BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

APRIL, 1944

A II—ORGANIC CHEMISTRY

CONTENTS

Published by the

BUREAU OF CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

(Supported by the Chemical Society, the Society of Chemical Industry, the Physiological Society, the Biochemical Society, the Anatomical Society of Great Britain and Ireland, and the Society for Experimental Biology.)

Offices of the Bureau: 56 VICTORIA STREET, LONDON, S.W.1 *Telephone:* VICTORIA 5215

BUREAU OF CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

PUBLICATIONS OF THE BUREAU

ABSTRACTS SECTIONS

A I—GENERAL, PHYSICAL AND INORGANIC CHEMISTRY.
A II—ORGANIC CHEMISTRY.
A III—PHYSIOLOGY. BIOCHEMISTRY. ANATOMY.
B I—CHEMICAL ENGINEERING AND INDUSTRIAL INORGANIC CHEMISTRY.
B II—INDUSTRIAL ORGANIC CHEMISTRY.
B III—AGRICULTURE, FOODS, SANITATION, ETC.
C—ANALYSIS AND APPARATUS.

COLLECTIVE INDEXES

DECENNIAL INDEX 1923—1932. QUINQUENNIAL INDEX 1933—1937.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A II—Organic Chemistry.

APRIL, 1944.

I.—ALIPHATIC.

Modern methods of preparative organic chemistry. XI. Oxidations with selenium dioxide. G. Stein. **XIII. Hydrogenation with Raney catalysts.** R. Schröter. **XIV. Boron fluoride as catalyst of chemical reactions.** D. Kästner (*Angew. Chem.*, 1941, **54**, 146—152; 229—234, 252—260; 273—281, 296—304).—Reviews.

Reaction of hydrogen atoms with propylene. B. S. Rabinovitch, S. G. Davis, and C. A. Winkler (*Canad. J. Res.*, 1943, **21**, **B**, 251—257).—The principal products of the reaction between H atoms and C_3H_6, studied by the Wood–Bonhoeffer method over the temp. range 30—250°, are C_3H_8, C_2H_6, and CH_4. No unsaturated products appear to be formed. The nature and proportions of the products are independent of temp. A mechanism is suggested based on the formation of an active Pr radical as the primary step. H. W.

Action of anisole with *aaa*-trichloro-β-methyl-Δ$^{\beta}$-propene. C. C. Price and H. D. Marshall (*J. Org. Chem.*, 1943, **8**, 532—535).—$CCl_3{\cdot}CMe{:}CH_2$ (I) is very resistant to attack by Br in CCl_4 or aq. $KMnO_4$ and does not dissolve in conc. H_2SO_4. Addition of HCl or HBr is not practicable because of the ease with which it undergoes the allylic rearrangement. In presence of HF as catalyst, (I) and *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2$ smoothly yield *aa-dichloro-γ-*p*-anisyl-β-methyl-*Δ$^{\alpha}$*-propene* (II), b.p. 124—126°/4 mm., oxidised by CrO_3 to *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$. $CH_2Cl{\cdot}CMe{:}CCl_2$, formed by allylic rearrangement of (I) under the influence of HF, gives very little (II) when treated with *p*-$OMe{\cdot}C_6H_4{\cdot}NH_2$ and HF under the same conditions. The formation of (II) from (I) may therefore be interpreted as a direct addition of the base to the double linking in (I) in opposition to Markovnikov's rule; the additive product then gives (II) by loss of HCl. It is, however, possible that the dissociation of (I) gives a resonating ion common to both the allylic rearrangement and the Friedel–Crafts reaction. H. W.

Reactions of monovinylacetylene with chlorine and bromine. K. Rengert and H. J. Schumacher (*Ber.*, 1940, **73**, [*B*], 1025—1042).—$CH_2{:}CH{\cdot}C{:}CH$ (I) and Br, when illuminated at 60—150°/100 mm., give a liquid mixture, $C_4H_4Br_4$, b.p. 172—180°/20 mm., the low v.p. of which prevents investigation of the kinetics; the thermal reaction also interferes. Thermal interaction of Cl_2 with (I) is a chain reaction up to 650 mm., leading to a mixture, $C_4H_4Cl_4$, b.p. 90—110°/25 mm., or, if an excess of (I) is used, mainly to a product (II), $C_4H_4Cl_2$, b.p. 35°/40 mm. Investigation of the kinetics is complicated by the stepwise reaction, rearrangement of (II), polymerisation, and addition of Cl_2 to the polymers. H_2 and O_2, if introduced, take part in the reaction. R. S. C.

[Laboratory] preparation of nitroethane. H. McCombie, B. C. Saunders, and F. Wild (*J.C.S.*, 1944, 24—25).—Et_2SO_4 (100 g.) is shaken for 20 hr. with $NaNO_2$ (100 or 150 g.) in H_2O (125 or 187 g.). The best yield is 46% (65% on Et_2SO_4 not recovered), based on $Et_2SO_4 \rightarrow NaEtSO_4$. More $EtNO_2$ is obtained by distilling solid $NaEtSO_4$, $NaNO_2$, Na_2CO_3, and a little H_2O above 100°. S. A. M.

Reduction of nitroparaffins in liquid ammonia. G. W. Watt and C. M. Knowles (*J. Org. Chem.*, 1943, **8**, 540—543).—$EtNO_2$, Pr$^{\alpha}NO_2$, Pr$^{\beta}NO_2$, Bu$^{\alpha}NO_2$, and Bu$^{\beta}NO_2$ dissolve in and react with liquid NH_3 at −33·5° to form relatively unstable NH_4 salts of the type $CHR{:}N(\rightarrow O){\cdot}ONH_4^+$. All are colourless, cryst. solids which decompose slowly with liberation of NH_3. Qualitatively the decreasing order of stability of the corresponding NH_4 salts is Pr$^{\beta}NO_2$ > Bu$^{\beta}NO_2$ > Pr$^{\alpha}NO_2$ > Bu$^{\alpha}NO_2$ > $EtNO_2$. When Na is added to liquid NH_3 containing a nitroparaffin with an excess of NH_4Br the quantity of H_2 liberated is almost exactly equiv. to that of the Na taken. Removal of the solvent and decomp. of the NH_4 salts results in recovery of the nitroparaffins. Addition of Na to solutions of these nitroparaffins in liquid NH_3 results in the liberation of H_2, the formation of white ppts. (probably of Na salts), and, after addition of NH_4Br, the isolation of the corresponding alkylhydroxylamines, solutions of which readily reduce Ag_2O–NH_3 at room temp. The yields are low owing to slow and incomplete reduction and to the difficulties in separating small quantities of these products from relatively large quantities of inorg. salts. The following must be prepared under anhyd. conditions: p-*nitrobenzaldoxime Et*, m.p. 122—123°, *Pr*$^{\alpha}$, m.p. 77—78°, and *Bu*$^{\beta}$, m.p. 80—81°, *ether*. iso-*Propylhydroxylamine hydrochloride* and n-*butylhydroxylamine platinichloride* are described. M.p. are corr. H. W.

Polymerisation of vinyl ethers. I. Vinyl *n*-butyl ether. M. F. Schostakovski and I. F. Bogdanov (*J. Appl. Chem. Russ.*, 1942, **15**, 249—259).—$OBu^{\alpha}{\cdot}CH{:}CH_2$ (I) prepared (not quite pure) from Bu$^{\alpha}$OH and C_2H_2, b.p. 92—93°, is polymerised by $SnCl_4$ or $FeCl_3$ to an oil (n and η of 1% solutions in C_6H_6 given). The heat of polymerisation is 11·6—14·4 kg.-cal. per 100 g.; to prevent overheating the mixture of monomer and catalyst is either cooled (to keep the temp. at 40—60°) or diluted with polymer. Some η vals. are given for (I)–Bu$^{\alpha}$OH mixtures. J. J. B.

Rôle of neighbouring groups in replacement reactions. VII. Methoxyl group. S. Winstein and R. B. Henderson (*J. Amer. Chem. Soc.*, 1943, **65**, 2196—2200; cf. A., 1943, II, 228).—Owing to interaction of neighbouring groups, reaction of CHMeBr·CHMe·OMe or *trans*-1-bromo-2-methoxy*cyclo*hexane (I) occurs substantially without inversion. threo-, b.p. 55·6—55·7°/40 mm., and erythro-*β-Bromo-γ-methoxy-*n*-butane*, b.p. 55·7—56·2°/40 mm., are obtained by *trans*-addition to $(CHMe{:})_2$ by NHBrAc + H_2SO_4 (trace) in MeOH at < 0°. The following are prepared by known methods: threo-, b.p. 126·4—126·5°/752 mm. (*α-naphthylurethane*, m.p. 84—85°; *acetate*, b.p. 154·8—155·4°/750 mm.), and erythro-*γ-methoxy-*n*-butan-β-ol*, b.p. 132·3—132·5°/748 mm. (*α-naphthylurethane*, m.p. 111—112°; *acetate*, b.p. 153·4—154·0°/749 mm.); *trans*-2-methoxy*cyclo*hexanol (from the oxide by H_2SO_4–MeOH), b.p. 72·5—73·2°/100 mm. (3:5-*dinitrobenzoate*, m.p. 101—102°; *acetate*, b.p. 87·5—88·0°/10 mm.). (I) could not be resolved by brucine. R. S. C.

Fructose-1:6-diphosphoric acid and fructose-6-monophosphoric acid. C. Neuberg, H. Lustig, and M. A. Rothenburg (*Arch. Biochem.*, 1943, **3**, 33—44).—Ba H_2 *d*-fructose-1:6-diphosphate (I) was prepared from the strychnine H salt by treatment with $Ba(OH)_2{,}H_2O$ in MeOH, $[\alpha]_D^{17}$ +4·04° to +4·15° (free acid), reducing power (K salt) 0·48 times that of *d*-fructose, and resistant to Br–H_2O. The Ba H salt was prepared by treating (I) with HBr at 3° and pptn. with EtOH. Partial hydrolysis of fructose-1:6-diphosphates (Ca salt with HCl, Ba salt with HBr) at 35° gave 50% yield of Ba *d*-fructose-6-phosphate, $[\alpha]_D^{19}$ +3·58° (Ba salt), reducing power (K salt) 0·82 times that of *d*-fructose, and resistant to Br–H_2O. E. R. S.

Invert soaps. II. Dimethyl-butyl-, octyl-, -dodecyl-, and -hexadecyl-sulphonium iodides. R. Kuhn and O. Dann (*Ber.*, 1940, **73**, [*B*], 1092—1094; cf. A., 1944, II, 115).—RSMe and MeI–N_2 at ~20° give dimethyl-butyl-, *-octyl-*, *-dodecyl-*, and *-hexadecyl-sulphonium iodide*, all cryst. but very hygroscopic. RHal and NaSMe in EtOH at room temp. to −10° (exothermic) and then the b.p. give Me octyl, b.p. 100·5—102·5°/17—18 mm., *dodecyl*, b.p. 163—165°/19 mm., and *hexadecyl sulphide*, m.p. 19·5—20·5°. SMe_2RI is surface-active if R = $C_{\geq 8}$; SMe_2RI are effective against *B. coli* and staphylococci, respectively, at the following concns.: R = Me, Bu, or octyl >2%, $C_{12}H_{25}$ 0·1, 0·2%, and $C_{16}H_{33}$ 0·5, 0·02%; for $C_{12}H_{25}{\cdot}SMeCl{\cdot}CH_2Ph$ the concns. are 0·1 and 0·067, for $C_{12}H_{25}{\cdot}NMe_2Br{\cdot}CH_2Ph$ 0·0167 and 0·02%, respectively. R. S. C.

Methanetri-β-propionic acid.—See A., 1944, III, 33.

Reaction of sodium triphenylmethyl with esters of αβ-unsaturated acids.—See A., 1944, II, 99.

Glycidyl esters of aliphatic acids. E. B. Kester, C. J. Gaiser, and M. E. Lazar (*J. Org. Chem.*, 1943, **8**, 550—556).—*Glycidyl laurate*, b.p. 126°/1 mm., 290° (decomp.)/760 mm., m.p. 21°, *myristate*, b.p. 146°/1 mm., 310° (decomp.)/760 mm., m.p. 33·5—34·5°, *palmitate* (I), b.p. 170°/1 mm., m.p. 44·5—45·0°, *stearate*, b.p. 193°/1 mm., m.p. 50·5—51·3°, and *oleate*, b.p. 185°/1 mm., m.p. −1°, and *β-methylglycidyl myristate*, b.p. 130°/1 mm., m.p. 21·5°, are obtained by boiling the requisite Na salt with epichlorohydrin (II) (or β-methylepichlorohydrin) in excess. The best results are obtained under atm. pressure and strictly anhyd. conditions. The use of increased pressures shortens the time of reaction considerably but the increased temp. favours the formation of quantities of material of high b.p. With imperfectly dried reactants at atm. pressure

50—60% of materials polymerised or of high b.p. are produced. An excess of (II) is preferable to PhMe or light petroleum to produce fluidity of the soap suspension. (II) does not react satisfactorily with Na_2 sebacate and *glycidyl sebacate*, m.p. 44°, is best obtained from glycidol and sebacyl chloride in PhMe containing NEt_3 as acceptor for HCl in place of C_5H_5N, thus enabling NEt_3,HCl to be almost quantitatively filtered off. (I) is obtained similarly The soaps are best obtained by neutralising the fatty acid in $COMe_2$ with 5N-NaOH. Glycidyl esters of the mixed acids of babassu, soya-bean, walnut, and castor oils and rosin have been prepared. H. W.

Synthesis of *d*(−)-β-phosphoglyceric acid and *d*(+)-α-phosphoglyceric acid. C. Neuberg (*Arch. Biochem.*, 1943, **3**, 105—112).—*d*(−)-Glyceric acid was phosphorylated by $EtPO_3$, and the insol. Ba H *d*(−)-β-phosphoglycerate obtained in 70% yield; Ag *d*(+)-α-phosphoglycerate was obtained also in 7% yield. The synthetic and natural products are identical. E. R. S.

Quantitative effect of *X*-rays on ascorbic acid in simple solution and in mixtures of naturally occurring compounds.—See A., 1944, III, 284.

Mechanism of ketol formation from pyruvate and aldehydes. R. L. Berg and W. W. Westerfeld (*J. Biol. Chem.*, 1944, **152**, 113—117).—Oxidation of $(CHMe{\cdot}OH)_2$, CHMeAc·OH, and Ac_2 by KIO_4 leads to rupture of the linking between the substituted C atoms and conversion of the substituent OH groups into CHO while the CO groups are transformed into CO_2H. Oxidation of the 4-C ketol produced in the enzymic reaction between pyruvate (I) and EtCHO gives AcOH and EtCHO, thereby identifying the ketol as CHEtAc·OH. Association of CO of the ketol with the 2-C portion of the structure derived from (I) makes doubtful the possibility of intermediate compound formation between EtCHO and (I) prior to the decarboxylation of the latter. H. W.

Reaction of ethylenediamine with Zeise's salts. A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 243—246; cf. A., 1940, I, 267).—$(CH_2{\cdot}NH_2)_2$ (I) and aq. Zeise's salt $[K(PtC_2H_4Cl_3)]$ afford a complex, *Pt ethylene ethylenediamine dichloride*, $(C_2H_4{\cdot}PtCl_2{\cdot}NH_2{\cdot}CH_2)_2$ (II); no cycle is formed, but (I) unites two central atoms as a bridge. Evaporation of the mother-liquor from (II) at 100° (bath) gives C_2H_4 and $(CH_2{\cdot}NH_2)_2PtCl_2$. (I) and the butadiene salt, $K_2[(PtCl_3)_2C_4H_6]$, afford the very long-chain complex, *Pt butadiene ethylenediamine dichloride* (III); the bridges between two central atoms are formed by butadiene on the one hand and (I) on the other. (II) and (III) are decomposed by boiling H_2O. The probable reason why (I) does not follow Tschugaev's rule when there is a C_2H_4 mol. in the inner sphere is the instantaneous formation of an insol. ppt. $[(PtCl_2{\cdot}C_2H_4)_2(CH_2{\cdot}NH_2)_2]$, when an attempt is made to introduce (I). A. T. P.

Synthesis of amino-acids from substituted cyanoacetic esters. P. E. Gagnon, R. Gaudry, and F. E. King (*J.C.S.*, 1944, 13—15).—Alkylcyanoacetic esters are converted into hydrazides, to which the Curtius reaction is applied (cf. Darapsky, A., 1936, 1494). $CN{\cdot}CHPr^{\beta}{\cdot}CO_2Et$ gives a syrupy hydrazide, which gives 60% yield of valine (PhNCO gives α-N-*phenylcarbamido*isovaleric *acid*, m.p. 149°). $CN{\cdot}CH_2{\cdot}CO_2Et$ (I) and CH_2PhBr give 44% yield of $CH_2Ph{\cdot}CH(CN){\cdot}CO_2Et$, b.p. 165—173°/15 mm. [*hydrazide* (II), m.p. 123—124°], and 23% yield of *Et* α-*cyano*-ββ-*dibenzylacetate*, b.p. 190—200°/15 mm. (*hydrazide*, m.p. 235—237°); (II) gives 50% yield of phenylalanine (*phenylcarbamyl derivative*, m.p. 168—170°). (I) and anisyl chloride give 48% yield of *Et* α-*cyano*-β-*anisylpropionate*, b.p. 165—170°/0·2 mm.; the *hydrazide*, m.p. 122—123°, gives 30% yield of *O*-methyltyrosine, but if conc. HCl–AcOH is used in place of the usual 20% HCl for the final hydrolysis of the urethane, tyrosine is obtained (yield 11%). (I) and $OPh{\cdot}[CH_2]_3{\cdot}Br$ give *Et* α-*cyano*-δ-*phenoxyvalerate* (40% yield), b.p. 175—190°/0·7 mm.; the *hydrazide*, m.p. 85°, gives a 40% yield of α-*amino*-δ-*phenoxyvaleric acid*, m.p. 265—267° (decomp.), with which PhNCO forms a *phenylureide*, m.p. 158°. (I) and $Br{\cdot}[CH_2]_3{\cdot}CO_2Et$ give 40% yield of *Et*$_2$ α-*cyanoadipate*, b.p. 178—186°/15 mm.; the *dihydrazide*, m.p. 128°, cannot be converted into the desired ornithine. Similarly (I) and $Br{\cdot}[CH_2]_4{\cdot}CO_2Et$ give 30% yield of *Et*$_2$ α-*cyanopimelate*, b.p. 183—197°/12 mm., the *dihydrazide*, m.p. 115—116°, from which cannot be converted into lysine. S. A. M.

Raman spectrum of glycine.—See A., 1944, I, 78.

New mode of formation of β-alanine. C. Enders [with Zellweger] (*Naturwiss.*, 1943, **31**, 209).—A substance promoting the growth of yeast and considered to the β-alanine is obtained when AcCHO is heated with 40% NH_3 at 100°. It is also formed in neutral or slightly acid solution from AcCHO and glycine. The mechanism of the change is discussed. H. W.

Complex compounds of diguanide with bivalent metals. VII.—See A., 1944, I, 89.

Optical antipodes of pantothenic acid. R. Kuhn and T. Wieland (*Ber.*, 1940, **73**, [*B*], 1134).—Resolution of *dl*-pantothenic acid by quinine in $COMe_2$–EtOH or COMeEt gives *d*- and *l*-acids, $[\alpha]_D^{20}$ ±27° in H_2O. The *d*-acid has 45—50 × 10^6 SbmE units of activity per g.; the *l*-acid is inactive (cf. A., 1942, II, 297; 1944, II, 36). R. S. C.

Analogues of pantothenic acid. III. Preparation of growth-inhibiting analogues related to *N*-pantoyltaurine (Miss) J. Barnett (*J.C.S.*, 1944, 5—8; cf. A., 1942, II, 250; III, 621).—$NH_2{\cdot}[CH_2]_2{\cdot}SH$ [from $(CH_2)_2NH$ and H_2S](2 : 4-*dinitrobenzoylthioether*, m.p. 93·5—94·5°) and pantolactone (α-hydroxy-ββ-dimethylbutyrolactone) (I) in a sealed tube in vac. (100°, 1 hr.) give N-*pantoyl*-β-*aminoethylthiol* (II), a yellow oil (86% pure), highly toxic to rats. $(NH_2{\cdot}[CH_2]_2)_2S_2$ and (I) in abs. MeOH (reflux, 1 hr.) give *bis*-(N-*pantoyl*-β-*aminoethyl*) *disulphide* (III), m.p. 141—144°. $(NH_2{\cdot}[CH_2]_2)_2S$ (IV) and (I) in abs. MeOH (cold, 12 hr.; reflux, 1 hr.) give *bis*-(N-*pantoyl*-β-*aminoethyl*) *sulphide* (V), a viscous oil. (IV) and Br–H_2O give *bis*-β-*aminoethyl sulphoxide dihydrobromide*, m.p. 201—202° (quant. yield, ~100% pure); this with NaOEt gives the *sulphoxide* (VI), a syrup [*dihydrochloride* (VII), m.p. 220°; 97% pure]. (VI) and (I) in abs. MeOH (20°, 3 days) give *bis*-(N-*pantoyl*-β-*aminoethyl*) *sulphoxide* (VIII), a syrup (~92% pure); after 3 months in a sealed tube. $COMe_2$ extracts a compound, m.p. 143—144°, identical with (III). (IV) or (VII) and $KMnO_4$ in 50% AcOH give 50% yield of *bis*-β-*aminoethyl sulphone dihydrochloride*, m.p. 226—228°; the sulphone and (I) in abs. MeOH (reflux, 1 hr.) give *bis*-(N-*pantoyl*-β-*aminoethyl*) *sulphone* (IX), a syrup. (II) and (III) inhibit the growth *in vitro* of *Lactobacillus arabinosus* to approx. the same degree as pantoyltaurine, (V), (VIII), and (IX) to a smaller degree; rats are more susceptible to *Streptococcus hæmolyticus* in presence of any of these substances than in their absence. S. A. M.

Dimethanesulphonimide, a strong acid. B. Helferich and H. Grünert (*Ber.*, 1940, **73**, [*B*], 1131—1133).—$NH(SO_2Me)_2$ is best (~90%) obtained by adding 5N-NaOH (4) and $MeSO_2Cl$ (2 mols.) to conc., aq. NH_4Cl (1 mol.) at 0°. It is a strong acid (cf. A., 1942, II, 297); 0·1, 0·01, and 0·001N. solutions have pH 1·27, 2·20, and 3·25, respectively. With $CHMeN_2$ it gives *dimethanesulphonethylimide* (100%), m.p. 94—95° (corr.), also obtained (47%) from NH_2Et,HCl (1 mol.), $MeSO_2Cl$ (2·6), and NaOH (4·7 mols.) at 0—5°. NH_2R,HCl (I), $MeSO_2Cl$ (1 mol.), and NaOH (2—2·21 mols.) at 2—5° give *methanesulphon-ethylamide*, b.p. 105·5—107° (corr.)/0·3 mm., and -*methylamide* (~60%), b.p. 118°/0·3 mm. [with some *dimethanesulphonmethylimide*, m.p. 115·5—116·5° (corr.)]. R. S. C.

Trimethylacetic acid. Isolation and degradation of pivalazide. A. Bühler and H. E. Fierz-David (*Helv. Chim. Acta*, 1943, **26**, 2123—2136).—The behaviour of *pivalazide* (I) contradicts the theory that an enolisable CO or a vicinal C:C linking is essential for the Curtius transformation of azides. Survey of the literature leads to the conclusion that at present there is no experimentally established theory of the isomerisation incident to the Hofmann and Curtius degradations. Freshly sublimed pivaloylhydrazine, m.p. 56—57°, in 2N-HCl at −5° to −3° is converted by $NaNO_2$ into (I), a mobile, odourless liquid, m.p. 0°, which can (generally) be distilled unchanged in a high vac.; it is less advantageously prepared from $Bu^{\gamma}COCl$ and NaN_3. It passes quantitatively at 100° into N_2 and $Bu^{\gamma}NCO$, b.p. 84·6° (corr.), a colourless liquid with a pleasant odour, which does not solidify at −30° and could not be polymerised by prolonged irradiation. The following are described: NN′-*di*tert.-*butyl*-, m.p. 242°, N-*phenyl*-N′-tert.-*butyl*-, m.p. 153° (corr.), and *N*-*tert*.-butyl-*carbamide*, m.p. 242°; $NHBu^{\gamma}{\cdot}CO_2Me$, b.p. 56°/11 mm., $NHBu^{\gamma}{\cdot}CO_2Et$, b.p. 74°/11 mm., m.p. 30—21°, NH_2Bu^{γ}, b.p. 44° (hydrochloride, m.p. 273—275°). H. W.

Modern methods of preparative organic chemistry. X. Syntheses with diazomethane. B. Eistert (*Angew. Chem.*, 1941, **54**, 99—105, 124—131).—A review.

II.—SUGARS AND GLUCOSIDES.

Methanesulphonates of the sugar group. III. B. Helferich and H. Jochinke (*Ber.*, 1940, **73**, [*B*], 1049—1052; cf. A., 1939, II, 468).—β-Di*iso*propylidenefructose and $MeSO_2Cl$ in C_5H_5N at 0° give 2 : 3-4 : 5-di*iso*propylidene-*d*-fructopyranose 1-methanesulphonate (85%), m.p. 125—126°, $[\alpha]_D^{21}$ −29·3° in $CHCl_3$, converted by H_2SO_4–MeOH–H_2O into syrupy fructose 1-methanesulphonate. Di*iso*propylidenesorbose gives similarly 2 : 3-4 : 6-*diisopropylidene*-l-*sorbofuranose* 1-*methanesulphonate* (~70%), m.p. 116—117°. α-Di*iso*propylidenefructose gives 1 : 2-4 : 5-*diisopropylidene*-d-*fructopyranose* 3-*methanesulphonate* (>90%), m.p. 104—105°, $[\alpha]_D^{22}$ −161·4° in $CHCl_3$, converted by boiling H_2SO_4–MeOH–H_2O into syrupy *d*-fructose 3-methanesulphonate or, by shorter treatment, into 1 : 2-iso*propylidene*-d-*fructopyranose* 3-*methanesulphonate* (I) (variable yield up to 70%), m.p. 133° (decomp.), $[\alpha]_D^{19}$ −138° in $COMe_2$. With $MeSO_2Cl$–C_5H_5N at 0°, (I) gives 1 : 2-iso*propylidene*-d-*fructopyranose* 3 : 4 : 5-*trimethanesulphonate*, m.p. 128—130°, $[\alpha]_D^{20}$ −115·5° in $CHCl_3$, or with Ac_2O–C_5H_5N at 37° gives 1 : 2-iso*propylidene*-d-*fructopyranose* 4 : 5-*diacetate* 3-*methanesulphonate* (>90%), m.p. 84—86°. Phenyl-β-*d*-fructopyranoside with $MeSO_2Cl$–C_5H_5N at 0° gives *phenyl*-β-d-*fructopyranose tetramethanesulphonate* (>85%), m.p. 197° (decomp.), $[\alpha]_D^{19}$ −135·3° in C_5H_5N, or at −19° gives, after

acetylation, impure *phenyl-β-*d-*fructopyranoside triacetate* 1-*methanesulphonate* (II), whence boiling NaOMe–MeOH gives *phenyl-β-fructopyranoside* 1-*methanesulphonate*, m.p. 120° (decomp.), $[\alpha]_D^{20}$ −172·2° in C_5H_5N, which by reacetylation gives pure (II), m.p. 127—128°, $[\alpha]_D^{19}$ −135·4° (does not react with NaI–$COMe_2$ at 125—130°). R. S. C.

Splitting of sucrose by ultrasound.—See A., 1944, I, 88.

Starch. XI. Highly methylated starch. Sugars obtained by fission. K. Hess, H. A. Schulze, and B. Krajnc. **XII. Comparison of end-group content, viscosity, and osmotic pressure of starch and its components.** K. Hess and E. Steurer (*Ber.*, 1940, **73**, [*B*], 1069—1076, 1076—1079).—XI. When methylated potato starch (40—41% OMe) is treated with Na, liquid NH_3, and MeI in PhOMe, the product contains usually ~44—45·5% of OMe; high OMe content is obtained only if not too much Na is used, an excess causing back-hydrolysis. MeI–Ag_2O similarly gives variable results up to 45·6% of OMe. Hydrolysis of a product containing 45·55% of OMe gives methyl-tetra- 3·99, -tri- 86·7, -di- 4·77, and -mono-methylglucoside 2·27%. It is concluded that methylation is still incomplete but may involve structural changes.

XII. Data on the end-group content, η, and osmotic pressure of starch (potato; maize) and amylo- and erythro-amylose are recorded. They are considered too inconsistent to serve as a basis for final generalisation. R. S. C.

Limit dextrins and starch. XII. Preparation and constitution of a difficultly hydrolysable disaccharide ("*iso*maltose") from starch. K. Ahlborg and K. Myrbäck (*Biochem. Z.*, 1941, **308**, 187—195; cf. A., 1944, II, 8; III, 67).—The prep. of *iso*maltose (I) from maize starch by hydrolysis with 0·2N-H_2SO_4 followed by removal of glucose and fractional pptn. with EtOH is described. Hydrolysis of a limit dextrin with takadiastase gives 20% yield of (I). The theoretical yield is calc. to be ~36%, whence it is concluded that the mol. of the limit dextrin with mol. wt. 700—1000 contains one (I) unit. The action of pancreatin on potato starch shows that it contains one (I) for every 15—20 maltose units. Since amylose is probably not branched, amylopectin must contain one (I) to every 10 maltose units. The structure of (I) is shown by methylation followed by hydrolysis, which yields 2 : 3 : 4-tri- and 2 : 3 : 4 : 6-tetra-methyl-glucose. J. N. A.

Phosphorylase of waxy maize.—See A., 1944, III, 289.

Amorphin, a glycoside in *Amorpha fruticosa*, L. F. Acree, jun., M. Jacobson, and H. L. Haller (*J. Org. Chem.*, 1943, **8**, 572—574).—The seeds of *A. fruticosa*, L., give the colour reaction in the Durham test which heretofore has been considered sp. for rotenone and the rotenoids, but no compounds of this class could be isolated from them. The product responsible for the positive reaction is *amorphigenin* (I), $C_{32}H_{22}O_7$, the aglycon of the glycoside, amorphin (II), $C_{33}H_{40}O_{16}$. (I) has m.p. 191—192°, does not reduce Fehling's solution before or after acid hydrolysis, and gives a negative phenol test. (II) has m.p. 151—151·5°, does not reduce Fehling's solution until after acid hydrolysis, and gives a positive Durham and orcinol test and a negative phenol test. A substance, m.p. 218°, which gives a positive Durham test has been isolated in quantity too small for extended examination. H. W.

III.—HOMOCYCLIC.

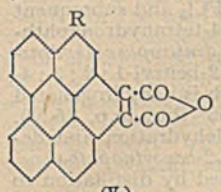
Action of ultra-violet light on liquid benzene. C. B. Allsopp and B. Szigeti (*J.S.C.I.*, 1944, **63**, 31—32).—When liquid C_6H_6 is irradiated in presence of air with ultra-violet light of λ 2537 A., small quantities of five different substances can be separated by chromotographic fractionation of the products. The absorption spectrum of one of them resembles those of the diphenylpolyenes, and another yields a bromophenylhydrazone. None of them has been definitely identified.

2 : 3 : 5-Trimethylnaphthalene in coal tar. O. Kruber (*Ber.*, 1940, **73**, [*B*], 1174—1175).—The first cryst. sulphonic acids obtained by partial sulphonation (with 92% H_2SO_4) of a neutral, heavy oil fraction, b.p. 286—289°, readily yield 2 : 3 : 5-*trimethylnaphthalene* (I), b.p. 285°/762 mm., m.p. 25·3° (picrate, m.p. 124°; styphnate, m.p. 148°), after purification through the K salts. The hydrocarbon from subsequent sulphonates requires purification through the picrate, which is successful only if much preliminary enrichment has been effected by sulphonation. Its constitution is established by its oxidation by CrO_3 in AcOH at 60° to 2 : 3 : 5-*trimethyl*-1 : 4-*naphthaquinone*, m.p. 128°, which is further oxidised by aq. $KMnO_4$ at 60—70° to 3 : 1 : 2-$C_6H_3Me(CO_2H)_2$, m.p. 154°, or to 2 : 3 : 1-$C_6H_3Me_2{\cdot}CO_2H$ if excess of $KMnO_4$ is used at 100°. H. W.

Syntheses in the naphthalene group. III. Syntheses of 2-benzyl-naphthalenes. W. Borsche, P. Hofmann, and H. Kuhn [and, in part, R. Manteuffel] (*Annalen*, 1943, **554**, 23—40; cf. A., 1937, II, 18, 257).—α-Phenacylcinnamic acid (I) is hydrogenated (Pd–C in EtOAc) to *α-phenacyl-β-phenylpropionic acid*, reduced (Zn–Hg and HCl in boiling MeOH) followed by hydrolysis to γ-phenyl-α-benzyl-*n*-butyric acid, b.p. 198°/1 mm., m.p. 54—55°, also obtained by hydrogenation (Pd–C in EtOAc) of (I) or of phenylbenzylcrotonolactone. This is converted by treatment with PCl_3 and subsequent distillation in vac. into 1-keto-2-benzyl-1 : 2 : 3 : 4-tetrahydronaphthalene (II), b.p. 176°/1 mm., m.p. 53—54° (2 : 4-*dinitrophenylhydrazone*, m.p. 53—54°), reduced (Clemmensen) to 2-benzyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 195°/13 mm., which is dehydrogenated by Se at 280—300° to 2-$C_{10}H_7{\cdot}CH_2Ph$, m.p. 58° (lit., m.p. 35·5°). (II) is transformed by MgPhBr followed by dehydration and dehydrogenation (Se) of the product into 1-*phenyl*-2-*benzylnaphthalene*, m.p. 87—88°. $(CH_2Ph)_2CH{\cdot}CH_2{\cdot}COCl$ is cyclised by distillation to 1-*keto*-3-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. ~170°/1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 220°), which is reduced and dehydrogenated to (III), m.p. 57—58°. 2-$C_{10}H_7{\cdot}COPh$ is reduced by N_2H_4,H_2O at 220—230° to 2-$C_{10}H_7{\cdot}CH_2Ph$, m.p. 58° (picrate, m.p. 93°). 1-$C_{10}H_7{\cdot}COPh$ is transformed similarly into 1-$C_{10}H_7{\cdot}CH_2Ph$, m.p. 57·5—58° (picrate, m.p. 103—104°). Na β-anisoylpropionate, PhCHO, and Ac_2O at 100° afford p-*anisylbenzylidenecrotonolactone*, m.p. 176—177°, converted by Na_2CO_3 in boiling aq. MeOH into α-p-*methoxyphenacylcinnamic acid*, m.p. 171°, which is hydrogenated to *α-p-methoxyphenacyl-β-phenylpropionic acid*, m.p. 132°; this is reduced (Clemmensen) to *α-benzyl-γ-p-anisyl*-n-*butyric acid*, b.p. ~200°/1 mm., m.p. 77°, which is cyclised to 1-*keto*-7-*methoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (III), b.p. 202—204°/1 mm., m.p. 120—121° (2 : 4-*dinitrophenylhydrazone*, m.p. 223°). Reduction (Clemmensen) followed by dehydrogenation (Se) of (III) leads to 7-*methoxy*-2-*benzylnaphthalene*, m.p. 75·5° (*picrate*, m.p. 92—93°). *γ-p-Anisylbutyric acid*, m.p. 53—55°, is smoothly obtained by hydrogenation (Pd–C in EtOAc) of γ-keto-γ-*p*-anisyl-*n*-butyric acid. *γ-Keto-γ-phenyl-γ-anisylidenebutyric acid*, m.p. 179°, is reduced catalytically and subsequently according to Clemmensen to *γ-phenyl-α-4-methoxybenzylbutyric acid*, m.p. 87°; this gives successively 1-*keto*-2-4′-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 65° (2 : 4-*dinitrophenylhydrazone*, m.p. 195°), and 2-4′-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 69°, but the subsequent dehydrogenation does not appear to proceed smoothly. Reduction of 2-anisoylnaphthalene by N_2H_4 affords 2-4′-*hydroxybenzylnaphthalene*, m.p. 98° (*picrate*, m.p. 125—126°). Na β-anisoylpropionate, *p*-OMe·C_6H_4·CHO, and Ac_2O at 100° afford p-*anisyl-anisylidene-crotonolactone*, m.p. 175—176°, converted by prolonged boiling with Na_2CO_3 in aq. MeOH into p-*methoxy-α-4-methoxyphenacylcinnamic acid*, m.p. 191°, which is reduced directly to γ-p-*anisyl-α-4-methoxybenzyl*-n-*butyric acid*, m.p. 112°; this is treated with PCl_3 and then cyclised to 1-*keto*-7-*methoxy*-2-4′-*methoxybenzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 233—236°/1 mm., m.p. 90·5° (2 : 4-dinitrophenylhydrazone, m.p. 200°), which is reduced (Clemmensen) and then dehydrogenated (Se at 280—300°) to 7-*methoxy*-2-4′-*methoxybenzylnaphthalene*, m.p. 121·5°. Na β-veratroylpropionate, PhCHO, and Ac_2O at 100° give 3 : 4-*dimethoxyphenylbenzylidenecrotonolactone* (IV), m.p. 139—140°, converted by Na_2CO_3 in boiling aq. MeOH into α-3 : 4-*dimethoxyphenacylcinnamic acid*, m.p. 212°, and by boiling NaOMe–MeOH with immediate acidification into *Me* α-3 : 4-*dimethoxyphenacylcinnamate*, m.p. 121—122°, which is transformed by N_2H_4,H_2O at 120—130° into 3-*keto*-6-3′ : 4′-*dimethoxyphenyl*-4-*benzyl*-2 : 3 : 4 : 5-*tetrahydropyridazine*, m.p. 173—174°. The ester is hydrogenated to *Me α-3 : 4-dimethoxyphenacyl-β-phenylpropionate*, m.p. 136—137° (corresponding *acid*, m.p. 140°), which is reduced (Clemmensen) to γ-3 : 4-*dimethoxyphenyl-α-benzylbutyric acid*, b.p. ~240°/1 mm., also obtained by catalytic hydrogenation of (IV) and converted into 1-*keto*-6 : 7-*dimethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 143° (2 : 4-*dinitrophenylhydrazone*, m.p. 227°). Gradual addition of NaOMe in MeOH to Me β-veratroylpropionate and PhCHO in MeOH at 30° leads to *β-veratroyl-β-benzylidenepropionic acid*, m.p. 124—126°; this is hydrogenated (Pd–C) in EtOAc) to the corresponding saturated acid, which is reduced (Clemmensen) to the non-cryst. γ-3 : 4-*dimethoxyphenyl-β-benzyl*-n-*butyric acid*, b.p. ~220°/1 mm. The corresponding non-cryst. 1-*keto*-6 : 7-*dimethoxy*-3-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (2 : 4-*dinitrophenylhydrazone*, m.p. 239°) is dehydrogenated to 6 : 7-*dimethoxy*-2-*benzylnaphthalene*, m.p. 105—106°, which does not give a colour with $FeCl_3$. H. W.

Perylene and its derivatives. LI. A. Zinke, U. Noculak, R. Skrabal, and H. Troger (*Ber.*, 1940, **73**, [*B*], 1187—1192).—Gradual addition of Br to a solution of perylene in boiling C_6H_6 gives a *tetrabromoperylene* (I), m.p. 310°, which gives a dark green colour in conc. H_2SO_4 and a more freely sol. (probably non-homogeneous) tetrabromoperylene (II), m.p. (indef.) 198—203°, which dissolves in warm conc. H_2SO_4 to a blue solution becoming violet and then dirty red when further heated. Under similar conditions 3 : 9-dibromoperylene gives (I) and a further tetrabromoperylene (III), m.p. 250—251°, whereas the 3 : 10-Br_2-compound gives a tetrabromoperylene (IV), m.p. 265°, softens at 254°. It is uncertain whether (II), (III), and (IV) are isomeric compounds or identical products in different stages of purity. Hot conc. H_2SO_4 transforms (I), (II), (III), and (IV) into quinones which are non-cryst. and sol. in alkali. (I) and conc. H_2SO_4 at 90° give a *product* with the approx. composition of a dibromoperylenequinone. Attempts to establish the position of Br in (I), (II), (III), and (IV) by use of $(CH{\cdot}CO)_2O$ are shown to be useless since no reaction occurs with

3 : 4 : 9 : 10-tetra-chloro- or -nitro-perylene although the 1 : 12-positions are free. Condensation with $(CH{\cdot}CO)_2O$ is not completely inhibited by the presence of substituents since 3 : 9-dichloroperylene gives a *compound* [(V), R = Cl] and 3 : 9-dibenzoylperylene affords a *substance* [(V), R = Bz]. Treatment of this with $AlCl_3$ at 170—180° gives varying results; it is decarboxylated by NaOH–CaO to 1 : 12-benzperylene, m.p. 272°, the Bz groups being removed. Decarboxylation of 4 : 5-*benz*-1 : 2-*diphenylaceperylene*-Bz1 : Bz2-*dicarboxylic anhydride* leads to a *hydrocarbon*, m.p. 279°, with the composition of the expected diphenylacebenzperylene but it is doubtful whether both Ph groups are still present. Condensation of tribenzoylperylene with $(CH{\cdot}CO)_2O$ in boiling $PhNO_2$ yields *tribenzoyl*-1 : 12-*benzperylene*-Bz1 : Bz2-*dicarboxylic anhydride*.



(V.)

H. W.

Invert soaps. III. Benzylmethyldialkylammonium chlorides. R. Kuhn, D. Jerchel, and O. Westphal (*Ber.*, 1940, **73**, [*B*], 1095—1100; cf. A., 1944, II, 90).—CH_2PhCl and $NMeR_2$ at 110—120° give *benzylmethyldi-butyl*-, m.p. 181°, *-hexyl*-, m.p. 58°, *-octyl*- (I), m.p. 68°, *-dodecyl*- (II) (prep. in EtOH at 120° and then 90°), m.p. 96°, and *-cetyl-ammonium chloride* (III) (prep. in EtOH at 100°), m.p. 99°. *Dimethyldi-hexyl*-: m.p. ~35°, and *-tetradecyl-ammonium methosulphate*, m.p. 129—130°, and *methylethyldidodecylammonium iodide*, m.p. 149°, and nitrate, m.p. 14°, are also prepared. Surface activity reaches a sharp max. at (II). For $CH_2Ph{\cdot}NMeR_2Cl$, efficiency against *Streptobacterium plantarum* is a max. with (II). Efficiency against staphylococci, *B. coli*, *E. typhi*, and Friedländer bacillus is a max. at (I); against paratyphoid-*B* bacteria, (II) is as effective as (I).

R. S. C.

Aniline homologues in coal tar. O. Kruber and L. Rappen (*Ber.*, 1940, **73**, [*B*], 1178—1184).—The most volatile fractions obtained in the separation of quinoline (I) are acetylated and the Ac derivatives are separated from one another by fractional crystallisation. The total primary bases constitute only 0·12% of crude (I). The presence of *o*-, *m*-, and *p*-toluidine, *m*-4-, *p*-, *m*-5- (II), and *o*-3-xylidine is established. The three toluidines are present in tar in about the same ratio as the three cresols. Among the xylidines as among the xylenols the *m*-compounds, particularly (II), predominate.

H. W.

Reactions of 3-nitro-1-naphthylamine, including anil formation, bromination, and the preparation of 1 : 2 : 3 : 4-tetrabromonaphthalene. H. H. Hodgson and D. E. Hathway (*J.C.S.*, 1944, 21—22).—3 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ (I) [*Bz*, m.p. 220°, p-*toluenesulphonyl*, m.p. 200°, *CHPh*:, m.p. 122°, o-, m.p. 194°, m-, m.p. 188°, and p-*nitrobenzylidene*, m.p. 242° (sinters at 235°), and p-*hydroxybenzylidene* derivative, m.p. 233°] and Zn–Ac_2O–NaOAc give 1 : 3-$C_{10}H_6(NHAc)_2$, m.p. 264°. (I)–$NaNO_2$–AcOH–H_2SO_4, followed by Cu_2O–EtOH, afford an almost quant. yield of 2-$C_{10}H_7{\cdot}NO_2$. Br (1 or 2 mols.)–$CHCl_3$ converts (I) into 2 : 4-*dibromo*-3-*nitro*-1-*naphthylamine*, m.p. 182° (*Ac* derivative, m.p. 202°). 3 : 2 : 4 : 1-$NO_2{\cdot}C_{10}H_4Br_2{\cdot}N_2HSO_4$ and Cu_2O–EtOH yield 1 : 3-*dibromo*-2-*nitronaphthalene*, m.p. 130·5°; CuBr–HBr (*d* 1·7) at <20° affords 1 : 3 : 4-*tribromo*-2-*nitronaphthalene*, m.p. 218° (reduced by aq. $Na_2S_2O_4$–EtOH to the corresponding *amine*, m.p. 163°), and CuCl–HCl (*d* 1·16) gives 4-*chloro*-1 : 3-*dibromo*-2-*nitronaphthalene*, m.p. 198° (*amine*, m.p. 161°). 1 : 2 : 3 : 4-*Tetrabromonaphthalene*, m.p. 196°, is obtained from 1 : 3 : 4 : 2-$C_{10}H_4Br_3{\cdot}N_2HSO_4$.

A. T. P.

Chromophoric naphthalene nucleus.—See A., 1944, I, 52.

"Carpasemine" isolated from *Carica papaya* seeds. T. B. Panse and A. S. Paranjpe (*Proc. Indian Acad. Sci.*, 1943, **18**, **A**, 140—144).—"Carpasemine" (I) (A., 1941, II, 381) is identified as benzylthiocarbamide, m.p. 165° (Ac derivative, m.p. 131°; *methiodide*, m.p. 103—105°). (I) is transformed by boiling 20% NaOH into NH_3, $CH_2Ph{\cdot}NH_2$ (hydrochloride, m.p. 245—246°), and $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$, m.p. 148—149° (*Ac* derivative, m.p. 130°), oxidised ($KMnO_4$) to an unidentified *compound*, m.p. 205—207°. A synthesis of (I) starting from $CH_2Ph{\cdot}CN$ is recorded.

H. W.

Complex compounds of diguanide with bi- and ter-valent metals. VI. Copper, nickel, and cobaltic phenyldiguanide-*p*-sulphonic acid. P. Rây and S. K. Siddhanta (*J. Indian Chem. Soc.*, 1943, **20**, 250—252; cf. A., 1942, II, 254).—Dicyanodiamide and boiling aq. *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ give *phenyldiguanide*-p-*sulphonic acid* (I), *p*-$^-SO_3{\cdot}C_6H_4{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}C(:NH){\cdot}NH_3^+$, m.p. 265—268° (decomp.), which behaves as an ampholyte. Aq. $CuSO_4,5H_2O$ (at 50—60°) or $NiCl_2,6H_2O$ (at 100°) added to (I) in an excess of aq. NH_3 affords the *Cu*$^{\cdot\cdot}$, $+H_2O$, or *Ni*$^{\cdot\cdot}$ complex, $+2H_2O$ (probably *trans*-forms). $CoCl_2,6H_2O$ and aëration yields the *Co*$^{\cdot\cdot\cdot}$ complex, $+5H_2O$.

A. T. P.

Derivatives of diphenylsulphonamides. I. Preparation of 2′-aminodiphenyl-4-sulphonamide. A. H. Popkin. **II. Derivatives of 2′-aminodiphenyl-4-sulphonamide.** A. H. Popkin and (Miss) G. M. Perretta (*J. Amer. Chem. Soc.*, 1943, **65**, 2043—2045, 2046—2048).—I. Adding *o*-$C_6H_4Ph{\cdot}NHAc$ (I) to $ClSO_3H$ at <10° and then heating at 60° gives 2′-*acetamidodiphenyl*-4-*sulphonyl chloride* (II), m.p. 149—150·5°, converted by hot, conc., aq. NH_3 into the *amide*, m.p. 201—202°, which with hot, conc., aq. HCl–MeOH gives 2′-*aminodiphenyl*-4-*sulphonamide* (III), m.p. 186—187°. *o*-$C_6H_4Ph{\cdot}NO_2$ and $ClSO_3H$ give, as above, 2′-*nitrodiphenyl*-4-*sulphonyl chloride* (IV), m.p. 78—80°, and thence the *amide*, m.p. 203—204°, which with Sn–conc. HCl–EtOH yields (III). 2′-*Aminodiphenyl*-4-*sulphonic acid*, decomp. >250°, is obtained from (II) by boiling 18% aq. HCl or from (I) by 96% H_2SO_4 at 120°; when it is diazotised in 10% H_2SO_4 at room temp. and then heated at 60° and the Na_2 salt resulting is fused with NaOH at 270—290°, *o*-$OH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}OH$-*p*, m.p. 161·5—162·5° [diacetate, m.p. 94·5—96·5° (lit. 94°)], is obtained, thus proving the structure.

II. (II) is unstable when kept. NH_2R and (II) or (IV) in C_5H_5N–$COMe_2$ at 50° and then room temp. give *o*-$NHAc{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR$-*p* or *o*-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NHR$-*p*, respectively, converted by HCl–MeOH or Sn–conc. HCl–MeOH respectively into *o*-$NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR$-*p*, which are inactive against *E. coli in vitro* and streptococci in mice. The following are described: 2′-*aminodiphenyl*-4-*sulphon-anilide*, m.p. 100—100·5° (*Ac* derivative, m.p. 163·5—164·5°), *-benzylamide*, m.p. 106·5—107° (*Ac* derivative, m.p. 161—162°), -o-, m.p. 165—165·5° (*Ac* derivative, m.p. 173·5—175°), and -p-*xenylamide*, m.p. 169—170° (*Ac* derivative, m.p. 196—196·5°); 2′-*nitrodiphenyl*-4-*sulphon-anilide*, m.p. 155·5—156·5°, *-benzylamide*, m.p. 128·5—130°, -o-, m.p. 161—162°, and -p-*xenylamide*, m.p. 164—165°; N^4-2″-*acetamido*-, m.p. 231·5—232·5°, N^4-2″-*amino*-, m.p. 197·2—198·2°, and N^4-2″-*nitro-diphenyl*-4′-*sulphonylsulphanilamide*, m.p. 239·5—240°; 2′-2‴-*acetamido*-, m.p. 148·5—150° (decomp.), 2′-2‴-*amino*-, m.p. 263—264°, and 2′-2‴-*nitro-diphenyl*-4″-*sulphonamidodiphenyl*-4-*sulphonamide*, m.p. 173—174°.

R. S. C.

Decomposition of the diazonium salts of 4-nitro-1-naphthylamine by sodium sulphite and sodium acetate. Preparation of 4 : 4′-dinitro-1 : 1′-azonaphthalene. H. H. Hodgson, D. E. Nicholson, and G. Turner [with, in part, J. Habeshaw] (*J.C.S.*, 1944, 15—17).—Rapid addition of aq. Na_2SO_3 to 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}N_2Cl$ (or $\cdot N_2HSO_4$) (I) + NaOAc (excess) at 0° yields 4 : 4′-*dinitro*-1 : 1′-*azonaphthalene* (II), m.p. 334°, and a trace of 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}OH$. Excess of NaOAc alone initiates an oxidation–reduction reaction with (I) and affords (II), 4 : 4′-dinitro-1 : 1′-dinaphthyl (III), m.p. 246°, and (by a simultaneous decomp. by H_2O or OH′) some 4 : 4′-*dinitronaphthalene*-1′ : 2-*azo*-1-*naphthol* (IV), m.p. 278° (also obtained from 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}N_2Cl$ and 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}OH$ in aq. $NaHCO_3$). (I) and aq. Na_2SO_3 at 0° afford numerous substances, including (II) (10—20%), (III), and 1-$C_{10}H_7{\cdot}NO_2$; no (IV) is formed. In the above reactions, 4 : 4′-*dinitronaphthalene*-1′ : 2-*azo*-1-*naphthylamine*, m.p. 274°, is not obtained, but is prepared from 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}N_2Cl$ and 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ in AcOH–NaOAc. Mechanisms of reactions are postulated, and colour reactions recorded. (II) gives a bright blue colour with H_2SO_4, suggesting that salt formation has produced a di-indamine-like structure.

A. T. P.

Replacement of the diazonium by the nitro-group. General method based on decomposition of the aryldiazonium cobaltinitrites. H. H. Hodgson and E. Marsden (*J.C.S.*, 1944, 22—24).—Aryldiazonium *cobaltinitrites* (I), $(ArN_2)_3Co(NO_2)_6$, are prepared by adding $Na_3Co(NO_2)_6$ to a solution of ArN_2Cl neutralised with $CaCO_3$. They decompose on heating, sometimes with explosive violence, and couple with alkaline β-$C_{10}H_7{\cdot}OH$. (I) (Ar = Ph, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}$, and *p*-$C_6H_4Cl{\cdot}$) with Cu_2O in conc. aq. $NaNO_2$ give $PhNO_2$ (75·5%), *o*- (67·4%), *m*- (72%), and *p*-$C_6H_4(NO_2)_2$ (75%), and *p*-$C_6H_4Cl{\cdot}NO_2$ (82·5%), respectively. Small amounts of 1- (20%) and 2-$C_{10}H_7{\cdot}NO_2$ (16·9%) are obtained similarly from (I) (Ar = 1- and 2-$C_{10}H_7$), but $CuSO_4$–Cu_2O–$NaNO_2$ gives 68 and 60%, respectively. Using the latter method, *o*- and *p*-toluidine and *o*- and *p*-anisidine also give >60% of the respective NO_2-compounds.

A. T. P.

Interpretation of the Sandmeyer reaction. IV. Catalysed decomposition of diazonium cations by anionoid complexes with special reference to those of cobalt and ferric iron. H. H. Hodgson, S. Birtwell, and J. Walker (*J.C.S.*, 1944, 18—19; cf. A., 1943, II, 28).—% Yields of *m*- and *p*-$C_6H_4Cl{\cdot}NO_2$ (I) obtained by decomp. of *m*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ with metallic salts in boiling HCl (*d* 1·16) are recorded in parentheses: HCl alone (47·3; 54·4), hydrated $AlCl_3$ (54·4; 60·7), $SbCl_3$ (31·6; 37·1), anhyd. $CaCl_2$ (47·3; 54·4) hydrated $CoCl_2$ (60·7; 70·9), CuCl, hydrated $CuCl_2$, or anhyd. $FeCl_3$ (67·5; 77·6), anhyd. $ZnCl_2$ (47·3; 54·4); the use of $CrCl_3$, $SnCl_4$, $NiCl_2$, and $HgCl_2$ is also examined in the case of (I). At the acid concn., $FeCl_3$ or $CuCl_2$ is as efficient as CuCl. $CoCl_2$ in the blue complex anionoid condition catalyses the reaction, whereas in the pink cationoid state it loses its catalytic influence. The results support the mechanism previously suggested (A., 1942, II, 52, 254).

A. T. P.

Decomposition of diazotised 1 : 6-dinitro-2-naphthylamine by precipitated copper in organic solvents. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1944, 10—11).—1 : 6 : 2-$(NO_2)_2C_{10}H_5{\cdot}N_2HSO_4$ is added to pptd. Cu in a solvent at 15° (cf. Cu_2O method; A., 1943, II, 158); if MeOH is used, no CH_2O is formed and a yield of 58% of 1 : 6-$C_{10}H_6(NO_2)_2$ results. Yields are recorded using other solvents, *e.g.*, EtOH (57·5), Pr$^\beta$OH (54·5), Bu$^\alpha$OH (36·5), COMeEt (44·5), and $Cl{\cdot}[CH_2]_2{\cdot}OH$ (36%) (cf. *loc. cit.*). 2 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$

is deaminated similarly to 2-$C_{10}H_7$·NO_2 in MeOH (35) or EtOH (33·5%). A. T. P.

Colour and constitution. VIII. Coupling of the four *m*-halogenophenols and the chromoisomerism of the 3-halogeno-4-benzeneazophenols, explained on resonance theory. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1944, **60**, 43—45; cf. A., 1943, II, 361).—The unique mono-coupling of *m*-C_6H_4F·OH in position 4, and the mono- and di-coupling of the other three *m*-C_6H_4Hal·OH in the 4- and 2 : 4-positions, are discussed from the viewpoint of H bonding and theory of resonance. The consequent chromoisomerism which arises both in the 3-halogeno-4-benzeneazophenols and in 3 : 2-NO_2·$C_{10}H_6$·NH_2 is explained. A. T. P.

***p*-Diphenylyl iodoacetate.** L. C. Hensley and S. E. Hazlet (*J. Amer. Chem. Soc.*, 1943, **65**, 2256).—CH_2Br·CO_2·C_6H_4Ph-*p* or CH_2Cl·CO_2·C_6H_4Ph-*p* with KI in $COMe_2$ at room temp. and then the b.p. give 77·8 and 18·3%, respectively, of p-*diphenylyl iodoacetate*, m.p. 113·5—114·3°. R. S. C.

Reduction products of *o*-nitrophenyl esters of arylsulphonic acids. L. C. Raiford and J. R. Shelton (*J. Amer. Chem. Soc.*, 1943, **65**, 2048—2051).—*o*-NO_2·C_6H_4·O·SO_2Ar (*A*) and its derivatives are reduced by $SnCl_2$–EtOH–conc. HCl to NH_2-esters without migration of acyl; mixed aliphatic acyl arylsulphonyl derivatives of *o*-NH_2·C_6H_4·OH and its substitution products are stable. Latimer's theory (A., 1930, 9) does not account for this difference between arylsulphonyl and purely aliphatic derivatives. (*A*) are prepared from *o*-NO_2·C_6H_4·OH etc. and $ArSO_2Cl$ in C_5H_5N. The following are described. *o*-NO_2·C_6H_4 benzene-, m.p. 64° (lit. 75°), *p*-toluene-, m.p. 81°, p-*bromo*-, m.p. 98·5°, and m-*nitro-benzene-sulphonate*, m.p. 88°; 4 : 6-*dibromo*-2-*nitrophenyl benzenesulphonate*, m.p. 131·5°, p-*toluenesulphonate*, m.p. 141°, p-*bromo*-, m.p. 131°, and m-*nitro-benzenesulphonate*, m.p. 113°; 3-*bromo*-5-*nitro*-p-*tolyl benzenesulphonate*, m.p. 155°, p-*toluenesulphonate*, m.p. 127°, p-*bromo*-, m.p. 151°, and m-*nitro-benzenesulphonate*, m.p. 98°; 4-*bromo*-2-*nitrophenyl*, m.p. 88—89°, 4-*nitro*-m-*tolyl*, m.p. 83—84°, 6-*bromo*-4-*nitro*-m-*tolyl*, m.p. 119—120°, and 2 : 6-*dibromo*-4-*nitro*-m-*tolyl benzenesulphonate*, m.p. 124—126°; 4-*bromo*-2-*nitrophenyl*, m.p. 101°, 6-*bromo*-4-*nitro*-m-*tolyl*, m.p. 86—87°, and 4-*nitro*-m-*tolyl* p-*bromobenzenesulphonate*, m.p. 91—92°; o-*aminophenyl benzenesulphonate*, m.p. 86°, *p*-toluenesulphonate, m.p. 98·5° (lit. 102°), p-*bromo*-, m.p. 111—112°, and m-*amino-benzenesulphonate*, m.p. 125—126°; 6-*bromo*-4-*amino*-m-*tolyl*, m.p. 100°, and 3-*bromo*-5-*amino*-p-*tolyl benzenesulphonate*, m.p. 95°; 4 : 6-*dibromo*-2-*aminophenyl* p-*toluene*-, m.p. 129—130°, and p-*bromobenzene-sulphonate*, m.p. 128°; 3-*bromo*-5-*amino*-p-*tolyl* p-*toluene*-, m.p. 88°, and p-*bromobenzene-sulphonate*, m.p. 112—113°. R. S. C.

Synthesis and properties of aryl vinyl ethers. M. F. Schostakovski and M. S. Burmistrova (*J. Appl. Chem. Russ.*, 1942, **15**, 260—266).—PhOH containing 10—15% of H_2O, C_2H_2 at 10—18 atm., and NaOH afford at 180° OPh·CH:CH_2, b.p. 155—156° (only slightly hydrolysed by 2% H_2SO_4); if PhOH is dry, a polymer is formed. Similarly are prepared o-*tolyl*, b.p. 167—168·5°, m-*tolyl*, b.p. 173—174·5°, p-*tolyl*, b.p. 175·5°, α-*naphthyl*, b.p. 257—258·5°, and *benzyl* (I), b.p. 183—184°, *vinyl ether*. The mol. refraction of the ethers, except (I), is by 0·8—1 > expected, and all the ethers, except (I), polymerise on heating. J. J. B.

Preparation of 6-nitro-1-naphthol, improved methods for the decomposition of diazo-naphthols, and new reactions of nitro-naphthols. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1944, 8—10).—6-Nitro-2-diazo-1-naphthol (I) [from 1 : 6 : 2-$(NO_2)_2C_{10}H_5$·NH_2], explodes at 150—151° (lit. 142—145°, 151—157°), is converted by Cu_2O–EtOH in AcOH–H_2SO_4 at 55—80° into 6 : 1-NO_2·$C_{10}H_6$·OH (II), new m.p. 181—182° (*acetate*, m.p. 121°; *benzoate*, m.p. 147·5—148°). (I) and aq. HCl–CuCl at 100° (bath) give 2-*chloro*-6-*nitro*-1-*naphthol*, m.p. 179—180°, converted by Br–AcOH at 60—90° into its 4-*Br*-derivative, m.p. 199°. 2-*Bromo*-6-*nitro*-1-*naphthol*, m.p. 164·5—165·6°, is similarly obtained from (I). (II) and Br–AcOH at room temp. give the 4-*Br*-derivative, m.p. 238°, and at 100° (bath) afford 2 : 4-*dibromo*-6-*nitro*-1-*naphthol*, m.p. 210° [also obtained from (I) and Br–AcOH at 110° without evolution of HBr]. (I) in AcOH–H_2SO_4 and saturated aq. KI (+ Cu powder) at 95° yield 2-*iodo*-6-*nitro*-1-*naphthol*, m.p. 214—215° (decomp.) (discolours >200°). (II) and $Hg(OAc)_2$–AcOH give 6-*nitro*-1-*naphthol*-4-*mercuriacetate*, m.p. >360° (shrinks at 300°), converted by I in 30% aq. KI at 90—100° into 4-*iodo*-6-*nitro*-1-*naphthol*, m.p. 214—216°. 4 : 5-*Dinitro*-1-*diazo*-2-*naphthol* (III) [from 2 : 4 : 5 : 1-$(NO_2)_3C_{10}H_4$·NH_2], decomp. slowly if heated gradually, explodes at 160° on rapid heating, is converted by Al + a little Cu in boiling EtOH into 4 : 5 : 2-$(NO_2)_2C_{10}H_5$·OH, m.p. 237—238° (lit. ~230°). 1-*Bromo*-4 : 5-*dinitro*-2-*naphthol*, m.p. 218—220°, is obtained from (III) and 30% HBr–CuBr at 100° (bath). β-$C_{10}H_7$·NH·SO_2·C_6H_4Me-*p* with Br–AcOH at 90°, followed by hydrolysis (cold, conc. H_2SO_4) and diazotisation, affords 6-*bromo*-2-*diazo*-1-*naphthol*, m.p. 214° (decomp.) (darkens ~145°; shrinks ~160°), converted by Al–Cu–Devarda's alloy in boiling EtOH into 6 : 1-$C_{10}H_6Br$·OH. 1 : 6 : 2-$(NO_2)_2C_{10}H_5$·NH·SO_2·C_6H_4Me-*p* after hydrolysis, diazotisation, and immediate addition to β-$C_{10}H_7$·OH in aq. NaOH at <10° gives 1 : 6-*dinitro*-2-*naphthaleneazo*-β-*naphthol*, m.p. 310°. M.p. are corr. A. T. P.

Phenols of the heavy oil of coal tar. II. O. Kruber and A. Marx (*Ber.*, 1940, **73**, [*B*], 1175—1177).—Fractional extraction with 4—5% NaOH of a phenol mixture, b.p. 248—252°, leads to the isolation of 5-*hydroxyhydrindene* (I), b.p. 251°/760 mm., m.p. 54—55° [*phenylurethane*, m.p. 155°; *oxyacetic acid*, m.p. 157°; *benzoate* (II), m.p. 110°], and 3 : 4 : 5-*trimethylphenol* (III), b.p. 248°/758 mm., m.p. 106° (phenylurethane, m.p. 148°; *oxyacetic acid*, m.p. 149°). (III) forms mixed crystals with (I) which can be removed as (II). H. W.

ββ-Di-*p*-hydroxyphenylpropane.—See B., 1944, II, 65.

Alkylpyrocatechols.—See B., 1944, II, 65.

Invert soaps. IV. Quaternary salts of aminophenyl ethers. R. Kuhn and D. Jerchel (*Ber.*, 1940, **73**, [*B*], 1100—1105; cf. A., 1944, II, 95).—*o*-NO_2·C_6H_4·OK, *n*-$C_{12}H_{25}Cl$, and a little $ZnCl_2$ in EtOH at 180° give o-NO_2·C_6H_4 (55—65%), b.p. 201—203°/3·5 mm., hydrogenated (PtO_2; EtOH) to o-NH_2·C_6H_4 n-$C_{12}H_{25}$ *ether*, m.p. 39°, b.p. 188—189°/3 mm. (*hydrochloride*), which with Me_2SO_4 at ~150° gives *o*-NMe_2·C_6H_4 *n*-$C_{12}H_{25}$ *ether* (80%), b.p. 220°/3 mm. [*methylmethosulphate* (I), m.p. 102—104°]. *p*-NO_2·C_6H_4·OK gives similarly p-NO_2·C_6H_4, m.p. 55°, and thence *p*-NH_2·C_6H_4 (*hydrochloride*, m.p. 103—106°), and (by Me_2SO_4) *p*-NMe_2·C_6H_4 *n*-$C_{12}H_{25}$ ether [*methylmethosulphate* (II), m.p. 118—120°]. *m*-NMe_2·C_6H_4·OK gives m-NMe_2·C_6H_4 n-$C_{12}H_{25}$ *ether*, m.p. 28—29° [*methylmethosulphate* (III), m.p. 82—83°]. The bactericidal and bacteriostatic activity of (I)—(III) are quantitatively similar to those of *n*-$C_{12}H_{25}$·NMe_2Br·CH_2Ph. R. S. C.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1944, III, 33.

Rôle of neighbouring groups in replacement reactions. VII. Methoxyl group.—See A., 1944, II, 90.

Action of anisole with αaa-trichloro-β-methyl-Δβ-propene.—See A., 1944, II, 89.

Behaviour of hydrogenated anisoles towards lithium phenyl.—See A., 1944, II, 114.

Synthesis of 1 : 4-epoxy*cyclo*hexane. R. C. Olberg, H. Pines, and V. N. Ipatiev (*J. Amer. Chem. Soc.*, 1943, **65**, 2260).—Passing *cis*- or *trans-cyclo*hexane-1 : 4-diol over activated Al_2O_3 at 275° gives 28 or 73%, respectively, of 1 : 4-*epoxy*cyclo*hexane*, b.p. 120·1°/760 mm., converted by 48% HBr into *trans*-1 : 4-dibromo*cyclo*hexane. R. S. C.

Restricted rotation in arylolefines. VII. New synthesis of hindered β-substituted β-arylacrylic acids. R. Adams and C. W. Theobald (*J. Amer. Chem. Soc.*, 1943, **65**, 2208—2211; cf. A., 1943, II, 10).—Di-*o*-substitution only slightly reduces the ease with which CPh:C·CO_2H undergoes addition reactions. 2 : 4 : 6 : 1-$C_6H_2Me_3$·COMe and PCl_5 at 60° (3 hr.) and then 100° (45 min.) give 2 : 4 : 6 : 1-$C_6H_2Me_3$·$CCl:CH_2$ (50%), b.p. 122—124°/25 mm., -$C_6H_2Me_3$·CO·CH_2Cl (19%), m.p. 62—63°, and some *α-mesitylvinyl* H_2 *phosphate*, m.p. 229—232°. 2 : 4 : 6 : 1-$C_6H_2Me_3$·C:CH with MgEtBr–Et_2O and then CO_2 at <0°/2·5—3 atm. gives *mesitylpropiolic acid* (I) (43%), m.p. 165—167° (decomp.), which with gaseous HCl in AcOH at 80—90° gives *β-chloro-β-mesitylacrylic acid* (67%), m.p. 145—146°, obtained also (71%) from 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CH_2·CO_2H by $POCl_3$–PCl_5 at 0°. With HBr–AcOH (79% yield) or, less well, aq. HBr at room temp. (I) gives *β-bromo-β-mesitylacrylic acid*, m.p. 135—135·5°. 2 : 3 : 4 : 6 : 1-C_6HMe_4·COMe (II) and PCl_5–PCl_3–$POCl_3$ at, successively, 0°, room temp., 55°, and 65—70° give α-iso*durylvinyl chloride* (III), b.p. 225°/745 mm., with *ω-chloroacetoisodurene*, m.p. 88—88·5°, b.p. 144°/6 mm., and ? α-*iso*durylvinyl H_2 phosphate, m.p. 184—184·5°. NaOEt converts (III) in boiling EtOH into iso*durylacetylene* (~65%), b.p. 86°/1 mm., which affords, as above, iso*durylpropiolic* (67%), m.p. 164—164·5° (decomp.), and thence *β-chloro-* (90%), m.p. 185°, and (by aq. HI at room temp.) *β-iodo-β-iso**durylacrylic acid* (90%), m.p. 183—184°. MgEtBr–Et_2O and then CO_2 converts (II) into *β-keto-β-iso**durylpropionic acid* (71%), m.p. 113—114° (decomp.). M.p. are corr. R. S. C.

Synthesis of amino-acids from substituted cyanoacetic esters.—See A., 1944, II, 91.

Condensation of aldehydes with malonic acid. XV. Condensation of 5-bromo- and 3 : 5-dibromo-salicylaldehyde; influence of dissimilar groups. K. C. Pandya and (Miss) R. B. K. Pandya (*Proc. Indian Acad. Sci.*, 1943, **18**, A, 164—170; cf. A., 1941, II, 170).—Condensation of *o*-OH·C_6H_4·CHO with $CH_2(CO_2H)_2$ is facilitated by the presence of Br or Cl in the aromatic nucleus. By reason of the ready sublimation of 2 : 5 : 1-OH·C_6H_3Br·CHO condensation with $CH_2(CO_2H)_2$ in presence of a little C_5H_5N at 100° proceeds somewhat slowly, giving 5-*bromo*-2-*hydroxycinnamic acid* (I), m.p. 150—152° (yield 50—55%) (no colour with $FeCl_3$; decolorises Baeyer's reagent), and 5-*bromosalicylidenemalonic acid*, m.p. 175° (decomp.) (yield 24%), which passes at 180° into (I). At 100—105° in absence of a

condensing agent the reactants afford 6-*bromocoumarin*-3-*carboxylic acid*, m.p. 200° (yield 92·5%), with small amounts of a compound, m.p. 241° (decomp.). 2 : 3 : 5 : 1-OH·$C_6H_2Br_2$·CHO (**II**), fused NaOAc, and Ac_2O at 170—180° afford 6 : 8-dibromocoumarin, m.p. 176°, in ~33% yield. (**II**), $CH_2(CO_2H)_2$, and a little C_5H_5N at 110° give a substance, m.p. 323—327°, darkens at 210°, which contains Br but not OH, CHO, or CO_2H, 3 : 5-*dibromo*-2-*hydroxycinnamic acid*, m.p. 185—187° (yield 31%), and 3 : 5-*dibromosalicylidenemalonic acid*, m.p. 157—159° (yield 22%). In absence of a condensing agent the reactants afford 6 : 8-*dibromocoumarin*-3-*carboxylic acid*, apparently dimorphous, m.p. 224—226°. H. W.

Reaction of sodium triphenylmethyl with esters of $\alpha\beta$-unsaturated acids. W. D. McPhee and E. G. Lindstrom (*J. Amer. Chem. Soc.*, 1943, **65**, 2177—2180).—CPh_3Na does not cause enolisation of CHMe:CH·CO_2Et in Et_2O, but by 1 : 4-addition gives [CPh_3·CHMe·CH·CO_2Et]Na (**I**), whence H_2O and then boiling 10% KOH–EtOH gives *β-triphenylmethyl*-n-*butyric acid* (**II**), m.p. 213·5—215·5° (214—216°) after sintering (*p-bromophenacyl* ester, m.p. 174—176° after sintering) (cf. Michael *et al.*, A., 1943, II, 192). Adding BzCl to (**I**) *in situ* gives a glass, whence distillation gives $CHPh_3$ and impure CPh_3·CHMe·CHBz·CO_2Et (**III**), hydrolysed by KOH in boiling 75% EtOH to (**II**) and BzOH; hydrolysis of (**III**) to a ketone was impracticable. ~2 mols. of CH_2:CH·CO_2Me are required to discharge the colour of 1 mol. of CPh_3Na; hydrolysis of the product affords, with difficulty, *γγγ-triphenyl*-n-*butyric* (**IV**) (16%), m.p. 153—156° (p-*bromophenacyl* ester, m.p. 193·5—194·5°), and *α-β′β′β′-triphenylethylglutaric acid* (18%), m.p. 205—206° (*bis*-S-*benzylthiuronium* salt, m.p. 144—144·5°). CPh_3Na and $(CH_2)_2O$ in Et_2O give *γγγ-triphenyl*-n-*propyl alcohol* (96%), m.p. 107—108°, b.p. 208—212°/3 mm., converted by red P–I at 165° into the iodide, m.p. 173·5—174·5° (cf. Wooster *et al.*, A., 1934, 1095), the Grignard reagent of which with gaseous CO_2 gives 19% of (**IV**), sinters 148°, m.p. 154—156° (*p*-bromophenacyl ester, sinters 192°, m.p. 194—195·5°). R. S. C.

Reformatsky reaction with benzylideneaniline. H. Gilman and M. Speeter (*J. Amer. Chem. Soc.*, 1943, **65**, 2255—2256).—CHPh:NPh, $CH_2Br·CO_2Et$ (gives 54% yield) or $CH_2Br·CO_2·CH_2Ph$ (gives 40% yield), and Zn in boiling PhMe give, after or without hydrolysis, β-anilino-β-phenylpropiolactam, m.p. 154°. Use of CHMeBr·CO_2Et gives 85% of β-anilino-β-phenyl*iso*butyrolactam, m.p. 109—110°. R. S. C.

Anhydrides of peptides and dehydrogenated peptides. J. E. Tietzman, D. G. Doherty, and M. Bergmann (*J. Biol. Chem.*, 1943, **151**, 387—394).—Acetyldehydrophenylalanyldehydrophenylalanine (**I**) and C_5H_5N–H_2O (1 : 1) at 100° (bath), followed by 2N-HCl at 0°, afford *anhydroacetyldehydrophenylalanyldehydrophenylalanine* (**II**), m.p. 210—212° (decomp.), also obtained similarly, but more slowly, at 37·5° (20 days), or from the azlactone of (**I**) at 100° (bath). Hydrogenation (2 H_2; Pd-black in EtOH at 20—25° for 150 hr.) of (**II**) yields *anhydroacetylphenylalanylphenylalanine*, m.p. 203—204° (decomp.) (*Me* ester, m.p. 135—137°) (decomposed by boiling HCl to phenylalanine), and an *acetylphenylalanylphenylalanine* (**III**), m.p. 246—248° (decomp.). The azlactone of the Bz analogue of (**I**) and C_5H_5N–H_2O (1 : 2) at 100° (bath) give *anhydrobenzoyldehydrophenylalanyldehydrophenylalanine*, m.p. 258—259° (decomp.). The crude azlactone from glycine, PhCHO, and Ac_2O–NaOAc with boiling H_2O (2 hr.) (cf. Dakin, A., 1929, 811) gives a *product*, $C_{20}H_{16}O_3N_2$, m.p. 254—255° (decomp.) (structure suggested); it forms Na, NH_4, and C_5H_5N salts. The azlactone of acetylbis(dehydrophenylalanyl)-dehydrophenylalanine and $COMe_2$ in N-NaOH at room temp. yield *anhydrobis*(*dehydrophenylalanyl*)*dehydrophenylalanine azlactone*, m.p. 288—289° (decomp.). Hydrogenation (2 H_2; Pd in aq. $NaHCO_3$) of (**I**) or acetyldehydrophenylalanyl-*dl*-phenylalanine affords (**III**) and an *isomeride*, m.p. 183—185°. Acetyldehydrophenylalanylglycine at 180° in vac. gives only a tar, and neither it nor its Bz analogue could be transformed by C_5H_5N–H_2O into anhydropeptides. A. T. P.

Cyclic fatty acids. *cyclo*Hexylgeranylacetic acid. L. Leder-Pakendorf (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 757—760).—Adding Et *cyclo*hexylmalonate and then geranyl chloride to Na powder in xylene–PhMe gives *Et* cyclo*hexylgeranylmalonate* [*Et α-carbethoxy-α*-cyclo*hexyl-δθ-dimethyl-*$\Delta^{\gamma\eta}$-n-*decadienoate*], b.p. 201—203·5°/5 mm., the derived (50% KOH) oily acid from which at 40—150° gives α-cyclo*hexyl-δθ-dimethyl-*$\Delta^{\gamma\eta}$-*decadienoic acid* (**I**), b.p. 213—214°/7 (? 17) mm. (*Et* ester, b.p. 215—218°/25 mm.), reduced by H_2–Pd–Pt–C in EtOH to α-cyclo*hexyl-δθ-dimethyl*-n-*decoic acid* (**II**), b.p. 218—219°/14 mm. (**I**) and (**II**) are only feebly toxic, but are effective against *Lupus vulgaris*, *Lepra*, and [(**I**) much more effective than (**II**)] tubercle bacilli. R. S. C.

Chemotherapeutic study of *p*-nitrobenzoyl and related compounds. C. Siebenmann and R. J. Schnitzer (*J. Amer. Chem. Soc.*, 1943, **65**, 2126—2128).—*cyclo*Hexanol (2 mols.) and *p*-$NO_2·C_6H_4$·COCl (**I**) (1 mol.) in C_5H_5N at <20° and then at the b.p. give cyclo*hexyl* p-*nitrobenzoate* (**II**), m.p. 51·5—52·5°. Resorcinol (2 mols.) and (**I**) (1 mol.) in C_5H_5N at 100° give *resorcinol mono-*, m.p. 175—177°, and some *di*-p-*nitrobenzoate*, m.p. 185—186° [best obtained by use of an excess of (**I**)]. The following are similarly prepared. *Pyrocatechol mono-*, m.p. 151—152°, and *di-*, m.p. 162—165°, quinol mono-, m.p. 190—194°, and di-, m.p. 252—257°, *pyrogallol mono-*, m.p. 193—197°, and *tri-*, m.p. 229—231°, 4-hexylresorcinol mixed (**III**) (m.p. 60—72°) mono- and di-, *inositol hexa-* (prep. without a solvent at 180—200°), m.p. 310—315°, -p-*nitrobenzoate*; cyclo*hexyl* 3 : 5-*dinitrobenzoate*, m.p. 109—111°; p-*nitrobenz-morpholide*, m.p. 101—106°, *-piperidide*, m.p. 115—118°, and -cyclo*hexylamide*, m.p. 203—204°; 3 : 5-*dinitrobenz-morpholide*, m.p. 184—187°, and *-piperidide*, m.p. 143—144·5°; 1 : 4-*di*-p-*nitrobenzoylpiperazine*, m.p. 318°. *p*-$NH_2·C_6H_4·SO_2·NH_2$ (**IV**) (0·11) and (**I**) (0·23 mol.) in C_5H_5N at <30° and then 100° give N^1N^4-*di-*, m.p. 268° (decomp.), hydrolysed by boiling 30% NaOH to N^1-*p*-nitrobenzoylsulphanilamide (**V**), m.p. 218—219° (lit. 235—240°). 1 mol. each of (**I**) and (**IV**) in C_5H_5N give N^4-p-*nitrobenzoylsulphanilamide*, m.p. 260°. N^1-Benzoyl- (**VI**), m.p. 178—180° (lit. 181·2—182·3°), and N^1N^4-dibenzoyl-sulphanilamide, m.p. 252° (decomp.) (lit. 268—270°), are also prepared. Most of these compounds have little or no anticoccal activity. (**II**) is slightly active against strepto- but not against pneumo-cocci. (**III**) is effective against pneumoccoci. (**V**) is extremely effective against meningococci in mice, and (**VI**) is sp. against pneumococci. The N^1N^4-derivatives of (**IV**) are quite inactive, as are the 3 : 5-dinitrobenzoyl derivatives. R. S. C.

Isomorphism of organic compounds. VI. H. Lettré [with H. Barnbeck, P. Lehmann, and M. Stier] (*Ber.*, 1940, **73**, [*B*], 1150—1152).—*p*-OMe·$C_6H_4·CO_2H$ (**I**) gives eutectics with BzOH and *p*-$C_6H_4R·CO_2H$ (R = OH, Me, Cl, Br, and I). OMe therefore resembles OH in inability of isomorphous replacement by other substituents. (**I**) forms additive compounds (1 : 1) with *o-*, *m-*, and *p*-$NO_2·C_6H_4·CO_2H$. *r*-OH·CHPh·CO_2H (**II**) gives only a eutectic with *r-p*-OMe·C_6H_4·CH(OH)·CO_2H (**III**). Similar observations are made with (+)-*p*-OMe·C_6H_4·CH(OH)·CO_2H and (+)- and (−)-OH·CHPh·CO_2H. (**II**) and (**III**) form a system of two true racemates in which the racemic forms are not isomorphous. The sterically similar forms do not give mixed crystals and a partial racemate does not arise from the sterically opposite modifications. H. W.

Rearrangement of benzyl ethers of salicylic acids. D. S. Tarbell and V. P. Wystrach (*J. Amer. Chem. Soc.*, 1943, **65**, 2146—2149).—2 : 3 : 5 : 1-OH·$C_6H_2Cl_2·CO_2$H (**I**), CH_2PhCl, K_2CO_3, and NaI in boiling COMeEt–H_2O give *Me* 3 : 5-*dichloro*-2-*benzyloxybenzoate*, m.p. 42·5—43·5°, hydrolysed by KOH–H_2O–MeOH to the *acid* (**II**), m.p. 148—148·5°. At 153° (**II**) gives *CH_2Ph* 3 : 5-*dichlorosalicylate* (**III**) (65—72%), m.p. 109·5—110·5° [also obtained from (**I**) (as Na salt) by $CH_2Ph·OH$ and a little NEt_3 at 135°], (**I**) (20%), and 8—10% of CO_2, but no other decarboxylation product. In $NPhMe_2$ at 155° (**II**) gives 51% of (**III**) and 25% of (**I**); (**III**) is also obtained slowly in boiling AcOH, but (**II**) is unchanged in PhMe–xylene at 116—117°. *o*-$CH_2Ph·O·C_6H_4·CO_2$H at 185—190° gives *o*-OH·$C_6H_4·CO_2·CH_2Ph$ (35%), *o*-OH·$C_6H_4·CO_2$H (17—~35%), and 5 : 2 : 1-$CH_2Ph·C_6H_3$(OH)·$CO_2·CH_2Ph$ (a little; identified by hydrolysis). 5 : 2 : 1-$NO_2·C_6H_3$(OH)·CO_2Et, m.p. 97—97·5° (lit. 93°), gives, as above, *Et* 5-*nitro*-2-*benzyloxybenzoate*, m.p. 75—75·5°, which with KOH–H_2O–MeOH at the b.p. gives 5 : 2 : 1-$NO_2·C_6H_3$(OMe)·CO_2H, m.p. 159·5—160·5° (lit. 161°), but at room temp. gives 5-*nitro*-2-*benzyloxybenzoic acid*, m.p. 166—166·5°. At 175° this gives *CH_2Ph* 5-*nitrosalicylate* (63%), m.p. 83·5—85·5° [also prepared from 5 : 2 : 1-$NO_2·C_6H_3$(OH)·CO_2Na and CH_2PhCl], and 5 : 2 : 1-$NO_2·C_6H_3$(OH)·CO_2H (28%). The reaction mechanism is discussed. M.p. are corr. R. S. C.

Effect of heat on the β-naphthylmethyl and 9-phenanthrylmethyl ether of 3 : 5-dichlorosalicylic acid. D. S. Tarbell and V. P. Wystrach (*J. Amer. Chem. Soc.*, 1943, **65**, 2149—2153).—The 9 : 10-ethylenic linking of phenanthrene is sufficiently "aliphatic" to cause rearrangement of 9-phenanthrylmethyl ethers to resemble that of allyl (A., 1942, II, 258) rather than that of CH_2Ph ethers (cf. preceding abstract). This is not so for the 1 : 2-linking of $C_{10}H_8$, since β-$C_{10}H_7·CH_3$ resemble CH_2Ph ethers. β-$C_{10}H_7·CH_2Cl$ with 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2·CO_2$Me (**I**) and NaOH in aq. COMeEt and then KOH–MeOH–EtOH gives 3 : 5-*dichloro*-2-*β-naphthylmethoxybenzoic acid* (**II**) (50%), m.p. 142—142·5° (decomp.), which at 147—148° gives *β-naphthylmethyl* 3 : 5-*dichlorosalicylate* (**III**) (67%), m.p. 138·5—139° [identified by hydrolysis to 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2·CO_2$H (**IV**) and β-$C_{10}H_7·CH_2·OH$], CO_2 (9·5%), and (**IV**) (~10%). (**III**) is also obtained when (**II**) is crystallised from AcOH. HCl passed into phenanthrene, conc. HCl, and 40% CH_2O at 94° gives 9-chloromethylphenanthrene (**V**) (21%), m.p. 101·5—102° [picrate, m.p. 101·5—102° (lit. 99·5—100·5°)], which with (**I**), NaI, and K_2CO_3 in aq. COMeEt gives *Me* 3 : 5-*dichloro*-2-9′-*phenanthrylmethoxybenzoate* (56%), m.p. 162·5—163·5°. Hydrolysis with alkali then yields the derived *acid* (**VI**), m.p. 174·5—175°, which at 229° gives CO_2 (75%), (**IV**) (29·8%), and 9-3′ : 5′-*dichloro*-2′-*hydroxyphenyl*-10-*methyl*-[? 9-3′ : 5′-*dichloro*-2′-*hydroxybenzyl*-]*phenanthrene* (41%), m.p. 136·5—137·5° (*acetate*, m.p. 208—208·5°). (**VI**) is unchanged in boiling AcOH. 9-Phenanthroyl chloride, 2 : 4 : 1-$C_6H_3Cl_2·OH$ (**VII**), and $AlCl_3$ in CS_2 give 2 : 4 : 1-*$C_6H_3Cl_2$* 9-*phenanthroate* (14%), m.p. 183—184°, which with EtOH gives some of the *Et* ester, m.p. 114·5—115°. (**V**), (**VII**), NaI, and K_2CO_3 in aq. COMeEt give 9-2′ : 4′-*dichlorophenoxymethylphenanthrene* (60%), m.p. 125—125·5°, which at 279—280° (not 240°) yields (**VII**) as sole product isolated. Mg,

(V), and a trace of MeI in boiling Et_2O–C_6H_6 give, after treatment with aq. NH_4Cl, *αβ-di-9-phenanthrylethane* (59%), m.p. 252·5—254·5°, and a little (?) 9-methylphenanthrene. Zn–HCl–EtOH is without effect on (V). M.p. are corr. R. S. C.

Synthesis of phenolic acid esters. I. Depsides. C. J. Cavallito and J. S. Buck (*J. Amer. Chem. Soc.*, 1943, **65**, 2140—2142).—$OH{\cdot}C_6H_4{\cdot}CO_2Na$ and CH_2PhCl (1·1 mol.) in boiling aq. EtOH give up to 40% of CH_2Ph *p-*, m.p. 111°, *o-*, b.p. 158°/3 mm., and *m-hydroxybenzoate*, m.p. 70°. 2 : 4 : 1-$(OH)_2C_6H_3{\cdot}CO_2H$ and CH_2PhCl (1·05 mol.) in boiling KOH–EtOH–H_2O give *CH_2Ph* 2 : 4-*dihydroxybenzoate*, m.p. 60°, b.p. 215°/2 mm. Similar use of an excess of CH_2PhCl gives *CH_2Ph* p-*benzyloxybenzoate*, m.p. 115°, hydrolysed by alkali to *p*-$CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$, m.p. 188°. Similarly are prepared *o-*benzyloxy-, m.p. 70°, 2 : 4-*di-*, m.p. 180°, and 3 : 4 : 5-tri-benzyloxybenzoic acid, m.p. 189°. The benzyloxy-acids with $SOCl_2$ give the acid chlorides, which with CH_2Ph esters of OH-acids give $CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2Ph$ etc., whence H_2–spongy Pd in dioxan at 50°/40 lb. gives the free depsides. Thus are obtained: *p*-benzyloxy-, m.p. 110°, and 3 : 4 : 5-*tribenzyloxy-benzoyl chloride*, m.p. 115°; *CH_2Ph* p-, m.p. 166°, m-, m.p. 107°, and o-p′-*benzyloxybenzoyloxybenzoate*, m.p. 73°; *CH_2Ph* p-o′-*benzyloxybenzoyloxy-*, m.p. 71°, 2 : 4-*di*-p-*benzyloxybenzoyloxy-*, m.p. 111°, and p-3′ : 4′ : 5′-*tribenzyloxybenzoyloxy-benzoate*, m.p. 107°; *p-*, m.p. ~270°, *m-* m.p. 247°, and o-p′-*hydroxybenzoyloxybenzoic acid*, m.p. 180°; p-o′-*hydroxy-*, m.p. 210°, p-3′ : 4′ : 5′-*trihydroxy-*, m.p. 255—260°, and 2 : 4-*di*-p-*hydroxy-benzoyloxybenzoic acid*, m.p. ~210°. R. S. C.

Action of sodium on ethyl β-methylbutane-αβδ-tricarboxylate. III. Synthesis of *cis-allo*santenic acid. IV. R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **20**, 243—246; 247—249; cf. A., 1943, II, 371).—III. $CO_2Et{\cdot}CH_2{\cdot}CMe(CN){\cdot}CH(CN){\cdot}CO_2Et$ and EtOH–NaOEt–MeI at room temp., then boiling, give *Et_2 γδ-dicyano-γ-methylpentane-αδ-dicarboxylate*, b.p. 185°/5 mm., converted by boiling conc. HCl, followed by EtOH–H_2SO_4 at 110°, into *Et_3 γ-methylpentane-αγδ-tricarboxylate* (I), b.p. 154°/5 mm. [free acid, m.p. 178° (cf. Sen-Gupta, A., 1933, 1049)]. (I) and Na in boiling C_6H_6 give *Et_2* 2 : 3-*dimethyl*cyclo*pentanone*-3 : 5-*dicarboxylate*, b.p. 135°/4 mm., which with boiling 6% HCl affords 2 : 3-dimethyl*cyclo*pentanone-3-carboxylic acid, a liquid (*semicarbazone*, decomp. 204°); its *Et* ester (HCl–EtOH), b.p. 99°/4 mm. and anhyd. HCN (+ a little KCN) at 9° yield a cyanohydrin, dehydrated by $POCl_3$–C_5H_5N at 145—150° and then hydrolysed by boiling conc. HCl to a mixture, m.p. 140—145°, of santenenic and *iso*santenenic acid. The mixture is hydrogenated (PtO_2, AcOH, room temp., 1 atm.) to 2 : 3-dimethyl-*cyclo*pentane-1 : 3-dicarboxylic acid, converted by AcCl into *cis-allo*santenic anhydride (II), m.p. 92°, and some isomeric santenic acids. Hydrolysis of (II) with EtOH–KOH yields *cis-allo*santenic acid, m.p. 151—152° (cf. Enkvist, A., 1933, 822).

IV. $CO_2Et{\cdot}[CH_2]_2{\cdot}CMe(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$ and Na–C_6H_6, followed by $CH_2Br{\cdot}CO_2Et$, give *Et_3* 4-*methyl*cyclo*pentanone*-2 : 4-*dicarboxylate*-2-*acetate*, b.p. 170°/5 mm., hydrolysed by boiling conc. HCl to 4-methyl*cyclo*pentanone-4-carboxylic-2-acetic acid (*Et_2* ester, b.p. 145°/6 mm.), reduced (Clemmensen) to 1-*methyl*cyclo-*pentane*-1-*carboxylic*-3-*acetic acid* (III), m.p. 124—125°. Et 3-methyl*cyclo*pentanone-3-carboxylate and $CH_2Br{\cdot}CO_2Et$–Zn afford esters, converted by $POCl_3$–C_6H_6 into unsaturated esters, b.p. 125°/4 mm., and thence by H_2–PtO_2–EtOH at room temp. and 1 atm., followed by boiling 10% aq. KOH–EtOH, into (III). (III) is probably identical with the acid, m.p. 126°, described by Banerjee (A., 1941, II, 16) as the 2-acetic acid. A. T. P.

Sulphonated esters, amides, and imides of *cis*-3 : 6-*endo*methylene-hexahydrophthalic acid.—See B., 1944, II, 66.

Synthesis of condensed ring compounds. XI. A tricyclic compound [obtained] by the di-inene double addition reaction. W. Nudenberg and L. W. Butz (*J. Amer. Chem. Soc.*, 1943, **65**, 2059—2060; cf. A., 1943, II, 330).—δ-1-Hydroxy*cyclo*pentyl-β-methyl-Δ$^{\gamma}$-*n*-butinen-β-ol, b.p. 124°/5 mm., and $KHSO_4$ at 160—180° give δ-Δ^1-cyclo*pentenyl-β-methyl-*Δ$^{\alpha}$-*buten-*Δ$^{\gamma}$-*inene* (62%), b.p. 81°/13 mm., which with $(CH{\cdot}CO)_2O$–CO_2 at 110—120° and then 150—160° gives 8-*methyl*-7 : 12-cyclo*penta*[a]*naphthitadiene*-5 : 6 : 10 : 11-[1-*methyl*-5 : 6-*trimethylene*-2 : 3 : 4 : 6 : 7 : 8-*hexahydronaphthalene*-3 : 4 : 7 : 8-]*tetracarboxylic anhydride* (13%), m.p. 168—170° (vac.) [absorption max. at 2500 A. (ε 18,000) in EtOH]. δ-1-*Hydroxy*-2-*methyl*cyclo*pentyl-β-methyl-*Δ$^{\gamma}$-n-*butinen-β-ol* (prep. in 70% yield), b.p. 122—123°/1—2 mm., in boiling 15 : 37 (vol.) H_2SO_4–H_2O gives δ-2-methyl-Δ^1-*cyclo*pentenyl-β-methyl-Δ$^{\alpha}$-buten-Δ$^{\gamma}$-inene (38%), b.p. 85—95° (90°)/13—14 mm., which with Me_2 fumarate (3 mols.)–N_2 at 190—200° gives (?) *Me_4* 4 : 8-*dimethyl*-7 : 12-cyclo*penta*[a]-*naphthitadiene*-trans-trans-5 : 6 : 10 : 11-[1 : 6-*dimethyl*-5 : 6-*trimethylene*-2 : 3 : 4 : 6 : 7 : 8-*hexahydronaphthalene*-trans-trans-3 : 4 : 7 : 8]-*tetracarboxylate*, a glass, whence N_2H_4 yields no cryst. product. *Me_4* $\Delta^{8(14):9}$-chrysitadiene-*trans-trans*-6 : 7 : 11 : 12-tetracarboxylate and N_2H_4,H_2O in boiling MeOH give a *Me_2* ester *dihydrazide*, m.p. 161—168° (decomp.). M.p. are corr. R. S. C.

Preparation of *p*-aminobenzaldehyde, and the mechanism of the reactions of sodium polysulphides with *p*-nitrotoluene. H. G. Beard and H. H. Hodgson (*J.C.S.*, 1944, 4—5).—*p*-$C_6H_4Me{\cdot}NO_2$ and Na_2S_x in boiling aq. EtOH–NaOH (90 min.) give *p*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ (I) in yields of 35—40 ($x = 1$), 45·3 ($x = 2$), 53·4 ($x = 3$), and 72—75% ($x = 4$); much by-product results when $x = 5$. In absence of an alcohol (EtOH is more efficient than MeOH or Pr$^{\alpha}$OH) or of free alkali the optimum yield of (I) falls to 31 or <10%, respectively. A mechanism of the reaction is postulated.

[With R. R. Davies.] (I) (52%) and its *o*-Cl-derivative (48%) are prepared by a modification of Geigy's process (G.P. 86,874), using the respective nitrotoluene and 17% aq. NaOH + S. A. T. P.

Reaction of *p*-bromophenacyl bromide with chloride ions. H. H. Pokras and H. I. Bernstein (*J. Amer. Chem. Soc.*, 1943, **65**, 2096—2097).—*p*-$C_6H_4Br{\cdot}CO{\cdot}CH_2Br$ (I) and NaCl or KCl (excess) in boiling 62% EtOH give p-*bromophenacyl chloride* (II), also obtained (m.p. 117—118°; 80%) from PhBr, $CH_2Cl{\cdot}COCl$, and $AlCl_3$. Use of 1 mol. of NaCl causes only partial conversion, but the reverse change could not be effected. Solubilities of (I) and (II) in 62% EtOH at 25° are 0·332±0·008 and 0·278±0·01 g. per 100 c.c., respectively. Mixtures of (I) and (II) melt at intermediate temp. (mixed m.p. diagram given). Formation of (II) may obscure identification of compounds contaminated with NaCl. R. S. C.

Fluorine derivatives of acetophenone and ethylbenzene. J. H. Simons and D. F. Herman (*J. Amer. Chem. Soc.*, 1943, **65**, 2064—2066).—Fluorination may be effected by active AgF ($AgF_{1\cdot6}$) in liquid HF or by F_2 in liquid HF. Gradual replacement of Cl in C_2PhCl_5 by F progressively increases the difficulty of further exchange; exchange starts at $C_{(\alpha)}$. $COPh{\cdot}CHBr_2$ and $AgF_{1\cdot6}$ in liquid HF at 75° (not other methods) give $COPh{\cdot}CHF_2$ (40%), b.p. 83—85°/29 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 221—223°), converted by warm 5% NaOH into $OH{\cdot}CHPh{\cdot}CO_2H$. COPhMe, F_2, and Ag_2O in HF at 0° give $COPh{\cdot}CHF_2$ (20·2%) with small amounts of CF_4 and BzF. $COPh{\cdot}CCl_3$ and $AgF_{1\cdot6}$ in HF at <0° give *ωω-dichloro-ω-fluoro-* (48·7%), b.p. 111—112°/24 mm., and *ω-chloro-ωω-difluoro-acetophenone* (8·5%), b.p. 84—85°/25 mm., both converted by warm 10% NaOH into BzOH but failing to give 2 : 4-dinitrophenylhydrazones; a little BzF is also formed; $COPh{\cdot}CF_3$ could not be obtained thus from $COPh{\cdot}CCl_3$ or the products. $COPh{\cdot}CCl_3$ and PCl_5 at 220° give C_2PhCl_5 (84%), b.p. 155—156°/15 mm., which with HF at 145°/>300 lb. gives *αβββ-tetrachloro-α-fluoroethylbenzene* (I) (51·1%), b.p. 246°/731 mm., 123—126°/14 mm., *βββ-trichloro-αα-difluoroethylbenzene* (II) (29·8%), b.p. 219°/731 mm., 100°/16 mm., and small amounts of BzF and (?) $CPhF_2{\cdot}CCl_2F$. With SbF_3–$SbCl_5$ at 170—180° (I) gives (II) (47·3%), *ββ-dichloro-ααβ-trifluoroethylbenzene* (III) (6·7%), b.p. 177—178°/731 mm., 94—95°/42 mm., and a little BzF. Repeated treatment of (II) with $AgF_{1\cdot6}$–HF at 180° gives 19·9% of *β-chloro-ααββ-tetrafluoro-* (IV), b.p. 152—153°/733 mm., 1·3% of *pentafluoro-ethylbenzene*, b.p. 128—129°/733 mm., and 16% of (III), $SbCl_5$ and (III) in HF at 180°/>400 lb. give 15% of (IV) and a small amount of C_2PhF_5 (not obtained pure by this method). R. S. C.

Preparation and properties of mesityl-2 : 4 : 6-trimethylbenzylglyoxal [αγ-dimesitylpropane-αβ-dione]. R. P. Barnes and A. E. Brandon (*J. Amer. Chem. Soc.*, 1943, **65**, 2175—2177).—$CHR{:}CH{\cdot}COR$ (R = mesityl) and H_2O_2 in NaOH–H_2O–MeOH at 30° give *βγ-epoxy-αγ-dimesitylpropan-α-one*, geometrical *isomerides*, m.p. (I) 95° and (II) 110°; illumination of (I) in EtOH gives (II), but the reverse change could not be effected. In boiling NaOH–MeOH–H_2O, (II) gives *β-hydroxy-αγ-dimesityl-*Δ$^{\beta}$-*propen-α-one* (III), m.p. 143°; (I) gives mainly the geometrical *isomeride* (IV), m.p. 128°, and a little (III). (III) and (IV) give red colours with $FeCl_3$–EtOH and are respectively ~70% and ~40% enolic (Kurt Meyer), but are not interconvertible. Br in MeOH converts (III) or (IV) into *γ-bromo-αγ-dimesitylpropane-αβ-dione* (V), yellow, m.p. 137—148°, converted by boiling conc. HCl–MeOH into the colourless enolic *form* (VI), m.p. 143°, and by KI and a little AcOH in $COMe_2$ into (III). (VI) gives a dark brownish-green colour with $FeCl_3$–EtOH and is ~5% enolic (Kurt Meyer). With boiling Ac_2O–KOAc, (V) or (VI) gives *γ-bromo-β-acetoxy-αγ-dimesityl-*Δ$^{\beta}$-*propen-α-one*, m.p. 133—134°, whence boiling conc. HCl–MeOH yields (VI). R. S. C.

Preparation and properties of mesityl-*p*-methoxybenzylglyoxal. R. P. Barnes and H. Delaney (*J. Amer. Chem. Soc.*, 1943, **65**, 2155—2157).—2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}COMe$ and *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ in NaOH–H_2O–EtOH at room temp. give *mesityl* p-*methoxystyryl ketone*, m.p. 103—104°, which with H_2O_2 in NaOH–H_2O–EtOH at ~35° gives the *oxide*, an oil, converted by boiling NaOH–MeOH–H_2O in 10 min. into *β-hydroxy-γ-*p-*anisyl-α-mesityl-*Δ$^{\beta}$-*propen-α-one*, m.p. 97—98°. This is 99% enolic (Kurt Meyer) in EtOH, with alkaline H_2O_2 gives *p*-anisic and mesitoic acids, and with Br–$CHCl_3$ gives *γ-bromo-γ-*p-*anisyl-α-mesitylpropane-αβ-dione*, an oil, converted by KOAc in boiling AcOH into *β-hydroxy-γ-acetoxy-γ-*p-*anisyl-α-mesityl-*Δ$^{\beta}$-*propen-α-one* (I), m.p. 128—129°. (I) gives a red colour with $FeCl_3$, is 83% enolic, is unchanged by AcCl, but with boiling KOAc–Ac_2O gives *βγ-diaceloxy-γ-*p-*anisyl-α-mesityl-*Δ$^{\beta}$-*propen-α-one* (II), m.p. 96°. Hydrolysis of (I) or (II) by conc. H_2SO_4 gives the white, cryst. enediol (III), which gives a bluish-green colour with $FeCl_3$, decolorises indophenol, and, when kept, is converted by autoxidation into an orange peroxide and then into deep yellow α-p-*anisyl-γ-mesityl-*

propane-αβγ-trione, m.p. 106°. (**III**) is thus much less stable than its *o*-anisyl analogue (A., 1943, II, 66). R. S. C.

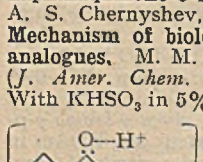
Polycyclic compounds. III. Benzonaphthone [*peri*naphthindenone] bromide, the primary product of interaction of bromine and benzonaphthone. A. M. Lukin (*Bul. Acad. Sci. U.R.S.S., Cl. Sci. chim.*, 1941, 565—572).—Contrary to Brass and Clar (A., 1940, II, 75) the primary interaction product of benzonaphthone and Br is the dibromide. The monobromide is an intermediate stage, as is the complex formed by the mono- and di-bromides. V. B.

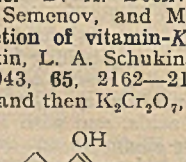
Ionone. II. Optical resolution of *dl*-α-ionone. H. Sobotka, (Miss) E. Bloch, H. Cahnmann, (Misses) E. Feldbau, and E Rosen (*J. Amer. Chem. Soc.*, 1943, **65**, 2061—2062; cf. A., 1944, II, 78).—*dl*-α-Ionone and *l*-menthydrazide, $[\alpha]_D^{23}$ −76·7° in 95% EtOH, in boiling EtOH containing a little NaOAc and AcOH give the difficultly separable l-, m.p. 185°, $[\alpha]_D^{22}$ −320° in EtOH, and d-*α-ionone*-l-*menth-hydrazone*, m.p. 176°, $[\alpha]_D^{23}$ +230° in EtOH, whence distillation with *o*-$C_6H_4(CO)_2O$ in steam yields *l*-, $[\alpha]_D^{27}$ −406° (2 : 4-*dinitrophenylhydrazone*, m.p. 133°; *p*-chlorobenzoylhydrazone, m.p. 200—201°), and *d*-α-ionone, $[\alpha]_D^{23}$ +347° (2 : 4-*dinitrophenylhydrazone*, m.p. 129°; *p*-chlorobenzoylhydrazone, m.p. 196—198°), which differ in odour. β-Ionone-*l*-menth-hydrazone, m.p. 178°, [α] −35°, *dl*-α-ionone-2 : 4-dinitrophenylhydrazone, m.p. 143°, and -*p*-chlorobenzoylhydrazone, m.p. 214°, are also described. Use of the active compounds for investigating the α⟷β-ionone equilibration is discussed. R. S. C.

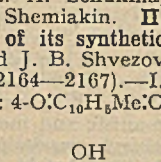
Volatile vegetable substances. XXVI. Ionones. Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1943, **26**, 2151—2165).—α-Ionone (**I**) [semicarbazone, m.p. 142—143° (lit. 137—138°); *δ-phenylsemicarbazone*, m.p. 186·5—187°; 2 : 4-dinitrophenylhydrazone, m.p. 151° (lit. 147—148°)] is readily obtained pure through the H sulphite or oxime. β-Ionone (**II**) is obtained pure by hydrolysis of the semicarbazone (**III**), m.p. 148·5—149°, becomes yellow at >100°, with aq. *o*-$C_6H_4(CO_2H)_2$ in a current of steam; the *δ-phenylsemicarbazone* has m.p. 157·5—158° and is stable to light and air whereas a *phenylsemicarbazone*, m.p. 151—152°, obtained from (**III**) and NH_2Ph at 180°, rapidly becomes yellow in air. The reactions of (**I**), (**II**), and methyl-α-ionone (**IV**) with NaOEt–EtOH and according to Legal, Rosenthaler, Ehrlich–Müller, and Hanriot are described in detail. Reduction of (**I**), (**II**), and (**IV**) with Na in boiling EtOH gives dihydro-α-ionol (**V**), b.p. 126—127°/10 mm. (acetate, b.p. 131—132°/10 mm.), differing in physical consts. from the product of Palfray *et al.* (A., 1937, II, 108), dihydro-β-ionol, b.p. 132—133°/10 mm., m.p. 41° [allophanate, m.p. 162·5—163° (lit. 171·5°); acetate, b.p. 137—138°/10 mm.], and *dihydromethyl-α-ionol*, b.p. 136—138°/10 mm. (*acetate*, b.p. 141—142°/10 mm.), respectively. Hydrogenation (PtO_2 in 90% AcOH at 70°) of (**V**) affords cis-*tetrahydroionol*, b.p. 130—131°/10 mm. (*allophanate*, m.p. 162—162·5°), oxidised to cis-*tetrahydroionone* (*semicarbazone*, m.p. 183—184°; 2 : 4-*dinitrophenylhydrazone*, m.p. 120—120·5°). It is probable that the product obtained by Kandel (A., 1939, II, 169) is the *trans*-isomeride. *α-Methyltetrahydroionol*, b.p. 138—139°/10 mm., is similarly obtained. (**I**) is hydrogenated (Raney Ni in 95% EtOH at 65°) to dihydro-α-ionone, b.p. 119—120°/10 mm. [semicarbazone, m.p. 167—167·5° (lit. 171—172°)]. The dihydroionol obtained by hydrogenation (Raney Ni in 95% EtOH at 65°) is non-homogeneous and appears to contain ~22% of ketones. (**I**) is dehydrated by I to 1 : 1 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 107—108°/10 mm.; under like conditions (**IV**) gives the 1 : 1 : 6 : 7-Me_4-compound, b.p. 120—122°/10 mm. Parachors, mol. surface energies, and dipole moments of the ionones and the corresponding alcohols indicate that the former possess a *cis*-ethylenic structure and that the butenyl or Bu chain is coiled into an open ring. M.p. are corr. H. W.

Reaction between quinones and metallic enolates. XVIII. Mechanisms. L. I. Smith, R. T. Arnold, and J. Nichols (*J. Amer. Chem. Soc.*, 1943, **65**, 2131—2134; cf. A., 1944, II, 54).—The varying modes of reaction of bromopolymethylbenzoquinones with $CHNa(CO_2Et)_2$ or other anionoid reagents are correlated and shown to be rational on the basis of possible modes of resonance. Similar explanations can be applied also outside this series of compounds. R. S. C.

Vitamin-*K* group. I. Synthesis of potassium 2-methyl-1 : 4-naphthaquinone-3-sulphonate. D. A. Bochvar, L. A. Schukina, A. S. Chernyshev, N. G. Semenov, and M. M. Shemiakin. **II. Mechanism of biological action of vitamin-*K* and of its synthetic analogues.** M. M. Shemiakin, L. A. Schukina, and J. B. Shvezov (*J. Amer. Chem. Soc.*, 1943, **65**, 2162—2164, 2164—2167).—I. With $KHSO_3$ in 5% H_2SO_4 and then $K_2Cr_2O_7$, 1 : 2 : 4-O:$C_{10}H_5$Me:O

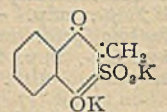
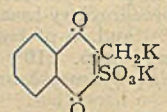

(III.)


(IV.)


(V.)

(**I**) gives >9% of K 2-methyl-1 : 4-naphthaquinone-3-sulphonate (**II**) (cf. Fieser and Fieser, A., 1935, 585; Moore, A., 1941, II, 369). By use of aq. $KHSO_3$ (no acid) at 115—120° and then $K_2Cr_2O_7$ or, better, aq. Cl_2 ~60% of (**II**) is obtained. The reaction mechanism is (**I**)⟶(**III**)⟶(**IV**)⟶(**V**) and thence, by oxidation, (**II**). The change (**IV**) → (**V**) is accelerated by H· or OH′, but for (**I**) the reverse change to (**I**) is accelerated by H· to a greater degree so that the total effect of acid is unfavourable; for 1 : 4-O:$C_{10}H_6$:O (**VI**) the total effect is favourable (cf. *loc. cit.*). (**II**) has only slightly less anti-hæmorrhagic effect than has (**I**) (cf. Moore, *loc. cit.*; Baker *et al.*, A., 1942, II, 285; Menotti, A., 1943, II, 303; a different method of test is used).

II. Biological activity of (**I**) and its derivatives is held to be due to biological degradation to *o*-$C_6H_4(CO_2H)_2$ (**VII**) or its derivatives. (**VII**) and particularly its Et_2 ester and diamide have vitamin-*K* activity. In boiling H_2O (30 hr.) (**I**) (20 g.) gives (**VII**) (0·9 g. isolated as anhydride) and a (?) quinhydrone, m.p. >350°; 1·2 g. of (**VII**) is obtained by boiling aq. KOH (45 min.). In H_2O (5 hr.), (**II**) (20 g.) gives 0·8 g. of (**VII**) and 3·3 g. of a *quinhydrone* (**VIII**), m.p. 243—244° (decomp.) (oxidised to a quinone by Cl_2 and reduced to a quinol by Zn–AcOH). In 25% aq. KOH at room temp., (**II**) gives the yellow K_2 salt (**IX**), which in H_2O rapidly gives (**VII**) and (**VIII**) but by further treatment with 25% KOH gives the orange-red K_2 salt (**X**) and thence, by acid, regenerates (**II**). Generation of

(**IX.**)   (**X.**)

(**VII**) depends on formation of a 2-CHR: derivative, which explains why (**I**), but no other 2-alkyl derivatives, is antihæmorrhagic and why substitution at $C_{(3)}$ usually has little effect. R. S. C.

Perylene and its derivatives. L. A. Zinke, H. Troger, and E. Ziegler (*Ber.*, 1940, **73**, [*B*], 1042—1048; cf. A., 1937, II, 142).—Contrary to Zinke *et al.* (A., 1927, 1190), perylene (**I**), *o*-$C_6H_4(CO)_2O$, and $AlCl_3$ (or $AlCl_3$–NaCl) at 170° give *di*-o-*carboxybenzoylperylene*-A_1, m.p. >360°, and -A_3, sinters from 260°, m.p. 292—296°, o-*carboxybenzoylperylene*-A_2, m.p. 277—278° (sinters 260°), and *diphthaloylperylene*-B_1 (violet-blue vat) and -B_2 (blue-green vat). In boiling $PhNO_2$, -A_3 gives -B_1 and ? a half-cyclised acid; -A_1 gives similarly ? impure -B_2. $(CH_2{\cdot}COCl)_2$, (**I**), and $AlCl_3$ in CS_2 give *γ-keto-γ-3-perylenyl*-n-*butyric acid*, darkens 240°, m.p. 255° (*Br*$_4$-derivative, m.p. 190°; *Me*, m.p. 183°, and *Et* ester, m.p. 168°), converted by Ac_2O into ? 2 : 3-*succinylperylene*. $(CH_2{\cdot}CO)_2O$ and (**I**) give impure products. R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Organ extracts. III. Unsaponifiable lipoids from arteriosclerotic aortas. E. Hardegger, L. Ruzicka, and E. Tagmann (*Helv. Chim. Acta*, 1943, **26**, 2205—2221).—The comminuted material is extracted exhaustively with $COMe_2$ and neutral lipoids result after removal of acids and substances readily sol. in H_2O from the extract. These are hydrolysed successively with $Ba(OH)_2$ and KOH (whereby alterations of the native material are not excluded) and the unsaponified residue is separated into its components by crystallisation and chromatography over Al_2O_3. 370 human aortas yield 127 g. of unsaponifiable matter from which is obtained ~90 g. of cholesterol (**I**) containing (according to $[\alpha]_D$) ~5·6% of dihydrocholesterol. On average 1 aorta contains ~240 mg. of total (**I**) compared with 5—50 mg. in the normal organ. From the residual (**I**)-poor unsaponifiable matter are isolated: $\Delta^{3:5}$-cholestadien-7-one (**II**), m.p. 114—114·5°, $[\alpha]_D$ −299°±5° in $CHCl_3$ (*oxime*, m.p. 176—178°; *semicarbazone*, m.p. 206·5—207·5°); $\Delta^{4:6}$-cholestadien-3-one (**III**), m.p. 79·5—81°, $[\alpha]_D$ +35°±2° in $CHCl_3$ (oxime, m.p. 176—177°); *cholestane*-3(β) : 5 : 6(trans)-*triol* (**IV**), m.p. 244—245° (softens at 227°) (diacetate, m.p. 165—167°), which does not give a colour reaction with $SbCl_3$, $C(NO_2)_4$, or $CCl_3{\cdot}CO_2H$; 7(β)-hydroxycholesterol (**V**), m.p. 188—188·5°, $[\alpha]_D$ −93°±2° in $CHCl_3$ (*dibenzoate*, m.p. 151·5—152·5°); batyl alcohol; unidentified *substance A*, m.p. 301—303°, $[\alpha]_D$ −61°±17° in $CHCl_3$; *substance B*, m.p. 301—301·5°, $[\alpha]_D$ +25·5°±3° in $CHCl_3$; *substance C*, m.p. 79·5—80°, $[\alpha]_D$ ±0°±1° in $CHCl_3$; *substance D*, m.p. 219—221°, $[\alpha]_D$ −66°±3° in $CHCl_3$, saturated towards $C(NO_2)_4$, which gives a red colour with $SbCl_3$ in $CHCl_3$ and a blue colour with $CCl_3{\cdot}CO_2H$ in $CHCl_3$; *substance E*, m.p. 68—69°, $[\alpha]_D$ +17°±4° in $CHCl_3$, which gives a marked yellow-brown colour with $C(NO_2)_4$. Provisionally, the possibility cannot be excluded that (**II**), (**III**), (**IV**), and (**V**) [with the possible exception of (**II**)] do not exist pre-formed in the aortas but are formed during the working up from (**I**). H. W.

Organ extracts. IV. Unsaponifiable lipoids from swine spleen. V. Prelog, L. Ruzicka, and P. Stein (*Helv. Chim. Acta*, 1943, **26**, 2222—2242).—The material is extracted with $COMe_2$ and the extract is treated with hot MeOH into which the bulk of the unsaponifiable matter passes, leaving the fatty acid glycerides undissolved. From the MeOH extract the bulk of the cholesterol (**I**) is separated by crystallisation from $COMe_2$. What remains is hydro-

lysed by NaOH–MeOH and much of the fatty acids are separated as the insol. Ba salts, which retain a considerable proportion of the residual unsaponifiable matter, the removal of which is described. This is then treated with Girard's reagent *T* and the reacted and unchanged portions are chromatographed over Al_2O_3. The following are isolated: Δ^5-cholestene-3(β) : 7(α)-diol [7(α)-hydroxycholesterol], m.p. 168—170°, $[\alpha]_D^{21}$ −12·3°±3° in $CHCl_3$ (dibenzoate, m.p. 170·5°, $[\alpha]_D^{21}$ +97°+5° in $CHCl_3$), which does not give a colour with $C(NO_2)_4$ and with $SbCl_3$, $CCl_3{\cdot}CO_2H$, and Lifschütz reagent gives the colours typical of hydroxycholesterols; Δ^4-cholestene-3(β) : 6-diol, m.p. 254°, $[\alpha]_D^{20}$ +8·4°±4° in C_5H_5N (diacetate, m.p. 132—133°, $[\alpha]_D^{20}$ −12°±3° in $CHCl_3$; dibenzoate, m.p. 181°, $[\alpha]_D^{20}$ −73·0°±2·5° in $CHCl_3$); cholestan-3(β)-ol-6-one, m.p. 128—129°, $[\alpha]_D^{18}$ −13·6°±3° in $CHCl_3$; $\Delta^{3:5}$-cholestadien-7-one, m.p. 114°, $[\alpha]_D^{14}$ −305°±4° in $CHCl_3$; $\Delta^{4:6}$-cholestadien-3-one (oxime, m.p. 173·5—175°); *substance*, $C_{27}H_{46}O_2$, m.p. 155·5—156°, $[\alpha]_D^{19}$ −132°±4° in $CHCl_3$, which gives the colour reactions typical of hydroxycholesterols, gives a *monoacetate*, m.p. 110—111°, $[\alpha]_D^{20}$ −118°±4° in $CHCl_3$, and a *monobenzoate*, m.p. 134—135°, $[\alpha]_D^{20}$ −79°±3° in $CHCl_3$, cannot be pptd. with digitonin, and is oxidised by $Al(OPh)_3$ and $COMe_2$ to $\Delta^{4:6}$-cholestadien-3-one (oxime, m.p. 172—174°); in EtOH it does not exhibit absorption in the ultraviolet; it gives a marked depression of m.p. with Δ^6-cholestene-3 : 5-diol, of which it is very possibly a stereoisomeride; batyl alcohol, m.p. 64·5—65·5°, $[\alpha]_D^{21}$ +5·3°±1·5° in $CHCl_3$ (*bisphenylurethane*, m.p. 98·5—99°); (?) palmitylsphingosine, m.p. 90—91°, $[\alpha]_D^{16}$ ±0°±3° in $CHCl_3$; *compound* A, $C_{27}H_{46-48}O$, m.p. 210—216°, $[\alpha]_D^{17}$ −74·8°±2° in $CHCl_3$, which does not give a yellow colour with $C(NO_2)_4$; *substance* B, $C_{25}H_{48}O_3$, m.p. 200—201°, $[\alpha]_D^{19}$ −5·7°±3° in $CHCl_3$, which does not give the hydroxycholesterol colour reactions or a yellow colour with $C(NO_2)_4$, does not give a ppt. with digitonin, and is not identical with cholestane-3(β) : 5 : 6-(*trans*)-triol or -3(β) : 5 : 6-(*cis*)-triol; *substance* C, m.p. 86—87°, which does not give a yellow colour with $C(NO_2)_4$. As impurities a hydrocarbon, $C_{25}H_{52}$, m.p. 53·5—54°, and friedelin, m.p. 255—259°, are isolated. According to their constitution, all the isolated steroids can be represented as oxidation or transformation products of (I). In this and similar researches it has been found possible to isolate from organ extracts all derivatives of (I) which have been identified from the autoxidation or photo-oxidation of (I). It cannot therefore be decided definitely whether the transformation products of (I) isolated from organ extracts are present as such in the organism or are produced during the working up. The biochemical significance of the isolation of the steroids is therefore very difficult to evaluate. The total result is, however, valuable. Since steroids with 18, 19, and 21 C atoms have only so far been isolated from the sexual tract, the adrenals, and urine, their occurrence appears provisionally to be characteristic of these sources. M.p. are corr. H. W.

Steroids and sex hormones. LXXXVIII. 3(α)-Hydroxy*allo*œtiocholanic acid. P. A. Plattner and A. Fürst (*Helv. Chim. Acta*, 1943, **26**, 2266—2273).—Oxidation of 3(β)-hydroxy*allo*œtiocholanic acid by CrO_3 in AcOH gives 3-keto*allo*œtiocholanic acid (I), m.p. 260—262°, the yield of which is greatly diminished by the simultaneous formation of *isoallo*œtiolithobilianic acid. Similar oxidation of the hydrogenation product of $\Delta^{5:6}$-3(β)-hydroxypregnen-20-one gives 20-*keto*-23-allo*pregnane*-2 : 3-*diacid*, m.p. 219—219·5°, $[\alpha]_D$ +93·8° in $CHCl_3$. Hydrogenation (PtO_2 in AcOH containing HBr at 60°) of (I) gives 3(α)-*acetoxy*allo*œtiocholanic acid*, m.p. 215—218°, $[\alpha]_D$ +50·3° in $CHCl_3$; the *Me* ester (II), m.p. 199—202°, $[\alpha]_D$ +54·5° in $CHCl_3$, is hydrolysed to 3(α)-*hydroxy*allo*œtiocholanic acid* (III), m.p. 281—284°, $[\alpha]_D$ +45·3° in $CHCl_3$ (*Me* ester, m.p. 178—181°, $[\alpha]_D$ +52·6° in $CHCl_3$). Similar hydrogenation of larger quantities of crude (I) gives a product from which cryst. derivatives of (III) cannot be separated. From the ethereal solution of the hydrogenated product separates a substance of high m.p. from which by esterification (CH_2N_2) and chromatography *Me*$_3$ isoallo*œtiolithobilianate*, m.p. 82—83°, $[\alpha]_D$ +47·2° in $CHCl_3$, is isolated. Esterification and acetylation of the more sol. products lead to *Me* allo*œtiocholanate*, m.p. 140—142°, $[\alpha]_D$ +55·4° in $CHCl_3$ (*acid*, m.p. 225—227°, $[\alpha]_D$ +55·8° in $CHCl_3$), and *Me* 3(β)-*bromo*allo*œtiocholanate*, m.p. 135°, $[\alpha]_D$ +59·3° in $CHCl_3$. Me 3(β)-hydroxy- is converted by PBr_3 in boiling C_6H_6 into *Me* 3(α)-*bromo*allo*œtiocholanate*, m.p. 160°, $[\alpha]_D$ +69·8° in $CHCl_3$. *Me* 3(β)-p-*toluenesulphonyloxy*allo*œtiocholanate*, m.p. 147°, $[\alpha]_D$ +80·1° in $CHCl_3$, from the OH-ester and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in dry C_5H_5N at 0° and then at room temp., is converted by anhyd. NaOAc in boiling AcOH into (II) (yield 50%) and *Me* $\Delta^{2:3}$- or $\Delta^{3:4}$-allo*œtiocholenate*, m.p. 129—131°, $[\alpha]_D$ +94·8° in $CHCl_3$, hydrogenated (PtO_2 in AcOH) to Me *allo*œtiocholanate, m.p. 142—144·5°, $[\alpha]_D$ +53·3° in $CHCl_3$. M.p. are corr. H. W.

Bile acids and related substances. XXVIII. 12(α)-Hydroxycholanic acid. M. Sorkin and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 2097—2101; cf., A., 1942, II, 412).—Hydrogenation (Raney Ni–MeOH at 20°) of Me 12-ketocholanate (I) gives a mixture of Me 12(α)- (II) and 12(β)- (III) -hydroxycholanate, partly separated chromatographically, after which (III) can be caused to crystallise. Crude (II) is hydrolysed to 12(α)-*hydroxycholanic acid* (IV), m.p. 109—115°, $[\alpha]_D^{12}$ +37·9°±2° in $COMe_2$, also obtained by treating Me 3-keto-12(α)-acetoxycholanate with $N_2H_4{\cdot}H_2O$ and NaOEt–EtOH at 180°. 12(β)-Hydroxycholanic acid has $[\alpha]_D^{12}$ +43·5°±2° in $COMe_2$. The constitution of (IV) is established by methylation (CH_2N_2) followed by oxidation (CrO_3 in AcOH at room temp.) to (I). Substitution of NaOH–MeOH for pure MeOH in the hydrogenation of Me 3(α)-hydroxy-12-ketocholanate so favours the production of 3(α) : 12(α)-dihydroxycholanic acid that the greater part of it can be separated pure by two crystallisations; a simplified method is described for the separation of the remainder of it from deoxycholic acid. M.p. are corr. (block); limit of error ±2°. H. W.

Steroids and sex hormones. LXXXIX. Simple digitaloid lactones with *allo*cholane configuration. P. A. Plattner, L. Ruzicka, and A. Fürst (*Helv. Chim. Acta*, 1943, **26**, 2274—2278).—3(α)-Acetoxy-*allo*œtiocholanic acid is converted by $SOCl_2$ in boiling C_6H_6 into the chloride, which with CH_2N_2 in C_6H_6–Et_2O at −10° affords 21-*diazo*-3(α)-*acetoxy*allo*pregnan*-20-*one*, decomp. 156—158°, $[\alpha]_D$ +141·6° in $CHCl_3$, converted by AcOH at 100° into 3(α) : 21-*diacetoxy*allo*pregnan*-20-*one*, m.p. 165°, $[\alpha]_D$ −92·1° in $CHCl_3$. This is converted by Zn and $CH_2Br{\cdot}CO_2Et$ in C_6H_6–dioxan followed by treatment with boiling dil. HCl and Ac_2O–C_5H_5N at room temp. into 20 : 21-*dihydroxy*-3(α)-*acetoxynor*allo*cholanolactone* (I), m.p. 255° (loss of H_2O), $[\alpha]_D$ +56° in $CHCl_3$. (I) is converted by prolonged boiling with Ac_2O into $\Delta^{20:22}$-21-*hydroxy*-3(α)-*acetoxy*-, m.p. 230°, $[\alpha]_D$ +19° in $CHCl_3$, and thence by 2N-HCl in dioxan at 100° into $\Delta^{20:22}$-3(α) : 21-*dihydroxy*-, m.p. 243—244° $[\alpha]_D$ +10° in $CHCl_3$, -*nor*allo*cholenolactone*. 3(β)-Acetoxy*allo*œtiocholanic acid similarly gives 21-diazo-3(β)-acetoxy*allo*pregnan-20-one, m.p. 131—132°, $[\alpha]_D$ +134·4° in $CHCl_3$, which gives 3(β) : 21-diacetoxy*allo*pregnan-20-one, m.p. 151—152·5°, $[\alpha]_D$ +80·8° in $CHCl_3$, converted into $\Delta^{20:22}$-21-*hydroxy*-3(β)-*acetoxynor*allo*cholenolactone*, m.p. 193—194°, $[\alpha]_D$ +1° in $CHCl_3$. Likewise *allo*œtiocholanic acid yields 21-*diazo*allo*pregnan*-20-*one*, m.p. 120—121° (decomp.), $[\alpha]_D$ +151·3° in $CHCl_3$, which gives successively 21-*acetoxy*allo*pregnan*-20-*one*, m.p. 200°, $[\alpha]_D$ +101·8° in $CHCl_3$, and $\Delta^{20:22}$-21-*hydroxynor*allo*cholenolactone*, m.p. 170°, $[\alpha]_D$ +1·3° in $CHCl_3$. M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. Ætiocholane-3(α) : 12(β)-diol-17-one. H. Reich and T. Reichstein (*Helv. Chim. Acta*, 1943, **26**, 2102—2109).—Me 3(α) : 12(β)-diacetoxycholanate is oxidised by CrO_3 in AcOH at ~75° and the product is divided into acidic (I) and neutral (II) portions. Direct crystallisation of (II) leads to the removal of unchanged material and the residue is hydrolysed by alkali. The acids thus isolated contain some deoxycholic acid and a *lactone*, $C_{25}H_{38}O_5$, m.p. 285—288°, which is probably a monoacetate corresponding to the lactone obtained by Miescher *et al.* (A., 1939, II, 160) by the oxidation of cholesteryl acetate dibromide and is converted by energetic acetylation into a *diacetate*, $C_{27}H_{40}O_6$, m.p. 271—274°. The relatively small amounts of neutral, unsaponifiable substances are treated with Girard's reagent *T*, thus leading to the isolation of pregnane-3(α) : 12(β)-diol-20-one (identified as the diacetate) and ætiocholane-3(α) : 12(β)-diol-17-one (*diacetate*, m.p. 162—162·5°, $[\alpha]_D^{15}$ +176·0°±2°, $[\alpha]_{5461}^{15}$ +213·7°±2° in $COMe_2$). (I) is completely hydrolysed, methylated (CH_2N_2), and fractionally hydrolysed whereby Me 3(α) : 12(β)-diacetoxyætiocholanate is largely unaffected. All the yields are very poor. M.p. are corr. (block); limits of error ±2°. H. W.

D-Homosteroids.—See B., 1944, III, 33, 34.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Characterisation of carboxylic acids by carbodi-imides. X. Optically active carbodi-imides. F. Zetzsche and A. Fredrich (*Ber.*, 1940, **73**, [*B*), 1114—1123).—*l*-Menthylamine (I) and CS_2 in PhMe at ~50° and then the b.p. give 83% of *s*-di-*l*-menthylthiocarbamide, m.p. 201°, $[\alpha]_D$ −125·6° in $CHCl_3$ (in this and other cases), converted by HgO in CS_2 at room temp. into *carbodi*-l-*menthylimide*, $C(:NR)_2$ (82%), b.p. 213—215°/14 mm., $[\alpha]_D$ −101·4°, which gives no ureides. *p*-$NMe_2{\cdot}C_6H_4{\cdot}NCS$ (II) and (I) in Et_2O at room temp. give N-p-*dimethylaminophenyl*-N′-l-*menthylthiocarbamide* (87%), m.p. 149—150°, $[\alpha]_D$ −80·3°, and thence N-p-*dimethylaminophenyl*-N′-l-*menthylcarbodi-imide* (III) (67%), m.p. 50—52°, $[\alpha]_D$ −70·3°. With HCO_2H in Et_2O, (III) gives N-p-*dimethylaminophenyl*-N′-l-*menthylcarbamide*, m.p. 229—230°, $[\alpha]_D$ −62·9°, and with stearic acid in C_5H_5N at 100° or, in other cases, RCO_2H in Et_2O at room temp. gives N-*stearoyl*-, m.p. 115—116°, $[\alpha]_D$ −33·2°, N-*benzoyl*-, m.p. 115—116°, $[\alpha]_D$ −55·0°, N-p-*bromobenzoyl*-, m.p. 216—218°, $[\alpha]_D$ −48·8°, N-*cinnamoyl*- m.p. 148—149°, $[\alpha]_D$ −59·7°, and N-*piperoyl*-N- (or N′-)p-*dimethylaminophenyl*-N′- (or N-)l-*menthylcarbamide*, m.p. 190—192°. Bornylamine hydrochloride (IV), $[\alpha]_D$ −5·3°, gives similarly *s*-dibornylthiocarbamide (55%), sinters 225°, m.p. 227—228°, $[\alpha]_D$ −19·4°, and thence *carbodibornylimide* (84%), m.p. 229—231°, which gives N-*benzoyl*-NN′-*dibornylcarbamide*, sinters 148°, m.p. 150—152° (but no other urcide), and with AcOH or $H_2C_2O_4$ in dioxan gives dibornylcarbamide, sublimes from 300°, decomp. ~345° (lit. sublimes >290°). The base from (IV)

with (II) gives N-p-*dimethylaminophenyl*-N'-*bornylthiocarbamide*, m.p. 181°, $[\alpha]_D$ −11·1°, and thence the *carbodi-imide*, m.p. 31—34°, b.p. 203—204°/0·12 mm., $[\alpha]_D$ −11·9°, which yields, as above, N-p-*dimethylaminophenyl*-N'-*bornylcarbamide*, m.p. 199—200°, and the *CHMeBr·CO*, m.p. 139—140°, *Bz*, m.p. 137—138°, and *cinnamoyl* derivatives, m.p. 139—140°, thereof. *s*-Di*cyclo*hexylthiocarbamide, m.p. 180—181°, is obtained in 95·8% yield from the base and CS_2 in PhMe. N'-cyclo*Hexyl*-N-p-*dimethylaminophenylthiocarbamide* (prep. as above; 92% yield), m.p. 131—132°, gives the *carbodi-imide*, b.p. 175—176°/0·6 mm., *carbamide* (VI), m.p. 187—188°, and the *crotonyl*, m.p. 107—108°, *stearoyl*, m.p. 80—81°, *CHMeBr·CO*, m.p. 138—139°, *CHEtBr·CO*, m.p. 120—121°, *Bz*, sinters 140°, m.p. 141—142°, and *cinnamoyl* derivative, m.p. 160—161°, thereof. Similarly are prepared $CS(NH{\cdot}CH_2Ph)_2$ (95·4% yield) and *carbodibenzylimide* (VII) (76%), b.p. 208—210°/18 mm., which is unstable and gives a *dimer*, m.p. 102—103° [reacts more slowly than does (VII)]. In C_5H_5N at 100° (VII) with BzOH gives *benzoyl*-NN'-*dibenzylcarbamide*, m.p. 98—99°, but with AcOH or *n*-$C_5H_{17}{\cdot}CO_2H$ gives $CO(NH{\cdot}CH_2Ph)_2$, m.p. 166—167°. N-p-*Dimethylaminophenyl*-N'-*benzylthiocarbamide* has m.p. 127—128°. With $CH_2{:}CH{\cdot}CO_2H$, α-bromopalmitic acid, or $CHMeBr{\cdot}CH_2{\cdot}CO_2H$, (V) gives only (VI). No ureide is obtained from (III) by $CHMeBr{\cdot}CO_2H$, $CHEtBr{\cdot}CO_2H$, $C_{14}H_{29}{\cdot}CHBr{\cdot}CO_2H$, or $CHMeBr{\cdot}CH_2{\cdot}CO_2H$. Formation of ureides thus depends on the nature of both the acid and carbodi-imide (cf. C., 1944, Part 2). R. S. C.

ω-Nitrocamphene. P. Lipp, H. Bräucker, and H. Sauer [with, in part, J. Gerdes] (*Ber.*, 1940, **73**, [*B*], 1146—1150; cf. A., 1940, II, 136).—Reduction of ω-nitrocamphene (I) with Zn dust and AcOH gives mainly tricyclal (II) containing a small proportion of camphenilanealdehyde, separated from (II) as its enol acetate and identified by oxidation to *iso*camphenilanic acid (III), m.p. 117·5—118·5° (corr.). In addition to (II) and in the ratio ~3 : 1 there is produced 2-acetoxy*apo*camphanealdehyde [*semicarbazone*, m.p. 216·5—217·5° (corr.)], readily converted by air and more readily by other oxidising agents into 2-acetoxy*apo*camphanecarboxylic acid, m.p. 121—122° (corr.) [corresponding *chloride*, b.p. 111—113°/0·3 mm., m.p. ~60°, and *amide*, m.p. 99—100° (corr.)]. This is hydrolysed to 2-hydroxy*apo*camphanecarboxylic acid, m.p. 225—226° (lit. m.p. 237°), which is oxidised ($KMnO_4$–KOH) to ketopinic acid, m.p. 232·5—234° (corr.). The non-carboxylic compounds contain essentially the two *iso*camphanols, removed as the *p*-nitrobenzoates, which are only partly separable from one another by crystallisation (small amounts of a p-*nitrobenzoate*, m.p. 148—149°, are isolated); the alcohols from the remaining mixture of *p*-nitrobenzoates are oxidised to (III). The nitrile, b.p. 93·5—96°/8 mm., of (III) or camphenilanic acid is indifferent towards *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$. In contrast to the complete change in system caused by additions to (I) in strongly acid solution the *iso*camphane skeleton is changed only in part and in part remains intact in a slightly acid medium. H. W.

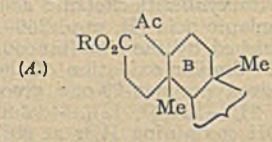
Rearrangement of camphorquinone. I. Formation and reactions of the inactive modifications of 2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid. R. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **20**, 301—306).—Synthetic camphor is oxidised with SeO_2 to *dl*-camphorquinone (cf. Evans *et al.*, A., 1934, 299), which with conc. H_2SO_4 gives dl-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylic acid* (I), m.p. 109° (cf. *d*-acid, Manasse and Samuel, A., 1898, i, 147; 1903, i, 45; Bhagvat and Simonsen, A., 1927, 250) [*monohydrate*, m.p. 73—74°; *semicarbazone*, m.p. 230—231°; *Me* ester, b.p. 100°/4 mm.; *Et* ester (II), b.p. 120°/6 mm.]. Clemmensen reduction of (I) gives 1 : 2 : 2-*trimethyl*cyclo*hexane*-3-*carboxylic acid*, b.p. 118°/5 mm. (p-*phenylphenacyl ester*, m.p. 114°), the *Me* ester, b.p. 95°/12 mm., of which when dehydrogenated by Se at 340° in a sealed tube for 28 hr. gives *o*-xylene and *o*-xylene-3-carboxylic acid. Treatment of (II) with $Et_2C_2O_4$ and NaOEt gives an oxalyl derivative, which loses CO on heating to yield *Et*$_2$ 2 : 3 : 3-*trimethyl*cyclo*hexan*-1-*one*-4 : 6-*dicarboxylate* (III), b.p. 155°/6 mm. (violet colour with $FeCl_3$–EtOH), which in a closed tube with NaOEt at 150—200° for 24 hr. gives *Et*$_3$ *αββ-trimethylpentane-αγε-tricarboxylate*, b.p. 160°/4 mm. (no colour with $FeCl_3$–EtOH). Treatment of this with Na and C_6H_6 regenerates (III), hydrolysis of which with either KOH–H_2O–EtOH or dil. HCl re-forms (I). S. A. M.

New derivatives of 4-phenylcamphor. S. S. Nametkin and T. V. Scheremeteva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 131—134).—4-Phenyl- (I) and 4-*p*-aminophenyl-camphor (II) (*Ac* derivative, m.p. 181—184°) are prepared by modified methods. (I) and 100% H_2SO_4 at 35—40° give 4-p-*sulphophenylcamphor*, m.p. 189—190° (*Ba*, +6H_2O, and *Pb* salt, +8H_2O). 4-p-*Hydroxyphenylcamphor*, m.p. 125°, is obtained by decomp. of the aq. diazonium solution from (II) at room temp. (I) and $HCO_2C_5H_{11}$-*iso* + Na yield 4-*phenyl*-3-*hydroxymethylenecamphor* (III), m.p. 50—54° (*Bz* derivative, m.p. 149—150°), converted by prolonged action of aq. AcOH at room temp. into 3-*aldehydo*-4-*phenylcamphor*, m.p. 91—95° (does not give a Bz derivative). 4-Phenylcamphorquinone, m.p. 142—143°, is obtained from (III) and 1% $KMnO_4$ in cold dil. alkali, and 4-*p*-nitrophenylcamphor and SeO_2–Ac_2O afford 4-p-*nitrophenylcamphorquinone*, m.p. 137°. A. T. P.

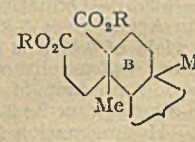
A tricyclic compound obtained by the di-inene double-addition reaction.—See A., 1944, II, 101.

Triterpenes. LXXXII. Degradation of diacetoxynorlupanone and acetylbetulic acid to acetoxybisnorlupandicarboxylic acid. L. Ruzicka and E. Ray (*Helv. Chim. Acta*, 1943, **26**, 2143—2151).—Diacetoxynorlupanone (A., 1941, II, 71) in C_5H_5N is partly hydrolysed by KOH–EtOH at room temp. to *dihydroxynorlupanone 2-acetate*, m.p. 293°, $[\alpha]_D$ −7°, oxidised by CrO_3 in AcOH at room temp. to *acetoxynorlupanonic acid* (I), m.p. 253°, $[\alpha]_D$ −10°. The corresponding *Me* ester (II), m.p. 235°, $[\alpha]_D$ −16°, is partly hydrolysed to Me norlupanolonate, m.p. 253°, $[\alpha]_D$ −45°, identical with the product obtained by Ruzicka *et al.* (A., 1941, II, 72) by the oxidation of Me acetylbetulate, the constitution of which is thereby established. (I) is hydrogenated (PtO_2 in AcOH) to *acetylnorlupandiolic acid*, m.p. 289°, $[\alpha]_D$ +10°, which could not be lactonised. (II) is oxidised by SeO_2 in hot AcOH to *Me acetoxynorluponalonate*, m.p. 184°, $[\alpha]_D$ −16°, further oxidised by 30% H_2O_2 in boiling AcOH and then esterified to *Me acetoxybisnorlupandicarboxylate* (III), m.p. 182°, $[\alpha]_D$ −13°. Acetylbetulic acid is oxidised by SeO_2 in boiling AcOH to *acetyl-lupenalolic acid*, m.p. 295°, $[\alpha]_D$ +11°, which does not give a yellow colour with $C(NO_2)_4$ and yields a yellow solution in conc. H_2SO_4 which rapidly becomes red. It is oxidised by CrO_3 in AcOH to *acetylbisnorlupanoldicarboxylic anhydride*, m.p. 352°, $[\alpha]_D$ +32°, *acetyl-lupenoldicarboxylic acid*, m.p. ~300°, $[\alpha]_D$ +14°, which does not give a colour reaction with $C(NO_2)_4$, and (after esterification) (III). Hydrolysis of (III) by KOH–MeOH gives *Me*$_2$ *hydroxybisnorlupandicarboxylate*, m.p. 210°, $[\alpha]_D$ −13°, and the corresponding *Me*$_1$ ester, m.p. 296°. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$ (*l* = 1). The experiments further confirm the presence of the *iso*propenyl group in the C skeleton of betulin. The formulation of lupane derivatives by Jones *et al.* (A., 1942, II, 60) and Kon *et al.* (*ibid.* 60) is criticised adversely. H. W.

Triterpenes. LXXXIII. Oxidative degradation of rings A and B in hederagenin. L. Ruzicka, J. Norymberski, and O. Jeger (*Helv. Chim. Acta*, 1943, **26**, 2242—2250).—Repetition of the work of Kitasato *et al.* (A., 1932, 1035; 1933, 612) confirms the composition of the hydroxytetracarboxylolactone Me_3 ester $C_{30}H_{46}O_8$ (I) and thus brings indirect evidence of the attachment of $C_{(30)}$ of the oleanolic acid skeleton to C of the ring. Hederagenin is converted by 33% HBr–AcOH into diacetylhederageninlactone, m.p. 248—248·5°, hydrolysed by KOH–EtOH to hederageninlactone (II), m.p. 358—360° (high vac.). Hederageninbromolactone is oxidised by CrO_3 in AcOH containing a little conc. H_2SO_4 to (?) hedragonebromolactone and acidic products, debrominated (Zn dust in AcOH) and then converted by HBr–AcOH into hedragenone dicarboxylolactone, m.p. 266—267°, $[\alpha]_D$ +23·7° (Me_2 ester, m.p. 199—200°, $[\alpha]_D$ +28·5°). (II) is oxidised by CrO_3 in boiling AcOH to hedragonclactone, m.p. 309—310° (vac.), $[\alpha]_D$ +44·0, and the ketohydroxydicarboxylolactone (III) (*A*; R = H), m.p. 263—264°. The corresponding Me ester is oxidised by CrO_3 and H_2SO_4–AcOH and



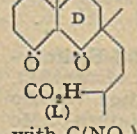
(*A.*)



(*B.*)

the product is dissolved in Et_2O which is extracted successively with aq. $KHCO_3$ and Na_2CO_3. The former extract gives (III), sparingly sol. in Et_2O, and the hydroxycarboxylolactone (*B*; R = H), m.p. 238—239°, converted by CH_2N_2 in Et_2O–$CHCl_3$ into the *Me*$_2$ ester, m.p. 170—170·5°, and passing when heated at 240—250°/high vac. into the *pyroketone*, $C_{27}H_{40}O_3$, m.p. 288—289° (high vac.), $[\alpha]_D$ +152°. The portion of the $KHCO_3$ extract which is freely sol. in Et_2O after esterification with CH_2N_2 affords (I), m.p. 199—200°, $[\alpha]_D$ −16·6°. The Na_2CO_3 extract yields (III). M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.

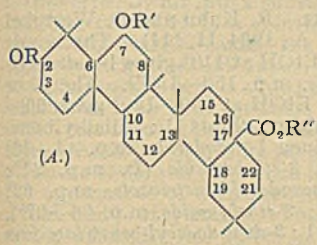
Triterpenes. LXXXIV. New evidence of the different position of the carboxyl group in oleanolic and glycyrrhetic acid. L. Ruzicka, O. Jeger, and W. Ingold (*Helv. Chim. Acta*, 1943, **26**, 2278—2282).—Energetic oxidation of oleanolic and deoxoglycyrrhetic acid with SeO_2 gives dienedione derivatives converted by CrO_3 into oxides, which when treated drastically with alkali suffer fission of ring E with production of different acids. This behaviour is not compatible with the formulation of Kon *et al.* (A., 1942, II, 148, 418), according to which only one acid should be produced. Me $\Delta^{10:11\cdot13:18}$-2-acetoxyoleadiene-12 : 19-dione-20-carboxylate is oxidised by CrO_3 in AcOH at 90° and then at room temp. to *Me* $\Delta^{10:11}$-13 : 18-*oxido*-2-*acetoxyoleanene*-12 : 19-*dione*-20-*carboxylate*, m.p. 282—283°, $[\alpha]_D$ +86° in $CHCl_3$, which is transformed by 10% KOH at 200° into the *nor-acid* (I), m.p. 241°, $[\alpha]_D$ +101° in C_5H_5N, +131° in $COMe_2$ (non-cryst. *Me* ester), which gives a marked enol reaction with $FeCl_3$ in EtOH and a yellow colour with $C(NO_2)_4$. M.p. are corr. H. W.



(I.)

Triterpenes. LXXXV. Sumaresinolic acid. L. Ruzicka, O. Jeger, A. Grob, and H. Hösli (*Helv. Chim. Acta*, 1943, **26**, 2283—

2300).—Sumaresinolic acid (**I**) belongs to the oleanolic acid (**II**) group and, like hederagenin, siaresinolic and echinocystic acid, to the sub-group of hydroxyoleanolic acids. The position of 1 OH in (**I**) is not definitely assigned but it must be attached to $C_{(7)}$ or $C_{(8)}$ in ring B. In formula *A* (R = R′ = R″ = H) OH is placed arbitrarily at $C_{(7)}$; $C_{(8)}$ cannot be excluded. In the following formulæ *x* indicates 7 or 8. The relationship of (**I**) to (**II**) is established by chemical reactions and comparison of $[\alpha]_D$ for analogous derivatives of the acids. Extraction of Sumatra gum benzoin with boiling EtOH and treatment of the extract with NaOH leads through the Na salt (**III**) to (**I**), m.p. 298°, $[\alpha]_D$ +54·0°, converted by CH_2N_2 in Et_2O at 0° into the Me ester (**IV**), m.p. 220—221°, $[\alpha]_D$ +46·7°, also obtained from (**III**) and Me_2SO_4 and hydrolysed with great difficulty (Claisen solution at 200° for 12 hr.) to (**I**). The Et ester has m.p. 212°, $[\alpha]_D$ +44·7°. (**IV**) is transformed by Ac_2O in C_5H_5N at room temp. into *Me* 2-*acetylsumaresinolate* (**V**), m.p. 227°, $[\alpha]_D$ +40·6°, converted by mild alkaline hydrolysis into (**IV**). *Et* 2-*acetylsumaresinolate* has m.p. 231°. Passage of HCl into a solution of (**V**) in AcOH at room temp. affords *Me* 2-*acetylanhydrosumaresinolate*, m.p. 174—175°, $[\alpha]_D$ +48°, obtained analogously but in poorer yield from (**IV**). *Me diacetylsumaresinolate* (**VI**), m.p. 258°, $[\alpha]_D$ +25·3°, is obtained from HCl, Ac_2O, and (**V**) at 100° and subsequently at room temp. or from (**V**) and BF_3–Et_2O in Ac_2O at room temp. Mild hydrolysis converts (**VI**) into *Me* x-*acetylsumaresinolate*, m.p. 134—135° (loss of MeOH of crystallisation and softening ~100°), $[\alpha]_D$ +48·0°, reacetylated by Ac_2O in C_5H_5N at room temp. to (**VI**) and drastically hydrolysed to (**IV**). (**I**) is oxidised by CrO_3 in AcOH at room temp. to $\Delta^{12:13}$-x-*keto*-2-*hydroxyoleanene*-28-*carboxylic acid* (**VII**), m.p. 286—287°, $[\alpha]_D$ +31·6°, converted by Ac_2O in C_5H_5N into a mixed *anhydride*, $C_{34}H_{50}O_7$, m.p. 312°, of the ketoacetoxy-acid and AcOH, which is well adapted to the isolation of homogeneous (**VI**). *Me* $\Delta^{12:13}$-x-*keto*-2-*hydroxysumaresenecarboxylate* (**VIII**), m.p. 205—206°, is obtained analogously from (**IV**) or from (**VI**) and CH_2N_2. (**V**) is oxidised by CrO_3 to *Me* $\Delta^{12:13}$-x-*keto*-2-*acetoxyoleanene*-28-*carboxylate* (**IX**), m.p. 285—286°, $[\alpha]_D$ +44·9°, converted by mild hydrolysis into (**VIII**), which is reacetylated to (**IX**) and by drastic hydrolysis gives (**VII**). It appears to be unchanged by N_2H_4,H_2O and NaOEt–EtOH at 210—220° but is quantitatively reduced (Clemmensen) to the 13 : 28-*lactone* of x-*keto*-13-*hydroxy*-2-*acetoxyoleanane*-28-*carboxylic acid* (**X**), m.p. 324—326° (high vac.), $[\alpha]_D$ +4·6°. Gradual addition of Br–$CHCl_3$ to (**IX**) in boiling $CHCl_3$ leads to a *compound*, $C_{33}H_{49}O_5Br$, m.p. 215—225° (decomp.), $[\alpha]_D$ +38·6°, and an isomeric *Br-ketone*, m.p. 293—294·5°, $[\alpha]_D$ +81°; both substances give a yellow colour with $C(NO_2)_4$. Prolonged contact of (**IX**) with 33% HBr–AcOH at room temp. gives (**X**), hydrolysed by alkali to the 2 : 13-(*OH*)$_2$-derivative, m.p. >370°. (**X**) is oxidised by SeO_2 in dioxan at 200—210° to an acidic substance and the 13 : 28-*lactone* of enol-7 : 8-diketo-13-hydroxy-2-acetoxyoleanane-28-carboxylic acid, m.p. 265—267°, $[\alpha]_D$ −30°, which could not be acetylated by Ac_2O in C_5H_5N or by Ac_2O and the BF_3–Et_2O complex, and is hydrolysed by boiling 5% KOH–MeOH to the corresponding 2-*OH*-derivative, m.p. 325—327°, into which it is re-converted by Cu_2O–BF_3–Et_2O. Slow oxidation of (**IV**) by CrO_3 and H_2SO_4 in AcOH at room temp. affords *Me* $\Delta^{12:13}$-2 : x-*diketo-oleanene*-28-*dicarboxylate*, m.p. 190—191° after loss of MeOH of crystallisation at 110—114°, $[\alpha]_D$ +35·2° [*oxime*, m.p. 265—267° (decomp.); *semicarbazone*, m.p. 257—258° (decomp.)], which gives a marked yellow colour with $C(NO_2)_4$. The non-cryst. *Me* $\Delta^{12:13}$-2-keto-*x*-acetoxyoleanene-28-carboxylate, obtained analogously from the 2-OH-compound, gives an *oxime*, m.p. 151—152° (decomp.), and a *semicarbazone*, m.p. 216—218° (decomp.). (**VI**) is oxidised by SeO_2 in boiling AcOH to *Me* $\Delta^{12:13-18:19}$-2 : x-*diacetoxyoleadiene*-28-*carboxylate*, m.p. 234—235° $[\alpha]_D$ −156·0°, which gives a brown colour with $C(NO_2)_4$; in dioxan at 200° the product is *Me* $\Delta^{10:11-13:18}$-12 : 19-*diketo*-2 : x-*diacetoxyoleadiene*-28-*carboxylate* (**XI**), m.p. 230—231°, $[\alpha]_D$ −189° (a second *modification*, m.p. 211°, is sometimes obtained), which does not give a yellow colour with $C(NO_2)_4$ and is hydrolysed by very prolonged boiling with 10% KOH–MeOH to $\Delta^{10:11-17:18}$-12 : 19-*diketo*-2 : x-*dihydroxy*-28-*noroleadiene* (**XII**), m.p. 300—302°, $[\alpha]_D$ +228° (2-*acetate*, m.p. 264°, $[\alpha]_D$ +212°), and $\Delta^{10:11-13:18}$-12 : 19-diketo-2 : x-dihydroxyoleadiene-28-carboxylic acid, which passes in boiling xylene into (**XII**). (**XI**) is transformed by boiling 5% HCl–MeOH into *Me* $\Delta^{10:11-13:18}$-12:19-*diketo*-2-*hydroxy*-x-*acetoxyoleadiene*-28-*carboxylate*, m.p. 310—312°, which does not give a yellow colour with $C(NO_2)_4$. With N_2H_4,H_2O in EtOH at 200° (**XII**) gives a *pyridazine* derivative, $C_{29}H_{42}O_2N_2$, decomp. ~350°, $[\alpha]_D$ +283°. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$. H. W.



Triterpene resinols and related acids. XV. Dehydration of α-amyrin and α-amyradienol with phosphoric oxide : *l*-α-amyradiene and *l*-α-amyratriene. E. S. Ewen, A. E. Gillam, and F. S. Spring (*J.C.S.*, 1944, 28—30).—Dehydration of α-amyrenonol with AcOH–HI gives α-*amyradienone*-III, m.p. 179°, $[\alpha]_D^{20}$ +170°. α-Amyradienol (I) with PCl_5 yields α-*dichloroamyradiene*, m.p. 128—129°, $[\alpha]_D^{21}$ +407°, which with AcOH–Zn affords d-α-*amyratriene*, m.p. 131—133°, $[\alpha]_D$ +439°. Dehydration of (**I**) with P_2O_5 leads to l-α-*amyratriene*, m.p. 140—142°, $[\alpha]_D^{20}$ −450°, which contains a conjugated triene system (absorption spectrum). The ethenoid linking of α-amyrin must consequently be situated in the vicinity of the OH. All rotations are in $CHCl_3$. F. R. S.

Chemical composition of *Calotropis gigantea*. I. Wax and resin components of the latex. P. B. R. Murti and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1943, **18, A**, 145—159).—The latex of *C. gigantea* is converted by EtOH into a soft coagulum (*A*) and an aq. alcoholic solution (*B*). (*A*) is transformed by successive extractions with boiling EtOH and Et_2O into a sticky solid which has not been investigated completely, a small amount of a substance, m.p. 248—250°, and a residue which is hydrolysed to AcOH and $Pr^{\beta}CO_2H$ and mixtures of resinols which are separated into their components by acetylation or benzoylation followed by fractional crystallisation. Thus are obtained : α-*calotropeol* (**I**), $C_{30}H_{50}O$, m.p. 204—205°, $[\alpha]_D^{32}$ +102·0° in C_6H_6 (*acetate*, m.p. 250—251°, $[\alpha]_D^{30}$ +98·0° in C_6H_6; *benzoate*, m.p. 273—274°, $[\alpha]_D$ +743° in C_6H_6), which gives a bright pink solution immediately with the Liebermann–Burchard reagent, an orange-yellow solution with deep green fluorescence with Salkowski's reagent, and appears to contain one double linking; β-*calotropeol*, $C_{30}H_{50}O$, m.p. 216—217° (*benzoate*, m.p. 279—280°, $[\alpha]_D^{33}$ +69·0° in C_6H_6; *acetate*, m.p. 238°, $[\alpha]_D^{30}$ +43·9°), which resembles (**I**) in its colour reactions; a mixture of β-amyrin and tetracyclic resinols. (*B*) yields to Et_2O–$CHCl_3$ a cryst. substance (? mixture), m.p. ~242°, indicated by its colour reactions and solubility to belong to the cardiac poisons and containing N and S; CaC_2O_4 is also present in very fine subdivision. H. W.

VI.—HETEROCYCLIC.

Additive compounds of organo-magnesium derivatives with furanoid compounds. E. Cherbuliez and M. K. Araqui (*Helv. Chim. Acta*, 1943, **26**, 2251—2252).—Coumarone, coumaran, diphenylene oxide (**I**), or methylcodeine (**II**) in C_6H_6 is added to MgMeI, MgEtBr, MgPhBr, or $CH_2Ph{\cdot}MgCl$ in Et_2O. The Et_2O is distilled off and the residual solution is boiled for 0·5—2 hr., whereby the additive *compound* is gradually pptd., usually almost quantitatively. Substitution of C_6H_6 by PhMe does not alter the change. Substances closely allied to (**II**) such as thebaine and deoxycodeine react with organo-magnesium compounds in Et_2O with rupture of the furanoid ring. (**I**) is obtained in 28% yield by heating PhOH with PbO at 170° until H_2O ceases to be evolved and then distilling the product rapidly with a free flame. H. W.

Transformation products of simpler benzopyrylium compounds. P. Karrer, C. Trugenberger, and G. Hamdi (*Helv. Chim. Acta*, 1943, **26**, 2116—2120; cf. A., 1943, II, 101; Pratt *et al.*, *J.C.S.* 1923, **123**, 745).—3 : 4′-Dimethoxy-2-phenylbenzopyrylium ferrichloride (**I**), m.p. 150—151° (lit. 135°), is obtained directly by passing HCl into a solution of *o*-OH·C_6H_4·CHO (**II**) and *p*-OMe·C_6H_4·$CO{\cdot}CH_2{\cdot}$OMe (**III**) in abs. EtOH; the corresponding *chloride* (**IV**), m.p. 109°, is almost quantitatively obtained by passing HCl into (**II**) and (**III**) in AcOH. (**I**) is transformed by hot MeOH containing NaOAc into the *Me ether* (**V**) of the carbinol base, m.p. 149°, more readily prepared from (**IV**) and cold MeOH; the corresponding *Et ether* has m.p. 132°. (**V**) and BzO_2H in $CHCl_3$ give 2 : 3 : 4′-*trimethoxyflavanone*, m.p. 220°, hydrolysed (HCl in boiling aq. MeOH) to 4′-methoxyflavanol, m.p. 230° (lit. 225°). (**V**) and Br in $CHCl_3$ afford 3 : 4′-*dimethoxy*-2-*phenylbenzopyrylium perbromide*, m.p. 143°, reconverted into (**V**) by MeOH. COPh·CH_2·OMe and (**II**) in anhyd. HCO_2H saturated with dry HCl at room temp. give 3-*methoxy*-2-*phenylbenzopyrylium chloride*, m.p. 119° (corresponding *perbromide*, m.p. 122°), converted by H_2O into the corresponding carbinol *base*, m.p. 121°, which in hot EtOH smoothly gives the *Et ether*, m.p. 124°. H. W.

Reaction between quinones and metallic enolates. Mechanisms.—See A., 1944, II, 103.

1 : 3-Dioxans.—See B., 1944, II, 35.

***lin.*-Dibenzothionaphthen in coal tar.** O. Kruber and L. Rappen (*Ber.*, 1940, **73**, [*B*], 1184—1186).—The solid residue obtained from the C_5H_5N mother-liquors used in the purification of chrysene from coal tar are extracted with EtOH containing 10% of xylene. The undissolved material is oxidised by 30% H_2O_2 in AcOH at 100° to dibenzothionaphthen sulphone (**I**), m.p. 231°, thus establishing the presence of *lin.*-dibenzothionaphthen (**II**) in coal tar. Successive addition of S and $AlCl_3$ to 2-$C_{10}H_7$Ph at 110° and subsequent heating of the mixture to 200° give a product from which (**I**) can be obtained by oxidation but from which (**II**) could not be isolated. Brasan is transformed by molten KOH at 280—320° into 3-*hydroxy*-2-*o*-*hydroxyphenylnaphthalene*, converted into (**II**), m.p. 160° (picrate, m.p. 128°), by distillation with P_2S_5 in a vac. The distillate contains also a substance which is oxidised (H_2O_2 in AcOH) to a *sulphone*, m.p. 264°. H. W.

Piperidine derivatives.—See B., 1944, II, 35.

Iron derivatives of heterocyclic acids. I. Ferric complexes of chelidamic acid. J. H. Gorvin (*J.C.S.*, 1944, 25—28).—Picolinic acid and $Fe(OH)_3$ give *tripicolinato-iron* (+H_2O), decomp. 282° (corr.), and *di-(4-chloropicolinato)hydroxo-iron*, darkens 260—270°, is obtained from the Cl-acid. Chelidamic acid with $Fe(OH)_3$ forms *dichelidamatoferric acid* (+$2H_2O$) (I), which affords NH_4 (+$2{\cdot}5H_2O$), NEt_4 (+$2H_2O$), o-*toluidine*, C_5H_5N, *quinoline*, *quinine*, *Na* (+$2H_2O$), *K* (+$2H_2O$), *Ag* (+$2H_2O$), *Ba* (+$2{\cdot}5H_2O$), *di*-p-*toluidine* (+H_2O), decomp. 220—225°, and *dinor*-d-ψ-*ephedrine* salts; Ag_3 and *triaquo-ferric dichelidamato-oxoferrate* (+$4H_2O$). (I) contains one free and one masked CO_2H, and gives rise to two series of H_2O-sol. salts. The light-absorption of the complexes has been studied. F. R. S.

Azo-dyes. I. Preparation and bacteriostatic properties of azo-derivatives of 2 : 6-diaminopyridine. R. N. Shreve, M. W. Swaney, and E. H. Riechers (*J. Amer. Chem. Soc.*, 1943, **65**, 2241—2243).—2 : 6-*Diamino-3-arylazopyridine monohydrochlorides* are prepared in which aryl = Ph (I), m.p. 137°, *o*-, m.p. 184°, *m*-, m.p. 123·2°, and *p*-tolyl, m.p. 151·3°, *o*-, m.p. 193°, *m*-, m.p. 99·5°, and *p*-anisyl, m.p. 192°, *o*-, m.p. 127°, and *m*-OEt·C_6H_4, m.p. 114·3°, *o*-, m.p. 189°, *m*-, m.p. 209·4°, and *p*-OH·C_6H_4, m.p. 232°, *m*-C_6H_4Cl, m.p. 259°, *o*-, m.p. 209·5°, *m*-, m.p. 141°, and *p*-C_6H_4I, m.p. 198°, 5 : 1 : 2-, m.p. 222°, and 6 : 1 : 3-OH·C_6H_3Me, m.p. 203—204°, 3 : 1 : 4-, m.p. 233°, 4 : 1 : 2-, m.p. 265°, and 5 : 1 : 2-NO_2·C_6H_3Me, m.p. 251°, 2 : 5 : 1-OMe·C_6H_3Cl, m.p. 204°, 5 : 2 : 1-NO_2·C_6H_3(OMe), m.p. 226°, 4 : 1 : 3-OMe·C_6H_3Me, m.p. 174·5°, 1 : 3 : 2-$C_6H_3Me_2$, m.p. 122°, *o*-, m.p. 135·6°, and *p*-C_6H_4Ph, m.p. 230·5°, *p*-PhN_2·C_6H_4, m.p. 203—204°, *o*-CO_2Me·C_6H_4, m.p. 177°, and *o*-CO_2Et·C_6H_4, m.p. 170°. M.p. are corr. Solubilities in H_2O are recorded, that of (I) being much the highest. For bacteriostatic properties, see A., 1944, III, 295. R. S. C.

Invert soaps. V. Quaternary salts of isomeric hydroxyquinoline ethers. R. Kuhn and O. Westphal (*Ber.*, 1940, **73**, [*B*], 1105—1108; cf. A., 1944, II, 98).—3-Amino- is obtained (92%) from 3-bromo-quinoline by conc., aq. NH_3 and CuO at 140—150°. The K salt (pptd. by KOEt–EtOH) of 3-hydroxyquinoline with *n*-$C_{12}H_{25}Br$ in EtOH at 180° gives 3-n-*dodecyloxyquinoline*, m.p. 42° [*methyl-methosulphate* (I), m.p. 115—116°]. 8-n-*Dodecyloxyquinoline*, m.p. 25°, b.p. 225°/3 mm. [*hydrochloride*, m.p. 73—80°; *methylmethosul-phate* (II), m.p. ~23°], is similarly prepared. *n*-$C_{12}H_{25}Cl$ gives 6-n-*dodecyloxyquinoline*, m.p. 45°, b.p. 235°/2 mm. [*hydrochloride*, m.p. 150—151°; *methylmethosulphate* (III), m.p. 70° (decomp.)]. Bactericidal and bacteriostatic activities of (I), (II), (III), and *n*-$C_{12}H_{25}$·NMe_2Br·CH_2Ph are very similar. R. S. C.

Polarisation of fluorescence and anisotropy of molecules of dyes.—See A., 1944, I, 77.

*cyclo***Tetramethylenepyrazolone. III. Molecular compounds.** H. Ruhkopf (*Ber.*, 1940, **73**, [*B*], 1066—1068; cf. A., 1940, II, 108).—By mixed m.p. diagrams [only eutectics and m.p. of compounds (in parentheses below) are recorded] it is shown that 1-phenyl-2-methyl-3 : 4-*cyclo*tetramethylene-5-pyrazolone form 1 : 1 additive *compounds* with CHPhEt·CO·NH_2 (m.p. 92°), CHPhPr^a·CO·NH_2 (m.p. 78°), $CHPh_2$·CO·NH_2 (m.p. 125°), and phenylethylhydantoin (m.p. 146°), and a 1 : 2 additive *compound*, m.p. 128°, with α-allyl-Δ^γ-pentenoylcarbamide, but no compound with CHR_2·CO·NH_2 (R = Et, Pr^a, or allyl), α-*cyclo*hexenyl-*n*-propionamide, CH_2Ph·CO·NH_2, CHRR′·CO·NH·CO·NH_2 (R = R′ = Et or Pr; R = Ph, R′ = Et), or diketopyrazolidine. It is similarly shown that no compounds are formed from (*a*) 1-phenyl-2-methyl-3 : 4-*cyclo*trimethylene-5-pyrazolone with CHPhEt·CO·NH_2, $CHPh_2$·CO·NH_2, or CHR_2·CO·NH·CO·NH_2 (R = Et, Pr, or allyl), (*b*) 1-phenyl-2 : 3-dimethyl-5-pyrazolone with CHPhEt·CO·NH_2 or phenacetin, or (*c*) 4-dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone (I) with CHR_2·CO·NH_2 (R = Et or Ph), CHPhEt·CO·NH_2, or phenacetin, but that (I) gives a 1 : 1 additive *compound*, m.p. 147°, with phenylethylhydantoin. From these results general rules are propounded. R. S. C.

Pyrimidines.—See B., 1944, III, 34.

Synthesis of carbazo-condensed systems from α- and α′-amino-nicotines. V. Synthesis of 3-phenylpyriminazole and its nicotine analogue. J. L. Goldfarb and M. S. Kondakova (*J. Appl. Chem. Russ.*, 1942, **15**, 151—163; cf. 1937, A., II, 473).—2-Aminopyridine (I) and CHPhBr·CO·CO_2H in aq. $NaHCO_3$ yield, besides COPh·CH_2·OH and CH_2Ph·CO_2H, 3-phenylpyriminazole-2-carboxylic acid, m.p. 201—202° (decomp.) (*hydrochloride*, m.p. 225—227°; *hydrobromide*, m.p. 246°; *platinichloride*, m.p. 243—247°; *picrate*, m.p. 205—207°), which at 210—220° gives 3-*phenylpyriminazole*, m.p. 97—98°, b.p. 188—192°/6 mm. (*hydrobromide*, m.p. 195°; *platinichloride* does not melt up to 285°; *picrate*, m.p. 236°), giving with aq. $KMnO_4$ (I) and with Br–H_2O a Br additive product. 2-Aminonicotine (II) and CHPhBr·CO·CO_2H in aq. $NaHCO_3$ give 7-(*N*-methylpyrrolidyl)-3-phenylpyriminazole-2-carboxylic acid, which could not be isolated but gave a *picrate*, m.p. 210—211° (decomp.), and at 230—240° afforded 7-(N-*methylpyrrolidyl*)-3-*phenylpyriminazole*, m.p. 94—95° [*picrate*, m.p. 240° (decomp.)], which is oxidised by CrO_3 to (II). J. J. B.

Pyridylquinolines.—See B., 1944, II, 66.

Invert soaps. VI. Triazolium salts. R. Kuhn and O. Westphal (*Ber.*, 1940, **73**, [*B*], 1109—1113; cf. A., 1934, II, 111).—The K salt of 1 : 2 : 4-triazole and *n*-$C_{12}H_{25}Cl$ in EtOH at 110° gives 1-n-*dodecyl*-1 : 2 : 4-*triazole*, m.p. 39° [*ethobromide*, m.p. 150—152°]. The K or Na salt of benztriazole with AlkCl in EtOH at 100—120° gives 60—80% of 1-alkylbenztriazole but AlkBr affords 1 : 3-dialkylbenztriazolium bromide. Thus are obtained 1-n-*dodecyl*-, m.p. 44—46° [3-*methylmethosulphate*, m.p. ~25°; 3-*ethobromide* (I), m.p. 27°; *butylobromide*, m.p. 33°], and 1-n-*hexadecyl-benztriazole*, m.p. 62° (3-*methylmethosulphate*, m.p. 76—77°; 3-*ethobromide*, m.p. 96—97°), 1 : 3-*dioctyl*-, m.p. 147—148°, and 1 : 3-*di-n-dodecyl-benztriazolium bromide*, m.p. 141—143°, and 1 : 3-*dibenzylbenztriazolium chloride*, m.p. 207—209°. Bactericidal and bacteriostatic activities of the salts against six bacteria are recorded. The activity of (I) is of exceptional degree. R. S. C.

Fluorescence of chlorophyll.—See A., 1944, I, 77.

Constitution of yeast-ribonucleic acid. VII. Diffusion coefficients and mol. wts. W. E. Fletcher, J. M. Gulland, D. O. Jordan, and (in part) H. E. Dibben. **VIII. Electrometric titration of the acid groups.** W. E. Fletcher, J. M. Gulland, and D. O. Jordan (*J.C.S.*, 1944, 30—33, 33—39; cf. A., 1944, II, 85).—VII. Diffusion coeffs. suggest that yeast-ribonucleic acids (I) of different origins have mol. wts. ranging between those corresponding with 8 and 18 hypothetical tetranucleotides. Deamination of B.D.H. (I) under the special conditions described does not diminish the mol. wt., confirming the conclusion that phospho-amide groups are not essential links between nucleotides in that acid. Less controlled conditions cause extensive mol. degradation.

VIII. Electrometric titration of samples of (I) indicates that (I) has four acid dissociations per tetranucleotide when existing as a polytetranucleotide, three of which are primary dissociations, and one a secondary dissociation of H_3PO_4. The deaminated acid is similarly constituted. Mild hydrolysis reduces the mol. wt. of the polytetranucleotide, and the titration results suggest that a further secondary dissociation of H_3PO_4 becomes free. These data necessitate a modification of the formula previously proposed for (I); this is discussed in relation to the existing mol. wt. and enzyme data. F. R. S.

Nucleic acids. XVI. Constitution of thymonucleic acid. Position of the linking between bases and deoxyribose. H. Bredereck, G. Müller, and (Miss) E. Berger. **XVII. Nucleotide syntheses. Synthesis of uridylic acid.** H. Bredereck, and (Miss) E. Berger (*Ber.*, 1940, **73**, [*B*], 1058—1065, 1124—1125).—XVI. Linkage of the sugar to positions 9 and 3 is proved for purine and pyrimidine deoxyribonucleotides, respectively (cf. Gulland *et al.*, A., 1938, II, 128, 296). Adding Me_2SO_4 and aq. NaOH to Na thymonucleate at 30—35° and pH 8—9 gives a Na salt (I) containing 7 NMe and 2 OMe; further methylation slightly increases the OMe but not the NMe content. Fission of (I) by emulsin at 37° and pH 4·9 causes an increase of 4 equivs. in acidity so that the methylated acid is tetrabasic; one Me is probably present as phosphoric ester. Passing gaseous HCl into (I) in 95% MeOH gives 1 : $N_{(6)}$-dimethyladenine,

CH<(N——C·C(:NMe)·NMe)(NH·C————N:CH) (*picrate*, m.p. 235°), also obtained (picrate, m.p. 236°) from adenosine by Me_2SO_4–NaOH and then HCl–MeOH. With 25% H_2SO_4 at 175—180° (I) gives 1 : $N_{(6)}$-dimethylcytosine, NH·CO·NMe / CH:CH·C:NMe (*picrate*, m.p. 222°) [also obtained (picrate, m.p. 218°) from cytidine nitrate by Me_2SO_4–NaOH and then 25% H_2SO_4 at 175—180°], and (? 1-)methylthymine, m.p. 210° (A., 1908, i, 835, m.p. 202—205°), but no methylguanine. Me_2SO_4–NaOH and then HCl–MeOH converts guanosine into a dimethylguanine (*hydrochloride*, m.p. 275°; *picrate*, m.p. 214°).

XVII. Triphenylmethyluridine (A., 1933, 149) with $(OPh)_2POCl$ in C_5H_5N at −18° and then aq. NaOH at 100° gives uridylic acid, isolated as brucine salt, sinters 188°, m.p. 195°, $[\alpha]_D^{20}$ −54·8°. Known processes yield 3 : 5-*benzylideneguanosine*, m.p. 295° (2-*acetate*, m.p. 263°), *guanosine 2-acetate*, m.p. ~180°, and *guanosine 5-CPh_3 ether*, amorphous (2-*acetate*, amorphous). R. S. C.

Aminothiazoles and benzenesulphonimidothiazolines etc.—See B., 1944, II, 34, 35.

Ring fissions with thiazolium salts. A. Schöberl and M. Stock (*Ber.*, 1940, **73**, [*B*], 1240—1252).—Addition of CH_2PhBr to 2 : 4-dimethylthiazole gives 3-benzyl-2 : 4-dimethylthiazolium bromide (I), m.p. 171°. Interaction of COMe·CH_2Cl with MeCS·NHPh at 15—20° gives S-*acetonylthioacetanilide hydrochloride*, which passes when heated or boiled with alkali and subsequently acidified into 3-phenyl-2 : 4-dimethylthiazolium chloride, transformed by KI into the corresponding iodide (II), which gives an intense blue colour with phosphotungstic acid and a red colour with Na nitroprusside after addition of NH_3. The initially yellow solution of (I) in 2N-

NaOH becomes colourless when heated but addition of acid does not cause liberation of H_2S and there is no production of PbS on boiling with alkali plumbite; the parallel experiment with aneurin is positive. In alkaline solution (I) is immediately oxidised by I and is converted by air into a substance, m.p. (indef.) 96—97°. Gradual addition of AcOH to a solution of (I) or (II) in 2N-NaOH–EtOH containing $NaNO_2$ causes the development of an intense yellow colour which does not appear to be very sensitive. When 9(18)-phosphotungstic acid is added to solution of (I), (II), or aneurin (III) which has been kept for some time an intense blue colour appears which can be used in the detection and determination of thiazolium salts. Addition of freshly prepared Na nitroprusside solution to aq. solutions of (I) and (II) which have been treated with 2N-NH_3 causes the appearance of a cherry-red colour which attains its max. after a time and is very stable. The colour does not appear in 2N-NaOH and is markedly less stable in 0·1N-NaOH than in NH_3. It is not given by (III). The test can be used quantitatively. Increase of temp. (55—60°) facilitates the development of the colour, which does not then reach its full intensity since decomp. is also facilitated. The solutions are rapidly bleached by exposure to light. They are, however, stable for days in the dark. They should be prepared in a subdued red light and exposed as briefly as possible to the photometer light. NH:CMe·SH and OH·CH:CCl·CO_2Et are condensed and then hydrolysed to *2-methylthiazole-5-carboxylic acid*, m.p. 209° (decomp.) (*Et* ester, b.p. 117—120°/19 mm.), not identical with the acid thus described in the literature. 2-Methylthiazole-4 : 5-dicarboxylic acid, m.p. 169°, loses CO_2 at 175° with production of a monocarboxylic acid, m.p. 143—145°, softens at 130°. H. W.

Reactions of benzthiazole derivatives. IV. 1-Thiocyanobenzthiazole. W. H. Davies and W. A. Sexton (*J.C.S.*, 1944, 11—13).—1-Thiocyanobenzthiazole (I) is not stable to prolonged storage and decomposes fairly rapidly when heated. With many reagents, *e.g.*, NaOH and Na_2S, it is converted into derivatives of 1-thiolbenzthiazole. With MeOH, (I) gives mainly *Me benzthiazyl-1-thioncarbamate*, m.p. 175° (*Et* compound, m.p. 163°, from EtOH). The mechanism of this reaction is discussed. F. R. S.

Cyanine type dyes.—See B., 1944, II, 58, 90, 91.

Dioxazine dyes.—See B., 1944, II, 69.

VII.—ALKALOIDS.

Fluorescent alkaloid in rye-grass (*Lolium perenne*, L.). I. Introduction. R. E. R. Grimmett and J. Melville. **II. Extraction from fresh rye-grass and separation from other bases.** R. E. R. Grimmett and D. F. Waters. **III. Extraction and properties.** I. Reifer and N. O. Bathurst. **VI. Investigation of a volatile base C_6H_7N.** F. B. Shorland, E. P. White, and R. E. R. Grimmett (*New Zealand J. Sci. Tech.*, 1943, **24**, B, 149—150, 151—155, 155—159, 179—185; cf. A., 1944, III, 282; also C, 1944, Part 2).—I. A neutral or acid EtOH extract of the basal shoots of rye-grass, from which anthocyanins and fat-sol. pigments have been removed, gives an intense greenish fluorescence on addition of NH_3. This is due to an alkaloid, named *perloline* (I). Other alkaloids are present in smaller amount.

II. The only other pasture species to give comparable yields of (I) is tall fescue. For bulk extraction, grass of >0·02% alkaloid content is chosen by spot testing. 60—70% of (I) in the grass is extracted by 0·75% HCl. Neutralisation with $Ca(OH)_2$ and adjustment of pH to 7·5 with Na_2CO_3 gives a sludge containing 50—60% of (I) in the extract; if tannic acid is also added, 90% is pptd.; approx. quant. extraction of the sludge is effected by excess of Na_2CO_3 and EtOH. (I) is finally separated from other bases by its greater basicity, and its hydrochloride is crystallised out of a solution conc. below 50°. Fraction "B" contains other $CHCl_3$-sol., Et_2O-insol. bases, similar to (I), but less fluorescent. Fraction "C" contains an Et_2O-sol. *base*, subliming at 295° (180°/0·04 mm.), decomp. 316°; the *hydrochloride* (subliming at 297°, decomp. 317°) gives a bright blue fluorescence in aq. solution, and characteristic ppts. with KI_3, $KBiI_4$, $KHgI_3$, $AuBr_3$, and $HgCl_2$. Fraction "D" (II) was sol. in ligroin and had an odour like C_5H_5N.

III. Dried ground rye-grass leaves are extracted with EtOH and AcOH. Dried unground grass is extracted with 1% H_2SO_4. Purification of (I) is carried out by partition between $CHCl_3$ and dil. HCl; after 7 crystallisations from H_2O, the hydrochloride analyses for $C_{36}H_{22}O_3N_4(OMe)_4,2HCl$. 0·2 p.p.m. can be detected in daylight by the fine green fluorescence of solutions in $CHCl_3$ or EtOH, which are not stable to direct sunlight. Ppts. are given with $AgNO_3$, picric acid, $HgCl_2$, $KBiI_4$, $KHgI_3$, phospho-molybdic and -tungstic acids, $AuCl_3$, $PtCl_4$, KI_3, and NH_4 reineckate, and colours with $NaVO_3$–H_2SO_4 (brown) and Ti_2O_3–H_2SO_4 (brick-red). Oxidation ($KMnO_4$ or H_2O_2) gives a colourless base with blue fluorescence, and reduction ($TiCl_3$) a non-fluorescent material. The alkaloid content of rye-grass varies with environmental conditions from traces to 0·1%.

VI. (II) is almost entirely a *base*, C_6H_7N, b.p. 134—138° (*picrate*, m.p. 154—156°, *mercurichloride*, m.p. 151—152°), which can be reduced catalytically to a H_6-derivative (*hydrochloride* m.p. 169—171°; 3 : 5-*dinitrobenzoate*, m.p. 110—112°). (II) is not a picoline; possible formulæ are discussed. S. A. M.

VIII.—ORGANO-METALLIC COMPOUNDS.

Mode of reaction of lithium phenyl. V. Behaviour of halogenated anisoles towards lithium phenyl. G. Wittig and G. Fuhrmann (*Ber.*, 1940, **73**, [*B*], 1197—1218).—The halogenated anisoles are allowed to react with LiPh in Et_2O under comparable conditions and investigation is made of the products formed after addition of H_2O or $COPh_2$. In the reaction of the *o*-halogenoanisoles it is found that I is replaced rapidly and Br more slowly by Li whereas Cl and F (the latter more rapidly than the former) give the Li halide with consequent formation of *o*-C_6H_4Ph·OMe. H between OMe and halogen in the *meta*-compounds is readily exchanged for Li and in consequence of this action the formation of C_6H_4Ph·OMe and LiHal predominates. In comparison the exchange of halogen for metal, which is observed only with *m*-C_6H_4I·OMe, recedes into the background. Common to *para*-substituted anisoles is the replacement of "mobile" H by metal which is facilitated by increasingly electronegative character of the halogen and with *p*-C_6H_4F·OMe results in the production of *p*-C_6H_4Ph·OMe. *p*-C_6H_4I·OMe and *p*-C_6H_4Br·OMe also exchange their halogen for Li. The exchangeability of aromatically bound H for Li depends on the polarisation of C-H linkings by electronegative substituents such as OMe or F and is explicable by the theory of induced alternating polarities. Since the acidifying effect diminishes with increasing distance only H in the *ortho*-position is replaceable and the entry of Li to the C_6H_6 nucleus is facilitated by the presence of 2 *meta*-substituents between which the Li enters. The influence of OMe and the 4 halogens on the action is qualitatively but not quantitatively similar to the effect on the acidity of AcOH. The theory fails to explain the observation that the exchange of H for Li is considerably facilitated by an accumulation of negative substituents even in the *para*-position. Here the alternating induction is subsidiary to a second effect which behaves as a "general effect" from C to C and, for example, causes the acidifying effect of a halogen in a fatty acid to diminish with increasing distance from CO_2H. Steric effects are also obvious. If Li replaces H *ortho* to halogen as has been established for PhF and is observed with *m*-halogenoanisoles, the halogen becomes so reactive and the subsequent production of Ph_3 derivatives under the further influence of LiPh is so rapid that in only one case it has been possible to trap the metallic compound as the carbinol by use of $COPh_2$. A polarising counter action of Li corresponds with the polarising action of halogen. An electronic explanation of the replaceability of halogen by Li is advanced. The following appear new: 1 : 6(or 1 : 8)-*dimethoxy*-9 : 9-*diphenylfluorene*, m.p. 201—202°; 1-*methoxy*-, dimorphic, m.p. 180·5—181° and 193—194°, converted by Br in boiling AcOH into 2(or 4)-*bromo*-1-*methoxy*-9 : 9-*diphenylfluorene*, m.p. 222·5—223°; 5-*iodo*-, m.p. 136—137°, 5-*chloro*-, m.p. 118—119°, and 5-*fluoro*-3-*methoxytriphenylcarbinol*, m.p. 129·5—131°. *m*-C_6H_4Ph·OMe is converted by successive treatments with LiPh in Et_2O and $COPh_2$ into 2-*methoxy*-4-*phenyltriphenylcarbinol*, m.p. 138·5—139·5°. Under similar treatment veratrole gives 2 : 3-*dimethoxytriphenylcarbinol*, m.p. 110—111·5°. 1 : 2 : 3-$C_6H_3(OMe)_3$ is converted by LiPh in Et_2O followed by $COPh_2$ and then by 2N-NaOH into 1 : 3 : 2-$(OMe)_2C_6H_3$·ONa (whence the benzoate, m.p. 114—116°); other products are unchanged material, CPh_3·OH, and 2 : 3 : 4-trimethoxytriphenylcarbinol, m.p. 140—140·8° (lit. 139°). 1 : 3 : 5-$C_6H_3(OMe)_3$ when treated similarly yields 2 : 4 : 6-trimethoxytriphenylcarbinol, m.p. 114—115° (lit. 110—111°). H. W.

Mercury diallyl. K. V. Vijayaraghavan (*J. Indian Chem. Soc.*, 1943, **20**, 318; cf. A., 1942, II, 41).—CH_2:CH·CH_2·HgI (I) and conc. aq. KCN give $(CH_2$:CH·$CH_2)_2$Hg (II). Fresh aq. suspensions of (I) give a faint odour of (II) with $Na_2S_2O_3$, Na_2S, or KI on keeping or gently warming; on heating Hg and complex inorg. Hg salts are formed. (I) in EtOH with Na_2S or $Na_2S_2O_3$ ppts. Hg and gives inorg. complex salts; with KI–EtOH it gives a faint odour of (II) on warming, but K_2HgI_4 on heating. (I) in $COMe_2$ with NaI gives a faint odour of (II), but is mainly unchanged. S. A. M.

IX.—PROTEINS.

Denaturation changes in ovalbumin with urea, radiation, and heat. J. H. Clark (*J. Gen. Physiol.*, 1943, **27**, 101—111).—When 10—50% of $CO(NH_2)_2$ (I) is added to isoelectric solutions of ovalbumin (II) the pH val. is altered to ~5·2—5·8 depending on the concn. of (I). The extent of the denaturation produced by (I) depends on concns. of (I) and (II) and also on the temp. of the solution. 0·9% (II) solution is not denatured by 20% (I); it is denatured slowly by 25% and rapidly by 35% (I) at room temp. At higher temp. 30% (I) is rapidly effective. Denaturation of (II) by ultra-violet radiation or heat is accompanied by structural changes but the mol. has a fair degree of symmetry except at the isoelectric point, and

there is no association or dissociation of the mol. within the pH range outside the zone in which aggregation follows denaturation. Denaturation of (II) by (I) causes no change in optical rotation until the concn. of (I) is high enough to dissociate the mol. The optical rotation of fresh native (II) does not vary over the pH range 3·4—10·5, but it is increased ~100% after boiling the solution for 5 min. at pH 3·4 or 6·4—7·2, and the increase is the greater the nearer is the pH to the isoelectric point. In presence of (I) a (I)–protein complex is formed in which the protein is denatured but is not pptd. because of the dispersive action of (I); this prevents pptn. of protein exposed to ultra-violet radiation and subsequent heating to 40° because the complex is not decomposed at 40°. Decomp. occurs at 55—58° so that aggregation results at a temp. < that of rapid heat-denaturation. This is not due to an acceleration of heat-denaturation or to decrease in the temp. of heat-denaturation but results from the effect of heat on the complex which liberates the (I)-denatured protein and causes its pptn. J. N. A.

Invert soaps. I. Action of invert soaps on albuminous substances. R. Kuhn and H. J. Bielig [in part, with O. Dann] (*Ber.*, 1940, **73**, [*B*], 1080—1091).—Invert soaps ppt. the echinochrome symplex from H_2O or aq. Na_2CO_3, the ppt. retaining the dye tenaciously (cf. Kuhn *et al.*, A., 1943, III, 738). In dil. AcOH invert soaps liberate the dye (removed by Et_2O) with pptn., and subsequent addition of Na_2CO_3 ppts. the almost colourless protein. A 1% solution of invert soap gives with chloroplastin a ppt. containing all the chlorophylls and carotenoids in extractable (Et_2O, C_6H_6) form; as the concn. of n-$C_{12}H_{25}$·SMe_2I (I) added is increased, the amount of dye liberated slowly increases; this amount suddenly becomes much greater, approx. when the drop no. of the soap solution is a max. (0·2% solution); an approx. parallelism also exists between the amount of dye liberated and the surface activity of various sulphonium iodides. ~30 mols. of (I) are needed to liberate 1 mol. of chlorophyll-*a* when up to one sixth of the dye is liberated; complete liberation of the dye requires much more (I). Normal soaps do not affect chloroplastin. The carotene of yellow carrots is present as symplex in non-extractable form but is at once liberated by 1—1·5% invert soap solutions. Invert soaps do not split chromoproteins. CH_2Ph·NMe_2Br·$C_{12}H_{25}$-n (II) does not ppt., and prevents coagulation of, the yellow enzyme of yeast or of oxyhæmoglobin (III) by heat; its action on (III) is antagonised by Na deoxycholate. Methæmoglobin is pptd. by ~1% invert soap solution. Catalase is unaffected by an equal vol. of 0·1—10% (II) at pH 7·2—5·4, but is pptd. and inactivated by a 1% solution at pH 8·2 (Na_2CO_3). Ferritin (IV) is completely pptd. from 2 c.c. of 0·1% solution by 1 c.c. of a 1 : 300, but not 1 : 350, solution of (II); the (IV) is denatured but the Fe is not liberated; 1 mol. of (II) ppts. 1·03 atom of Fe. Invert soaps ppt. oxyhæmocyanin from dil. Na_2CO_3 (not dil. AcOH), the fresh (not old) ppt. being sol. in an excess of soap or $(NH_4)_2SO_4$ and dissolving also if the original mixture is warmed; Cu is not liberated. Ovoverdin is split by 0·00005% invert soap solution (colour change to the red of astaxanthin), but pptn. of the protein requires 0·0005% soap solution. Gelatins and ovalbumin (V) are pptd. by invert soaps if the pH is such that the protein is present as anion; for proteins having isoelectric point near pH 7·2 the CO_2 content of the solution is important. With (V), SH is liberated before pptn. occurs. The concn. of the soaps required for bactericidal action is approx. that (0·001—0·00002%) required for pptn. of proteins. The action of invert soap on genes resembles that of *X*-rays. Isolation of β-carotene (from carrots) and of lycopene (from tomatoes) is described. R. S. C.

Crystalline muscle phosphorylase.—See A., 1944, III, 218.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin and related compounds. LXIII. Ultra-violet absorption spectra of ethanol lignins. R. F. Patterson and H. Hibbert (*J. Amer. Chem. Soc.*, 1943, **65**, 1869—1873; cf. A., 1943, II, 346).—Absorption spectra are recorded for the fractions of spruce and maple lignins and for ethanolysis products from OH·CHMe·COAr and OH·$[CH_2]_2$·COAr (Ar = vanillyl). Comparisons with those of known ingredients and related compounds (*loc. cit.*) confirm the aromatic nature of lignin, the existence of OH-derivatives of 4 : 3 : 1-OH·C_6H_3(OMe)·COEt in both lignins and of 4 : 3 : 5 : 1-OH·C_6H_2(OMe)$_2$·COEt in spruce lignin, and conjugation (to an unkown extent) between the aryl nucleus and the side-chain. R. S. C.

Lignin. XII. Sulphite liquor from beech wood. H. Friese and G. Stoeck [with, in part, R. Konau] (*Ber.*, 1940, **73**, [*B*], 1135—1145; cf. A., 1938, II, 331).—The liquor is repeatedly evaporated with H_2O under diminished pressure to remove volatile acids and taken to dryness after neutralisation with $CaCO_3$. Treatment with boiling EtOH and MeOH gives pure *d*-xylose (I), isolable by direct crystallisation. The non-cryst. residue in acetylated to a protein sol. in $CHCl_3$ and H_2O but not in Et_2O and containing ~36% OAc with Ca, S, and OMe, and an Et_2O-sol. fraction free from Ca and S but containing 71·8% OAc and 2·1% OMe. Hydrolysis gives (I) and fermentable hexoses, mainly mannose. Glucose is probably present. Methylpentoses, ketoses, uronic acids, and, probably, arabinose and galactose are absent. (I) frequently contains OMe in non-glucosidic union. The extractions remove sugars almost quantitatively. Their amount is 26—30% of the dry residue but depends on the boiling. (I) constitutes ~76% of the free carbohydrates. The remaining portion of the alcoholic extract separable by acetylation is a *lignin–carbohydrate* compound (Ca 4·2, S 6·5, OMe 11·0, OAc 36·5, C 45·2, H 4·7%). Extraction of the residue from the alcoholic extractions with 80% MeOH gives a brown solid (25—35% of the initial material, dependent on the duration of boiling). It contains Ca 6, S 6, OMe 11% and gives only small amounts of sugar acetates when drastically treated. The residue from the acetylation is a pale brown lignin–carbohydrate compound which contains little combined lignin. Hydrolysis with dil. H_2SO_4 is incomplete but sulphacetolysis leads to Et_2O-sol. sugar acetates with OAc 68·8, OMe 2·34% but no Ca or S. Ultrafiltration of the remaining material leaves a brown powder with C 52 H 4·7, OMe 16, S 5·1, and Ca 4·0%. The ultrafiltrate on pptn. with MeOH gives a substance with C 41·7, H 5·1, OMe 10·5, S 7·3, and Ca 8·5%; the MeOH contains $Ca(OAc)_2$, $(HCO_2)_2Ca$, and small amounts of Ca ligninsulphonate. H. W.

Oxidative degradation of pectin in aqueous solution. Viscosimetric determinations. H. Deuel (*Helv. Chim. Acta*, 1943, **26**, 2002—2025).—The irreversible oxidative degradation of pectin (I) in aq. solution is followed viscosimetrically. Ascorbic acid (II) and similar enediols degrade (I) in the presence of O_2, the change being accelerated by increase of temp., and occurring most rapidly at the neutral point. Decomp. of (I) and oxidation of (II) are inter-related. Dehydroascorbic acid has a weak degrading action. At room temp. H_2O_2 in small concn. causes decomp. of the mol. of (I); increase of temp. causes very marked acceleration; this degradation occurs more rapidly in the presence of (II), Fe^{II} salts, N_2H_4, and NH_2OH. The oxidation of (I) is decelerated by EtOH and sucrose and inhibited by H_2S, SO_2, and I. The degradation of (I) described above is externally similar to hydrolysis by pectinase and oxidative decomp. by HIO_4 but the reaction mechanism is different. Activated H_2O_2 and autoxidising (II) degrade the most varied carbohydrates on addition to (I). H. W.

Gliotoxin, the antibiotic principle of *Gliocladium fimbriatum*. I. Production, physical and biological properties. J. R. Johnson, W. F. Bruce, and J. D. Dutcher (*J. Amer. Chem. Soc.*, 1943, **65**, 2005—2009).—Prep. of gliotoxin, new formula $C_{13}H_{14}O_4N_2S_2$, $[\alpha]_D^{25}$ −290±10° in EtOH, −270°±10° in C_5H_5N, −255±10° in $CHCl_3$, +111° → 0° in 5 days in NaOH–EtOH–H_2O, is described. The mol. wt. is best determined cryoscopically in $NHPh_2$, other solvents giving erroneous or erratic results. Crystallo-optical properties and solubilities [much the greatest in C_5H_5N (at 100°) or dioxan] in 16 solvents are described. The absorption spectrum (detailed) resembles that of indole and tryptophan, indicating presence of an indole nucleus. For physiological properties see A., 1944, III, 292. R. S. C.

Formation of a nicotinamide-like substance from various amino-acids and related compounds. M. R. Bovarnick (*J. Biol. Chem.*, 1943, **151**, 467—475).—The reaction between asparagine (I) and glutamic acid (II) that results in the formation of a nicotinamide-like substance (III) is catalysed by Mn (best; 10 times amount of (III)] and Fe salts (Mg, Ca, Al, Cr, Co, Ni, and Cu have little effect), and is promoted by aëration. Certain NH_2-acids and non-N dibasic acids are capable of substituting for (II) in the reaction. In order of decreasing activity are methionine [as active as (II)], proline, citrulline, ornithine, α-ketoglutaric acid, glutaric acid, maleic acid, arginine, phenylalanine, hydroxyproline, fumaric acid, tyrosine, oxalacetic acid, lysine, serine, threonine, and malic acid. All the terminal-substituted C_5 NH_2-acids react. The only effective substitute for (I) is glutamine. The NH_4 salts of aspartic, α-ketoglutaric, maleic, and malic acids when heated with (II) produce small amounts of nicotinamide activity, although their Na salts are inactive. With many mixtures of (I) + NH_2-acid, much more activity is produced by treating with H_2O_2 for 2 days at room temp., then autoclaving (15 min.), than at 100° (48 hr.); also small amounts of nicotinamide activity are produced from many NH_2-acids and from the NH_4 salts of several dicarboxylic acids by H_2O_2 alone, in absence of (I) and (II). Reaction mechanisms are discussed. A. T. P.

Hypericin and a non-fluorescent, photosensitive pigment from St. John's wort (*Hypericum perforatum*).—See A., 1944, III, 232.

INDEX OF AUTHORS' NAMES, A II.

APRIL, 1944.

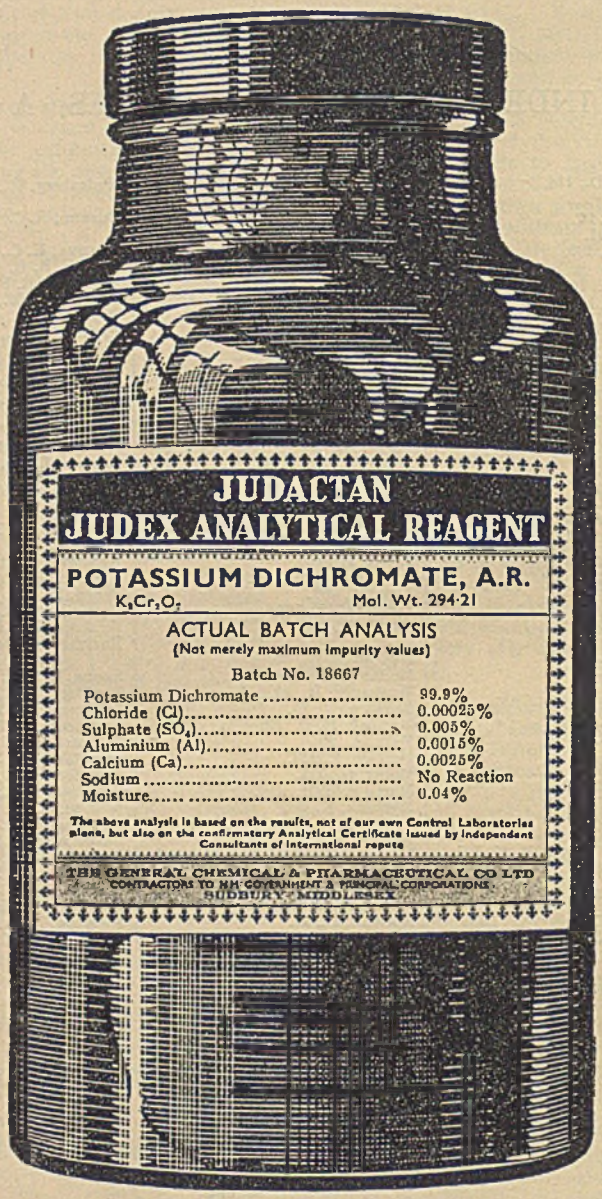
JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL

BATCH

ANALYSIS



Each Batch subjected to INDEPENDENT ANALYSIS before label is printed

You are invited to compare the above actual batch analysis with the purities guaranteed by the specifications of any competing maker in this country or abroad

THE GENERAL CHEMICAL & PHARMACEUTICAL CO. LTD.

Chemical Manufacturers, Judex Works, Sudbury, Middlesex

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD., BUNGAY, SUFFOLK.