomethyleneglucosaccharate*, m.p. 96—97°. D. G.

Formation of " active racemates " between organic compounds of sulphur and selenium. A. Fredga (*Arkiv Kemi, Min., Geol.*, 1944, **17**, A, No. 17, 15 pp.).—*r*-Thioacetic-α-propionic acid (**I**), from $CHMeBr{\cdot}CO_2H$ and $SH{\cdot}CH_2{\cdot}CO_2H$, has m.p. 87—88°. Reduction of (−)-$(S{\cdot}CHMe{\cdot}CO_2H)_2$ by Na–Hg and treatment of the product with $CH_2Cl{\cdot}CO_2Na$ gives (−)-thioacetic-α-propionic acid (**II**), m.p. 79—80°, $[\alpha]_D^{25}$ −172·9° in EtOAc (cf. Fitger, *Diss., Lund*, 1924). The corresponding (+)-*acid* (**III**) has m.p. 79—80°, $[\alpha]_D^{25}$ +172·7° in EtOAc, +173·3° in AcOH, +169·6° in abs. EtOH, +153·0° in $COMe_2$, +95·0° in $CHCl_3$, +109·8° in 0·4N-HCl, and +55·0° in neutral aq. solution. *r*-Thio-αβ-dipropionic acid, m.p. 72—72·5°, is obtained from $SH{\cdot}CHMe{\cdot}CO_2H$ and $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$. Reduction of $(S{\cdot}CHMe{\cdot}CO_2H)_2$ by Na–Hg and treatment of the product with $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$ affords (+)-*thiodi-αβ-propionic acid* (**IV**), $[\alpha]_D^{25}$ +131·1° in EtOAc, +129·7° in AcOH, +129·2° in abs. EtOH, +125·2° in $COMe_2$, +111·1° in $CHCl_3$, +104·4° in 0·4N-HCl, +69·6° in neutral aq. solution. The similarly prepared (−)-*acid* (**V**) has $[\alpha]_D^{25}$ −131·0° in EtOAc. r-*Selenoacetic-α-propionic acid* (**VI**), m.p. 65—66°, is obtained by the successive action of Na–Hg and $CHMeBr{\cdot}CO_2H$ on $(Se{\cdot}CH_2{\cdot}CO_2H)_2$ or of Na–Hg and $CH_2Cl{\cdot}CO_2H$ on $(Se{\cdot}CHMe{\cdot}CO_2H)_2$. The (+)-*acid* (**VII**), obtained by successive treatments of (+)-$(Se{\cdot}CHMe{\cdot}CO_2H)_2$ with Na–Hg and $CH_2Cl{\cdot}CO_2H$ has m.p. 60·5—61·5°, $[\alpha]_D^{25}$ +149·4° in EtOAc, +166·2° in AcOH, +150·4° in abs. EtOH, +137·1° in $COMe_2$, +123·7° in $CHCl_3$, +116·4° in 0·4N-HCl, and +40·7° in neutral aq. solution. r-*Seleno-αβ-dipropionic acid* (**VIII**), m.p. 72·5—73·5°, is obtained by reduction of $(Se{\cdot}[CH_2]_2{\cdot}CO_2H)_2$ in presence of neutralised $CHMeBr{\cdot}CO_2H$ but not through $(Se{\cdot}CHMe{\cdot}CO_2H)_2$ and β-halogenopropionic acids. It is best resolved into its optical components by quinine in aq. $COMe_2$, thus leading to the (−)-*acid* (**IX**), two forms, m.p. 53·5—54·5° and 61·5—62·5°, $[\alpha]_D^{25}$ −124·2° in EtOAc, −121·0° in AcOH, −121·4° in abs. EtOH, −119·3° in $COMe_2$, −110·5° in $CHCl_3$, −109·6° in 0·4N-HCl, and −52·3° in neutral aq. solution (*quinine* salt, +3·33° in H_2O). M.p. diagrams show that (**I**) and (**VI**) are true racemates. (**III**) and (**VII**) give an almost rectilinear m.p. curve indicating isomorphism whilst (**II**) and (**VII**) give an active racemate. (**I**) and (**VI**) do not give a completely isomorphous series but probably a sequence of isodimorphous mixed crystals. (**IV**) and (**IX**) doubtless give an active racemate but observations are impeded by the occurrence of (**IX**) in two cryst. forms. (**VIII**) and the corresponding S acid, (**V**), and (**IX**) show extensive, possibly complete miscibility in the solid phase. H. W.

Catalytic formation of long-chain aldehydes.—See B., 1944, II, 272.

Carbonyl reduction by thioacetal hydrogenolysis. M. L. Wolfrom and J. V. Karabinos (*J. Amer. Chem. Soc.*, 1944, **66**, 909—911).—A general method is described for converting CO into CH_2 by conversion (by EtSH, $ZnCl_2$, and NaOH at 5°—room temp.) into $>C(SR)_2$, followed by hydrogenation of the crude products in presence of Raney Ni in boiling 70% EtOH. It is applied to 3 sugar acetates, 1 free sugar, and 5 other CO-compounds. Thus are obtained 1-deoxy-*D*-galactitol [*L*-fucitol] penta-acetate (66% from *D*-galactose penta-acetate), 1-deoxy-*D*-glucitol [1-deoxy-*l*-sorbitol, *L*-gulomethylitol] penta-acetate (60% from *D*-glucose penta-acetate), 2-deoxy-*D*-mannitol [-*l*-sorbitol, -*D*-glucitol] penta-acetate (20% from *D*-fructose penta-acetate), 1-deoxy-*D*-galactitol (24% from *D*-galactose), PhMe (65% from PhCHO), PhEt (66% from COPhMe), n-C_7H_{16} (50% from $COMe{\cdot}C_5H_{11}$-n and 40% from n-$C_6H_{13}{\cdot}CHO$), and CH_2Ph_2 (77% from $COPh_2$). MeCHO is isolated from the reaction mixture after reduction of $C_6H_{13}{\cdot}CH(SEt)_2$. R. S. C.

Condensations. XXVI. Acylation of methyl ketones with aliphatic esters by means of sodium amide. Synthesis of β-diketones of the type, COR·CH$_2$·COR′. J. T. Adams and C. R. Hauser. **XXVII. Preparation of potassium triphenylmethide and its use in condensations.** R. Levine, E. Baumgarten, and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 1220—1222, 1230—1231; cf. A., 1944, II, 211).—XXVI. Adding COMeR (1 mol.) and then $R'CO_2Et$ (2 mols.) to $NaNH_2$ (2 mols.) in Et_2O gives $CH_2(COEt)_2$ (57% with 13% of COEt·CHMe·COMe), b.p. 78—80°/30 mm. (Cu salt, m.p. 209—210°), $CH_2(COPr^{\alpha})_2$ (68%), b.p. 101—102°/2 mm. (Cu salt, m.p. 156—157°), n-*dodecane-εη-dione* (80%), b.p. 109—110°/20 mm. (Cu salt, m.p. 136—137°), *ββ-dimethyl*-n-*decane-γε-dione* (52% with some $Bu^{\alpha}CO{\cdot}NH_2$ and $COBu^{\alpha}{\cdot}CHPr^{\alpha}{\cdot}CO_2Et$), b.p. 116—119°/20 mm. (no Cu salt), *βι-dimethyl*-n-*decane-εη-dione* (76%), b.p. 115—116°/20 mm. (blue Cu salt, m.p. 157—158°), n-*tridecane-ζθ-dione* (68%), b.p. 162—164°/20 mm. (blue Cu salt, m.p. 119—120°), *ββζζ-tetramethyl*-n-*heptane-γε-dione* (28%), b.p. 96—97°/20 mm. (purple Cu salt, m.p. 197—198°), CH_2Ac_2 (54%), $COMe{\cdot}CH_2{\cdot}COBu^{\gamma}$ (43%), b.p. 70—71°/20 mm. (Cu salt, m.p. 191—192°), $COEt{\cdot}CH_2{\cdot}COBu^{\alpha}$ (70% with 2% of $COMe{\cdot}CHEt{\cdot}COEt$), b.p. 84—76°/20 mm. (Cu salt, m.p. 157—158°), and $COMe{\cdot}CH_2{\cdot}COPr^{\beta}$ (42%), b.p. 66—67°/20 mm. (Cu salt, m.p. 171—172°). 1 mol. of $NaNH_2$ gives about half these yields; a reaction mechanism to account for this is proposed.

XXVII. $CHPh_3$ and KNH_2 in liquid NH_3 give $KCPh_3$, which after replacement of NH_3 by Et_2O is used effectively for self-condensation of $Bu^{\beta}CO_2Et$ and condensation of $Pr^{\beta}CO_2Et$ with BzCl or EtI, and for conversion of COMeEt into $COEt{\cdot}CH_2{\cdot}CO_2H$. The $CHPh_3$ recovered is re-used. R. S. C.

Acetylene derivatives. XXXIII. Conversion of divinyl ketones. Addition of hydrogen chloride to ββ-dimethyldivinyl ketone. I. N.

Nazarov and T. D. Nagibina (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 206—215).—Addition of 1 mol. of HCl to CH_2:CH·CO·CH:CMe_2 (**I**) (b.p. 42—43°/8 mm.) yields *vinyl β-chloroisobutyl ketone*, b.p. 57—60°/8 mm. (decomp.). Addition of 2 mols. of HCl gives a *β-chloroethyl β'-chloroisobutyl ketone*, b.p. 92—94°/9 mm. (decomp.). With a 1% solution of KOH in EtOH (**I**) forms δ-ethoxy-β-methyl-Δβ-hexen-δ-one; polymerisation of (**I**) also occurs. Hydrolysis (6% H_2SO_4) of δ-methoxy-β-methyl-Δβ-hexen-δ-one yields 2 : 2-dimethyltetrahydro-4-pyrone. Addition of 2 mols. of HCl to phorone with subsequent hydrolysis yields 2 : 2 : 6 : 6-*tetramethyltetrahydro-4-pyrone*, b.p. 73—75°/17 mm. V. B.

Solubilities of high mol. wt. symmetrical normal aliphatic tertiary amines.—See A., 1944, I, 221.

Steric strain and anomalous base strength of normal aliphatic amines.—See A., 1944, I, 224.

Preparation of *sec.*- and *tert.*-amines. C. Prévost and H. C. de Mauny (*Compt. rend.*, 1943, **216**, 771—772).—$NHEt_2$ and excess of cold 33% aq. CH_2O give NEt_2·CH_2·OH, convertible by HCl in C_6H_6 into CH_2Cl·NEt_2,HCl, which with MgBuCl, MgMeI, or MgPhBr affords *n*-C_5H_{11}·NEt_2, b.p. 155°/760 mm., NEt_3, or CH_2Ph·NEt_2, b.p. 209°/755 mm. NHMe·CH_2·OH similarly leads to CH_2Ph·NHMe, b.p. 181°/760 mm. (aurichloride, m.p. 138°). A. T. P.

Preparation of diamines from keto-nitriles.—See B., 1944, II, 247.

Manufacture of *sec.* diamines.—See B., 1944, II, 248.

Reaction between amines and unsaturated compounds containing halogen attached to one of the ethylenic carbon atoms. III. Influence of a *gem*-dimethyl group. H. C. Murfitt and J. C. Roberts (*J.C.S.*, 1944, 371—373; cf. A., 1938, II, 335).—CH_2:CBr·CO_2Et (**I**) with $NHMe_2$ in EtOH gives *Et αβ-bis(dimethylamino)propionate*, b.p. 95—96°/14 mm. [*picrate*, m.p. 122—123° (decomp.); *platinichloride*, m.p. 190° (decomp.), changes at 186°], also obtained from CH_2Br·$CHBr$·CO_2Et (**II**) and $NHMe_2$. (**I**) or (**II**) and piperidine (**III**) yield (?) *Et αβ-dipiperidinopropionate*, b.p. 175—176·5°/13 mm. (no cryst. picrate). CMe_2Br·$CHBr$·CO_2Et, b.p. 112—114°/18 mm. (from CMe_2:CH·CO_2Et and Br), with NaOEt gives *Et α-bromo-ββ-dimethylacrylate* (**IV**), b.p. 88—89°/13 mm., which with (**III**) in EtOH yields impure *Et α-piperidino-ββ-dimethylacrylate*, b.p. 122—124°/18 mm. [*platinichloride*, m.p. 183° (decomp.), softens at 179°]. With $NHMe_2$ (**IV**) gives *Et α-dimethylamino-ββ-dimethylacrylate*, b.p. 76—78°/18 mm. (deliquescent *hydrochloride*). The *gem*-Me_2 thus diminishes the reactivity towards addition across the double linking. D. G.

Phosphorylcholine. E. Baer and C. S. McArthur [with, in part, D. B. Mundell] (*J. Biol. Chem.*, 1944, **154**, 451—460).—Phosphorylation of choline with $(OPh)_2POCl$ in C_5H_5N gives diphenylphosphorylcholine, isolated as the *aurichloride*, m.p. 122—123°, decomposed by Ag to *diphenylphosphorylcholine chloride*, m.p. 133—134° (?), which is catalytically hydrogenated (PtO_2) to phosphorylcholine chloride, isolated as the Ba salt. No secondary reaction products are formed. The rates of hydrolysis of phosphorylcholine (**I**) in acid at 100° and 125° and alkali at 125° are comparable with those of α- and β-glycerophosphoric acid, and glyceric acid-3-phosphoric acid. True and pseudo-choline-esterase do not hydrolyse (**I**). F. R. S.

Tri(hydroxymethyl)aminomethane derivatives. I. Polyhydroxyamines. J. S. Pierce and J. Wotiz (*J. Amer. Chem. Soc.*, 1944, **66**, 879—881).—$(OH·CH_2)_3C·NH_2$ (**I**) (4 mols.) (*hydrochloride*, m.p. 149—150°; *hydrobromide*, m.p. 133—134°) and Br·$[CH_2]_n$·Br (1 mol.) in boiling EtOH give *NN'-di-ββ'β''-trihydroxy*-tert.-*butyl-ethylene-*, m.p. 205—206°, *-propylene-αγ-*, m.p. 170—171°, and *-hexamethylenediamine dihydrobromide*, m.p. 160·5—162°. $OH·CH(CH_2Cl)_2$ (1 mol.) and (**I**) (2 mols.), best in boiling EtOH, give *β-hydroxy-NN'-di-ββ'β''-trihydroxy*-tert.-*butylpropylene-αγ-diamine*, an oil (*dihydrochloride*, m.p. 186—188°; *dihydrobromide*, m.p. 160—162°). $NH([CH_2]_2·OH)_2$ (**II**) (1 mol.) with epichlorohydrin (1 mol.) in EtOH at ~30° (cooling) and then (**I**) (1 mol.) in boiling EtOH gives *β-hydroxy-NN-di-β-hydroxyethyl-N'-ββ'β''-trihydroxy*-tert.-*butylpropylene-αγ-diamine dihydrochloride*, m.p. 139—141°; *β-hydroxy-NNN'N'-tetra-β-hydroxyethylpropylene-αγ-diamine dihydrochloride*, m.p. 98—100°, is similarly obtained by two-stage reaction with (**II**). $NHEt·[CH_2]_2·OH$ leads similarly to *β-hydroxy-N-ethyl-N-β-hydroxyethyl-N'-ββ'β''-trihydroxy*-tert.-*butylpropylene-αγ-diamine dihydrochloride*, a syrup. $(Cl·[CH_2]_3)_2O$ (1 mol.) and (**I**) (2 mols.) in EtOH at 100° give *γγ'-di-(ββ'β''-trihydroxy*-tert.-*butylamino)-n-propyl ether dihydrochloride*, an oil, but $(Cl·[CH_2]_2)_2O$ (1 mol.) and (**II**) (2 mols.) in EtOH at 150° yield *4-ββ'β''-trihydroxy*-tert.-*butylmorpholine hydrochloride*, m.p. 184—185°. $OH·CH_2·CH(OH)·CH_2Cl$ (1 mol.) and (**II**) (2 mols.) in boiling EtOH give *βγ-dihydroxy-n-propyl-ββ'β''-trihydroxy*-tert.-*butylamine hydrochloride*, a syrup; $OH·[CH_2]_2·Cl$ or $OH·[CH_2]_3·Br$ leads similarly to β-hydroxyethyl- (*hydrochloride*, a syrup) and γ-hydroxy-*n*-propyl-ββ'β''-trihydroxy-*tert.*-butylamine (*hydrobromide*, a syrup). Purification of the products is difficult. Many of the bases dissolve $Fe(OH)_3$, $Bi(OH)_3$, and other metal hydroxides. R. S. C.

Synthesis of β-amino-acids. IV. β-Aminononoic acid and its derivatives. V. M. Rodionov and V. A. Zvorkina (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 216—232).—*β-Aminobutyric acid hydrochloride*, m.p. 109·5—110·5°, is obtained from $CH_2(CO_2H)_2$ and MeCHO–NH_3 in EtOH. *β-Aminononoic acid* (**I**), m.p. 205° (*hydrochloride*, m.p. 135·5—136°; *Bz* derivative, m.p. 129·5—131°; *urethane* derivative, m.p. 80°), results in 23% yield from heptaldehyde, $CH_2(CO_2H)_2$, and NH_3 in EtOH. KCNO yields the corresponding *uraminic acid*, (**II**), m.p. 127—128°. The *amide*, m.p. 185—186°, of (**I**) is obtained through $SOCl_2$. With hot HCl (**II**) gives a mixture of *n-hexylhexa-hydropyrimidine* and *-dihydropyrimidine*. V. B.

Manufacture of β-alanine.—See B., 1944, II, 247.

Preparation of *l*-leucyl-*l*-glutamic acid anhydride. Its behaviour towards proteinases. N. Lichtenstein (*J. Amer. Chem. Soc.*, 1944, **66**, 1103—1104).—*dl*-$CHBu^{\beta}Br$·COBr (1·25 mols.) and *l*-glutamic acid (1 mol.) in aq. alkali give a solution whence crystallisation yields *l*-leucyl-*l*-glutamic acid (**I**), $[\alpha]_D^{18}$ +10·2° in N-HCl, converted in β-$C_{10}H_7$·OH at 170—180° into the *anhydride*, m.p. 213—215°, $[\alpha]_D^{18}$ −47·4° in 0·1N-NH_3, which in HCl regenerates (**I**) and is unaffected by a glycerol extract of pancreatin, pancreatic proteinase, or papain. R. S. C.

Configuration of valylvaline in gramicidin. H. N. Christensen (*J. Biol. Chem.*, 1944, **154**, 427—436).—Valylvaline, separated as the free dipeptide and as the Bz derivative under various conditions from gramicidin hydrolysates, is the pure optically inactive *dl* form, *d*(−)-valyl-*d*(−)-valine + *l*(+)-valyl-*l*(+)-valine, since the p-*phenylphenacyl* ester, m.p. 201°, of the Bz derivative is identical with the synthetic *r*-form. The findings indicate that no substantial quantities of the other two possible isomerides are present in the hydrolysates. Hence optically inactive valylvaline could not have arisen by racemisation. These conclusions suggest that *Bacillus brevis* joins together in gramicidin only valines of like configuration. The p-*phenylphenacyl* ester of benzoyl-*d*(−)-valyl-*l*(+)-valine and its optical enantiomorph has m.p. 141—142°; the mixed *Et* ester has m.p. 152°, whilst the *Et* ester of benzoyl-*d*(−)-valyl-*d*(−)-valine and its enantiomorph has m.p. 153°. F. R. S.

Synthesis of tyrosyltyrosyltyrosine and tyrosyltyrosyltyrosyltyrosine. A. E. Barkdoll and W. F. Ross (*J. Amer. Chem. Soc.*, 1944, **66**, 951—956).—*N*-Carbobenzyloxytyrosyltyrosine (**I**), + H_2O (A., 1934, 809), with $CHMeN_2$ gives the *Et* ester (**II**), m.p. 159—160·5°. *N*-Carbobenzyloxy-*O*-acetyltyrosine Et ester (**III**) (*loc. cit.*) with H_2–Pd-black in 0·2N-HCl–EtOH gives *tyrosyltyrosine Et* ester *hydrochloride* (**IV**), m.p. 216° (decomp.), also obtained similarly from (**II**) or from tyrosyltyrosine (**V**) by HCl–EtOH at 0°. Hydrogenation of the *Me* ester (prep. by CH_2N_2–MeOH), m.p. 174—175°, of (**I**) gives *tyrosyltyrosine Me* ester *hydrochloride*, m.p. 210°. With N-NaOH and then Ac_2O–dioxan–H_2O–NaOH, (**III**) gives *N-carbobenzyloxy-O-acetyltyrosyl-O-acetyltyrosine*, m.p. 209—210°, which is converted into an oil by PCl_5, probably owing to attack on the peptide linking. The Et ester of (**V**) [prep. from (**IV**) by $NaHCO_3$ in EtOAc–H_2O] with *N*-carbobenzyloxy-*O*-acetyltyrosyl chloride (**VI**) (modified prep.) in EtOAc gives *N-carbobenzyloxy-O-acetyltyrosyltyrosyltyrosine Et* ester (**VIII**), m.p. 211°, which with, successively, H_2–Pd-black–HCl–EtOH–dioxan, $NaHCO_3$–EtOAc–H_2O, and HCl–EtOAc at 0° give *tyrosyltyrosyltyrosine Et* ester *hydrochloride* (**IX**), m.p. 231—231·5° after darkening and sintering. 1·1N-NaOH hydrolyses (**VII**) to *N-carbobenzyloxytyrosyltyrosyltyrosine*, m.p. 182—183°, whence H_2–Pd-black and a trace of AcOH in MeOH yield *tyrosyltyrosyltyrosine* (**X**), + $2H_2O$, m.p. 181—182° [with HCl–EtOH gives (**IX**)]. N_2H_4 and (**III**) in EtOH give *N-carbobenzyloxytyrosyltyrosine hydrazide*, + H_2O, m.p. 246° (decomp.), which gives only indefinite products with the Et ester of (**V**). Pure (**VI**) with (**VIII**) in EtOAc gives *N-carbobenzyloxy-O-acetyltyrosyltyrosyltyrosyltyrosine Et* ester, m.p. 235·5—236·5°, hydrolysed by N-NaOH to the *acid*, +MeOH, darkens at 220°, m.p. 224—225° (decomp.), whence H_2–Pd-black and a trace of AcOH in MeOH yield *tyrosyltyrosyltyrosyltyrosine* (**XI**), a glass. Tyrosine (**XII**), (**V**), and (**X**) have similar absorption max. (2750, 2760, and 2765 A., respectively) but increasing $E_{max.}$ (1350, 2850, and 4160, respectively). (**XII**) is almost insol., (**V**) and (**X**) are freely sol., but (**XI**) only slightly sol. in H_2O. In EtOH or MeOH solubility increases regularly from the mono- to the tetra-peptide. (**X**) and (**XII**) give ppts. with Millon's reagent. *N-Carbobenzyloxy-O-acetyltyrosine Me* ester [prep. from the acid (**XIII**) by CH_2N_2–MeOH], m.p. 73—74·5°, with H_2–Pd-black in 0·27N-HCl–MeOH gives tyrosine Me ester hydrochloride, but in AcOH gives *O*-acetyltyrosine Me ester [*hydrochloride*, m.p. 201° (decomp.)]. Similarly, H_2–Pd-black converts (**XIII**) in AcOH into *O*-acetyltyrosine [*hydrochloride*, m.p. 223° (decomp.)]. When (**I**) or (**II**) is treated with HCl–EtOH at 0°, esterification is accompanied by partial hydrolysis of the O·CO·O·CH_2Ph, but at the b.p. both reactions are complete; these are general reactions since they occur also with *N*-carbobenzyloxyglycine and its *Et* ester, m.p. 35·5—36·5°. R. S. C.

Synthesis of methionine containing isotopic carbon and sulphur. G. W. Kilmer and V. du Vigneaud (*J. Biol. Chem.*, 1944, 154,

247—253).—$CH_2Ph·^{34}SH$, obtained from CH_2PhCl and ^{34}S (from $Na_2{}^{34}SO_3$), with $CH_2Cl·^{13}CH_2Cl$, obtained from $^{13}CH_2Me·NH_2$ (from $Na^{13}CN$), gives $CH_2Ph·^{34}S·^{13}CH_2·^{13}CH_2Cl$, converted by methods previously described into isotopic methionine, $^{34}SMe·[^{13}CH_2]_2·CH(NH_2)·CO_2H$. F. R. S.

Hydrolysis of tartaramides. M. Badoche (*Compt. rend.*, 1943, **216**, 892—895).—A mechanism is given to explain the non-racemisation of *d*-tartaramide on alkaline hydrolysis, through an intermediate enolamine. A. T. P.

Structure-chemical investigations. XIII. Malondithioamide. H. Lehr, W. Guex, and H. Erlenmeyer (*Helv. Chim. Acta*, 1944, **27**, 970—972).—$CH_2(CN)_2$ is converted by H_2S in EtOH containing KOEt at −10° and then at >50° into *malondithioamide* (**I**), m.p. 212° after decomp., converted by warm CH_2AcCl into *di-4-methyl-2-thiazolylmethane dihydrochloride*, m.p. 221° (decomp.), and by $COPh·CH_2Br$ in warm AcOH into *di-4-phenyl-2-thiazolylmethane*, m.p. 119—120°. With $(CO·CH_2Br)_2$ (**I**) gives a pale yellow, amorphous product which rapidly darkens, possibly denoting the conversion of a chain polymeride, in part at any rate, into a macrocyclic compound. H. W.

Reduction of nitroguanidine. Oxidation potentials of the nitroguanidine–nitrosoguanidine and nitrosoguanidine–aminoguanidine systems.—See A., 1944, I, 251.

Composition and constitution of ethylenebiguanide. K. Chakravarty and P. Ray (*J. Indian Chem. Soc.*, 1944, **21**, 41—43).—Attempts to prepare ethylenebiguanide from $(CH_2·NH_2)_2$,2HCl and dicyanodiamide according to Dittler (A., 1908, i, 924) give ethylenedibiguanide $[CH_2·NH·C(:NH)·NH·C(:NH)·NH_2]_2$ isolated as the *sulphate* $(+1·5H_2O)$. Its constitution is confirmed by the isolation of the *compounds*, $C_6H_{14}N_{10}Cu,H_2SO_4,2·5H_2O$ and $C_6H_{14}N_{10}Cu,2HCl$. F. R. S.

Guanylurea salts.—See B., 1944, II, 248.

Preparation of ethyl monoalkylcyanoacetates by simultaneous condensation–reduction. E. R. Alexander and A. C. Cope (*J. Amer. Chem. Soc.*, 1944, **66**, 886—888).—Simultaneous condensation and hydrogenation (Pd–C; 1—2 atm.) of CORR′ and $CN·CH_2·CO_2Et$ gives, usually, good yields of $CRR′·CH(CN)·CO_2Et$. For aldehydes piperidine acetate and AcOH, and for ketones NH_4OAc–AcOH, are the best condensing agents. For ketones EtOH, for C_{2-4}-aldelydes AcOH, and for other aldehydes dioxan is the best solvent. Use of PtO_2 leads to reduction of CN, and Raney Ni is inactivated by the AcOH. $COPr^n_2$ gives only a 39% yield, and $COBu^\beta_2$ gives an impure product. $CH_2(CO_2Et)_2$ does not react thus. The following are new: *Et α-cyano*-n-*nonoate*, b.p. 111—113°/1 mm., *-βδ-dimethyl*-n-*hexoate*, b.p. 117—119°/8 nm., *-β-methyl*-n-*octoate*, b.p. 135—137°/8 mm., and *-β-methyl*-n-*nonoate*, b.p. 112—115°/1 mm. R. S. C.

Cleavage of (dialkylvinyl)alkylcyanoacetic esters by sodium alkoxides. E. M. Osman and A. C. Cope (*J. Amer. Chem. Soc.*, 1944, **66**, 881—886).—Cleavage of $CHR:CR′·CR″(CN)·CO_2R‴$ by NaOAlk–AlkOH at 30—80° to unsaturated nitriles and alkyl carbonates is very facile owing to the electron-attracting properties of CHR:CHR′ and CN; variation of R″ affects the results as expected from the electronic properties of R″; variation of R‴ has little effect, except that cleavage is slow when R‴ = Me. The reaction is useful for the prep. of unsaturated nitriles, which are obtained mostly in the Δ^α-form. Hydrolysis by KOH–$(CH_2·OH)_2$ gives 49—81% of mixed Δ^α- and Δ^β-acids. Cleavage of malonic ester derivatives is much slower. The following are described. *Et α-cyano-αβ-dimethyl-*Δ^β-n-*pentenoate*, b.p. 106—108°/11 mm., *α-cyano-αβδ-trimethyl-*Δ^β-n-*hexenoate*, b.p. 129—133°/20 mm., *α-cyano-α-methyl-β*-n-*propyl-*Δ^β-n-*hexenoate*, b.p. 128—129°/12 mm., and *α-cyano-αβ-dimethyl-*Δ^β-n-*octenoate*, b.p. 132—136°/12 mm.; *Me*, b.p. 114—116°/8 mm., and *Pr$^\beta$ α-cyano-β-methyl-α-ethyl-*Δ^β-n-*hexenoate*, b.p. 139—142°/23 mm.; *αβ-dimethyl*-n-*pentenonitrile*, b.p. 64°/17 mm., *-n-hexenonitrile*, b.p. 73—77°/14—16 mm., and *-n-octenonitrile*, b.p. 96—98°/9 mm.; *α-methyl-β-ethyl*-n-*pentenonitrile*, b.p. 74—76°/17 mm.; *β-methyl-α-ethyl-* (**I**), b.p. 76—78°/8 mm., *β-methyl-α*-n-*propyl-*, b.p. 98°/14 mm., *β-methyl-α*-iso*propyl-*, b.p. 81—84°/9 mm., *αβδ-trimethyl-*, b.p. 74—76°/9 mm., and *α-methyl-β*-n-*propyl-*, b.p. 88—90°/8 mm., *-n-hexenonitrile*; mixed *αβ-dimethyl-*, b.p. 115—118°/10 mm., *β-methyl-α*-n-*propyl-*, b.p. 131—133°/10 mm., *αβδ-trimethyl-*, b.p. 132—140°/20 mm., and *α-methyl-β*-n-*propyl*-n-*hexenoic*, b.p. 129—133°/9 mm., and *αβ-dimethyl*-n-*octenoic acid*, b.p. 137—140°/10 mm. H_2–Pd–C reduces (**I**) in EtOH to *β-methyl-α-ethyl*-n-*hexonitrile*, b.p. 71—72°/7 mm., hydrolysed, as above, to $CHMePr^\alpha·CHEt·CO_2H$, b.p. 230° (amide, m.p. 96—97°). Adding (**I**) to $NaNH_2$ in C_6H_6 (exothermal) and then boiling gives *β-methyl-α-ethyl-*Δ^α-n-*hexenoamidine* (27—53%), b.p. 99—101°/1 mm., unstable when kept (*picrate*, m.p. 136·5—137·5°). R. S. C.

II.—SUGARS AND GLUCOSIDES.

Starch. XXVII. Preparation of glucose 1-phosphate. P. Bernfeld, C. de Traz, and C. Gautier (*Helv. Chim. Acta*, 1944, **27**, 843—844).—A detailed description is given of the prep. of glucose 1-phosphate, isolated as the K salt, by the enzymic phosphorolysis of starch. H. W.

Isolation of fructose 1-phosphate from biological material [liver].—See A., 1944, III, 743.

Synthesis of *DL*-threose. Preparation of *DL*-erythrose tribenzoate. W. W. Lake and J. W. E. Glattfeld (*J. Amer. Chem. Soc.*, 1944, **66**, 1091—1095).—*DL*-Threonic acid (**I**) (modified prep.) and BzCl in C_5H_5N at ≯ room temp. give DL-*threonolactone dibenzoate* (**II**), m.p. 142·5°. *K* DL-threo-*γ-chloro-αβ-dihydroxybutyrate* (prep. in EtOH) at 180—190°/0·1—0·5 mm. gives DL-*threonolactone* (**III**) (83%), b.p. 151—151·5°/0·5 mm., hydrolysed by H_2O at 70—80° to (**I**) and converted by BzCl–C_5H_5N into (**II**). By the method of Glattfeld *et al.* (A., 1935, 72), (**III**) gives DL-*threonamide*, m.p. 116°, converted by BzCl–C_5H_5N at room temp. into the *tribenzoate*, m.p. 155°. With N_2O_3 in AcOH at 15—20° this gives DL-*threonic acid tribenzoate*, *forms*, m.p. 95—98° and 121°, the *chloride* (prep. by $SOCl_2$), m.p. 113·5°, of which with H_2–Pd–$BaSO_4$ in xylene yields DL-*threose tribenzoate* (**IV**), m.p. 99—99·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 182°). NaOMe–MeOH at −15° or 0·3N-$Ba(OH)_2$ at 0° hydrolyses (**IV**) to *DL*-threose, a syrup [osazone, m.p. 167—168° (darkens; bath preheated at 165°)], which is oxidised by Br to (**I**) [isolated as (**II**)]. Oily *DL*-erythronamide, similarly obtained, gives the *tribenzoate*, m.p. 208°, and thence DL-*erythronic acid tribenzoate*, m.p. 151·5—152°, the *chloride*, m.p. 103·5°, of which does not yield cryst. *DL*-erythrose. M.p. are corr. R. S. C.

Optical activity of the copper complexes of polysaccharides and substituted methylglucosides. R. R. Reeves (*J. Biol. Chem.*, 1944, **154**, 49—55).—The four methyl-*β*-methylglucopyranosides show widely different optical behaviour when dissolved in cuprammonium hydroxide solution (**I**). The optical activity of methyl-2-methyl-*β*-glucoside in H_2O and in (**I**) so closely resembles that of the polysaccharide from *Phytomonas tumefaciens* that it is suggested that this polysaccharide is composed of glucopyranose units linked chiefly through the 2 position. The optical behaviour of a 3-linked polysaccharide and several 4-linked polysaccharides is similar to that of the correspondingly substituted methylglucosides. The shift in the optical rotation of glucopyranoside polysaccharides in (**I**) may be used to classify glucose polysaccharides and furnish information regarding their structure. F. R. S.

Carbanilates of α- and β-methyl-*d*-glucosides. W. M. Hearon, G. D. Hiatt, and C. R. Fordyce (*J. Amer. Chem. Soc.*, 1944, **66**, 995—997).—α- or β-Methyl-*d*-glucoside 2 : 3 : 4-triacetate and PhNCO in C_5H_5N exothermally and then at 90° give α-, m.p. 147—148°, [α] +145° in $CHCl_3$, and *β-methyl*-d-*glucoside* 2 : 3 : 4-*triacetate* 1-*carbanilate*, m.p. 147—148°, [α] +15° in $CHCl_3$, respectively, hydrolysed by 0·5% HCl–MeOH at the b.p. to α-, m.p. 131—133°, [α] +115° in C_5H_5N, and *β-methyl*-d-*glucoside* 1-*carbanilate*, m.p. 144—145°, [α] −9° in C_5H_5N, respectively. 4 : 6-Benzylidene-α- and -β-methyl-*d*-glucoside gives similarly the 2 : 3-*dicarbanilates*, m.p. 216—217°, [α] +40° in $CHCl_3$, and m.p. 247—248°, [α] −50° in $CHCl_3$, hydrolysed by 0·75% HCl–MeOH at the b.p. to α-, m.p. 151—153°, [α] +55° in C_5H_5N (4 : 6-*diacetate*, m.p. 189—190°, [α] +124° in C_5H_5N), and *β-methyl*-d-*glucoside* 2 : 3-*dicarbanilate*, m.p. 219—220°, [α] −103° in C_5H_5N (4 : 6-*diacetate*, m.p. 217—218°, [α] −22° in C_5H_5N), respectively. α- and β-Methyl-*d*-glucoside 6-CPh_3 ether give similarly the 2 : 3 : 4-*tricarbanilates*, m.p. 229—231°, [α] +52° in $CHCl_3$, and m.p. 232—234°, [α] −5° in $CHCl_3$, hydrolysed by 1% HCl–MeOH to α-, m.p. 192—193°, [α] +84° in $CHCl_3$, and *β-methyl*-d-*glucoside* 2 : 3 : 4-*tricarbanilate*, m.p. 234·5°, [α] +6° in C_5H_5N. [α] are $[\alpha]_D^{25}$. R. S. C.

Hydrolysis of maltohexaose and the products obtained thereby, principally maltotriose. K. Myrbäck and E. Leissner (*Arkiv Kemi, Min., Geol.*, 1944, **17**, **A**, No. 18, 22 pp.).—The concn. of the products of the hydrolysis of maltohexaose at time *t* is calc. on the following assumptions: (*a*) that all glucosidic linkings independent of the position and no. of the saccharide linkings are attacked at the same rate, (*b*) that the glucosidic linkings of the disaccharide are attacked with a velocity k_2 and all other linkings with a different velocity k_1, (*c*) that a terminal linking of all saccharides is resolved at a rate k_1 and all other linkings at a rate k_2, (*d*) that all linkings of a saccharide with *n* units are resolved at the same rate k_n, whereby $k_n = Ck_{n+1}$; calculation is made for the special case in which $C = 1·2$. In hydrolysates of this kind the sum of monosaccharide (glucose) (**I**) + disaccharide (maltose) (**II**) is customarily determined by fermentation. In such a hydrolysate (**I**) is not determined and from its amount the concn. of the remaining hydrolytic products is calc. on the above assumptions. It is found, however, that maltotriose (**III**) in addition to (**I**) and (**II**) is fermentable. It is therefore possible that the composition of starch hydrolysates in which (**I**) and (**II**) have been determined by fermentation differs markedly from that which has been assumed. (**III**), like (**II**), is not attacked by amylase. H. W.

Sugar in the cerebroside of the spleen in Gaucher's disease.—See A., 1944, III, 755.

Constitution of the tannin from Indian teripods. H. G. Biswas (*J. Indian Chem. Soc.*, 1944, **21**, 32—34).—Extraction with EtOH

of the pod cases of *Caesalpinia digyna* yields a *tannin*, m.p. 205—212° (decomp.), which on hydrolysis yields gallic acid and glucose. Acetylation (Ac_2O–C_5H_5N at room temp.) gives a *nona-acetate*, m.p. 206—208° (decomp.). The hydrolysis data are in fair agreement with the tannin being monodigalloylglucose. C. R. H.

Catalposide, the heteroside of *Catalpa* fruits. H. Colin, G. Tanret, and (Mlle.) M. Chollet (*Compt. rend.*, 1943, **216**, 677—679).—Catalposide, softens ~160°, m.p. 165°, resolidifies, darkens at ~190°, remelts 212° (block), $[\alpha]_D^{15}$ −149° (anhyd.) in H_2O, is hydrolysed by H_2SO_4 or emulsin to *β-d*-glucose and an unstable aglucone. R. S. C.

Lead tetra-acetate oxidations in the sugar group. VIII. Preparation and proof of structure of *N*-acetyl-*D*-glucofuranosylamine. R. C. Hockett and L. B. Chandler (*J. Amer. Chem. Soc.*, 1944, **66**, 957—960; cf. A., 1944, II, 214).—*aldehydo-D*-Glucose pentaacetate (I) in 29% aq. NH_3 at 50—60° gives *acet*-D-*glucofuranosylamide* (II), m.p. 189—191° (decomp.), $[\alpha]_D^{22\cdot4}$ +86·7° → +85·8° in H_2O in 10 days, converted by Ac_2O–C_5H_5N at 75—80° or Ac_2O–NaOAc at 90° into the *amide tetra*-O-*acetate*, m.p. 82·5—84·5°, $[\alpha]_D^{25}$ +32·7° in $CHCl_3$, which could not be obtained from (I) by NH_2Ac. *D-α-Glucoheptoseoxime*, m.p. 100—101°, $[\alpha]_D^{22}$ −6·3° → 0·9° in $CHCl_3$ in 70 hr., with Ac_2O–NaOAc at 100° gives *D-α-glucoheptonitrile hexa-acetate*, m.p. 85·5—87·5° (lit. 112·5—113·5°, $[\alpha]_D^{24\cdot8}$ +24·3° in $CHCl_3$), whence 29% aq. NH_3 at 50° gives (II), m.p. 192—194°. With $Pb(OAc)_4$, (II) gives an oxidation curve of type IV with production of CH_2O. Attempts to prepare *D*-xylose diacetamide and cryst. *D*-guloseoxime or *D*-gulonitrile pentaacetate failed. The mechanism of formation of NHAc-derivatives of sugars is discussed. R. S. C.

Chemistry of tissues. I. Chondroitin from cartilage. H. G. Bray, J. E. Gregory, and M. Stacey (*Biochem. J.*, 1944, **38**, 142—146).—Chondroitin sulphate (I), isolated from bovine nasal septa and bovine and human trachea, is degraded and methylated to a sulphate-free product of low mol. wt. The amide of 2 : 3 : 4-trimethyl-α-methylglucuronoside and 3 : 4 : 6-trimethyl-*N*-acetyl-α-methylchondrosaminide are isolated from an acid hydrolysate. (I) has a branched chain structure of glucuronic acid and chondrosamine residues. Some of the glucuronic acid units are terminal groups which are combined by glycosidic linkings through their $C_{(1)}$ atom. R. L. E.

Adsorption of fatty acid by the linear component of corn starch. T. J. Schoch and C. B. Williams (*J. Amer. Chem. Soc.*, 1944, **66**, 1232—1233).—Extracting commercial maize starch with 81% aq. dioxan increases its I-affinity from 4·1—4·4% to 5·3%; the fatty acid is selectively adsorbed on the linear components (*A*), thus reducing the I-affinity. Heating 2% defatted maize starch paste (3 l.) in an autoclave, adding oleic acid (200 ml), and cooling slowly gives a 29% yield of *A* as a microcryst. floc having I-affinity 14·5% after extraction by MeOH; the non-pptd., branched chain has, after extraction, I-affinity <0·2%. The purest *A* has I-affinity 19·0%, whence it is calc. that defatted maize starch contains 28% of *A*. R. S. C.

Mol. wt. of cellulose. Measurements of average degree of polymerisation. O. A. Battista (*Ind. Eng. Chem.* [*Anal.*], 1944, **16**, 351—354).—Data on η and concn. are given for five samples of purified cellulose covering a degree of polymerisation from 300 to 3000. A plot of log η/c against c, and of the log of the relative η function at 0·5% concn. against degree of polymerisation, give straight lines. The data have been used to derive a mathematical expression by means of which the val. of the η function at 0·5% concn. may be converted to degree of polymerisation data equiv. to vals. obtained by extrapolation of η–concn. data to infinite dilution. J. D. R.

Form and mobility of cellulose molecule.—See A., 1944, I, 240.

III.—HOMOCYCLIC.

Acetylene derivatives in the C_6 alicyclic series. M. Mousseron (*Compt. rend.*, 1943, **217**, 155—157).—The optical activity of methyl*cyclo*hexane, substituted in the 3-position by groups containing C:C, is increased by the C:C (notably when distant from the ring), by the lengthening of the C side-chain (for a fixed (C:C); the *cis*- has a higher rotation than the *trans*-isomeride. The presence of an intranuclear double linking in the corresponding *cyclo*hexenes also raises the optical activity. The *cis*-, b.p. 58°/25 mm., $[\alpha]_{546}$ −6·3°, and *trans*-, b.p. 60°/25 mm., $[\alpha]_{546}$ −3·45°, -3-acctylenyl, *cis*-, b.p. 75°/25 mm., $[\alpha]_{546}$ −7·6°, and *trans*-, b.p. 77°/25 mm., $[\alpha]_{546}$ −4·45°, -Δ$^{\alpha}$-propinenyl, *cis*-, b.p. 74°/25 mm., $[\alpha]_{546}$ −8·35°, and *trans*-, b.p. 78°/25 mm., $[\alpha]_{546}$ −4·72°, -Δ$^{\beta}$-propinenyl, *cis*-, b.p. 94°/25 mm., $[\alpha]_{546}$ −11·87°, and *trans*-, b.p. 98°/25 mm., $[\alpha]_{546}$ −6·71°, -Δ$^{\beta}$-butinenyl, and *trans*-3-Δ$^{\alpha}$-, b.p. 95°/25 mm., $[\alpha]_{546}$ −5·3°, and -Δ$^{\gamma}$-, b.p. 92°/25 mm., $[\alpha]_{546}$ −7·74°, -butinenyl derivatives of methyl*cyclo*hexane are described. 1-Methyl-3-acetylenyl- and -3-Δ$^{\alpha}$-propinenyl-Δ^{3}-*cyclo*hexene have $[\alpha]_{546}$ +75·2° and +88·4°, respectively. Me 3-methyl-*cyclo*hexyl-butinenoate, b.p. 155°/25 mm., $[\alpha]_{546}$ −6·92° (free acid, $[\alpha]_{546}$ −7·63°), and -pentinenoate, b.p. 175°/25 mm. $[\alpha]_{546}$ −9·47°, are prepared. F. R. S.

Sulphonic acids of aromatic compounds.—See B., 1944, II, 274.

Sulphonation of phenylpropylenes. C. M. Suter and W. E. Truce (*J. Amer. Chem. Soc.*, 1944, **66**, 1105—1109).—Adding CPhMe:CH_2 (0·94 mol.) to dioxan (2·0), SO_3 (1·69 mols.), and $(CH_2Cl)_2$ (400 g.) at 20—25°, keeping at 5°, and adding to aq. $Ba(OH)_2$ gives *Ba β-phenylpropene-αγ-disulphonate* (reduces $KMnO_4$ and decolorises aq. Br) and thence the *di*-S-p-*chlorobenzylthiuronium* salt (I), m.p. 215—217°. Adding CPhMe:CH_2 (54) to SO_3 (85), dioxan (176), and CCl_4 (500 g.) at 10—15° gives the corresponding *dioxan* salt (II) and thence the Na_2 salt. At 0° much monosulphonic acid is also formed. Treating (II) with PCl_5 in $(CH_2Cl)_2$ at the b.p. and then room temp., removing HCl by H_2O, and adding liquid NH_3 gives *β-phenylpropene-αγ-disulphonamide*, m.p. 197—200°. OH·CPh$(CH_2Cl)_2$ [prep. from $CO(CH_2Cl)_2$ by MgPhBr] and Na_2SO_3 in H_2O at 100° give β-hydroxy-β-phenylpropane-αγ-disulphonic acid (*di*-S-p-*chlorobenzylthiuronium* salt, m.p. 164—166°), the Na_2 salt of which with Ac_2O at about the b.p. or with $POCl_3$–PCl_5 at 75° and then hot aq. NaOH etc. yields (I). CH_2Ph·CH:CH_2 with SO_3, dioxan, and $(CH_2Cl)_2$ at <20° and then aq. $Ba(OH)_2$ gives *Ba β-hydroxy-γ-phenylpropane-α-sulphonate* (III) (derived S-p-*chlorobenzylthiuronium* salt, m.p. 156—158°) [and a resin (see below)], which with aq. $KMnO_4$ at 100° gives BzOH, does not decolorise aq. Br, and with PCl_5–$(CH_2Cl)_2$ at 100° and then NH_3 gives *γ-phenyl-Δ$^{\alpha}$-propene-α-sulphonamide*, m.p. 65—67°. CHPh:CH·CH_2Cl (IV) with, successively, Na_2SO_3, PCl_5–$(CH_2Cl)_2$, and NH_3 gives *α-phenyl-Δ$^{\alpha}$-propene-γ-sulphonamide*, m.p. 126—127°. The Na_2 salt derived from (III) is converted by Ac_2O at 120° into *Na β-acetoxy-γ-phenylpropane-α-sulphonate* (V), m.p. 171—174°, which at 210—215° yields AcOH and *Na α-phenyl-Δ$^{\alpha}$-propene-γ-sulphonate* [derived S-p-*chlorobenzylthiuronium* salt (VI), m.p. 196—198°], also obtained from (IV) by Na_2SO_3. CH_2Ph·CH:CH_2 and aq. Br–KBr at 90° give CH_2Ph·CH(OH)·CH_2Br (70%), converted by Na_2SO_3 and then Ac_2O into (V). (VI) is also obtained from the resin accompanying (III). CHPh:CHMe with SO_3, dioxan, and $(CH_2Cl)_2$ at 15—20° and then aq. $Ba(OH)_2$ gives impure Ba α-phenyl-Δ$^{\alpha}$-propene-β-sulphonate (with $KMnO_4$ gives BzOH) and thence the *Na* (VII), +H_2O, m.p. ~180°, and S-p-*chlorobenzylthiuronium* salt, m.p. 162—163°. At 230° (VII) gives CH_2Ph·CH:CH_2 + Na_2SO_4 and with PCl_5–CCl_4 and then NH_3 gives *α-phenyl-Δ$^{\alpha}$-propene-β-sulphonamide* (VIII), m.p. 138—139°. CHPh:CHMe with aq. Br or HOCl gives mixtures. CHMeBr·CHPh·OH (from COPh·CHMeBr) with hot aq. Na_2SO_3 gives *Na α-hydroxy-α-phenylpropane-β-sulphonate*, decomp. >250° (derived *S*-p-chlorobenzylthiuronium salt, m.p. 184—185°), and thence by PCl_5 etc. yields (VIII). R. S. C.

Addition products of dienes to toluene. B. A. Arbusov and E. V. Kuznetzov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 311—313).—Butadiene (I), PhMe, and finely-dispersed Na at 90°/5 atm. for 10 hr. yield an oil, b.p. 80—220°/16 mm., which affords four *adducts*, viz., from 1 mol. of PhMe and 1, 2, 3, or 4 mols. of (I), of b.p. 92—94°, 140—142°, 188—191°, and 210—220°, all at 16 mm., and yields (based on above oil) of 50, 27, 20, and 3%, respectively. The 1 : 1 adduct, α-phenyl-Δ$^{\gamma}$-pentene, is cyclised by 90% H_2SO_4 (method: Bogert *et al.*, A., 1929, 642) to 1-methyltetrahydronaphthalene, b.p. 153—155°/55 mm., dehydrogenated by S to 1-$C_{10}H_7$Me. The 1 : 2 adduct, ι-phenyl-Δ$^{\beta\zeta}$-nonadiene, similarly gives a hydrogenated ethylbenznaphthalene or hydrogenated methylphenanthrene, but the structure is not clear, and attempted dehydrogenation affords no pure compound. Tetrahydronaphthalene and (I) give 15% of an adduct, b.p. 140—142°/16 mm., probably a methylbenznaphthalene, cyclised to a substance, b.p. 148—150°/16 mm. Δ$^{\beta\delta}$-Hexadiene and PhMe with Na at 70° in an autoclave (10 hr.) give *ζ-phenyl-ε-methyl-Δ$^{\gamma}$-hexene*, b.p. 106—110°/16 mm. A. T. P.

Photochemical processes in aromatic compounds.—See A., 1944, I, 255.

***o*-Substituted diphenyls.** S. H. Zaheer and S. A. Fasech (*J. Indian Chem. Soc.*, 1944, **21**, 27—28).—2-Chloro- (I), -bromo-, -iodo- (II), and -cyano- have been prepared (Sandmeyer) from 2-aminodiphenyl. An 80% yield of *o*-C_6H_4Ph·MgI is obtained from (II) and flaked Mg in boiling Et_2O–H_2. *o*-C_6H_4Ph·MgCl (32% yield) is formed from Mg and (I) in an evacuated sealed tube at 210—215°/6 hr. C. R. H.

Dissociation of hexa-arylethanes. XVI. Alkyl and halogen derivatives. C. S. Marvel, H. W. Johnston, J. W. Meier, T. W. Mastin, J. Whitson, and C. M. Himel (*J. Amer. Chem. Soc.*, 1944, **66**, 914—918; cf. 1944, II, 217).—*p*-Bu$^{\gamma}$ has a remarkable promoting effect on the dissociation of C_2Ar_6. The following % of dissociation in C_6H_6 are determined magnetometrically (m.p. in parentheses are those of derived *peroxides*): tetra-*m-cyclo*hexylphenyldi-*p*- (m.p. 169—170°) 39, tetra-*p-cyclo*hexyldi-*m*- 16, and di-*p-tert.*-butylphenyltetra-*m-cyclo*hexylphenylethane (m.p. 163—164·5°) 20; di-*m*- (m.p. 185—186°) 33—42 and di-*o*-tolyl- (m.p. 159—161°) 65—68, di-*m*- 38—40 and di-*o*-bromophenyl-tetra-*p-tert.*-butylphenylethane 94; diphenyltetra-*p*- 5·3—7·6, tetraphenyldi-*m*- (m.p. 173—174°) 4—5·8, diphenyltetra-m- (m.p. 169—170°) 3·9—5·5, and hexa-*p*-fluorophenylethane 3·8; [*m*-C_6H_4Me·C(C_6H_4Me-*p*)$_2$]$_2$ 2·1%. Boiling *p*-$C_6H_4Bu^{\gamma}$·CO_2H (prep. from *p*-$C_6H_4Bu^{\gamma}$·MgBr), EtOH, C_6H_6, and H_2SO_4 in a Soxhlet apparatus over $CaCl_2$ give the *Et* ester (I)

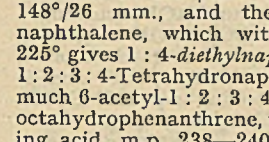
(75%), b.p. 120—120·5°/4 mm. Heating *p*-amino*cyclo*hexylbenzene and a little Zn dust in AcOH with continuous removal of H_2O gives the NHAc-compound, m.p. 129—130°, which with Fe and Br in AcOH at 30—40° (exothermic) gives 2-bromo-4-*cyclo*hexylacetanilide (71·5%), m.p. 122—123°, hydrolysed by EtOH–conc. HCl to the NH_2-compound, the hydrochloride, m.p. 207° (decomp.), of which gives (diazo-reaction; HPO_2) m-*bromo*cyclo*hexylbenzene* (**II**) (79%), b.p. 122—123°/4 mm. Adding Br to $PhBu^{\gamma}$ and a little Fe powder at 0—5° gives *p*-$C_6H_4Bu^{\gamma}Br$ (75%), b.p. 80—81°/2 mm. *p*-$C_6H_4Bu^{\gamma}\cdot NO_2$ and H_2–Raney Ni give *p*-$C_6H_4Bu^{\gamma}\cdot NH_2$, b.p. 90—93°/3 mm. Prep. as for (**II**) yields m-*bromo*-p-tert.-*butylbenzene*, b.p. 222—223°/740 mm. Grignard reaction yields m-cyclo*hexylbenzoic acid*, m.p. 120—121°; esterification as for (**I**) yields its *Et* ester, b.p. 137—139°/3 mm., and other esters required for preps. below. *m*-$C_6H_4Me\cdot MgBr$ and (**I**) give, after conversion into the Et ether, *di*-m-*tolyl*-p-tert.-*butylphenylcarbinol* (67%), m.p. 79—80°, and similar preps. yield o-*tolyldi*-p-tert.-*butylphenylcarbinol*, m.p. 129·5—130°, o-*bromophenyldi*-p-tert.-*butylphenylcarbinol*, m.p. 136·5—137°, *phenyldi*-p-*fluorophenylcarbinol*, m.p. 100°, (p-$C_6H_4F)_3C\cdot OH$, m.p. 94°, *diphenyl*-m-*fluorophenylcarbinol*, m.p. 117°, *phenyldi*-m-*fluorophenylcarbinol*, m.p. 114—114·5°, *tri*-m-*fluorophenylcarbinol*, m.p. 118·5—119°, and m-*tolyldi*-p-*tolylcarbinol*, m.p. 95—96°; other carbinols required for preps. below were oils. AcCl in C_6H_6 converts the appropriate carbinols into *phenyldi*-p-, m.p. 50—51°, and -m-*chlorophenyl*-, m.p. 57—59°, *di*-m-cyclo*hexylphenyl*-p-cyclo*hexylphenyl*-, m.p. 151—152°, and *di*-p-cyclo*hexylphenyl*-m-cyclo*hexylphenyl*-, m.p. 172—173°, *di*-m-cyclo*hexylphenyl*-p-tert.-*butylphenyl*-, m.p. 133—134°, *di*-m-tert.-*butylphenyl*-p-cyclo*hexylphenyl*-, m.p. 127—129°, o-, m.p. 171—172°, and m-*tolyldi*-p-tert.-*butylphenyl*-, m.p. 132—133°, o-, m.p. 135—136°, and m-*bromophenyldi*-p-tert.-*butylphenyl*-, m.p. 144—145°, *diphenyl*-m-*fluorophenyl*-, m.p. 84—84·5°, *phenyldi*-m-*fluorophenyl*-, m.p. 72·5—73°, *tri*-m-*fluorophenyl*- (prep. in EtOAc), m.p. 92—93°, *tri*-m-*chlorophenyl*-, m.p. 90—92°, and m-*tolyldi*-p-*tolyl*-, m.p. 67—69°, -*methyl chloride*. R. S. C.

Thiocarbonyls. I. Condensation of thioacetophenone with activated nickel. J. K. Cline, E. Campaigne, and J. W. Spies (*J. Amer. Chem. Soc.*, 1944, **66**, 1136—1137).—Trithioacetophenone, m.p. 121—122·1° (corr.), and Raney Ni in xylene–N_2 at 145—150° give, by "Wurtz" reaction, *trans*-$(CPhMe:)_2$ (18%) (cf. Mozingo *et al.*, A., 1943, II, 293). Cu is ineffective. R. S. C.

Synthesis of eudalene. R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **20**, 393—398).—*o*-$C_6H_4Me\cdot CH_2\cdot CH(CO_2Et)_2$ with $CH_2Br\cdot CO_2Et$ in cold EtOH–NaOEt gives *Et* γ-o-*tolylpropane-αββ-tricarboxylate*, b.p. 186°/5 mm., which on hydrolysis and loss of CO_2 yields o-*methylbenzylsuccinic acid*, m.p. 172° (previous shrinking) (anhydride, b.p. 270°/50 mm.; *anilic acid*, m.p. 157—158°; *anil*, m.p. 114°). Cyclodehydration (H_2SO_4) then gives 1-*keto*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-3-*carboxylic acid* (**I**), m.p. 164° (*semicarbazone*, m.p. 255°), reduced (Clemmensen) to 5-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-3-*carboxylic acid*, m.p. 132° [*Et* ester (**II**), b.p. 132°/4 mm.]. (**II**) with excess of MgMeI gives the 5-*methyltetrahydronaphthyldimethylcarbinol*, b.p. 145°/5 mm., dehydrogenated (Se at 230—300° for 24 hr.) to eudalene, b.p. 112°/6 mm. (styphnate, m.p. 120°). The structure of (**I**) was confirmed by independent synthesis as follows: 4-methyl-1-hydrindone [*semicarbazone*, decomp. 260°; phenylhydrazone, m.p. 139° (decomp.) (lit. 133°)] (improved prep. from β-*o*-tolylpropionic acid) with HCO_2Et in presence of Na gives the unstable 2-OH·CH: derivative, which after successive treatment with AcOH–NH_2OH,HCl at 70° and aq. EtOH–KOH gives β-3-*carboxy*-o-*tolylpropionic acid*, m.p. 172° [Et_2 ester (**III**), b.p. 150°/5 mm.]. (**III**) with Na in C_6H_6 followed by $CH_2Br\cdot CO_2Et$, and subsequent alkaline hydrolysis gave γ-3-*carboxy*-o-*tolylpropane*-αβ-*dicarboxylic acid*, m.p. 217—218°, the Et_2 ester, b.p. 178°/4 mm., of which yields (**I**) after treatment with Na followed by acid hydrolysis. J. N. A.

Jacobsen rearrangement. VIII. Cyclic systems. Mechanism. R. T. Arnold and R. A. Barnes (*J. Amer. Chem. Soc.*, 1944, **66**, 960—964; cf. A., 1941, II, 6).—A mechanism for the Jacobsen reaction, in which resonance plays a decisive rôle, is proposed. In H_2SO_4, 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene gives 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene, but 5 : 6-tetramethylenehydrindene (**I**) gives 5 : 6-benzhydrindene [2 : 3-trimethylenenaphthalene]. In H_2SO_4 2 : 3- gives 1 : 2-, but with $AlCl_3$ at 100° and then room temp. gives 1 : 3-diethyl-5 : 6 : 7 : 8-tetrahydronaphthalene, structures being proved by dehydrogenation by Pd–C at 200—240° to the appropriate $C_{10}H_6Et_2$. In H_2SO_4 5-*methyl*-6-*ethylhydrindene* (**II**) (see below) gives a 4 : 6- but with $AlCl_3$ gives a 4 : 6-dialkylhydrindene, structures being proved by oxidation. With H_2SO_4 5 : 6-*trimethylenehydrindene* (**III**) (see below) gives a tar but with $AlCl_3$ gives a 5 : 6-trimethylene-4-alkyl- and 4 : 7-dialkyl-hydrindene, structures being proved by oxidation to benzenecarboxylic acids. 5-Chloromethylhydrindene (**IV**) with H_2–Pd–$BaSO_4$ (or –PtO_2) in EtOH at 45—50 lb. gives 5-methylhydrindene, b.p. 86—88°/19 mm., converted by Ac_2O and $AlCl_3$ in $PhNO_2$ at 30° into 6-acetyl-5-methylhydrindene, b.p. 152—158°/11 mm., which with HNO_3 gives 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$ and with Zn–Hg–HCl–H_2O–AcOH gives (**II**), b.p. 112—116°/11 mm. Hydrindene, $(EtCO)_2O$, and $AlCl_3$ in $PhNO_2$ give 5-*propionylhydrindene* (**V**), b.p. 159°/12 mm. (*oxime*, m.p. 95—96°). $CHNa(CO_2Et)_2$ and (**IV**) in EtOH give Et_2 5-*hydrindenylmalonate*, b.p. 158—165°/3 mm., and thence β-5-*hydrindenylpropionic acid* (91%), m.p. 82—84°, also obtained (m.p. 85—86°) from (**V**) by H_2–S–NH_3–H_2O at 150—155°. PCl_5 in C_6H_6 then yields the acid chloride, converted by $SnCl_4$–C_6H_6 into 5 : 6-*benzhydrind*-1-*one*, whence HCl–Zn–Hg–AcOH–H_2O–PhMe yields (**III**), m.p. 52—54°, b.p. 116—120°/9 mm. (**I**) gives a 4 : 7-Br_2-derivative, m.p. 141·5—142·5°. $CPhEt{:}CH\cdot CO_2Et$ with H_2–Cu chromite at 250°/2800 lb. yields $CHPhEt\cdot[CH_2]_2\cdot OH$, b.p. 145—148°/26 mm., and thence 1-keto-4-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which with MgEtBr–Et_2O and then Pd–C–CO_2 at 225° gives 1 : 4-*diethylnaphthalene*, m.p. 16·5—17°, b.p. 165°/25 mm. 1 : 2 : 3 : 4-Tetrahydronaphthalene with Ac_2O and $AlCl_3$ in CS_2 gives much 6-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene and some 9-acetyloctahydrophenanthrene, m.p. 50·5—51·5° (oxidised to the corresponding acid, m.p. 238—240°). Octahydroanthracene with Ac_2O and $AlCl_3$ in cold $(CHCl_2)_2$ gives the 9-*Ac* derivative, m.p. 72—72·5°, b.p. 169°/3 mm., converted by aq. KOCl into the 9-*CCl*$_3$·*CO* derivative, $+H_2O$, m.p. 123·5—124·5°. The picrate of 2 : 3-$C_{10}H_6Et_2$ has m.p. 126—128°. R. S. C.

Constitution of "cyclised" vitamin-*A*. P. Meunier, R. Dulou, and (Mlle.) A. Vinet (*Compt. rend.*, 1943, **216**, 907—908).—The following structure is assigned to "cyclised" vitamin-*A* ("axerophthene") (**I**). Vitamin-*A* and PBr_3 in C_5H_5N at 0°, then KI in boiling $COMe_2$ (method: Kuhn *et al.*, A., 1934, 395), give a compound identical in properties with (**I**), and ozonisation affords CH_2O, thus supporting the terminal CH_2. A. T. P.



Direct aromatic amination: reaction of hydroxylamine-*O*-sulphonic acid. R. N. Keller and P. A. S. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 1122—1124).—$NH_2\cdot O\cdot SO_3H$–$AlCl_3$, HN_3 in light, or HN_3–$AlCl_3$ aminates the C_6H_6 ring of aromatic compounds, the active agent being NH or NH_2^+. NH_3, N_2H_4, and/or NH_2OH are formed as by-products. $NH_2\cdot O\cdot SO_3H$–$AlCl_3$ at 95—105° converts PhMe into (mainly *p*-)toluidine (30—51%), C_6H_6 into NH_2Ph (28%), *o*-xylene into *o*-4- + *o*-3-xylidine (21%), *m*-xylene into *m*-4-xylidine (16%), *p*-xylene into *p*-xylidine (13%), PhCl into *o*- + *m*- + *p*-$C_6H_4Cl\cdot NH_2$ (2·3%), $PhNO_2$ into *m*-$NO_2\cdot C_6H_4\cdot NH_2$ (~1%), and PhOMe into $OMe\cdot C_6H_4\cdot NH_2$ (a trace). HN_3 converts PhMe in ultra-violet light at 15±2° into toluidine (a little); HN_3–$AlCl_3$ gives mixed (mainly *p*- + *o*-)toluidine; $PhNO_2$ gives, by either method, a trace of amine. $AlCl_3$ and HN_3 in $(CHCl_2)_2$ or light petroleum at room temp. give much NH_3 or N_2H_4, respectively. R. S. C.

Separation of 3-nitro-1- and 4-nitro-2-naphthylamine by maleic anhydride, and monobromination of 4-nitro-2-naphthylamine. H. H. Hodgson and D. E. Hathway (*J.C.S.*, 1944, 385—387; cf. A., 1944, II, 127).—4 : 2- (**I**), new m.p. 98·5° (*p-nitrobenzoyl*, m.p. 169°, and *azo-β-naphthol* derivative, m.p. 240°), and 3 : 1-$NO_2\cdot C_{10}H_6\cdot NH_2$ (**II**) are separated by preferential acylation of (**I**) by $(CH\cdot CO)_2O$ (**III**) to give 4-*nitro*-2-*naphthylmaleamic acid* (**IV**), m.p. 193°. Further additions of (**III**) give mixtures, followed by pure 3-*nitro*-1-*naphthylmaleamic acid*, m.p. 170°. (**IV**) is hydrolysed to (**I**) by boiling aq. EtOH–H_2SO_4. A thermal analysis diagram is constructed to determine the requisite amount of (**III**); the eutectic (73°) is 65 : 35 of (**I**) : (**II**). (**I**) is only monobrominated by >2 equivs. of Br in $CHCl_3$ to 1-*bromo*-4-*nitro*-2-*naphthylamine*, m.p. 153° (*Ac* derivative, m.p. 177°), convertible (diazo-reaction) into 1 : 4-$C_{10}H_6Br\cdot NO_2$, new m.p. 87°. 1 : 3-$C_{10}H_6(NO_2)_2$ and aq. $Na_2S_2O_4$ (≡ monoreduction) give 50% unchanged + 50% of 1 : 3-$C_{10}H_6(NH_2)_2$. A. T. P.

Phenylthiocarbamides. Contribution to the study of the triad –N·C·S–. XIV. Mechanism of desulphurisation. XV. Action of copper acetate on phenylthiocarbamide. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1944, **21**, 63—66, 67—70).—XIV. A new mechanism for desulphurisation is put forward. Reaction is probably initiated by the formation of mol. compounds of thiocarbamides with metal hydroxides, etc., through co-ordination at S. A second mobile H (from N to S) is essential.

XV. At ordinary temp. $Cu(OAc)_2$ with $NHPh\cdot CS\cdot NH_2$ (**I**) gives Hector's base and the simultaneously formed CuOAc forms a complex with more (**I**). In boiling solutions, desulphurisation to NHPh·CN also takes place even in presence of considerable [AcOH]. F. R. S.

Structure and activity of sulphanilamides.—See A., 1944, III, 694.

Resolution and properties of the *meso*-form of αβ-diamino-α-phenylpropane. W. Froentjes and K. M. Dijkema (*Rec. trav. chim.*, 1943, **62**, 722—728).—$NH_2\cdot CHPh\cdot CHMe\cdot NH_2$ is separated by fractional crystallisation of the Ni tetrammine perchlorates into the *meso*- (**I**), b.p. 111—112°/9 mm. (yellow salt), and *r*-form, b.p. 109—110°/9 mm. (blue salt; picrate, m.p. 233°). (**I**) is resolved by crystallisation of the *d*- and *l*-ditartrates from MeOH. The d- and l-*bases* (+2H_2O) (*sulphates*; picrates, m.p. 222°) have equal, opposite rotations in Et_2O and as ions in H_2O, but in the pure state the *d*-, *e.g.*, $[\alpha]_{5893}$ +4·2°, has a much lower val. than the *l*-form, $[\alpha]_{5893}$ −46°. Other vals. of [α] and rotatory dispersion curves are given. D. G.

Preparation and diazotisation of *p*-aminomonomethylaniline. H. H. Hodgson and E. Marsden (*J.C.S.*, 1944, 398—400).—Hantzsch's failure to diazotise *p*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$ (I) (cf. A., 1902, i, 324) was apparently due to the presence of some *p*-$C_6H_4(NH_2)_2$, which catalyses the decomp. of diazo-compounds, and originates during the reduction of *p*-$NO{\cdot}C_6H_4{\cdot}NHMe$ (II) with Zn–AcOH, by fission of Me. Reduction of (II) or *p*-$NO_2{\cdot}C_6H_4{\cdot}NHMe$ with Fe and a little $FeSO_4$ or $Fe(NH_4)_2(SO_4)_2$ in boiling H_2O (1 hr.) gives (I) (*picrate*, m.p. 206°), with no rupture of Me. (I) is diazotised by <1 equiv. of HNO_2, added to excess of 10% aq. NaOH, unchanged (I) collected, and the filtrate coupled with β-$C_{10}H_7{\cdot}OH$ to give p-*methylaminobenzeneazo-β-naphthol* (III), m.p. 123° (*hydrochloride*, m.p. 197—202°), also obtained from *p*-$NAcMe{\cdot}C_6H_4{\cdot}N_2Cl$ and β-$C_{10}H_7{\cdot}OH$, followed by hydrolysis with boiling aq. HCl–EtOH. Similarly prepared from (I) and <1 mol. of HNO_2 are *p*-$C_6H_4X{\cdot}NHMe$ (X = Cl, Br); where X = I, the derivative is unstable and is converted into *p-iodo-*N*-nitrosomethylaniline*, m.p. 112°. (I) with >2 mols. of HNO_2, followed by alkaline β-$C_{10}H_7{\cdot}OH$, yields *p*-N-*nitrosomethylaminobenzeneazo-β-naphthol*, m.p. 178°, also obtained from (III) and HNO_2. A. T. P.

Azoxysulphones; preparation and properties, and observations on the structure of diazotates. W. V. Farrar and J. M. Gulland (*J.C.S.*, 1944, 368—371).—Chloramine-*T* (I) and ArNO yield azoxysulphones, regarded as resonance hybrids (cf. II and IIa). Thus, (I) and PhNO

(II.) $ArN(O)N{\cdot}SO_2{\cdot}C_6H_4Me\text{-}p$ $\leftrightarrow$ $ArN^{+}(O^{-}){=}N{\cdot}SO_2{\cdot}C_6H_4Me\text{-}p$ (IIa.)

in C_5H_5N at room temp. for 12 hr., then at 80° for 2 hr., afford *Ph* p-*tolyl azoxysulphone* (III), m.p. 112—113°. Similarly (I) and the appropriate ArNO yield the pale yellow o-*tolyl* p-*tolyl*, m.p. 82°, *di*-p-*tolyl*, m.p. 106°, and m-*nitrophenyl* p-*tolyl*, m.p. 122·5—124°, and the bright yellow p-*phenetyl* p-*tolyl azoxysulphone*, m.p. 128—128·5°. Similarly prepared from *p*-$NO{\cdot}C_6H_4{\cdot}NAlk_2$ are p-*dimethylaminophenyl* (purple-red), m.p. 182° (decomp.), and *p-diethylaminophenyl* p-*tolyl* (bright red), m.p. 178—179° (decomp.), and *p-dimethylaminophenyl Ph azoxysulphone* (bronze), m.p. 175—176° (decomp.), which may be represented by resonance of the azoxysulphone form with a quinonoid form; in conc. acid, where hydrolysis is absent, the cation is colourless. *Ph_2 azoxysulphone* (IV), m.p. 123°, is obtained from $PhSO_2{\cdot}NClNa$ (chloramine-*B*) and PhNO in C_5H_5N. With (I), *p*-$NO{\cdot}C_6H_4{\cdot}OH$ and 5 : 1 : 2-$NO{\cdot}C_6H_3Me{\cdot}OH$ give tars, and *p*-$NO{\cdot}C_6H_4{\cdot}NH_2$ and *p*-$NO{\cdot}C_6H_3{\cdot}NHMe$ afford amorphous products of possibly complex constitution. *p*-$O{:}C_6H_4{:}O$ and (I) in cold EtOH give ill-defined substances. *N*-NO-compounds do not react in similar manner to the *C*-NO-derivatives. When heated alone, all monoazoxysulphone derivatives decompose violently at ~180—200°, with evolution of SO_2. *m*-$C_6H_4(NO)_2$ and (I) in C_5H_5N at 80° for 2 hr. yield m-*phenylene bis-*(p-*tolyl azoxysulphone*), m.p. 208° (decomp.) (darkens >200°). (III) and Zn–AcOH–EtOH give *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}NHPh$; it is attacked only slowly by boiling dil. mineral acid, acid $Na_2Cr_2O_7$, or $KMnO_4$; cold conc. HNO_3 has no action. On distilling with 50% aq. H_2SO_4, (III) yields PhOH; PhN_2HSO_4 is formed from (III) and conc. H_2SO_4 at <10°, and 1 : 2-$NPh{:}N{\cdot}C_{10}H_6{\cdot}OH$ is obtained from (III), 95% EtOH, β-$C_{10}H_7{\cdot}OH$, and a little 30% aq. NaOH (boil for 2 min.); (III) with boiling 30% aq. NaOH for 30 min. yields benzene *iso*diazotate. Thus the primary hydrolysis product of (III) is a *n*-diazotate. Theoretical implications of the hydrolysis, with special relation to Angeli's views on *n*- and *iso*-diozotates, are discussed. (IV) and conc. H_2SO_4 at 0°, followed by dilution and boiling, afford $PhSO_3H$. A. T. P.

Synthesis of iodosulphobenzeneazo- and iodocarboxybenzeneazo-derivatives of naphthol- and naphthylamine-sulphonic acids. C. J. Klemme and H. Bang (*J. Org. Chem.*, 1944, **9**, 254—258).—The dyes have been synthesised for testing as radiographic opaques. The following are obtained by coupling the requisite naphthol- or naphthylamine-sulphonic acid with diazotised 4 : 3 : 5 : 1-$NH_2{\cdot}C_6H_2I_2{\cdot}SO_3H$ or 4 : 3 : 5 : 1-$NH_2{\cdot}C_6H_2I_2{\cdot}CO_2H$: Na_2 salts of 2-(2′ : 6′-di-iodo-4′-sulphobenzeneazo)-1-naphthol-4-sulphonic acid and -1-naphthylamine-4-sulphonic acid and Na_3 salt of 2-(2′ : 6′-di-iodo-4′-sulphobenzeneazo)-1-naphthylamine-4 : 8-disulphonic acid; Na_2 salts of 2-(2′ : 6′-di-iodo-4′-carboxybenzeneazo)-1-naphthol-4-sulphonic acid and -1-naphthylamine-4-sulphonic acid and Na_3 salt of 2-(2′ : 6′-di-iodo-4′-carboxybenzeneazo)-1-naphthylamine-4 : 8-disulphonic acid. H. W.

Interaction of aromatic diazo-compounds with β-ketonic esters. V. V. Feofilaktov (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1941, 521—530).—*n*-Valine (I), *n*-leucine (II), and *dl*-tyrosine have been prepared from Et *n*-propyl-, *n*-butyl-, and *p*-methoxybenzyl-acetoacetates and PhN_2X, the resulting α-CO-acid phenylhydrazones being reduced to the α-NH_2-acids. (I) and (II) have also been prepared using diazotates from *o*- and *p*-toluidine, *m*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, α- and β-$C_{10}H_7{\cdot}NH_2$, and sulphanilic acid. The *p*-tolylhydrazone of *n*-butyrylformic acid occurs in two modifications, m.p. 134—135° and 123—131°. Et acetylsuccinate reacts with diazotates forming *Et* 4-*arylazo*-1-*arylpyrazol*-5-*one*-3-*carboxylates*, *e.g.*, from *o*-, m.p. 95—96°, *m*-, m.p. 146—147°, and *p*-toluidine, m.p. 143—144°, *p*-nitroaniline, m.p. 246—248°, sulphanilamide, m.p. 258—260°, naphthionic acid, benzidine. Sulphanilic acid affords up to 80% of tartrazine Et_1 ester, hydrolysed by NaOH to tartrazine (Na_3 salt). Bromotetronic acid may be used in this reaction in place of tetronic acid, forming mono- and di-arylhydrazones derived from the latter, *e.g.*, α-p-*nitrobenzeneazo-*, m.p. 214°, α-m-*toueneazo-*, m.p. 172°, α-1-*naphthaleneazo-*, m.p. 148—150°, and α-2-*naphthaleneazo-β-ketobutyrolactone*, m.p. 212°. Et αγ-dibromoacetoacetate similarly affords *Et γ-bromo-α-1-naphthaleneazoaceto-acetate*, m.p. 165°. Cyclic β-ketonic esters undergo this reaction with opening of the ring. Et *cyclo*hexanonecarboxylate thus affords the *phenylhydrazone* of Et H α-ketopimelate, α-form, m.p. 89·5—90°, β-form, m.p. 142—143°, hydrolysed to *α-ketopimelic acid phenylhydrazone*, α-form, m.p. 144—145°, β-form, m.p. 131—132°. Reduction of this affords α-aminopimelic acid, m.p. 215—216°. Et *cyclo*pentanonecarboxylate similarly gives the lower homologues of these compounds. Et camphorcarboxylate gives Et 3-benzeneazo-camphor-3-carboxylate, hydrolysed to the *ketohomocamphoric acid phenylhydrazone*, m.p. 166°, reduced to *α-aminohomocamphoric acid*, m.p. 185°. 2-Cyano*cyclo*pentanone undergoes a similar reaction. G. A. R. K.

Evidence for the *iso*nitrile and nitrile structures of Hantzsch's aryl *syn*- and *anti*-diazocyanides. H. H. Hodgson and E. Marsden (*J.C.S.*, 1944, 395—398).—Although Hantzsch's formula for the *anti*-diazocyanides is correct, that for the aryl *syn*-diazocyanides does not explain the reactions. The *syn*- and *anti*-forms exhibit differences in chemical activity which are accounted for by *iso*nitrile and nitrile structures, respectively. The colours of both *syn*- and *anti*-compounds indicate covalent linkings between the diazo- and $\cdot\overset{+}{N}{:}\overset{-}{C}$ and $\cdot C{:}N$ groups, respectively. There is close analogy between the *syn*-diazocyanides and diazo*iso*cyanates. Temp. is of prime importance in transforming *syn*- into *anti*-diazocyanide, which occurs rapidly with the *p*-nitro- and *p*-chloro-benzene derivatives, even in Et_2O at ~0°. With *o*- and *p*-chloro- or -bromo-, and *p*-nitro-*syn*- and -*anti*-benzenediazocyanides (method of prep.: Le Fèvre *et al.*, A., 1938, II, 229), MgMeI in Et_2O affords complexes, the *anti* being of a deeper red colour than the *syn*. Decomp. with $2N\text{-}H_2SO_4$ at 0° yields ~20% of MeCHO from the *syn*-complexes only, probably as follows: $C_6H_4R{\cdot}N{:}N{\cdot}\overset{+}{N}{:}\overset{-}{C} + MgMeI \rightarrow C_6H_4R{\cdot}N{:}N{\cdot}C(Me){\cdot}MgI \rightarrow C_6H_4R{\cdot}N{:}N{\cdot}C(Me){:}NH \rightarrow MeCHO$. The non-coupling *p*-nitrobenzenediazocarboxylamide (I) (stable CN linking) with Br in $CHCl_3$, AcOH, or C_6H_6 yields probably a perbromide, which readily loses Br to give p-*nitrobenzenediazo-*N*-bromocarboxylamide hydrobromide* (II), *p*-$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NHBr,HBr$, m.p. ~81° (decomp.). (II) couples with α- or β-$C_{10}H_7{\cdot}NH_2$ in $CHCl_3$ or C_6H_6 (indicates a Hofmann rearrangement), and with β-$C_{10}H_7{\cdot}OH$ in aq. EtOH or aq. NaOH (not in $CHCl_3$, C_6H_6, or abs. EtOH) (with hydrolysis to *p*-$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH{\cdot}OH$), to give the corresponding *p*-nitrobenzeneazo-derivatives. In each case, the formation of intermediate diazo*iso*cyanate with its weak N·N linking precedes coupling. The coupling with α- and β-$C_{10}H_7{\cdot}NH_2$ in the above media supports the polarisation theory of Hodgson (A., 1943, II, 8). Aëration of (II) in cold H_2O for 1—1·5 hr. gives some (I) and the filtrate then couples with alkaline β-$C_{10}H_7{\cdot}OH$ to give 1 : 2-$NPh{:}N{\cdot}C_{10}H_6{\cdot}OH$. (II) and cold 20% aq. NaOH give 4 : 4′-dinitrodiazoaminobenzene, also obtained from *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2HSO_4$ and aq. KCNO at 0°. The formation of *syn*-cyanides in mineral acid medium parallels that of diazoamino-compounds in similar media. Attempts to isolate a diazo-cyanate or *-iso*cyanate from neutral *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ with KCNO or AgCNO were unsuccessful because of the facile decomp. of the resulting diazo-compound. The views of Le Fèvre *et al.* (*loc. cit.*), with particular reference to the dipole moment data, are discussed. A. T. P.

Separation of *m*- and *p*-cresol.—See B., 1944, II, 274.

Nuclear methylation of phenolic substances. (Miss) M. G. Barclay, A. Burawoy, and G. H. Thomson (*J.C.S.*, 1944, 400—404; cf. A., 1944, II, 157).—4 : 1 : 3 : 5-$OH{\cdot}C_6H_2Me(CH_2{\cdot}OH)_2$ (I), distilled at >250° alone or in presence of very weak alkalis, gives much *p*-cresol (II), some *m*-4-xylenol (III), and a little mesitol (IV); in presence of mild alkalis, *e.g.*, $Ca(OH)_2$, $Mg(OH)_2$, borax, the amount of (IV) increases to 12—18% by wt. of (I). This reaction is characteristic of all hydroxymethylphenols and other substances capable of forming anhydrohydroxymethylphenols at high temp. The analogous behaviour of (I) and *p*-aminoaryl alcohols (*loc. cit.*) is shown by the formation of anhydrides, which then undergo disproportionation to yield methylated phenols and amines, respectively, and oxidised resins serving as a source of H; both also condense to a varying degree, controlled by the presence of alkalis, to form substances of high mol. wt. containing CH_2 linkings, which decompose to form mainly the original phenol or amine. Distillation of 4 : 1 : 3-$OH{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}OH$ or of 3-piperidinomethyl-*p*-cresol with $Ca(OH)_2$ yields mainly (III), and a little (II) + (IV). Distillation of $CH_2(C_6H_3Me{\cdot}OH\text{-}5 : 2)_2$ with Na_2CO_3 gives almost pure (II), but with $Ca(OH)_2$ yields mainly (II) and a little (III) + (IV), a similar mixture also being obtained from 4-hydroxy-3 : 5-bis-(6-hydroxy-2-

methylbenzyl)toluene in presence of Na_2CO_3 or $Ca(OH)_2$. $CH_2(C_6H_3Me{\cdot}OH\text{-}5:4)_2$ and Na_2CO_3 or $Ca(OH)_2$ afford mainly *o*-cresol and traces of (**IV**). $CH_2[C_6H_2Me(OH){\cdot}CH_2{\cdot}OH\text{-}5:4:3]_2$ (**V**), m.p. 163° [prep. from *o*-cresol (1 mol.), NaOH (1·25 mols.), and aq. CH_2O for 1 week], distilled alone gives *o*-cresol, (**III**), *m*-2-xylenol (**VI**), and traces of (**IV**), but in presence of $Ca(OH)_2$ much (**III**), (**VI**), and (**IV**), with only a little *o*-cresol. 2 : 1 : 3 : 5-$OH{\cdot}C_6H_2Me(CH_2{\cdot}OH)_2$, m.p. 94°, gives, in presence of $Ca(OH)_2$, (**III**) + (**VI**) and a little (**IV**); the yield of (**IV**) is small owing to condensation to (**V**). 3 : 5-Dimethyl-2-piperidinomethylphenol with $Ca(OH)_2$ yields *m*-5-xylenol, 2 : 3 : 5 : 1-$C_6H_2Me_3{\cdot}OH$ (**VII**), and a little 2 : 3 : 5 : 6 : 1-$C_6HMe_4{\cdot}OH$ (**VIII**). 1 : 3 : 5 : 2 : 6-$OH{\cdot}C_6HMe_2(CH_2{\cdot}OH)_2$ with $Ca(OH)_2$ gives mainly (**VII**) + (**VIII**); no trace of 3 : 4 : 5-tri-, 2 : 3 : 4 : 5-tetra-, or penta-methylphenol was found, suggesting that these substances are not *p*-substituted derivatives of *m*-5-xylenol (cf. Caldwell *et al.*, A., 1939, II, 523). Distillation of 1-piperidinomethyl-2-naphthol gives β-$C_{10}H_7{\cdot}OH$ + 1 : 2-$C_{10}H_6Me{\cdot}OH$ (**IX**), the yield of (**IX**) being higher in presence of $CaCO_3$, whereas $Ca(OH)_2$ decreases the amount of β-$C_{10}H_7{\cdot}OH$ and (**IX**); traces of 1-$C_{10}H_7Me$ (**X**) are isolable. 2 : 2′-Dihydroxy-1 : 1′-dinaphthylmethane distilled alone or with Na_2CO_3 or $Ca(OH)_2$, yields much β-$C_{10}H_7{\cdot}OH$ and <2% of (**IX**) + (**X**). A mixture of phenolic substances forming a mixture of hydroxymethyl- or aminomethyl-phenols can be used: thus condensation of (**II**), CH_2O, and $Ca(OH)_2$ and distillation gives (**III**), (**II**), and (**IV**); the mixture on similar condensation and distillation affords 30% of (**IV**). Similarly (**IV**) is obtained from *o*-cresol and PhOH, a 20% yield of 2 : 3 : 4 : 6 : 1-$C_6HMe_4{\cdot}OH$ (**XI**) from *m*-cresol, and 30% of (**VIII**) from *m*-5-xylenol. A mixture of (**IV**) and (**XI**) results on similar treatment of the cresylic acids. A. T. P.

Relation of œstrogenic activity to structure in 4 : 4′-dihydroxydiphenylmethanes. E. E. Reid and (Miss) E. Wilson (*J. Amer. Chem. Soc.*, 1944, **66**, 967—969).—The appropriate ketone (1 mol.) and PhOH (3 mols.) in conc. HCl at room temp. (1 day to 20 weeks) or faster with gaseous HCl give ~90% of *ββ-di*-p-*hydroxyphenyl*-n-*heptane*, m.p. 101° (*dibenzoate*, m.p. 118°), *-octane*, m.p. 88° (*dibenzoate*, m.p. 114°), and *-γ-methylbutane*, m.p. 194° (*dibenzoate*, m.p. 204°), *ζζ-di*-p-*hydroxyphenyl*-n-*undecane*, m.p. 148·5° (*dibenzoate*, m.p. 94°), 1 : 1-di-*p*-hydroxyphenyl-4-methyl*cyclo*hexane, m.p. 179° (dibenzoate, m.p. 149·5°), *αα-di*-p-*hydroxyphenyl*-α-p-*anisylethane*, m.p. 245° (*dibenzoate*, m.p. 221°), $(p\text{-}OH{\cdot}C_6H_4)_2C(CH_2Ph)_2$, m.p. 193° (dibenzoate, m.p. 223°), and [from $(CH_2Ac)_2$] $[(p\text{-}OH{\cdot}C_6H_4)_2CMe{\cdot}CH_2]_2$, m.p. 302° (decomp.) (tetrabenzoate, m.p. 247°). Œstrogenic activity of the series, $(p\text{-}OH{\cdot}C_6H_4)_2CRR'$ is a max. at R = R′ = Pr^{α} in contrast to the stilbene series (Campbell, A., 1941, II, 62). R. S. C.

Dibenzfuran. XXI. Benzene and diphenyl intermediates for 1 : 9-derivatives. H. Gilman and J. R. Thirtle (*J. Amer. Chem. Soc.*, 1944, **66**, 858—859; cf. A., 1944, II, 303).—Metallation of 1 : 2 : 4-$C_6H_3(OMe)_3$ by $LiBu^{\alpha}$ in boiling Et_2O–N_2 occurs almost exclusively at position 3, since subsequent treatment with I or CO_2 gives 1-*iodo*-2 : 3 : 6-*trimethoxybenzene* (**I**) (51%), m.p. 108—108·5°, or 2 : 3 : 6 : 1-$(OMe)_3C_6H_2{\cdot}CO_2H$ (47%), m.p. 149—150° (lit. 145—146°) (*Me*, m.p. 57—57·5°, and *Et* ester, m.p. 42·5—43°, obtained with difficulty), respectively. Cu powder converts (**I**) at 185—190° and then 210—215° (N_2) into 2 : 3 : 6 : 2′ : 3′ : 6′-*hexamethoxydiphenyl* (76·4%), m.p. 125—125·5°, which with HNO_3–Ac_2O at the b.p. gives the 5 : 5′-$(NO_2)_2$-compound (**II**), m.p. 151—151·5°. HNO_3–AcOH at 60° converts (**I**) into 1-*iodo*-5-*nitro*-2 : 3 : 6-*trimethoxybenzene*, m.p. 119·5—120°, converted by H_2–Pd–$CaCO_3$ in EtOH at 30 lb. into 1 : 3 : 4 : 6-$(OMe)_3C_6H_2{\cdot}NO_2$, m.p. 128—129°, and by Cu powder at 210° and then 230° into (**II**). Attempts to prepare dibenzfuran derivatives are without effect or produce tars. R. S. C.

Vinyl alcohols. IX. Esters of αβ-dimesitylvinyl alcohol. R. C. Fuson, L. J. Armstrong, and W. J. Shenk, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 964—967).—The alcohol produced by dehydration of hydromesitoin or *iso*hydromesitoin (A., 1943, II, 261) is shown to be *ββ-dimesitylvinyl alcohol* by the prep. of esters of the *αβ*-dimesityl isomerides and demonstration that these alcohols are too readily ketonised to exist in the free state. CHMesBr·COBr (Mes = mesityl here and below) (prep. from $OH{\cdot}CHMes{\cdot}CO_2H$ by PBr_3 at 100°), b.p. 138—139°/9 mm., with granulated Zn in Et_2O gives a solution of CHMes:CO, which could be isolated only as *dimer*, m.p. 197—200°, but which with MgMesBr–Et_2O and then BzCl gives trans-*αβ-dimesitylvinyl benzoate*, m.p. 147—148°. In NaOH–EtOH–H_2O at the b.p. this undergoes hydrolysis and ketonisation to $COMes{\cdot}CH_2Mes$ (**I**); it shows no active H (Grignard machine) and gives no Cu derivative; its structure is thus proved. With MgMeI, (**I**) evolves 0·96 CH_4 but then regenerates (**I**); other attempts to prepare its enol also failed. MgEtBr and (**I**) in Et_2O give, after treatment with BzCl or AcCl, cis-*αβ-dimesitylvinyl benzoate*, m.p. 104—105·5° [no active H; hydrolysis gives (**I**)], or *acatate*, m.p. 68—69°, b.p. 188—193°/4 mm., respectively. *Mesitylglyoxalhydrazone*, m.p. 129—131°, HgO, $CaSO_4$, and a trace of KOH–EtOH in light petroleum give *mesityldiazomethane*, m.p. 59—61° (decomp.), whence no ketene could be obtained but whence boiling H_2O yields $CH_2Mes{\cdot}CO_2H$. 2 : 4 : 6 : 1-$C_6H_2Et_3{\cdot}CHBr{\cdot}COBr$ (prep. as above), b.p. 140—142°/5 mm., with Zn in Et_2O–Bu_2O gives a keten solution, whence H_2O yields 2 : 4 : 6 : 1-$C_6H_2Et_3{\cdot}CH_2{\cdot}CO_2H$. 2 : 4 : 6 : 1-$C_6H_2Pr^{\beta}_3{\cdot}COMe$ and SeO_2 give 2 : 4 : 6 : 1-$C_6H_2Pr^{\beta}_3{\cdot}CO{\cdot}CHO$ (**II**), b.p. 138—143°/7·5 mm., converted by 10% KOH at 100° into 2 : 4 : 6-*triiso*propyl*mandelic acid*, m.p. 163—164° (corr.) (*Me* ester, m.p. 94—95°), which with H_2SO_4–$COMe_2$ at 0° gives the *dioxolone*, m.p. 165—165·5°, and thence (N_2H_4,H_2O–EtOH) the *hydrazide*, m.p. 156—157°. HgO etc. converts the *hydrazone*, m.p. 153—154° (decomp.), of (**II**) into the diazo-compound, decomp. 104° or 125°, whence H_2O yields 2 : 4 : 6 : 1-*triisopropylphenylacetic acid* (**III**), m.p. 146—146·5°. 2 : 4 : 6 : 1-$C_6H_2Pr^{\beta}_3{\cdot}CH_2Cl$ with CuCN in C_5H_5N at 210—220° gives 2 : 4 : 6-*triisopropylbenzyl cyanide*, m.p. 81—82°, b.p. 129—130°/4 mm., converted by KOH–H_2O–diethylene glycol at the b.p. into (**III**) but by KOH–EtOH into the *amide*, m.p. 170—171°. R. S. C.

Vinyl alcohols. X. ββ-Diarylvinyl alcohols. R. C. Fuson, P. L. Southwick, and S. P. Rowland (*J. Amer. Chem. Soc.*, 1944, **66**, 1109—1112; cf. supra).—$CMes_2{:}CH{\cdot}OH$ (Mes = mesityl here and below) (**I**), m.p. 129—129·5° (A., 1943, II, 261) [*acetate* (**II**), m.p. 132·5—133°; *benzoate*, m.p. 175·5—176°], is obtained (80%) with a *dimer*, m.p. 189—191°, and a *trimer*, m.p. 290—292°, from hydromesitoin by 55% H_2SO_4 at 100° and from *iso*hydromesitoin (**III**) similarly or, less well, by boiling AcOH–conc. HCl, P_2O_5, or heating at 285°. It is unaffected by O_2 in $COMe_2$. $KMnO_4$ does not affect (**II**) whilst O_3 in CCl_4 gives $CHMes_2{\cdot}CO_2H$; hydrogenation at 200°/3000 lb. yields CH_2Mes_2. Attempts to ketonise (**I**) failed: boiling HCl–MeOH yields the *Me ether* (**IV**), m.p. 129—130°, also obtained from (**III**) by HCl–MeOH at room temp. and converted by HI–AcOH into $(CHMes{:})_2$; the *Et ether*, m.p. 96—97°, is obtained from (**I**) by HCl–EtOH. (**I**) is unaffected by Hg–Zn–HCl–AcOH, but with Zn dust at 300° or HI–AcOH at 100° gives $(CHMes{:})_2$ and with H_2–Raney Ni–EtOH at 200° gives *ββ-dimesitylethyl alcohol* (**V**), m.p. 118—119° (*acetate*, m.p. 164—165°; *benzoate*, m.p. 151·5—152·5°) (and a little CH_2Mes_2), which is also obtained from (**I**) by H_2–Cu chromite. With CrO_3–AcOH at room temp. (**V**) yields $COMes_2$, with aq. H_2SO_4 at 100° gives $(CHMes{:})_2$, and with red P–I–AcOH–H_2O gives $(CH_2Mes)_2$ [also obtained similarly from (**I**)]. O_3 in CCl_4 oxidises (**I**) to mesitoin, CrO_3–AcOH at room temp. or SeO_2 yields mesitil, $KMnO_4$ in aq. $COMe_2$, KOH–EtOH, or NaOCl gives a dimeric *product* (**VI**), $C_{40}H_{46}O_2$, m.p. 184·5—185° (decomp.). (**VI**) contains 1 active H, gives violet to red colours in solution at 70°, is unaffected by H_2–PtO_2 at 1 atm., and with hot HCl–MeOH or –EtOH gives a *compound*, $C_{35}H_{41}O_2$, m.p. 180—181°. CrO_3–AcOH oxidises (**III**) to $MesCO_2H$. With red P–I–AcOH–H_2O, (**III**) gives $(CH_2Mes)_2$, with HI–AcOH at 100° or conc. H_2SO_4 at 0° gives $(CHMes{:})_2$, and with PCl_5–$POCl_3$ at room temp. gives *αβ-dichloro-αβ-dimesitylethane*, m.p. 176—179°, also obtained similarly from (**I**) and (? with a diastereoisomeride) from $(CHMes{:})_2$ by PCl_5–$CHCl_3$ [crystallisation from MeOH gives also some (**IV**)], and converted by EtOH–KOH into *dimesitylacetylene*, m.p. 127—128·5°. With Cu chromite in EtOH–N_2 at 200°/1500 lb., (**III**) gives MesCHO. iso*Duraldehyde*, m.p. 22—25°, b.p. 112—114°/3 mm., in O_2 gives $ArCO_2H$ and with Mg–MgI_2 gives *hydro*iso*duroin*, m.p. 225·5—226·5° (with some $CAr_2{:}CH_2$), converted by boiling H_2SO_4–AcOH into *ββ-diisodurylvinyl alcohol*, m.p. 149·5—151·5° (*benzoate*, m.p. 156·5—158°), unaffected by air. R. S. C.

Toxic principles of poison ivy. II. Preparation and properties of diphenylmethylene ethers of pyrocatechols.—See A., 1944, II, 346.

Effect of bases on the hydrogenation of alkylphenols in the presence of Raney nickel. H. E. Ungnade and (Miss) D. V. Nightingale (*J. Amer. Chem. Soc.*, 1944, **66**, 1218—1220).—Hydrogenation (Raney Ni) of an alkylphenol is promoted by a small amount of its Na salt, best in absence of solvent (cf. A., 1944, II, 160). Differences in rate of hydrogenation of isomerides are removed by this catalysis, but the ratio of stereoisomeric *cyclo*hexanols formed is unaffected except at high temp. R. S. C.

Semihydrobenzoin and semipinacolic transformations in the α-phenyl-β-methyl- and -ethyl-Δ$^{\gamma}$-butene-αβ-diol series. Y. Deux (*Compt. rend.*, 1943, **216**, 776—778; cf. A., 1939, II, 265).—$CHPh{:}CMe{\cdot}CH{:}CH_2$ and HgO–I in Et_2O–H_2O give $CHPhI{\cdot}CMe(OH){\cdot}CH{:}CH_2$, which with conc. aq. $AgNO_3$ affords *γ-phenyl-Δ$^{\delta}$-penten-β-one* (**I**), b.p. 110—111°/14 mm. (*oxime*, m.p. 101—102°; *semicarbazone*, m.p. 138—139°) (semipinacolic change), hydrogenated (Raney Ni) to $CHPhEt{\cdot}COMe$ (*semicarbazone*, m.p. 187—188°). $CHPhCl{\cdot}CMe(OH){\cdot}CH{:}CH_2$, m.p. 84—85°, and MgEtBr give (**I**), also obtained from HNO_2 and $NH_2{\cdot}CHPh{\cdot}CMe(OH){\cdot}CH{:}CH_2$ (*picrate*, m.p. 213—214°) (prepared from the corresponding epoxide and excess of NH_3 at 110—120° in a sealed tube). *α-Phenyl-β-ethyl-Δ$^{\gamma}$-butene-αβ-diol*, m.p. 93—94° (*di*-p-*nitrobenzoate*, m.p. 107—108°), prepared from the corresponding epoxide and acidulated H_2O at 70—80° for 2 hr., is converted by 30% H_2SO_4 into *α-phenyl-α-ethyl-Δ$^{\beta}$-butenaldehyde*, b.p. 116—117°/15 mm. (*semicarbazone*, m.p. 160°; *oxime*, m.p. 98—99°) (semihydrobenzoin change).
$NH_2{\cdot}CHPh{\cdot}CEt(OH){\cdot}CH{:}CH_2$ (*picrate*, m.p. 145—146°) and HNO_2 give $CH_2{:}CH{\cdot}CHPh{\cdot}COEt$ (*loc. cit.*). A. T. P.

Halogenohydrins obtained by the action of hydracids on stilbene oxide. D. Reulos (*Compt. rend.*, 1943, **216**, 774—776).—*trans-αβ-*

Epoxy-αβ-diphenylethane (stilbene oxide) (**I**) and excess of conc. HCl in Et_2O afford, by a Walden inversion, cis-*β-chloro-αβ-diphenylethanol*, m.p. 77° (p-*nitrobenzoate*, m.p. 103—104°), transformed into (**I**) by aq. KOH, and by $SOCl_2$ in $CHCl_3$ into *cis*-$(CHPhCl)_2$. (**I**) and HBr (*d* 1·38) similarly yield *β-bromo-αβ-diphenylethanol*, m.p. 86° (p-*nitrobenzoate*, m.p. 121—122°), convertible into (**I**) by aq. KOH or into $(CHPhBr)_2$, m.p. 237°, by PBr_3; (**I**) and HI give the *β-I*-compound, m.p. 95—96°, readily decomposed with liberation of I. A. T. P.

Dehydration of *cyclo*hexane-1 : 4-diol. Synthesis of 1 : 4-epoxy-*cyclo*hexane. R. C. Olberg, H. Pines, and V. N. Ipatiev (*J. Amer. Chem. Soc.*, 1944, **66**, 1096—1099).—*trans*- (**I**), m.p. 142°, and *cis-cyclo*Hexane-1 : 4-diol (**II**), m.p. 107° (mixed m.p. curve given), are separated by way of the diacetates, m.p. 103° and 33—34°, respectively. Passing (**I**) in MeOH over activated Al_2O_3 at 275° gives Δ^3-*cyclo*hexenol (**III**) 11·4 and 1 : 4-*epoxycyclohexane* (**IV**) (b.p. 120·1°) 73%; (**II**) gives similarly 28 and 27%, respectively, and a 1 : 1 mixture affords 20·6 and 33·5%, respectively. Increasing the temp. reduces the amount of (**IV**), none being formed at 406°. At 350—400° there are obtained also *cyclo*hexadienes, *cyclo*hexene (**V**), methyl*cyclo*hexene, CH_2O, Me_2O, diene polymers, and at 400° a little $CO + H_2$ (from CH_2O). (**V**) is probably formed by hydrogenation of (**IV**) by MeOH to *cyclo*hexanol and subsequent dehydration. In EtOH at 300° only 21·4% of (**IV**) and at 340° none is formed; in $COMe_2$ at 300° 17% of (**IV**) and at 340° none is formed. Boiling the diol over activated Al_2O_3 slowly gives 48·6 mols. of (**IV**) and 18·3 mols. of (**III**). Use of I, $KHSO_4$, H_2SO_4, HBr, or Br gives no (**IV**). Boiling 48% HBr converts (**IV**) into *trans*-1 : 4-dibromo*cyclo*hexane, m.p. 112—113°. R. S. C.

Magnesium dehalogenation of *cis*-chlorohydrins of α-substituted *cyclo*hexanediols; exclusive formation of alkyl*cyclo*hexanones by semipinacolic transformation. M. Tiffeneau, (Mme.) B. Tchoubar, and S. Le Tellier (*Compt. rend.*, 1943, **216**, 856—860; cf. A., 1934, 1098).—2-Chloro*cyclo*hexanone and MgMeI give cis-2-*chloro*-1-*methyl*-cyclo*hexanol* (**I**), b.p. 83—84°/13 mm., purified from some *trans*-compound by removal of the latter as epoxide by aq. KOH. (**I**) and 1 mol. of MgEtBr yield 2-methyl*cyclo*hexanone (semicarbazone, m.p. 189°). Similarly prepared, using MgEtBr or $MgBu^aBr$, are cis-2-*chloro*-1-*ethyl*-, b.p. 96—100°/18 mm., or -1-*butyl*-cyclo*hexanol*, b.p. 96—99°/18 mm., and thence 2-ethyl- (semicarbazone, m.p. 165°) or 2-butyl-*cyclo*hexanone (semicarbazone, m.p. 145°), respectively. 2-*Chloro*-1 : 4-*dimethyl*-, b.p. 92—94°/17 mm., or 2-*chloro*-1 : 5-*dimethyl*-cyclo*hexanol*, b.p. 88—90°/14 mm., afford 2 : 4-dimethyl- (semicarbazone, m.p. 190°) or 2 : 5-dimethyl-*cyclo*hexanone (semicarbazone, m.p. 170°), respectively. Thus the dehalogenation of *cis*-chlorohydrins of *cyclo*hexanediols gives *cyclo*hexanones, whereas the *trans*-isomerides yield *cyclo*pentyl ketones. Mechanisms of reactions are discussed. A. T. P.

Alicyclic sulphur compounds. M. Mousseron (*Compt. rend.*, 1943, **216**, 812—814).—2-Chloro*cyclo*hexanol (**I**) and thiol*cyclo*hexane [Na derivative (**II**)] in hot EtOH give 2-*hydroxydi*cyclo*hexyl sulphide* (**III**), b.p. 170°/12 mm.; similarly prepared are 2-*hydroxydi*cyclo*pentyl sulphide*, b.p. 157°/12 mm., and 2-cyclo*pentylthiol*cyclo*hexanol*, b.p. 165°/12 mm. (**II**) and epoxy*cyclo*hexane (**IV**) give a mixture, b.p. 170°/12 mm., of two stereoisomerides of (**III**). Na_2S_2–EtOH yields *di*-(2-*hydroxy*cyclo*pentyl*) *disulphide*, m.p. 70—71°, and [from (**I**)] *di*-(2-*hydroxy*cyclo*hexyl*) *disulphide* (**V**), m.p. 156—157°; (**IV**) similarly gives stereoisomerides. (**V**) and Sn–HCl afford *di*-(2-*hydroxy*cyclo-*hexyl*) *sulphide*, m.p. 71° (*Et*$_1$, b.p. 165°/15 mm., and *Et*$_2$ *ether*, b.p. 190°/15 mm.) (probably through 2-thiol*cyclo*hexanol by loss of H_2S), also obtained from (**IV**) and H_2S or KHS. (**II**) and 2-chloro*cyclo*-hexylamine give 2-*aminodi*cyclo*hexyl sulphide*, b.p. 160°/15 mm. [*hydrochloride*, m.p. 200° (decomp.)]; Na_2S_2 yields *di*-(2-*amino*-cyclo*hexyl*) *disulphide*, b.p. 200°/15 mm. [*hydrochloride*, m.p. 230° (decomp.)]. Epithiomethene*cyclo*hexane (liquid) (from Na_2S and 1-thiocyano-1-thiocyanomethyl*cyclo*hexane) is converted by hot H_2O into *di*-(1-*hydroxymethyl*cyclo*hexyl*) *sulphide*, m.p. 55°, also obtained from Na_2S and 1-chloro-1-hydroxymethyl*cyclo*hexane (Tiffeneau *et al.*, A., 1937, II, 414). The appropriate Mg 3-methyl-*cyclo*hexyl chloride and SO_2, followed by $KMnO_4$ oxidation of the product, give, through the K salts, $[\alpha]_{546}$ +2·02° in H_2O, and $[\alpha]_{546}$ +1·25° in H_2O, respectively, the cis-, m.p. 95°, $[\alpha]_{546}$ +2·16° in C_6H_6, and trans-3-*methyl*cyclo*hexanesulphonic acid*, m.p. 93°, $[\alpha]_{546}$ +1·44° in C_6H_6. A. T. P.

Condensation of 4-chloro-3 : 5-dinitrobenzaldehyde with malonic acid in presence of organic bases. D. S. Mittal (*J. Indian Chem. Soc.*, 1944, **21**, 34).—C_5H_5N, piperidine, and quinoline (0·15 mol.) successfully catalyse the condensation of equimol. mixtures of 3 : 5 : 4 : 1-$(NO_2)_2C_6H_2Cl$·CHO and $CH_2(CO_2H)_2$. Yields of 84—92% of 4-*chloro*-3 : 5-*dinitrocinnamic acid*, m.p. 82°, are obtained. C. R. H.

Antispasmodics. VI. F. F. Blicke and R. F. Feldkamp (*J. Amer. Chem. Soc.*, 1944, **66**, 1087—1091; cf. A., 1944, II, 14).—1-$C_{10}H_7$·CH_2·CO_2Et (prep. from 1-$C_{10}H_7$·CH_2Cl by KCN and then hot H_2SO_4–EtOH), b.p. 180—181°/15 mm., $Et_2C_2O_4$, and NaOEt in EtOH give an ester, which at 175°/15 mm. yields CO and 1-$C_{10}H_7$·$CH(CO_2Et)_2$ (69%), m.p. 62° (lit. 59—60°). The derived Na compound (prep. in xylene) with RI in boiling C_6H_6 gives 22—75·6% of pure *Et*$_2$ 1-*naphthyl-methyl*-, m.p. 46—47°, b.p. 170—171°/2—3 mm., *-ethyl*-, m.p. 48—49°, b.p. 171—174°/3 mm., -n-*propyl*-, m.p. 51—52°, b.p. 182—184°/4 mm., and -n-*butyl-malonate*, 1-$C_{10}H_7$·$CR(CO_2Et)_2$, m.p. 53—54°, b.p. 185—188°/4 mm., hydrolysed by boiling KOH–EtOH–H_2O to the malonic acids, which at 180° yield α-1-naphthyl-propionic, m.p. 148—149° (lit. 148°), -n-*butyric*, m.p. 86—87°, -n-*valeric* (**I**), b.p. 190°/4 mm., and -n-*hexoic acid* (**II**), m.p. 64—65°, b.p. 183°/3 mm. $C_{10}H_8$, $COCl$·CO_2Et, and $AlCl_3$ in $(CHCl_2)_2$ give 69% of mixed esters, separated by picric acid into 1- (46%), b.p. 167°/3 mm., and 2-$C_{10}H_7$·CO·CO_2Et, b.p. 161—165°/2—3 mm., hydrolysed by Na_2CO_3 in boiling aq. EtOH to the acids, m.p. (**III**) 112—113° and 92—93°, respectively (cf. lit.). MgRBr and (**III**) in Et_2O give 1-$C_{10}H_7$·CPh(OH)·CO_2H, softens ~90°, m.p. (complete) 147°, *α-hydroxy-α-1-naphthyl-n-valeric*, m.p. 139—140°, and -n-*hexoic acid*, m.p. 116—117°, reduced by red P and I to 1-$C_{10}H_7$·$CHPh$·CO_2H, (**I**), and (**II**), respectively. The basic alkyl chloride and CHArR·CO_2H in boiling $Pr^\beta OH$ give: *β-diethylaminoethyl α-1-naphthyl-acetate hydrochloride*, m.p. 128—130°, *-propionate hydrochloride*, m.p. 98—100°, and -n-*butyrate hydrochloride* (**IV**), m.p. 117—119°, and *α-phenyl-α-1-naphthylacetate hydrochloride*, m.p. 124—126°; the *β-piperidinoethyl* ester *hydrochlorides*, m.p. 122—124°, (**V**) 115—117°, 139—140°, and 167—168°, respectively; the *γ-diethylamino-n-propyl* ester *hydrochlorides*, m.p. 110—111°, 90—94°, 97—98°, and (**VI**) ~107°, respectively. The *β-morpholinoethyl* ester *hydrochlorides*, m.p. 131—132°, 148—149°, 167—168°, and ~110°, respectively, are obtained from CHArR·COCl and the basic alcohol in C_6H_6 at 0° and then the b.p. *β*-Piperidinoethyl chloride, b.p. 69°/12 mm., gives a hydrochloride, m.p. 229—230° (lit. 208°, 231°). The esters have antispasmodic action at 1 : $\lessgtr 10^5$ to 1 : $\lessgtr 2 \times 10^6$, the morpholino-esters being least, and (**IV**)—(**VI**) being most, effective. R. S. C.

Nitro-amino-derivatives of *o*-bromobenzoic acid. H. Goldstein and G. Preitner (*Helv. Chim. Acta*, 1944, **27**, 888—891).—Gradual addition of 5 : 2 : 1-NHAc·C_6H_3Br·CO_2H to HNO_3 (*d* 1·5) gives 2-*bromo*-6-*nitro*-5-*acetamidobenzoic acid*, m.p. ~250° (decomp.), also obtained by oxidising 6 : 1 : 2 : 5-NO_2·C_6H_2MeBr·NHAc (**I**) with aq. $KMnO_4 + MgSO_4$. It is hydrolysed by boiling 10% KOH to 2-*bromo*-6-*nitro*-5-*aminobenzoic acid*, m.p. 218°. Nitration of 1 : 2 : 5-C_6H_3MeBr·NHAc gives mainly 4 : 1 : 2 : 5-NO_2·C_6H_2MeBr·NHAc (**II**) with some (**I**) and 2-*bromo*-4 : 6-*dinitro*-5-*acetamidotoluene*, m.p. 224—225° (cf. Cohen *et al.*, *J.C.S.*, 1914, **105**, 513). (**II**) is oxidised to 2-*bromo*-4-*nitro*-5-*acetamido*-, m.p. 208°, hydrolysed to 2-*bromo*-4-*nitro*-5-*amino*-, m.p. 236·5°, *-benzoic acid*. M.p. are corr. H. W.

Synthesis of alkyl and dialkylaminoalkyl esters of 5-fluoro-2-nitro- and -2-amino-benzoic acid. L. S. Fosdick and R. Q. Blackwell (*J. Amer. Chem. Soc.*, 1944, **66**, 1165—1166).—5-*Fluoro*-2-*nitrobenzoyl chloride* (prep. from the acid by $SOCl_2$), b.p. 130—140°/6—7 mm., yields, by the usual methods, *Me*, m.p. 36·5—37°, *Et*, m.p. 43·5—44°, Pr^a, b.p. 127—128°/3 mm., Bu^a, b.p. 152°/7 mm., NR_2·$[CH_2]_2$ [R = Me (*hydrochloride*, m.p. 154—155°), Et (*hydrochloride*, m.p. 147·5—148·3°), Pr^a (*hydrochloride*, m.p. 131—131·5°), and Bu^a (*hydrochloride*, m.p. 74·5—75·5°)], and NR_2·$[CH_2]_3$ [R = Et (*hydrochloride*, m.p. 137·5—138·2°), Pr^a (*hydrochloride*, m.p. 122—122·5°), and Bu^a (*hydrochloride*, m.p. 98·3—99·3°)] 5-*fluoro*-2-*nitrobenzoate*, reduced (PtO_2) to *Me*, b.p. 105°/2 mm., *Et*, b.p. 110°/2 mm., Pr^a, b.p. 116°/2 mm., Bu^a, b.p. 130°/2 mm., NR_2·$[CH_2]_2$ [R = Me (*hydrochloride*, m.p. 175°), Et (*hydrochloride*, m.p. 125°), Pr^a (*hydrochloride*, m.p. 165°), and Bu^a (*hydrochloride*, m.p. 125°)], and NR_2·$[CH_2]_3$ [R = Et (*hydrochloride*, m.p. 133—134°), Pr^a (*hydrochloride*, m.p. 145°), and Bu^a (*hydrochloride*, m.p. 107—108°)] 5-*fluoro*-2-*aminobenzoate*, respectively. The aminoalkyl NH_2-esters produce anæsthesia of long duration but are irritant and toxic. R. S. C.

Action of trimethylgallazide on cresols. R. O. Pepe (*Anal. Asoc. Quím. Argentina*, 1941, **29**, 124—128).—*o-*, *m-*, and *p*-Cresol in NaOH with 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CON_3 in $COMe_2$ yield o-, m.p. 102°, m-, m.p. 124°, and p-*tolyl* 3 : 4 : 5-*trimethylgallate*, m.p. 89°. F. R. G.

Action of trimethylgallazide on monomethyl ethers of diphenols. R. O. Pepe (*Anal. Asoc. Quím. Argentina*, 1942, **30**, 235—239).—3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CON_3 in $COMe_2$ with *o-*, *m-*, and *p*-OMe·C_6H_4·OH in NaOH yields o-, m.p. 115°, m-, m.p. 102°, and p-*anisyl* 3 : 4 : 5-*trimethoxygallate*, m.p. 89°. F. R. G.

5 : 8-Dichloro-2-naphthoic acid and -2-naphthylamine. H. Goldstein and P. Viaud (*Helv. Chim. Acta*, 1944, **27**, 883—888).—2-$C_{10}H_7$·CN and Cl_2 in glacial AcOH–I (trace) at 110—120° in bright light give 5 : 8 : 2-$C_{10}H_5Cl_2$·CN, hydrolysed by AcOH–H_2SO_4–H_2O to 5 : 8 : 2-$C_{10}H_5Cl_2$·CO_2H, m.p. 301°. This is converted by MeOH–H_2SO_4 into the *Me* ester (**I**), m.p. 145·5°, and by $SOCl_2$ or PCl_5 into the *chloride*, m.p. 102°, which yields the amide, m.p. 224°, and *anilide*, m.p. 226°. (**I**) and boiling N_2H_4,H_2O afford 5 : 8-*dichloro*-2-*naphthoylhydrazine* (**II**), m.p. 212°, which yields *hydrazones* with $COMe_2$, m.p. 192°, PhCHO, m.p. 239°, *p*-NO_2·C_6H_4·CHO, m.p. 284°, and COPhMe, m.p. 204°. (**II**) is transformed by I in boiling EtOH into NN′-*di*-5 : 8-*dichloro*-2-*naphthoylhydrazine*, m.p. 342°. $NaNO_2$ and

H_2SO_4 convert (**II**) into the azide (**III**), m.p. ~108° (decomp.), which with the requisite boiling alcohol affords *Me*, m.p. 161°, and *Et*, m.p. 141°, N-5 : 8-*dichloro*-2-*naphthylcarbamate*. Boiling glacial AcOH converts (**III**) into NN′-*di*-5 : 8-*dichloro*-2-*naphthylcarbamide*, m.p. ~327°. (**III**) and boiling Ac_2O afford (after hydrolysis) 5 : 8 : 2-$C_{10}H_5Cl_2{\cdot}NH_2$ (*Bz* derivative, m.p. 203°), also obtained by chlorinating (β-$C_{10}H_7{\cdot}NH_2)_2,H_2SO_4$ in 80% H_2SO_4 and converted by diazotisation followed by treatment with boiling dil. H_2SO_4 into 5 : 8-*dichloro*-2-*naphthol*, m.p. 143° (*Me ether*, m.p. 74°). 5 : 8-*Dibromo*-2-*naphthol*, m.p. 147° (*Me ether*, m.p. 83°), is derived from 5 : 8 : 2-$C_{10}H_5Br_2{\cdot}NH_2$. M.p. are corr. H. W.

Sulphocarboxylic acids. III. Acid amide-like autocondensation of 3-amino-5-sulphobenzoic acid. P. Ruggli and H. Dahn (*Helv. Chim. Acta*, 1944, **27**, 867—882; cf. A., 1942, II, 197).—The prep. of H_2O-sol. org. compounds of approx. polymeric-homologous character and almost const. solubility in H_2O is described. The corresponding azo-dyes are very similarly adsorbed by Al_2O_3. The NH_2-acids and their dyes are not substantive to cotton in dil. Na_2CO_3; adsorption is not pronounced and the data cannot readily be reproduced. At any rate no such differences are found as might be expected from the great difference in mol. wt. This is possibly due to the very similar solubility. 3 : 5 : 1-$NO_2{\cdot}C_6H_3(SO_3H){\cdot}CO_2H$ gives a *Sr* H_2 salt (+$2H_2O$), *dipyridinium* salt, loses C_5H_5N at ~160° leaving the pyridinium H salt, m.p. 202—203°, and a *di*(*benzylthiuronium*) salt, m.p. 173—174°. The presence of 3 : 5 : 1-$NO_2{\cdot}C_6H_3(SO_2Cl){\cdot}COCl$ in 3 : 5 : 1-$NO_2{\cdot}C_6H_3(SO_2Cl){\cdot}CO_2H$ (**I**) (cf. Shah *et al.*, A., 1933, 1293) is determined by the formation of the alkali-insol. dianilide under the action of NH_2Ph. 3 : 5 : 1-$NH_2{\cdot}C_6H_3(SO_3H){\cdot}CO_2H$ is readily obtained by catalytic reduction (H_2 at 80°/50 atm.–Raney Ni in neutral solution) of the NO_2-compound. The normal Sr salt (+$2H_2O$), sol. in 8·3 parts of H_2O at 20°, *monopyridinium*, softens greatly with evolution of C_5H_5N at 176—178°, and non-cryst. benzylthiuronium salt are described. The acid and Sr salt give a blue, the pyridinium a yellow, fluorescence in ultra-violet light. Neutralisation of an aq. suspension of 3 : 5 : 1-$NH_2{\cdot}C_6H_3(SO_3H){\cdot}CO_2H$ at 70—80° with powdered $Sr(OH)_2$ and subsequent alternate additions of (**I**) and $Sr(OH)_2$ give the *Sr* (+$8H_2O$ and +$3H_2O$) salt of 3-3′-nitro-5′-carboxybenzenesulphonamido-5-sulphobenzoic acid; the acid and benzylthiuronium salt are non-cryst. Reduction [$FeSO_4$ and $Sr(OH)_2$] of the NO_2-acid affords the 3′-NH_2-acid, softens at 120—130°, chars at >300° [*Sr* salt (also *hexahydrate*)], and thence by diazotisation the corresponding N_2-acid, very sparingly sol. in hot H_2O. The conversion of (**I**) into 3 : 5 : 1-$NO_2{\cdot}C_6H_3(SO_3H,C_5H_5N){\cdot}CO{\cdot}C_5H_5NCl$ is described. Treatment of (**I**) with C_5H_5N followed by 3 : 5 : 1-$NH_2{\cdot}C_6H_3(SO_3H){\cdot}CO_2H$ leads to 3-3′-nitro-5′-sulphobenzamido-5-sulphobenzoic acid [*tri*(*benzylthiuronium*) salt, m.p. 180°], which is relatively stable to hydrolysis. It is reduced by $FeSO_4$ and $Sr(OH)_2$ or catalytically (Raney Ni) to the 3′-NH_2-compound (**II**), chars at >320°, the purity of which is best controlled by potentiometric titration of ·NH_2 with $NaNO_2$. This gives an internal *diazonium* salt, chars at ~320°, which couples with β-$C_{10}H_7{\cdot}OH$ to an azo-dye, m.p. 237—238°. (**II**) and (**I**) give 3-(3′-3″-nitro-5″-sulphobenzamido-5′-sulphobenzamido)-5-sulphobenzoic acid [*tetra*(*benzylthiuronium*) salt, m.p. 179°], reduced to the 3″-NH_2-acid, chars at >300° (Sr salt), which is converted into the diazo-compound, decomp. ~170°, m.p. 210°; this couples with β-$C_{10}H_7{\cdot}OH$ in C_5H_5N to a dye, m.p. 235—236°. H. W.

Condensation of 2-acetylnaphthalene with diethyl succinate. W. S. Johnson and A. Goldman (*J. Amer. Chem. Soc.*, 1944, **66**, 1030—1037).—Contrary to Stobbe *et al.* (A., 1911, i, 374), 2-$C_{10}H_7Ac$ and $(CH_2{\cdot}CO_2Et)_2$ with NaOEt in Et_2O give 18% of β-carbethoxy-γ-2-naphthyl-*cis*-Δ^β-pentenoic acid (**I**) (*A*) (R = Et, R′ = H), m.p. 119—119·5° (119—119·6°), but with NaOEt (~1 mol.) in boiling

$$\underset{2\text{-}C_{10}H_7{\cdot}C{\cdot}Me}{CO_2R{\cdot}C(:CH{\cdot}CO_2R')} \qquad \underset{2\text{-}C_{10}H_7{\cdot}C{\cdot}Me}{CO_2R'{\cdot}CH_2{\cdot}C(:CO_2R)}$$

(*A*.) (*B*.)

EtOH give 21% of cryst. (**I**) and an oil, which by treatment with $Ba(OH)_2$ and then AcCl gives the *anhydride* (**II**), m.p. 155·5—156°, of β-*carboxy*-γ-2-*naphthyl*-cis-Δ^β-*pentenoic acid* (**III**) (*A*) (R = R′ = H) (see below) with larger amounts of the *anhydride* (**IV**), m.p. 116—116·5°, of the trans-*dicarboxylic acid* (**V**) (*B*) (R = R′ = H) (see below). Structures are proved as follows. In boiling $Ba(OH)_2$–H_2O–EtOH, (**I**) gives (**III**), m.p. 179·5—180·5° (decomp.) [a further impure crop, m.p. 163—165° (decomp.), could not be purified; cf. Stobbe *et al.* (*loc. cit.*)], whence AcCl at room temp. yields (**II**). Boiling EtOH containing a drop of H_2SO_4 converts (**II**) into *Et* β-*carboxy*-γ-2-*naphthyl*-cis-Δ^β-*pentenoate* (**VI**) (*A*) (R = H, R′ = Et), *forms*, m.p. 118·5—119° and 105—105·5°, which is also obtained by partially esterifying (**III**) in EtOH–C_6H_6 + a little H_2SO_4 with continuous removal of H_2O. Such treatment with EtOH–C_6H_6–H_2SO_4 converts (**I**) into the cis-*Et*$_2$ ester (*A*) (R = R′ = Et), b.p. 184—186°/0·05—1 mm., which is also obtained from (**VI**) by boiling HCl–EtOH and is reconverted into (**I**) by partial hydrolysis by $Ba(OH)_2$–EtOH–H_2O. Hydrolysis of (**IV**) by 2% NaOH yields (**V**), m.p. 167—168° (decomp.), reconverted into (**IV**) by AcCl. EtOH + a little H_2SO_4 converts (**IV**) into *Et* β-*carboxy*-γ-2-*naphthyl*-trans-Δ^β-*pentenoate* (**VII**) (*B*) (R = H, R′ = Et), m.p. 102—102·5°, whence hydrolysis and then dehydration regenerates (**IV**) and H_2SO_4–EtOH–C_6H_6 (as above) yields the oily trans-*Et*$_2$ ester, converted by partial hydrolysis into β-*carbethoxy*-γ-2-*naphthyl*-trans-Δ^β-*pentenoic acid* (**VIII**) (*B*) (R = Et, R′ = H), an oil (derived *anilide-acid*, m.p. 153—154°). With O_3 in EtOAc and then Raney Ni at room temp. and finally the b.p., (**I**), (**VI**), or (**VII**) yields 39—42% of 2-$C_{10}H_7Ac$. With a little NaOAc in boiling AcOH–Ac_2O, (**VI**) gives *Et* 3-*methyl*-6 : 7-*benz*-1-*indone*-2-*acetate* (**IX**), m.p. 96·5—97°, and (**II**). With HNO_3 at 190—200° (**IX**) gives 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$, with boiling conc. HCl gives the *lactone* (**X**), m.p. 168·5—169° [with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ gives a *compound*, $C_{17}H_{17}O_4N_3$, m.p. 244° (decomp.) (bath preheated at 239°)], of 3-*hydroxy*-3-*methyl*-6 : 7-*benz*-1-*hydrindone*-2-*acetic acid* (**XI**) (see below), and with H_2–30% Pd–C in EtOAc gives *Et* 3-*methyl*-6 : 7-*benz*-1-*hydrindone*-2-*acetate*, m.p. 70·2—70·6°. 5% NaOH at room temp. hydrolyses (**X**) to (**XI**), m.p. 169—169·5° (decomp.) [a *form*, m.p. 148·5—150° (decomp.), may also exist] [and red, amorphous material, m.p. 227—235° (decomp.)], which regenerates (**X**) in presence of traces of acid. (**I**) is largely unchanged by NaOAc–AcOH–Ac_2O, giving only a trace of (**II**), but with HF yields (**X**). NaOAc–AcOH–Ac_2O cyclises (**VIII**) to *Et* 4-*acetoxy*-1-*methylphenanthrene*-2-*carboxylate* (**XII**) (78%), m.p. 127·5—128°, hydrolysed by boiling HCl–EtOH to the 4-*OH*-ester (**XIII**), m.p. 178·5—179°, whence Me_2SO_4–aq. NaOH yields *Et* 4-*methoxy*-1-*methylphenanthrene*-1-*carboxylate*, m.p. 74—74·5°, and thence the 4-*OMe-acid*, m.p. 225—225·5°, which with Cu powder in quinoline at 205°, rising to 220°, gives 4-methoxy-1-methylphenanthrene, m.p. 78—79° [picrate, m.p. 183—184° (lit. 182—183°)]. 5% KOH–EtOH hydrolyses (**XII**) to 4-*hydroxy*-1-*methylphenanthrene*-2-*carboxylic acid* (**XIV**), m.p. 253—254° (decomp.; uncorr.) (*acetate*, m.p. 227·5—229°), which is too sensitive for decarboxylation. (**VII**) is not cyclised by NaOAc–Ac_2O–AcOH, yielding only a little (**IV**). HF cyclises (**III**) to 3-*methyl*-6 : 7-*benz*-1-*indone*-2-*acetic acid*, m.p. 215·5—219·5° [could not be obtained from (**IX**)], and some (**X**), and (**V**) gives (**XIV**). The crude product of the original condensation, after separation of much (**I**), is cyclised by NaOAc, whereby (**VIII**) yields (**XII**) and the remaining (**I**) can be isolated; it is thus shown to contain 29% of (**I**) and 30% of (**VIII**); full esterification (to diesters, b.p. 203—206°/2—3 mm.), partial hydrolysis, and then cyclisation indicates 47% of (**I**) and 38% of (**VIII**). Unless otherwise stated, m.p. are corr. R. S. C.

Vitamin-*A* aldehyde (axerophthal). E. G. E. Hawkins and R. F. Hunter (*J.C.S.*, 1944, 411).—Vitamin-*A* aldehyde (**I**), max. at 6570 A. ($SbCl_3$), bands at 3680 and 3500 A. (2 : 4-*dinitrophenylhydrazone*, m.p. 208—209°, prepared in aq. EtOH–HCl–H_2 at 60°; band at 4350 A.), is prepared from vitamin-*A* alcohol (**II**), $Al(OPr^\beta)_3$, MeCHO, and C_6H_6 at 70° for 48 hr. in a sealed tube. Purification is effected by " cyclisation " of unchanged (**II**) and chromatography. Ponndorff reduction with $Al(OPr^\beta)_3$ converts (**I**) into (**II**). In solution, (**I**) is oxidised rapidly at 0° to yield (chromatographic separation) a product which shows bands at 3300 A. and 6180—6200 A. ($SbCl_3$); it differs from (**II**) in that the ultra-violet absorption spectrum is unaltered after treatment with HCl–EtOH. Adding NaOEt–EtOH to (**I**) in $COMe_2$ at −5°, and keeping at room temp. for 2½ hr., gives axerophthylideneacetone, reduced by $Al(OPr^\beta)_3$ to axerophthylidene*iso*propyl alcohol. A. T. P.

Reaction of α-chloroketones with alkali. W. D. McPhee and E. Klingsberg (*J. Amer. Chem. Soc.*, 1944, **66**, 1132—1136).—$COMe{\cdot}CH_2Ph$, b.p. 105—106°/23 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 155·5—156·5°), with SO_2Cl_2–CCl_4 at 45° gives $COMe{\cdot}CHPhCl$ (**I**) (84%), b.p. 115—118°/16 mm., which with $PhSO_2Na$ in boiling 95% EtOH gives α-*benzenesulphonylbenzyl Me ketone* (88%), m.p. 120·5—122·5°. With NaOMe in boiling MeOH, (**I**) gives $Ph{\cdot}[CH_2]_2{\cdot}CO_2Me$ (**II**) (60%), α-*hydroxybenzyl Me ketone Me*$_2$ *acetal* (**III**) (14%), m.p. 63—65°, and $Ph{\cdot}[CH_2]_2{\cdot}CO_2H$ (**IV**) (9%) (cf. Richard, A., 1934, 191; 1935, 979; Aston *et al.*, A., 1942, II, 247), but in MeOH containing a little H_2O gives 48% of (**IV**) and 20% of (**III**). With 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ (**V**) or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, (**III**) gives the bis-derivatives of BzCOMe. $CH_2Ph{\cdot}COCl$ with CH_2N_2 (2 mols.) in Et_2O and then gaseous HCl (cf. Bradley *et al.*, A., 1939, 68) gives *benzyl chloromethyl ketone* (83%), b.p. 133—135°/19 mm. (derived *benzenesulphonylmethyl ketone*, m.p. 89·5—90·5°), which with NaOMe–MeOH gives readily 80% of (**II**). $Ph{\cdot}[CH_2]_2{\cdot}COCl$ gives similarly $Ph{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH_2Cl$ (85%), m.p. 39—40° (2 : 4-dinitrophenylhydrazone, m.p. 145—146°), which with NaOMe–MeOH and a little H_2O gives a mixture, b.p. 112—116°/2 mm., of $Ph{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH_2{\cdot}OH$ (**VI**) and $Ph{\cdot}[CH_2]_2{\cdot}C(OMe)_2{\cdot}CH_2{\cdot}OH$ (and 8% of $Ph{\cdot}[CH_2]_3{\cdot}CO_2H$), which after boiling in EtOH + a drop of HCl yields (**VI**) (*phenylhydrazone*, m.p. 114·5—115·5°). *Et* α-*chloro*-α-*benzylacetoacetate* (prep. from $CH_2Ph{\cdot}CHAc{\cdot}CO_2Et$ by SO_2Cl_2 at 0°), b.p. 121—125°/1 mm., in boiling H_2SO_4–AcOH–H_2O gives α-*chloro*-β-*phenylethyl Me ketone* (84%), b.p. 97—99°/4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 138·5—139·5°), which with NaOMe–MeOH + H_2O gives $\beta\beta$-*dimethoxy*-δ-*phenyl*-n-*butan*-γ-*ol* (54%), b.p. 119—121°/6 mm. This is unaffected by (**V**) in the cold (hydrolysed hot) but after treatment

with hot HCl–EtOH yields $CH_2Ph{\cdot}CO{\cdot}COMe$ [phenylosazone, m.p. 169·5—171° (lit. 172—173°)] and, when kept in Et_2O, gives a *lactolide*, $C_{22}H_{28}O_4$, m.p. 180—182·5°. *S-Benzylthiuronium γ-phenyl-n-butyrate*, m.p. 141—141·5°, and *β-phenylisobutyrate*, m.p. 144—144·5°, are also described. The products, b.p. 104°/0·04 mm. and m.p. 40—41°, of Eastham *et al.* (A., 1944, II, 162) are 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}[CH_2]_2{\cdot}CO_2R$ in which R = Et (lit. b.p. 193°/20 mm.) and Me (lit. m.p. 37°, 38—39°), respectively. M.p. are corr.

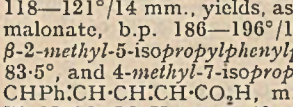
R. S. C.

Reversibility of the benzoin reaction. J. Romo A. (*Ciencia*, 1943, **4**, 216—217).—Benzoin, anisoin, and piperoin in EtOH with $(NH_4)_2CO_3$ and KCN yield the substituted hydantoins obtained by Bucherer *et al.* (A., 1934, 1231) under the same conditions from PhCHO etc. It is concluded that the reaction $2C_6H_4R{\cdot}CHO \rightarrow C_6H_4R{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_4R$ is reversible. Benzil under these conditions yields 5-phenylhydantoin together with EtOBz.

F. R. G.

New aspects of the *ortho*-effect. Cyclic ketones related to acetophenone. R. G. Kadesch (*J. Amer. Chem. Soc.*, 1944, **66**, 1207—1213).—6 : 9-*Dimethylbenzsuberone* (I) (see below) behaves towards MgMeI and NH_2OH as a highly hindered ketone [cf. acetomesitylene (II)] in contrast to 4 : 7-dimethyl-1-indanone (III) and 1-keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (IV). This is due to the CO of (I) being forced out of co-planarity with the C_6H_6 ring by incorporation into the C_7-ring, so that approach of reagents is blocked by the neighbouring Me, whereas the CO is held co-planar in the C_5- and C_6-rings of (III) and (IV). This also explains the hindrance exhibited by (II), but not by 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CHO$, the CHO being too small. Thus *o*-groups are necessary for hindrance but not alone sufficient. 2 : 1-$C_{10}H_6Me{\cdot}COMe$ (V) is hindered, showing that the CH of the adjoining nucleus is sterically effective. (III), m.p. 77—78°, is obtained from 2 : 5 : 1-$C_6H_3Me_2{\cdot}CO{\cdot}[CH_2]_2{\cdot}Cl$ by hot conc. H_2SO_4. 3 : 5 : 1-$C_6H_3Me_2{\cdot}CH_2Br$ (prep. from *s*-$C_6H_3Me_3$ by Br in air at 135—155°; 49% yield) and $CHNa(CO_2Et)_2$–EtOH at 60—70° give Et_2 3 : 5-dimethylbenzylmalonate, b.p. 198—205°/24 mm.; the derived *acid*, m.p. 147—148°, at 175—185° yields *β*-m-5-*xylylpropionic acid*, m.p. 45—46·5°, and thence, by way of the chloride, 5 : 7-*dimethyl*-1-*indanone*, m.p. 76—77°. 2-*Chloromethyl*-p-*cymene* (prep. from *p*-cymene in 59% yield), b.p. 118—121°/14 mm., yields, as above, Et_2 2-methyl-5-*iso*propylbenzylmalonate, b.p. 186—196°/13 mm., the derived *acid*, m.p. 163°, *β*-2-*methyl*-5-*isopropylphenylpropionic acid*, softens 69°, m.p. 83—83·5°, and 4-*methyl*-7-*iso*propyl-1-*indanone*, m.p. 107°.

$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$, m.p. 160—164°, yields (H_2–colloidal Pd) $Ph{\cdot}[CH_2]_4{\cdot}CO_2H$, m.p. 56—58°, and thence benz-1-suberone (VI), b.p. 141·5—143°/14 mm. 2 : 5 : 1-$C_6H_3Me_2{\cdot}CO{\cdot}[CH_2]_2{\cdot}Cl$ yields, as above, *δ-keto*-δ-p-*xylyl*-n-*butane-αα-dicarboxylic acid*, m.p. 117—118° (decomp.) [Et_2 ester, b.p. 215—218° (decomp.)/15 mm.)], *δ-keto*-δ-p-*xylyl*-n-*valeric*, m.p. 72—73° (also obtained from *p*-xylene and $COCl{\cdot}[CH_2]_3{\cdot}COCl$), and (Clemmensen) δ-p-*xylyl*-n-*valeric acid*, m.p. 36·5—37·5°, the chloride (prep. by $SOCl_2$) of which with $AlCl_3$ in CS_2 gives (I) (41%), b.p. 121—131°/1 mm. Adding 2 : 1-$C_{10}H_6Me{\cdot}MgBr$ (VII) to AcCl gives 2-$C_{10}H_7Me$ and 2 : 1-$C_{10}H_6MeBr$ with only small amounts of (V) (reverse addition gives none). 2 : 1-$C_{10}H_6Me{\cdot}CO_2H$ [prep. from (VII) by CO_2] with $SOCl_2$ gives the chloride, b.p. 115—120°/1—2 mm., which with MgMeI gives 82% of (V), b.p. 122—126°/1 mm. (*ω-CHPh:* derivative, m.p. 136·5—137·5°).



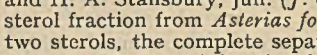
(VI.)

R. S. C.

Action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate. V. R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **20**, 399—402; cf. A., 1944, II, 101).—The product (*A*) of the action of Na on Et_3 β-methylbutane-αβδ-tricarboxylate (A., 1943, II, 371) when reduced (Na–Hg) and subsequently esterified gives *Et*$_2$ 3-*hydroxy*-1-*methylcyclopentane*-1 : 4-*dicarboxylate*, b.p. 145°/5 mm., converted by $POCl_3$ and C_5H_5N, followed by hydrolysis, into 1-*methyl*-Δ^3-*cyclopentene*-1 : 3-*dicarboxylic acid* (I), m.p. 168°. None of the isomeric 1-methyl-Δ^3-*cyclo*pentene-1 : 2-dicarboxylic acid was detected, which would be the case if (*A*) contained Et_2 3-methyl*cyclo*pentanone-2 : 3-dicarboxylate (cf. Baker, A., 1931, 957). Reduction (H_2, PtO_2, AcOH) of (I) gives a mixture of saturated acids from which *cis*-1-methyl*cyclo*pentane-1 : 3-dicarboxylic anhydride, m.p. 81°, was obtained by action of AcCl. Hydrolysis yielded the *cis*-acid identical with a sample synthesised as follows: dehydration ($POCl_3$–C_5H_5N) of the cyanohydrin of Et 3-methyl*cyclo*pentanone-3-carboxylate followed by hydrolysis gives a mixture (m.p. 155—162°) of unsaturated acids from which *cis*- and *trans*-1-methyl*cyclo*pentane-1 : 3-dicarboxylic acids were obtained on hydrogenation (H_2–PtO_2). (*A*) is therefore Et_2 3-methyl*cyclo*pentanone-3 : 5-dicarboxylate.

J. N. A.

Constituents of pyrethrum flowers. XVI. Heterogeneous nature of pyrethrolone. F. B. LaForge and W. F. Barthel (*J. Org. Chem.*, 1944, **9**, 242—249).—Pyrethrolone (I) is a mixture of components differing with respect to the nature of the side-chain. These components can be partly separated by distillation and show marked differences in *n*. Determination of C-Me in successive fractions shows that one component has the conjugated system of double linkings and the other contains a side-chain terminating with the group C:CHMe. The acetate and Me ether are shown to be mixtures corresponding to the two systems of unsaturation. The heterogeneous nature of (I) explains the apparent discrepancies between absorption results and chemical facts and revisions of the formulæ of Gillam *et al.* (A., 1942, II, 415) become unnecessary. (I) consists predominatingly of the compound



H. W.

Polyenes. II. Purification of β-ionone. W. G. Young, S. J. Cristol, L. J. Andrews, and S. L. Lindenbaum (*J. Amer. Chem. Soc.*, 1944, **66**, 855—857; cf. A., 1944, II, 261).—β-Ionone (I) of max. purity (ε 10,700 at 296 mμ.) is obtained from its semicarbazone by cold conc. H_2SO_4 (cf. Heilbron *et al.*, A., 1943, II, 60), but other methods cause partial decomp.; notably distillation in steam with *o*-$C_6H_4(CO)_2O$ gives 80—90%-pure (I). (I) is not affected by cold conc. or dil. H_2SO_4, and only slowly by hot dil. H_2SO_4.

$CHPh{:}CH{\cdot}CH{:}CH{\cdot}COMe$ and (I) react with BzO_2H in C_6H_6 or PhMe at 8° much faster than do Δ^α-mono-unsaturated ketones (*A*) until 1 mol. of BzO_2H is absorbed and thereafter react as slowly as do (*A*); thus the hindrance to addition observed with C:C·C:C·CO is not observed with C:C·C:C·CO.

R. S. C.

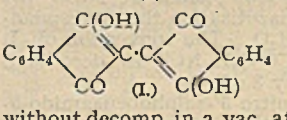
Reported total asymmetric synthesis. J. M. O'Gorman (*J. Amer. Chem. Soc.*, 1944, **66**, 1041).—2-Formyl*cyclo*hexanone with hot MeI–10% EtOH–NaOEt or, better, the Na salt thereof with MeI–PhMe gives 2-formyl-2-methyl*cyclo*hexanone, α $0 \pm 0·7°$ or $\pm 0·1°$, respectively.

R. S. C.

Trimeric glyoxal. G. M. Dyson (*Chem. and Ind.*, 1944, 342—343).—Trimeric glyoxal (I) may be converted into tetrahydroxy-*p*-benzoquinone by atm. oxidation of its aq. solution in Na_2CO_3, usually in presence of a bisulphite. The benzenoid skeleton must exist in (I), which is probably 1 : 1 : 2 : 3 : 4 : 4 : 5 : 6-octahydroxy-Δ^2-*cyclo*hexenone. (Cf. Raudnitz, A., 1944, II, 346.)

F. R. S.

Indene derivatives. III. Constitution and reactions of bishydroxyindone. Photochemical reduction of triketohydrindene. A. Schönberg and R. Moubasher (*J.C.S.*, 1944, 366—367; cf. A., 1943, II, 136).—The violet bis-1 : 3-indanedione (bisdiketohydrindene) (cf. Wanag, A., 1937, II, 199; 1939, II, 326; Eck *et al.*, A., 1935, 1492) is the dienol (I) in the solid state and is renamed bishydroxyindone. It dissolves readily in aq. NaOH and with CH_2N_2–Et_2O gives an orange *Me ether* (II), m.p. ~122° (decomp.) (depends on rate of heating), reconverted into (I) by conc. H_2SO_4 at 50°. (I) sublimes without decomp. in a vac. at 340°. It is stable to O_2 at room temp., but is oxidised (O_2; Se) at 340° to *o*-$C_6H_4(CO)_2O$, also obtained similarly from (II). (I) is more reactive than 5 : 12-dihydroxynaphthacene-6 : 11-quinone (III), although the corresponding resonance structures of (I) and (III) are similar. (III) is only sparingly sol. in aq. NaOH and does not react with CH_2N_2, probably owing to a 6-membered chelate ring (similarly *o*-$OH{\cdot}C_6H_4{\cdot}COMe$ does not react with CH_2N_2). The red triketohydrindene is photochemically reduced to the colourless hydrindantin, turns red at ~200° and decomposes at higher temp., by $Pr^\beta OH$ in sunlight for 10 days.



(I.)

A. T. P.

IV.—STEROLS AND STEROID SAPOGENINS.

Physico-chemical constants of cholesterol and its ozonide.—See A., 1944, I, 236.

Resinification of cholesterol. A. H. Roffo and L. M. C. Urquiza (*Anal. Asoc. Quím. Argentina*, 1942, **30**, 177—196).—Cholesterol exposed to ultra-violet light from a Cd-vapour lamp is converted into an orange transparent resin, the absorption spectrum and intensity of fluorescence of which have been examined. Resinification is considered as a complex oxidation accompanied by a progressive decrease in m.p., *d*, and I val., and an increase in acidity.

F. R. G.

Marine products. XV. Sterols of starfish. II. W. Bergmann and H. A. Stansbury, jun. (*J. Org. Chem.*, 1944, **9**, 281—289).—The sterol fraction from *Asterias forbesi* is a complex mixture of at least two sterols, the complete separation of which has not been accomplished. Prolonged fractional crystallisation of the sterol mixture (I) or of the acetates derived therefrom suggests that the least sol. component is identical with stellasterol (II). The discrepancy between the m.p. of the benzoates derived from (I) and of stellasteryl benzoate (III) depends on isomerisation induced by HCl when (II) is heated with BzCl so that (III) is a mixture of isomerides such as is also produced when (II) is treated with BzCl and C_5H_5N and the product subjected to HCl. Complete separation could not be effected by crystallisation of (I), its acetate or benzoate, chromatography of the acetates over Al_2O_3, or bromination of the acetates which destroys most of the material but gives a very small amount of an unknown *dibromide*, $C_{31}H_{50}O_2Br_2$, m.p. 184—185°. Subsequent work is done with (I), the degree of unsaturation of which suggests

the presence of di-unsaturated (**II**) and a mono-unsaturated sterol which is termed stellastenol (**IV**). All fractions of starfish sterols and their derivatives are slightly dextrorotatory, indicating the absence of the $\Delta^{5:6}$ double linking; also they all give a green colour reaction with Br usually regarded as typical of sterols with a double linking at $C_{(6)}$. Hence it is assumed as a working hypotheses that (**II**) and (**IV**) have a double linking in the γ- (7 : 8), δ- (8 : 9), or α- (8 : 14) -position. The presence of a double linking in the side-chain of (**II**) is established by ozonolysis, giving *d-αβ*-dimethylbutaldehyde isolated as the 2 : 4-*dinitrophenylhydrazone*, m.p. 119—120°, $[\alpha]_D^{14}$ +14·1°. l-*αβ-Dimethylbutaldehyde*-2 : 4-*dinitrophenylhydrazone*, derived from ergosterol, has m.p. 124—124·5°, $[\alpha]_D^{24}$ −37·7°. The mixed m.p. of the two derivatives is 119—122·5°. Bearing in mind that partial racemisation of the aldehydes is difficult to prevent it appears justifiable to conclude that the aldehydes are optical antipodes and that (**II**) has the side-chain $CHMe{\cdot}CH{:}^{24}CHMePr\beta$ in which the optical configuration at $C_{(24)}$ is the opposite of that of ergosterol. Preliminary studies show the presence of inert double linkings in (**I**). Thus a mixture of acetates with 1·4 double linkings absorbed ~0·5 mol. of H_2 with Pt-black catalyst in AcOH at room temp. and atm. pressure, giving a homogeneous *α-stellastenyl acetate*, m.p. 105—106°, $[\alpha]_D^{23}$ +12·5°, hydrolysed to *α-stellastenol*, m.p. 123—125°, $[\alpha]_D^{21}$ +19·8° (3 : 5-*dinitrobenzoate*, m.p. 196·5—197·5°). This is isomerised by HCl in $CHCl_3$ at 0° to *β-stellastenyl acetate*, m.p. 94—96°, $[\alpha]_D^{26}$ +19° (hydrolysed to *β-stellastenol*, m.p. 122—124°, $[\alpha]_D^{22}$ +29·5°), which is hydrogenated at room temp. to *stellastanol* (**V**), m.p. 143°, $[\alpha]_D^{22}$ +22° (*acetate*, m.p. 138—139°, $[\alpha]_D^{24}$ +13·5°; 3 : 5-*dinitrobenzoate*, m.p. 204—205°). The optical activites of the two stellastenols and (**V**) agree with the general rule that α-unsaturated sterols have a less positive and β-unsaturated sterols a more positive rotation than the corresponding saturated sterols. (**V**) is isomeric with ergostanol and campestanol and like the latter it differs from ergostanol in the configuration at $C_{(24)}$. The starfish sterols are C_{28} compounds and are the first principal sterols of this order to be found in animal tissue. This complexity is difficult if not impossible to reconcile with the hypothesis of the exogenous origin of the sterols of marine invertebrates. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

Marine products. XVI. 7-Dehydroclionasterol. W. Bergmann, A. M. Lyon, and M. J. McLean (*J. Org. Chem.*, 1944, **9**, 290—292).—Clionasteryl acetate is oxidised by CrO_3 in AcOH at 60—65° to 7-*ketoclionasteryl acetate*, m.p. 172—173°, $[\alpha]_D^{27}$ −99·44°. This is reduced by $Al(OPr\beta)_3$ in $Pr^\beta OH$ and then hydrolysed to a mixture of diols; the form of higher m.p. gives a *dibenzoate*, m.p. 159—160°, $[\alpha]_D^{24}$ +93·4°, which is transformed by protracted boiling with $NPhMe_2$ into 7-*dehydroclionasteryl benzoate*, m.p. 133—135° (turbid; clear at 138°), also obtained from the dibenzoate of the form of lower m.p. This is hydrolysed by KOH–MeOH to 7-*dehydroclionasterol* (**I**), m.p. 138°, $[\alpha]_D^{26}$ −98·2°, which becomes yellow when kept. Better results are obtained by hydrolysing the mixed dibenzoates with NaOMe in MeOH–C_6H_6 and treatment of the product with boiling $NPhMe_2$; (**I**) is then isolated as the digitonide and the latter is converted directly by boiling Ac_2O into 7-*dehydroclionasteryl acetate*, m.p. 139—140°, $[\alpha]_D^{24}$ −71·6°, the absorption spectrum of which is identical with that of ergosteryl acetate. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

Bile acids and related substances. XXX. Simplified preparation of 3(α) : 12(α)-dihydroxyætiocholanic acid. V. Wenner and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 965—969).—Me 3(α) : 12(β)-dihydroxyætiocholanate is partly acetylated by boiling Ac_2O–C_6H_6, giving unchanged material, the diacetate, a little of the 12- and (mainly) the amorphous 3-acetate (**I**). Oxidation of (**I**) by CrO_3 in AcOH at 16° yields *Me* 12-*keto*-3(α)-*acetoxyætiocholanate* (**II**), m.p. 152—154°, $[\alpha]_D^{14}$ +151·5°±2° in $CHCl_3$, hydrolysed to the 3(α)-*OH*-ester (**III**), m.p. 169—170°, $[\alpha]_D^{13}$ +144·0°±1° in $CHCl_3$. (**II**) or (**III**) is hydrogenated (Raney Ni in alkaline solution) to Me 3(α) : 12(α)-dihydroxyætiocholanate, m.p. 182—183°, $[\alpha]_D^{14}$ +51·9±2° in MeOH (3-*monoacetate*, m.p. 155—156°, $[\alpha]_D^{15}$ +52·3°±2° in $COMe_2$). M.p. are corr. (block); limit of error ±2°. H. W.

Comparison of methods for the preparation of dehydroandrosterone. S. Schreyer (*Anal. Asoc. Quím. Argentina*, 1941, **29**, 141—148).—The yield of dehydroandrosterone obtained from cholesteryl acetate dibromide by CrO_3 is not related to O consumed. The experimental conditions of Butenandt *et al.* (A., 1936, 77) give a higher yield than those of Ruzicka *et al.* (A., 1935, 1125) or Wallis *et al.* (A., 1935, 1242). F. R. G.

Constituents of the adrenal cortex and related substances. LXIX. Action of lead tetra-acetate on cholestenone. E. Seebeck and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 948—950).—The product obtained by oxidising Δ^4-cholesten-3-one with $Pb(OAc)_4$ in AcOH–Ac_2O at 70° (cf. A., 1939, II, 552) is the 2-*OAc*-derivative, m.p. 141—142°, $[\alpha]_D^{15}$ +65·5°±1° in $CHCl_3$, since it is converted by hydrogenation and subsequent hydrolysis into cholestane-2 : 3-diol (possibly a mixture of stereoisomerides) which is oxidised by CrO_3 in AcOH to the homogeneous dicarboxylic acid, m.p. 196—197° (Me_2 ester, m.p. 62—64°), also prepared according to Windaus *et al.* (A., 1914, i, 1066) by oxidation of cholestan-3(β)-ol. M.p. are corr. (block); limits of error ±2°. H. W.

Constituents of the adrenal cortex and related substances. LXVIII. Pregnane-3(α) : 11(α)-diol-20-one and -3(β) : 11(α)-diol-20-one. J. von Euw, A. Lardon, and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 821—839).—Me 3(β)-11(α)-dihydroxybisnorcholanate is converted when heated with MgPhBr into the amorphous carbinol, the amorphous acetate of which is transformed by boiling AcOH into *αα-diphenyl-β-11(α)-hydroxy-3(β)-acetoxyætiocholanyl-*Δ^α*-propene*, m.p. 282—284°. Ozonisation at −10° and fission of the ozonide by Zn dust and AcOH gives $COPh_2$ and a mixture which, after acetylation, is separated chromatographically into *pregnan-3(β)-ol-11 : 20-dione acetate* (**I**), m.p. 169—170°, $[\alpha]_D^{13}$ +89·1°±1·5° in $COMe_2$, and *pregnane-3(β) : 11(α)-diol-20-one* 3-*monoacetate* (**II**), m.p. 163—164°, $[\alpha]_D^{12}$ +115·2°±1·5° in $COMe_2$. Ozonisation at −80° with use of 1 mol. proportion of O_3 and immediate fission of the ozonide leads almost exclusively to (**II**). Alkaline hydrolysis (KOH–MeOH) at 20° of (**I**) and (**II**) gives *pregnan-3(β)-ol-11 : 20-dione* (**III**), m.p. 152—153° (becomes opaque at 100°), and *pregnane-3(β) : 11(α)-diol-20-one* (? hydrate), m.p. 255—260°. (**II**) is readily oxidised by CrO_3 in AcOH to (**I**). By a similar series of changes Me 3(α) : 11(α)-dihydroxybisnorcholanate is transformed into *αα-diphenyl-β-11(α)-hydroxy-3(α)-acetoxyætiocholanyl-*Δ^α*-propene*, m.p. 242—245°, and thence into *pregnane-3(α) : 11(α)-diol-20-one* 3-*monoacetate* (**IV**), m.p. 182—184° $[\alpha]_D^{13}$ +147·5°±1·5° in $COMe_2$, hydrolysed to *pregnane-3(α) : 11(α)-diol-20-one*, m.p. 222—225°, and oxidised by CrO_3 in AcOH to *pregnan-3(α)-ol-11 : 20-dione acetate* (**V**), m.p. 132—133°, or, frequently, 138° when heating is slow (in one experiment hexagonal plates, m.p. 134—137°, were observed), $[\alpha]_D^{13}$ +121·7°±3° in $COMe_2$; pregnan-3(α)-ol-11 : 20-dione has m.p. 172—174°.

Pregnan-12(β)-ol-3 : 20-dione is converted by anthraquinone-2-carboxyl chloride and C_5H_5N in C_6H_6 into the *anthraquinone-2-carboxylate*, m.p. 208—209°, which passes at 295—300°/0·05 mm. into Δ^{11}-pregnene-3 : 20-dione, m.p. 131—133°, transformed by NHAcBr and NaOAc,$3H_2O$ in dil. AcOH, into 12-bromopregnan-11(α)-ol-3 : 20-dione, m.p. 245—246° (decomp.) [the by-products afford (on oxidation) Δ^9-pregnene-3 : 12 : 20-trione, m.p. 182—183°]. This is oxidised to 12-*bromopregnane*-3 : 11 : 20-*trione*, m.p. 192—193°, debrominated by Zn dust and NaOAc in AcOH to pregnane-3 : 11 : 20-trione (**VI**), m.p. 161—162°. This when partly hydrogenated (PtO_2 in AcOH) and then pptd. with digitonin and treated with Girard's reagent *T* gives mainly (**III**) characterised as (**II**), also obtained directly by chromatography of the acetylation–hydrogenation product. The by-products of the hydrogenation, if necessary after hydrolysis, are re-converted by cautious oxidation into (**VI**), whereby a good yield of (**III**) is secured. (**III**) (as acetate) is partly hydrogenated to pregnane-3(β) : 20-diol-11-one 3-monoacetate, m.p. 200—201°, identified as the *diacetate*, m.p. 209—210°, and fully hydrogenated to *pregnane*-3(β) : 11(α) : 20-*triol* 3-*monoacetate*, double m.p. ~75° and 166—167°, which is converted by Ac_2O and C_5H_5N at 70° into the 3 : 20-*diacetate*, m.p. 209—210°, by CrO_3 in AcOH into pregnane-3(β) : 20-diol-11-one 3-monoacetate, m.p. 199—200°, and by $Al(OPh)_3$ in C_6H_6–$COMe_2$ at 98° into (**II**).

Pregnane-3(α) : 12(β)-*diol*-20-*one dianthraquinone-2'-carboxylate* (**VII**), m.p. 283—284°, is hydrolysed by $NH_2{\cdot}CH_2{\cdot}CO_2K$ in EtOH–dioxan or KOPh with excess of PhOH in EtOH–dioxan to the 12-*monoanthraquinone-2'-carboxylate* (**VIII**), m.p. 230—231°, which rapidly becomes green on exposure to air and gives an *acetate* (**IX**), m.p. 174—175°. (**VIII**) is oxidised by CrO_3 in AcOH at 18° to pregnan-12(β)-ol-3 : 20-dione anthraquinone-2'-carboxylate, m.p. 209—210°. Pregnane-3(α) : 12(β)-diol-20-one 3-monoacetate, m.p. (indef.) 95—110°, is converted into (**IX**) and a *substance*, m.p. 225—226°. Pregnane-3(α) : 12(β)-diol-20-one and BzCl in C_5H_5N at 20° give the *dibenzoate*, m.p. 183—184°, partly hydrolysed by KOH–MeOH to the 12-*monobenzoate*, m.p. 160—161°, which gives a non-cryst. 3-acetate. At 290°/high vac. (**IX**) gives unchanged material, $\Delta^{3:11}$-*pregnadien*-20-*one* (**X**), m.p. 125—127°, and Δ^{11}-*pregnen*-3(α)-*ol*-20-*one acetate* (**XI**), m.p. 136—137° (hydrolysed to the alcohol, m.p. 125—126°, which is oxidised to Δ^{11}-pregnene-3 : 20-dione, m.p. 132—134°).

Δ^{11}-*Pregnen*-3(α)-*ol*-20-*one anthraquinone-2'-carboxylate* (**XII**) has m.p. 240—242°. (**VII**) at 290—320°/0·02 mm. passes into (**X**) with some (**XII**) and (?) Δ^3-*pregnen*-12(β)-*ol*-20-*one anthraquinone-2'-carboxylate*, m.p. 190—192°, and some unchanged material. (**XI**), NHAcBr, and NaOAc in dil. AcOH at 16° afford 12-*bromopregnane*-3(α) : 11(α)-*diol*-20-*one* 3-*monoacetate*, m.p. 213—214°, oxidised to 12-*bromopregnan*-3(α)-*ol*-11 : 20-*dione acetate*, m.p. 194—195°. This is converted by Zn dust, NaOAc, and AcOH into (**V**). Δ^9-*Pregnen*-3(α)-*ol*-12 : 20-*dione acetate*, double m.p. 150—152° and 162—164°, is described. Energetic hydrogenation of (**V**) leads to *pregnane*-3(α) : 11(α) : 20-*triol* 3-*monoacetate*, m.p. 83—85°, converted by $Al(OPh)_3$ in $COMe_2$ into (**IV**). M.p. are corr. (block); limit of error ±2°. H. W.

Introduction of the 3-keto-Δ^4-conjugated system in the deoxycholic acid series. B. Riegel and A. V. McIntosh, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 1099—1103).—3 : 12-Dihydroxycholic esters are con-

verted by $Al(OBu^{\gamma})_3$ and *cyclo*hexanone in boiling PhMe directly into 12-hydroxy-3-keto-esters. Thus are obtained Me 12-hydroxy-3-keto-cholanate (I) (63%), m.p. 140·5—142°, *-norcholanate* (II) (65%), m.p. 143—145°, *-bisnorcholanate* (78%), m.p. 203—204°, and -ætiocholanate (37%), m.p. 139—141·5°. With Br–AcOH at room temp. (1·75 min.) these give 4-*Br*-esters, m.p. 134—134·5°, 178·5—180°, 206—207°, and a resin, respectively, which in boiling C_5H_5N yield Me 12-hydroxy-3-keto-Δ^4-cholenate (III), m.p. 144—145° (lit. 150—152°), -Δ^4-*norcholenate* (IV), m.p. 136·5—137°, -Δ^4-*bisnorcholenate* (V), m.p. 164—167° (? 175—176°), and -Δ^4-*ætiocholenate* (VI), m.p. 152—153°, respectively. (III)—(VI) have characteristic absorption max. at 241—241·5 mμ., ε being 14,470, 16,320, 14,100, and 14,940, respectively. Me 3 : 12-diacetoxy-cholanate and *-norcholanate*, m.p. 153—153·4°, in 0·5N-KOH–EtOH at room temp. give 3-hydroxy-12-acetoxy-cholanic and *-norcholanic acid* (82·5%), m.p. 219—221°, oxidised by CrO_3–AcOH to 3-keto-12-acetoxy-cholanic and -norcholanic acid, respectively, and thence, by hydrolysis followed by treatment with MeOH and a little AcCl, (I) and (II), respectively. *Me* 3 : 12-*diacetoxy-bisnorcholanate*, m.p. 165—167°, and -ætiocholanate, m.p. 149—150·5°, and 12-*hydroxy*-3-*keto*-Δ^4-*bisnorcholenic acid*, m.p. 210—220°, are also prepared. M.p. are corr. R. S. C.

Steroids and sex hormones. XCIX. Synthesis of 12-*epi*-14-deoxydigoxigenin. L. Ruzicka, P. A. Plattner, and J. Pataki (*Helv. Chim. Acta*, 1944, **27**, 988—994).—3(α) : 12(β)-*Diacetoxypregnan*-20-*one* (I), m.p. 114—115°, $[\alpha]_D^{17}$ +165·5° in $CHCl_3$, obtained by acetylation of the 3(α)-OH-compound, m.p. 208°, $[\alpha]_D^{17}$ +158° in $CHCl_3$, is converted by Zn and $CH_2Br{\cdot}CO_2Et$ followed by hydrolysis into 3(α) : 12(β) : 20-*trihydroxynorcholanic acid*, m.p. 221—222°, $[\alpha]_D^{16\cdot5}$ +46·4° in EtOH. The *Me* ester, m.p. 158—159°, $[\alpha]_D^{16\cdot5}$ +33·7° in $CHCl_3$, does not readily lose H_2O when boiled with Ac_2O but is converted into the *triacetate* (II), m.p. 162·5—163·5°, $[\alpha]_D^{16\cdot5}$ +70·2° in $CHCl_3$. When sublimed at 170°/high vac., (II) gives a non-cryst. material from which after hydrolysis, hydrogenation, and re-acetylation Me diacetylnordeoxycholate is obtained. (I) is oxidised by $Pb(OAc)_4$ in AcOH–Ac_2O at 68—72° to 3(α) : 12(β) : 21-triacetoxypregnan-20-one, m.p. 150·5—151° (lit. 114—115°), $[\alpha]_D^{14\cdot5}$ +156·9° on $CHCl_3$, $[\alpha]_D^{13}$ +153·2° in $COMe_2$, which with Zn and $CH_2Br{\cdot}CO_2Et$ followed by Ac_2O–C_5H_5N gives 12-epi-14-*deoxydigoxigenin* 3 : 12-*diacetate* [$\Delta^{20:22}$-21-*hydroxy*-3(α) : 12(β)-*diacetoxynorcholenolactone*], m.p. 180—181°, $[\alpha]_D^{15}$ +107·9° in $CHCl_3$, hydrolysed by 2N-HCl in dioxan at 100° to 12-epi-14-*deoxydigoxigenin*, m.p. 253—255°, $[\alpha]_D^{15}$ +51·5° in $CHCl_3$. M.p. are corr. (vac.). H. W.

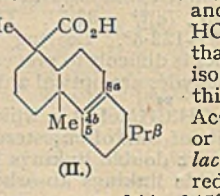
V.—TERPENES AND TRITERPENOID SAPOGENINS.

Terpene series. I. Dehydration of alcohols in the terpene series under pressure and in presence of dilute aqueous salt solutions. V. N. Ipatiev and H. Pines (*J. Amer. Chem. Soc.*, 1944, **66**, 1120—1122).—In aq. $MgCl_2$ at 230°/70 atm. terpineol or *p*-menthane-1 : 8-diol gives α-terpinene [liquid tetrabromide, an oil; $(CH{\cdot}CO)_2O$ *adduct*, m.p. 64—65°, and the corresponding *acid*, m.p. 127—128°], dipentene [tetrabromide, m.p. 124—125° (photomicrograph)], and a terpene [*tetrabromide*, m.p. 96° (photomicrograph)]; dehydration occurs without ring-change since hydrogenation and then dehydrogenation (Pt–Al_2O_3) gives *p*-cymene. Similar treatment of dihydroterpineol gives *p*-methyl*iso*propyl*cyclo*hexane and *dl*-*p*-menthene (I), of menthol gives mainly (I), and of *iso*borneol gives camphene (II) and a small amount of a liquid isomeride (III). Borneol is more stable, but in aq. $MgCl_2$ at 285—295° gives (II) and an isomeride (IV), m.p. −15° (more at higher temp.). HCl converts (III) or (IV) into *iso*bornyl chloride and hydrogenation gives *iso*bornylene. R. S. C.

Action of selenium dioxide on camphor and α-substituted camphors. J. Vène (*Compt. rend.*, 1943, **216**, 772—774).—Camphor and excess of SeO_2 in boiling EtOH give 27% of camphorquinone (I); the yield is 88—90% in PhMe or xylene, and 95% in a little Ac_2O. SeO_2 and α-hydroxycamphor give 40% of (I) in EtOH (2 hr.), or 85% in absence of solvent (15 min.). α-Bromocamphor is almost unattacked by SeO_2 in Ac_2O at 135°, but in absence of solvent at 145—150° (6 hr.) yields 55% of (I); α-chlorocamphor behaves similarly, giving 30% of (I). Ethylcamphor and SeO_2 at 180—190° for 2 hr. yield 12% of (I), whereas benzylcamphor is dehydrogenated with SeO_2 at 200° to give 95% of benzylidenecamphor, stable to SeO_2 at 200°. α-Oximinocamphor and SeO_2 at 85° (violent reaction) afford 23% of camphor-α-mononitrile and 27% of camphoric anhydride; a similar slower reaction occurs in EtOH or PhMe. A. T. P.

Saponins and sapogenins. XXIV. Norechinocystenol-*A* and norechinocystenone-*A*. G. H. Harris and C. R. Noller (*J. Amer. Chem. Soc.*, 1944, **66**, 1005—1006; cf. A., 1944, II, 21).—The CO-ester acetate, in which the CO is β- to the CO_2H of echinocystic acid (A., 1939, II, 333), with N_2H_4,H_2O and NaOEt–EtOH at 200° gives *norechinocystenol*-A (I), m.p. 188—191°, $[\alpha]_D^{25}$ +15·1° in $CHCl_3$ (*acetate*, m.p. 217—220°, $[\alpha]_D^{21}$ +21·6° in $CHCl_3$), the CO being reduced, the Ac removed, and the CO_2H eliminated. CrO_3–AcOH oxidises (I) to *norechinocystenone*-A (II), m.p. 159—162°, $[\alpha]_D^{21}$ +30·8° in $CHCl_3$. (I) differs from oleanol and (II) differs from oleanone (cf. A., 1940, II, 311). R. S. C.

Resin acids. Structure of the lactone of hydroxytetrahydroabietic acid. R. F. B. Cox (*J. Amer. Chem. Soc.*, 1944, **66**, 865—870).—The following reactions favour Ruzicka's formula (A., 1941, II, 69) for abietic acid against Fieser's (A., 1938, II, 108) and indicate that lactonisation of hydroxytetrahydroabietic acid occurs at $C_{(4b)}$. With MgMeI in Et_2O–C_6H_6 and then aq. NH_4Cl the lactone (I) gives $\Delta^{4b:8a}$- (II), m.p. 185—186°, $[\alpha]_D$ −36° in EtOH, and $\Delta^{4b:5}$-*dihydroabietic acid* (III), m.p. 147—148°, $[\alpha]_D$ +68° in EtOH. (II) and (III) are stable in boiling AcOH, but in HCl–EtOH regenerate (I); (III) lactonises faster than (II) does, but unlactonised acid is thereby isomerised to (II); (II) is not isomerised by this method. (III) is hydrogenated (PtO_2; AcOH) faster than is (II). With NOCl–AcOH or OBu·NO–HCl, (II) gives a blue 8*b*-*NO-lactone*, m.p. 91·5—92°, $[\alpha]_D$ −925° in EtOH, reduced by Na_2S–EtOH–H_2O to the 8*b*-NH_2-*lactone*, m.p. 144—145°, $[\alpha]_D$ +1° in EtOH, and hydrolysed to (I) by hot HCl–AcOH. NOCl–AcOH converts (III) into the 5-*oximino-lactone*, m.p. 184—185°, $[\alpha]_D$ −30° in $CHCl_3$, which with mineral acid undergoes Beckmann rearrangement. R. S. C.



(II.)

VI.—HETEROCYCLIC.

Furfuryl furoate by condensation from furfuraldehyde. E. R. Nielsen (*J. Amer. Chem. Soc.*, 1944, **66**, 1230).—Dissolution of Na (18 g.) in furfuryl alcohol (250 g.) + C_6H_6 (750 c.c.) at the b.p. and gradual addition of distilled furfuraldehyde (1350 g.) gives furfuryl 2-furoate (77·8%), forms, m.p. 18·5° and 27·5°, b.p. 121°/1·5 mm. R. S. C.

Gossypol. IV. Behaviour of gossypol as an *o*-hydroxy-aldehyde : formation of α-pyrones and flavylium salts. B. Krishnaswamy, K. S. Murty, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 370—376).—Gossypol (I) condenses with $CH_2Ac{\cdot}CO_2Et$ to form a *pyrone*, $C_{38}H_{34}O_{10}$, m.p. >330°, with $CH_2(CO_2Et)_2$ to a *pyrone*, $C_{34}H_{28}O_8(CO_2Et)_2$, m.p. 248—250°, with COPhMe (HCl) to a flavylium *salt*, $C_{46}H_{40}O_6Cl_2$, m.p. 295—297°, and with ω : 4-dihydroxyacetophenone (+HCl) to a flavylium *salt*, $C_{46}H_{40}O_8Cl_2$ (+$3H_2O$), m.p. >320°. These reactions indicate the presence of 2 *o*-OH–CHO groups in (I). The dianilino-compound of (I) also undergoes the reactions smoothly, indicating that it is easily split up into (I) and NH_2Ph under the reaction conditions. F. R. S.

Synthesis of coumarins from *o*-hydroxyaryl alkyl ketones. V. Formation of coumarins from *o*-hydroxyphenyl benzyl ketones. D. Chakravarti and B. C. Bera (*J. Indian Chem. Soc.*, 1944, **21**, 44—46).—5-Methyl-, 5-chloro-, and 3-chloro-2-methoxy-5-methyl-phenyl benzyl ketones condense (Reformatsky) with $CH_2Br{\cdot}CO_2Et$ and $CHMeBr{\cdot}CO_2Et$ to give OH-esters, which on dehydration ($SOCl_2$–C_5H_5N) and demethylation (HI) yield coumarins. The following are described: *Et* 2-*methoxy*-5-*methyl*-β-*benzylcinnamate*, b.p. 200—205°/3 mm.; 4-*benzyl*-6-*methylcoumarin*, m.p. 148°; 2-*ethoxy*-5-*methylphenyl benzyl ketone*, b.p. 200—201°/5 mm.; *Et* 2-*ethoxy*-5-*methyl*-β-*benzylcinnamate*, b.p. 210—215°/5 mm.; *Et* 2-*methoxy*-α-β-*benzyl*-α : 5-*dimethylcinnamate*, b.p. 203°/2·5 mm.; 4-*benzyl*-3 : 6-*dimethylcoumarin*, m.p. 136°; *Et* 5-*chloro*-2-*methoxy*-β-*benzyl*-, b.p. 208°/4 mm., and 5-*chloro*-2-*methoxy*-β-*benzyl*-α-*methyl*-*cinnamate*, b.p. 212°/2 mm.; 6-*chloro*-4-*benzylcoumarin*, m.p. 101°, and its 3-*Me* derivative, m.p. 162°; 3-*chloro*-2-*hydroxy*-5-*methylphenyl benzyl ketone*, m.p. 110° (2-*OMe*-compound, b.p. 195—200°/3·5 mm.); *Et* 3-*chloro*-2-*methoxy*-5-*methyl*-β-*benzylcinnamate*, b.p. 210—215°/4·5 mm. (α : 5-*Me*$_2$ derivative, b.p. 210°/2 mm.); and 8-*chloro*-4-*benzyl*-6-*methylcoumarin*, m.p. 161° (3 : 6-*Me*$_2$ derivative, m.p. 173°). F. R. S.

4-Hydroxycoumarins. IV. Esters of 4-hydroxycoumarins. M. A. Stahmann, L. H. Graf, C. F. Huebner, S. Roseman, and K. P. Link. **V. Condensation of αβ-unsaturated ketones with 4-hydroxycoumarin.** M. Ikawa, M. A. Stahmann, and K. P. Link. **VI. Glucosides of 4-hydroxycoumarins.** C. F. Huebner, S. A. Karjala, W. R. Sullivan, and K. P. Link (*J. Amer. Chem. Soc.*, 1944, **66**, 900—902, 902—906, 906—909; cf. A., 1944, II, 166).—IV. 3 : 3′-Alkylidenebis-4-hydroxycoumarins with RCOCl in C_5H_5N at 0° and then 25° give 3 : 3′-methylenebis-4-hydroxycoumarin diacetate (I), *dipropionate* (II), m.p. 247—248°, *di*-n-, m.p. 227—228°, and -iso-*butyrate*, m.p. 233—234°, *di*-n-, m.p. 224—225°, and -iso-*valerate*, m.p. 220—221°, *di*-n-*hexoate*, m.p. 225—226°, *di*-n-*heptoate*, m.p. 215—216°, *dibenzoate* (III), m.p. 263—264°, *di*-αα-*dimethylpropionate*, m.p. 210—211°, *di*(*benzylcarbonate*), m.p. 188—189°, *di*(*acetylsalicylate*), m.p. 253—256°, *di*(*carbomethoxysalicylate*) (IV), m.p. 213—216°, *di*-(o-*benzyloxybenzoate*) (V), m.p. 212—213°, *di*-o-, m.p. 250—252°, and -p-*chlorobenzoate*, m.p. 288—291°, and *di*-2-*furoate*, m.p. 298—300°, 3 : 3′-*ethylidene*-, m.p. 209—210°, 3 : 3′-*propylidene*-, m.p. 203—204°, and 3 : 3′-*butylidene*-*bis*-4-*hydroxycoumarin dibenzoate*, m.p. 226—227°, 3 : 3′-*propylidene*-, m.p. 202—203°, and 3 : 3′-*butylidene*-*bis*-4-*hydroxycoumarin diacetate* (VI),

m.p. 210—211°. 4-*Acetylsalicyloxy-*, m.p. 183—185°, and 4-*o-benzyloxybenzoyloxy-* (**VII**), m.p. 173—175°, -3-*phenylcoumarin* are similarly obtained. 3 : 3′-Methylene- (**VIII**), -propylidene-, and -butylidene-bis-4-hydroxycoumarin are also diacetylated by boiling Ac_2O alone, but the 3 : 3′-benzylidene- and -ethylidene-coumarins are thus dehydrated to the 4 : 4′-epoxy-compounds. The CHPh:compound is dehydrated also by BzCl–C_5H_5N. Aq. NaOH hydrolyses (**I**) or (**II**) to the parent OH-compound; 1 mol. of NaOEt in boiling EtOH converts (**I**), (**II**), or (**VI**) into the epoxy-compounds and EtOAcyl, probably by way of the monoester since this is also converted into the epoxy-compound by 1 mol. of NaOEt. Boiling aq. NaOAc converts (**IV**) into the epoxy-compound (63%), (**VIII**) (35%), o-OH·C_6H_4·CO_2H, and traces of *o*-CO_2Me·O·C_6H_4·CO_2H. 2 mols. of NaOEt in boiling EtOH convert (**III**) into (**VIII**) and some epoxy-compound. Hydrogenation (Raney Ni; 100°/1900 lb.; dioxan) of (**V**) gives 3 : 3′-*methylenebis-4-salicyloxycoumarin*, m.p. 223—225°, and [Pd–C–AcOH–EtOAc at 1 atm., which has no effect on (**V**)] of (**VII**) gives 4-*salicyloxy-3-phenylcoumarin*, m.p. 185—187°.

V. Michael condensation of 4-hydroxycoumarin (**IX**) with unsaturated ketones, COR·CH:CR′R″, occurs best in boiling C_5H_5N or for CHPh:CH·COMe in boiling H_2O and yields (**IX**) substituted at $C_{(3)}$ by ·CR′R″·CH_2·COR. With CH_2N_2 these give 3-OMe-compounds but they are cyclised by boiling 4% HCl–MeOH and then methylated to yield substances (*A*). Michael condensation with NaOEt, HCl, or piperidine in EtOH leads to mixtures of the primary products with (*A*). Thus are obtained 4-*hydroxy-3-γ-keto-α-methyl-*n-*butyl-* (44%), m.p. 141° [*Me ether*, b.p. 170° (bath)/0·5 mm.], -3-*γ-keto-αα-dimethyl-*n-*butyl-* (**X**) (13%) m.p. 212°, -3-*γ-keto-α-phenyl-*n-*butyl-* (**XI**) (40%), m.p. 161° (*Me ether*, m.p. 127°), -3-*γ-keto-α*-p-*anisyl-*n-*butyl-* (45%), m.p. 160° [*Me ether*, b.p. 240° (bath)/0·5 mm.], -3-*γ-keto-α-*4′-*hydroxy-*3′-*methoxyphenyl-*n-*butyl-* (18%), m.p. 181°, -3-*γ-keto-αγ-diphenyl-*n-*propyl-* (37%), m.p. 160° (*Me ether*, m.p. 91°), -3-*γ-keto-α-phenyl-γ-*o-*hydroxyphenyl-* (**XII**) (34%), m.p. 194°, -*coumarin* and 2-*methoxy-*2 : 4-*dimethyl-* (29%), m.p. 124°, -2 : 4 : 4-*trimethyl-* (80%), m.p. 102°, -4-*phenyl-*2-*methyl-* (**XIII**) (83%), m.p. 166°, -4-p-*anisyl-*2-*methyl-* (75%), m.p. 163°, -4-4′-*hydroxy-*3′-*methoxyphenyl-* (82%), m.p. 187°, -2 : 4-*diphenyl-* (13%), m.p. 205°, and -4-*phenyl-*2-*o-hydroxyphenyl-* (50%), m.p. 194° (decomp.), -3 : 4-*dihydrocoumarino-*3′ : 4′-5 : 6-1 : 2-*pyran*. HCl–H_2O–EtOH converts (**XI**) into 2-*ethoxy-*4-*phenyl-*2-*methyl-*3 : 4-*dihydrocoumarino-*3′ : 4′-5 : 6-1 : 2-*pyran*, m.p. 177°. In boiling HCl–H_2O–MeOH (1 : 5 : 5), (**XIII**) regenerates (**XI**) but in boiling NaOH–H_2O–MeOH (1 : 5 : 5) gives a salt, *o*-CO_2Na·C_6H_4·C<O·CMe(OMe) / C(CO$_2$Na)—> CHPh, which yields (**XIII**) by ring-closure on acidification. When ketones, *o*-OH·C_6H_4·CH:CH·COR, are used in the Michael condensation, the primary products suffer spontaneous dehydration to (*B*); thus are obtained 4-*acetonyl-* (69%), m.p. 263° (decomp.), 4-*phenacyl-* (76%), m.p. 240° (decomp.), and 4-*o-hydroxyphenyl-coumarino-*4′ : 3′-2 : 3-*benz-*4-*pyrone* (75%), m.p. 241° (decomp.). Dehydration, but without cyclisation, also accompanies formation of (**X**), yielding 34% of 2 : 4-*diketo-*3-*αγ-dimethyl-*Δβ-*butenylidenechroman*, m.p. 93°. Structures are proved by synthesis of (**XI**) also from 3 : 3′-benzylidenebis-4-hydroxycoumarin by NaOH. The Michael condensation of (**IX**) fails with CHPh:CH·CO_2Et, CHPh:C(CO_2Et)$_2$, phorone, CO(CH:CHPh)$_2$, or furfurylideneacetone. *o*-OH·C_6H_4·COMe and *o*-OH·C_6H_4·CHO in aq. NaOH at 85° give 2 : 2′-*dihydroxy-β-phenylacrylophenone* (14%), m.p. 160° (decomp.) (*dibenzoate*, m.p. 114°). The primary Michael products and (*A*) have potent anticoagulant properties.

VI. Treating the appropriate 4-hydroxycoumarins in aq. NaOH (1 mol.) with $AgNO_3$ (1·02 mol.) gives the Ag salts, which with acetobromoglucose (**XIV**) and $CaSO_4$ in C_6H_6 yield *β-*4-*hydroxy-* (40%), m.p. 178—179°, $[\alpha]_D^{25}$ −63·2° in $CHCl_3$, *β-*4-*hydroxy-*6-*methyl-* (36%), m.p. 168—170°, $[\alpha]_D^{25}$ −24·9° in C_6H_6, and *β-*4-*hydroxy-*6-*phenyl-coumarin glucoside tetra-acetate* (**XV**) (47%), m.p. 156—158°, $[\alpha]_D^{25}$ −58·4° in C_6H_6, and 3 : 3′-*methylenebis-*4-*coumarin monoglucoside tetra-acetate* (**XVI**) (25%), sinters at 185° [giving 3 : 3′-methylene-4 : 4′-epoxydicoumarin (**XVII**), m.p. 290°], whence a trace of NaOMe in MeOH yields *β-*4-*hydroxy-* (90%), m.p. 201—202°, $[\alpha]_D^{25}$ −106° in MeOH, and *β-*4-*hydroxy-*6-*methyl-coumarin glucoside* (90%), m.p. 223—224°, $[\alpha]_D^{25}$ −86° in C_5H_5N. The free hydroxycoumarin with (**XIV**), $CaSO_4$, and a few drops of quinoline (no yield in absence thereof or in presence of a large amount) in C_6H_6 gives *ββ′-*3 : 3′-*methylenebis-*4-*hydroxycoumarin diglucoside octa-acetate* (**XVIII**), m.p. 167—168°, $[\alpha]_D^{30}$ +58·0° in C_6H_6, and 4-*hydroxy-*3-7′-*coumarino-*4″ : 3″-2′ : 3′-*benzpyranylcoumarin glucoside tetra-acetate*, m.p. 234—235°, $[\alpha]_D^{25}$ −9·0° in C_5H_5N. The glucosides or their acetates reduce Fehling's solution after boiling for a few min. owing to their rapid hydrolysis by alkali which is due to the high acidity of the enol. In Ba(OMe)$_2$–MeOH at room temp. (**XV**) gives 4-hydroxy-3-phenylcoumarin (81%) and α-methylglucoside, and (**XVIII**) gives (**XVII**) (59%). In boiling Ba(OMe)$_2$–MeOH, (**XVIII**) gives 59%, and in boiling NaOMe–MeOH (**XVI**) gives 55—86%, of (**XVII**). The mechanism of the methanolysis is discussed. R. S. C.

Keten acetals. XIV. Reactions of keten acetal with quinones. S. M. McElvain and E. L. Engelhardt (*J. Amer. Chem. Soc.*, 1944, **66**, 1077—1083; cf. A., 1944, II, 130).—Contrary to earlier views (A., 1942, II, 227), quinones and CH_2:C(OEt)$_2$ (**I**) give 4-hydroxy-1-ethoxybenzfurans. Substitution by Me hinders and finally stops the addition. In the benzoquinone series, substitution by Br facilitates reaction which occurs by addition at a nuclear C, but in the naphthaquinone series the Br is partly replaced. The product obtained (*loc. cit.*) from *p*-O:C_6H_4:O by (**I**) is shown to be 4-*hydroxy-*1-*ethoxybenzfuran*; with Ac_2O it gives a monoacetate and with MgMeI evolves 1 CH_4 without addition; with HBr in dioxan at room temp. (24 hr.) it gives 4-hydroxycoumaran-1-one (**II**) (67%), m.p. 189—191°; in boiling 75% EtOH it gives 2 : 5 : 1-(OH)$_2$$C_6H_3$·$CH_2$·$CO_2$Et (47%), converted into (**II**) by boiling 10% HCl; it is unaffected by (**I**) or $CHMeN_2$, as also is (**II**), but with *iso*-C_5H_{11}·ONa–EtI in boiling *iso*-C_5H_{11}·OH, (**I**) or (**II**) gives 4-*ethoxycoumaran-*1-*one*, m.p. 89—90°. *p*-OH·C_6H_4·OEt (modified prep.), CH_2:CH·CH_2Br, and K_2CO_3 in $COMe_2$ give *quinol Et allyl ether* (80%), m.p. 39—40°, converted in boiling NPhEt_2 into 4-*ethoxy-*2-*allylphenol* (89·5%), b.p. 184—185°/50 mm., the *acetate*, b.p. 161—162°/1·5 mm., of which with, successively, O_3–AcOH, H_2O_2–AcOH–H_2O, NaOEt–EtOH, and HCl gives (**II**) (14·5%). 1 : 2 : 6 : 4-O:$C_6H_2Me_2$:O (modified prep.) and (**I**) at 150° (not at 125° or in boiling xylene) give a tar containing 7% of 4-*hydroxy-*1-*ethoxy-*3 : 5-*dimethylbenzfuran*, m.p. 100—101°, hydrolysed by hot 75% EtOH to *Et* 3 : 6-*dihydroxy-*2 : 4-*dimethylphenylacetate*, m.p. 147—148°, whence boiling 25% HCl yields 4-*hydroxy-*3 : 5-*dimethylcoumaran-*1-*one* (56%), m.p. 143—144°. 1 : 2 : 5 : 4-O:$C_6H_2Me_2$:O (modified prep.) and (**I**) react only at 150°, giving tarry polymers and a small amount of the quinol, which may be derived from 1 : 4 : 2 : 5 : 6-(OH)$_2$$C_6HMe_2$·CH:C(OEt)$_2$. Duroquinone does not react with (**I**). 1 : 4-O:$C_{10}H_6$:O and (**I**) at 90° give a tar containing 2% of 4′-*hydroxy-*4-*ethoxynaphtha-*1′ : 2′-1 : 2-*furan*, m.p. 106—108°, whence boiling 75% EtOH yields 4-*hydroxy-*5 : 6-*benzcoumaran-*1-*one*, m.p. 204—205°. 1 : 2 : 4-O:C_6H_3Br:O (modified prep.) reacts with (**I**), giving 10% of EtBr and a product whence hot 75% EtOH yields (? 6-)*bromo-*4-*hydroxycoumaran-*1-*one* (26·5%), m.p. 202—204°, converted by methylation etc. into (? 3-)*bromo-*2 : 5-*dimethoxyphenylacetic acid*, m.p. 194—195° (could not be oxidised to ArCO_2H). 1 : 2 : 5 : 4-O:$C_6H_2Br_2$:O and (**I**) in boiling C_6H_6 give, after treatment with 75% EtOH, *Et* 2 : 5-*dibromo-*3 : 6-*dihydroxyphenylacetate* (40%), m.p. 126—127°, but 1 : 2 : 6 : 4-O:$C_6H_2Br_2$:O reacts in Et_2O to give only a tar (a trace of EtBr is formed). 1 : 2 : 4-O:$C_{10}H_5$Br:O (modified prep.) and (**I**) at 125° give EtBr (40%) and a product whence 75% EtOH yields xanthopurpurin Et_2 ether (20·6%); the primary product, 1 : 4 : 2-O:$C_{10}H_5$(:O)·CH:C(OEt)$_2$, has reacted with a second mol. of (**I**). 1 : 2 : 3 : 4-O:$C_{10}H_4Br_2$:O (modified prep.) and (**I**) in boiling C_6H_6 give *Et* 3-*bromo-*1 : 4-*naphthaquinone-*2-*acetate* (57·6%), m.p. 124—125°. 1 : 2 : 3 : 4-O:$C_{10}H_4$MeBr:O reacts with (**I**) at 125°, yielding ~25% of EtBr and tars. R. S. C.

Constitution of trimeric glyoxal. H. Raudnitz (*Chem. and Ind.*, 1944, 327).—"Trimeric glyoxal" is 2 : 3 : 6 : 7-*tetrahydroxy-*1 : 4 : 5 : 8-"*naphthodioxan*" (**I**), formed by way of [CH(OH)$_2$]$_2$. With H_2SO_4 in $COMe_2$, (CHO)$_2$ gives the 2 : 3-6 : 7-(CMe$_2$:)$_2$-*derivative*, m.p. 207° (cf. Fischer *et al.*, A., 1926, 599), of (**I**), which contains no OH or CO and in hot mineral acid regenerates (CHO)$_2$ and $COMe_2$. (See also A., 1944, II, 340.) R. S. C.

Toxic principles of poison ivy. II. Preparation and properties of diphenylmethylene ethers of pyrocatechols. H. S. Mason (*J. Amer. Chem. Soc.*, 1944, **66**, 1156—1158; cf. A., 1943, II, 447).—Conversion of *o*-C_6H_4(OH)$_2$ (**I**) into its monoallyl ether and thence 3-allylpyrocatechol, m.p. 73—74° (lit. 70—72°), is described. CPh_2Cl_2 and (**I**) in warm C_6H_6 or, best, pinene at 100° (cf. Sachs *et al.*, A., 1904, i, 878) give good yields of *o*-C_6H_4:$O_2$$CPh_2$, m.p. 94—94·6°. 3-n-*Propyl-*, m.p. 41·5—42°, and 4-tert.-*butyl-pyrocatechol CPh$_2$: ether*, m.p. 138—139°, are similarly prepared. These ethers are readily hydrolysed by dil. boiling HCl–EtOH and disrupted by hydrogenolysis (Pd; EtOH), but are stable to hot 25% KOH–EtOH or MgBu^{a}Br. R. S. C.

Photochemical reactions. VIII. Reaction of ethylenes with phenanthraquinone. A. Schönberg and A. Mustafa (*J.C.S.*, 1944, 387; cf. A., 1944, II, 142).—In sunlight, phenanthraquinone (**I**) reacts readily with stilbene (9 days), styrene (4 days), CPh_2:CHPh (4 days), or CH_2:CPh_2 (16 days) in C_6H_6 to give photo-*products*, m.p. ~260° (red melt) (**II**), m.p. ~130° (decomp.), m.p. ~225° (decomp.) (**III**), or m.p. 202—203° (orange melt), respectively, considered to be 5 : 6-*oo*-diphenylene-2 : 3-dihydro-1 : 4-dioxans, *e.g.*, (**II**) = (*A*), R = Ph. All four products yield (**I**) with conc. H_2SO_4 at room temp.; (**II**) or (**III**) at ~270° or ~235° in CO_2 give (**I**) and stilbene or CPh_2:CHPh, respectively. A. T. P.

Ichthynone, $C_{23}H_{20}O_7$, m.p. 203—204°, α ±0° (contains 2 OMe) [dibromide, m.p. 234—235°; phenylhydrazone, m.p. 195—200° (decomp.); H_1-compound, m.p. 233—234°], from *Ichthyomethia piscipula*.—See A., 1944, III, 708.

Amino-ketones. III. β-Tetrahydro*iso*quinolino-ketones and [their] derivatives. Reactions with Grignard reagents. N. H. Cromwell and J. S. Burch (*J. Amer. Chem. Soc.*, 1944, **66**, 872—873; cf. A., 1944, II, 352).—Tetrahydro*iso*quinoline with CHPh:CH·COMe or CHPh:CH·COPh in 95% EtOH at, successively, the b.p., room temp., and 0° gives δ-*tetrahydroisoquinolino*-δ-*phenyl*-n-*butan*-β-*one* (**I**) (59%), m.p. 71—72°, and β-*tetrahydroisoquinolino*-β-*phenylpropiophenone* (**II**) (83%), m.p. 90—91° (*oxime*, m.p. 173—175°), respectively. The *oxime* (prep. by NH_2OH,HCl–NaOAc–MeOH–H_2O at, successively, the b.p., room temp., and 0°), m.p. 155—157°, of (**I**) with Na–EtOH gives γ-*amino*-α-*tetrahydroisoquinolino*-n-*butylbenzene* (32%), b.p. 178—180°/1 mm. (*Bz* derivative, m.p. 159—161°). MgPhBr and (**I**) or MgMeI and (**II**) in Et_2O give δ-*tetrahydroisoquinolino*-βδ-*diphenyl*-n-*butan*-β-*ol* (43—45%), m.p. 115—116°. MgMeI and (**I**) give β-*tetrahydroisoquinolino*-β-*phenyl*-tert.-*amyl alcohol* [2-(γ-*hydroxy*-α-*phenyl*-γ-*methyl*-n-*butyl*)*iso*quinoline] (47%), m.p. 95—96°. MgPhBr and (**II**) give β-*tetrahydroisoquinolino*-αaγ-*triphenyl*-n-*propyl alcohol*, m.p. 78—80°. R. S. C.

Interaction of iodine with some ketones in presence of pyridine. L. C. King (*J. Amer. Chem. Soc.*, 1944, **66**, 894—895).—COArAlk (I) and I (1 mol.) in an excess (2 mols. required for the reaction) of C_5H_5N at 100° give 1-phenacyl-, m.p. 215—219°, 1-α-*naphthoylmethyl*-, m.p. 219—220°, 1-*anthroylmethyl*-, m.p. 235—237°, and 1-α-*methylphenacyl-pyridinium iodide*, m.p. 152—153° (derived *perchlorates*, m.p. 189—190°, 176—177°, 227—230°, and 141—142°, respectively), which with NaOH in boiling H_2O or 50% EtOH give BzOH, α-$C_{10}H_7$·CO_2H, 1-anthroic acid, and BzOH, respectively. R. S. C.

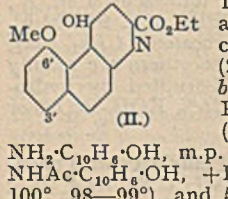
Production of aminosulphanilamidopyridines.—See B., 1944, III, 186.

Excretion of metabolic products of sulphapyridine in the dog. J. V. Scudi (*Proc. Soc. Exp. Biol. Med.*, 1944, **55**, 197—199; cf. A., 1940, III, 758).—Following oral administration of sulphapyridine, a *hydroxysulphapyridine*, m.p. 180—181° (corr.), and a H_2O-sol. *hydroxysulphapyridine glucuronide* [as the *Ag* salt or the *brucine* salt, m.p. 215° (decomp.)] have been isolated from dog urine. F. R. S.

Structure and synthesis of pyridoxamine and pyridoxal. S. A. Harris, D. Heyl, and K. Folkers (*J. Biol. Chem.*, 1944, **154**, 315—316).—Treatment of 3-hydroxy-2-methyl-5-hydroxymethyl-4-methoxymethylpyridine with NH_3 at 120—140° gives the -4-aminomethyl compound (pyridoxamine), m.p. 193—193·5°. Oxidation ($KMnO_4$) of pyridoxine gives an aldehyde, the oxime of which on decomp. with HNO_2 and treatment with EtOH–HCl affords a cyclic acetal. This is hydrolysed to 3-hydroxy-4-formyl-2-methyl-5-hydroxymethylpyridine (pyridoxal). F. R. S.

8-Hydroxyquinaldine as an analytical reagent. L. L. Merritt, jun., and J. K. Walker (*Ind. Eng. Chem.* [*Anal.*], 1944, **16**, 387—389).—Technique for the prep. of 8-hydroxyquinaldine is recorded (cf. C., 1944, Part 4). J. D. R.

Derivatives of 7- and 10-methoxybenz(f)quinoline. A. C. Mueller and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1944, **66**, 860—862).—Stirring 2 : 8-NH_2·$C_{10}H_6$·SO_3H and KOH at 260° gives 2 : 8-NH_2·$C_{10}H_6$·OH (74%), the *N*-Ac derivative (prep. by boiling Ac_2O–AcOH), m.p. 215—216° (lit. 210—211°), of which with Me_2SO_4–2N-NaOH at 30° gives 2-*acetamido*-8-*methoxynaphthalene* (70%), m.p. 163—164°. Boiling conc. aq. HCl–EtOH then gives 8-*methoxy*-2-*naphthylamine hydrochloride* (81%), cryst., which with CO_2Et·CO·CHNa·CO_2Et (**I**) and a drop of conc. HCl in EtOH at room temp. gives the oily anil, which, introduced into mineral oil at 260°, yields *Et* 4-*hydroxy*-6′-*methoxy*-5 : 6-*benzquinoline*-2-*carboxylate* [1-*hydroxy*-10-*methoxybenz*(f)*quinoline*-3-*carboxylate*] (**II**) (61%), m.p. 181—183°. This is hydrolysed by boiling 2N-alkali to the corresponding *acid* (*hydrochloride*, cryst., hydrolyses in H_2O), which at the m.p. (250°) gives CO_2 and 4-*hydroxy*-6′-*methoxy*-5 : 6-*benzquinoline* (**III**) (28%), m.p. 180—182°. Probably owing to steric hindrance the OH in (**III**) could not be replaced by halogen. 2 : 5-NH_2·$C_{10}H_6$·OH, m.p. 198—200° (lit. 199·5°), gives similarly 2 : 5-NHAc·$C_{10}H_6$·OH, +H_2O, m.p. 117—121°, and anhyd., an oil (lit. 100°, 98—99°), and 5-*methoxy*-2-*naphthylamine*, m.p. 71—72°, unstable (N-*Ac* derivative, m.p. 151—152°; *hydrochloride*, cryst.), which with (**I**) etc. gives an anil, converted in mineral oil at 250° into *Et* 4-*hydroxy*-3′-*methoxy*-5 : 6-*benzquinoline*-2-*carboxylate* [cf. (**II**)], m.p. 256—258°, and thence as above into the corresponding *acid*, m.p. 292—295° (decomp.), and (at 295°, later 280°) 4-*hydroxy*-3′-*methoxy*-5 : 6-*benzquinoline* [1-*hydroxy*-7-*methoxybenz*(f)*quinoline*] (55%), m.p. 308—311°. With boiling $POCl_3$ this gives 4-chloro- (74%), m.p. 118—119°, and thence 4-*morpholino*-, m.p. 136—137°, and 4-*piperidino*-, m.p. 116—117°, -3′-*methoxy*-5 : 6-*benzquinoline*.



(II.)

R. S. C.

Hydantoins. III. Chemical constitution and hypnotic action. A. Novelli, Z. M. Lugones, and P. Velasco (*Anal. Asoc. Quím. Argentina*, 1942, **30**, 225—231; cf. A., 1941, II, 334).—Intraperitoneal injection in white rats of a no. of substituted hydantoins showed hypnotic action only for 5 : 5-diphenyl-, 5-phenyl-5-ethyl-, and 5-phenyl-5-*n*-propyl-hydantoin. The following are new: 5-*phenyl*-5-*amyl*-, m.p. 125—127°, -5-*hexyl*-, m.p. 140—142°, -3-N-*methyl*-5-n-*propyl*, m.p. 134—135°, -1 : 3-N-*dimethyl*-5-n-*propyl*-, m.p. 92°; 5-p-*tolyl*-5-n-*propyl*-, m.p. 189—190°, -3-N-*methyl*-5-n-*propyl*-, m.p. 116—117°, -1 : 3-N-*dimethyl*-5-n-*propyl*-, m.p. 77—78°; 5-p-*bromophenyl*-5-n-*propyl*-, m.p. 207—208°; 5-cyclo*hexyl*-5-*phenyl*-, m.p. 236—237°; 5 : 5-o-*diphenylene*-3-N-*methyl*-, m.p. 248—250°; 5 : 5-o-*diphenylene*-1 : 3-N-*dimethyl*-, m.p. 205—206°; 5 : 5-*diphenyl*-3-N-*methyl*-, m.p. 215°; 5 : 5-o-*phenylenetrimethylene*-1 : 3-N-*dimethyl*-, m.p. 140°, and -3-N-*methyl*-, m.p. 184·5°; 5 : 5-*aminodiphenylene*-, m.p. 310—312°; 5-2′-*phenanthryl*-3-N-*methyl*-5-*ethyl*-, m.p. 189—190°, and -1 : 3-N-*dimethyl*-5-*ethyl*-, m.p. 150°; 5 : 5-2′-*methyl*-5-iso*propyl*cyclo*pentamethylene*-3-N-*methyl*-, m.p. 165°, and -1 : 3-N-*dimethyl*-*hydantoin*, m.p. 117—118°. The m.p. of 5 : 5-2′-methyl-5′-*iso*propyl*cyclo*pentamethylenehydantoin is now recorded as 257°. F. R. G.

1-Methylhistidine. I. Synthesis of *dl*-1-methylhistidine. W. Sakami and D. W. Wilson (*J. Biol. Chem.*, 1944, **154**, 215—222).—4(5)-Hydroxymethylglyoxaline from *d*-fructose is oxidised (HNO_3) to glyoxaline-4(5)-aldehyde, methylated (Me_2SO_4–$COMe_2$) to 1-methylglyoxaline-5-aldehyde, which condenses ($NHEt_2$–C_5H_5N) with 2-thio-3-acetylhydantoin (improved prep.) to 2-*thio*-(1′-*methyl*-5′-*glyoxalinylmethylidene*)*hydantoin*. Reduction and hydrolysis (HI–P) of this compound affords *dl*-1-methylhistidine, isolated as the bis-3 : 4-dichlorobenzenesulphonate, m.p. 251—252°, and identical with the product obtained by hydrolysis of anserine with $Ba(OH)_2$. F. R. S.

***N*-Desylarylamines in Leuckart's reaction.** A. Novelli and J. C. Somaglino (*Anal. Asoc. Quím. Argentina*, 1943, **31**, 147—152).—NHPh·CHPhBz reacts with RCO·NH_2 (R = H, Me, Et) to give the same glyoxaline derivatives as benzoin, NHPh being replaced by NH·COR. 4 : 4′-*Dimethoxy*-N-*desylaniline*, m.p. 115° (from anisoin and NH_2Ph at 140° in CO_2), with HCO·NH_2, and *p*-C_6H_4Me·NH·CHPhBz with NH_2Ac behave similarly. F. R. G.

Abnormal quaternary salts of bispyridinium derivatives of nicotinic acid. J.-A. Gautier and E. Leroi (*Compt. rend.*, 1943, **216**, 619—620).—Nicotinic acid and $[CH_2]_nHal_2$ (n = 2 or 3) give monoacid salts, $(CO_2^-$·$C_5H_4N^+$·$[CH_2]_n$·$N^+C_5H_4$·$CO_2H)Hal^-$, whence $AgNO_3$ gives the dibetaines, CO_2^-·$C_5H_4N^+$·$[CH_2]_n$·$N^+C_5H_4$·CO_2^-. Diacid salts cannot be prepared in this series but are readily formed from pyridine-2- or -4-carboxylic acid. R. S. C.

Synthetic amino-acids. Reactions of 2 : 5-diketo-3 : 6-di-β-chloroethylpiperazine. H. R. Snyder and M. E. Chiddix (*J. Amer. Chem. Soc.*, 1944, **66**, 1000—1002).—2 : 5-Diketo-3 : 6-di-β-chloroethylpiperazine (**I**) (A., 1943, II, 72) loses HCl with great ease. *E.g.*, in boiling NaOH–EtOH it gives 2 : 5-*diketo*-3 : 6-*divinylpiperazine* (**II**) (62%), m.p. 192·5° (corr.) (instantaneous) or decomp. >240° (slow heating). Attempts to prepare the $(CN·[CH_2]_2)_2$ compound and to condense (**I**) with $CH_2Ac·CO_2Et$ also led to (**II**), which was either isolated as such or identified after hydrolysis by conc. HCl as α-amino-γ-butyrolactone hydrochloride, m.p. 199—200°. However, some reactions of (**I**) occur normally. Thus, with morpholine or piperidine at 85°, rising to 125°, with KCNS–$COMe_2$ at room temp. and then the b.p. or CH_2Ph·SH–NaOEt–EtOH at the b.p. it gives 2 : 5-*diketo*-3 : 6-*di*-β-*morpholino*- (~40%), m.p. 229—232° (corr.), -*piperidino*-, m.p. 242—243° (corr.), -*thiocarbamido*- (~15%), m.p. 207—208° (corr.), or -benzylthiol- (~50%), m.p. 173—174° (corr.) (lit. 165°, 176°), -ethylpiperazine, respectively. R. S. C.

Non-Markovnikov addition in reactions of 2 : 5-diketo-3 : 6-divinylpiperazine. H. R. Snyder and M. E. Chiddix (*J. Amer. Chem. Soc.*, 1944, **66**, 1002—1004).—Non-Markovnikov addition of HCl and RSH occurs with 2 : 5-diketo-3 : 6-divinylpiperazine (**I**) (preceding abstract), probably owing to its ·CH(NH)·CO acting as a *m*-directing group. Thus, gaseous HCl or HBr in AcOH gives 2 : 5-diketo-3 : 6-di-β-chloroethyl- (**II**) and -3 : 6-*di*-β-*bromoethylpiperazine* (**III**), m.p. 221° (decomp.) [reconverted into (**I**) by hot H_2O]. With MeSNa, (**II**) or (**III**) gives methionine anhydride and thence methionine [Bz derivative, m.p. 151—151·5° (lit. 143—145°)]. CH_2Ph·SNa and (**II**) give 2 : 5-*diketo*-3 : 6-*di*-β-*benzylthiolethylpiperazine*, m.p. 177—178°, hydrolysed by boiling aq. HCl to CH_2Ph·S·$[CH_2]_2$·CH(NH_2)·CO_2H, m.p. 226—230° (decomp.) (lit. 190—191°). H_2S and (**I**) in EtOH containing a little AcOH at room temp. gives 2 : 5-*diketo*-3 : 6-*di*-β-*thiolethylpiperazine*, m.p. 185—186° (decomp.), whence hot conc. HCl yields homocysteinethiolactone hydrochloride. M.p. are corr. R. S. C.

Arylamino-heterocyclic compounds. I. Synthetic method. II. Arylaminopyrimidines. C. K. Banks (*J. Amer. Chem. Soc.*, 1944, **66**, 1127—1130, 1131).—I. Heterocyclic compounds containing nuclear "active" halogen react with aromatic amines in H_2O, fastest (5 examples) in 2N-HCl; the reaction is slower in more dil. acid or H_2O and addition of NaOH greatly decreases the rate.

Efficiency is HCl > H_2SO_4 > tartaric acid, but the differences are not large. An excess of HCl causes hydrolysis. An electronic mechanism is suggested. The reaction does not apply to compounds containing N·C:C·Hal nor to aromatic or aliphatic halides.

II. The following are obtained from 4-chloro-2-aminopyrimidine in boiling very dil. HCl. 2-*Amino*-4-*anilino*-*pyrimidine* (**I**), m.p. 155—156° (*Ac*$_2$, m.p. 170°, and *Ac*$_1$ derivative, m.p. 176—178°; *hydrochloride*, m.p. 184—185°), and -6-*methylpyrimidine*, m.p. 170—172°; 2-*amino*-4-p-*carboxyanilino*-, m.p. 295—297° (decomp.) (*diethylaminoethyl* ester *trihydrochloride* and *Na* salt, m.p. >250°), -4-o- (*dihydrochloride*, m.p. indefinite, >200°), -4-*m*- (*hydrochloride*, m.p. 178—180°), and -4-p-*hydroxyanilino*-, m.p. 245—247° (decomp.) (*hydrochloride*, m.p. 275—277°), -4-2′ : 6′-dihydroxyanilino- (*dihydrochloride*, m.p. 123—124°), -4-*p*-anisidino- (*hydrochloride*, m.p. 276—278°), -4-3′ : 4′-dimethoxyanilino- (*hydrochloride*, m.p. 270°), -4-*p*-acetamidoanilino- (*dihydrochloride*, m.p. 299—300°), -4-*p*-acetylanilino- (*hydrochloride*, m.p. 275—276°), -4-m-2′-*xylidino*-, m.p. 186—187°, -4-p-, m.p. 193—195°, and -4-o-*xenylamino*-, m.p. 130—132°, -4-α-*naphthylamino*-, m.p. 133—134°, and -4-*morpholino*-, m.p. 157—161°, -*pyrimidine*. 4-Amino-2-anilino- (*hydrochloride*, m.p. 149—150°) and 2 : 4-*dianilino*-*pyrimidine*, m.p. 136—138° (*hydrochloride*, m.p. 194—195°), are similarly obtained. (**I**) has pressor action on anæsthetised dogs equal to that of benzedrine but of shorter duration. R. S. C.

Hydrogenation of basic nitriles in presence of Raney nickel. W. Huber (*J. Amer. Chem. Soc.*, 1944, **66**, 876—879).—Hydrogenation of basic heterocyclic nitriles in presence of Pd–ZrO_2, Pd–C, or PtO_2 in Ac_2O, HCl–EtOH, H_2SO_4–EtOH, HCl–AcOH, or H_2SO_4–AcOH at 25—55°/55—80 lb. is slow and gives much *sec.*-amine. In presence of Raney Ni and 3—4 mols. of NH_3 in MeOH or, less well, EtOH, PrβOH, BuOH, dioxan, Bu^a_2O, or HCO·NH_2 at 60—200 lb. it is rapid (30—80 min. for 0·5 mol.) and gives excellent yields of primary with 0—5% of *sec.*-amine; vigorous shaking is essential; use of <2·5 mols. of NH_3 increases the amount of *sec.*-amine. Details are given for hydrogenation of 4-amino-2-methyl- and 2 : 4-diaminopyrimidine-5-nitrile, 4-phenyl-1-benzylpiperidine-4-nitrile, pyridine-3-nitrile, 4-methyl-5-cyanomethylthiazole, $NEt_2·[CH_2]_3·CN$, and furan-3-nitrile. The following are incidentally described: 4-*phenyl*-1-*benzyl*-4-*aminomethylpiperidine*, m.p. 71—72°, b.p. 224—226°/1 mm. [*dihydrochloride*, m.p. 202—204° (decomp.)]; di-2-methyl-4-amino-5-pyrimidylmethylamine [*tetrahydrochloride*, m.p. 357° (decomp.); (? tetra)picrate, m.p. 269—270° (decomp.)], which, when formed in presence of NH_3–Ni, is often hydrolysed to 4-amino-2-methyl-5-hydroxymethylpyrimidine; *di*-δ-*diethylaminobutylamine*, b.p. 125—126°/2 mm. (hygroscopic hydrochloride; *tripicrate*, m.p. 90—93°). R. S. C.

***d*-Ribobenziminazole. A correction.** G. R. Barker, (Miss) K. R. Cooke, and J. M. Gulland (*J.C.S.*, 1944, 339).—The properties of *d*-ribobenziminazole (cf. A., 1944, II, 85) are now shown to be in agreement with those described by Richtmeyer *et al.* (cf. A., 1942, III, 248). F. R. S.

Some aminopyridoquinolines and their quaternary salts. R. D. Haworth and W. O. Sykes (*J.C.S.*, 1944, 311—314).—8-*Bromo*-6-*aminoquinoline*, m.p. 148° [*hydrochloride* (+2H_2O), m.p. >275°; Ac derivative, m.p. 199°], prep. by reduction ($SnCl_2$–HCl) of the NO_2-compound, with *m*-$NO_2·C_6H_4·SO_3H$ (Skraup) gives 7-bromo-6 : 5-2′ : 3′-pyridoquinoline, m.p. 147—149° (lit. 150°) [*hydrochloride*, m.p. >325°; *monomethiodide*, m.p. 305° (decomp.)], which with aq. NH_3 (sealed tube at 180—200°) affords the 7-NH_2-compound, m.p. 213—215° [*methochloride* (+H_2O), m.p. 272° (decomp.); *Ac* derivative, m.p. 188°, and its *methiodide* (+H_2O), m.p. 283° (decomp.)]. 4 : 1 : 3-$C_6H_3Br(NH_2)_2$ (improved prep. through the *diformyl* derivative, m.p. 179—180°) with *m*-$NO_2·C_6H_4·SO_3H$ (Skraup) yields 8-bromo-5 : 6-2′ : 3′-pyridoquinoline (*monohydrochloride*, m.p. 268—274°), aminated to the 8-NH_2-compound (**I**), [*hydrochloride*, m.p. 295° (decomp.)], also obtained from the 8-OH-compound [*dihydrochloride*, m.p. 315° (decomp.)], which is prepared from 5-amino-8-hydroxyquinoline sulphate (Skraup). The Ac derivative of (**I**), m.p. 198° (lit. 201°), is methylated with difficulty using *p*-$C_6H_4Me·SO_2Me$; after hydrolysis (HCl), 8-*amino*-5 : 6-2′ : 3′-*pyridoquinoline methochloride hydrochloride* (+H_2O), m.p. 280° (decomp.), is obtained. F. R. S.

Action of formamide on the arylacetonitriles. I. A. Novelli (*Anal. Asoc. Quím. Argentina*, 1943, **31**, 23—31).—PhCN, heated with NH_4HCO_3 and HCO_2H, yields NH_2Bz. $CH_2Ph·CN$ similarly gives $CH_2Ph·CO·NH_2$, together with 2-*benzyl*-1 : 3 : 5-*triazine*, m.p. 155—156° [*hydrochloride*, blackens 220°, m.p. 225—226°; *methiodide*, softens 158°, m.p. 172°; *mercurichloride*, m.p. 185—187°; *picrate*, decomp. ~198°, m.p. 207° (decomp.)], which is oxidised ($KMnO_4$) to BzOH. 1-$C_{10}H_7·CH_2·CN$ similarly gives 1-$C_{10}H_7·CH_2·CO·NH_2$ together with 2-α-*naphthyl*-1 : 3 : 5-*triazine*, softens 190°, m.p. 193—194·5° [*methiodide*, m.p. 282° (decomp.); *mercurichloride*, m.p. 195—197°; *picrate*, m.p. 205° (decomp.)]. F. R. G.

Hydantoins. II. Dihydantoins. A. Novelli (*Anal. Asoc. Quím. Argentina*, 1941, **29**, 181—184).—(COPh·$[CH_2]_n)_2$ (*n* = 2 or 3) with NaCN and NH_4HCO_3 yield αδ-*di*-[5-(5-*phenylhydantoinyl*)]*butane*, m.p. 291—292·5°, and αζ-*di*-[5-(5-*phenylhydantoinyl*]*hexane*, m.p. 260—265°, which have no hypnotic action on rats. F. R. G.

Experiments on the synthesis of purine nucleosides. V. Coupling of pyrimidine derivatives with diazonium salts. Method for the preparation of 5-aminopyrimidines. B. Lythgoe, A. R. Todd, and A. Topham. **VI. Synthesis of 9-*d*-xylosido-2-methyladenine and of 6-*d*-xylosidamino-2-methylpurine.** J. Baddiley, B. Lythgoe, and A. R. Todd (*J.C.S.*, 1944, 315—317, 318—322).—V. In order to introduce a 5-NH_2-group into 6-amino-4-glycosidaminopyrimidines which would preclude hydrolysis of the sugar linkage, 4 : 6-diaminopyrimidines have been coupled with diazonium compounds, giving 5-azo-compounds; catalytic hydrogenation of these products yields 4 : 5 : 6-triaminopyrimidines. $CH_2(CN)_2$ in EtOH–H_2O–NaOAc with diazotised *p*-$NO_2·C_6H_4·NH_2$ gives *p-nitrobenzeneazomalononitrile*, m.p. 222° (decomp.); the p-*Cl*-compound (**I**), m.p. 188—190° (decomp.), is similarly prepared. 4 : 6-Diaminopyrimidine with diazotised *p*-$NO_4·C_6H_4·NH_2$ and aq. $NaHCO_3$ affords 4 : 6-*diamino*-5-p-*nitrobenzeneazo*-2-*methylpyrimidine*, m.p. >360°, reduced (H_2–Ni) to the 4 : 5 : 6-(NH_2)$_3$-compound (**II**), m.p. 252—254°, also obtained by reducing the 4 : 6-*dianimo*-5-*benzeneazo*-derivative, m.p. 311° (decomp.), from benzeneazomalononitrile and acetamidine hydrochloride (**III**). 4 : 6-Diamino-6-methylpyrimidine with diazotised *p*-$C_6H_4Cl·NH_2$ yields 4 : 6-*diamino*-5-p-*chlorobenzeneazo*-2-*methylpyrimidine*, m.p. 340—342° (decomp.), also obtained from (**I**) and (**III**). 4 : 6-*Diamino*-5-p-*chlorobenzeneazopyrimidine*, m.p. 301—302° (decomp.), reduced to (**II**), and the -5-p-*NO*$_2$-compound, m.p. >360°, are similarly prepared. 4-Methyluracil is similarly converted into 2 : 6-*dihydroxy*-5-p-*chlorobenzeneazo*-4-*methylpyrimidine*, m.p. 235° (decomp.). The structural conditions governing the coupling of pyrimidine derivatives and their relation to those governing nitrosation are surveyed.

VI. Diazotised *p*-$NO_2·C_6H_4·NH_2$ in aq. $NaHCO_3$ with 6-amino-4-*d*-xylosidamino-2-methylpyrimidine gives 6-*amino*-4-d-*xylosidamino*-5-p-*nitrobenzeneazo*-2-*methylpyrimidine*, m.p. 230° (decomp.), which on hydrogenation (H_2–Ni) affords a mixture of the corresponding 5-aminopyrimidine with *p*-$C_6H_4(NH_2)_2$. 6-*Amino*-4-d-*xylosidamino*-5-(2′ : 4′-*dichlorobenzeneazo*)-2-*methylpyrimidine* (**IV**) (+ 2·5H_2O), m.p. 218—219° (decomp.), similarly prepared with HCS_2Na following hydrogenation, yields the 6-*amino*-5-*thioformamido*-4-d-*xylosidamino*-derivative (+H_2O), m.p. 232° (decomp.), which gives only small amounts of purine. Acetylation (Ac_2O–C_5H_5N) of (**IV**) leads to 6-*amino*-4-*triacetyl*-d-*xylosidamino*-5-(2′ : 4′-*dichlorobenzeneazo*)-2-*methylpyrimidine*, decomp. ~230°, which after hydrogenation and treatment with HCS_2H gives the 6-*amino*-5-*thioformamido*-4-*triacetyl*-d-*xylosidamino*-compound, m.p. 148° (decomp.); this with boiling C_5H_5N in N_2 affords (loss of H_2S) a mixture of 6-*triacetyl*-d-*xylosidamino*-2-*methylpurine* (+C_5H_5N), m.p. 204—205° [deacetylated to 6-d-*xylosidamino*-2-*methylpurine* (**V**), m.p. 218° (decomp.), $[\alpha]_D^{19}$ −32° in H_2O], and 9-d-*xylosido*-2-*methyladenine* (**VI**), m.p. 288° (decomp.), $[\alpha]_D^{19·5}$ −26° in H_2O. (**V**) could not be deaminated by HNO_2, but its hydrolysis (0·1N-H_2SO_4) product, 2-methyladenine (**VII**), is deaminated to 2-*methylhypoxanthine*, m.p. >360°, indicating that in (**V**) the xylose residue is present in a 6-xylosidamino-group. Methylation (MeOH–NaOMe–MeI) of (**VII**) affords 2 : 7-, m.p. 338° (decomp.), and 2 : 9-*dimethyladenine* (**VIII**), m.p. 238°, required for purposes of comparison with (**V**). 6-*Amino*-4-*methylamino*-2-*methylpyrimidine*, m.p. 239—240°, obtained from the corresponding 4-Cl-compound and NH_2Me, with diazotised *p*-$C_6H_4Cl·NH_2$ gives the -5-p-*chlorobenzeneazo*-derivative, m.p. 207° (decomp.), which after hydrogenation and treatment with HCS_2Na leads to 6-*amino*-5-*thioformamido*-4-*methylamino*-2-*methylpyrimidine*, m.p. 189° (decomp.), cyclised to (**VIII**). Hydrolysis (N-H_2SO_4) of (**VI**) affords (**VII**) and *d*-xylose, and deamination (HNO_2) of it gives 9-d-*xylosidamino*-2-*methylhypoxanthine* (+H_2O), m.p. 203°. Ultraviolet absorption spectra of (**V**), (**VI**), (**VII**), and (**VIII**) and its 2 : 7-analogue are compared. F. R. S.

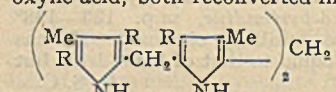
Convenient preparation of synthetic xanthopterin. J. R. Totter (*J. Biol. Chem.*, 1944, **154**, 105—108).—Reduction (Na–Hg) of leucopterin gives Na dihydroxanthopterin, which with $AgNO_3$ affords xanthopterin and with HCl yields dihydroxanthopterin, both in good yield. F. R. S.

Pyrrole series. XII. Condensation of pyrroles with bromine. Self-oxidation and a new type of displacement reaction. A. H. Corwin and P. Viohl. **XIII. Anomalous reaction of dipyrrylmethanes leading to a new class of heterocyclic compounds.** A. H. Corwin and R. C. Ellingson. **XIV. Formation of dipyrrolopyridones in the course of a proposed porphyrin synthesis.** A. H. Corwin and S. R. Buc (*J. Amer. Chem. Soc.*, 1944, **66**, 1137—1146, 1146—1151, 1151—1156; cf. A., 1944, II, 276).—XII. Et 2 : 4-dimethylpyrrole-3-carboxylate (**I**) and Br in MeOH at −60° or, less well, KOH–MeOH at 0—10° give the 5-Br-derivative (**II**), which with Br [best (75·3%), 4 atoms] in AcOH at 10—15° gives *Et*$_2$ 3 : 5 : 4′-*trimethyl*-5′-*bromodi*-2-*pyrrylmethene*-4 : 3′-*dicarboxylate hydrobromide* (**III**), m.p. 153° (decomp.), also obtained from (**I**) by Br in Et_2O–AcOH at −5° to 0°. Bromination of (**I**) is much faster than that of (**II**). Contrary to Fischer's view, formation of (**III**) thus proceeds: (**I**) + 2Br →

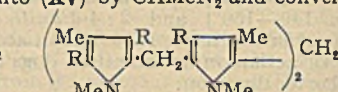
(II) + HBr; (II) + Br→Et 2-bromo-3-methyl-5-bromomethylpyrrole-4-carboxylate (IV) + HBr; (II) + (IV) →(III). Formation of (III) is limited by a HBr-catalysed self-oxidation of (II) to yield HBr and Et_2 3 : 5 : 3′ : 5′-tetramethyldi-2-pyrrylmethene-4 : 4′-dicarboxylate (V) [derived base (VI), decomp. 190°], so that the rate of evolution of HBr exceeds that of consumption of Br by (II); in accordance with this view, (II) contains active Br, liberating I from KI. Two reaction mechanisms are discussed, each being partly supported by the following reactions. Et_2 3 : 5 : 3′ : 5′-tetramethyldi-2-pyrrylmethane-4 : 4′-dicarboxylate [obtained from (VI) by hydrogenation], m.p. 230° (slight decomp.), (II), and a little HBr in dioxan at room temp. give (VI). The free base from (III) with (I) in Et_2O at 0° gives *Et* 5″-*bromo*-3 : 5 : 3′ : 5′ : 4″-*pentamethyltri*-2-*pyrrylmethane*-4 : 4′ : 3″-*tricarboxylate* (VII) (95·5%), m.p. 210° (decomp.), whence HCl–Et_2O at 0° or HBr–AcOH at 40° and then aq. NH_3 regenerates the base from (III) (73% and 43%, respectively). Et 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate and (II) in AcOH at 40° give, after treatment with NH_3, *Et* 3′-*bromo*-2 : 5 : 4′-*trimethyldi*-2-*pyrrylmethene*-4 : 5′-*dicarboxylate*, m.p. 135—136° (decomp.). However, Et_2 3-methyl-5-bromomethylpyrrole-2 : 4-dicarboxylate does not condense with (II). (III), (I), and a little HBr in AcOH at 50° give (V). H_2–Pd–C at 2 atm. reduces (VII) to Et_3 3 : 5 : 3′ : 5′ : 4″-*pentamethyltri*-2-*pyrrylmethane*-4 : 4′ : 3″-*tricarboxylate*, m.p. 224—225°. 3-*Carbethoxy*-4-*methylpyrrole*-5-*carboxylic acid* (prep. from the Et_2 ester by KOH in boiling 80% EtOH), m.p. ~230° (evolution of CO_2), in boiling glycerol yields Et 3-methyl- (46%), m.p. 73°, and thence Et 2-formyl-3-methyl-pyrrole-4-carboxylate, m.p. 122°, which with (I) and HCl in Et_2O at 0° and then aq. NH_3 yields Et_2 3 : 5 : 3′-trimethyldi-2-pyrrylmethene-4 : 4′-dicarboxylate (VIII), m.p. 147° (decomp.). The hydrobromide of (VIII) with Br–AcOH at 50° and then aq. NH_3 gives Et_2 5′-*bromo*-3 : 5 : 3′-*trimethyldi*-2-*pyrrylmethene*-4 : 4′-*dicarboxylate*, m.p. 151° (decomp.). (VIII), (I), and a trace of $KHSO_4$ in Et_2O give Et_3 3 : 5 : 3′ : 5′ : 3″-*pentamethyltri*-2-*pyrrylmethane*-4 : 4′ : 4″-*tricarboxylate*, decomp. 222°.

XIII. Treating 3-carbalkoxydi-2-pyrrylmethanes with alkali (Na; $NaCPh_3$ in dioxan; NaOAlk) gives 6-keto-1 : 2 : 3 : 6-tetrahydropyrrolo-2′ : 3′-4 : 5-pyridino-1 : 2-1″ : 2″-pyrroles ["dipyrrolo-(1 : 2-*a*,2′ : 3′-*d*)pyridine-4(9)-one"; this numbering is as (*A*)], which fluoresce like lubricating oil. For this condensation the 1′-N must be unsubstituted and at least as acidic as the 1-N; if the 1-N is the more acidic, the alkali reacts at this point and ring-closure of the 3-CO_2Alk with the 1′-N is impossible. Mixed m.p. in this series are unreliable and re-esterification in presence of NaOAlk is very facile, so that care is essential in identification. Structures assigned below are held to be proved by the reactions of the isomerides. The compound, m.p. 204°, obtained (A., 1943, II, 72) from Et_3 1 : 4 : 3′ : 5′-tetramethyldi-2-pyrrylmethane-3 : 5 : 4′-tricarboxylate (IX) by Na, is Et_2 6-*keto*-1′ : 4′ : 3″ : 5″-*tetramethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole*-5′ : 4″-*dicarboxylate* (X). The violet-red colour formed in alkali is due to carbenium salt formation. (X) is unaffected by conc. H_2SO_4, HCl–EtOH at 0°, boiling H_2SO_4–AcOH–H_2O, or ketone reagents. 3-Carbomethoxy-5-carbethoxy-2 : 4-dimethylpyrrole (prep. from CHMeAc·CO_2Me, OH·N:CAc·CO_2Et, Zn dust, and NaOAc in aq. AcOH at 90°, rising to 110°; 68% yield), m.p. 130—131°, with Na in PhMe at 98—110° and then Me_2SO_4 at 90° gives 3-*Me* 5-*Et* 1 : 2 : 4-*trimethylpyrrole*-3 : 5-*dicarboxylate* (76%), m.p. 78—80°, whence SO_2Cl_2 yields 4-*Me* 2-*Et* 1 : 3-*dimethyl*-5-*chloromethylpyrrole*-2 : 4-*dicarboxylate*, m.p. 69—71° (and a by-product, m.p. 85—87°). With (I) in boiling MeOH this gives 3-*Me* 5 : 4′-Et_2 1 : 4 : 3′ : 5′-*tetramethyldi*-2-*pyrrylmethane*-3 : 5 : 4′-*tricarboxylate* (XI) (82%), m.p. 139°, whence $NaCPh_3$ in dioxan yields (X), m.p. 197—199° or, after longer reaction, 189—190°; the difference in m.p. is due to partial re-esterification and pure (X) is obtained by treating this product with NaOEt. Et_2 1 : 3-dimethyl-5-chloromethylpyrrole-2 : 4-dicarboxylate and (I) in hot MeOH give 4′-*Me* 3 : 5-Et_2 1 : 4 : 2′ : 5′-*tetramethyldi*-2-*pyrrylmethane*-3 : 5 : 4′-*tricarboxylate* (84%), m.p. 134°, whence $NaCPh_3$ in dioxan gives 4″-*Me* 5′-*Et* 6-*keto*-1′ : 4′ : 3″ : 5″-*tetramethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole*-5′ : 4″-*dicarboxylate*, m.p. 194°. OH·N:CAc·CO_2Me (prep. described) with CH_2Ac·CO_2Et etc. as above gives 5-carbomethoxy-3-carbethoxy-2 : 4-dimethylpyrrole (54%), m.p. 164°, and thence as above the 1 : 2 : 4-Me_3 ester, m.p. 86—87°, and 2-*Me* 4-*Et* 1 : 3-*dimethyl*-5-*chloromethylpyrrole*-2 : 4-*dicarboxylate* (82%), m.p. 99—100°. This with (I) in MeOH yields 5-*Me* 3 : 4′-Et_2 1 : 4 : 3′ : 5′-*tetramethyldi*-2-*pyrrylmethane*-3 : 5 : 4′-*tricarboxylate* (58%), m.p. 130—131°, which with $NaCPh_3$ in dioxan yields impure 5′-*Me* 3″-*Et* 6-*keto*-1′ : 4′ : 3″ : 5″-*tetramethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole*-5′ : 3″-*dicarboxylate* (XII), m.p. 188—189°, obtained pure (m.p. 210—211°) by treatment with NaOMe. With NaOMe, (IX) or (XI) gives (X), and with NaOEt either gives pure (XII).

XIV. Et_4 4 : 4-dimethyldi-2-pyrrylmethane-3 : 5 : 3′ : 5′-tetracarboxylate (XIII) with 1 mol. of NaOH in hot EtOH gives 58% of Na_1 and some Na_2 salt, separated by extraction with H_2O and fractional pptn. therefrom by NaCl; 2 mols. of NaOH lead to mainly the Na_2 salt. Et_3 4 : 4′-*dimethyldi*-2-*pyrrylmethane*-3 : 5 : 3′-*tricarboxylate*-5′-*carboxylic acid* [with $CHMeN_2$ yields (XIII)] in glycerol + a little quinoline at 240° (or 285°) gives Et_3 4 : 4′-*dimethyldi*-2-*pyrrylmethane*-3 : 5 : 3′-*tricarboxylate* (XIV) (86·5%), m.p. 187° (and ? an *isomeride*, m.p. 184—185°), which with CH_2O–conc. HCl–EtOH at the b.p. gives the *substance* (XV), m.p. 216—217° (decomp.), whence NaOH yields no cryst. acid. With 1 mol. of NaOH in hot EtOH, (XIV) gives a small yield of an acid, m.p. >205°, which in hot glycerol yields a substance, m.p. >250°. With 0·05 mol. of NaOH in hot aq. EtOH, (XIV) gives Et_2 6-*keto*-4′ : 4″-*dimethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole*-5 : 3″-*dicarboxylate* (34%), darkens 235°, decomp. 245°. Condensation of Et_2 4 : 4′-dimethyldi-2-pyrrylmethane-3 : 3′-dicarboxylate by NaOH (1 mol.) in boiling 60% EtOH and heating the product in glycerol gives 6-*keto*-4 : 4″-*dimethyl*-1 : 2 : 3 : 6-*tetrahydropyrrolo*-2′ : 3′-4 : 5-*pyridino*-1 : 2-1″ : 2″-*pyrrole* (poor yield), cryst. Partial hydrolysis of the Et_4 ester (XVI) gives the 3 : 3′-Et_2 and 3 : 3′ : 5′-Et_3 ester of 1 : 4 : 1′ : 4′-tetramethyldi-2-pyrrylmethane-3 : 5 : 3′ : 5′-tetracarboxylic acid, both reconverted into (XV) by $CHMeN_2$ and converted



(XV.) (R = CO_2Et)



(XIX.) (R = CO_2Et)

by heating in glycerol + a little quinoline into Et_2 1 : 4 : 1′ : 4′-*tetramethyldi*-2-*pyrrylmethane*-3 : 3′-*dicarboxylate* (XVII), m.p. 164—165°, and Et_3 1 : 4 : 1′ : 4′-*tetramethyldi*-2-*pyrrylmethane*-3 : 5 : 3′-*tricarboxylate* (XVIII), m.p. 127—129°, respectively. With paraformaldehyde and a little AcOH in boiling BuOH, (XVIII) yields the *substance* (XIX) (89%), m.p. 147—149°. Partial hydrolysis of (XVIII) gives an acid [reconverted into (XVIII) by $CHMeN_2$], decarboxylation of which gives (XVII). R. S. C.

Amino-ketones. II. Synthesis of α-diamines from α-amino-ketones. N. H. Cromwell and H. Hoeksema (*J. Amer. Chem. Soc.*, 1944, **66**, 870—871; cf. A., 1943, II, 108).—ω-*Morpholinoacetophenoxime* (prep. from the ketone by NH_2OH,HCl–KOH–H_2O–MeOH at 20°), m.p. 147—149°, with H_2–Raney Ni in EtOH at 50° (NH_3 inhibits reduction) gives 10%, with H_2–Pd–C–AcOH gives 15%, with H_2–Pd–C–HCl–AcOH gives 10%, or with Na–EtOH gives 26% of β-*morpholino*-α-*phenylethylamine* (I), b.p. 134°/2 mm. ω-*Piperidinoacetophenoxime*, *forms*, m.p. 117—118·5° and 136—138·5°, with Na–EtOH gives 24% of β-*piperidino*-α-*phenylethylamine* (II), b.p. 128°/3 mm. No diamine is obtained by catalytic hydrogenation of β-amino-ketoximes, probably owing to loss of the β-amino-radical to give unsaturated oximes. Low yields of (I) and (II) by Na–EtOH are due partly to loss of NH_3 during distillation of the product. *Bz* derivatives, m.p. 143—144° and 135—136°, of (I) and (II), respectively, are potent local anæsthetics. R. S. C.

Phenylthiocarbamides. Contribution to the study of the triad –N·C·S–. XIII. Action of sulphur monochloride on *N*-phenyl-*N*-methylthiocarbamide. Formation of thiodiazoles. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1944, **21**, 17—18).—The compound formed by the interaction of S_2Cl_2 with a $CHCl_3$ solution of NPhMe·CS·NH_2 is 2-imino-3-methyl-2 : 3-dihydrobenzthiazole and not either of the compounds suggested by Dost (A., 1906, i, 351). NHPh·CS·NH_2 gives 2-aminobenzthiazole under the same conditions. C. R. H.

Vasosulpha compounds. W. F. Hamilton, M. F. George, jun., E. Simon, and F. M. Turnbull (*J. Amer. Pharm. Assoc.*, 1944, **33**, 142—145; cf. A., 1944, III, 756).—Dissolution of the appropriate ephedrine alkaloid and sulpha drug in warm, dil., aq. Na_2SO_3, followed by cooling, yields *ephedronium sulphathiazole*, m.p. 206°, and *sulphadiazine*, m.p. 192—193°, and *deoxyephedronium sulphathiazole*, m.p. 118—120°, and *sulphadiazine*, m.p. 187—189° (all m.p. corr.). F. O. H.

Organo-metallic derivatives of methylbenzthiazole. Magnesium compounds. C. Courtot and S. Tchelitcheff (*Compt. rend.*, 1943, **217**, 201—203).—The Mg compound from methylbenzthiazole with CO_2 gives *benzthiazolylacetic acid*, m.p. 112—113°, with $COMe_2$ forms *benzthiazolylmethyldimethylcarbinol*, m.p. 79°, with some benzthiazolylmethyl alcohol, and with $COPh_2$, *diphenylbenzthiazolylmethylcarbinol*, m.p. 194—195°, is obtained. F. R. S.

Organo-metallic derivatives of methylbenzthiazole and of benzthiazole. C. Courtot and S. Tchelitcheff (*Compt. rend.*, 1943, **217**, 231—233).—Methylbenzthiazole reacts with $NaNH_2$ to give the *Na* derivative, which with the appropriate reagent yields: 2-β-phenylethylbenzthiazole, with some dibenzylbenzthiazolylmethane (CH_2PhCl); 2-*n*-amylbenzthiazole, b.p. 152—153°/15 mm., and methyldibutylbenzthiazole, b.p. 176°/15 mm. ($Bu^{\alpha}Cl$); methyl-*iso*-butylbenzthiazole, b.p. 167°/15 mm. ($Bu^{\beta}Cl$); 2-*iso*hexylbenzthiazole, b.p. 172—175°/25 mm. ($C_5H_{11}Br$); α-benzthiazolyl-Δ^{γ}-butene, b.p. 153°/15 mm., and δ-benzthiazolyl-$\Delta^{\alpha\zeta}$-heptadiene, b.p. 198°/15 mm., m.p. 126° (CH_2:CH·CH_2Br); and 2-*p*-nitro- and -amino-

phenylbenzthiazole (p-$C_6H_4Cl{\cdot}NO_2$). The *Li* derivative of methylbenzthiazole with *cyclo*hexyl chloride gives benzthiazolyl*cyclo*hexylmethane, b.p. 189—190°/15 mm. (picrate, m.p. 118°), and with $C_2H_4Cl_2$ yields αδ-dibenzthiazolylbutane, m.p. 87° (picrate, m.p. 92—93°). F. R. S.

Derivatives of phenothiazine. H. Gilman and D. A. Shirley (*J. Amer. Chem. Soc.*, 1944, **66**, 888—893).—Phenothiazine (**I**), o-$C_6H_4I{\cdot}NO_2$, Cu-bronze, and K_2CO_3 in boiling xylene give 10-o-*nitro*- (44%), m.p. 156—157°, reduced by Sn–HCl to 10-o-*amino-phenylphenothiazine* (95%), m.p. 139—139·5°, which with the hygroscopic hydrochloride, m.p. 64—68° (lit. 62—64°), of $NEt_2{\cdot}[CH_2]_3{\cdot}Cl$ (prep. from the alcohol by $SOCl_2$–$CHCl_3$; b.p. 73—75°/20 mm.) at 130—140° gives 10-o-γ-*diethylamino*-n-*propylaminophenylphenothiazine* (49%), b.p. 215—230°/<0·5 mm. Similarly are prepared 10-3′-*nitro*-p-*tolyl*-, m.p. 179·5—180°, 10-3′-*amino*-p-*tolyl*-, m.p. 140—140·5°, 10-3′-γ-*diethylamino*-n-*propylamino*-p-*tolyl*-, b.p. 270° (bath)/<0·5 mm., 10-3′-*nitro*-p-*anisyl*-, m.p. 184—186°, 10-3′-*amino*-p-*anisyl*-, m.p. 180—181°, 10-3′-γ-*diethylamino*-n-*propylamino*-p-*anisyl*-, b.p. 220—235°/<0·5 mm., 10-3′-*nitro*-o-*anisyl*-, m.p. 159—160°, 10-4′-*chloro*-2′-*nitrophenyl*-, m.p. 185—186·5°, 10-4′-*chloro*-2′-*aminophenyl*-, m.p. 125·5—126°, and 10-4′-*chloro*-2′-γ-*diethylamino*-n-*propylaminophenyl*-, b.p. 270—280°/2 mm., -*phenothiazine*. With LiBuᵃ and the p-$C_6H_4Me{\cdot}SO_2{\cdot}[CH_2]_2{\cdot}Cl$ in Et_2O, (**I**) gives 10-β-chloroethylphenothiazine (47%), m.p. 96—97° (5-*oxide*, m.p. 154—155°), which with the appropriate amine and Cu-bronze at the b.p. gives 10-β-*diethylamino*- (67%), b.p. 161—165°/<0·5 mm., 10-β-*di*-n-*propylamino*-, b.p. 225—230°/1 mm., 10-β-*morpholino*-, m.p. 74·5—75·5°, b.p. 198—201°/<0·5 mm., and 10-β-6′-*methoxy*-8′-*quinolylamino*- [prep. by Cu powder at 140—150° (N_2)], m.p. 118·5—119·5°, -*ethylphenothiazine*. 10-γ-*Chloro*-, m.p. 60°, 10-γ-*diethylamino*- (**II**), b.p. 170—182°/<0·5 mm. (*dipicrate*, m.p. 103—104°), 10-γ-*di*-n-*propylamino*-, b.p. 257—265°/1—2 mm., 10-γ-*diallylamino*-, b.p. 245—260°/1 mm., and 10-γ-*piperidino*-, b.p. 255—265°/1—2 mm., -n-*propylphenothiazine* are similarly prepared. p-$OMe{\cdot}C_6H_4{\cdot}NHPh$ (prep. from p-$OMe{\cdot}C_6H_4{\cdot}NHAc$ by PhBr, Na_2CO_3, and Cu powder, followed by hydrolysis). m.p. 106° (lit. 105°), S, and a little I at 140—150° and later 175° give 3-methoxyphenothiazine (45—51%), m.p. 158—159° (lit. 163°, 159°) (*Ac* derivative, m.p. 121—122·5°), which affords, as above, 3-methoxy-10-γ-chloro-, an oil, -10-γ-*di*-n-*propylamino*-, b.p. 250—265°/2 mm., and -10-γ-*diethylamino*-n-*propylphenothiazine*, b.p. 220—225°/<0·5 mm. p-$C_6H_4Me{\cdot}NHPh$, S, and a little I at 280° give 3-*methylphenothiazine*, m.p. 166—168°. Conc. HNO_3 converts 10-acetyl- or 10-ethyl-phenothiazine in AcOH into 3 : 7-dinitro-10-acetyl-, m.p. 265—267° (cf. lit.), and 3-*nitro*-10-*ethyl-phenothiazine* 5-*oxide*, m.p. 204·5—205°, respectively. AlkBr, (**I**), Cu powder, and Na_2CO_3 in boiling C_6H_6 gives 10-*allyl*-, b.p. 187—195°/1 mm., or at 170—180° 10-n-*decyl*-, b.p. 183—185°/<0·5 mm. (3-NO_2-derivative 5-*oxide*, m.p. 102·5—103°), and 10-n-*octadecyl-phenothiazine*, m.p. 53° (5-*oxide*, m.p. 98°). 10-*Phenyl*-, m.p. 170—171°, and 3-*nitro*-10-*phenyl-phenothiazine* 5-*oxide*, m.p. 223·5—224·5°, are also prepared. (**I**), its 10-alkylaminoalkyl and 10 other derivatives have no effect on avian malaria, except that (**II**) is doubtfully active in 12·5-mg. doses. Phenothiazine derivatives have very slight toxicity to canaries. R. S. C.

Metallation of 10-phenyl- and 10-ethyl-phenothiazine. H. Gilman, P. R. Van Ess, and D. A. Shirley (*J. Amer. Chem. Soc.*, 1944, **66**, 1214—1216).—10-Ethylphenothiazine (**I**) (prep. from phenothiazine (**II**) and Et_2SO_4 in EtOH at 120—130°; 56% yield], m.p. 101—103°, with LiBuᵃ in Et_2O–N_2 and then CO_2 gives 6% of 10-*ethylphenothiazine*-4- (or -2-)*carboxylic acid*, m.p. 178—179° (*Me* ester, m.p. 111—112°), converted by boiling, conc. HI into m-$C_6H_4Ph{\cdot}CO_2H$, m.p. 138—139°, which is also obtained (m.p. 140°; 2·5% yield) from m-$C_6H_4I{\cdot}CO_2Me$ by K_2CO_3 and Cu-bronze in boiling NH_2Ph and then boiling 15% KOH–EtOH. The 3-Hg·OAc derivative, m.p. 151—153°, of (**I**) with aq. NaCl gives the HgCl derivative, which in I–KI–H_2O–CCl_4 gives 3-*iodo*-10-*ethylphenothiazine* (80%), m.p. 126—127°, whence MgBuᵃBr–I and then CO_2 gives 10-*ethylphenothiazine*-3-*carboxylic acid*, m.p. 197·5—198·5°. 10-Phenylphenothiazine [prep. from (**II**) by PhI, Cu powder, and Na_2CO_3 at the b.p.], m.p. 94·5°, with LiBuᵃ and then CO_2 gives 10-*phenylphenothiazine*-4-(or -2-)*carboxylic acid* (9·5%), m.p. 258—258·5° (*Me* ester, m.p. 133—134°), converted by boiling, conc. HI into m-$CO_2H{\cdot}C_6H_4{\cdot}NPh_2$. 10-p-, m.p. 221—221·5° (*Me* ester, m.p. 140·5—141·5°), and 10-m-*carboxyphenylphenothiazine*, m.p. 254—255° (*Me* ester, m.p. 98—99°), are also obtained from (**II**) by p- and m-$C_6H_4I{\cdot}CO_2Et$, respectively, with Cu powder and K_2CO_3, followed by aq. NaOH or HCl–MeOH. R. S. C.

Total synthesis of 2 : 3 : 4 : 5-tetrahydrobiotin. L. C. Cheney and J. R. Piening (*J. Amer. Chem. Soc.*, 1944, **66**, 1040—1041).—Preliminary data are given for the following reactions. $Cl{\cdot}[CH_2]_3{\cdot}Br + CH_2(CO_2Et)_2 \rightarrow Cl{\cdot}[CH_2]_3{\cdot}CH(CO_2Et)_2 \rightarrow Cl{\cdot}[CH_2]_4{\cdot}CO_2Et \rightarrow$ [+ $CH_2(CO_2Et)_2$] Et_2 n-*pentane*-αα′γ-*tricarboxylate*, b.p. 165—170°/4 mm. → the *tricarboxylic acid*, m.p. 82° → ($SOCl_2$; decarboxylation) α-*chloropimelic acid*, m.p. 89—90° → ($SH{\cdot}[CH_2]_2{\cdot}CO_2H$; esterification) β-*carboxyethyl* αε-*dicarbethoxy*-n-*amyl sulphide*, b.p. 210—213°/3 mm. → (Dieckmann) Et_2 3-*ketotetrahydrothiophen*-4-*carboxylate*-2-*valerate* → *oxime* → (dry HCl) Et_2 3-*aminothiophen*-4-*carboxylate*-2-*valerate*, m.p. 43—44° → 3-*amino*-4-*carbethoxythiophen*-2-*valeric acid*, m.p. 97—97·5° → the N-*Bz* derivative, m.p. 126·5—127·5° → the *hydrazide*, m.p. 140—141° → the *azide*, decomp. 99—100° → (boiling EtOH) 3-*benzamido*-4-*carbethoxyamino*-2-*thienylvaleric acid*, m.p. 156·5—157·5° → (hydrolysis; $COCl_2$) 2′-*keto*-2′ : 3′-*dihydroglyoxalino*-4′ : 5′-1 : 2-*thiophen*-4-*valeric acid*, m.p. 253—254° (decomp.), the absorption spectrum of which [max. at 260 mμ. (ε 17 × 10^{-3})] resembles those of 2′-*keto*-4-γ-*phenoxy*-, m.p. 174—174·5°, -*benzyloxy*-, m.p. 127—127·5°, and -*hydroxy*-n-*propyl*-2′ : 3′-*dihydroglyoxalino*-4′ : 5′-1 : 2-*thiophen*, m.p. 138—139°. R. S. C.

Hemicyanine dyes.—See B., 1944, II, 244.

VII.—ALKALOIDS.

Pyrolysis of nicotine to myosmine. C. F. Woodward, A. Eisner, and P. G. Haines (*J. Amer. Chem. Soc.*, 1944, **66**, 911—914).—Pyrolysis of nicotine over SiO_2 chips gives NH_3, NH_2Me, HCN, C_5H_5N, 3-methyl-, 3-ethyl-, and 3-vinyl-pyridine, 3 : 2′-nicotyrine, myosmine (**I**), and higher-boiling products. At 555—570° up to 18·1% of (**I**) is obtained, but the yield is much less at 700° or over activated Al_2O_3 at 500°. R. S. C.

Erythrina alkaloids. XIV. Isolation and characterisation of erysothiovine and erysothiopine, new alkaloids containing sulphur. K. Folkers, F. Koniuszy, and J. Shavel, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 1083—1087; cf. A., 1943, II, 74).—After removal of free alkaloids, the light petroleum extract of *E. glauca* seeds in H_2O gradually yield *erysothiovine* (**I**), $C_{20}H_{23}O_7NS$, $+H_2O$ (lost at 140°/vac.), m.p. 187°, $[\alpha]_D^{25}$ +208° in EtOH, and, more slowly at 0°, *erysothiopine* (**II**), $C_{19}H_{21}O_7NS$, $+H_2O$ (lost at 100°/vac.), m.p. 168—169°, $[\alpha]_D^{25}$ +194° in EtOH. In hot 1—2% mineral acid, (**I**) gives erysovine (**III**) and $CO_2H{\cdot}CH_2{\cdot}SO_3H$ (**IV**) (NH_2Ph, m.p. 187—189°, and *sulphapyridine* salt, m.p. 162—163°). Hydrolysis of (**II**) similarly gives erysopine (**V**). The ester group of (**I**) and (**II**) contains the combined SO_3H of (**IV**), since the Ca and Ba salts of (**IV**) are insol. and those of (**I**) and (**II**) are sol. (**I**) is isolated also from *E. pallida*, Britton & Rose, and *E. poeppigiana*. No " thio "-alkaloid is isolated from *E. sandwicensis*, Deg. Threshold doses for curare action (frog) are: erysonine 100, erysodine 15, (**V**) 4, (**III**) 3, (**I**) and (**II**) 1 mg. per kg. body wt. R. S. C.

Alkaloids of the Leguminosæ. VIII. Alkaloids of *Podalyria* species. IX. Isolation of β-phenylethylamine from *Acacia* species. X. Isolation of anagyrine from *Cytisus linifolius* Lam. XI. Alkaloids of the genera *Cytisus* and *Genista*. XII. Alkaloids of *Calycotome spinosa* (L.) Link. XIII. Isolation of tryptamine from some *Acacia* species. E. P. White (*New Zealand J. Sci. Tech.*, 1944, **25**, B, 137—138, 139—142, 143—146, 146—151, 152—157, 157—162).—VIII. Lupanines (**I**) are extracted (Soxhlet) from three species of *Podalyria*, determined by titration, the optical isomerides separated by hot hexane, and identified by m.p. of methiodides, perchlorates, and aurichlorides, alone and mixed with authentic specimens. *P. sericea*, R. Br., tops and seeds contain *d*-(**I**) with less *dl*-, *P. buxifolia*, Willd., *dl*- with a trace of *l*-, and *P. calyptrata*, Willd., pure *l*-, $[\alpha]_D$ −79° in EtOH.

IX. The alkaloids are extracted in a Soxhlet apparatus, or by repeated soaking with 5% HCl with intermittent heating. The tops of eight species forming a distinct morphological group (uninerval phyllodes and flowers in racemes) contain relatively high concns. of $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ (**II**); their seeds contain only traces. The tops of three other species contain traces of (**II**) and small amounts of another alkaloid not yet purified. 20 other species are alkaloid-free. (**II**) is identified by m.p. of its hydrochloride, *mercurichloride* (165°), *mercuri-iodide* (182°), picrate, and aurichloride, alone and mixed with specimens synthesised from $CH_2Ph{\cdot}CN$. Substances allied to (**II**) have previously only been found in low concns. (mainly in parasites and fungi), and are possible intermediates in the biogenesis of tetrahydroisoquinoline alkaloids.

X. Soxhlet extraction of the seeds of *Cytisus linifolius*, Lam., gives ~1% of cytisine (**III**), while the tops yield ~1% of anagyrine (**IV**), with ~0·1% of other bases. The alkaloids are identified by analysis and m.p. of their salts, alone and mixed with authentic specimens, and by slide reactions. (**IV**) gives slide reactions with $KCdI_3$, $AuCl_3$, $HgCl_2$, K_2HgI_4, $AuBr_3$, picric acid, KI_3, and $KBiI_4$.

XI. The genera *Cytisus* and *Genista* can be divided into six groups according to their alkaloid contents: (i) sparteine (**V**) only, (ii) mainly (**I**), with or without some (**V**), (iii) (a large group) (**III**) or allied bases, with no (**V**), (iv) (**III**) or allied bases, with (**V**), (v) calycotomine, sometimes with traces of other alkaloids, (vi) alkaloid-free.

XII. Soxhlet extraction of the seeds of *Calycotome spinosa* with 2% AcOH in 50% EtOH yields ~1% of bases; tops contain only traces. The chief component, named *calycotomine* (**VI**), $C_{10}H_9(OMe)_2(NH)(OH)$, m.p. 139—141°, $[\alpha]_D^{20}$ +21° in H_2O, forms a *hydrochloride*, m.p. 193°, $[\alpha]_D$ +15° in H_2O, a *picrate monohydrate*, m.p. 163—166°, a *perchlorate*, m.p. 176—177°, a *mercurichloride*, m.p. 118—119°, a *Bz*$_2$ derivative, m.p. 120—122°, and a nitroso-amine. Methylation with CH_2O and HCO_2H gives the N-*Me*

derivative (**VII**) (*hydrochloride*, m.p. 216°), with MeI, the *hydriodide* of (**VII**), m.p. 228—229°, and with Me_2SO_4 and NaOH, quaternary material. (**VI**) itself has no phenolic reactions, but demethylation gives an *o*-dihydric phenol (intense green colour with $FeCl_3$). (**VI**) gives characteristic slide reactions, particularly with $AuBr_3$, KI_3, picric acid, $HgCl_2$, and $KCdI_3$. It reacts negatively for *C*-Me and for indole, whilst $KMnO_4$–NaOH oxidation gives an insol. *substance*, $C_{11}H_{11}O_4N$, m.p. 316°, blue-fluorescent in EtOH, and two other fractions, all containing N and OMe. Traces of *dl*-(**VI**) (*hydrochloride*, m.p. 193°) are also present. Another trace alkaloid is named *calycotamine* (*hydrochloride*, $C_{11}H_{15-17}O_3N$,HCl, m.p. 206°, $[\alpha]_D$ +20° in H_2O); it has 2 OMe and no NMe, like (**VI**), but is distinct from it.

XIII. *Acacia floribunda* tops contain up to 0·2% of a mixture of (**II**) and tryptamine (3-ω-aminoethylindole) (**VIII**); flowers contain up to 1%, whilst *A. pruinosa* tops contain 0·04%. *A. longifolia* flowers and tops contain up to 0·2% of alkaloids, including (**II**), but not (**VIII**). (**VIII**) is identified by the reactions characteristic for 3-substituted indoles, by its m.p. and that of its hydrochloride and picrate (alone and mixed with specimens synthesised by reduction of the product from Mg indolyl iodide and $CH_2Cl{\cdot}CN$), and by slide reactions (particularly with $KBiI_4$ and picric acid). It has not formerly been found in plants. S. A. M.

Antiplasmodial action and chemical constitution. VII. Derivatives of quinine and *iso*quinine. T. S. Work (*J.C.S.*, 1944, 334—335).—Reduction of crude quininal, obtained by ozonolysis of quinine, with H_2–Pd–C, gives quinonol, isolated as the dihydrobromide (*monosulphate*, m.p. 149°). Decomp. of the ozonide of β-*iso*quinine with H_2O affords 3-*acetyl*-6′-*methoxyrubanol*, m.p. 198—200°, reduced catalytically to the 3-OH·$[CH_2]_2$ derivative (*dihydrobromide*, m.p. 192—194° (decomp.)], which is a diastereoisomeride of the substance previously obtained (cf. Henry *et al.*, A., 1937, II, 266). Although active, none of the compounds showed antiplasmodial action equal to that of quinine. F. R. S.

Quaternary salts of scopolamine.—See B., 1944, III, 169.

Ultra-violet absorption spectrum of ibogaine.—See A., 1944, I, 212.

Aconite alkaloids. XV. Nature of the ring system and character of the nitrogen atom. L. C. Craig, L. Michaelis, S. Granick, and W. A. Jacobs (*J. Biol. Chem.*, 1944, **154**, 293—304).—Hydrolysis (1·056N-NaOH) of delphinine gives *delphonine* (**I**) a resin, m.p. 76—78°; *pyrodelphonine* (**II**) and *α-ketodelphonine* (**III**) are similarly obtained. MeI and (**I**), followed by removal of I with Ag_2O, afford N-*methyl*-de-*delphonine* (**IV**). Aconine, (**I**), heteratisine, and tetrahydroatisine in solution as bases all show a strong absorption between 2200 and 2600 A, and it appears probable that the absorption must be due to a conjugated unsaturation of some kind, indicating that the ring structure of the aconite alkaloids, at least in the form of free bases, could be of tetracyclic character. The hydrochlorides of these bases absorb in a manner which could be ascribed possibly to a single double bond as modified by the N and OH groups present. (**III**) is a cyclic amide and shows an absorption spectrum very similar to that of (**I**) in alkaline solution. The absorption spectrum of (**IV**) indicates the presence of an additional double bond. That of (**II**) indicates a new double bond but different in arrangement from that of (**IV**). F. R. S.

Synthesis of *ON*-dimethylanalobine. L. Marion (*J. Amer. Chem. Soc.*, 1944, **66**, 1125—1127).—The following reactions are recorded. CHAr:CH·CO_2H (Ar = 3 : 4 : 1-CH_2O_2:C_6H_3) → (electrolytic) Ar·$[CH_2]_2$·CO_2H (65·2%) → (PCl_5; aq. NH_3) Ar·$[CH_2]_2$·CO·NH_2 (use of $SOCl_2$ leads to β-x-*chloro*-3 : 4-*methylenedioxyphenylpropionamide*, m.p. 146°) → Ar·$[CH_2]_2$·NH_2 (**I**) (51·3%) {picrate, m.p. 180·5° [lit. 174° (uncorr.)]}. *m*-Cresol → 5 : 1 : 2-OH·C_6H_3Me·NO_2 → 5 : 1 : 2-OMe·C_6H_3Me·NO_2 (18%) → 2 : 5 : 1-NO_2·C_6H_3(OMe)·CH_2·CO·CO_2H (78%), m.p. 137° → (H_2O_2–NaOH) 2-*nitro*-5-*methoxyphenylacetic acid*, m.p. 178·5°. With PCl_5–$CHCl_3$ and then (**I**) in $CHCl_3$–aq. NaOH, this yields 2-*nitro*-5-*methoxyphenylacet*-β-3′ : 4′-*methylenedioxyphenylethylamide*, m.p. 188°, converted by PCl_5 in $CHCl_3$ into 6 : 7-*methylenedioxy*-1-2′-*nitro*-5′-*methoxybenzyl*-3 : 4-*dihydro*isoquinoline, m.p. 168°, the *methiodide*, m.p. 205°, of which with Zn dust in hot aq. HCl gives 6 : 7-*methylenedioxy*-1-2′-*amino*-5′-*methoxybenzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline *dihydrochloride* (65—74%), m.p. 268°. By diazotisation, heating, and then treating with Zn dust in hot HCl this gives *dl-ON*-dimethylanalobine, an oil [*hydrochloride*, m.p. 266° (decomp.); *picrate*, m.p. 226°], the *methiodide*, m.p. 241°, of which in hot alkali yields *ON*-dimethylanalobinemethine, m.p. 100° (*picrate*, m.p. 258°) (cf. Manske, A., 1938, II, 298). R. S. C.

Alkaloid $C_{17}H_{13-15}$(OH)(OMe)N, m.p. 238°, $[\alpha]_D^{24}$ −77·47° in $CHCl_3$ (benzoate, m.p. 124—125°), and alkaloid $C_{17}H_{13}(OMe)_4N$,0·5H_2O, m.p. 152·5—153°, $[\alpha]_D^{24}$ −214·22° in EtOH, −187·93° in $CHCl_3$ [picrate, m.p. 242—245°; styphnate, m.p. 247—249°; methiodide, m.p. 273—274° (decomp.)], from *Argemone hispida*.—See A., 1944, III, 707.

VIII.—ORGANO-METALLIC COMPOUNDS.

Aromatic mercury salts.—See B., 1944, III, 169.

Zinc alkyls from *sec.*-alkyl halides. H. Soroos and M. Morgana (*J. Amer. Chem. Soc.*, 1944, **66**, 893—894).—Adding 1 : 1 $Pr^{\beta}Br$–$Pr^{\beta}I$ to Zn–Cu initially at 50° and later maintained at 20° gives an oil, (?) $ZnPr^{\beta}Hal$, which at 90—200°/1 mm. (liquid N_2 trap) gives 85% of $ZnPr^{\beta}_2$, for which $\log P = 7{\cdot}987 - 1858/(t + 230)$. A similar reaction, initiated at 60° and continued at 25°, gives 72% of *Zn di-sec.-butyl*, b.p. 56°/4 mm. The products inflame in air and decompose slowly in diffused light with deposition of Zn. R. S. C.

IX.—PROTEINS.

Electrophoretic evidence for complex formation in casein.—See A., 1944, III, 763.

Optical constants of zinc insulin crystals. G. L. Keenan (*J. Amer. Pharm. Assoc.*, 1944, **33**, 183—184).—Published data are reviewed. Standard reference samples of cryst. insulin showed a crystal habit of a cube or rhombohedron with twinning. Birefringence was positive and vals. of n were n_ϵ 1·562 and n_ω 1·550 (both ±0·002). F. O. H.

Aromatic sulphonic acids as reagents for peptides. Partial hydrolysis of silk fibroin. W. H. Stein, S. Moore, and M. Bergmann (*J. Biol. Chem.*, 1944, **154**, 191—201).—By determining the approx. solubilities of a no. of aromatic sulphonates of various peptides it was shown that these salts could be used to ppt. peptides selectively. The acid hydrolysis of silk fibroin was followed by the Van Slyke HNO_2 and the ninhydrin methods, and after 40 hr. contained ~75% of dipeptides. From this mixture glycyl-*l*-alanine was pptd. as the 2 : 5-dibromobenzenesulphonate, and then *l*-alanylglycine as the 2 : 6-di-iodophenol-4-sulphonate. J. F. M.

Protein–formaldehyde reaction. I. Collagen. E. R. Theis. **II. Wool.** E. R. Theis and M. M. Lams (*J. Biol. Chem.*, 1944, **154**, 87—97, 99—103).—I. Collagen (**I**) and CH_2O were allowed to react in 0·1N-KCl, for 72 hr. at 20°, the pH being adjusted by addition of either HCl or NaOH. The mixture was then analysed for N content, for bound acid or base, and for fixed CH_2O. The results show that fixation of CH_2O with (**I**) in no way affects the acid-binding capacity of (**I**) but does affect the base-binding capacity. No shift in the isoionic point could be shown to be due to CH_2O fixation. Correlation between data for shrinkage temp. and CH_2O fixation is shown.

II. Purified wool keratin (**II**) was treated as in Part I (KOH in place of NaOH) with and without CH_2O. The acid- and base-binding capacity curve without CH_2O is similar to the titration curves obtained by other workers. The acid- and base-binding capacity of CH_2O-treated (**II**) shows no change in the acid zone or at the zero combination point. The CH_2O fixation by (**II**) is given and is somewhat similar to that obtained for (**I**). An interpretation of the data is given. F. R. S.

Action of 1 : 2-epoxides on proteins. H. Fraenkel-Conrat (*J. Biol. Chem.*, 1944, **154**, 227—238).—Epoxides, such as $(CH_2)_2O$, propylene oxide, and epichlorohydrin, are suitable reagents for the esterification of protein CO_2H groups in aq. solution at room temp. Through treatment of cryst. egg-albumin and β-lactoglobulin with these compounds, preps. of modified protein have been obtained, which differ from the original material in that their isoelectric points are shifted as much as 3 pH units towards the alkaline side and they contain considerably fewer CO_2H, phenolic, NH_2, and SH groups than the untreated proteins. The only property of the proteins not appreciably affected by the treatment is the no. of their total basic groups. F. R. S.

Chemical nature of blood-proteins. I—III.—See A., 1944, III, 716.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Esters of lignin derivatives. J. C. Clark and F. E. Brauns (*Paper Trade J.*, 1944, **119**, *TAPPI Sect.*, 53—56).—Treatment with the acyl chloride in C_5H_5N at room temp. or 70—85° gives the *benzoates* and *p-toluenesulphonates* of alkali spruce lignin *A* (**I**), PhOH spruce lignin *A* (**II**), and PhOH Willstätter spruce lignin (**III**). The *undecoate* of (**I**) and *propionate*, *butyrate*, *valerate*, and 3 : 5-*dinitrobenzoate* of (**III**) are similarly prepared. Ac_2O–C_5H_5N gives the acetates. PhNCO in dioxan at the b.p. gives *phenylurethanes*. Analyses indicate introduction of 4—5 aliphatic but 4 aromatic (except 5 Bz) acyl groups into (**I**), 7—8 groups into (**II**), and 5—6 groups into (**III**). An additional OH group may be formed from (**I**) by fission of an O-ring by alkali. R. S. C.

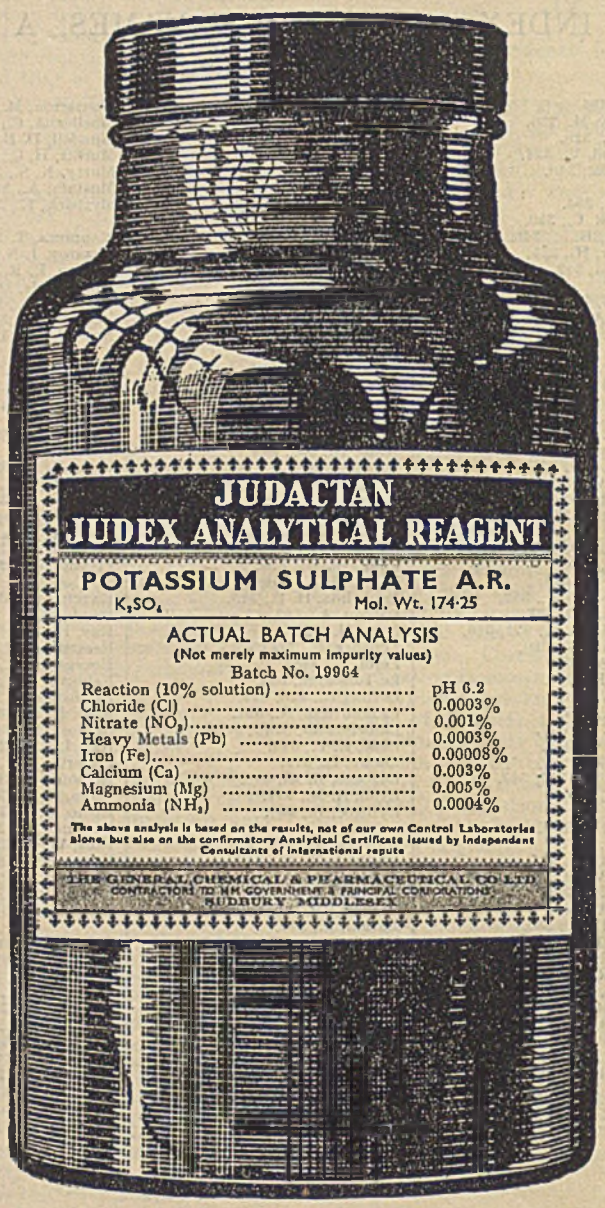
INDEX OF AUTHORS' NAMES, A II.

NOVEMBER, 1944.

JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL BATCH ANALYSIS



Each Batch subjected to INDEPENDENT ANALYSIS before label is printed

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