BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1942.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

I.—ALIPHATIC.

Strength of carbon–hydrogen and carbon–carbon bonds. Carbon–hydrogen bond strengths in methane and ethane.—See A., 1942, I, 258.

Catalytic polymerisation of olefines in presence of phosphoric acid.—See A., 1942, I, 302.

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Thermal reaction of ethylene with acetylene.—See B., 1942, II, 209.

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Reactions of bromine with carbon tetrachloride and tetrachloroethylene following neutron capture and isomeric nuclear transition.—See A., 1942, I, 306.

Calculation of steric hindrance.—See A., 1942, I, 259.

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Preparation of nitrohydroxy-compounds of the paraffin series.—See B., 1942, II, 212.

Organic acid synthesis.—See B., 1942, II, 213.

Preparation of organic acids from olefines and carbon monoxide.—See B., 1942, II, 213.

Mixed electrolyses of nitrate with *n*-valerates and *iso*butylacetates. M. Rudin (*Helv. Chim. Acta*, 1942, **25**, 636—640).—The products of the mixed electrolysis of nitrate and *n*-valerate are *n*-octane, Bu^aOH characterised as $Bu^aO{\cdot}NO$, Bu^aNO_3, and $Bu^aCO_2Bu^a$, $(CHMe{:})_2$, leading to butane-$\beta\gamma$-diol dinitrate, and an octanediol dinitrate. *iso*Butylacetic acid [γ-methyl-*n*-valeric acid] similarly affords $\beta\eta$-dimethyloctane, (?) *iso*amyl nitrite, and nitrates or *iso*butylacetates of a decanol, b.p. 106—108°/22 mm., or decanediol, b.p. 133—140°/14 mm. H. W.

Formation of carbonyl compounds by the enzymic oxidation of unsaturated fatty acids. H. Süllmann (*Helv. Chim. Acta*, 1942, **25**, 521—523).—CO-compounds, capable of forming hydrazone, dihydrazone, and osazone derivatives, are formed during the oxidation of linolenic acid by lipoxidase. H. W.

Dihydroxystearic acid of castor oil; its constitution and structural relationship to the θ-, ι-dihydroxystearic acids, m.p. 132° and 95°, respectively. G. King (*J.C.S.*, 1942, 387—393; cf. A., 1939, II, 5).—Dry HCl is passed through the naturally occurring dihydroxystearic acid (**I**), m.p. 141°, of castor oil at 160°, to give mixed chlorohydroxystearic acids, converted by boiling 2N-NaOH– or -KOH–EtOH into (d-)*oxidostearic acid* (**II**), m.p. 59·5°, $[\alpha]_D^{19}$ +0·29° in EtOH, hydrolysed by 7N-KOH at 170° (sealed tube) to *r*-dihydroxystearic acid (**III**), m.p. 95°. (**I**) and conc. HCl at 160° afford chlorohydrins and thence (**II**), with (probably) θ- and ι-ketostearic acid. *r*-Dihydroxystearic acid (**IV**), m.p. 332°, and dry HCl at 160° give chlorohydrins and thence *r*-oxidostearic acid, m.p. 59·5° [not identical with (**II**), but identical with the acid obtained from oleic acid by HOCl, followed by NaOEt–EtOH], and (**III**). (**III**) by the above procedure yields *r*-oxidostearic acid, m.p. 55·5° (identical with that obtained by autoxidation of elaidic acid), and thence (**IV**). The optical inversion involved in these transformations probably occurs during hydration of the oxide ring, and it is concluded that (**I**) is an active component of (**IV**). Configurations are assigned to the acids. A. T. P.

Autoxidation of "oxygen-active" acids. I. Gravimetric and volumetric course of the addition of oxygen to the methyl esters. W. Treibs (*Ber.*, 1942, **75**, [*B*], 203—210).—In uncatalysed action Me elæostearate rapidly absorbs 2 atoms of O; further absorption takes place very slowly and ceases before complete reaction with 3 O. In contrast to the other acids there is no elimination of H_2O in the absence of a catalyst but such is induced by impurities in the air and filter-paper used as a support for the ester. Me linoleate absorbs 4 O and loses 1 H_2O; further action of O_2 causes the production of large fragments. Me linolenate consumes 5 O and loses 2 or 1 H_2O according to conditions. Syneresis does not lead to formation of large fragments. The hexaenic ester of liver oils reacts with 7 O and eliminates 1 H_2O; further oxidation is not observed. H. W.

Oxalic acid from sawdust.—See B., 1942, II, 209.

Formation of complexes of tartaric and metatungstic acids.—See A., 1942, I, 305.

β-Methylallyl-substituted malonic ester.—See B., 1942, II, 214.

Manufacture of succinic anhydride.—See B., 1942, II, 214.

Alkylsuccinic acids. I. *n*-Tetradecyl- and *n*-hexadecyl-succinic acids. S. U. Mehta and K. S. Nargund (*J. Univ. Bombay*, 1942, **10**, *Part* 5, 141—142).—n-*Hexadecane-aaβ-tricarboxylic acid*, m.p. 135°, on pyrolysis gives *n*-tetradecylsuccinic acid, m.p. 110° (lit. 121°) (Me_2, b.p. 220°/20 mm., and Et_2 ester, b.p. 230°/20 mm.; anhydride, m.p. 74°; *imide*, m.p. 98—99°; *monoanilide*, m.p. 124—125°; *mono-p-toluidide*, m.p. 118—120°). n-*Octadecane-aaβ-tricarboxylic acid*, m.p. 135°, on pyrolysis gives n-*hexadecylsuccinic acid*, m.p. 89—90°, (Me_2, b.p. 205—210°/10 mm., and Et_2 ester, b.p. 215—220°/10 mm.; *anhydride*, m.p. 63°; *imide*, 94—95°). W. C. J. R.

Purification of maleic anhydride.—See B., 1942, II, 214.

Effect of inorganic salts on ketone decomposition of oxaloacetic acid.—See A., 1942, I, 302.

Synthesis of aminopropanols. I. O. Hromatka (*Ber.*, 1942, **75**, [*B*], 131—138).—1-γ-Hydroxypropylpiperidine, b.p. 223°/750 mm. (hydrochloride, m.p. 151°; picrate, m.p. 69°; methiodide, m.p. 133—134°; benzoate hydrochloride, m.p. 190—191°; *p*-nitrobenzoate hydrochloride, m.p. 211°), is prepared by heating piperidine (**I**) with $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ and $CH_2{:}CH{\cdot}CH_2{\cdot}ONa$ (**II**) at 100°, or by reduction of Et β-piperidinopropionate, b.p. 123°/20 mm. [from (**I**) and $CH_2{:}CH{\cdot}CO_2Et$], by Na–EtOH or by H_2 at 203°/234 atm. in presence of a $CuO–Cr_2O_3$ catalyst. (**II**) and morpholine at 108° slowly give 4-γ-hydroxypropylmorpholine, b.p. 143—145°/28 mm. (*picrate*, m.p. 136—137°; *aurichloride*, m.p. 125—127°; *benzoate hydrochloride*, m.p. 190°; p-*nitrobenzoate hydrochloride*, m.p. 238°). $NHEt_2$ and (**II**) at 110—120° give $NEt_2{\cdot}[CH_2]_3{\cdot}OH$, b.p. 122°/70 mm., in 46·7% yield. Under similar conditions $NHMeBu^\beta$ affords $NMeBu^\beta{\cdot}[CH_2]_3{\cdot}OH$ (**III**) (*benzoate picrate*, m.p. 96—98°; p-*nitrobenzoate hydrochloride*, m.p. 152—154°). (**III**) is also obtained by the reduction (Na–EtOH at 130°) of *Et β-methyl*sec.*-butylaminopropionate*, b.p. 102—105°/13 Torr. $CHMeBu^\beta{\cdot}NHMe$ gives γ-*methyl-β'-iso*hexylaminopropan-a-*ol*, b.p. 115—120°/13 Torr (p-*nitrobenzoate hydrochloride*, m.p. 127—128°). NHPhMe and (**II**) at 108° afford *methyl-γ-hydroxypropylaniline*, b.p. 180—185°/25 Torr. $NHPr^\beta_2$ and $NHBu^\beta_2$ could not be caused to react with $CH_2{:}CH{\cdot}CO_2Et$. H. W.

Formation of glycine from serine. F. Leuthardt and B. Glasson (*Helv. Chim. Acta*, 1942, **25**, 245—249).—Hippuric acid is formed from serine and BzOH but the yield of glycine obtained on hydrolysis is < that obtained with glutamine under similar conditions. H. W.

Structural specificity of choline and betaine in trans-methylation.—See A., 1942, III, 619.

Stereoisomeric aa′-iminodipropionic acids. P. Karrer and R. Appenzeller (*Helv. Chim. Acta*, 1942, **25**, 595—599).—*l*(+)-*aa′-Iminodipropionic acid*, m.p. 247° (corr.; decomp.), $[\alpha]_D^{14}$ +12·1° in H_2O, is obtained by condensation of *d*(+)-$CHMeBr{\cdot}CO_2H$ with *l*(+)-$NH_2{\cdot}CHMe{\cdot}CO_2H$ in presence of NaOH; the l-*acid*, m.p. 247° (corr.; decomp.), $[\alpha]_D^{15}$ −11·0° in H_2O, is obtained analogously from the (−)-acids. meso-*aa′-Iminodipropionic acid*, m.p. ~232—233° (decomp.), is derived by use of a (−)- with a (+)-reactant, the Walden inversion being complete. H. W.

***β-dl-a′β'*-Dihydroxy-*β'*-methylbutyramidopropionic acid.** W. Schindler and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 551—554).—$CMe_2{:}CH{\cdot}CO_2H$ is oxidised by OsO_4 and $AgClO_3$ and then esterified (CH_2N_2) to *Me aβ-dihydroxy-β-methylbutyrate*, b.p. 58—60°/0·2 mm. (corresponding amide and hydrazide are non-cryst.). $CMe_2{:}CH{\cdot}COCl$ and $NH_2{\cdot}[CH_2]_2{\cdot}CO_2Et$ give *Et β-dimethylacrylamidopropionate*, b.p. 115—117°/0·08 mm., hydrolysed to the *acid*, m.p. 100—101°. This is oxidised by OsO_4 and $AgClO_3$ and then esterified to *Me* β-dl-*$\alpha'\beta'$-dihydroxy-β'-methylbutyramidopropionate*, b.p. 105—108° (bath)/

0·005 mm. (*benzylthiuronium* salt of the corresponding acid, m.p. 154—156°). H. W.

Ureides containing a quaternary carbon atom.—See B., 1942, II, 216.

Pyrolysis of methyl and ethyl cyanides. B. S. Rabinovitch and C. A. Winkler (*Canad. J. Res.*, 1942, **20, B**, 69—72).—HCN is a primary product of the thermal decomp. of MeCN at 865° and 675°. Final products are H_2, CH_4, HCN, C, small quantities of C_2 hydrocarbons, and products of high b.p. The products of the thermal decomp. of EtCN are H_2, CH_4, C_2H_6, C_2H_4, HCN, MeCN, acrylonitrile, C, small amounts of succinonitrile, and compounds of higher b.p. A. J. M.

II.—SUGARS AND GLUCOSIDES.

Supersensitive Schiff's aldehyde reagent. Demonstration of a free aldehyde group in certain aldoses. W. C. Tobie (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 405—406).—The reagent is a 0·05% solution of basic fuchsin in 0·1% aq. SO_2. With aldose sugars a pink colour is formed. J. D. R.

So-called *iso*sucrose. H. H. Schlubach and B. Middelhoff (*Annalen*, 1942, **550**, 134—140).—The action towards enzymes of *iso*sucrose obtained by Irvine *et al.* (A., 1929, 683) from the octa-acetate, m.p. 133·5°, and NaOMe supports the view that it is an isomeride of turanose; it is regarded as *iso*turanose. A. T. P.

Preparation of aldehydo-acylated ribose.—See B., 1942, II, 216.

Heart glucosides. XIX. Lactone ring of scilliroside. A. Stoll and J. Renz (*Helv. Chim. Acta*, 1942, **25**, 377—391).—The doubly unsaturated, 6-membered lactone ring of scilliroside (**I**) is characterised by the presence of OAc in the α-position to CO. The possibility of " isomerisation " proves that (**I**), like scillarene *A* (**II**) has a *tert.*-OH at $C_{(14)}$. The action of KOH–MeOH on (**I**) is in essence similar to that on (**II**) but the product does not form stable, homogeneous alkali enolates. With $Ba(OMe)_2$ (**I**) slowly yields a cryst. non-homogeneous ppt. which after acidification reacts to only a slight extent with CH_2N_2; the substance appears to react mainly in the carbonyl form but homogeneous products could not be isolated. (**I**) and KOH–MeOH yield *Me deacetylscillirosidate* (**III**), converted by *o*-$C_6H_4(NH_2)_2$ into a *quinoxaline* derivative, $C_{37}H_{50}O_{10}N_2$. The corresponding acid loses CO_2 when treated with H_2O_2 but a homogeneous oxidation product could not be obtained. The reactions, however, decide the location of Ac in (**I**). With Ac_2O (**III**) gives an amorphous *hexa-acetate*, m.p. (indef.) 130—140°. (**III**) loses H_2O in EtOH–AcOH and becomes isomerised to the amorphous *Me deacetylisoscillirosidate* (**IV**), decomp. ~210°, which does not react with CH_2N_2 and gives an amorphous *dinitrophenylhydrazone*, decomp. 160—170°. (**IV**) is converted by Ac_2O–C_5H_5N into the cryst. *penta-acetate* (**V**), m.p. 242°, $[\alpha]_D^{20}$ −46° in MeOH. The *penta-acetate* of the corresponding Et ester has m.p. 228°, $[\alpha]_D^{20}$ −44° in MeOH. Hydrogenation (PtO_2 in MeOH) of (**V**) gives a *substance*, $C_{39}H_{56}O_{14}$, m.p. 138°, $[\alpha]_D^{20}$ −5·6° in MeOH, deacetylated by $Ba(OMe)_2$ in MeOH at 0° to the *compound*, $C_{31}H_{48}O_{10}$, $[\alpha]_D^{20}$ −25° in MeOH, and deacetylated and demethylated by NaOH–MeOH to the *substance*, $C_{30}H_{46}O_{10}$, m.p. 210°, $[\alpha]_D^{20}$ −26° in MeOH. M.p. are corr. H. W.

Carboxyl content of fibre- and wood-cellulose. E. Husemann and O. H. Weber (*J. pr. Chem.*, 1942, [ii], **159**, 334—342).—Determination of the CO_2H content of purified celluloses (**I**) by the " reversible methylene-blue method " shows that wood-(**I**) contain 1 CO_2H for 103—109 glucose residues whereas fibre-(**I**) have very high glucose vals. The high CO_2H content of cotton after purification with ClO_2 and NaOH is caused by slight impurity (pectins). Comparison of the glucose vals. with the viscosimetrically determined mean degrees of polymerisation shows the fibre-(**I**) to be approx. monocarboxylic acids, thus indicating that CO_2H is formed by oxidation of the terminal reduced glucose residues. Wood-(**I**) are polycarboxylic acids in which a macromol. contains 9—12 CO_2H and thus resemble the xylans which with the degree of polymerisation 150 have a xylose val. 16. The function of CO_2H in the plant cell is discussed. H. W.

Cupriethylenediamine as a solvent for cellulose fractionation. F. L. Straus and R. M. Levy (*Paper Trade J.*, 1942, **114**, *TAPPI Sect.*, 211—215; cf. B., 1942, II, 224).—A method is described for the fractional pptn. of cellulose (flax and cotton) (**I**), from its solution in 0·5M-$Cu(OH)_2$–$(CH_2{\cdot}NH_2)_2$ (**II**) by means of 8N-H_2SO_4 at 25°, each fraction being centrifuged, washed, dried, redissolved in (**II**), and its η measured. The amount of (**I**) in each fraction is then determined in an aliquot portion by complete pptn. with H_2SO_4 followed by oxidation with $K_2Cr_2O_7$. The nature of the (**I**)–(**II**) complex is discussed mathematically in relation to the results obtained. H. A. H.

III.—HOMOCYCLIC.

Kinetics of the formation and decomposition of di*cyclo*pentadiene. E. Baur and S. Fratter (*Helv. Chim. Acta*, 1941, **24**, 768—782).—Manometric determinations of the formation and dissociation of di*cyclo*pentadiene at 149°, 165·5°, 180°, and 195° and 109—638 mm. disclose systematic departures from the requirements of Guldberg's kinetic postulate. In the sense of Baur's kinetics, these discrepancies indicate onesidedness of the production of equilibrium. H. W.

Light absorption of geometrical isomerides and structure of vitamin-*D*. H. P. Koch (*Chem. and Ind.*, 1942, 273—275).—For *cis–trans*-isomerides or pairs of substances containing geometrically isomeric chromophores, the *cis*-form shows a much smaller extinction coeff. (ε). Steric hindrance is considered to be responsible for the feeble light absorption properties of various 2-methyl-Δ^1-*cyclo*hexene derivatives. The abnormally low ε for vitamin-*D* (calciferol) supports the postulated structure; the factors preventing free rotation to form the stable *trans*-configuration are unknown. H. B.

Raman spectra of monoalkylbenzenes and monoalkyl*cyclo*hexanes.—See A., 1942, I, 258.

Bromination of *o*-nitrotoluene. Steric effect of bromine on the relative yields of the 4- and 6-bromo-derivatives. D. R. Mehta and P. Ramaswami Ayyar (*J. Univ. Bombay*, 1942, **10, A**, *Part* 5, 99—109).—Thermal analysis of the reaction products of the bromination of *o*-$C_6H_4Me{\cdot}NO_2$ (**I**) in the presence of C_5H_5N, $Fe_2(SO_4)_3$–H_2SO_4, Fe, Fe–I (the most effective catalyst), Sb, $SbCl_3$, and $SbCl_5$ shows an average yield of 57% of 1 : 4 : 2- and 43% of 1 : 6 : 2-$C_6H_3MeBr{\cdot}NO_2$ (**I**) with Cl_2 affords 66% of 1 : 6 : 2-$C_6H_3MeCl{\cdot}NO_2$; the lower yield with Br may be due to its larger at. vol. W. C. J. R.

Sesquiterpenes. LIII. Synthesis of 5-methylazulene. P. A. Plattner and H. Roniger (*Helv. Chim. Acta*, 1942, **25**, 590—594).—5-Chloromethylindane is dehalogenated (H_2–Pd–C in EtOH) to *5-methylindane*, b.p. 74°/11 mm., converted by treatment with $CHN_2{\cdot}CO_2Et$ at 130—140° and then at 165°, followed by hydrolysis and distillation over Pd–C, into *5-methylazulene* [*picrate*, m.p. 110·5°; additive *compound*, m.p. 151·5°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$]. M.p. are corr. H. W.

Preparation of β-amino-α-phenylpropane.—See B., 1942, II, 273.

Antiplasmodial action and chemical constitution. V.—See A., 1942, II, 288.

Molecular compounds of carbamide derivatives. E. Ochiai and S. Kuroyanagi (*J. pr. Chem.*, 1941, [ii], **159**, 1—12; cf. A., 1939, II, 363).—F.p. diagrams show that compound formation does not occur between $NH_2{\cdot}CO{\cdot}NH{\cdot}COEt$ (**I**), m.p. 204° (lit. 210—211°), and *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$ (**II**) or 2-thiol-4-methylthiazole (**III**). $CO(NH{\cdot}COEt)_2$ (**IV**), however, gives 1 : 1 mol. *compounds* with (**II**), (**III**), $NH_2{\cdot}CO{\cdot}NHPh$ (**V**), and $NH_2{\cdot}CS{\cdot}NHPh$ (**VI**), and 2 : 1 *compounds* with *m*-$C_6H_4(OH)_2$ (**VII**) and $NHPh_2$. Compounds are not formed from (**IV**) and pyramidone, veronal, *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, or sulphathiazole, from (**VI**) and (**II**), (**VII**), or (**V**), from $NH_2{\cdot}CS{\cdot}NH{\cdot}CH_2Ph$, $NH_2{\cdot}CS{\cdot}NHAc$, or Et 2-thiol-4-methylglyoxaline-5-carboxylate with (**II**) and (**VII**). (**III**) yields *compounds* with (**VII**) (3 : 1) and (**II**) (1 : 1). Although $CO(NH_2)_2$ does not give a compound with (**I**) or (**V**), it forms a 1 : 1 *compound* with (**IV**). A. T. P.

Carbimides. Reaction between phenylcarbimide and sodium phenylacetylide. A. Tyabji (*J. Univ. Bombay*, 1942, **10, A**, *Part* 5, 110—113).—PhNCO and CNa:CPh in Et_2O (2 days) afford a *compound*, $C_{29}H_{21}O_3N_3$, m.p. 260°, and *isomerides*, $C_{22}H_{16}O_2N_2$, m.p. 201° (**I**) and 186° (**II**). (**I**) yields a Br_1-derivative, m.p. 190—191°. Attempted prep. of the phenylcarbamate of 4-hydroxy-2-phenylquinoline for comparison with (**I**) or (**II**) was unsuccessful. W. C. J. R.

Theory of the benzidine rearrangement. A. Pongratz and K. Scholtis (*Ber.*, 1942, **75**, [*B*], 138—145).—$(NPhAc)_2$ is not attacked by cold MeI or conc. acids, thus showing that formation of benzidine (**I**) from $(NHPh)_2$ (**II**), is an ionic change when effected by conc. acids; this view is supported by the existence of salts of (**II**) with conc. acids and their established isomerisation in aq. and non-aq. media. The change occurs with the cation since the isomerisation of unsymmetrical hydrazobenzenes invariably yields exclusively the corresponding unsymmetrical (**I**) form and not mixed forms as would be expected from an extra-mol. course of the change. The suggested scheme is: (**II**) $+2HX \rightarrow [(NH_2Ph)_2]X_2 \rightarrow [C_6H_4{\cdot}NH_2]_2X_2$. The transformation by MeI is regarded as a cryptoionic change. The driving force of the isomerisation is the considerable difference in energy content of the two systems. NPhAc·NHPh and MeI at 100° yield *N-acetyl-N′N′-dimethylbenzidine methiodide di-iodide*, m.p. 205—206°, converted by Na_2SO_3 into *N-acetyl-N′N′-dimethylbenzidine methiodide*, m.p. 228° after softening. $(NPhAc)_2$ and MeI do not react at 100° but in presence of MeOH a primary hydrolysis occurs with ultimate resulting formation of $[C_6H_4{\cdot}NMe_2I]_2I_4$ (**III**). (**II**) and cold MeI in a closed vessel shielded from light rapidly give *hydrazobenzene dihydriodide*; this is also obtained from the reactants at 100° but is then accompanied by (**III**) if the reaction is prolonged. $(NPhMe)_2$ and MeI give *dimethylhydrazobenzene dimethiodide*. (**II**) and MeI under N_2 at 100° yield benzidine dihydriodide, m.p. >270°, which with MeI and MeOH at 100° gives (**III**) and tetra-

methylbenzidine dimethiodide whereas the last-named is formed almost exclusively from (I) under like conditions. Prolonged heating of $(C_6H_4{\cdot}NMe_2)_2$,2HI with MeI and MeOH at 100° in an air-free tube leads to (III). (II) and MeBr in a sealed tube at room temp. slowly yield *hydrazobenzene dihydrobromide*. H. W.

Course of the coupling of dialkylated anilines. K. Holzach and A. Simon (*Ber.*, 1942, **75**, [*B*], 166—167).—4-*Nitro*-, m.p. 122°, 2-*chloro*-4-*nitro*-, m.p. 85·5°, 2 : 4-*dinitro*-, m.p. 110° and 6-*bromo*-2 : 4-*dinitro*-, m.p. 122°, -4′-*di*-n-*butylazobenzene* are obtained by coupling the requisite diazonium salt with $NPhBu^{\alpha}_2$. There is no evidence of the elimination of an alkyl group or production of a monoalkyl dye. The presence of strongly negative substituents does not inhibit normal coupling. H. W.

Solubilisation of diazoimino-compounds.—See B., 1942, II, 279.

Mixed triaryl thiophosphates.—See B., 1942, II, 279.

Aquo-ammono-phosphoric acids. II. Preparation of *N*-substituted derivatives of the phenyl esters of amido- and diamido-phosphoric acids. L. F. Audrieth and A. D. F. Toy (*J. Amer. Chem. Soc.*, 1942, **64**, 1337—1339).—*N*-Substituted derivatives of (*a*) Ph_2 amido- and (*b*) Ph diamido-phosphates can be prepared by aminolysis either of the corresponding chlorophosphates or of the $POCl_3$–PhOH–C_5H_5N reaction mixture. The latter method is satisfactory for (*b*), but is not recommended for (*a*). *Ph di*(*methylamido*)-, m.p. 103—105°, *di*(cyclo*hexylamido*)-, m.p. 124—125°, and *di*(*morpholido*)-*phosphate*, m.p. 85—86°, and *Ph*$_2$ *methylamido*-, m.p. 95°, cyclo*hexylamido*-, m.p. 104—105°, and *morpholido-phosphate*, m.p. 72·5—73·5°, are new. W. R. A.

Cleavage of ethers by boron bromide. I. Common ethers. F. L. Benton and T. E. Dillon (*J. Amer. Chem. Soc.*, 1942, **64**, 1128—1129).—R_2O (R = Et, Pr$^{\beta}$, or Bu$^{\alpha}$) (3 mols.) and BBr_3 (1 mol.) give good yields of ROH + RBr. PhOPr$^{\beta}$, PhOBu$^{\alpha}$, *o*-$C_6H_4Br{\cdot}OMe$, and 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}OMe$ give good yields of phenol and alkyl halide. $CH_2Ph{\cdot}OPr^{\alpha}$ gives $Pr^{\alpha}OH$ (71%) and CH_2PhBr (75%). R. S. C.

Synthesis of allyl and propenyl essential oils. General method. L. Bert (*Compt. rend.*, 1941, **213**, 873—874).— $OR{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CHCl$ (from PhOR, $CH_2Cl{\cdot}CH{:}CHCl$, and $AlCl_3$ or Zn dust) afford (with other products) (i) $OR{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CH_2$ by Na (alone or in Et_2O or a C_6H_6 hydrocarbon), (ii) $OR{\cdot}C_6H_4{\cdot}CH{:}CHMe$ by treatment with KOH–R′OH (whence $OR{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OR'$) then Na + EtOH. Estragol, safrole, methyleugenol, elemicin, anethole, *iso*safrole, *iso*-methyleugenol, *iso*elemicin, and asarone have been thus obtained. W. C. J. R.

Reduction of aromatic nitro- and polynitro-compounds. XV. Cathodic reduction of nitrophenol ethers. K. Brand and W. Schreber [with, in part, E. Heck] (*Ber.*, 1942, **75**, [*B*], 156—165; cf. A., 1935, 482).—The cathodic reduction of *o*-nitrophenyl acetate or benzoate is rendered impossible by the ease with which the esters are hydrolysed, but satisfactory results are obtained with o- (**I**), b.p. 154°/16 mm., f.p. 30·5°, and p- (**II**), b.p. 166°/14 mm., f.p. 21·2° *-nitrophenyl OMe·CH*$_2$ *ether*, obtained from $CH_2Cl{\cdot}OMe$ and the dry Na or Li salt of the NO_2-phenol. Reduction of (**I**) at a Hg cathode [anolyte is aq. Na_2CO_3 free from NaCl; catholyte is a solution of (**I**) in EtOH–H_2O–NaOAc] gives a mixture of the expected azoxy- (**III**) and hydrazo- (**IV**) -ethers, which are not isolated. (**III**) is converted by HCl into 2 : 2′-azoxyphenol, m.p. 153°. (**IV**) is oxidised by air to 2 : 2′-*dimethoxymethoxyazobenzene*, m.p. 103·5° hydrolysed by HCl to 2 : 2′-azophenol, m.p. 174° (whence 2 : 2′-azoanisole, m.p. 154·5°, and 2-hydroxy-2′-methoxyazobenzene, m.p. 122°). Under these conditions the yields of (**III**) and (**IV**) are small, but if a Ni is substituted for a Hg cathode the yield of (**IV**) is increased to 40—60% and (**III**) is obtained in small quantity. At a Ni cathode (**II**) gives a 69—70% yield of 4 : 4′-*dimethoxymethoxyazobenzene*, m.p. 82—83°, not apparently accompanied by the azoxy-ether. It is hydrolysed to 4 : 4′-azophenol, m.p. 211°. With MeOH–NaOMe (**I**) and (**II**) exchange $OMe{\cdot}CH_2$ for Me before reduction to the azoxyanisole occurs. p-$NO_2{\cdot}C_6H_4{\cdot}OLi$ (+3H_2O) is described. H. W.

Thermal rearrangement of *m*-acetamidophenyl allyl ether. R. T. Arnold, J. McCool, and E. Schultz (*J. Amer. Chem. Soc.*, 1942, **64**, 1023—1025).—*m*-$NHAc{\cdot}C_6H_4{\cdot}OH$, $CH_2{:}CH{\cdot}CH_2Br$, and K_2CO_3 in $COMe_2$ give m-*acetamidophenyl allyl ether*, m.p. 87—88°, rearranged in boiling $NPhMe_2$–H_2 or –N_2 (not in ligroin, b.p. 200—220°) into 5-*acetamido*-2-*allylphenol*, m.p. 160·5—162° [*acetate* (**I**), m.p. 132—133°]. H_2–PtO_2 and (**I**) in EtOH give (after hydrolysis with aq. K_2CO_3) 5-*acetamido*-2-*propylphenol* (**II**), m.p. 173·5—174°, hydrolysed by HCl to 5 : 2 : 1-$NH_2{\cdot}C_6H_3Pr^{\alpha}{\cdot}OH$, m.p. 132—132·5° [with Ac_2O gives the *acetate*, m.p. 117·5—118°, of (**II**), converted thereinto by aq. Na_2CO_3 + NaOH], which is also obtained by the method of Hartung *et al.* (A., 1941, II, 131), who obtained a form, m.p. 109—110°. 3 : 4 : 1-$NO_2{\cdot}C_6H_3Pr^{\alpha}{\cdot}NH_2$ [prep. from 1 : 2 : 4-$C_6H_3Pr^{\alpha}(NO_2)_2$ by H_2S–NH_3–H_2O–EtOH], m.p. 59—59·5°, gives (diazo-reaction) 3-*nitro*-, m.p. 46·5—47·5°, reduced by H_2–Pt in EtOH to 3-*amino*-4-n-*propylphenol*, m.p. 152—153° (acetylation gives oils). R. S. C.

Action of thionyl chloride on β-naphthol and 1-hydroxy-2-naphthoic acid. J. W. Airan and S. V. Shah (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 128—130).—β-$C_{10}H_7{\cdot}OH$, $SOCl_2$, and $BiCl_3$ in Et_2O or C_6H_6 afford 2 : 2′-dihydroxy-1 : 1′-dinaphthyl sulphide, m.p. 212°, whilst 1 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ similarly yields 4 : 4′-dihydroxy-3 : 3′-dicarboxy-1 : 1′-dinaphthyl sulphide, m.p. 265°. W. C. J. R.

Interaction of sulphuryl chloride and naphthol derivatives. J. W. Airan and S. V. Shah (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 131—134).—α-$C_{10}H_7{\cdot}OH$, SO_2Cl_2, and $BiCl_3$ in Et_2O afford 4 : 1-$G_{10}H_6Cl{\cdot}OH$; 2 : 1-$C_{10}H_6Ac{\cdot}OH$ similarly gives 4-*chloro*-2-*acetyl*-1-*naphthol*, m.p. 116° (*acetate*, m.p. 82°); 1 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ yields 1 : 4 : 2-$OH{\cdot}C_{10}H_5Cl{\cdot}CO_2H$ (*acetate*, m.p. 102°); 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ gives 3 : 4 : 2-$OH{\cdot}C_{10}H_5Cl{\cdot}CO_2H$ (*acetate*, m.p. 186°). W. C. J. R.

Preparation of alkali formaldehydesulphoxylate–diaminodiphenyl sulphide or sulphone reaction products.—See B., 1942, II, 279.

Dielectric polarisation of benzyl alcohol.—See A., 1942, I, 293.

Synthesis of "heavy" *dl*-adrenaline. G. R. Clemo and G. A. Swan (*J.C.S.*, 1942, 395—397).—All six H of *o*-$C_6H_4(OH)_2$ exchange with D_2O in alkaline solution at 100°, although replacement of the last is very slow. The "*heavy*" *pyrocatechol*, m.p. 104°, used for subsequent reactions, was approx. $C_6HD_5O_2$. With $CD_2Cl{\cdot}CO_2D$ and $POCl_3$ at 55—60°, followed by hot D_2O, it affords "heavy" chloroacetylpyrocatechol, m.p. 172° (85·5 atoms % D), converted by $CD_3{\cdot}ND_2$ in D_2O at room temp. into "heavy" adrenalone, and thence by hot dil. D_2O–D_2SO_4 into the "heavy" sulphate, which is reduced (D_2, Pd–C, D_2O) to "heavy" *dl*-adrenaline (90 atoms % D, *i.e.* $C_9H_{11\cdot3}D_{11\cdot7}O_3N$). Its physiological action is almost indistinguishable from that of "light" *dl*-adrenaline. A. T. P.

Substituted cinnamic acid esters and amides.—See B., 1942, II, 280.

Attempted direct synthesis of β-substituted cinnamic acids. B. D. Patel and K. V. Bokil (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 123—127).—Condensation of $CH_2Ac{\cdot}CO_2Et$ (**I**) with phenolic ethers in presence of varying [H_2SO_4] is studied; concns. <80% are ineffective. 80% H_2SO_4 yields substituted butyric acids and/or esters and more complex acids (**II**) formed by addition of (**I**) to any cinnamic acid (**III**) or ester formed. 85% H_2SO_4 gives (**II**) and sulphonated acids. Contrary to Limaye (A., 1940, II, 129) no substituted (**III**) has been obtained. PhOEt and (**I**) yield *ββ-di*-p-*phenetylbutyric acid*, m.p. 60—62° (anilide, m.p. 135°), also obtained from *p*-$OEt{\cdot}C_6H_4{\cdot}CMe{:}CH{\cdot}CO_2H$ and PhOEt in 80% H_2SO_4. *o*-$C_6H_4Me{\cdot}OMe$ and (**I**) yield *ββ-di*-6-*methoxy*-m-*tolylbutyric acid*, m.p. 131—132° (anilide, m.p. 141—142°); *m*-$C_6H_4Me{\cdot}OMe$ yields 4 : 7-dimethylcoumarin, m.p. 132—133°; *p*-$C_6H_4Me{\cdot}OMe$ gives 4 : 6-dimethylcoumarin, m.p. 150—151°. W. C. J. R.

Synthesis of 3′ : 5′-di-iodothyronine. P. Block, jun., and G. Powell (*J. Amer. Chem. Soc.*, 1942, **64**, 1070—1074).—Iodination of thyronine gives mixtures (cf. lit.). *K* 2 : 6-*di-iodo*-4-*nitrophenoxide* best (~80%) prepared from *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$ by ICl–AcOH–H_2O etc. at 95°, with Me_2SO_4–K_2CO_3–$PhNO_2$ at 130° gives the Me ether (85%), reduced by Fe–AcOH to 4 : 2 : 6 : 1-$NH_2{\cdot}C_6H_2I_2{\cdot}OMe$ (90%), m.p. 105° (lit. 100°). A diazo-reaction ($OBu{\cdot}NO$–H_2SO_4–AcOH at 15—18°; then H_2SO_4–H_2O at 110°) then yields 2 : 6-*di-iodoquinol* 1-*Me ether* (75%), m.p. 125—125·5° (derived *Me*$_2$ *ether*, m.p. 56°, also obtained from 4 : 3 : 5 : 1-$NO_2{\cdot}C_6H_2I_2{\cdot}OH$ by way of the quinone), which with *p*-$C_6H_4Cl{\cdot}NO_2$–KOH–H_2O (little) at 130° (later 160°) gives 3′ : 5′-*di-iodo*-4-*nitro*-4′-*methoxydiphenyl ether* (70%), m.p. 124—124·5°, reduced by H_2–$Pd(OH)_2$–$CaCO_3$ in EtOH–NaOH (little) to *p*-$NH_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}OMe$-*p* (**I**) and by Fe filings + powder in EtOH–H_2O–AcOH at 100° to 3′ : 5′-*di-iodo*-4-*amino*-4′-*methoxydiphenyl ether* (90%), m.p. 105·5° [hydrochloride, m.p. 232—233°; Ac derivative, m.p. 176·5°, hydrogenated as above to (**I**)]. By the Sandmeyer reaction this yields p-3′ : 5′-*di-iodo*-4′-*methoxyphenoxybenzonitrile* (40%), softens at 133·5—134·5°, m.p. 138·5—139·5°, reduced (Stephen) to the *aldehyde* (55%), m.p. 119° after softening, which by way of the azlactone gives *α-benzamido*-p-3′ : 5′-*di-iodo*-4′-*methoxyphenoxycinnamic acid* (85%), m.p. 230—231°. With red P–HI–AcOH–H_3PO_2 and then HBr this gives, first, 3′ : 5′-*di-iodothyronine Me ether*, decomp. 212° (preheated at 190°), and then mainly 3′ : 5′-*di-iodothyronine*, decomp. 206° (preheated at 190°) [reduced by H_2–$Pd(OH)_2$–$CaCO_3$ in aq. NaOH to thyronine], which is <¼ as active (? inactive) as thyroxine. R. S. C.

Syntheses in the chaulmoogric acid series. IV. Synthesis of β-*dl*-Δ^2-*cyclo*pentenylpropionic acid, a new homologue of chaulmoogric acid. K. V. Bokil and K. S. Nargund (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 118—122).—Reduction (Na–Hg, 80% EtOH) of Et *cyclo*pentanone-2-carboxylate-5-β-propionate (cf. Cook *et al.*, A., 1934, 1002) and dehydration (Ac_2O) of the OH-acid yields a mixture separated by fractionation of the Ba salts from EtOH. The less sol. salt gives an unsaturated dibasic *acid*, $C_9H_{12}O_4$, m.p. 128—129°. The sol. salt gives mixed Et esters whence the Et ester, b.p. 90—92°/7 mm., of β-Δ^2-cyclo*pentenylpropionic acid*, b.p. 127—129°/7 mm. Et Δ^1- or Δ^2-*cyclo*pentene-1-carboxylate is reduced (Na, EtOH) to Δ^1-cyclo*pentenylcarbinol*, b.p. 57/10 mm. (p-*nitrobenzoate*, m.p. 36—37°). W. C. J. R.

Synthesis of anti-leprosy drugs. I. New synthesis of κ-*cyclo*hexylundecoic acid, an analogue of dihydrohydnocarpic acid. (Miss)

B. C. Pandya, K. S. Nargund, and K. V. Bokil (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 114—117).—Et potassio*cyclo*hexanone-2-carboxylate (modified prep.) and Et κ-bromoundecoate in C_6H_6 afford *Et* cyclo*hexanone-2-carboxylate-2-κ-undecoate*, b.p. 260—265°/13 mm., hydrolysed by boiling conc. HCl to 2-*carbethoxy*cyclo*hexanone-2-κ-undecoic acid*, b.p. 260—265°/3 mm., and by KOH–MeOH to the crude dibasic acid, which on distillation gives κ-2-*keto*-cyclo*hexylundecoic acid*, m.p. 61—62° (Et ester, b.p. 210—215°/3 mm.; semicarbazone, m.p. 134—135°), reduced (Clemmensen) to κ-*cyclo*hexylundecoic acid, m.p. 57—58° (Et ester, b.p. 193—195°/3 mm.; *amide*, m.p. 107—108°). W. C. J. R.

Derivatives of 3 : 5-di-iodohippuric acid. B. K. Blount, J. C. L. Resuggan, and F. A. Robinson (*Quart. J. Pharm.*, 1942, **15**, 16—20). —3 : 5-*Di-iodo*-4-*hydroxyhippuric acid* (**I**), m.p. 223—224° [O-*Ac*, m.p. 205—206°, and O-*benzyl*, m.p. 216—218° (Et ester, m.p. 164—165°), derivatives], prepared from glycine and *p*-OAc·C_6H_4·COCl followed by hydrolysis and iodination, yields a very sol. Na_2 salt. When injected intravenously into rabbits there is 100% excretion (begins ~75 min. after injection; complete in ~2·5 hr.). The toxicity is 1·8 times as great as that of iodoxyl (**II**). 3 : 5-*Di-iodo*-4-*carboxymethoxyhippuric acid*, m.p. 227° (Et_2 ester, m.p. 112—113°), from $CH_2Cl·CO_2Et$ and the Et ester of (**I**) followed by hydrolysis, is nearly 1·4 times as toxic as (**II**) when tested on rats and nearly twice as toxic when tested on mice. J. N. A.

Alkanolamines. XI. Monoalkylamino-alcohols and their esters. C. B. Kremer and E. Waldman (*J. Amer. Chem. Soc.*, 1942, **64**, 1089—1090).—$NH_2·CMe_2·CH_2·OH$ and RBr in boiling EtOH give *β-ethyl-*, m.p. 75·5—76·5°, b.p. 162—163°, -n-, m.p. 59·5—60·5°, b.p. 183—185°, and -iso-*propyl-*, m.p. 43—45°, b.p. 165—166°, -n-, m.p. 69·5—70°, b.p. 195—196°, and -iso-*butyl-*, m.p. 51—52·5°, b.p. 185—186°, -n-, m.p. 60—60·5°, b.p. 216—217°, and -iso-*amyl-*, m.p. 76·5—77°, b.p. 205—207°, -*amino*iso*butyl alcohol*, converted by *p*-$NO_2·C_6H_4·COCl$ in C_5H_5N at 30—40° (not in alkali) into the p-*nitrobenzoates*, m.p. 206·5—207° (impure), 185—185·5°, 140—141° (impure), 163·5—164°, 165—166°, 151—151·5°, and 168—168·5°, respectively. In conc. HCl at +40—45° powdered Sn then gives the hygroscopic *p*-aminobenzoate hydrochlorides (not detailed). R. S. C.

Amidine salts of aminobenzoic acids.—See B., 1942, II, 280.

Dimorphism of amylcaine hydrochloride. H. R. Kreider and A. R. Menotti (*J. Amer. Chem. Soc.*, 1942, **64**, 1227—1228).—Dimorphic forms, m.p. 153·5° (corr.) and 176° (2 pseudomorphs), of *p*-$NH_2·C_6H_4·CO_2·[CH_2]_2·NH·C_5H_{11}$-*n*,HCl are described with photomicrographs. R. S. C.

Rearrangement of 3 : 5-dichloro-4-crotyloxybenzoic acid. D. S. Tarbell and J. W. Wilson (*J. Amer. Chem. Soc.*, 1942, **64**, 1066—1070; cf. A., 1942, II, 258).—Alkaline hydrolysis of 4 : 3 : 5 : 1-$OH·C_6H_2Cl_2·CO_2Et$ (**I**) (prep. from *p*-$OH·C_6H_4·CO_2Et$ by SO_2Cl_2 in 81% yield), m.p. (+H_2O) 108—116° (decomp.) and (anhyd.) 111—112°, gives the acid (89%), m.p. 268—269° (lit. 265°). (**I**) with, best (63%; 22% pure), CHMe:CH·CH_2Br and NaOH in boiling, aq. $COMe_2$ and subsequent hydrolysis (Claisen's alkali) gives 3 : 5-*dichloro*-4-*crotyloxybenzoic acid* (**II**), m.p. 150—152° [structure proved by oxidation by alkaline $KMnO_4$ to 2 : 6-*dichloro*-4-*carboxyphenoxyacetic acid* (78%), m.p. 248—250°, not obtained from (**I**) and $CH_2Br·CO_2Et$]. Rearrangement of (**II**) to 4 : 2 : 6 : 1-CHMe:CH·$CH_2·C_6H_2Cl_2$·OH (**III**) (61%) (*phenylurethane*, m.p. 149—150°) occurs without inversion at 165—175°, but in $NPhMe_2$ at 155° only decarboxylation occurs. 78% of 2 : 6 : 1-$C_6H_3Cl_2·OH$ is obtained from 4 : 3 : 5 : 1-$OH·C_6H_2Cl_2·CO_2H$ in $NPhMe_2$ at 155°, later 190°. 4 : 2 : 6 : 1-$C_6H_2Bu^aCl_2·OH$, b.p. 111—115°/3 mm. (*phenyl-*, m.p. 143—144°, and *α-naphthyl-urethane*, m.p. 142—143°), is obtained from (**III**) by H_2–PtO_2 in EtOH and by Clemmensen reduction of 3 : 5-*dichloro*-4-*hydroxybutyrophenone* (**IV**), m.p. 96—97°. 2 : 6-*Dichlorophenyl* n-*butyrate* [prep. by $(Pr^aCO)_2O$–C_5H_5N at 100°], b.p. 118—119°/3 mm., with $AlCl_3$ in $PhNO_2$ at room temp. gives 2 : 6 : 1-$C_6H_3Cl_2·OH$ (~57%) but at 140—150° (no solvent) gives (**IV**) (59%). 2 : 6-*Dichlorophenyl acetate*, b.p. 125—126°/17 mm., gives similarly 3 : 5-*dichloro*-4-*hydroxyacetophenone* (69%), m.p. 164—165·5°, converted by MgEtBr into *β*-3 : 5-*dichloro*-4-*hydroxyphenylbutan-β-ol* (56%), m.p. 116—117°, which with a trace of I at 185° gives 2 : 6-*dichloro*-4-(?)*α-methylpropenyl-* (88%), b.p. 161—163°/17 mm., and thence (H_2–PtO_2; EtOH) -4-sec.-*butyl-phenol*, m.p. 68—70° (*phenylurethane*, m.p. 100—101°). 2 : 6-*Dichlorophenyl allyl ether* (prep. by CH_2:CH·CH_2Br and K_2CO_3 in COMeEt), b.p. 89—90°/2 mm., at 193—200° (N_2) gives 2 : 6-*dichloro*-4-*allyl-* (~57%), m.p. 33—35°, b.p. 104—108°/3 mm., and 6-*chloro*-2-*allyl-phenol* (~10%) (**V**), b.p. 61—63°/1 mm. (*α-naphthylurethane*, m.p. 125—126°). o-*C_6H_4Cl allyl ether* (prep. in $COMe_2$), b.p. 108—110°/15 mm., at the b.p. gives 89% of (**V**). R. S. C.

***p*-Sulphonamidobenzamidine.**—See B., 1942, III, 189.

Attempted synthesis of homo*iso*vanillic acid. O. Hromatka (*Ber.*, 1942, **75**, [*B*], 123—131).—Attempts from *o*-$NO_2·C_6H_4·OMe$ and *o*-$C_6H_4Cl·OMe$ are described. 3 : 4 : 1-$NO_2·C_6H_3(OMe)·CH_2Cl$ is converted by KCN in aq. EtOH at 65—70° into 3-*nitro*-4-*methoxyphenylacetonitrile*, m.p. 86—87°, b.p. 175°/0·3 mm., reduced (H_2, Pd–C, MeOH at 19·5°) to 3-amino-4-methoxyphenylacetonitrile (**I**) (*hydrochloride*, m.p. 202°; picrate, m.p. 180°); attempts to diazotise the base were unsuccessful. (**I**) and 85% H_2SO_4 at 50° give 3-*nitro*-4-*methoxy-* (**II**), m.p. 155°, whereas at 95° the product is -4-*hydroxy-*, m.p. 162°, -*phenylacetamide*. (**II**) is converted by boiling aq. NaOH into 3-*nitro*-4-*methoxyphenylacetic acid* (**III**), m.p. 132°, reduced (as above) to the 3-NH_2-acid, m.p. 105°, which yields red resins and a small amount of *p*-$OMe·C_6H_4·CH_2·CO_2H$ when diazotised and boiled with H_2O. (**II**) is reduced to 3-*amino*-4-*methoxyphenylacetamide*, m.p. 164°. 2N-NaOMe–MeOH at 120° converts (**III**) into 2 : 2′-*dimethoxyazoxybenzene*-5 : 5′-*diacetic acid*, m.p. 195—196°. 4 : 3 : 1-$OMe·C_6H_3Cl·CH_2Cl$, m.p. 38° (obtained in 89·7% yield by saturating *o*-$C_6H_4Cl·OMe$ in an excess of 40% CH_2O with HCl at 96°), and KCN in boiling $Pr^{\beta}OH$ give 3-*chloro*-4-*methoxyphenylacetonitrile*, m.p. 55°, hydrolysed by KOH–H_2O–EtOH to the *acid* (**IV**), m.p. 98°, which is oxidised by $KMnO_4$ to 4 : 3 : 1-$OMe·C_6H_3Cl·CO_2H$, m.p. 213°. NaOMe in MeOH at 185° converts (**IV**), into 3-*chloro*-4-*hydroxyphenylacetic acid*, m.p. 107°. With KOH–NaOH at 220° (**IV**) gives 2 : 4 : 1-$OH·C_6H_3(OMe)·CH_2·CO_2H$, m.p. 130°, which when distilled affords 5-*methoxycoumaranone*, m.p. 56°, and with CH_2N_2 gives 2 : 4 : 1-$(OMe)_2C_6H_3·CH_2·CO_2H$. 3 : 3′-*Dichloro*-4 : 4′-*dimethoxydiphenylmethane*, m.p. 78°, is obtained from *o*-$C_6H_4Cl·OMe$, CH_2O, $ZnCl_2$, and HCl at 90°. H. W.

Phenylglutaric acids. III. αα-Diphenylglutaric acid. J. J. Trivedi, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 135—136; cf. A., 1937, II, 195; 1938, II, 188).—$CHPh_2·CN$, I·$[CH_2]_2·CO_2Et$, and EtOH–NaOEt give after hydrolysis (20% NaOH at room temp.) *γ-cyano-γγ-diphenylbutyric acid*, m.p. 161—162°, hydrolysed (conc. HCl, 160—170°, 6 hr.) to *αα-diphenylglutaric acid*, m.p. 193—194° [*anhydride* (**I**), m.p. 142—143°; *monoanilide*, m.p. 208°; *mono*-p-*toluidide*, m.p. 168°]. (**I**) at 180—190° in dry NH_3 yields *αα-diphenylglutarimide*, m.p. 158—159°. W. C. J. R.

***cyclo*Hexane series. VI. Stereoisomeric forms of 4- and 3-methyl-*cyclo*hexane-1 : 1-dicarboxylic acid, and conclusive chemical evidence for the multiplanar *cyclo*hexane ring.** R. D. Desai, R. F. Hunter, and G. S. Sahariya (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 168—172). —1-Carboxy-4-methyl-1-*cyclo*hexylacetic acid-*A*, m.p. 173°, and -*B*, m.p. 137°, with successively PCl_5, Br first at room temp. (sunlight) and then at 50—60°, and HCO_2H, yield the *-α-bromoacetic acid*-A, m.p. 152° [with the *β-lactone*, m.p. 110° (previous sintering) (*NH_2Ph* salt +H_2O, m.p. 160°), of (**I**) (below)], and -B, m.p. 132°, respectively, hydrolysed (2N-aq. Na_2CO_3) to the -1-*carboxylic*-1-*glycollic acid*-A (**I**), m.p. 134°, and -B, m.p. 138°, respectively, oxidised (alkaline $KMnO_4$) to the -1 : 1-*dicarboxylic acid*-A, m.p. 170° (decomp.), and -B, m.p. 175° (decomp.), respectively. Similarly 1-carboxy-3-methyl-1-*cyclo*hexylacetic acid-*A*, m.p. 163°, and -*B*, m.p. 108—109°, yield the *-α-bromoacetic acid*-A, m.p. 142°, and -B, m.p. 155°, respectively, -1-*carboxylic*-1-*glycollic acid*-A, m.p. 166°, and -B, m.p. 134°, respectively, and -1 : 1-*dicarboxylic acid*-A, m.p. 171—172° (decomp.), and -B, m.p. 185° (decomp.), respectively. The existence of the above pairs of stereoisomeric 1 : 1-dicarboxylic acids supplies the first proof of the multiplanar forms of the *cyclo*hexane ring. A. Lı.

Sulphur studies. XVIII. Sulphonium derivatives from *p*-phenylphenacyl bromide. R. W. Bost and H. C. Schultze (*J. Amer. Chem. Soc.*, 1942, **64**, 1165—1167; cf. A., 1941, II, 332).—*p*-$C_6H_4Ph·CO·CH_2Br$ (**I**) and Alk_2S, in, best, boiling abs. MeOH give p-*phenylphenacyldialkylsulphonium bromides* (*A*), which with the Ag salts of strong acids give the derived other sulphonium salts. Sulphonium salts of weak acids (AcOH, BzOH, *o*-$OH·C_6H_4·CO_2H$, *p*-$NH_2·C_6H_4·SO_2·NH_2$) cannot be isolated and with H_2S give the sulphonium H sulphide, which decomposes to give p-*phenylphenacyl mercaptan*, m.p. 109° (2 : 4-dinitrophenylhydrazone, m.p. 159°), and R_2S. (*A*) and the derived *nitrates*, *H sulphates*, and *sulphanilates*, respectively, are described in which the alkyl are *Me_2*, m.p. 148°, 136°, —, and 166° (and the normal *sulphate*, m.p. 148°), *Et_2*, m.p. 131°, 125°, 157°, and 139°, *Pr^{α}_2*, m.p. 117°, 118°, 152°, and an oil, *Bu^{α}_2*, m.p. 96—107°, 138°, 172°, and an oil, *Me Et*, m.p. 139°, 134°, 155°, and 163°, *Me Pr^{α}*, m.p. 131°, 121°, an oil, and 158°, *Me Bu^{α}*, m.p. 119°, 137°, 168°, and 146° (and the *benzenesulphonate*, m.p. 129—134°), and *diallyl*, m.p. 72°, —, —, —. COPh·CH_2Br and $MeSBu^{\alpha}$ in abs. MeOH give SMe_2BuBr. *p*-Phenylphenacyldi-*n*- and -*iso*-amylsulphonium bromides are oils. R. S. C.

Constitution of natural tannins. VIII. Colouring matters derived from anthracene-9-aldehyde. A. Russell and W. B. Happoldt, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1101—1103; cf. A., 1941, II, 173).—9-Anthraldehyde (improved prep.) and COArMe in HCl–EtOAc at room temp. give 27—71% of *Ph*, m.p. 122—123°, o-*benzoyloxy-*, m.p. 151°, o-, m.p. 159—160°, m-, m.p. 202°, and p-*hydroxy-*, m.p. 241—242°, 2 : 6-, m.p. 224°, and 2 : 5-*dibenzoyloxy-*, m.p. 171°, 2 : 5-, m.p. 146°, and 2 : 4-*diacetoxy-*, m.p. 188°, 2 : 5-, m.p. 228·5°, and 2 : 4-*dihydroxy-* (prep. in boiling KOH–MeOH–N_2), m.p. 199°, 2 : 3 : 4-*tribenzoyloxy-*, m.p. 161—162°, 2 : 4-, m.p. 139°, and 2 : 6-*dimethoxyphenyl*, m.p. 202°, p-*diphenylyl*, m.p. 212—213°, and *β-$C_{10}H_7$* *β*-9-

anthranylvinyl ketone, m.p. 163°. 2 : 4 : 1-(OH)$_2$C$_6$H$_3$·COMe gives *7-hydroxy-2-9′-anthranylbenzopyrone* (59%), m.p. 212—220°. R. S. C.

***anti*-Phenyl phenylthiolmethyl ketoxime. Attempted synthesis of benzo-*m*-thiazine derivatives.** E. Vinkler (*J. pr. Chem.*, 1941, [ii], **159**, 115—120).—SPh·CH$_2$·COPh affords the anti-*oxime* (**I**), m.p. 81—82°, converted (PCl$_5$–Et$_2$O) into SPh·CH$_2$·CO·NHPh, m.p. 82—83° (also obtained from SPh·CH$_2$·CO$_2$H and NH$_2$Ph at 150°). (**I**) could not be converted into the *syn*-form. A. T. P.

Condensation of *o*-anisylsuccinic anhydride with *o*- and *m*-tolyl methyl ethers. B. S. Mehta, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1942, **10**, **A**, *Part 5*, 137—140; cf. A., 1940, II, 132).—*o*-Anisylsuccinic anhydride (**I**), *o*-C$_6$H$_4$Me·OMe, and AlCl$_3$ in PhNO$_2$ or C$_6$H$_2$Cl$_4$ give *β*-6-*methoxy*-m-*toluoyl*-*α*-*o*-*anisylpropionic acid* (44—54%), m.p. 183° [with MeOH–HCl gives a pyrylium compound, m.p. >300°; *Me* (via Ag salt), m.p. 101°, and *Et* ester, m.p. 63—65°], and *β*-6-*methoxy*-m-*toluoyl*-*β*-*o*-*anisylpropionic acid* (42—49%), m.p. 140—141° (*semicarbazone*, m.p. 200°; *Me*, m.p. 113°, and *Et* ester, m.p. 93°). 4 : 3 : 1-OMe·C$_6$H$_3$Me·COMe, *o*-OMe·C$_6$H$_4$·CHO (**II**), and 50% aq. NaOH afford 6-*methoxy*-m-*tolyl* *o*-*methoxystyryl ketone*, m.p. 79°, which did not react with KCN or Br. (**I**) similarly condenses with *m*-C$_6$H$_4$Me·OMe to give *β*-5-*methoxy*-*o*-*toluoyl*-*α*-*o*-*anisylpropionic acid* (**III**) (58—60%), m.p. 151—152° (*Me*, m.p. 115°, and *Et* ester, m.p. 122°), and *β*-5-*methoxy*-*o*-*toluoyl*-*β*-*o*-*anisylpropionic acid* (20—27%), m.p. 125°. 5-*Methoxy*-*o*-*tolyl* *o*-*methoxystyryl ketone*, b.p. 210—215°/11 mm. [from 4 : 2 : 1-OMe·C$_6$H$_3$Me·COMe and (**II**)], with KCN gives a product hydrolysed to (**III**). W. C. J. R.

Self-condensation of acetyl*cyclo*hexene. E. R. H. Jones and H. P. Koch (*J.C.S.*, 1942, 393—395).—The two dimerides, m.p. 205° [*mono-oxime*, m.p. 254° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 293°] and new m.p. 130° [*mono-oxime*, m.p. ~250° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 212—213°], formed from 1-acetyl*cyclo*hexene by NaNH$_2$–Et$_2$O (cf. Rapson *et al.*, A., 1935, 1498) are probably stereoisomeric *α*- and *β*-9-*keto*-12-*acetyltetradecahydrophenanthrene*, respectively. They both yield (Se at 300°) phenanthrene and show no high-intensity absorption in the ultra-violet. A third condensation product is probably 1-*keto*-3-Δ$^{1'}$-cyclo*hexenyl*-Δ^2-*octahydronaphthalene*, m.p. 85° [*oxime*, m.p. 232° (decomp.); *semicarbazone*, m.p. 213°; 2 : 4-*dinitrophenylhydrazone*, m.p. 228°], dehydrogenated by Pd–C at 340° (in CO$_2$) to 2-C$_{10}$H$_7$Ph. 1-Acetyl-2-methyl*cyclo*hexene does not undergo self-condensation with NaNH$_2$–Et$_2$O. A. T. P.

Antihæmorrhagic activity of sulphonated derivatives of 2-methylnaphthalene. B. R. Baker, T. H. Davies, L. McElroy, and G. H. Carlson (*J. Amer. Chem. Soc.*, 1942, **64**, 1096—1101).—Heating 1 : 2 : 4-O:C$_{10}$H$_5$Me:O with aq. NaHSO$_3$ or KHSO$_3$ at 100° and then cooling at 0° and adding COMe$_2$ ppts. the biologically active *Na* or *K* salt (**I**), respectively, of the 1 : 1 additive compound. Concn. of the mother-liquor and addition of KCl yields *K* 2-*methyl*-1 : 4-*naphthaquinol*-3-*sulphonate* (**II**), which has <0·1 times the biological potency of (**I**). (**I**) and (**II**) are differentiated by formation of the corresponding S-*benzylthiuronium* salts, m.p. 127—129° (decomp.) and 138—139° (decomp.), respectively. With K$_2$Cr$_2$O$_7$–H$_2$SO$_4$–H$_2$O at 25°, (**II**) or the initial crude reaction product gives readily *K* (**III**) and thence S-*benzylthiuronium* 2-*methyl*-1 : 4-*naphthaquinone*-3-*sulphonate*, m.p. 156—157°; the *Na* salt is similarly obtained. (**III**) is reconverted into (**II**) by Na$_2$S$_2$O$_4$ and with alkaline KMnO$_4$ gives *o*-C$_6$H$_4$(CO$_2$H)$_2$ (**IV**). The structure of (**II**), (**III**), etc. is proved as follows. 2 : 1 : 4-C$_{10}$H$_5$Me(OAc)$_2$ (**V**) with ClSO$_3$H in CHCl$_3$ at room temp. gives *Na* 2-*methyl*-1 : 4-*naphthaquinol*-3-*sulphonate diacetate*, m.p. 148—150° (decomp.), oxidised by CrO$_3$–AcOH–H$_2$O–KCl to (**III**) and converted by HNO$_3$–H$_2$O into 3-*nitro*-2-*methyl*-1 : 4-*naphthaquinone*, m.p. 124·5—125·8°. KMnO$_4$ oxidises this to (**IV**), and H$_2$–PtO$_2$ in AcOH yields 3-amino-2-methyl-1 : 4-naphthaquinol, isolated as *hydrochloride*, m.p. 205—207° (decomp.), or *triacetate* (**VI**) (prep. at 80—100°), m.p. 214—215° (with boiling Ac$_2$O–NaOAc gives the *tetra-acetate*, m.p. 173—174·5°), and oxidised by FeCl$_3$–HCl–H$_2$O to 3-*amino*-2-*methyl*-1 : 4-*naphthaquinone*, m.p. 162—162·5°, which in hot 10% NaOH gives phthiocol. With NH$_3$ in aq. MeOH at 45°, (**V**) gives 2-*methyl*-1 : 4-*naphthaquinol* (*mono*-)*acetate*, m.p. 124·5—125·8°, the 3-p-*nitrobenzeneazo*-derivative, m.p. 274—276°, of which with KMnO$_4$ gives (**IV**) and with H$_2$–catalyst in AcOH and then Ac$_2$O–NaOAc at 100° gives (**VI**) and thence (boiling 10% NaOH–air) phthiocol. The stability of (**I**) to K$_3$Fe(CN)$_6$ etc. greatly exceeds that of (**II**). The 3-sulphonate is formed by way of the active additive compound, since the yield of (**III**) and the amount of reducible material (potentiometric) increase if the initial heating is prolonged. The rate of conversion (followed by titration with 2 : 6-dichlorophenol-indophenol) is decreased by increase in acidity. The bearing of the results on the use of commercial preps. ("Hykinone") is noted. R. S. C.

Sulphonation of 1-aminoanthraquinone compounds.—See B., 1942, II, 280.

IV.—STEROLS AND STEROID SAPOGENINS.

7-Benzoyloxysterols and their use in preparation of 7-dehydrosterols. O. Wintersteiner and W. L. Ruigh (*J. Amer. Chem. Soc.*, 1942, **64**, 1177—1179).—7(*α*)-Benzoyloxycholesteryl benzoate with NaOMe–MeOH–C$_6$H$_6$ at room temp. gives, after chromatography, 7(*α*)-*benzoyloxycholesterol* (**I**), m.p. 110—115°, [*α*]$_D^{24}$ +111° in CHCl$_3$ [absorption max. at 230 (*ε* 12,750) and 272 m*μ*. (*ε* 740); 3 : 5-*dinitrobenzoate*, m.p. 162—163°, [*α*]$_D^{24}$ +80·5° in CHCl$_3$; p-*toluenesulphonate*, m.p. varies, 90° to 100° (decomp.), with KOAc–MeOH gives an impure compound, m.p. 153·5—155·5°; no digitonide]. Pyrolysis (2 mm.) or boiling in NPhMe$_2$–CO$_2$ converts (**I**) into 7-dehydrocholesterol, m.p. 142·5—143·5°, [*α*]$_D^{28}$ −121° in CHCl$_3$ (3 : 5-dinitrobenzoate, m.p. 209·5—210·5°, [*α*]$_D^{26}$ −38·3° in CHCl$_3$) (cf. lit.). 7(*α*)-Benzoyloxystigmasteryl benzoate, m.p. 183·5—185° (lit. 156—158°, 184—186°), with NaOMe–MeOH–C$_6$H$_6$ at 23—25° gives 7(*α*)-*benzoyloxystigmasterol*, m.p. 154·5—156·5°, resolidifies, remelts at 193°, [*α*]$_D^{24}$ +100·8° in CHCl$_3$ (no digitonide; 3 : 5-*dinitrobenzoate*, m.p. 150·5—152·5°), converted in boiling NPhMe$_2$ into 7-dehydrostigmasterol, m.p. 150—152·5°, [*α*]$_D^{27}$ −104·0° in CHCl$_3$, −109·8° in C$_6$H$_6$ [absorption max. at 282 m*μ*. (*ε* 10,800); *benzoate*, m.p. 178·5—180°, [*α*]$_D^{26}$ −48·5° in CHCl$_3$]. R. S. C.

Sterols. CXLI. 3(*α*) : 11 : 12-Trihydroxycholanic acid. R. E. Marker, A. C. Shabica, E. M. Jones, H. M. Crooks, jun., and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 1228—1229).—Contrary to Longwell *et al.* (A., 1940, II, 95), 3(*α*) : 11-dihydroxy-12-ketocholanic acid with N$_2$H$_4$,H$_2$O, NaOEt, and EtOH at 200° gives 3(*α*) : 11 : 12-*trihydroxycholanic acid*, m.p. 136° (decomp.), converted by CrO$_3$–AcOH and then Hg–Zn–HCl into neolithobilianic acid (**I**). 11-Hydroxy-12-ketocholanic acid (**II**) gives similarly 11 : 12-dihydroxycholanic acid, m.p. 204—208°, and thence (**I**) [also obtained directly from (**II**) by CrO$_3$–AcOH]. R. S. C.

Sterol group. XLIV. Oxidation of phytosterols with the Oppenauer reagent. E. R. H. Jones, P. A. Wilkinson, and (in part) R. H. Kerlogue (*J.C.S.*, 1942, 391—393; cf. A., 1941, II, 251).—Cholesterol is oxidised [Al(OBu^t)$_3$–COMe$_2$–C$_6$H$_6$] to cholestenone (2 : 4-dinitrophenylhydrazone, m.p. 233°). Fucosterol yields *fucostadienone* (50%), m.p. 94—94·5° [*semicarbazone*, m.p. 238° (decomp.); *oxime*, m.p. 166—167°; 2 : 4-*dinitrophenylhydrazone*, m.p. 237°], and stigmasterol affords stigmastadienone (58%), m.p. 124·5—125° [*oxime*, m.p. 187—188°; 2 : 4-*dinitrophenylhydrazone*, m.p. 244—245° (decomp.); semicarbazone, new m.p. 238—239°]. *β*-Sitosterol (**I**), m.p. 136—137° [obtained from its acetate, m.p. 125° (16 crystallisations from EtOAc), and KOH–EtOH], is oxidised similarly to sitostenone (15%), m.p. 83—84° (2 : 4-*dinitrophenylhydrazone*, m.p. 247—248°), and a ketone (~10%), m.p. 143—145° (2 : 4-*dinitrophenylhydrazone*, m.p. 208—209°), probably a mixture. Absorption spectra of the ketones and their derivatives are in accordance with expectations. It is doubtful if (**I**) as described in the literature is a homogeneous substance. A. T. P.

Enolic ethers of keto*cyclo*pentanopolyhydrophenanthrenes.—See B., 1942, III, 189.

Diazoprogesterone.—See B., 1942, III, 189.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Syntheses in the camphor and terpene group. G. Komppa (*Ber.*, 1942, **75**, [*A*], 1—13).—A lecture. H. W.

Influence of anhydride or lactone formation on the rotatory power of the diacids or hydroxy-acids derived from *d*-camphor. J. Vène (*Compt. rend.*, 1941, **213**, 842—843).—[*α*] of all known lactones or anhydrides (except *β*-campholide) having the 1 : 2 : 2-trimethyl*cyclo*pentane nucleus (whether halogenated or not), derived from *d*-camphor, is negative, that of the corresponding OH- or dibasic acids positive. A. Li.

Alterations in molecular structure during chemical reactions. V. Neomenthol and phosphorus pentachloride. W. Hückel and K. Kümmerle (*Ber.*, 1942, **75**, [*B*], 115—120).—The action of PCl$_5$ on *d*- and *dl*-neomenthol (**I**) under conditions similar to those used for menthol (**II**) (A., 1937, II, 157) invariably gives menthene in amount which is variable and very dependent on slight variations in experimental technique. Chlorides are formed in considerable amount, mainly racemised neomenthyl chloride and *tert.*-4-chloromenthane (**III**) (ratio ~3 : 2) with a little *l*-menthyl and *d*-neomenthyl chloride (~1 : 1). A part of (**III**) is isolated as such whereas the other part changes to *p*-menthan-4-ol; two 4-chloromenthanes hydrolysed with differing readiness must therefore be formed, of which only one stereoisomeride is isolated. Substitution of OH by Cl in (**I**) is accompanied to a considerable extent by migration of the halogen to the *tert.* position at C$_{(4)}$. The almost complete racemisation of the *sec.* chloride proves that Cl in the *sec.* position at C$_{(3)}$ in the reaction product is not a result of simple substitution. In general, substitution of OH by Cl in (**I**) does not proceed in the same manner as in (**II**) and resembles the change with aliphatic alcohols. H. W.

Sesquiterpenes. LII. Degradation of dihydroguaiol by chromic acid. Preparation of 1 : 4 : 7-trimethylazulene. P. A Plattner and G. Magyar (*Helv. Chim. Acta*, 1942, **25**, 581—589).—Dihydroguaiol is oxidised by CrO$_3$ in AcOH at 70° to 2 : 8-dimethyldi*cyclo*-[0 : 3 : 5]-

decan-5-one (**I**), $[\alpha]_D$ −85·8° in EtOH (semicarbazone, m.p. 206°, $[\alpha]_D$ −80·5° in AcOH), and an *acid* (**II**), probably $CHMe<^{CH_2—CH_2}_{CH(CO_2H)}>CH\cdot CHMe\cdot[CH_2]_2\cdot CO_2H$, m.p. 186—187°, $[\alpha]_D$ ±0° in EtOH, +1·5° in 0·3N-KOH–EtOH (*Me*$_2$ ester, $[\alpha]_D$ −6·2° in EtOH), also obtained by ozonisation of *benzylidene*-2 : 8-*dimethyldi*cyclo-[0 : 3 : 5]-*decan*-5-*one*, m.p. 149°, $[\alpha]_D$ +124·1° in EtOH, prepared by the action of NaOH and PhCHO in EtOH on (**I**). Oxidation (Br–KOH in dioxan) of (**I**) gives a *Br*$_2$-derivative, m.p. 97—98°, and (**II**). Guaiazulene is obtained by treatment of (**II**) with $MgPr^\beta Br$ followed by dehydrogenation of the product by S at 200°/650 mm. (**I**) and MgMeI in Et_2O give 2 : 5 : 8-*trimethyldi*cyclo-[0 : 3 : 5]-*decan*-5-*ol*, m.p. 83°, $[\alpha]_D$ −10° in hexane, dehydrated by $KHSO_4$ at 180°/600 mm. to 2 : 5 : 8-*trimethyldi*cyclo-[0 : 3 : 5]-*decene*, b.p. 110—114°/12 mm., which is dehydrogenated by S at 200°/600 mm. to 1 : 4 : 7-trimethylazulene [additive compound, m.p. 177—178°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$]. M.p. are corr. (See also A., 1942, II, 280.) H. W.

VI.—HETEROCYCLIC.

Furoanilides.—See B., 1942, II, 272.

***dl*-Δ^3-Dehydro-α-tocopherol.**—See B., 1942, III, 189.

Chemistry of the lignan group of natural products. R. D. Haworth (*J.C.S.*, 1942, 448—456).—A lecture. F. R. S.

1 : 3-Dioxans.—See B., 1942, II, 255.

Synthesis of ethyl 1-methylpyrrolidine-2-acetate. F. E. King, J. W. Clifton, and H. T. Openshaw (*J.C.S.*, 1942, 422—424).—*Et*$_3$ ε-*phenoxypentane*-αββ-*tricarboxylate*, b.p. 203—205°/1 mm., obtained from Et ethanetricarboxylate and $OPh\cdot[CH_2]_3\cdot Br$ with NaOEt–EtOH, is hydrolysed (KOH) to the *acid*, m.p. 132—134°, which is decarboxylated at 150° to the *αβ-dicarboxylic acid* (**I**), m.p. 153° (*Br*$_2$-derivative, m.p. 145—146°). HBr and (**I**) give ε-*bromopentane*-αβ-*dicarboxylic acid*, m.p. 91—92°, which does not afford a recognisable product on treatment with Br. NH_3 and (**I**) yield the NH_4 salt, which on heating is converted into ε-*phenoxypentane*-αβ-*dicarboxylimide*, m.p. 85—86°, which with NaOBr gives a mixture containing ε-*phenoxy*-Δ$^\alpha$-*hexenoic acid*, m.p. 86°, obtained in purer form from $CH_2(CO_2H)_2$ and γ-phenoxybutyronitrile (*semicarbazone*, m.p. 118°). This acid and HBr–P–AcOH afford β*ε-dibromo*-n-*hexoic acid*, b.p. 154°/1 mm., which with NH_2Me–MeOH forms Et 1-methylpyrrolidine-2-acetate, converted by Na–PhMe–Et_2O followed by H_2SO_4 and picric acid into *Et β-keto-αγ-di*-(1-*methyl*-2-*pyrrolidyl*)*butyrate dipicrate*, m.p. 155—157° (decomp.), and not cuskhygrine dipicrate. F. R. S.

2 : 3 : 6-Triaminopyridine.—See B., 1942, II, 255.

Arylazopyridines.—See B., 1942, III, 190.

Synthesis of 2-methylpyrrolizidine. G. R. Clemo and T. A. Melrose (*J.C.S.*, 1942, 424—426).—3-Keto-4 : 5-dihydrodi-(1 : 2)-pyrrole with Zn–MeI gives a condensation *product*, m.p. 209° (by elimination of H_2O from 2 mols of ketone), and is reduced (Na–Hg) to the *pinacol*, m.p. 183—184°. CH_2:$CMe\cdot CO_2Me$ and HBr–AcOH yield *Me β-bromoisobutyrate*, b.p. 75°/22 mm. 5-Methyl-4 : 5-dihydrouracil is hydrolysed (HCl) to *β-carbethoxy*-n-*propylamine*, b.p. 71°/13 mm. (*picrate*, m.p. 108—109°), which with $CH_2Cl\cdot CO_2Et$–NaOAc affords *carbethoxymethyl-β-carbethoxy*-n-*propylamine*, b.p. 110°/1 mm. (picrolonate, m.p. 137—138°), converted by K–PhMe into *Et* 3-*hydroxy*-4-*methylpyrrole*-2-*acetate*, m.p. 85° (p-*nitrobenzoyl* derivative, m.p. 152°). Reduction (H_2–PtO_2) of Et pyrrole-2-acetate gives *Et pyrrolidine*-2-*acetate*, b.p. 110°/27 mm. (*picrolonate*, m.p. 146°), which with $CH_2Br\cdot CO_2Et$ yields the -1 : 2-*diacetate*, b.p. 125°/1 mm. This ester and K form 2-*ketopyrrolizidine*, b.p. 78°/1 mm. (*picrolonate*, m.p. 212—213°), which with Mg–MeI gives 2-*hydroxy*-2-*methylpyrrolizidine*, b.p. 95°/1 mm. (*picrolonate*, m.p. 198°). The carbinol and PCl_5 afford *dehydro*-2-*hydroxy*-2-*methylpyrrolizidine* (*picrolonate*, m.p. 169—170°), which is reduced (H_2–PtO_2) to 2-methylpyrrolizidine, b.p. 62°/25 mm., the *picrate*, m.p. 169—170°, of which is not identical with that obtained by Menschikoff (A., 1936, 1123). F. R. S.

Preparation of 8-hydroxyquinoline. F. E. King and J. A. Sherred (*J.C.S.*, 1942, 415—416).—8-Methoxyquinoline has been prepared by the Skraup reaction using As_2O_5 and is readily demethylated with boiling HBr. F. R. S.

Reaction of 4-chloroquinaldines and of 2-chlorolepidines with ammonia, and the preparation of the corresponding phenyl esters. O. G. Backeberg and J. L. C. Marais (*J.C.S.*, 1942, 381—383).—By passing NH_3 into a solution of 4-chloro-quinaldine or -quinoline in PhOH, 4-*amino*-6-, m.p. 209°, and -8-*methoxyquinaldine*, m.p. 233°, are formed, and these are also obtained by reduction of 4-*benzeneazo*-6-, m.p. 73°, and -8-*methoxyquinaldine*, m.p. 130°, respectively. By using the chlorolepidines in the same reaction, only 10% yields of the 2-aminolepidines are obtained and the products are mainly the Ph ethers, which are formed in theoretical yield in absence of NH_3. The following are described : 4-phenoxyquinoline [*picrate*, m.p. 179°; *platinichloride*, m.p. 220° (decomp.)]; 4-*phenoxy*-, m.p. 71·5°, 4-*phenoxy*-6-, m.p. 112°, and -8-*methoxy*-, m.p. 147°, -6-, m.p. 121°, and -8-*ethoxy-quinaldine*, m.p. 100°; 2-*phenoxy*-, m.p. 48°, 2-*phenoxy*-6-*methoxy*-, m.p. 70°, and -6-*ethoxy-lepidine*, m.p. 95°. When the chlorolepidines are heated (sealed tube) with $ZnCl_2,2NH_3$, the corresponding 2-*amino*-6-*methoxy*-, m.p. 174°, and -*ethoxy-lepidine*, m.p. 207°, are formed. Oxidation ($FeCl_3$) of the crude NHPh·NH-compound from the chlorolepidines gives 2-*benzeneazo*-6-*methoxy*-, m.p. 142°, and -6-*ethoxy-lepidine*, m.p. 162°. F. R. S.

Antiplasmodial action and chemical constitution. V. Carbinolamines derived from 6-methoxyquinoline. H. King and T. S. Work (*J.C.S.*, 1942, 401—404).—By the action of the appropriate alkyl halide on benzylhexylamine and removal of CH_2Ph by reduction (H_2–AcOH–PtO_2) the following are obtained : *benzyl*-n-*butyl*-, b.p. 170°/18 mm., n-*butyl*-, b.p. 201°/738 mm. (*hydrochloride*, m.p. 268°), *benzyl*-n-*amyl*-, b.p. 175—177°/15 mm., n-*amyl*-, b.p. 108°/15 mm. (*hydrochloride*, m.p. 275—276°), *benzyl*-n-*propyl*-, b.p. 155°/15 mm., n-*propyl*-, b.p. 171—181°/753 mm. (*hydrochloride*, m.p. 243°), *benzylethyl*-, b.p. 145°/13 mm., and *ethyl-hexylamine*, b.p. 158°/743 mm. (*hydrochloride*, m.p. 191°). Similarly prepared are *benzyl*-n-, b.p. 179°/12 mm. (*hydrochloride*, m.p. 199—200°), *benzyldi*-, b.p. 240°/12 mm., *benzyl*-n-*propyl*-, b.p. 185°/13 mm., *propyl*-, b.p. 119°/14 mm. (*hydrochloride*, m.p. 237°), *benzylethyl*-, b.p. 178°/11 mm. (*benzyldiethylnonylammonium iodide*, m.p. 64—65°), and *ethyl-nonylamine*, b.p. 103°/14 mm. (*hydrochloride*, m.p. 200—201°). Benzylnonylamine and MeI give *benzyldimethylnonylammonium iodide*, m.p. 89°, converted into the hydroxide and hydrosulphide, which in solution under reduced pressure affords *dimethylnonylamine*, b.p. 209°/741 mm. (*methiodide*, m.p. 170°). Nonyl iodide and NH_2Me in MeOH yield some *methyl-* (**I**), b.p. 95°/14 mm. (*hydrochloride*, m.p. 180—181°), but mainly *methyldi-nonylamine*, b.p. 190—192°/15 mm. Nonylamine and PhCHO give *benzylidenenonylamine*, b.p. 179°/14 mm., which with MeI, followed by 90% EtOH and HCl, forms (**I**). Condensation of the appropriate amine with 6-methoxy-4-quinolyl CH_2Br ketone hydrobromide followed by reduction gives *ethyl-* (*dipicrate*, m.p. 170°, *propyl-* (*dipicrate*, m.p. 169°), and *butyl-hexyl-* (*dipicrate*, m.p. 158—159°), and *methylnonyl-aminomethyl-* (*dipicrate*, m.p. 151°) and 2′ : 2′ : 6′-*trimethylpiperidinomethyl*-6-*methoxy*-4-*quinolylcarbinol* (*dipicrate*, m.p. 214°). The carbinolamines are inactive when tested on bird-malaria in canaries. F. R. S.

Synthesis of amines from amides through the amidodichlorides. T. S. Work (*J.C.S.*, 1942, 429—432).—*Cinchoninanilide*, m.p. 161—162°, prepared from cinchoninic acid, $SOCl_2$, and NH_2Ph, with PCl_5 followed by reduction ($SnCl_2$), gives N-*phenyl-lepidylamine* (**I**), m.p. 121°, and not the expected quinoline-4-aldehyde (Sonn–Müller reaction). Similarly, *cinchoninomethylamide*, m.p. 111°, affords N-*methyl-lepidylamine dihydrochloride*, m.p. 215—220° (decomp.). *Cinchoninodiethylamide*, b.p. 180°/2 mm. (*picrate*, m.p. 189°), does not undergo the reaction. 6-*Chlorocinchoninanilide*, m.p. 205°, with PCl_5 in $CHCl_3$ gives a mixture of the *hydrochloride* and an oil, converted by boiling NH_2Ph into NN-*diphenyl*-6-*chloro*-4-*quinolylamidine*, m.p. 207°. The hydrochloride and PCl_5 in $CHCl_3$ give an oil, which with CS_2 forms unstable orange needles (6-chlorocinchoninanilide amidodichloride ?), and is reduced ($SnCl_2$) to N-*phenyl*-6-*chlorolepidylamine*, m.p. 129° (*nitrosamine*, m.p. 131°). *Quinoline*-4-*aldehyde anil*, m.p. 85°, is reduced ($SnCl_2$) to (**I**). *Nicotinethylamide*, m.p. 57°, with PCl_5 followed by $SnCl_2$ yields a mixture of pyridine-3-aldehyde and 3-N-*ethylaminomethylpyridine* (*platinichloride* ; *picrate*, m.p. 207°). The mechanism of the reactions is discussed. F. R. S.

Antiplasmodial action and chemical constitution. VI. Compounds related to lepidylamine. T. S. Work (*J.C.S.*, 1942, 426—429).—Condensation of the appropriate aldehyde with diethyl-δ-aminoamylamine (**I**), followed by reduction (H_2–Pd–C), gives α-*diethylamino*-δ-*amyl-benzylamine*, b.p. 187—189°/25 mm., -p-*methoxy*-, b.p. 218°/17 mm., and -m-*amino-benzylamine*, b.p. 184—186°/25 mm., and -*lepidylamine* (dipicrate, m.p. 147—148°). Conversion of the cinchoninamide of δ-amino-α-diethylaminopentane by PCl_5 into the amidodichloride followed by reduction with $SnCl_2$ leads to the formation of the appropriate quinoline polyamines. Acetylsulphanilyl chloride (**II**) and lepidylamine followed by hydrolysis (NaOH) give N^1-*lepidylsulphanilamide*, m.p. 194° ; N^1-(6-*methoxylepidyl*)*sulphanilamide*, m.p. 194° (N^4-*Ac* derivative, m.p. 215°), is similarly prepared. α-*Diethylamino*-δ-*amyl*-6-*methoxylepidylamine* (*tripicrate*, m.p. 87—88°) is prepared from quininic acid. ζ-*Diethylaminohexanol*, b.p. 96—99°/2 mm., prepared from hexamethylene chlorohydrin and $NHEt_2$, with $SOCl_2$ gives *diethylamino*-ω-*chlorohexane*, b.p. 118—120°/19 mm., which does not condense successfully with lepidylamine. 5-Chloroisatin and $AcCO_2H$ afford 6-*chloroquinoline*-2 : 4-*dicarboxylic acid*, m.p. ~250° (decomp.), which is partly decarboxylated (boiling $PhNO_2$) to 6-*chlorocinchoninic acid* (**III**), m.p. 302°, the *Me* ester, m.p. 79·5°, of which yields the *amide*, m.p. 244°, converted (P_2O_5) into the *nitrile*, m.p. 164°, which is reduced (H_2–PtO_2–HCl) to 6-*chloro*-4-*aminomethylquinoline*, m.p. 90° [*dihydrochloride*, m.p. ~250° (decomp.)]. 6-Chlorolepidylamine and (**II**) give N^4-*acetyl*-N^1-(6-*chlorolepidyl*)*sulphanilamide*, m.p. 194°, hydrolysed (NaOH) to the N^1-*compound*, m.p. 200°. The acid chloride hydrochloride of (**III**) with (**I**) affords the 6-*chlorocinchonin-*

amide of *diethyl-δ-aminoamylamine*, m.p. 99°, which after conversion into the amidodichloride followed by reduction ($SnCl_2$) leads to *α-diethylamino-δ-amyl-6-chlorolepidylamine* (picrate, m.p. 97—99°). None of the polyamines containing the quinoline nucleus and none of the sulphonamides showed any antiplasmodial action. F. R. S.

Chemotherapeutic studies in the acridine series. IX. Chloroaminoacridines. F. R. Bradbury and W. H. Linnell (*J.C.S.*, 1942, 377—381).—4 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}CO_2Na$ and *m*-$C_6H_4Cl{\cdot}NH_2$ (Na_2CO_3–Cu–*n*-BuOH) give *3′-chloro-5-nitrodiphenylamine-2-carboxylic acid*, m.p. 221—222°, which with $POCl_3$ followed by HCl affords a mixture of chloronitroacridones, reduced ($SnCl_2$–HCl) to the corresponding NH_2-compounds, further reduced (Na–Hg) to 6-, m.p. 179—180°, and *8-chloro-2-aminoacridine* (**I**), m.p. 220—221°. 2 : 4 : 1-$(NO_2)C_6H_3{\cdot}CHO$, PhCl, and H_2SO_4 yield *4-nitro-*C-(*9-chlorophenyl*)-*anthranil* (**II**), m.p. 215°, and *8-chloro-2-nitro-10-hydroxyacridone*, m.p. 200° (-10-*OMe*-derivative, decomp. 241°); with $NaNO_2$–H_2SO_4 (**II**) gives 8-chloro-2-nitroacridone (also obtained if the original condensation be carried out in presence of $NaNO_2$), reduced ($SnCl_2$–HCl) to (**I**). 5 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}CO_2K$ and *m*-$C_6H_4Cl{\cdot}NH_2$ (K_2CO_3–Cu–*n*-BuOH) form *3′-chloro-4-nitrodiphenylamine-2-carboxylic acid*, m.p. 272—273° (decomp.), which on ring-closure leads to 5 : 6-, m.p. 201°, and 5 : 8-*dichloro-3-nitroacridine*, m.p. 223°. The 5 : 6-compound with HCl gives *6-chloro-3-nitro-*, m.p. >300°, reduced (Na–Hg) to the *-3-amino-acridine*, m.p. 211—212°. *8-Chloro-3-aminoacridone*, m.p. 267—269°, is obtained by reduction (Na–Hg) of mixed 6- and 8-chloro-3-nitroacridones, followed by fractionation. F. R. S.

Barbituric acids.—See B., 1942, III, 172.

Pyridylquinolines.—See B., 1942, II, 255.

Synthesis of N^1-substituted sulphanilamides. S. Rajagopalan (*Current Sci.*, 1942, **11**, 146).—The following are described : 4-, m.p. 189—190° (lit. 208°), and *ω-sulphanilamidoacetophenone*, m.p. 176—177° (decomp.); *ω-sulphanilamido-α-acetonaphthone*, m.p. 169°; N^4-*acetylsulphanilamidoguanidine*, m.p. 117—118°; 5-, m.p. 243—244° (decomp.), and *7-sulphanilamidoindazole*, m.p. 249—250° (decomp.); 3-$N^{4'}$-*acetylsulphanilamido*-1 : 2 : 4-*triazole*, m.p. 204°; 3-*sulphanilamidoindotriazine*, decomp. 200—201°. 3-Aminoindotriazine, m.p. 195—196° (decomp.), is obtained from isatin and aminoguanidine carbonate in AcOH. P. G. M.

Invert soaps. X. Sulphonamidotetrazolium salts : action on the glycolysis of lactic acid bacteria. D. Jerchel (*Ber.*, 1942, **75**, [*B*], 75—81).—CHMe:N·NHPh, diazotised *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, and cryst. NaOAc in EtOH at 0—10° give N-*phenyl*-N′-p-*sulphonamidophenyl*-C-*methylformazan*, $NHPh{\cdot}N{:}CR{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ [(**I**), R = Me], m.p. 235°. Analogously prepared are *compounds* in which R = Pr^a, m.p. 200°, *n*-C_6H_{13}, m.p. 18]°, *n*-C_7H_{15}, m.p. 176°, and *n*-$C_{11}H_{23}$, m.p. 167°. (**I**) is oxidised by $Pb(OAc)_4$ in dry $CHCl_3$ to *2-phenyl-3-p-sulphonamidophenyl-5-methyltetrazolium chloride*, $\begin{matrix}N{\cdot}NPh\\ \|\\ CR{-}N\end{matrix}\!\!>\!N^+{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2\}Cl^-$ [(**II**), R = Me], m.p. ~198°. *Compounds*, R = Pr^a, m.p. 179°, *n*-C_6H_{13}, m.p. 147°, *n*-C_7H_{15}, m.p. 142°, and *n*-$C_{11}H_{23}$ (**III**), m.p. 135°, are obtained similarly. Towards *Streptobacterium plantarum* (**III**) is about as active as diphenylundecyltetrazolium chloride or zephirol. H. W.

Bile pigments. XXXI. Intermediate compounds in the transformation of hæmins into bile pigments. E. Stier [with, in part, (Miss) K. Gangl] (*Z. physiol. Chem.*, 1942, **272**, 239—272).—Coproverdohæmin ester is reduced (Pd in 100% HCO_2H at 70—75°) to coproporphyrin I Me_4 ester which is accompanied by coproglaucobilin ester, m.p. 202°. This last substance is also obtained as a by-product of the oxidation of copro-ester-pyridinehæmochromogen, which is transformed by H_2O_2–O_2 into a complex mixture of pigments from which a cryst. material could not be obtained. Oxidation of meso-Me_2 ester-C_5H_5N-hæmochromogen by H_2O_2 and benzoylation of the product leads to *benzoyloxymesoporphyrin Me_2 ester*, m.p. (indef.) 197—199° after softening at 175° (complex *Zn* salt, m.p. 232°). It does not appear to be affected by attempted catalytic hydrogenation but is converted by NaOMe in boiling MeOH–dioxan into hydroxymesoporphyrin Me_2 ester. This with $Fe(OAc)_2$–NaCl at 100° yields hydroxymesohæmin Me_2 ester, converted by C_5H_5N at room temp. into an unseparated mixture of bile pigments. Protohæmin Me_2 ester is transformed by $N_2H_4{\cdot}H_2O$ in aq. C_5H_5N at 60° into the partly cryst. proto-Me_2 ester–C_5H_5N–hæmochromogen, which is oxidised and benzoylated to *benzoyloxyprotoporphyrin Me_2 ester*, m.p. 219° after softening at 195°. This is catalytically hydrogenated to benzoyloxymesoporphyrin Me_2 ester and converted by NaOMe in MeOH–dioxan into *hydroxyprotoporphyrin Me_2 ester*. Introduction of Fe then leads to hydroxyprotohæmin Me_2 ester, converted into a bile pigment, probably tetramethylhæmatoglaucobilin. Rhodohæmin Me_2 ester and $N_2H_4{\cdot}H_2O$ in C_5H_5N at 60° afford *rhodo-Me_2 ester-C_5H_5N-hæmochromogen*, m.p. 195° after softening at 182°, whence is obtained *benzoyloxyrhodoporphyrin Me_2 ester*, m.p. 205° after softening at 200°. *Phyllo-ester-C_5H_5N-hæmochromogen* in like manner affords *benzoyloxyphylloporphyrin Me ester*, m.p. (indef.) 224° after softening at 210°, hydrolysed to *hydroxyphylloporphyrin Me ester*. Phylloporphyrin with conc. H_2SO_4 and 20% oleum appears to yield δ-phyllorhodin.

Ætioxanthoporphinogen is transformed by HBr–AcOH at 140—150° into *hydroxyætioporphyrin* (**I**), decomp. 255°. Similarly mesoxanthoporphinogen gives *hydroxymesoporphyrin* (**IX**), m.p. 255—256°, converted by HCl–MeOH into the Me_2 ester, m.p. 171°. H. W.

Reactions of certain thiazoles and glyoxalines with picryl chloride and 2 : 4-dinitrochlorobenzene. J. McLean and G. D. Muir (*J.C.S.*, 1942, 383—386).—Thiazole (improved prep.) and picryl chloride (**I**) give a mixture of *thiazole hydrochloride*, m.p. 139—140°, and *picrylthiazole*, m.p. 172°. 2-Methylthiazole and (**I**) in $COMe_2$ afford *N-picryl-2-methylthiazolium chloride*, m.p. 126° (decomp. in hot EtOH), and a small amount of *picryl-2-methylthiazole*, m.p. 150°. 4-Methylthiazole and (**I**) yield 2-hydroxy-3-picryl-4-methyl-2 : 3-dihydrothiazole (cf. Tomlinson, A., 1937, II, 36). 5-Methylthiazole and (**I**) in $COMe_2$ form the *hydrochloride*, m.p. 81°, and *picryl-5-methylthiazole*, m.p. 111°. 2 : 4-Dimethylthiazole and (**I**) give the *hydrochloride*, m.p. 189°, whilst the 2 : 5-compound affords an $COMe_2$ additive *compound* (?) of picryl-2 : 5-dimethylthiazole, m.p. 172° (decomp.). 1 : 4-Dimethylglyoxaline with (**I**) yields N-*picryl*-1 : 4-*dimethylglyoxalinium chloride*, m.p. 179°, and with 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ forms N-(2 : 4-*dinitrophenyl*)-1 : 4-*dimethylglyoxalinium chloride*, m.p. 227°. N-(2 : 4-*Dinitrophenyl*)-1 : 5-*dimethylglyoxalinium chloride*, m.p. 253°, is similarly obtained. A mechanism for the varying reactions is put forward. F. R. S.

Structural-chemical investigations. VI. Reductive fission of 5-phenyl-4-methylthiazole. H. Erlenmeyer and M. Simon (*Helv. Chim. Acta*, 1942, **25**, 528—530).—CHPhBr·COMe and $HCS{\cdot}NH_2$ give *5-phenyl-4-methylthiazole*, b.p. 134—135°/25 mm. (*picrate*, m.p. 147°), reduced by Na and EtOH to $CH_2Ph{\cdot}CHMe{\cdot}NHMe$ (*platinichloride*, m.p. 198—199°; *phenylthiocarbamide* derivative, m.p. 134°). H. W.

Isosteric and structurally similar compounds. XVI. 4-Hydroxybenzthiazole. H. Erlenmeyer and H. Ueberwasser (*Helv. Chim. Acta*, 1942, **25**, 515—521).—*o*-$OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH_2$ is converted by Br in $CHCl_3$ into *2-amino-4-methoxybenzthiazole*, m.p. 152°, diazotised under strictly defined conditions and then transformed by Gattermann Cu and conc. HCl or HBr into 2-chloro- (**I**), m.p. 66°, or *2-bromo-*, m.p. 71°, *-4-methoxybenzthiazole*. (**I**) with red P and HI (*d* 1·7) in boiling AcOH gives 4-hydroxybenzthiazole, converted by oleum at the temp. of ice and salt into *4-hydroxybenzthiazole-5 : 7-disulphonic acid*, and by conc. H_2SO_4 at room temp. into the *-7-sulphonic acid*, which with I–KI in neutral solution gives *5-iodo-4-hydroxybenzthiazole-7-sulphonic acid* (*K* salt). *5-Chloro-2-methoxyphenylthiocarbamide*, m.p. 144—145° (NN′-5 : 5′-*dichloro*-2 : 2′-*dimethoxydiphenylthiocarbamide*, m.p. 165—166°), similarly affords *7-chloro-2-amino-4-methoxybenzthiazole*, m.p. 203°, diazotised and converted into 2 : 7-*dichloro-*, m.p. 124°, and *7-chloro-2-bromo-*, m.p. 141—142°, *-4-methoxybenzthiazole*. Partial dehalogenation of these compounds to *7-chloro-4-methoxybenzthiazole* (**II**), m.p. 92—94°, succeeds if the Raney Ni catalyst is kept saturated with H_2. *7-Chloro-4-methoxy-2-ethoxybenzthiazole* has m.p. 87—88°. (**II**) is dealkylated by 48% HBr at 170—180° to *7-chloro-4-hydroxy-*, m.p. 211° after partial sublimation, converted by I–KI in neutral solution into *7-chloro-5-iodo-4-hydroxy-*, m.p. ~195° (decomp.), *-benzthiazole*. H. W.

Highly *C*-alkylated 2-amino-1 : 3 : 4-thiodiazoles and their sulphanilamide derivatives. H. Arnold (*Ber.*, 1942, **75**, [*B*], 87—93).—Hydnocarpyl chloride and $NH_2{\cdot}CS{\cdot}NH{\cdot}NH_2$ (**I**) at 60—70° give *5-amino-2-norhydnocarpyl*-1 : 3 : 4-*thiodiazole*, m.p. 150—152° (*hydrochloride*, m.p. 112—114°), converted by *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in dry C_5H_5N at 60° into 5-p-*acetamidobenzenesulphonamido-2-norhydnocarpylthiodiazole*, m.p. 117—119°, which is hydrolysed to the 5-p-NH_2-compound, m.p. 117—118° (softens at 113°). Oleyl chloride and (**I**) at 110° yield *5-amino-2-α-Δ⁹-heptadecenyl*-1 : 3 : 4-*thiodiazole*, m.p. 150—160° (softens at 110°) (*hydrochloride*, m.p. 85—90°), which yields 5-p-*acetamidobenzenesulphonamido-2-α-Δ⁹-heptadecenyl*-1 : 3 : 4-*thiodiazole*, m.p. 104—106°, and the Ac-free *compound*, m.p. 109—111°. Analogously, CHPh:CH·COCl affords *5-amino-*, m.p. 233—235° (*hydrochloride*, m.p. 230—232°), 5-p-*acetamidobenzenesulphonamido-*, m.p. 202—204°, and 5-p-*aminobenzenesulphonamido-*, m.p. 285—286°, *-2-styryl*-1 : 3 : 4-*thiodiazole*. H. W.

VII.—ALKALOIDS.

***Strychnos* alkaloids. CXIV. Condensations of dihydro-ψ-strychnine and -brucine with acetic anhydride, malonic acid, and hydrocyanic acid.** H. Leuchs and K. D. Gundermann (*Ber.*, 1942, **75**, [*B*], 168—173).—Dihydro-ψ-strychnine (**I**) is converted by Ac_2O at 100° into *dihydrostrychnine-9-acetic acid* (**II**), m.p. 300—303° (vac.; decomp.), $[\alpha]_D^{20}$ +43·0° in H_2O [*Na* salt; *Me* ester, m.p. 227—228° (vac.; decomp.), and its *methiodide*], converted by Br–HBr into bromodihydrostrychnine-9-acetic acid, m.p. 290° (vac.). (**II**) is also obtained from (**I**) and $CH_2(CO_2H)_2$. (**I**) and KCN in AcOH afford *dihydrostrychnine-9-nitrile*, m.p. 283—286° (vac.; slight decomp.) (*hydrochloride*; *perchlorate*).

[With Y. Hwang.] Dihydro-ψ-brucine (**III**) is converted by Ac_2O and NaOAc at 100° into *dihydrobrucine-9-acetic acid* (**IV**), m.p. 282—284° (vac.; decomp.), $[\alpha]_D^{20}$ +33·1°/*d* in AcOH (*perchlorate*, decomp. 260—280°), and *N-acetyl*-sec.-ψ-*dihydrobrucine*, apparently two forms, m.p. 80—90°, becoming resinous at 155—185°, and m.p. ~160° (decomp.); with Ac_2O–C_5H_5N at 100° (**IV**) does not appear to be produced. (**IV**) does not react with NH_2OH in AcOH at 100°, and is not catalytically hydrogenated in HCl or AcOH. It gives a non-cryst. *Et* ester (*picrate*, m.p. 120—140°), and *Me* ester, m.p. 200° (vac.) [*picrate*, m.p. 231—235° (decomp.) after softening at 210°; *methiodide*, m.p. 190° decomp. ~218°]. (**IV**) is oxidised by 2N-HNO_3 at 0° to the quinone, $C_{23}H_{24}O_6N_2$ (*perchlorate*), reduced by SO_2 to the corresponding quinol (*perchlorate*). With CrO_3–dil. H_2SO_4 at 70—80° (**IV**) gives a *substance*, $C_{19}H_{24}O_7N_2$, m.p. 230—232° (vac.; decomp.) (softens at 220°). (**IV**), PhCHO, and NaOMe in boiling MeOH afford *benzylidenedihydrobrucine-9-acetic acid* [*perchlorate*, m.p. 245—255° (decomp.) (darkens at 180°)]. (**IV**) is also produced from (**III**) and $CH_2(CO_2H)_2$. With KCN in AcOH (**III**) yields *dihydrobrucine-9-nitrile*, m.p. 176—178° (vac.; decomp.) (*hydrochloride*; *perchlorate*). H. W.

Alkaloids from Koto-tzuzarafuji (*Stephania sasakii*, **Hayata**).—See B., 1942, III, 172.

Alkaloids of *Lycopodium* species. I. *L. complanatum*, L. R. H. F. Manske and L. Marion (*Canad. J. Res.*, 1942, **20, B**, 87—92).—From *L. complanatum*, L., the following alkaloids are obtained: lycopodine, $C_{16}H_{25}ON$ [*perchlorate*, m.p. 283° (decomp.)], nicotine (its first recorded occurrence in a pteridophyte), and the new compounds, *complanatine* (LI), $C_{18}H_{31}ON$, m.p. 169° (*perchlorate*, $+H_2O$, m.p. 194°), and *alkaloids* L2, $C_{18}H_{29}O_2N$, m.p. 97° (*perchlorate*, m.p. 231°), L3, $C_{18}H_{31}O_2N$ (*perchlorate*, m.p. 246°), L4, $C_{16}H_{27}N$ (*perchlorate*, $+0{\cdot}5H_2O$, m.p. 225°), L5, $C_{18}H_{28}O_3N_2$ (*perchlorate*, m.p. 282°), and *obscurine*, L6, $C_{18}H_{28}ON_2$ (*diperchlorate*, $+H_2O$, m.p. 299°, with some previous decomp.). Nicotine is also isolated from *Equisetum arvense*, L. Hydrolysis (dil. H_2SO_4) of the H_2O-insol. polysaccharides from (**I**) gives *d*-galactose. A. T. P.

VIII.—ORGANO-METALLIC COMPOUNDS.

Veratral-6-arsinic acid. A. A. Schamschurin (*J. Gen. Chem. Russ.*, 1941, **11**, 647—649).—6-Nitroveratrole on reduction with $FeSO_4$–aq. NH_3 gives 87% of 6-aminoveratrole, which by the Bart reaction affords 46% of 4 : 5-*dimethoxybenzaldehyde-6-arsinic acid*, m.p. ~300° (decomp.) (semicarbazone, m.p. 256°). The acid is stable to boiling 15% HCl and is oxidised by $KMnO_4$ to 4 : 5-*dimethoxy-2-carboxyphenylarsinic acid*, m.p. 300° (retains 1 H_2O at 100°). G. A. R. K.

Organic compounds of mercury. V. Interaction of mercury dialkyls with mercury salts of tribasic acids. N. N. Melnikov and M. S. Rokitzkaja (*J. Gen. Chem. Russ.*, 1941, **11**, 592—595).—Hg dialkyls do not react with Hg salts in org. solvents (cf. A., 1938, II, 166), but in presence of small amounts of H_2O good yields of alkyl Hg salts are obtained. The following have been prepared (% yield in parentheses): $(HgMe)_3PO_4$, decomp. 182° (80), $(HgEt)_3PO_4$, m.p. 179—180°, monohydrate, m.p. ~110° (98), $(HgEt)_3AsO_4$, m.p. 184—186° (75), $HgEt{\cdot}NO_3$, m.p. 86—86·5° (80—85), $(HgPr^{\alpha})_3PO_4$, m.p. 96° (98), $(HgBu^{\alpha})_3PO_4$, m.p. 75° (88), $(HgC_5H_{11}\text{-}iso)_3PO_4$, m.p. 105° (62). G. A. R. K.

Electric moments of organomercuric halides in dioxan.—See A., 1942, I, 293.

IX.—PROTEINS.

Oxazoline and thiazoline rings in proteins. S. Blackburn, W. R. Middlebrook, and H. Phillips (*Nature*, 1942, **150**, 57).—Activated peptide linkings which undergo methylation may be those which have undergone condensation with the side-chains of β-OH-acids giving rise to oxazoline rings. Free cysteine side-chains in reduced wool may form thiazoline rings. A. A. E.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Behaviour of some lignin preparations in the molecular still. J. F. Hechtman (*Paper Trade J.*, 1942, **114**, *TAPPI Sect.*, 259—264).—A pot still has been constructed so that the reservoir and condensing surfaces are removable for weighing. The distillation characteristics of native lignin (**I**), CH_2N_2-methylated lignin (**II**), fully methylated lignin (**III**), and Willstätter lignin (**IV**), all from black spruce, were examined. At 260°/1 μ. pressure, (**I**) gave 4% of distillate; both residue and condensate had the same OMe content as the original. Ultra-violet absorption curves and solubility characteristics indicated that the residue might be of higher and the condensate of lower mol. wt. than (**I**). At >290°/>1 μ. decomp. occurred. At 290°/1 μ. (**II**) gave 6% of condensate containing 17·7% OMe; the OMe content of the residue was 20·9% and of the original 21·1%. Even at 350°/1 μ. no distillate was obtained from (**III**), although non-condensable material was lost. Under the same conditions (**IV**) too yielded no condensate, and only 2% of volatile material was lost after 20 hr. At 260°/25—50 μ. (**IV**) gave a considerable condensate (OMe content 14·0%), but when air was replaced by N_2 no condensate was obtained even at 350°. The significance of these results is discussed. H. A. H.

XI.—ANALYSIS.

Micro-Kjeldahl nitrogen determination without use of titration procedure. W. H. Taylor and G. F. Smith (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 437—439).—The Wagner micro-Kjeldahl procedure is modified by absorption of the NH_3 in aq. H_3BO_3, dilution to a standard vol., and electrometric titration to a definite p_H, the results being interpreted by a preformed calibration curve. J. D. R.

Micro-determination of sulphur and halogens.—See A., 1942, I, 276.

Potentiometric titration of dibasic acids.—See A., 1942, I, 306.

Colorimetric estimation of arginine and histidine. H. T. Macpherson (*Biochem. J.*, 1942, **36**, 59—63).—Arginine is determined by a modification of Weber's method (A., 1930, 755) in which the $CO(NH_2)_2$ is added prior to the OBr′ and the colour developed in two stages [*i.e.*, by repetition of the addition of $CO(NH_2)_2$ and OBr′] to ensure max. and consistent colour development. Since the colour does not obey Beer's law a photometer is preferable to a colorimeter and 0·02±0·001 mg. may be determined. Histidine is determined by a modification of the method of Jorpes (A., 1932, 1270) in which the reaction with sulphanilic acid and $NaNO_2$ is carried out at room temp., Na_2CO_3 used for colour development, and the colour stabilised by slightly alkaline EtOH. The final colour may be measured in a colorimeter since it obeys Beer's law. H. G. R.

Determination of terpinyl acetate and other esters. H. M. Perry and T. F. West (*Analyst*, 1942, **67**, 159—161).—The B.P. 1932 method for the determination of esters with 0·5N-KOH–EtOH gives low results with terpinyl acetate, some other terpinyl esters, and menthyl valerate. Boiling ~1·5 g. of the sample with 40 ml. of 0·5N-KOH in $OH{\cdot}[CH_2]_2{\cdot}OEt$ for 30 min. completely saponified all the 30 esters tested except terpinyl propionate, which required 40 min. The reagent is suitable for determining terpenic alcohols after acetylation or formylation. Data are given for a no. of esters, alcohols, and essential oils. T. F. W.

Determination of quercetin-like substances using a Klett–Summerson photoelectric colorimeter. C. W. Wilson, L. S. Weatherby and W. Z. Bock (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 425—426).—The sample is mixed with a solution of citric and boric acids in anhyd. $COMe_2$ and the colour produced measured in a Klett–Summerson photoelectric colorimeter. Recovery of added quercetin was quant. J. D. R.

Gravimetric determination of flavines. B. A. Ellis (*Analyst*, 1942, **67**, 226—227).—Euflavine and acriflavine are determined directly by pptn. from aq. solution as the picrate, $C_{20}H_{17}O_7N_6$ (**I**). A certain excess of picric acid is necessary and (**I**) is washed with ice-cold H_2O, dried at 100°, and weighed. The filtrate may be used for determination of Cl′, due allowance being made for the Cl derived from the euflavine. Shell dressings are extracted with acidified EtOH, and after adding H_2O the extract is evaporated to low bulk, filtered, and (**I**) pptd. as above. Sterilisation of the dressings reduced the recoveries of flavines. S. B.

Colorimetric (*p*-dimethylaminobenzaldehyde–sulphuric acid) method for determining small quantities of atropine. R. P. Daroga (*J. Indian Chem. Soc.*, 1941, **18**, 579—584).—Conditions for the max. sensitivity of a colorimetric method for atropine (**I**) have been worked out. The test solution is treated with 0·1 c.c. of reagent (made as required by diluting a 20% solution of $p\text{-}NMe_2{\cdot}C_6H_4{\cdot}CHO$ in conc. H_2SO_4 with H_2O, 1 : 1) and warmed for 30 min. (steam-bath). After diluting to 25 c.c. the violet colour is matched against permanent standards in a tintometer. A linear relationship between concn. of (**I**) and colour intensity is shown to exist. W. C. J. R.

Determination of cystine content of proteins by means of sulphuric, hydrochloric, hydriodic, and mixtures of hydrochloric and formic acids. W. C. Hess and M. X. Sullivan (*J. Washington Acad. Sci.*, 1942, **32**, 130—132).—Similar vals. are obtained for cystine in a variety of proteins whatever hydrolysing agent is used, except that HI gives slightly higher vals. owing to non-formation of humin. P. G. M.

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SEPTEMBER, 1942.

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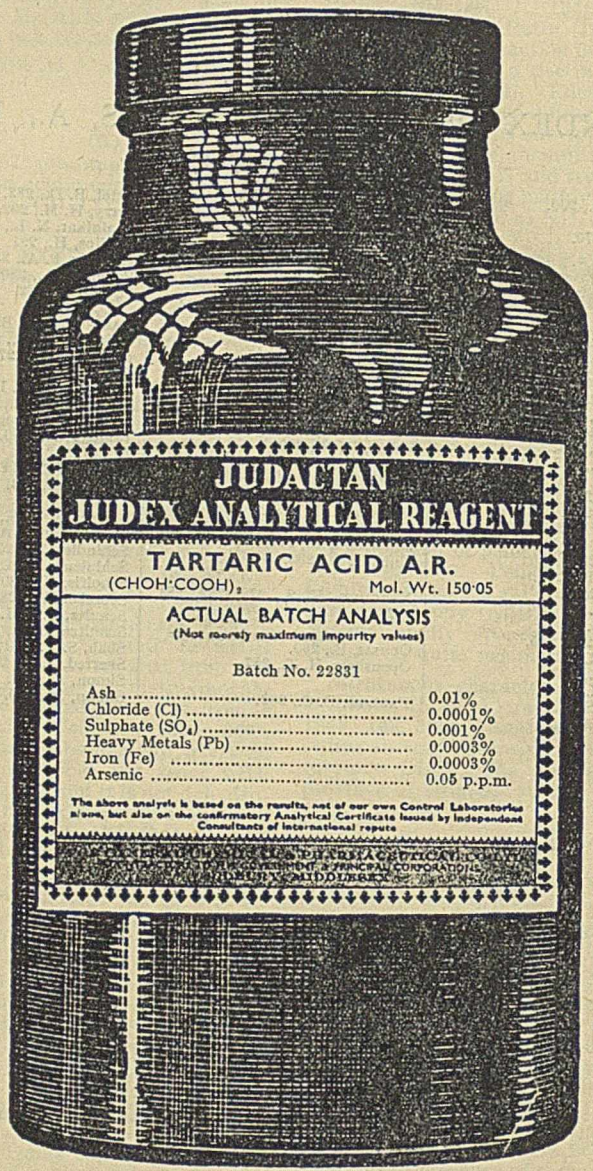

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