BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1941.

I.—ALIPHATIC.

Elimination reactions in organic chemistry. (A) **Mechanism.** M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, F. R. Webb, and L. I. Woolf. (B) **Tautomerism and elimination.** E. D. Hughes (*Nature*, 1941, **147**, 812—813, 813—814).—(A) A summary of work reconciling and rationalising the Hofmann and Saytzeff rules. Reactions of "onium" salts proceeding by mechanism *E*2 (attack of a base on an alkyl proton) display "Hofmann influences" (=*H*); those going by mechanism *E*1 (prior formation of a carbonium ion) show "Saytzeff influences" (=*S*). Halide reactions by both mechanisms are governed by (*S*). Within the range investigated, these statements are true irrespective of whether the alkyl groups are primary, *sec.*, or *tert.*, provided they are saturated. Introduction of suitably placed unsaturation increases the field of application of (*S*). The responsible mechanism for (*H*) is undoubtedly the inductive effect, whilst that for (*S*) involves resonance due to the quasi-conjugation [cf. A., 1940, I, 390; identical with the "hyperconjugation" of Mulliken *et al.* (A., 1941, I, 100)] of the C_γ·H electrons with the electrons transferred in elimination from the dissolving C_β·H linking to the forming C_α:C_β linking. The greater is the no. of C_γ·H linkings the larger will be this effect; a much more powerful effect of the same kind arises when, in place of quasi-conjugation, full conjugation is produced by the provision of γ-unsaturation as in the $CH_2Ph·CH_2·$ group. Independent electrostatic and resonance effects thus co-exist in elimination reactions, and being separately energised they may even work in opposition. Reactions involving the production of olefines from alcohols and ethers fall within the theoretical scheme outlined.

(B) The effect of alkyl groups on rate in the base-catalysed enolisation of ketones is of the Hofmann type. The base-catalysed equilibria of CAlkAlk′:CH·CO_2H are essentially dependent on the same internal mechanism as (*S*) (above). H. B.

Production of hydrocarbons by catalytic conversion of carbon monoxide. Hydrogenation of carbon monoxide to produce hydrocarbons having more than one carbon atom in the molecule. Production of hydrocarbons by conversion of carbon monoxide with hydrogen. Catalytic conversion of carbon monoxide with hydrogen into hydrocarbons.—See B., 1941, II, 289, 290.

Production of saturated hydrocarbons.—See B., 1941, II, 290.

Production of saturated hydrocarbons with branched or more highly branched chains from saturated hydrocarbons with branched or less branched chains.—See B., 1941, II, 246.

Catalytic aromatisation and isomerisation of ββδ-trimethylpentane. S. J. Green and A. W. Nash (*Nature*, 1941, **148**, 53—54).—Considerable formation of mixed xylenes, and some $C_{10}H_8$, accompanied by cracking, occurs with pure $CH_2Pr^\beta Bu^\gamma$ at 550° with a liquid catalyst-space velocity of 0·33 c.c. per c.c. per hr. and a 6 at.-% Mo oxide-activated Al_2O_3 catalyst in a mild steel tube. L. S. T.

Determination of freezing points and amounts of impurity in hydrocarbons from freezing and melting curves. B. J. Mair, A. R. Glasgow, jun., and F. D. Rossini (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 591—620).—Time–temp. freezing and melting curves are analysed and a procedure for determining the f.p. of a substance and the amount of impurity in it is developed to apply to cases in which a known portion of the curves represents thermodynamic equilibrium between liquid and cryst. phases. The method is shown to be applicable to hydrocarbons containing 0·6—11·5 mol.-% of solute. J. W. S.

Polymerisation of ethylene.—See B., 1941, II, 290.

Biochemical synthesis of carbon chains of isoprene type.—See A., 1941, III, 937.

Synthesis of hydrocarbons with conjugated ethylenic linkings. III. V. I. Esafov, V. M. Guliakov, V. V. Kargopoltzeva, A. P. Kulakova, G. V. Razmislov, and N. D. Toporov (*J. Gen. Chem. Russ.*, 1940, **10**, 1973—1977).—COMeEt and CaC_2 (7 hr. at 100°) yield *γ-methyl-Δγ-hepten-ε-one* (**I**), b.p. 164—165°. With MgEtBr in Et_2O this gives *γ-methyl-ε-ethyl-Δγε-heptadiene*, b.p. 154°, and with *iso*-C_5H_{11}·MgBr a mixture, b.p. 194—200°, of *γ-methyl-ε-isoamyl-Δγε-heptadiene* and *βζ-dimethyl-ε-ethyl-Δδζ-nonadiene*. The Grignard reaction did not take place as above in the cases of CH_2Ph·MgBr and (**I**) or mesityl oxide. R. T.

Manufacture of butadiene, chlorobutene, and trichlorobutane.—See B., 1941, II, 290.

Production of acetylene, acetone, and methyl acetate.—See B., 1941, II, 245.

Isomerisation of chloroalkanes.—See B., 1941, II, 247.

Production of alkyl halides from alkenes and hydrogen halide.—See B., 1941, II, 247.

Manufacture of alkyl chlorides.—See B., 1941, II, 291.

Manufacture of chloroform.—See B., 1941, II, 291.

Manufacture of nitromethane.—See B., 1941, II, 247.

Production of alcohols by catalytic hydrogenation of esters of carboxylic acids.—See B., 1941, II, 248.

Addition of βγ-unsaturated alcohols to the active methylene group. III. Scope and mechanism of the reaction. M. F. Carroll (*J.C.S.*, 1941, 507—511; cf. A., 1940, II, 266, 347).—At 150—250° in the presence of an alkaline catalyst (NaOAc, NaOEt, KOH) βγ-unsaturated alcohols with a compound containing an active CH_2 [$CH_2Ac·CO_2Et$, $CHBuAc·CO_2Et$, or $CH_2(CO_2Et)_2$] give normal additive products; from an alcohol ROH, the substances obtained are EtOH, CO_2, ROAc, $COMe_2$, CH_2AcR (or R′ where rearrangement occurs) and the olefine from ROH. With $CH_2Ac·CO_2Et$ and saturated alcohols, the ester is obtained. The reactivity of the groups attached to the active CH_2 is in the order: $CH_2(CO_2R)_2$ > R·CO·CH_2·CO_2R′ > R·CO·CHR′·CO_2R″ > R·CO·CH_2·COR′. The mechanism of the reactions is discussed, and the results are applied to explain some analogous reactions. F. R. S.

Search for a stable substituted vinyl alcohol. F. H. Stodola (*Science*, 1941, **93**, 452).—Alternative formulæ for the "substituted vinyl alcohol" and the corresponding ketone prepared by Fuson *et al.* (A., 1941, II, 222) are suggested. The behaviour of the alcohol on oxidation (CrO_3 in AcOH) is difficult to reconcile with the vinyl alcohol formula, without assuming an unprecedented αδ dehydrogenation. L. S. T.

Synthesis of primary βγ-unsaturated alcohols, glycols, and their derivatives. S. N. Chitrik (*J. Gen. Chem. Russ.*, 1940, **10**, 2098—2100).—The sole product of reaction of Mg with $(CH_2Br·CH:)_2$ in Et_2O is butadiene. *p*-$C_6H_4Me·SO_3·CH_2·CH_2Cl$ does not react with CHPh:CH·MgBr in Et_2O. R. T.

Purification of glycerol by crystallisation.—See B., 1941, II, 245.

Production of pentaerythritol.—See B., 1941, II, 248.

Manufacture of ethers from olefines.—See B., 1941, II, 248.

Effect of alkalinity or acidity on stability of ether.—See B., 1941, II, 245.

Action of oxides of nitrogen on unsaturated ethers. I. Action of nitrous anhydride on methyl allyl ether. N. J. Maslov (*J. Gen. Chem. Russ.*, 1940, **10**, 1915—1917).—OMe·CH_2·CH:CH_2 in Et_2O when saturated at −10° with N_2O_3 yields *Me γ(β)-nitro-β(γ)-nitrosopropyl ether*, m.p. 106—107°, reduced by $SnCl_2$ in HCl to OMe·CH_2·$CH(NH_2)$·CH_2·NH_2 [*dihydrochloride*, m.p. 214° (*platinichloride*); *dipicrate*, m.p. 210°]. R. T.

Acetone-[*iso*propylidene-]glyceraldehyde and optically active glycerides. IX. Configuration of natural batyl, chimyl, and selachyl alcohols. E. Baer and H. O. L. Fischer (*J. Biol. Chem.*, 1941, **140**, 397—410).—*l*(−)-*iso*Propylideneglycerol in $(CH_2$·$OMe)_2$ is added to a cold solution of Na–$C_{10}H_8$ in the same solvent. When the green colour has disappeared, *n*-$C_{18}H_{37}I$ is added and the solution is boiled for 48 hr. After removal of solvent and dihydronaphthalene at 160°/10—15 mm., d-iso*propylidene-α*-n-*octadecylglycerol* (**I**), m.p. 34—36°, $[\alpha]_D^{40}$ −12·6°, is isolated by distillation in a mol. still. l- (**II**), m.p. 32·5—33·5°, $[\alpha]_D^{40}$ +12·4°, and dl- (**III**), m.p. 32—33°, -iso*propylidene-α*-n-*octadecylglycerol* are obtained similarly. (**I**) is hydrolysed by 80% AcOH at 80° to d-*α*-n-*octadecylglycerol* (**IV**), m.p. 71—72°, $[\alpha]_D$ +0·8°, +0·7°, and +4·0° in $CHCl_3$ (*c* = 84, 3·83, and 1·0, respectively), identical with natural batyl alcohol, (**V**). (**II**) and (**III**) similarly afford l- (**VI**), m.p. 71—72°, $[\alpha]_D$ 0·0°, −1·6°, and −2·3° in $CHCl_3$ (*c* = 9·98, 3·17, and 1·10, respectively), and dl- (**VII**), m.p. 71—71·5°, -*α*-n-*octadecylglycerol*. (**IV**) gives an *α'β*-diacetate, readily interconvertible polymorphic forms, m.p. 34—34·5° and 42—43° respectively, $[\alpha]_D$ −7·6° in $CHCl_3$ free from EtOH, an *α'β*-diphenylurethane, m.p. 100·5—101·5°, $[\alpha]_D$ −6·4° in C_5H_5N, and an *α'β-di*-p-*nitrobenzoate*, m.p. 65·5—66·5°, $[\alpha]_D$ −27·9° in dry $CHCl_3$; the first two compounds are identical with those derived from (**V**). Similarly (**VI**) gives an *α'β-di*-*acetate*, varieties, m.p. 34—34·5° and 42—43°, respectively, $[\alpha]_D$ +7·6°, $[\alpha]_{5461}$ +8·6° in $CHCl_3$ free from EtOH, an *α'β-diphenylurethane*, m.p. 101—101·5°, $[\alpha]_D$ +6·5° in dry C_5H_5N, and an *α'β-di*-p-*nitrobenzoate*, m.p. 66·5—67°, $[\alpha]_D$ +29·1° in CCl_4. The *α'β-diacetate*, b.p. 180—183°/10^{-3} mm., m.p. 34—34·5°, *α'β-diphenylurethane*, m.p. 94·5—95°, and *α'β-di*-p-*nitrobenzoate*, m.p. 73·5—74°, of (**VII**) are described. The appropriate *iso*propylideneglycerol is transformed by *n*-$C_{16}H_{33}I$ into d- (**VIII**), $[\alpha]_D^{23}$ −11·9°, l- (**IX**), $[\alpha]_D$ +12·1°, and dl- (**X**) -iso*propylidene-α*-n-*hexadecylglycerol*. Hydrolysis of (**VIII**) gives d-*α*-n-*hexadecylglycerol*, m.p. 62·5—63·5°, $[\alpha]_D^{25}$ +3·0° in dry $CHCl_3$ (*α'β-diphenylurethane*, m.p. 97·5—98°, $[\alpha]_D$ −6·9° in dry C_5H_5N; *α'β-di*-p-*nitrobenzoate*, m.p. 52°, $[\alpha]_D$ −29·2° in dry $C_2H_2Cl_4$), identical with natural chimyl alcohol (**XI**). Similarly (**IX**) gives l-*α*-n-*hexadecylglycerol*, m.p. 63—64°, $[\alpha]_D^{22}$ ±0·0° (*c* = 10·1), $[\alpha]_D^{25}$ −1·3° (*c* = 3·22) and −2·2° (*c* = 1·13) in dry $CHCl_3$ (*α'β-diphenylurethane*, m.p. 97—98°, $[\alpha]_D$ +7·17° in dry C_5H_5N; *α'β-di*-p-*nitrobenzoate*, m.p. 52—53°, $[\alpha]_D$ +29·7° in dry $C_2H_2Cl_4$), and (**X**) affords dl-*α*-n-*hexadecylglycerol*, m.p. 62—63° (*α'β-diphenylurethane*, m.p. 92°; *α'β-di*-p-*nitrobenzoate*, m.p. 52—53°). (**V**) and (**XI**) therefore belong to the *d* series to which also selachyl alcohol can be assigned on account of its close relationship to (**V**).

The unsaponifiable matter from ratfish (*Chimaera monstrosa*) liver oil consists mainly of (**XI**) with a small proportion of (**V**). H. W.

Chemical warfare materials. XXIV. Determination of "yellow cross" [*ββ'*-dichlorodiethyl sulphide] by the spectrophotometric method. H. Mohler (*Helv. Chim. Acta*, 1941, **24**, 571—573).—$(Cl$·$[CH_2]_2)_2S$ may be determined spectrophotometrically in hexane using the band 202—203 mμ. A concn. >0·00003M. is necessary. Beer's law holds over the range 0·0003—0·0015M. F. J. G.

[Velocity of] hydrolysis of *ββ'*-dichlorodiethyl sulphide.—See A., 1941, I, 420.

Manufacture of organic anhydrides.—See B., 1941, II, 249.

Preparation of alkyl formates.—See B., 1941, II, 249.

Azeotropic distillation for dehydrating acetic acid.—See B., 1941, II, 289.

Configurational relationship of α-methylheptoic and γ-methylnonoic acids. P. A. Levene and M. Kuna (*J. Biol. Chem.*, 1941, **140**, 255—257).—α-Methylheptoic acid, $[\alpha]_D^{25}$ +8·48°, resolved by cinchonidine, by the usual reactions yields the Et ester, $[\alpha]_D^{25}$ +8·91°, β-methylheptan-α-ol, $[\alpha]_D^{25}$ −4·01°, and α-iodo-β-methylheptane, $[\alpha]_D^{25}$ +1·05°, which with $CH_2(CO_2Et)_2$ and NaOEt yields γ-methylnonoic acid, b.p. 92°/0·1 mm., $[\alpha]_D^{25}$ +0·46° (cf. A., 1932, 360). All [α] are homogeneous. A. Lt.

Polymorphism of unsaturated fatty acids C_{18}. G. Ravitsch, V. Volnova, and T. Kuzmina (*Acta Physicochim. U.R.S.S.*, 1941, **14**, 403—413).—The polymorphism of oleic acid (**I**) has been studied by means of photomicrography and of heating and cooling curves. Apparatus for determining cooling curves with very slow cooling is described. When (**I**) is very slowly cooled the break on the cooling curve usually observed at ~9° is resolved into two, at 11° and at 8·5°; this is attributed to contamination with saturated fatty acids. The heating curves show additional thermal effects at 20—21°, the position depending on the previous history of the sample. These indicate the existence of a new modification of (**I**), m.p. 20—20·5°, and this is confirmed by photomicrographs. F. J. G.

Alkenyl esters of unsaturated monocarboxylic acids of the C_nH_{2n-1}·CO_2H series. A. D. Petrov and V. D. Azatian (*J. Appl. Chem. Russ.*, 1940, **13**, 1602—1605).—Oleic, undecenoic, acrylic, and crotonic acid and Δ$^{\alpha}$-hexinene at 50—70° in presence of HgO and BF_3,Et_2O give COMeBu, but not the expected esters. At >30° and in Et_2O, *β*-Δ$^{\alpha}$-, b.p. 110°/30 mm., and *β*-Δ$^{\gamma}$-*hexenyl*, b.p. 89·5—92·5°/18 mm., and *β*-Δ$^{\alpha}$-*pentenyl crotonate*, b.p. 95°/30 mm., are obtained from Δ$^{\alpha}$- and Δ$^{\gamma}$-hexinene and Δ$^{\alpha}$-pentinene, respectively. R. T.

Separation and identification of fatty acids. III. Preparation of pure oleic and elaidic acid by the hydroxamic acid method. Y. Inouye and H. Yukawa (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 411—413; cf. A., 1940, II, 336).—*Oleohydroxamic acid*, m.p. 61°, obtained from olive oil by treatment with NH_2OH,HCl and NaOEt, is quantitatively converted into oleic acid by hydrolysis with boiling EtOH–dil. H_2SO_4. *Elaidohydroxamic acid*, m.p. 91°, prepared similarly, yields elaidic acid when hydrolysed under the same conditions. J. N. A.

Constitution of spiculisporic acid, a metabolic product of the mold fungus *Penicillium spiculisporum* (Lehman). M. Asano and Y. Kameda [with, in part, T. Naruse] (*J. Pharm. Soc. Japan*, 1941, **61**, 57—63).—Spiculisporic acid (**I**) is the lactone of γ-hydroxy-γδ-dicarboxypentadecoic acid, and not of the βδ-dicarboxy-acid as stated by Clutterbuck *et al.* (A., 1931, 1092). (**I**) affords γ-ketopentadecoic acid (**II**) (semicarbazone, m.p. 124—125°), identical with that obtained by condensing Me·$[CH_2]_{10}$·CO·CHNa·CO_2Et and CH_2Br·CO_2Et at 100° for 7 hr., followed by HI (*d* 1·7) at 100° (bath). $CO(CH_2$·$CO_2Et)_2$–NaOEt–CH_2Br·CO_2Et at 110° yield a substance, converted by *n*-$C_{10}H_{21}I$–NaOEt at 120° into a product reduced by Na–Hg to laurone, $CO(C_{11}H_{23}$-*n*$)_2$, and (**II**). (**I**) and red P–HI (*d* 1·7) at 190—210°, followed by Zn–AcOH, and then KOH–EtOH at 100° (bath), afford para-*tetradecane-αγδ-tricarboxylic acid* (**III**), m.p. 160—162° (*tri*-p-*phenylphenacyl* ester, m.p. 108—111°), and the meso-*αγδ-tricarboxylic acid* (**IV**), m.p. 109—111°. $CH_2(CO_2Et)_2$, Cl·$[CH_2]_2$·CO_2Et, and NaOEt afford $CH(CO_2Et)_2$·$[CH_2]_2$·CO_2Et, b.p. 126—128°/2 mm., converted into the Na derivative and then condensed with *n*-$C_{10}H_{21}$·CHBr·CO_2Et at 120—130° to *Et$_4$ tetradecane-αγγδ-tetracarboxylate*, b.p. 210—225°/2 mm., which on hydrolysis by 50% KOH–EtOH at 100° (bath) and then heating at 140—150° yields (**III**) and (**IV**). *n*-$C_{10}H_{21}$·$CNa(CO_2Et)_2$, CH_2Br·$CH(CO_2Et)$·CH_2·CO_2Et, and NaOEt at 140—150° afford *Et$_4$ tetradecane-βγδδ-tetracarboxylate*, b.p. 215—217°/1 mm., converted by hydrolysis (KOH–EtOH) and then decarboxylation (at 150—155°) into *tetradecane-αββ-tricarboxylic acid* (**V**), m.p. 145—147°; if (**I**) possessed the constitution attributed by Clutterbuck *et al.* (*loc. cit.*), it should yield (**V**). A. T. P.

α-Hydroxy-α-methylthiodiacetic acid. E. Larsson (*Svensk Kem. Tidskr.*, 1941, **53**, 1—5).—CO_2H·CH_2·S·CMe(OH)·CO_2H (**I**) [from SH·CH_2·CO_2H (**II**) and $AcCO_2H$] is completely dissociated into its components in alkaline solution. In 0·1N-HCl *k* = 0·015 and in H_2O *k* = 0·01—0·03. The formation and dissociation of (**I**) are both very rapid. Similar compounds are formed from (**II**) and CHO·CO_2H (*k* very small in acid solution and dissociation slow) and CH_2O (*k* = 0·3 in H_2O and dissociation rapid), but not $COMe_2$. M. H. M. A.

Basic catalysis of transformation and decomposition of monosaccharides. II. Epimerisation of arabinose by anions of weak acids in acid media. A. D. Braun and R. K. Konnova (*Biochimia*, 1940, **5**, 497—501).—Anions of weak acids cause epimerisation of arabinose in acid medium. Ketopentose, which is readily decomposed by acid, is thus produced from aldopentose by OAc′ ions, the resulting solution being almost free from aldopentose. $NHPh{\cdot}NH_2$ in presence of HSO_3' is used, *e.g.*, in urine analysis, to detect ketopentose in presence of aldoses and other aldehydes. W. McC.

Studies of the chemical properties of carbohydrates by means of heavy oxygen. I. Exchange reactions of oxygen between monoses and water. K. Goto and T. Titani (*Bull. Chem. Soc. Japan*, 1941, **16**, 172—177).—In H_2O containing an excess of ^{18}O at 100°, glucose, fructose, galactose, xylose, and arabinose exchange 1 O. In presence of acid or base >1 O is gradually exchanged although decomp. also occurs. R. S. C.

Active form of simple sugars. VII. Reactivity of fructose 1 : 6-diphosphate. A. V. Stepanov and B. N. Stepanenko (*Biochimia*, 1940, **5**, 567—573).—The proportions of HCN bound by fructose 1 : 1-diphosphate (**I**), fructose 1-monophosphate, and fructose during 2 hr. are 30, 13, and 0%, respectively. The high val. for (**I**) shows that much of this compound in the equilibrium mixture is in the keto-form. Phosphorylation of hexoses is accompanied by conversion from a cyclic form into an open-chain, more reactive keto-form. This conversion occurs gradually during the first stages of glycolysis, the six-C chain, which is most stable in free glucose, being finally disrupted. W. McC.

Enzymic hydrolysis of disaccharides and halogenosalicins. W. W. Pigman (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 1—8; cf. A., 1939, III, 99).—Enzymes of almond emulsin hydrolyse all of the disaccharides with β-glucosidic linkings so far tried, in agreement with the Weidenhagen theory. Rates of hydrolysis for gentiobiose (6-β-glucosido-*d*-glucose), 4-β-glucosido-*d*-mannose (**I**), and lactositol (4-β-glucosido-*d*-sorbitol) are compared with those of other disaccharides. Small changes in structure of the aglucone sugar have a large effect on rate of enzymic hydrolysis; *e.g.*, although (**I**) differs from cellobiose in the configuration of only one C atom, a very marked decrease is observed in the case of (**I**). Theoretical considerations are discussed, and mechanisms of reaction are suggested. Rates of enzymic fission for *p*-chloro-, -bromo-, and -iodo-salicins are similar, but the relative ease of fission is I- > Br- > Cl-derivative; introduction of halogen in the *p*-position of the salicin aglucone reduces the rate to $<\frac{1}{3}$ of the val. for salicin. A. T. P.

Hydrolysis of laminarin. Isolation of a new glucose disaccharide. V. C. Barry (*Sci. Proc. Roy. Dublin Soc.*, 1941, **22**, 423—429; cf. A., 1939, III, 409).—*Laminaribiose* (? glucose-3-β-glucoside), m.p. >90° (decomp.) (one specimen was cryst., m.p. 161—162°), $[\alpha]_D^{15}$ +20·8° (25 min.) in H_2O, +16·14° (21 hr.) (*osazone*, m.p. 195°, $[\alpha]_D^{19}$ −79·6° in EtOH; cf. Zechmeister *et al.*, A., 1934, 810), is present in the products of partial hydrolysis (N-$H_2C_2O_4$ or snail-juice) of laminarin (**I**). It is hydrolysed by emulsin to glucose. The constitution of (**I**) is discussed. A. Li.

Carbohydrate group of egg proteins. III. P. A. Levene (*J. Biol. Chem.*, 1941, **140**, 279—284).—The polysaccharide (**I**) from egg proteins (A., 1929, 1478) could not be satisfactorily methylated, but on hydrolysis (10N-HCl at room temp.) yields d-*mannoglucosaminide*, which when hydrolysed gives mannose and when reduced (Raney Ni at 75° under pressure) yields *mannitolchondrosaminide*, acetylated and hydrolysed (boiling 20% HCl) to glucosamine, but no mannose. (**I**) with 5% HNO_3 at 100° under pressure, then conc. HNO_3 at room temp., yields no mucic acid. A. Li.

Optical rotatory relationships exhibited by aromatic and aliphatic glucosides. W. W. Pigman and H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 9—25).—A comparison of rotations of numerous glucosides shows that aromatic groups (Ph and substituted Ph) produce rotational effects different from those produced by aliphatic radicals. When an aromatic nucleus is attached to an asymmetric C through an O linking, the rotatory contributions of other asymmetric C attached to the former C are greater by a fairly const. amount than when the attached group is aliphatic. Substituted phenyl-β-glucosides are much more lævorotatory than the aliphatic β-glucosides. Phenyl-β-glucosides when substituted by *o*-*p*-directing groups in any position, or *m*-directing groups in the *o*-position, have vals. of $[M]_D^{20}$ (in H_2O) of ~−17,000 to −20,000, whereas those of aliphatic β-*d*-glucosides are ~−6500 to −9500, except in the case of glucosides of *tert.* alcohols (~−4000); *m*-directing groups in *m*- or *p*-positions, however, cause an increase in val. and *p*-nitrophenyl-β-glucoside has a val. of $[M]_D^{20}$ −31,130. A marked decrease in val. is caused by substituting two groups in the *o*-positions of phenyl-β-glucoside, *e.g.*, the *o*-*o*′-xylenyl derivative has a val. of −4380 (cf. *o*-*p*-isomeride, −18,480). In a series of related glucosides, aliphatic or aromatic, the mol. rotations of the β-glucosides ∝ rotatory contributions of the glucosidic carbons. Vals. of $[M]_D$ and $[\alpha]_D$ for many α- and β-glucosides are recorded, with relevant literature. A parallelism observed between the dissociation consts. of phenols and the optical properties of the corresponding substituted phenyl-β-glucosides supports the view that the optical rotation is conditioned by the same intramol. electronic forces as those which control dissociation of phenolic H. β-*d*-α-Mannoheptose hexa-acetate (improved prep.), PhOH, and *p*-$C_6H_4Me{\cdot}SO_3H$ or $ZnCl_2$ at 100° (bath) give the acetylated glycoside, converted by MeOH–$Ba(OMe)_2$ into the *phenyl*-d-α-*mannoheptosides*, α-, m.p. 212°, $[\alpha]_D^{20}$ +207° in H_2O, and (more sol.) β-form, m.p. 189—190°, $[\alpha]_D^{20}$ −39·8° in H_2O. *Phenyl*-α-d-*taloside tetra-acetate*, m.p. 103·5—104°, $[\alpha]_D^{20}$ +97·4° in $CHCl_3$, affords *phenyl*-d-*taloside*, m.p. 165·5—166·5°, $[\alpha]_D^{20}$ +138° in H_2O. β-*d*-α-Glucoheptose hexa-acetate, PhOH, and $ZnCl_2$ give *phenyl*-d-α-*glucoheptoside penta-acetate*, α-, m.p. 154—155°, $[\alpha]_D^{20}$ +167° in $CHCl_3$, and β-form, m.p. 97°, $[\alpha]_D^{20}$ +8·0° in $CHCl_3$, deacetylated to *phenyl*-α-, m.p. 191—192°, $[\alpha]_D^{20}$ +163° in H_2O, and -β-d-α-*glucoheptoside*, m.p. 167—168°, $[\alpha]_D^{20}$ −89·7° in H_2O, respectively. A. T. P.

Constitution of butrin. P. S. Rao (*Current Sci.*, 1940, **9**, 492; cf. A., 1937, II, 445).—Butrin (**I**) and CH_2N_2 yield a *Me*$_1$ *ether*, hydrolysed to a monomethylbutein. Hence (**I**) is not a bioside but a diglucoside of butin with the sugar nuclei in different positions. E. M. W.

Syntheses of 2 : 4-dimethyl-β-methylglucoside. M. H. Adams, R. E. Reeves, and W. F. Goebel (*J. Biol. Chem.*, 1941, **140**, 653—661).—β-Methylglucoside 2 : 4 : 6-triacetate 3-*p*-toluenesulphonate is de-acetylated [$Ba(OMe)_2$ in dry MeOH at 0°] to the non-cryst. *β-methylglucoside* 3-p-*toluenesulphonate*, transformed by CPh_3Cl in C_5H_5N at 100° into the amorphous 6-*triphenylmethyl-β-methylglucoside* 3-p-*toluenesulphonate* (**I**), m.p. 76—78°, $[\alpha]_D^{22}$ −22·0° in $CHCl_3$ (2 : 4-*diacetate*, m.p. 145—147°, $[\alpha]_D^{25}$ +14·5° in $CHCl_3$). Repeated methylation of (**I**) by Ag_2O and MeI gives 6-*triphenylmethyl*-2 : 4-*dimethyl-β-methylglucoside* 3-p-*toluenesulphonate*, $[\alpha]_D^{25}$ −1·05° in $CHCl_3$, converted by HBr–AcOH into 2 : 4-*dimethyl-β-methylglucoside* 3-p-*toluenesulphonate*, $[\alpha]_D^{25}$ −2·3° in $CHCl_3$, and thence by Na–Hg in MeOH into 2 : 4-*dimethyl-β-methylglucoside* (**II**), dimorphous, m.p. 105—106° or 122—124°, $[\alpha]_D^{25}$ −18·6° in $COMe_2$, in very poor yield. Di*iso*propylideneglucose *p*-toluenesulphonate is converted by boiling 2% HCl–MeOH into a mixture of α- and β-methylglucoside 3-*p*-toluenesulphonates from which, after successive treatments with CPh_3Cl and Ac_2O–C_5H_5N, 6-*triphenylmethyl-α-methylglucoside* 2 : 4-*diacetate* 3-p-*toluenesulphonate*, m.p. 191—192°, $[\alpha]_D^{25}$ +72·8° in $CHCl_3$, is isolated. Gradual addition of solid KOH to di*iso*propylideneglucose dissolved in CH_2PhCl at 100° affords 3-benzyldi*iso*propylideneglucose, hydrolysed by dil. HCl to 3-benzylglucose, m.p. 138—141°, $[\alpha]_D$ +20·3° to +41·9° in H_2O (equilibrium) (lit. m.p. 127—128°, $[\alpha]_D$ +29·1°), which gives the non-cryst. 3-*benzyl*-6-*triphenylmethylglucose* (**III**), $[\alpha]_D^{25}$ +19·4° (equilibrium) in $CHCl_3$ [1 : 2 : 4-*triacetate*, m.p. 150—205° (mixture of α- and β-forms)]. (**III**) is methylated (MeI + Ag_2O) with great difficulty and the product of the reaction is converted by HBr–AcOH followed by Na and 95% EtOH into (**II**) in small yield. 2 : 4-Dimethyl-α-methylglucoside (**IV**) has m.p. 79—80°. (**II**) and (**IV**) are transformed by $NHPh{\cdot}NH_2$ into 4-methylglucosazone, thus establishing the presence of OMe at $C_{(2)}$. H. W.

Synthesis of glucosides. K. Nisizawa (*Bull. Chem. Soc. Japan*, 1941, **16**, 155—160).—β-*d*-Galactose penta-acetate (**I**), guaiacol (**II**), and *p*-$C_6H_4Me{\cdot}SO_3H$ (**III**) at 125—128° give a mixture, converted by boiling 0·2N-NaOMe–MeOH into β-*guaiacyl*-d-*galactoside* (**IV**), m.p. 203—204°, $[\alpha]_D^{20}$ −44·64° in H_2O, and a residue, which with Ac_2O–C_5H_5N at 100° gives

α-guaiacyl-d-*galactoside tetra-acetate* (V), m.p. 82—84°, $[\alpha]_D^{22}$ +227·6° in $CHCl_3$, and thence *α-guaiacyl*-d-*galactoside*, m.p. 140—142°, $[\alpha]_D^{21}$ +211·4° in H_2O. (IV), $[\alpha]_D^{28}$ −44·48° in H_2O, is better obtained by way of its *tetra-acetate*, m.p. 100—102°, $[\alpha]_D^{22}$ −16·71° in $CHCl_3$, from acetobromogalactose (VI), (II), NaOH, and a little H_2O in $COMe_2$ at room temp. At 100° (I), (II), and $ZnCl_2$ give mainly (V), but at 125° the same mixture is obtained as with (III). At 120°, (I), *m*-cresol, and $ZnCl_2$ give α-m-*tolyl*-d-*galactoside* (VII), m.p. 150—152°, $[\alpha]_D^{19}$ +207·0° in H_2O, by way of its *tetra-acetate*, m.p. 75—76°, $[\alpha]_D^{17}$ +178·0° in $CHCl_3$; at 125—128° with $ZnCl_2$ or (III) (cf. Helferich *et al.*, A., 1935, 201), mixed crystals (? a 1 : 1 additive *compound*), m.p. 175—178°, $[\alpha]_D^{13}$ +81·0° in H_2O, of (VII) and its β-analogue (m.p. 166—167°, $[\alpha]_D$ −44·3° in H_2O) are obtained. *p*-OH·C_6H_4·COMe and (VI) give (as above) *β-p-acetylphenyl*-d-*galactoside tetra-acetate* (52%), m.p. 146—147°, $[\alpha]_D^{28}$ −51·69° in C_6H_6, but (I) in presence of $ZnCl_2$ or (III) at 127—128° gives only the *α-galactoside*, m.p. 158—160°, $[\alpha]_D^{29}$ +226·2° in H_2O, by way of the *tetra-acetate*, m.p. 155—157°, $[\alpha]_D^{23\text{ or }29}$ +29·0° in $CHCl_3$. *o*-OH·C_6H_4·CHO, (VI), and Ag_2O in quinoline give *β-o-aldehydophenyl*-d-*galactoside*, m.p. 237—239°, $[\alpha]_D^{30}$ −23·6° in H_2O, by way of the *tetra-acetate* (21·6%), m.p. 107—109°, $[\alpha]_D^{23}$ −13·74° in $CHCl_3$. *s-m*-Xylenol, (VI), and NaOH in $COMe_2$ give *β-s-m-xylyl*-d-*galactoside*, m.p. 193—194°, $[\alpha]_D^{22}$ −43·0° in H_2O, by way of the *tetra-acetate* (24·6%), m.p. 116—117°, $[\alpha]_D^{23}$ −19·0° in C_6H_6; *β-p-allylphenyl*-d-*galactoside*, m.p. 196—198°, $[\alpha]_D^{20}$ −59·6° in N-NaOH (*tetra-acetate*, m.p. 140—141°, $[\alpha]_D^{23}$ −52·5° in C_6H_6), is similarly obtained. The procedure using (I) and $ZnCl_2$ at 127—128° or 130—132° yields *α-phenyl-*, $+H_2O$, m.p. 88—90°, $[\alpha]_D^{17}$ +199·2° in H_2O (*tetra-acetate*, m.p. 131—132°, $[\alpha]_D$ +175·5° in $CHCl_3$), *α-p-tolyl-*, m.p. 190—191°, $[\alpha]_D^{18}$ +178·0° in H_2O (*tetra-acetate*, $[\alpha]_D^{25}$ +162·0° in $CHCl_3$), and *α-o-anisyl-β-galactoside*, $+H_2O$, m.p. 150—153°, $[\alpha]_D^{18}$ +156·4° (amorphous tetra-acetate, $[\alpha]_D^{15}$ +170·5° in $CHCl_3$). BuOH, (VI), and Ag_2CO_3 at 60° give *β-butyl*-d-*galactoside*, m.p. 99—100°, $[\alpha]_D^{15}$ −8·4° in H_2O, by way of the *tetra-acetate*, m.p. 60—62°, $[\alpha]_D^{20}$ −13·8° in $CHCl_3$. R. S. C.

Constituents of the Chinese drug " chih-shih " (*Citrus fusca*, Lour., of the family Rutaceæ); derivatives of hesperitin. L. C. Waung (*J. Pharm. Soc. Japan*, 1940, **60**, 164—168).—Extraction of the fruits of *C. fusca*, Lour., with warm EtOH gives 6—7% of material, $C_{28}H_{34}O_{15}$, m.p. 236—237°, identical with the new hesperidin (I) of Kolle and Gloppe (A., 1936, 970). Hydrolysis (2% HCl or H_2SO_4) of (I) gives hesperitin (II), m.p. 224—226° (oxime, m.p. 230—231°). (II) is transformed by cold Ac_2O containing a trace of conc. H_2SO_4 into the monoacetate, m.p. 127°, which does not give a colour with $FeCl_3$ but becomes cherry-red under the influence of Mg + HCl, by Ac_2O at 100° into the *diacetate*, m.p. 127—129°, which gives a red colour with Mg + HCl and a dark violet colour with $FeCl_3$, and by NaOAc and boiling Ac_2O into a *tri-*, m.p. 165—167° (which is not coloured by Mg + HCl or by $FeCl_3$), and a *tetra-acetate*, m.p. 104—106°, which gives no colour with $FeCl_3$ but a positive reaction with Mg + HCl. The product of the action of an excess of CH_2N_2 on (II) in Et_2O is separated by MeOH into Me_2 esters, m.p. 133—136° (III) and 153—155° (IV) respectively, and a Me_1 ester, m.p. 161—163°, all of which give positive reactions with $FeCl_3$ and with Mg + HCl. (III) and (IV) are transformed by Ac_2O and concn. H_2SO_4 into the *monoacetate*, m.p. 153—154·5°. Glucose and rhamnose are obtained by hydrolysis of (I). H. W.

Glycerolysis of starch. Mol. wt. and viscosity of the products. Y. Tsuzuki (*Bull. Chem. Soc. Japan*, 1941, **16**, 161—170).—Increasing the duration or temp. (180—200°) of heating potato, wheat, or rice starch in glycerol causes greater decrease in α and $\eta_{sp.}$ of the product and its acetate and greater increase in (*a*) the glycerol content of the product and its acetate and (*b*) the Ac content of the acetate. The mol. wt. calc. from the glycerol content (end-group) agrees approx. with that determined by cryoscopy in $(CH_2Br)_2$. The equation, $\eta_{sp.}/c = K_m M + k$ (k = const.), gives K_m independent of chain length (cf. Meyer *et al.*, A., 1935, 1318). Wheat starch degrades more easily than does rice starch. R. S. C.

Hydrolysis and catalytic oxidation of cellulosic materials. R. F. Nickerson (*Ind. Eng. Chem.*, 1941, **33**, 1022—1026; cf. B., 1941, II, 111).—Curves relating time (t) and CO_2 evolved (C) are recorded for the hydrolysis of celluloses (I) of various origins and their derivatives by boiling HCl (2·4) + $FeCl_3$ (0·6 mol. per l.). With cotton-(I) and its rayon and other derivatives and linen-(I), t (corr. for the induction period of 0·4 hr.) $\propto C$, but with wood-(I) and its rayons the curves consist of two linear portions of different slopes. They indicate that on hydrolysis the formation of hydrocellulose results in a loss of available glucose; that mercerisation of cotton or dispersion of it in $Cu(NH_3)_4^{\cdot\cdot}$ increases the availability of glucose by increasing the amount of non-resistant (I) above the normal ~10%; and that the proportion of easily hydrolysed material in wood-(I) is > in cotton-(I). The theory that (I) consists entirely of chains of anhydroglucose units in various degrees of association, from a dense cryst. to an amorphous easily hydrolysed fraction, is confirmed. J. G.

Depolymerised cellulose and its hydrolysis. A. Buevskoi (*J. Appl. Chem. Russ.*, 1940, **13**, 1649—1659).—Depolymerisation is effected by treatment with 65—80% H_2SO_4 at −13° and 20°. The mol. wt. of the products falls with increasing $[H_2SO_4]$, temp., and duration of contact. Products of the mol. wt. 83,400 to 505 were isolated by fractional pptn. methods. The velocity of hydrolysis of the depolymerisation products is independent of their mol. wt.; it is, however, $\propto$ their solubility, rising abruptly with transition to homogeneous systems. R. T.

Manufacture of primary amines.—See B., 1941, II, 294.

Configurational relationships of aliphatic amines. P. A. Levene and M. Kuna (*J. Biol. Chem.*, 1941, **140**, 259—265).—α-Methylheptoic acid, $[\alpha]_D^{25}$ −7·8°, yields successively the chloride, b.p. 67—70°/12 mm., $[\alpha]_D^{25}$ −5·1°, and nitrile, b.p. 71—73°/14 mm., $[\alpha]_D^{25}$ −14·9°, and α-amino-β-methylheptane, b.p. 105—106°/113 mm., $[\alpha]_D^{25}$ +3·04° (hydrochloride, $[\alpha]_D^{25}$ +2·0° in H_2O) (with the *sec.* amine, b.p. 90—100°/1 mm., $[\alpha]_D^{25}$ +0·56°). n-C_5H_{11}·CHMe·$[CH_2]_3$·Br, $[\alpha]_D^{27\cdot5}$ +2·5°, with KCN yields δ-methyldeconitrile, b.p. 106—110°/11 mm., $[\alpha]_D^{25}$ +1·46°, reduced (Raney Ni) to inactive α-amino-ε-methyldecane (inactive hydrochloride). α-Ethylhexoic acid, $[\alpha]_D^{25}$ −3·54°, yields successively the chloride, b.p. 62—64°/10 mm., $[\alpha]_D^{25}$ −1·63°, and nitrile, b.p. 98—100°, $[\alpha]_D^{25}$ −4·80°, and α-amino-β-ethylhexane, b.p. 98—99°/90 mm., $[\alpha]_{5875\cdot6}^{25}$ −0·52° (hydrochloride, $[\alpha]_{5875\cdot6}^{25}$ −1·07° in H_2O). *d*-Nonan-δ-ol, b.p. 94—95°, $[\alpha]_D^{25}$ +0·57°, yields successively l-δ-*iodo-*, b.p. 98—99°/12 mm., $[\alpha]_D^{25}$ −1·72°, *-azido-*, b.p. 100°/23 mm., $[\alpha]_D^{25}$ −0·1°, and *-amino-nonane*, b.p. 113—114°, $[\alpha]_{5461}^{25}$ +0·52° (A., 1937, II, 447) (hydrochloride, $[\alpha]_{5461}^{25}$ −0·94° in H_2O). Rotations of some configurationally related amines are tabulated. [α] are homogeneous except where otherwise stated. A. Li.

Manufacture of quaternary ammonium compounds.—See B., 1941, II, 250.

Preparation of β-ethylaminoethanols.—See B., 1941, II, 295.

Manufacture of monosodium glutamate from gluten.—See B., 1941, II, 296.

Chondrosin. P. A. Levene (*J. Biol. Chem.*, 1941, **140**, 267—277).—*Chondrosin Me ester hydrochloride* (I), m.p. 165—170°, $[\alpha]_D^{30}$ +39·2° in MeOH, is reduced (Raney Ni under pressure) to Me *d*-chondrosaminido-*l*-gulonate; the *N-Ac* derivative of the *hepta-acetate* (Ac_2O in C_5H_5N), m.p. 122°, $[\alpha]_D^{25}$ −21·3° in EtOH, is methylated (Me_2SO_4, then CH_2N_2, then MeI–Ag_2O) to *Me* N-*acetyl*-d-*chondrosaminido*-l-*gulonate Me*$_7$ *ether*, m.p. 67°, $[\alpha]_D^{25}$ −4·8° in EtOH, reduced (Cu chromite at 175° under pressure) to N-*acetyltrimethylchondrosaminido-tetramethylsorbitol*, m.p. 55—57, $[\alpha]_D^{30}$ −44·2° in $CHCl_3$. The N-*acetylhexa-acetate* (Ac_2O + NaOAc), m.p. 99—100° (softening at 98°), $[\alpha]_D^{25}$ +12·2° in $CHCl_3$, of (I) is methylated (as above) to N-*acetylhexamethylchondrosin Me ester*, a syrup, $[\alpha]_D^{25}$ −5·2° in $CHCl_3$. A. Li.

Methionine and its derivatives. I. Detection. Y. Tsuchiya (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 465—475).—When MeSH is passed into a solution of 0·01—0·02 g. of isatin in 100 c.c. of conc. H_2SO_4 the yellow colour of the solution becomes grass-green. The reaction is inhibited by H_2S. 0·2 mg. of methionine (I) can be detected as follows by this reaction: 0·2—100 mg. of dried sample, mixed with 0·45—0·75 g. of NaOH and a little H_2O, is fused for 1—2 min. The melt is treated with dil. acid and the gases evolved are passed over $Pb(OAc)_2$ and then through the special reagent. Among the naturally occurring NH_2-acids only (I) gives the reaction, which is not given by mixtures of NH_2-acids and carbohydrates. A mixture of cystine and betaine gives the reaction and also compounds which contain the SMe group

such as SMe·$[CH_2]_2$·CH(OH)·CO_2H, SMe·$[CH_2]_3$·NH_2, and SMe·$[CH_2]_3$·OH; oxidised derivatives of (I) such as methionine sulphoxide, homocystine, and β-methylsulphonylpropionic acid yield only H_2S and do not give the reaction, which appears to be sp. for MeSH. J. N. A.

Synthesis of the aspartic acid analogue of glutathione (asparthione). G. M. Miller, O. K. Behrens, and V. Du Vigneaud (*J. Biol. Chem.*, 1941, **140**, 411—415).—*N*-Carbobenzyloxy-α-benzylaspartyl chloride and *S*-benzylcysteinylglycine Me ether in $CHCl_3$ at room temp. afford *N-carbobenzyloxy-α-benzyl-β-aspartyl-S-benzylcysteinylglycine Me ether*, m.p. 153°, hydrolysed (N-NaOH in dioxan) to the *acid*, m.p. 168—170°. This is converted by Na in liquid NH_3 into *β-aspartylcysteinylglycine* (*asparthione*), $[\alpha]_D^{25}$ −29·0° in H_2O. H. W.

Production of urea from ammonia and carbon dioxide containing inerts.—See B., 1941, II, 295.

Dimorphism of bromodiethylacetylcarbamide. A Watanabe (*J. Pharm. Soc. Japan*, 1940, **60**, 163—164).—Bromodiethylacetylcarbamide is obtained as a rhombic holohedral variety (*A*) by slow crystallisation of technical adalin (I) from MeOH or $COMe_2$ and as a monoclinic holohedral form (*B*), m.p. 118°, by rapidly cooling a somewhat more conc. solution of (I); crystallographic and optical data are recorded. *A* and *B* are stable at room temp. but at 70° *A* passes rapidly into *B* so that its true m.p. cannot be determined. *A* and *B* have the composition, $C_7H_{13}O_2N_2Br$. H. W.

Oxidising action of selenious acid. I. Organic sulphur compounds. A. E. A. Werner (*Sci. Proc. Roy. Dublin Soc.*, 1941, **22**, 387—392).—Mono-, di-, and tri-alkyl- and monoacylthiocarbamides, and thioamides with H_2SeO_3 give Se or Se + S. Strong acid suppresses the formation {by decomp. of [NRR′·C(NR″)·S]$_2$} of S, and in very strongly acid solutions no reduction occurs. Diacetylthiocarbamides react only in strongly acid solution. In EtOH or weak acid, thioalcohols give no ppt., thioacids a complex of H_2SeO_3 with the thioacid, but in very strongly acid solutions both give Se. Compounds containing S but not SH do not reduce H_2SeO_3. The significance of these results is discussed. A. Li.

Synthesis of methylenediureide and its polymeride-homologues. A. A. Vanscheidt, Z. K. Naumova, and E. P. Melnikova (*J. Gen. Chem. Russ.*, 1940, **10**, 1968—1972).—$CH_2(NH{\cdot}CO{\cdot}NH_2)_2$ condenses with CH_2O in aq. $Ba(OH)_2$ to the *compound*, $CH_2(NH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH)_2$, which with $CO(NH_2)_2$ in dil. HCl at room temp. yields the *compound*, $CO(NH{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$, m.p. 227°, with $CH_2(NH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$. R. T.

Preparation of aceto- and benzo-nitriles. Y. S. Gwan (*J. Indian Chem. Soc.*, 1941, 18, 164).—NH_2Ac and NH_2Bz with *p*-$C_6H_4Me{\cdot}SO_2Cl$ at 130—135° give good yields of the nitriles. A. Li.

Synthesis of succinonitrile.—See B., 1941, II, 251.

Action of olefine oxides on halides of arsine. II. M. S. Malinovski (*J. Gen. Chem. Russ.*, 1940, **10**, 1918—1922).—$AsCl_3$ saturated at room temp. with $(CH_2)_2O$ yields *tri-(β-chloroethyl) arsenite*, b.p. 190—195°/8 mm., with *di-(β-chloroethoxy)arsine chloride*, b.p. 168—175°/10 mm., and *β-chloroethoxyarsine dichloride*, b.p. 125—135°/10 mm. Epichlorohydrin (I) and $AsCl_3$ (10 days at room temp.) afford *tri-(β-chloro-α-chloromethylethyl) arsenite*, b.p. 188—193°/10 mm., and *β-chloro-α-chloromethylethoxyarsine dichloride*, b.p. 105—120°/10 mm. Propylene oxide (II) and $AsCl_3$ (10 days at room temp.) yield *di-(β-chloropropoxy)arsine chloride*, b.p. 185—190°/5 mm. $AsPhCl_2$ and $(CH_2)_2O$ (10 days at room temp.) afford *phenyldi-(β-chloroethoxy)arsine*, b.p. 190—193°/5 mm. $AsPhCl_2$ and (I) or (II) (10 days at room temp.) yield *phenyl-β-chloro-α-chloromethylethoxyarsine chloride*, b.p. 218—222°/5 mm., or *phenyl-β-chloropropoxyarsine chloride*, b.p. 190—195°/10 mm. R. T.

Co-ordinated mercury compounds with ethylene- and propylene-diamines. P. Neogi and K. L. Mondal (*J. Indian Chem. Soc.*, 1941, **18**, 146—148).—Equimol. amounts of $NH_2{\cdot}[CH_2]_3{\cdot}NH_2$ (pn) and Hg salts in EtOH yield H_2O-insol. *propylenediaminemercuric chloride*, m.p. >250° (decomp.), *bromide*, and *nitrate*. $NH_2{\cdot}[CH_2]_3{\cdot}NH_2$ salts with Hg salts in H_2O or EtOH yield H_2O-sol. *compounds*, [Hg(pn),2HCl]Cl_2, [Hg(pn),2HBr]Br_2, [Hg(pn),2HI]I_2, and [Hg(pn),2HNO_3]$(NO_3)_2$. $NH_2{\cdot}[CH_2]_2{\cdot}NH_2$,2$HNO_3$ similarly yields compounds [Hg(en)]$(NO_3)_2$ and [Hg(en),2HNO_3]$(NO_3)_2$. A. Li.

II.—HOMOCYCLIC.

***cyclo*Hexene derivatives.**—See B., 1941, II, 251.

Distribution of multiple linkings in ring systems. IV. Six-membered rings with the allene system of linkings. N. A. Domnin (*J. Gen. Chem. Russ.*, 1940, **10**, 1939—1949).—2′-Methyl*cyclo*hexanone in light petroleum and PCl_5 yield 2 : 2-*dichloro*-1-*methyl*cyclo*hexanone*, b.p. 62—64°/8 mm., which with 20% KOH in EtOH (5 hr. at the b.p.) affords 2-*chloro*-1-*methyl*-Δ¹-cyclo*hexene*, b.p. 44°/9 mm. This is chlorinated in $CHCl_3$ in presence of $NaHCO_3$ to 1 : 2-*dichloro*-1-*methyl*-Δ²-cyclo*hexene*, b.p. 80—82°/8 mm., and 1 : 2 : 2-*trichloro*-1-*methyl*cyclo*hexane*, b.p. 100—102°/8·5 mm. R. T.

Benz*cyclo*octatetraenes. I. W. S. Rapson and R. G. Shuttleworth (*J.C.S.*, 1941, 487—490).—*o-Iodobenzanilide*, m.p. 142·5°, and PCl_5–PhMe, followed by $SnCl_2$–HCl–Et_2O (ice-cooling), afford *o*-$C_6H_4I{\cdot}CHO$ (I), converted by $CH(OEt)_3$–EtOH–NH_4Cl into its Et_2 acetal, b.p. 159°/23 mm. (I) and Cu-bronze in an inert atm. at 200—220° give diphenyl-2 : 2′-dialdehyde, m.p. 63°, but attempts to prepare 1 : 2 : 3 : 4-dibenz-Δ$^{1:3:5:7}$-*cyclo*octatetraene (II) from it by reaction with succinic acid or Et_2 succinate failed. *o*-Iodocinnamaldehyde [from (I) and MeCHO in EtOH–$NHEt_2$] and *o*-$C_6H_4I{\cdot}CH_2{\cdot}CO_2H$ (improved prep.) (*Et* ester, m.p. 42—43°) with PbO–Ac_2O at 150—160° give *αδ-bis-o-iodophenyl-Δ$^{\alpha\gamma}$-butadiene* (III), isomerides, m.p. 249—250° (III) and 180—181° (IV), not converted into (II). (III) and Cu-bronze alone at 280° or in a little boiling quinoline yield intermol. condensation products (a *substance*, $C_{32}H_{24}I_2$, m.p. 200—202°, is isolable); in more dil. solution *trans*-αδ-diphenyl-Δ$^{\alpha\gamma}$-butadiene is formed. Cu-bronze and (IV) at 300° in an inert atm. (no reaction in quinoline) afford a *product*, ? $C_{48}H_{36}I_2$, m.p. ~200°. 2 : 2′-Dibromodiphenyl and Na give Ph_2 (cf. Mascarelli *et al.*, A., 1934, 62). $CHNaAc{\cdot}CO_2Et$ and *o*-$C_6H_4I{\cdot}COCl$ in Et_2O yield a product, hydrolysed by dil. H_2SO_4 to *o*-$C_6H_4I{\cdot}COMe$, b.p. 112°/4 mm. (*semicarbazone*, m.p. 178·5—179·5°), and *o*-$C_6H_4I{\cdot}CO_2Et$, b.p. 122°/4 mm., in approx. equimol. proportions. A. T. P.

Condensation of alcohols with aromatic hydrocarbons in presence of aluminium chloride. Condensation of *cyclo*heptanol with benzene and toluene. N. G. Sidorova and I. P. Tzukervanik (*J. Gen. Chem. Russ.*, 1940, **10**, 2073—2076).—Suberol and C_6H_6 condensed in presence of $AlCl_3$ yield cyclo*heptylbenzene*, b.p. 132—135°/28 mm., nitrated to p-*nitro*cyclo*heptylbenzene*, b.p. 203—210°/38 mm., from which p-cyclo*heptylaniline*, an oil (*Bz*, m.p. 173°, and *Ac* derivative, m.p. 136—137°), is prepared. With PhMe suberol yields a mixture of m- and p-cyclo*heptyltoluene*. R. T.

Polymerisation of styrene in heavy alcohol. (Mechanism of chain polymerisation of styrene in solution.) T. Yosida and T. Titani (*Bull. Chem. Soc. Japan*, 1941, **16**, 125—136).—Exchange of H of CHPh:CH_2 (I) or polystyrene is not observed when freshly prepared (I) (2 c.c.) is heated in a sealed tube for 22 hr. at 130° with 3·6% or 10·4% EtOD or with 9·8% or 11·5% $C_2H_4D{\cdot}OH$. The mechanism of polymerisation is discussed. J. L. D.

Free aryl radicals in the Fittig and Ullmann reactions. W. S. Rapson and R. G. Shuttleworth (*Nature*, 1941, **147**, 675).—A series of Ullmann, Fittig, and related reactions showed that one of the products formed on treating ArX (X = Cl, Br, or I) with Na or Cu is the compound, ArH. This is attributed to the formation of free aryl radicals in the reaction, from which ArH is formed either by reaction with the diluent when present, or by dismutation when the diluent is absent. The isolation of diphenyl-2- and -4-carboxylic acids from the reaction between PhI and EtOBz in presence of Cu-bronze supports this view. L. S. T.

Electrolysis of iodonium compounds. Attempt to prepare iodonium amalgam. E. V. Zappi and R. Mastropaolo F. (*Anal. Asoc. Quím. Argentina*, 1941, **29**, 88—94).—No amalgam is obtained by electrolysis, at 4·5 v. and 0° with an agitated Hg cathode, of diphenyl-, *o*- and *p*-dianisyl-iodonium hydrates. The products isolated consist of the corresponding aryl iodide and diaryl. F. R. G.

Velocity of decomposition of naphthalene, tetra- and deca-hydronaphthalene, and dodecane during destructive hydrogenation.—See A., 1941, I, 421.

Preparation of α-chloro-αββ-triphenylethylene. W. Tadros (*Nature*, 1941, **148**, 53).—SO_2Cl_2 (35 g.), $CPh_2{:}CHPh$ (prep. described) (50 g.) in CCl_4 (25 c.c.), and Bz_2O_2 (0·2 g.) are refluxed on a water-bath for 45 min. Excess of SO_2Cl_2 is removed by distillation under reduced pressure, and the oily residue recryst. twice from EtOH. The mother-liquors are conc., and the oil that separates is recryst. from EtOH. The yield of $CPh_2{:}CClPh$, m.p. 117°, is 45 g. L. S. T.

Certain peculiarities of reactions involving formation of conjugated double linkings. Preparation of δε-diphenyl-$\Delta^{\alpha\gamma\varepsilon\eta}$-octatetraene from γ-benzoylpropyl bromide. S. N. Chitrik (*J. Gen. Chem. Russ.*, 1940, **10**, 2095—2097).—$Bz{\cdot}[CH_2]_3{\cdot}Br$ and Na–Al in moist Et_2O yield *αβ-dibromo-δε-diphenyloctane-δε-diol*, m.p. 160—161°, converted by fusion in presence of sulphanilic acid into *δε-diphenyl-$\Delta^{\alpha\gamma\varepsilon\eta}$-octatetraene*, m.p. 84—85°. R. T.

Preparation of methyl halide [halogenomethyl] derivatives of aromatic hydrocarbons.—See B., 1941, II, 297.

Nitrous acid as a nitrating and oxidising agent. IV. *N*-Dialkylanilines. H. H. Hodgson and D. E. Nicholson (*J.C.S.*, 1941, 470—475; cf. A., 1936, 1501).—The behaviour of *N*-dialkylanilines towards excess of HNO_2 (2 or 5 times that required for nitrosation) in 5% or 15—16% HCl at 0° is studied. $NPhMe_2$ thus gives a 3 : 1 mixture of solid *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$,HCl (**I**) and *p*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$; the filtrate, when kept, affords *p*-$NO_2{\cdot}C_6H_4{\cdot}NMe{\cdot}NO$ (**II**), a little 2 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}NHMe$ (indicates some *m*-nitration), and still less (?) $(NO_2)_3C_6H_2{\cdot}NMe_2$. *p*-Nitrosation and *p*-nitration are considered to be simultaneous initial reactions. $NPhEt_2$ readily affords *p*-$NO_2{\cdot}C_6H_4{\cdot}NEt{\cdot}NO$ (**III**), whilst NHPhMe(Et) afford the respective *N*-NO-derivative, and thence (**II**) [or (**III**)]. NPhMeEt affords p-*nitrosomethylethylaniline*, m.p. 69°, converted on long keeping (with HNO_2) into (**II**) + (**III**) (~83 : 17). $CH_2Ph{\cdot}NPhMe$ (in aq. HCl–AcOH–$NaNO_2$) gives a mixture of 4-nitro- (**IV**) and some 2 : 4-dinitro-benzylmethylaniline (**V**), the former being converted by HNO_2 into (mainly) (**V**) and a little *p*-$NO_2{\cdot}C_6H_4{\cdot}N(NO){\cdot}CH_2Ph$ (**VI**). (**V**) and boiling conc. HCl yield 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NHMe$, whereas (**IV**) is similarly unchanged. $CH_2Ph{\cdot}NPhEt$ readily reacts to give (**VI**). In no case is the CH_2Ph group expelled by HNO_2 and Et is more readily removed than is Me. An improved prep. of (**I**) is described. A. T. P.

Production of diarylamines.—See B., 1941, II, 332.

Cu and Co^{III} 1-nitroso-β- and 2-nitroso-α-naphthylamine.—See A., 1941, I, 429, 430.

***N*^{1}-β-Aminoethyl- and *N*^{1}-β-diethylaminoethyl-sulphanilamide.** L. H. Amundsen and L. A. Malentacchi (*Science*, 1941, **93**, 286).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ with $NHAc{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ and $NEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ in $CHCl_3$ + aq. $NaHCO_3$ followed by hydrolysis (6N-HCl) gives N^1-*β-aminoethyl-* and N^1-*β-diethylaminoethyl-sulphanilamide dihydrochloride*, m.p. 217—220° (decomp.) and 190—195° (decomp.), respectively. L. S. T.

Sulphanilylguanidine. T. Dewing and S. Smith (*Nature*, 1941, **148**, 24).—Fusion of sulphanilamide with dicyanodiamide gives sulphanilylguanidine and not phenylguanidine-4-sulphonamide (cf. A., 1938, III, 937; Marshall *et al.*, A., 1941, III, 786). L. S. T.

Theory of aromatic substituents and rearrangement with special reference to the benzidine change. E. D. Hughes and C. K. Ingold (*J.C.S.*, 1941, 608—613; cf. A., 1926, 833).—Views expressed previously are modified. With the recognition of the quantal theory of mesomerism, theories involving "chronology" of electron displacements (those which specify a succession of electron displacements in an identical nuclear framework) are superseded. The mechanism of the benzidine rearrangement is discussed (cf. A., 1933, 1044; Robinson, *J.C.S.*, 1941, 220). An argument against homolysis of the N–N bond is that the benzidine change does not occur under conditions in which this form of dissociation is known to be considerable; heterolysis is assumed. Homolysis and heterolysis refer to bond fission according to schemes X·|·Y and X|··Y, respectively (dots denote shared electrons), independently of states of electrification of X and Y and any concomitant covalency changes. The transition state, although largely ionic, is partly covalent; the electronic system of the transition state is examined in detail. Stereochemical aspects of the benzidine change are discussed, and also the nature of the semidine rearrangement. A. T. P.

Comparison of hydrogenation of aliphatic and alicyclic azines. I. Azines of hexahydrobenzaldehyde and heptaldehyde. II. Azines of *cyclo*hexanone and ethyl propyl ketone. P. G. Ugriumov (*J. Gen. Chem. Russ.*, 1940, **10**, 1985—1994, 1995—1998).—I. Hexahydrobenzaldehyde and N_2H_4 yield the *azine* (**I**), b.p. 140—141°/3 mm., 166—167°/11 mm. The velocity of hydrogenation (Pt-black in EtOH) of (**I**) is considerably < of diheptylideneazine (**II**); the chief product formed is *NN′-dihexahydrobenzylhydrazine*, b.p. 140—142°/3 mm. [*hydrochloride*, m.p. 193—194°; *dihydrochloride*, m.p. 205—206° (decomp.); *NN′-Bz*$_2$ derivative, m.p. 146—146·5°], oxidised by PbO in Et_2O to *ω-azohexahydrotoluene*, $(\dot{N}{\cdot}CH_2{\cdot}C_6H_{11})_2$, b.p. 116—117°/3 mm., 164—166°/18 mm. (**II**) similarly yields *NN′-di-*n*-heptylhydrazine*, b.p. 118—119°/3 mm. (*dihydrochloride*, m.p. 160—170°; *NN′-Bz*$_2$ derivative, m.p. 48—49°), oxidised to *α-azoheptane*, $(\dot{N}{\cdot}C_7H_{15})_2$, b.p. 110—111°/2·5 mm., 144—145°/17 mm.

II. The velocity of hydrogenation of *cyclo*hexanoneazine is slightly > of $(CEtPr{:}\dot{N})_2$, which yields *NN′-diethyl-NN′-di-n-propylhydrazine*, b.p. 99·5—100°/10 mm. R. T.

Diazo-compounds. IV. Effect of polyhydric alcohols and of certain carbohydrates on tetrazotisation of *m*-phenylenediamine. V. V. Kozlov and B. I. Stepanov (*J. Gen. Chem. Russ.*, 1940, **10**, 1510—1523).—The yield of tetrazonium derivative obtained from *m*-$C_6H_4(NH_2)_2$ in presence of polyhydric alcohols (*A*) rises with increase in the no. of OH in the mol. of, and with increasing concn. of, (*A*). At the same mol. concn. the effect of various (*A*) increases in the order glycol < glycerol < glucose < mannitol < maltose < sucrose < raffinose. R. T.

Structure and properties of the so-called *p*-diazoimines. A. M. Simonov (*J. Gen. Chem. Russ.*, 1940, **10**, 1220—1229).—The following mesomerism of diazoimines is suggested: $\underbrace{NR{\cdot}C_6H_4{\cdot}N{:}N} \rightleftharpoons NR{:}C\langle^{CH{:}CH}_{CH{:}CH}\rangle C\langle^{N}_{\dot{N}}$, in which the second mesomeride is bipolar. Coupling with OH-compounds takes place in the same way as with ordinary diazo-compounds. The following are described: *compounds* of 2′ : 4′-dinitro-4-diazodiphenylamine (**I**) with *α*-$C_{10}H_7{\cdot}NH_2$, m.p. 257—258°, with $CH_2Ac{\cdot}CO_2Et$, m.p. 203·5—204°, with $CH_2Ac{\cdot}CO{\cdot}CO_2Et$, m.p. 180·5—182·5° (decomp.), and with 1-phenyl-3-methyl-5-pyrazolone, m.p. 283°. (**I**) and *p*-$O{:}C_6H_4{:}O$ in aq. NaOAc at 30° yield 2-(p-2′ : 4′-*dinitroanilinophenyl*)-p-*benzoquinone*, m.p. 241·5—242·5°. 2′ : 4′-*Dinitro-4-dimethylaminodiphenylamine methiodide*, m.p. 182° (decomp.), is readily converted by KOH in MeOH into the *compound*, 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}\bar{N}{\cdot}C_6H_4{\cdot}\dot{N}Me_3$, m.p. 218·5—220° (decomp.). R. T.

Alkylpyrocatechols.—See B., 1941, II, 333.

Co^{II} dinitroso-resorcinol and -orcinol and Co^{III} oximinodimedone.—See A., 1941, I, 430.

Syntheses of stilbene derivatives. II. Synthesis of *trans*-4 : 4′-dihydroxy-αβ-diethylstilbene. S. Kuwada, Y. Sasagawa, and M. Nisikawa (*J. Pharm. Soc. Japan*, 1940, **60**, 224—226; cf. A., 1940, II, 215).—$OH{\cdot}CHEt{\cdot}COEt$ and *p*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ (**I**) give *γδ-dihydroxy-γ-*p*-anisylhexane*, b.p. 143—144°/0·5 mm., m.p. 83—84° (*monoacetate*, m.p. 101—102°), isomerised by hot 30% H_2SO_4 to *γ-*p*-anisylhexan-δ-one*, b.p. 140—155°/14 mm. (*oxime*, m.p. 133·3°). This and (**I**) afford *γδ-di-p*-anisylhexan-*γ*-ol, m.p. 115—117°, which is dehydrated to *γδ-di-p*-anisyl-Δ*γ*-hexene, demethylated (Späth) to *γδ-di-p*-hydroxyphenyl-Δ*γ*-hexene (*trans*-4 : 4′-dihydroxy-*αβ*-diethylstilbene). H. W.

4 : 5-Methylenedioxychrysene. L. H. Briggs and (Miss) J. M. Wilson (*J.C.S.*, 1941, 500—501).—*α*-$C_{10}H_7{\cdot}CH_2{\cdot}CO_2K$ and 6-nitropiperonal in Ac_2O at 100° give 2-*nitro-*, m.p. 203·5—206·5°, and thence [Fe(OH)$_2$–aq. NH_3] 2-*amino*-4 : 5-*methylenedioxy-α-1′-naphthylcinnamic acid*, m.p. 161·5—163·5° (decomp.), which when diazotised (H_2SO_4–$C_5H_{11}{\cdot}O{\cdot}NO$ at 25—30°) and treated with Cu powder + Cu-bronze in aq. NaH_2PO_2 at 45° to b.p. gives a crude acid, decarboxylated (Cu-bronze at 200—240°/0·04 mm.) to 4 : 5-*methylenedioxychrysene*, m.p. 222—223° (picrate, m.p. 202—202·5°). A. T. P.

Sinomenine. XLVIII. Degradation of sinomenolquinone dibenzoate to 2 : 3 : 3′ : 4′-tetramethoxydiphenyl. K. Goto and H. Shishido (*Bull. Chem. Soc. Japan*, 1941, **16**, 170—172).—Sinomenolquinone dibenzoate (cf. A., 1929, 1187) and H_2O_2 in warm AcOH give 5 : 6′-*dibenzoyloxy*-4 : 5′-*dimethoxydiphenic acid*, m.p. 233—235° (decomp.) (*Me*$_2$ ester, m.p. 170—173°), converted by hot KOH–MeOH–H_2O in H_2 and then Me_2SO_4–KOH into 4 : 5 : 5′ : 6′-*tetramethoxydiphenic acid*, m.p. 206—208° (could not be resolved; *Me*$_2$ ester, sinters at 124°, m.p. 132°), which with Cu powder in quinoline at 240—250° gives 2 : 3 : 3′ : 4′-*tetramethoxydiphenyl*, m.p. 96—100°. R. S. C.

2 : 4-Dinitro-5-naphthylaminophenols.—See B., 1941, II, 332.

4 : 6-Diamino-3-methoxytoluene. K. I. Bogatscheva (*J. Appl. Chem. Russ.*, 1940, **13**, 1606—1607).—4 : 6 : 1 : 3-$(NO_2)_2C_6H_2Me$·OMe is reduced by Fe in aq. EtOH–HCl (1 hr. at the b.p.) to 4 : 6-*diamino*-3-*methoxytoluene*, m.p. 101°; with H_2SO_4–HNO_3 at 120° it yields 2 : 4 : 6-*trinitro*-3-*methoxytoluene*, m.p. 92°. R. T.

Ephedrine alkanesulphonates.—See B., 1941, III, 269.

Action of alkali on chemical and physiological properties of adrenaline. F. H. Shaw (*Austral. J. Exp. Biol.*, 1941, **19**, 151—155).—During the action of alkali on adrenaline (**I**) an intermediate is rapidly formed which is probably the corresponding *o*-quinone; it retains the physiological activity of (**I**). After 2—5 min. action, the physiological activity has disappeared; the final product is not adrenochrome and its exact nature is unknown. D. M. N.

Physico-chemical study of products of oxidation of adrenaline. I. Isolation of adrenochrome. J. S. Rozum and S. S. Urazovski (*J. Gen. Chem. Russ.*, 1940, **10**, 1573—1579).—Adrenochrome is shown by chromatographic analysis to be a mixture of $\not<$ 7 substances. Of these, a brown substance predominates. At any given p_H a state of dynamic equilibrium exists between all these substances. R. T.

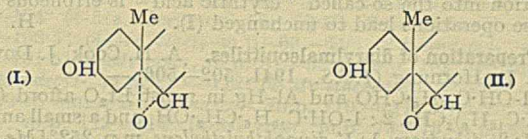
Sterols. XXII. Identity of bessisterol and spinasterol. S. Kuwada and S. Yosiki (*J. Pharm. Soc. Japan*, 1940, **60**, 161—162; cf. A., 1940, II, 218).—Comparison of α-spinastenol, spinastanol, and spinastanone and their derivatives with the corresponding compounds from α-bessistaenol establishes the identity of bessisterol with spinasterol. H. W.

Sterols. XXIII. Sterol from the seeds of *Momordica Cochinchinensis*, Spreng. S. Kuwada and S. Yosiki (*J. Pharm. Soc. Japan*, 1940, **60**, 232—233).—Extraction of the seeds with Et_2O followed by hydrolysis of the extract and purification of the unsaponifiable matter (*A*) through the 3 : 5-dinitrobenzoate and then chromatographically (Al_2O_3) leads to the isolation of a sterol, $C_{28}H_{46}O$, m.p. 156·5—163·5°, $[\alpha]_D^{22}$ +5·81°. Chromatography with the crude cryst. material from (*A*) gives a sterol, $C_{28}H_{46}O$,0·5H_2O, m.p. 163·5—167·5°, $[\alpha]_D^{22}$ +4·04° (acetate, m.p. 174·5—176·5°; benzoate, m.p. 196—198°), probably identical with cucurbitasterol (Lendle, A., 1938, III, 358). M.p. are corr. H. W.

Pentacyclic steroids. O. Rosenheim (*Nature*, 1941, **147**, 776—777).—Transannular tautomeric changes explain some of the reactions of *cis*-Δ^5-cholestene-3 : 4-diol, the formation of *i*-cholesterol from cholesterol, and the migration of Bz in 6-chloro-3-benzoyloxy-Δ^4-cholestene. L. S. T.

α-Œstradiol dimethyl and 17-methyl ether and related compounds. Y. Urushibara and T. Nitta (*Bull. Chem. Soc. Japan*, 1941, **16**, 179—182).—Figures given in parentheses below are min. œstrogenic doses (rats; μg. in oil). The Na derivative of α-œstradiol 3-Me ether (**I**) (4—5), m.p. 95—97°, and Me_2SO_4 in boiling Et_2O and later C_6H_6 give the *Me*$_2$ *ether* (<10, >5), m.p. 161—162°, also obtained from œstrone Me ether (15), Na, and Me_2SO_4 in C_6H_6 and converted by HI–AcOH into α-œstradiol 17-Me ether (<2·5), m.p 213·5—214·5° (3-benzoate, m.p. 165·5—166·5°; 3-*p*-toluenesulphonate, m.p. 124·5—125·5°). (**I**) gives the 17-acetate, m.p. 103·5—104·5°, 17-benzoate, m.p. 131—132°, and 17-*p*-toluenesulphonate, m.p. 160—161°. α-Œstradiol 17-*p*-toluenesulphonate (~100), m.p. 171—172°, di-*p*-toluenesulphonate, m.p. 172—173°, and 3-benzoate 17-*p*-toluenesulphonate, m.p. 184·5—185·5°, are prepared. Min. effective doses are œstrone 2 and diethylstilbœstrol 0·5 (*Me*$_2$ ether 5) μg. Duration of œstrus is recorded for numerous compounds. M.p. are corr. R. S. C.

Configurations of cholesterol oxides, Δ^4-cholestene- and cholestane-3 : 6-diols. Y. Urushibara (*Bull. Chem. Soc. Japan*, 1941, **16**, 182—185).—Known reactions establish configurations as follows. Cholesterol α- (**I**), m.p. 140—141°, and β-oxide (**II**), m.p. 136°; 5(β)-chloro-6(β)-hydroxycoprostan-3(β)-ol = "5-chloro-6-hydroxycholestanol"; Δ^4-cholestene-3(β) : 6(β)-, m.p. 257—258°, and -3(β) : 6(α)-diol, m.p. 178—179°; cholestane-3(β) : 6(β)-, m.p. 194—195°, and -3(β) : 6(α)-diol (**III**), m.p. 216°. This is confirmed by reduction of (**I**) to (**III**) by Na–C_5H_{11}·OH. R. S. C.



7-Hydroxy- and 7-keto-cholesterol.—See B., 1941, III, 269.

Recovery of pregnanediol.—See B., 1941, III, 269.

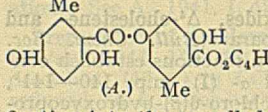
Zinc dust distillation of benzenoid compounds. Z. Nikuni, H. Hayashi, and S. Tsuji (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 414—418).—Distillation of guaiac resinic acid [α-3-hydroxy-4-methoxyphenyl-δ-4-hydroxy-3-methoxyphenyl-βγ-dimethyl-Δ$^\alpha$-butene] with Zn dust in H_2 yields 2 : 3-$C_{10}H_6Me_2$ and anthracene (**I**). CHPh:CH·CO_2H yields small amounts of stilbene, whilst CH_2Ph·CH_2·CO_2H yields a trace of (**I**) and much $C_{10}H_8$. CH_2Ph·CO_2H yields distilbene and a trace of (**I**). In every case an unidentified yellowish oil is also formed. J. N. A.

Reaction of acraldehyde with anthracene. A. G. Slobodski and V. I. Chmelevski (*J. Gen. Chem. Russ.*, 1940, **10**, 1199—1201).—Anthracene and CH_2:CH·CHO in presence of aq. SO_2 (3 hr. at 130°) yield an oily product, oxidised by Ag_2O to αβ-*endo*-9 : 10-dihydroanthracene-9 : 10-propionic acid. R. T.

Chloralamides. X. Reactivity of α-halogen in α-halogenochloral-nitro- and -bromo-methoxybenzamides. N. W. Hirwe, (Miss) K. D. Gavankar, and B. U. Patil (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 371—373).—The customary reactions lead to the following: α-*chloro*-, m.p. 149—150°, α-*methoxy*-, m.p. 144°, α-*ethoxy*-, m.p. 146—147°, α-*anilino*-, m.p. 168—169°, α-o-*toluidino*-, m.p. 151—152°, and α-p-*toluidino*-, m.p. 171—172°, -*chloral*-5-*nitro*-2-*methoxybenzamide*; α-*chloro*-, m.p. 150—151°, α-*bromo*-, m.p. 140°, α-*ethoxy*-, m.p. 147—149°, α-*anilino*-, m.p. 168—169°, α-o-*toluidino*-, m.p. 166—167°, α-p-*toluidino*-, m.p. 175—177°, and α-*phenoxy*-, m.p. 191—192°, -*chloral*-5-*bromo*-2-*methoxybenzamide*; α-*chloro*-, m.p. 109—110°, α-*anilino*-, m.p. 166—167°, α-o-*toluidino*-, m.p. 166—167°, and α-p-*toluidino*-, m.p. 173—174°, -*chloral*-3 : 5-*dibromo*-2-*methoxybenzamide*; α-*methoxychloral*-3-*nitro*-2-*methoxybenzamide*, m.p. 104—105°. Chloral-3 : 5-dinitro-2-methoxybenzamide and PCl_5 appear to afford 3 : 5-*dinitro*-2-*methoxybenz*-αβββ-*tetrachloroethyl imidochloride*, m.p. 19°. H. W.

Constitution of erythrin. Y. Sakurai (*J. Pharm. Soc. Japan*, 1941, **61**, 45—46).—Erythrin (**I**), $C_{20}H_{22}O_{10}$ (also +1H_2O), m.p. 148°, from *Roccella montagnei* from Java or *R. sp.* from Zanzibar, is converted by NaOAc and boiling Ac_2O into a *hexa-acetate*, m.p. 85°, and by CH_2N_2 into a *Me*$_3$ *ether* (**II**), m.p. 111° (*triacetate*, m.p. 110°). (**II**), anhyd. $COMe_2$, and $CuSO_4$ slowly give iso*propylidene-erythrin Me*$_3$ *ether* (**III**), m.p. 65°, whereas (**I**) yields iso*propylidene-erythrin*, m.p. 105°; both substances readily afford $COMe_2$ in presence of cold mineral acid. (**I**) is insol. in alkali carbonate but sol. in alkali hydroxide, by which it is transformed at 40° into Me orsellinate (**IV**) and *r*-erythritol (**V**), whereas in boiling MeOH it gives (**IV**) and picroerythrin, m.p. 136·5° (lit. 158°), further methanolised to (**IV**) and (**V**). (**II**) is hydrolysed by KOH–EtOH to orsellinic acid Me$_2$ ether, *iso*evernic acid, and (**V**), thus establishing the depside nature of both orsellinic acid components. Carbethoxy*iso*evernyl chloride is reduced (Rosenmund) to the aldehyde, which is decarboxylated and coupled with orsellinyl chloride Me$_2$ ether to *lecanorylaldehyde Me*$_3$ *ether*, m.p. 131°, unusually sensitive to light. This is oxidised to the *acid*, m.p. 179°, the chloride of which with *iso*propylidene-erythritol (**VI**) in C_5H_5N gives (**III**) and

thence (II). (VI) is $CMe_2{<}O{>}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ since it is oxidised by $Pb(OAc)_4$ to CH_2O and glyceraldehyde. (I) is therefore (*A*). The supposed conversion of (I) by dissolution in AcOH or in alkali with subsequent acidification into the so-called " erythric acid " is erroneous since these operations lead to unchanged (I).



(*A*.)

H. W.

Preparation of diarylmaleonitriles. A. H. Cook, J. Downer, and B. Hornung (*J.C.S.*, 1941, 502—506).—2 : 1-OH·$C_{10}H_6$·CHO and Al–Hg in moist Et_2O afford (2 : 1-OH·$C_{10}H_6$)$_2CH_2$, 2 : 1-OH·$C_{10}H_6$·CH_2·OH, and a small amount of 2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylethylene*, m.p. 252° [*Me*$_2$ *ether* (I), m.p. 222°]. 2-$C_{10}H_7$·OMe, $(CH_2O)_3$, and HCl–AcOH at <15° yield 2-*methoxy*-1-*chloromethylnaphthalene* (II), decomp. 120° (loses HCl); polymeric material is obtained at high temp. or from (II) at 120°. HCl is removed from (II) in $COMe_2$ by $AgNO_3$–EtOH at 30° to give s-2 : 2′-*dimethoxy*-1 : 1′-*dinaphthylethylene*, β-form, m.p. 145°; this and (I) are probably *cis*- and *trans*-isomerides. (II) and warm aq. $COMe_2$–$NaHCO_3$ afford 2 : 1-OMe·$C_{10}H_6$·CH_2·OH, whilst (II) and dil. KOH–EtOH at 40° yield 2-*methoxy*-1-*naphthylcarbinyl Et ether*, b.p. 173—175°/12 mm. (II) is converted by KCN–aq. $COMe_2$ at 30—35° into 2-*methoxy*-1-*naphthylacetonitrile* (III), m.p. 111° (*Br*-derivative, m.p. 145—146°, prep. by Br–$CHCl_3$), which does not give the corresponding diarylmaleonitrile with Br or I and bases. 2 : 1-OMe·$C_{10}H_6$·CH(OH)·CN and $SOCl_2$–C_6H_6 at room temp. yield *di*-2-*methoxy*-1-*naphthylcyanomethyl ether* (IV), m.p. 121°, whereas at higher temp. with excess of $SOCl_2$, or from (IV), 2-*methoxy*-1-*naphthylchloroacetonitrile*, m.p. 130°, is formed. The latter and warm C_5H_5N yield 2-*methoxy*-1-*naphthylcyanomethylpyridinium chloride*, m.p. 165° (slight decomp.), converted by aq. Na_2CO_3 into the orange 2-*methoxy*-1-*naphthylcyanomethylpyridinium enimine-betaine*, m.p. 150° (decomp.), which at 200°/0·001 mm. gives (III) and 2 : 2′-*dimethoxy*-1 : 1′-*dinaphthylmaleonitrile*, two stereoisomerides, α-, m.p. 255°, and β-, m.p. 290° (5% yield of each) (heating with Cu or Cu salts gives octanaphthylporphyrazines; $FeCl_3$ at 300° affords Fe porphyrazine pigments). *Cyanomethylpyridinium chloride* (V), m.p. 178°, and aq. K_2CO_3 or KOH give the corresponding betaine, which does not decompose to a nitrile; (V) and Bz_2O in $CHCl_3$–aq. K_2CO_3 yield ω-cyanophenacylpyridinium benzoate (cf. Kröhnke, A., 1939, II, 124). Neither (V) nor *acetamidopyridinium chloride*, m.p. 202—203°, gives any dimeric product on heating. CHClMe·CN affords a pyridinium salt and an unstable betaine. CHClPh·CN and C_5H_5N (2 days) give *α-cyanobenzylpyridinium chloride*, m.p. 159°, and thence the enimine-betaine, which at 120°/vac. yields diphenylmaleonitrile (~50% yield) (cf. Kröhnke, *loc. cit.*). Thus dimerisation appears to proceed only with arylhalogenoacetonitriles. $CH_2Ph{\cdot}CH(OH){\cdot}CN$ and PCl_5–C_6H_6 give *α-chloro-β-phenylpropionitrile*, b.p. 128—130°/13 mm., and thence the betaine, converted into cinnamonitrile. CHPh:CH·CH(OH)·CN and $SOCl_2$ give α-chloro-γ-phenyl-Δ$^{\beta}$-butenonitrile (no characteristic pyridinium salt or betaine is obtained), which when kept affords (probably) 2 : 5-*diphenyldihydroterephthalonitrile*, m.p. 114°. *p*-OMe·C_6H_4·CH(OH)·CN and $SOCl_2$ yield *α-chloro-α-p-anisylacetonitrile*, b.p. 153—155°/13 mm.; the pyridinium salt decomposes to *di*-p-*anisylmaleonitrile*, m.p. 186—187°, which gives a porphyrazine with Fe at 280—300°. 2 : 1-$C_{10}H_6$Me·CH_2Cl and KCN–85% EtOH give 2-*methyl*-1-*naphthylacetonitrile*, m.p. 78°; in presence of much H_2O, 2-*methyl*-1-*naphthylcarbinol*, m.p. 137—138°, is formed.

A. T. P.

Phthalic anhydride.—See B., 1941, II, 334.

Preparation of substituted phthalic anhydrides.—See B., 1941, II, 334.

Preparation of phenylacetaldehyde. A. K. Schumeiko (*J. Appl. Chem. Russ.*, 1941, **14**, 93—95).—Ph·$[CH_2]_2$·OH in C_6H_6 or PhMe is oxidised by $K_2Cr_2O_7$–H_2SO_4 (30 min. at room temp.) to $CH_2Ph{\cdot}CHO$ (40% yield).

R. T.

Oxidation of organic compounds with selenium dioxide. VII. Oxidation of substituted acetophenones. N. N. Melnikov and M. S. Rokitzkaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1439—1441).—The velocity of oxidation of $C_6H_4R{\cdot}COMe$ by SeO_2 in 75% AcOH at 30° rises in the order R = *m*-NO_2 < *p*-Br < *p*-Cl < H < *p*-OMe < *p*-Me < *p*-I. That of $CH_2Ph{\cdot}COMe$ is > that of *p*-$C_6H_4I{\cdot}COMe$.

R. T.

Dispersion spectra of crystalline and amorphous benzophenone.—See A., 1941, I, 397.

Pinacol–pinacolone rearrangement of phenyl-substituted benzopinacols. H. H. Hatt, A. Pilgrim, and (Miss) E. F. M. Stephenson (*J.C.S.*, 1941, 478—483).—*o*-$C_6H_4Ph{\cdot}COPh$ (I) (*anil*, m.p. 91—92°) and Zn–KOH–EtOH at 30° for 5 days afford *o-phenylbenzhydrol*, m.p. 71°, which is converted by warm H_2SO_4–AcOH (3 : 1) into 9-phenylfluorene. With Zn–AcOH at 25—30° for 10 days, or with Na–Et_2O in N_2, (I) gives s-*di*-o-*phenylbenzopinacol* (II), α- (+H_2O), m.p. 175° (decomp.), and β-form (+H_2O), m.p. 152—160° (boiling $CHCl_3$ converts β into α), also obtained in small yield from MgPhBr, Mg, and *o*-$C_6H_4Ph{\cdot}CO_2Me$ in N_2, but not formed by irradiation of (I) in Pr$^{\beta}$OH. (II) (α or β) and I in 20% NaOAc–AcOH yield (I). *m*-$C_6H_4Ph{\cdot}MgBr$ (prepared with active Mg in N_2) and PhCN yield m-*phenylbenzophenone*, m.p. 79°, b.p. 264—267°/25 mm. (*benzhydrol*, m.p. 81°), which by photochemical reduction in Pr$^{\beta}$OH affords s-*di*-m-*phenylbenzopinacol* (III), m.p. 178°, in 55% yield (20% yield by Zn–AcOH). Migratory aptitudes in the pinacol–pinacolone rearrangement are found to be *p*-, 3·7, and *m*-C_6H_4Ph, 0·4 (Ph = 1; *o*-C_6H_4Ph = 0), which agrees with the order suggested by Burton *et al.* (A., 1929, 1052), viz., α-$C_{10}H_7$ > β-$C_{10}H_7$ > *p*-C_6H_4Ph > *m*-C_6H_4Ph, in connexion with the stability of CAr_3. A comparison of agents [2% $HClO_4$ in anhyd. AcOH (3·75) or in AcOH + 4% H_2O (2·6); HI–AcOH (3·75); *p*-$C_6H_4Me{\cdot}SO_3H$–AcOH (3·9)] used with *s*-di-*p*-phenylbenzopinacol (IV), m.p. 198—201°, as substrate shows that the extent of migration of *p*-C_6H_4Ph (aptitude quoted) and Ph is independent of the agent, except in case of AcCl–AcOH–C_6H_6, which suggests increased migration of Ph. The migratory aptitude of *p*-C_6H_4Ph as obtained by Gomberg *et al.* (A., 1927, 245) is not confirmed. Wide differences in vals. for migratory aptitudes with various reagents are encountered with (II); agents other than $HClO_4$ bring about the pinacolone change so slowly that side reactions entirely supervene. (II)–HI–AcOH yield (I), whilst (II)–*p*-$C_6H_4Me{\cdot}SO_3H$–AcOH give 9-phenylfluorene. Rearrangement of (II) with $HClO_4$ affords solely *o-phenylbenzoyldiphenyl*-o-*diphenylylmethane* (V), m.p. 195·5°, which is unchanged by boiling 10% KOH–MeOH or –EtOH for 300 hr. Fission to methanes and mixed benzoic acids of (V) is carried out with KOH + a little *iso*-C_5H_{11}·OH, or better with KOH–NaOH (1 : 1) at 185—195°, and of (III) and (IV), after rearrangement, with KOH–NaOH (1 : 1) or KOH–MeOH. (V) gives some o-*phenyltriphenylmethane*, m.p. 138°. Fission of pure *o*-, *m*-, or *p*-$C_6H_4Ph{\cdot}COPh$ is carried out by KOH–NaOH (1 : 1) and cleavage figures are given.

A. T. P.

Synthesis of substances related to sterols. XXXV. Furfurylideneacetone as a reagent for the extension of ring systems. L. E. King and (Sir) R. Robinson (*J.C.S.*, 1941, 465—470).—2-Methyl*cyclo*pentanone, anhyd. HCN, and a little aq. KCN at 0° afford the cyanohydrin, converted by $SOCl_2$–C_5H_5N at 100° (bath) into 1-*cyano*-2-*methyl*-Δ^2-cyclo*pentene*, b.p. 68—70°/14 mm., hydrolysed by aq. KOH fo the 1-*carboxylic acid*, m.p. 125°. The corresponding Ba salt with $(HCO_2)_2Ba$ and sand at 150—200°/2 mm. yields 2-methyl-Δ^1-*cyclo*pentene-1-aldehyde, b.p. 70—75°/14 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 200°), which polymerises when kept. *cyclo*Pentanone, $CH(OEt)_3$, and NaOEt in Et_2O afford 2-ethoxymethylene*cyclo*pentanone, b.p. 115—122°/11 mm. (*semicarbazone*, m.p. 222—223°), which with MgMeI–Et_2O gives (probably) 2-*methyl*-1-*ethylidene*-Δ^2-cyclo*pentene*, b.p. 96—98°/11 mm. (no adduct with maleic anhydride in C_6H_6). 2-Methyl*cyclo*pentanone and $NaNH_2$–Et_2O, followed by $CH_2Cl{\cdot}CO_2Et$, afford *Et* 2-*methyl*cyclo*pentanone*-2-*acetate*, b.p. 130—133°/14 mm., purified by conversion with $Et_2C_2O_4$ and Na in light petroleum (3 days) into an oil, which loses CO at 180°/18 mm. to give *Et* 5-*carbethoxy*-2-*methyl*cyclo*pentanone*-2-*acetate*, b.p. 142—146°/0·5 mm., which is subsequently hydrolysed (conc. HCl) and esterified. *cis*-8-Methyl-6-hydrindanone and Br–AcOH–HBr afford a bromoketone (I), which with boiling dry C_5H_5N or quinoline gives an oily, saturated product from which a *semicarbazone*, m.p. 199°, is obtained. (I) and NMe_3–EtOH at 100° yield a quaternary bromide, m.p. 240°, converted by Ag_2O–90% EtOH into an oil, b.p. 112—118°/12 mm. (*semicarbazone*, m.p. 200°). *cis*-5-Hydrindanol and PBr_3 at <0° give 5-bromohydrindane, b.p. 104—105°/15 mm., which with boiling 20% KOH–EtOH gives a

mixture, b.p. 175—177°/750 mm., of Δ^4- and Δ^5-tetrahydrohydrindenes, oxidised by $KMnO_4$–aq. KOH at 40° to two acids, m.p. 173° and 101° (cf. Hückel *et al.*, A., 1935, 208). Hydrogenation ($SrCO_3$–Pd–MeOH) of 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene affords a hydrophenanthrol, converted by $Al(OBu^{\gamma})_3$–$COMe_2$–C_6H_6 into 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (**II**), m.p. 118—119° (through hydrolysis of mixed semicarbazones), which with Mg Δ^{γ}-butenyl bromide (method : Hibbit *et al.*, A., 1936, 713) yields a product cyclised by H_2SO_4–Ac_2O–AcOH to an acetate, hydrolysed by KOH–EtOH to 5-*hydroxy*-14-*methoxy*-3-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 18-*dodecahydrochrysene*, m.p. 161—168° (*p*-nitrobenzoate, m.p. 239°). The Na derivative (prep. by $NaNH_2$ in Et_2O) of 2-methyl*cyclo*hexanone with furfurylideneacetone (**III**) in Et_2O gives 2-*keto*-4-*furyl*-10-*methyl*-$\Delta^{1:9}$-*octahydronaphthalene*, b.p. 160—170°/0·05 mm., hydrogenated (Pd–$SrCO_3$–MeOH) to 2-keto-4-furyl-10-methyldecahydronaphthalene, the *semicarbazone*, m.p. 126°, of which with NaOEt–EtOH at 180° yields 1-*furyl*-9-*methyldecahydronaphthalene* (**IV**), b.p. 122—124°/0·4 mm., and a non-ketonic oil, b.p. 155—160°/0·4 mm. (**IV**) and HCl (*d* 1·16)–EtOH, followed by HCl–aq. AcOH, give an oil, oxidised by $KMnO_4$–$COMe_2$ to 9-*methyldecahydronaphthalene*-1-*carboxylic acid*, m.p. 164°. (**II**) and $NaNH_2$–Et_2O (in N_2) followed by (**III**) in Et_2O afford 6-*keto*-14-*methoxy*-4-*furyl*-3-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 9 : 10 : 11 : 18-*decahydrochrysene*, m.p. 172°. Et β-2-methoxy-6-naphthoylpropionate gives no new products in attempted Reformatsky reactions with Et α-bromo-propionate and -succinate. A. T. P.

Production of *cis*-androsterone.—See B., 1941, III, 269.

Hydroxyquinones. III. Constitution and synthesis of rapanone, the anthelmintic principle of *Rapanea Maximowiczii*, Koidz. M. Asano and K. Yamaguti (*J. Pharm. Soc. Japan*, 1940, **60**, 237—242).—Rapanone (**I**), m.p. 139—140°, is converted by BzCl and C_5H_5N into the *dibenzoate* (**II**), m.p. 88—90°, and by Zn powder and boiling Ac_2O into the *leucotetra-acetate* (**III**), m.p. 117—118°. (**I**) is decomposed by boiling 5% NaOH in H_2 into *α-ketopalmitic acid*, m.p. 65—66° (*oxime*, m.p. 81—82°), oxidised by alkaline H_2O_2 to *n*-pentadecoic acid (**IV**), identified as the *p*-toluidide, m.p. 92—93°. The synthesis of (**IV**) from Et myristate is described. Oxidation ($KMnO_4$–KOH) of (**I**) gives myristic acid, m.p. 51° (*p*-toluidide, m.p. 90—91°). 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CO·CH_2·CO_2Et, *n*-$C_{12}H_{25}I$, and NaOEt in boiling EtOH give *Et α*-3 : 4 : 5-*trimethoxybenzoylmyristate*, m.p. 54°, hydrolysed by boiling 1% KOH–EtOH to 3 : 4 : 5-*trimethoxymyristophenone*, m.p. 69°. This is converted by Na and boiling *iso*-C_5H_{11}·OH into 3 : 5-*dimethoxytetradecylbenzene*, b.p. 178°/0·02 mm., m.p. 43°, oxidised ($Na_2Cr_2O_7$, AcOH) to 6-*methoxy*-2-*tetradecyl*-p-*benzoquinone*, m.p. 81—82°, which with EtOH–NH_2Me and subsequent aëration yields 3 : 6-*di*(*methylamino*)-2-*tetradecyl*-p-*benzoquinone* (**V**), m.p. 143°. Acid hydrolysis of (**V**) affords 3 : 6-*dihydroxy*-2-*tetradecyl*-p-*benzoquinone* (**VI**), m.p. 139—140° [*dibenzoate* (**VII**), m.p. 94—95°; *leucotetra-acetate* (**VIII**), m.p. 121·5°]. The m.p. of (**I**) and (**II**) is not depressed by (**VI**) and (**VII**), respectively, whereas (**VIII**) causes a small but definite depression of the m.p. of (**III**). A similar series of changes gives successively *Et α*-3 : 4 : 5-*trimethoxybenzoyltridecoate*, m.p. 49—50°, 3 : 4 : 5-*trimethoxytridecophenone*, m.p. 61—62°, 3 : 5-*dimethoxytridecylbenzene*, m.p. 41·5—42·5°, 6-*methoxy*-, m.p. 82—83·5°, 3 : 6-*di*(*methylamino*)-, m.p. 141—142°, and 3 : 6-*dihydroxy*-2-*tridecyl*-p-*benzoquinone* (**IX**), m.p. 139—140° [*dibenzoate* (**X**), m.p. 91°; *leucotetra-acetate* (**XI**), m.p. 118°]. Since (**IX**), (**X**), and (**XI**) do not depress the m.p. of (**I**), (**II**), and (**III**), respectively, the identity of (**I**) and (**IX**) is regarded as established. H. W.

Hydroxyquinones. IV. Synthesis of dihydroxy-2-alkyl-*p*-benzoquinones. M. Asano and Z. Hase (*J. Pharm. Soc. Japan*, 1941, **61**, 1—6).—*Quinol di*-n-*dodecate* (prep. from quinol, $C_{11}H_{23}$·CO_2H, and $ZnCl_2$ at 140—165°), m.p. 83°, and CH_2N_2 give p-*dodecoxyanisole*, m.p. 32—33°. *n*-$C_{11}H_{23}$·COCl, *p*-$C_6H_4(OMe)_2$, and $AlCl_3$ in CS_2, first at room temp. and later at (?) >100°, give 2-n-*dodecoylquinol* 4-*Me ether* (**I**), m.p. 42—43° (2 : 4-*dinitrophenylhydrazone*, m.p. 121—124°), and 2-n-*dodecoylquinol*, m.p. 99° [with CH_2N_2 gives (**I**)]. Zn–Hg–HCl reduces (**I**) to 2-n-*dodecylquinol* 4-*Me ether*, m.p. 54—56°, b.p. 165—168°/0·3 mm., converted by $AlCl_3$ in hot C_6H_6 into 2-*n*-dodecylquinol, m.p. 109—111°, which with boiling aq. $FeCl_3$ gives 2-*n*-dodecoyl-*p*-benzoquinone, m.p. 74° (lit. 81°). With NH_2Me–EtOH this gives 1 : 3 : 6 : 2 : 4-O:$C_6H(NHMe)_2(C_{12}H_{25}$-*n*):O, m.p. 146—148°, hydrolysed by H_2SO_4–AcOH to 1 : 3 : 6 : 2 : 4-O:$C_6H(OH)_2(C_{12}H_{25}$-*n*):O (structure proved by oxidation by H_2O_2 to *n*-$C_{12}H_{25}$·CO_2H). Similarly are prepared : 2-n-*undecoyl*-, m.p. 73·5—74·5° [4-*Me ether*, m.p. 47·5—48·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 125—127°); *dibenzoate*, m.p. 93—94·5°], 2-n-*tetradecoyl*-, m.p. 101—103° (4-*Me ether*, m.p. 51—52°), 2-n-*hexadecoyl*-, m.p. 103—104° (4-*Me ether*, m.p. 59—60·5°), 2-n-*octadecoyl*-, m.p. 106—108·5° (4-*Me ether*, m.p. 63—64°), 2-n-*undecyl*-, m.p. 100—101·5° (4-*Me ether*, m.p. 51—52·5°, b.p. 162°/0·5 mm.), 2-n-*tetradecyl*-, m.p. 110—112° (4-*Me ether*, m.p. 57—60°, b.p. 195°/0·15 mm.), 2-n-*hexadecyl*-, m.p. 110—111°, and 2-n-*octadecyl*-, m.p. 112—114° (4-*Me ether*, m.p. 73—75, b.p. 226—228°/0·8 mm.), -*quinol*; 2-n-*undecyl*-, m.p. 57—59°, 2-n-*tetradecyl*-, m.p. 78—79°, 2-n-*hexadecyl*-, m.p. 82—83°, and 2-n-*octadecyl*-, m.p. 84—85°, -p-*benzoquinone*; 3 : 6-*di*(*methylamino*)-2-*n*-undecyl-, m.p. 145—148° (with H_2SO_4–AcOH gives embelin), -2-n-*hexadecyl*-, m.p. 140°, and -2-n-*octadecyl*-, m.p. 138—140°, -p-*benzoquinone*; 3 : 6-*dihydroxy*-2-n-*hexadecyl*-, m.p. 132—134° (*dibenzoate*, m.p. 93—95°), and -2-n-*octadecyl*-p-*benzoquinone*, m.p. 134—135° (*dibenzoate*, m.p. 92—93°). Reduction of the $(OH)_2$-quinone by Zn dust, Ac_2O, and a drop of H_2O at 100° and later, when cold, a little conc. H_2SO_4 gives 2 : 3 : 5 : 6-*tetra-acetoxy*-n-*hexa*-, m.p. 117—119°, and *-octa-decylbenzene*, m.p. 119·5—120·5°. R. S. C.

Hydroxyquinones. VI. Synthesis of dihydroxydialkylbenzoquinones. M. Asano and H. Takahashi (*J. Pharm. Soc. Japan*, 1941, **61**, 65—66).—$Et_2C_2O_4$, CH_2R·CO_2Et (R = *iso*-C_5H_{11}, *n*-C_7H_{15}, *n*-$C_{10}H_{21}$), and Na in Et_2O afford small amounts only of 3 : 6-*dihydroxy*-2 : 5-*di*isoa*myl*-, m.p. 177—178° (*dibenzoate*, m.p. 170°), -*di*-n-*heptyl*-, m.p. 143° (*dibenzoate*, m.p. 100°), and -*di*-n-*decyl*-*benzoquinone*, m.p. 131—132° (*dibenzoate*, m.p. 87°), and thence (Zn–Ac_2O + H_2O) 2 : 3 : 5 : 6-*tetra-acetoxy*-1 : 4-*di*isoa*myl*-, m.p. 162°, -*di*-n-*heptyl*-, m.p. 107°, and -*di*-n-*decyl*-*benzene*, m.p. 112°, respectively. A. T. P.

Peroxidase action. III. Oxidation of mesidine. N. B. Chapman and B. C. Saunders (*J.C.S.*, 1941, 496—500; cf. A., 1940, II, 283).—The system dil. aq. H_2O_2 (added gradually) and peroxidase oxidises mesidine (**I**) (2% solution) at room temp. and p_H 4·0—4·7 (dil. AcOH), when 2 : 6-*dimethyl*-p-*benzoquinone*-4-(2′ : 4′ : 6′-*trimethyl*)*anil* (**II**), m.p. 97°, separates gradually; a purified enzyme prep. gives 95% yield. Formation of (**II**) thus involves loss of Me, and the mechanism of reaction of discussed. (**I**) and H_2O_2–$FeSO_4$–dil. AcOH yield an amorphous product containing only traces of (**II**). (**I**)–PbO_2–AcOH–Et_2O afford (chromatographic analysis) azomesitylene, m.p. 75°. (**II**) with Zn dust in boiling Ac_2O–C_5H_5N gives the ON-*Ac*$_2$ derivative, m.p. 143°, of 4-hydroxy-2 : 6 : 2′ : 4′ : 6′-pentamethyldiphenylamine; hydrolysis (boiling 10% H_2SO_4) of (**II**) yields (**I**) and 1 : 2 : 6 : 4-O:$C_6H_2Me_2$:O (**III**), whilst (**I**) and (**III**), alone or in aq. AcOH (+a trace of $COMe_2$), give (**II**). (**I**) does not condense with 5-nitroso-*m*-2-xylenol. Oxidation ($K_2Cr_2O_7$–aq. NaOH at room temp.) of (**I**) gives (**II**) (8%), but equimol. mixtures of (**I**) with *m*-2- or *m*-5-xylenol afford 26 or 0—1%, respectively, of (**II**). A. T. P.

Phenol amidine reaction : detection of guanidine, guanidine derivatives, and carbamide by thymol and hypochlorite. W. R. Fearon (*Sci. Proc. Roy. Dublin Soc.*, 1941, **22**, 415—421; cf. Sakaguchi, *J. Biochem. Japan*, 1925, **5**, 13, 23).—At p_H 8·5—10, $CO(NH_2)_2$, NH:$C(NH_2)_2$, and NH_2·C(NH)·NHR (free or in protein form) with thymol (or a phenol containing H *para* to OH) and NaOCl give stable yellow quinonoid pigments probably of the type *p*-O:C_6H_4:N·C(NH)·NR·C_6H_3·OH-*p*. At p_H >11 only substituted guanidines react. The conditions and mechanism of this and the indophenol reaction are discussed. A. Li.

Hydroxyquinones. V. Synthesis of phthiocol, pigment of the tubercle bacillus. M. Asano and Z. Hase (*J. Pharm. Soc. Japan*, 1941, **61**, 55—57).—2-Methyl-1 : 4-naphthaquinone and NH_2Me–EtOH at room temp., aërated for 1 hr., yield 3-*methylamino*-, m.p. 127—129°, and thence (50% H_2SO_4–AcOH) 3-hydroxy-2-methyl-1 : 4-naphthaquinone (**I**) (phthiocol), m.p. 171—172° (*benzoate*, m.p. 129—130·5°; Ac_2O–Zn–NaOAc afford 1 : 2 : 4-*triacetoxy*-3-*methylnaphthalene*, m.p. 155·5—156°). *Et butyrophenone*-o-*carboxylate*, b.p. 160—163°/11 mm., and *iso*amyl nitrite in HCl–Et_2O give *α-oximino-butyrophenone*-o-*carboxylic acid* (**II**), m.p. 157° (decomp.), and

some 2 : 5-*di*-(*o*-*carboxyphenyl*)-3 : 6-*dimethyl*-1 : 4-*benzoquinonedioxime*, m.p. 273—274° (decomp.). (**II**) and aq. H_2SO_4 at 100° (bath) give *o*-*carboxyphenyl Et diketone*, m.p. 88—90°, the *Et* ester, b.p. 130°/3 mm., of which with NaOEt–Et_2O then affords (**I**). A. T. P.

III.—TERPENES.

Distribution of the double linkings in irone. A. E. Gillam and T. F. West (*Nature*, 1941, **148**, 114).—Irone shows an intense absorption band at 2280 A., and an inflexion near 3080 A., the two together being characteristic of a $\alpha\beta$-unsaturated ketone. The location of the intense band indicates the presence of a monosubstituted $\alpha\beta$-unsaturated ketone, probably CHR:CH·COR, and shows that the C:C·C:C·C:O structure is absent. The similarity between the absorption spectra of α-ionone (λ max. 2285 A.) and irone (λ max. 2280 A.) supports this view. L. S. T.

Catalytic transformations of terpenes. I. Action of activated clay on dipentene. G. A. Rudakov (*J. Gen. Chem. Russ.*, 1940, **10**, 1673—1681).—Dipentene is converted into terpinolene, and this in turn into α-terpinene, by boiling under reflux with fireclay treated with HCl. *p*-Cymene, Δ^3-*p*-menthene, and polyterpenes are also formed as secondary products, and, as these are more stable than are the primary ones, they alone survive prolonged treatment. R. T.

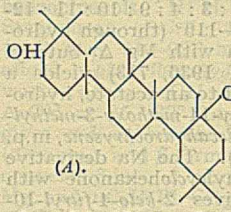
Halogen derivatives of fenchone, and their transformations. L. J. Briusova (*J. Gen. Chem. Russ.*, 1940, **10**, 1462—1470).—Chlorination of fenchone at 60—70° (Cu catalyst) yields *chlorofenchone*, b.p. 113—117°/12 mm. Bromofenchone, as obtained by Czerny (A., 1900, i, 675), is a mixture of products, including bromocamphor, 6-bromofenchone, and probably bromo*iso*fenchone. The mixture is converted by NaOEt in EtOH into a mixture of alcohols, of which borneol, probably *iso*fenchyl alcohol, and possibly fenchyl alcohol were identified. Reduction with Na in EtOH of the polybromide fraction of the bromination product gave an *alcohol*, $C_{10}H_{17}$·OH, b.p. 88·4—89°/13 mm. (*H phthalate*, m.p. 101—103°; *acetate*, b.p. 88—89°/10 mm.), oxidised by HNO_3 to fenchone. R. T.

***iso*Fenchone. II. *iso*Fenchoquinone and its derivatives, and hydroxy*iso*fenchones.** A. K. Rushentzeva and N. M. Delektorskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1653—1656; cf. A., 1941, II, 172).—*iso*Fenchone and SeO_2 in Ac_2O (5 hr. at 140—150°) yield *iso*fenchoquinone, m.p. 69—70° (lit., m.p. 49—50°) (*semicarbazone*, m.p. 165—166°; *phenylhydrazone*, m.p. 125—126°; *oxime*, m.p. 138·5—139·4°), reduced by Zn in AcOH to *hydroxyiso*fenchoquinone, obtained in two isomeric forms, m.p. 50—53° and 114—115°. R. T.

Order of reactions of hydrogenation and dehydrogenation.—See A., 1941, I, 421.

Triterpenes from Japanese *Skimmia* species. I. Skimmiol and skimmione. K. Takeda (*J. Pharm. Soc. Japan*, 1941, **61**, 63—65).—Extraction of the leaves of *Skimmia Japonica*, Thunb., and *S. repens*, Nakai (cf. Asahina, A., 1930, 1454), gives a neutral portion, m.p. 236—238°, which affords (chromatographic analysis) *skimmiol* (**I**), $C_{30}H_{50}O$, m.p. 279—281°, $[\alpha]_D^{19}$ +3·1° in $CHCl_3$ [*mono-acetate* (**II**), m.p. 298—299°, $[\alpha]_D^{23}$ +13·8° in $CHCl_3$, *-benzoate*, m.p. 287—289°, $[\alpha]_D^{17}$ +35·5° in $CHCl_3$, and *-formate*, m.p. 267—269°], and *skimmione* (**III**), $C_{30}H_{48}O$, m.p. 241—243°, $[\alpha]_D^{23}$ +12·2° in $CHCl_3$ [*mono-oxime*, m.p. 292—294°; *oxime acetate*, m.p. 224—225° (decomp.); *dibromide*, m.p. 211° (decomp.)], reduced (Clemmensen) to *skimmiene*, $C_{30}H_{50}$, m.p. 188—190°, $[\alpha]_D^{31}$ −20·5° in $CHCl_3$. (**I**) is oxidised by CrO_3 to (**III**). Catalytic hydrogenation of (**III**), followed by acetylation, affords (**II**). (**III**) is reduced by Na and *iso*-C_5H_{11}·OH to (**I**) and *iso*skimmiol (chromatographic separation), m.p. 267—269°. $[\alpha]_D^{22}$ +11·9° in $CHCl_3$ (*acetate*, m.p. 205—207°, $[\alpha]_D^{16}$ −31·8° in $CHCl_3$; *benzoate*, m.p. 274—275°, $[\alpha]_D^{13}$ −25·2° in $CHCl_3$). A. T. P.

Saponins. XVI. Constitution of nitro-compounds of the oleanolic acid series. II, III. S. Kuwada and K. Takeda (*J. Pharm. Soc. Japan*, 1940, **60**, 157—160, 249—250; cf. A., 1940, II, 221).—II. Nitration of acetyloleanolic acid (**I**) with fuming HNO_3 in AcOH and methylation (CH_2N_2) of the product affords *Me nitroacetyloleanolate* (**II**), decomp. 228°, $[\alpha]_D^{18}$ +98·5°. This when boiled with Zn dust and AcOH is converted into a neutral product separated by MeOH into ketoacetyloleanolactone (**III**) decomp. 317°, $[\alpha]_D^{24}$ +116·5°, *Me* iso*ketoacetyldihydro-oleanolate* (**IV**), m.p. 261—263°, $[\alpha]_D^{21}$ +6·4°, and Me ketoacetyldihydro-oleanolate (**V**), m.p. 198—199°, $[\alpha]_D^{24}$ −12·0°. (**III**) does not contain OMe, does not give an oxime or semicarbazone, has an absorption max. at 273 mμ., and is hydrolysed exclusively to keto-oleanololactone (**VI**), decomp. 322°, $[\alpha]_D^{24}$ +118·4°. (**IV**) contains 1 OMe, and has an absorption max. at 264 mμ.; on hydrolysis it affords solely *Me* iso*ketodihydro-oleanolate*, m.p. 220—221°. The absorption curve of (**V**) has a max. at 286 mμ. The Röntgen spectra of (**IV**) and (**V**) are distinct so that (**IV**) and (**V**) must be regarded as isomerides. Hydrolysis of (**V**) gives Me ketodihydro-oleanolate, m.p. 202—203°. Oxidation (CrO_3) of (**VI**) gives *keto-oleanonolactone*, m.p. 276—279°, $[\alpha]_D^{22}$ +155° (*oxime*, decomp. 276—277°; absorption max. at 272 mμ.). The changes recorded are in harmony with the constitution (*A*) for oleanolic acid. M.p. etc. are corr. and [α] are in $CHCl_3$.



(*A*).

III. Fuming HNO_3 in AcOH converts (**I**) into *nitroacetyloleanolic acid* (**VII**), decomp. 221—222°, $[\alpha]_D^{23}$ +95·5° in $CHCl_3$, hydrolysed by 5% KOH–MeOH to *nitro-oleanolic acid*, decomp. 229—230°, and methylated by CH_2N_2 to (**II**). (**VII**) is transformed by Zn dust and AcOH into neutral and acid products. The former are separated by MeOH into α- (**VIII**), decomp. 314°, and *β-ketoacetyloleanololactone* (**IX**), decomp. 286—288°, $[\alpha]_D^{17}$ +9·4° in $CHCl_3$. (**VIII**) and (**IX**) are distinguished from one another by the Röntgen diagrams. Under the influence of 10% KOH–MeOH (**VIII**) only loses Ac whereas (**IX**) is converted into *ketohydroxydihydro-oleanolic acid*, decomp. 304°. Probably (**VIII**) is a γ- and (**IX**) is a δ-lactone. The physical properties and certain derivatives of the so-called "ketoacetyl-lactone" obtained by oxidising (**I**) with CrO_3 agree completely with those of (**IX**). The acidic product is ketoacetyldihydro-oleanolic acid. H. W.

Position of the carboxyl group in oleanolic and related acids. P. Bilham and G. A. R. Kon (*Nature*, 1941, **147**, 745).—Evidence that the CO_2H is in one of the terminal rings is discussed. L. S. T.

Constituents of the branches of *Akebia quinata*, Decne. R. Kawaguchi and K. W. Kim (*J. Pharm. Soc. Japan*, 1940, **60**, 236).—"Akebigenin," obtained by hydrolysis of akebin, is a mixture of hederagenin and oleanolic acid. H. W.

Constituents of "senso." XI. Constitution of acetyl-ψ-deacetylbufotalin. S. Ohno (*J. Pharm. Soc. Japan*, 1940, **60**, 226—230; cf. A., 1939, II, 382, 438).—Acetyl-ψ-deacetylbufotalin (**I**) is oxidised by $KMnO_4$ to *ψ-ætiocholanic acid*, m.p. 180—183°, which does not give a cryst. phenacyl ester. The presence of a *tert.* OH at $C_{(14)}$ in it is established by the production of a lactone under the influence of HCl–EtOH. In the sterol nucleus of (**I**) there remains OH which cannot be acylated. To elucidate its nature the nuclear C_{17} ketone (*loc. cit.*) is oxidised by KOBr in alkaline solution, whereby little acid is produced and the sterol nucleus appears to be altered, by SeO_2 in AcOH, whereby an *o*-diketone is formed in small amount, and by CrO_3 in warm AcOH, giving a neutral substance, $C_{18}H_{28}O_4$, sol. in warm 2% $NaHCO_3$, and a dicarboxylic acid which readily loses CO_2 to yield a monocarboxylic acid. This partial decarboxylation is completed and lactonisation occurs during distillation in a high vac. The *lactone* (**II**) in C_5H_5N affords a *p-nitrobenzoate*, so that OH at $C_{(3)}$ is not involved in lactone formation and the *tert.* OH at β-$C_{(14)}$ is certainly not adapted thereto. Probably the active OH is at $C_{(9)}$ and *trans* to OH at $C_{(14)}$. This is shown by conversion of (**II**) by AcOH–HBr followed successively by 20% KOAc–EtOH and Ac_2O into a *deoxyacetyllactone*, $C_{18}H_{26}O_5$·$C_2H_4O_2$, which immediately decolorises $KMnO_4$. This is ozonised in $CHCl_3$ to a little of a neutral substance, an acid (**III**) which gives an orange-red colour with $FeCl_3$, but no $H_2C_2O_4$. (**III**) gives a distinct diazo-reaction, and yields a non-cryst. Me ester and a *semicarbazone*, $C_{21}H_{32}O_6$·CH_3ON_3, m.p. >280°, which does not give the diazo-change. (**III**) is therefore a β-CO-acid. It follows therefore that a *tert.* non-acylable OH is at $C_{(9)}$ and forms a link of the β-CO-lactone. Formulæ are suggested. H. W.

Constituents of *Zyzyphus vulgaris*, Lamark, var. *spinosus*, Bunge. II. Betulic acid. R. Kawaguchi and K. W. Kim (*J. Pharm. Soc. Japan*, 1940, **60**, 235—236).—Betulonic acid,

m.p. 253°, obtained by the oxidation of betulic acid, gives a *semicarbazone*, m.p. 282—283°. It is reduced catalytically to *dihydrobetulonic acid*, m.p. 256—257°, shown by comparison of its *semicarbazone*, m.p. 284—285°, to be identical with the acid obtained by oxidation of dihydrobetulin and dihydrobetulic acid. H. W.

Substitution reactions of dehydroabietic acid. II. W. P. Campbell and M. Morgana (*J. Amer. Chem. Soc.*, 1941, **63**, 1838—1843; cf. A., 1939, II, 30).—6-Sulphodehydroabietic acid (**I**) (modified prep.; 78% yield; cf. *loc. cit.*), $+3H_2O$, m.p. (immediate) 215° (evolution of H_2O), resolidifies, decomp. 227°, and Br or Br–NaBr in H_2O at 100° give 92% of 6-*bromodehydroabietic acid* (**II**), m.p. 200—202°, $[\alpha]_D^{25}$ +81° in EtOH (*Me* ester, m.p. 140·5—141°, $[\alpha]_D^{25}$ +71° in $COMe_2$), also obtained (impure acid, pure ester) from dehydroabietic acid by Br–CCl_4 at 60°. The structure of these acids is proved by conversion of (**I**) by 12% aq. NaOH–N_2 at 290° and then CH_2N_2–Et_2O into the known Me 6-hydroxydehydroabietate (27—44%), m.p. 158—161·5°. With conc. aq. NH_3 and CuBr at 200°, (**II**) gives 42% of 6-aminodehydroabietic acid (**III**), m.p. 211—214°, isolated (59%) as cryst. hydrochloride. Me 6 : 8-dinitrodehydroabietate (**IV**) (orientation rendered very probable by reactions given below) and boiling H_2S–NH_3–H_2O–MeOH give 91% of *Me* 8-*nitro*-6-*aminodehydroabietate* (**V**), m.p. 239—242°, $[\alpha]_D^{25}$ +105° in $COMe_2$ (impure hydrochloride, m.p. 247—248·5°; NN-*Ac*$_2$ derivative, m.p. 203·5—206°, $[\alpha]_D^{25}$ +97° in $COMe_2$). Reduction of the 6 : 8-$(NO_2)_2$-acid by Na_2S–NH_4Cl–aq. EtOH gives 11% of 8-*nitro*-6-*aminodehydroabietic acid* (**VI**), m.p. 285·5—286° (decomp.), $[\alpha]_D^{25}$ +117° in $COMe_2$ [isolated (22%) as hydrochloride; Me ester = (**V**)]. H_2SO_4–HNO_3 and (**III**) at <0° give a moderate yield of (**VI**) [m.p. 282·5—283° (decomp.); Me ester = (**V**), m.p. 241—243°]. Diazotisation (H_2SO_4–$NaNO_2$–H_3PO_4) of (**V**) and digestion of the diazonium salt in EtOH with or without Zn powder gives 40% of *Me* 8-*nitrodehydroabietate*, m.p. 194—195°, $[\alpha]_D^{25}$ +29° in $COMe_2$, and thence (H_2SO_4–HNO_3; 0°) (**IV**). With H_2SO_4–HNO_3, in yields varying according to the conditions, (**I**) gives 8-nitro-6-dehydroabietic acid (up to 81%) (Me$_2$ ester, m.p. 243·5—244°; cf. Hasselstrom *et al.*, A., 1941, II, 143) and (by way of 6-nitrodehydroabietic acid) 3—22% of 6 : 8-$(NO_2)_2$-acid. M.p. are corr. [N. B. Eddy] β-Dimethylaminodehydroabietinol Me ether hydrochloride has no analgesic and little toxic effect. R. S. C.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Luminescent oxidation of luciferin. P. N. Chakravorty and R. Ballentine (*J. Amer. Chem. Soc.*, 1941, **63**, 2030—2031).—Purified extracts of *Cypridina* luciferin (**I**) contain only C, H, and O. CO·CH_2·OH is present. With NH_2OH,AcOH it gives a micro-cryst. ppt., which is inactive towards luciferase (**II**) but is reactivated by acid hydrolysis. Luminescent oxidation involves R·CO·CH_2·OH → (**II**) RCO_2H (irreversible). The luminescent activity is restored by the reactions, RCO_2H → ($SOCl_2$) RCOCl → (CH_2N_2) RCO·CHN_2 → dil. H_2SO_4) RCO·CH_2·OH. Oxidation of the quinol nucleus is the reversible oxidation of (**I**) by O_2. R. S. C.

Action of organic nitrogen bases on cornstalk lignin. E. Fisher and R. S. Bower (*J. Amer. Chem. Soc.*, 1941, **63**, 1881—1883).—The amounts of cornstalk tissues or the lignin isolated therefrom by 72% H_2SO_4 which is dissolved by aq. or anhyd. mono-, di-, or tri-ethanolamine, morpholine–EtOH, or NEt_3 increase with the strength of the base. Compound formation is probable. R. S. C.

V.—HETEROCYCLIC.

Condensation of furan derivatives. XIII. Displacement of one aldehyde by another from carbonyl-ethylene compounds. V. V. Tschelincev and E. K. Nikitin (*J. Gen. Chem. Russ.*, 1940, **10**, 1453—1456).—The velocities of reaction of $COMe_2$ in aq. KOH with salicylaldehyde, vanillin, PhCHO, and furfuraldehyde are as 0·00125 : 0·00645 : 0·2 : 1. Each member of the series will displace the preceding ones from condensation with $COMe_2$. R. T.

Constitution of the condensation product of furfuraldehyde and aniline (Schiff's base). E. R. Riegel and (Miss) M. Hathaway (*J. Amer. Chem. Soc.*, 1941, **63**, 1835—1838).—The violet substance obtained from furfuraldehyde (**I**), NH_2Ph, and NH_2Ph,HCl (Stenhouse *et al.*, *Annalen*, 1870, **156**, 199) is 2-di-(*p*-aminophenyl)methylfurfuraldehyde monohydrochloride, $+H_2O$ (**II**) (cf. Zincke *et al.*, A., 1906, i, 33), since it is quantitatively tetrazotised in 95% EtOH and then coupled with 9 products to give *dyes*. Similar results are recorded for products from (**I**) and other bases. A mechanism is proposed to account for formation of NH_2Ph and 3-hydroxy-1-phenylpyridinium halide from (**II**) by boiling AcOH or, less well, EtOH. The violet substance obtained (König, A., 1904, i, 449) differs from (**II**) and does not react with HNO_2. R. S. C.

Benzopyrone series. IV. Synthesis of karanjin. T. R. Seshadri and V. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 404—410).—Karanjic acid (**I**) is converted (MeOH–conc. H_2SO_4) into its *Me* ester, m.p. 105—106°, transformed by MeI and anhyd. K_2CO_3 in boiling $COMe_2$ but not by Me_2SO_4–NaOH into *Me* O-*methylkaranjate*, also obtained directly by the prolonged action of K_2CO_3 and MeI on (**I**) in boiling $COMe_2$. It is hydrolysed by 25% aq. NaOH to O-*methylkaranjic acid*, m.p. 148°, which with PCl_5 in CCl_4 gives the *chloride*, m.p. 72°. This is condensed with Et αγ-dimethoxysodioacetoacetate (**II**) in Et_2O and the product is hydrolysed to 4-*methoxy*-5-ω-*methoxyacetylcoumarone*, m.p. 87—88°, which was also obtained by the protracted action in boiling $COMe_2$ of MeI and K_2CO_3 on 4-hydroxy-5-ω-methoxyacetylcoumarone (**III**), obtained in 95% yield by the action of KOH–anhyd. MeOH on karanjin (**IV**); very little (**I**) is produced by this method. Gradual addition of AcCl to (**I**) in well-cooled C_5H_5N leads to *acetylkaranjic acid*; the non-cryst. *chloride* is condensed with (**II**) to (**III**), from which (**IV**) is obtained in good yield by the action of Bz_2O and NaOBz at 180°. H. W.

Condensation of α-substituted acetoacetates with phenols. III. Pechmann condensation of ethyl α-(βββ-trichloro-α-hydroxyethyl)acetoacetate. IV. Condensation of cresols and other less reactive phenols with ethyl α-(βββ-trichloro-α-hydroxyethyl)acetoacetate. D. R. Kulkarni, R. L. Alimchandani, and N. M. Shah (*J. Indian Chem. Soc.*, 1941, **18**, 113—119, 123—126).—III. m-$C_6H_4(OH)_2$, 1 : 2 : 3- and 1 : 3 : 5-$C_6H_3(OH)_3$, α-$C_{10}H_7$·OH, and 1 : 3 : 5-$C_6H_3Me(OH)_2$ with CCl_3·CH(OH)·CHAc·CO_2Et (**I**) and $POCl_3$ give good yields of 7-*hydroxy*-, m.p. 207—208° (decomp.) (**II**) (*Me*$_2$ *ether*, m.p. 154—155°; *Ac*$_2$, m.p. 149—150°, and *Bz* derivative, m.p. 169—170°), 7 : 8- (**III**), m.p. 223° (decomp.) (*Me*$_3$ *ether*, m.p. 139°; *Ac*$_3$ derivative, m.p. 181°), and 5 : 7-*dihydroxy*-, m.p. 216—217°, -4-*methyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin* (*Ac*$_3$ derivative, m.p. 147—148°), 4-*methyl*-3-βββ-*trichloro*-α-*hydroxyethyl*-1 : 2-α-*naphthapyrone*, m.p. 231—232° (*Ac* derivative, m.p. 207—208°), and 5-*hydroxy*-4 : 7-*dimethyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin*, m.p. 223—224° (decomp.), respectively. (**II**) and (**III**) are reduced (Zn + AcOH) to 7-*mono*-, m.p. 254—255° (decomp.) *Ac* derivative, m.p. 169—170°), and 7 : 8-*di*-*hydroxy*-4-*methyl*-3-β-*chlorovinylcoumarin*, m.p. 231—232° (decomp.), which with Me_2SO_4 and aq. KOH in $COMe_2$ at 100° yield 2 : 4-*di*-, m.p. 172—173° (*Ag* salt), and 2 : 3 : 4-*tri*-*methoxy*-β-*methyl*-α-(β-*chlorovinyl*)*cinnamic acid*, m.p. 125—126° (*Ag* salt). With H_2SO_4 or P_2O_5 as catalyst, m-$C_6H_4(OH)_2$ and 1 : 3 : 5-$C_6H_3(OH)_3$ condense with (**I**) as above, but α-$C_{10}H_7$·OH does not condense. 1 : 2 : 3-$C_6H_3(OH)_3$ and 1 : 3 : 5-$C_6H_3Me(OH)_2$ with P_2O_5 do not condense, and with H_2SO_4 give uncrystallisable products. $AlCl_3$ is unsatisfactory.

IV. PhOH, α-$C_{10}H_7$·OH, *p*-$C_6H_4(OH)_2$, and 1 : 2 : 4-COMe·$C_6H_3(OH)_2$ give no cryst. products with (**I**). (**I**) with *p*-cresol and H_2SO_4 at <0° yields 4 : 6-*dimethyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin*, m.p. 202—203° (*Me ether*, m.p. 207°). (**I**) and *o*- and *m*-cresol in cold EtOH with H_2SO_4 yield γγγ-*trichloro*-β-4-*hydroxy*-3-, m.p. 186—187° (*Ac* derivative, m.p. 75°; *semicarbazone*, m.p. 256—257°), and -2-*methylphenylpropyl Me ketone*, m.p. 208—209° (decomp.) (*Ac* derivative, m.p. 104—105°; *semicarbazone*, m.p. 214°). A. Li.

Colouring matters of the flavone series. VI. Constituents of *Zinnia elegans* (Jacq.); synthesis of apigenin glucoside. T. Nakaoki (*J. Pharm. Soc. Japan*, 1940, **60**, 190—191; cf. A., 1939, II, 441).—The flowers yield apigenin glucoside (~1%), m.p. 226—227° (from aq. C_5H_5N) (5 : 7 : 4′-trihydr-

oxyflavone-7-glucoside), identical with that obtained by synthesis through apigeninglucose tetra-acetate. A. T. P.

Synthesis of nobiletin (5 : 6 : 7 : 8 : 3′ : 4′-hexamethoxyflavone). Z. Horii (*J. Pharm. Soc. Japan*, 1940, **60**, 246—248).—2-Hydroxy- is oxidised by $K_2S_2O_8$ and NaOH to 2 : 5-*dihydroxy*-3 : 4 : 6-*trimethoxyacetophenone*, m.p. 125—126°, partly methylated (Me_2SO_4 and K_2CO_3 in $COMe_2$ at 50°) to 2-*hydroxy*-3 : 4 : 5 : 6-*tetramethoxyacetophenone*, b.p. 148°/7 mm., which with veratroyl chloride and C_5H_5N at 100° affords the *veratroyl* derivative, m.p. 118·5—119·5°. This is isomerised by $NaNH_2$ in PhMe at 100° to 2-*hydroxy*-3 : 4 : 5 : 6-*tetramethoxy*-ω-*veratroylacetophenone*, m.p. 113·5—114·5°, converted by NaOAc and glacial AcOH at 100° or by conc. H_2SO_4 at 0° into 5 : 6 : 7 : 8 : 3′ : 4′-hexamethoxyflavone (**I**), m.p. 136·5—137·5°, identical with nobiletin. (**I**) is transformed by boiling 30% HCl into 5-hydroxy-6 : 7 : 8 : 3′ : 4′-pentamethoxyflavone, m.p. 144—145°. It is demethylated by HI (*d* 1·7) at 140° and then converted by Ac_2O and C_5H_5N into hexa-acetoxy-, m.p. 230·5—231·5°, and by BzCl and C_5H_5N at 100° into hexabenzoyloxy-flavone, m.p. 244—245°. H. W.

Tetrahydrocannabinol homologues with marihuana activity. IX. R. Adams, S. Loewe, C. Jelinek, and H. Wolff. **X.** R. Adams, C. M. Smith, and S. Loewe. **XI.** R. Adams, C. K. Cain, and S. Loewe (*J. Amer. Chem. Soc.*, 1941, **63**, 1971—1973, 1973—1976, 1977—1978; cf. A., 1940, II, 379).—Relative marihuana potencies are denoted *P* below relative to the *n*-amyl derivative. M.p. are corr. IX. 5 : 1 : 3-$C_6H_3R(OH)_2$, Et 5-methyl*cyclo*hexanone-2-carboxylate (**I**) and $POCl_3$ in C_6H_6 give 6″-*hydroxy*-5′-*methyl*-4″-n-*propyl*-, m.p. 233—235°, -n-*butyl*-, m.p. 199—200°, -n-*hexyl*-, m.p. 173—174°, -n-*heptyl*-, m.p. 172—173°, and -n-*octyl*-, m.p. 165—167°, -3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyrone*, converted by MgMeI into 6″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-n-*propyl*-, m.p. 145—146°, b.p. 185°/2 mm. (*P* 0·40±0·08), -n-*butyl*-, b.p. 178—180°/1 mm. (*P* 0·37±0·12), -n-*amyl*- (**II**) (*P* 1·00), -n-*hexyl*-, b.p. 190—192°/1 mm. (*P* 1·82±0·18), -n-*heptyl*-, b.p. 225—228°/0·05 mm. (*P* 1·05±0·15), and -n-*octyl*-, b.p. 215—220°/0·01 mm. (*P* 0·66±0·12), -3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyran*. 6″-Hydroxy-2 : 2 : 5′ : 4″-tetramethyl-3′ : 4′ : 5′ : 6′-tetrahydro-3 : 4 : 5 : 6-dibenzpyran, has *P* <0·2. 5-n-*Octylresorcinol* has b.p. 164—168°/4 mm.

X. 6″-Hydroxy-5′-methyl-4″-*n*-amyl-3′ : 4′ : 5′ : 6′-tetrahydro-3 : 4 : 5 : 6-dibenzpyrone [modified prep. from (**I**) and olivetol (**III**) by $POCl_3$–C_6H_6] with MgEtBr or $MgPr^nBr$ gives 6″-*hydroxy*-5′-*methyl*-3 : 3-*diethyl*-, b.p. 185—195°/0·02 mm. (*P* 0·12±0·024), and -*di*-n-*propyl*-, b.p. 200—204°/2 mm. (*P* 0·04±0·01), -4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzpyran*. Et 4- or 6-methyl*cyclo*hexanone-2-carboxylate, (**III**), and $POCl_3$ in C_6H_6 give 6″-*hydroxy*-4′-, m.p. 169—169·5°, and -6′-*methyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyrone*, m.p. 194—194·5°, and thence 6″-*hydroxy*-2 : 2 : 4′-m.p. 72—73° (*P* 0·137±0·01), and -2 : 2 : 6′-*trimethyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyran*, b.p. 181—185°/0·5—1·0 mm. (*P* 0·25±0·05). Et *cyclo*hexanone-2-carboxylate and (**III**) similarly give 6″-*hydroxy*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyrone*, m.p. 183—183·5°, and thence 6″-*hydroxy*-2 : 2-*dimethyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyran*, b.p. 175—180°/0·02 mm. (*P* 0·126±0·05). Condensation of pulegone and orcinol (**IV**) or olivetol gives compounds, as (**II**) but impure (absorption spectra), [α] depending on the amount of $POCl_3$ used; that corresponding with (**II**) has *P* 1·04±0·37 (cf. Ghosh *et al.*, A., 1941, II, 145).

XI. $CH_2Ac{\cdot}CO_2Et$ (**V**) and (**IV**) in 85% H_3PO_4 give 5-hydroxy-4 : 7-dimethylcoumarin, m.p. 258—259° (lit. 250°). (**V**), (**III**), and $POCl_3$ in boiling C_6H_6 give 5-*hydroxy*-4-*methyl*-7-n-*amylcoumarin*, m.p. 178—179°, converted by MgMeI in Bu_2O at 90° into 5-*hydroxy*-2 : 2 : 4-*trimethyl*-7-n-*amyl*-1 : 2-*benzpyran*, b.p. 140—142°/0·02 mm. (*P* 0·033±0·01). $CHBu^nAc{\cdot}CO_2Et$ with (**IV**) or (**III**) and $POCl_3$ in C_6H_6 at room temp. give 5-*hydroxy*-4 : 7-*dimethyl*-3-n-*butylcoumarin* (62%), m.p. 191—195° (and a trace of ? 7-hydroxy-4 : 5-dimethyl-3-*n*-butylcoumarin, m.p. 158—159°), and 5-*hydroxy*-4-*methyl*-3-n-*butyl*-7-n-*amylcoumarin* (66%), m.p. 140·5—141°, respectively, and from the latter 5-*hydroxy*-2 : 2 : 4-*trimethyl*-3-n-*butyl*-7-n-*amyl*-1 : 2-*benzpyran*, b.p. 176—177°/0·05 mm. (*P* 0·04±0·01). R. S. C.

Photochemistry of fluorescein dyes.—See A., 1941, I, 423.

2 : 6-Dichlorodiphenylene dioxide. S. Uyeo (*Bull. Chem. Soc. Japan*, 1941, **16**, 177—179).—2 : 6-Dinitrodiphenylene dioxide, m.p. 262°, and H_2–Pd–C in AcOH give quantitatively the $(NH_2)_2$-compound, m.p. 249°, which by a Sandmeyer reaction yields 2 : 6-*dichlorodiphenylene dioxide* (**I**), m.p. 207°. The dipole moment [Higasi], 0·62, of (**I**) indicates a folded structure and is < that (0·64) of diphenylene dioxide. R. S. C.

Aluminium chloride, a new reagent for the condensation of β-ketonic esters with phenols. V. Condensation of substituted resacetophenones with ethyl acetoacetate. C. V. Deliwala and N. M. Shah (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 352—358; cf. A., 1938, II, 152).—5-Ethylresacetophenone condenses with $CH_2Ac{\cdot}CO_2Et$ in dry $PhNO_2$ containing $AlCl_3$ at ~115° to 5-hydroxy-6-acetyl-4-methyl-8-ethylcoumarin, m.p. 168—169° (cf. Desai *et al.*, A., 1939, II, 173), reduced (Clemmensen) to 5-hydroxy-4-methyl-6 : 8-diethylcoumarin, m.p. 171°, and acetylated (Kostanecki) to 3′-acetyl-4 : 2′-dimethyl-6′-ethyl-7′ : 8′ : 6 : 5-chromono-α-pyrone, m.p. 173°. Condensation cannot be effected by conc. H_2SO_4. 5-Bromoresacetophenone and $CH_2Ac{\cdot}CO_2Et$ in dry $PhNO_2$ containing $AlCl_3$ at 115—120° and subsequently at 130° give 8-*bromo*-5-*hydroxy*-6-*acetyl*-4-*methylcoumarin*, m.p. 208—210° (*acetate*, m.p. 150°; *oxime*, m.p. >250°), which gives a cherry-red colour with $FeCl_3$ and a non-fluorescent, yellow solution in alkali; it is transformed by Ac_2O and NaOAc at 170—180° into 6′-*bromo*-4 : 2′-*dimethylchromono*-7′ : 8′-6 : 5-α-*pyrone*, m.p. 240—241°. Condensation does not succeed in the presence of $POCl_3$ or H_2SO_4. 5-Nitro-, 5-benzyl-, and ω-methoxy-resacetophenone, Me β-resacetophenonecarboxylate, 4 : 6- and 2 : 4-diacetylresorcinol do not condense or yield tarry material. 4 : 1-$C_{10}H_6Ac{\cdot}OH$ and $CH_2Ac{\cdot}CO_2Et$ afford 4-methyl-1 : 2-α-naphthapyrone, m.p. 172°, obtained also from 4 : 1-$COEt{\cdot}C_{10}H_6{\cdot}OH$. H. W.

Sulphur. XVII. Synthesis of sulphathiophen, 2-sulphanilamidothiophen. R. W. Bost and C. F. Starnes (*J. Amer. Chem. Soc.*, 1941, **63**, 1885—1886; cf. A., 1940, II, 296).—2-Aminothiophen stannichloride (modified prep.) and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ give 2-N^4-*acetylsulphanilamido*-, m.p. 196°, and thence (10·4% H_2SO_4) 2-*sulphanilamido-thiophen*, m.p. 156·5—157·5°. R. S. C.

Phenylhydantoins. H. R. Henze and L. M. Long (*J. Amer. Chem. Soc.*, 1941, **63**, 1936—1938).—$COPh{\cdot}[CH_2]_3{\cdot}Ph$, $(NH_4)_2CO_3$, and KCN in 50% EtOH at 60° give 5-*phenyl*-5-β-*phenylethylhydantoin* (67%), m.p. 201° (Na salt, strong anticonvulsant), which with Na and then Me_2SO_4 in abs. EtOH gives 5-*phenyl*-5-β-*phenylethyl*-3-*methylhydantoin* (not anticonvulsant), m.p. 144°. $COPh{\cdot}C_{11}H_{23}$-*n*, $(NH_4)_2CO_3$, and KCN in NH_2Ac at 110° give 5-*phenyl*-5-n-*undecylhydantoin*, m.p. 125°. $COR{\cdot}CH{:}CHPh$, $(NH_4)_2CO_3$, and KCN in H_2O at 59° or 60° give 5-styryl-5-methyl-, m.p. 222—223° [lit. 217° (decomp.)], -5-*ethyl*-, m.p. 214°, -5-n-*propyl*-, m.p. 171—174°, and -5-n-*butyl-hydantoin*, m.p. 125—130°. 5-Phenylhydantoin and Br–AcOH give the 5-Br-derivative, m.p. 210—215°, which with COPhMe at ~70° gives 5-*phenyl*-5-*phenacylhydantoin*, m.p. 221°. With KCN and $(NH_4)_2CO_3$ in $OH{\cdot}[CH_2]_3{\cdot}OH$ at 110° this gives 5 : 5′-*methylenebis*-5-*phenylhydantoin*, m.p. 358° (decomp.). M.p. are corr. R. S. C.

Reactions of 2-aminopyridine with diketones. I. Reaction of 2-aminopyridine with benzil. P. G. Sokov (*J. Gen. Chem. Russ.*, 1940, **10**, 1457—1461).—2-Aminopyridine (**I**) and benzil (60—90 min. at 200—225°) yield α-2-*pyridylaminodiphenylacetic acid*, melting with decomp. at 156°, giving 2-*pyridylaminodiphenylmethane* [2-*benzhydrylaminopyridine*], m.p. 104—105° (*hydrochloride*, m.p. 190—191°; *hydrobromide*, m.p. 195—196°; *picrate*, m.p. 183—184°), also prepared from (**I**) and $CHPh_2Br$, or from (**I**) and $OH{\cdot}CPh_2{\cdot}CO_2H$. R. T.

Preparation of sulphapyridine. B. Bobrański and I. M. Eker (*J. Appl. Chem. Russ.*, 1940, **13**, 1637—1641).—A 1 : 2 mixture of *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and 2-aminopyridine heated for 1 hr. at 100° gives acetylsulphapyridine (64% yield). This, heated for 1 hr. at 58—62° with 15% HCl, gives sulphapyridine in 75% yield. R. T.

Synthesis of 3-ethylpyridine. T. Ikeda and C. Ashizawa (*J. Pharm. Soc. Japan*, 1941, **61**, 42—45).—Nicotinoyl chloride hydrochloride and CH_2N_2 in dry Et_2O give a dark red resin, converted by warm AcOH into 3-acetoxyacetylpyridine, m.p. 83—84°, in very poor yield. 3-Acetylpyridine (hydrochloride, m.p. 174—177°; *semicarbazone*, m.p. 207—208°),

from Et nicotinate and EtOAc followed by boiling 10% HCl, is reduced by N_2H_4,H_2O at 120—130° followed by KOH at 150° to 3-ethylpyridine (picrate, m.p. 125—128°) and the *azine*, $C_{14}H_{14}N_4$, m.p. 108—109° (*dipicrate*, decomp. 241°). N_2H_4 *picrate*, decomp. 190°, is incidentally described. H. W.

Preparation of indole. F. T. Tyson (*J. Amer. Chem. Soc.*, 1941, **63**, 2024—2025).—Indole is best (46%) obtained from *o*-$C_6H_4Me{\cdot}NH{\cdot}CHO$ by KOBu$^\gamma$ (1·5 mol.) at 350—360°. Other proportions or use of KNH_2–NH_3, KOMe, or KOEt is less satisfactory and Na salts are useless. R. S. C.

7-Bromo-5-iodoisatin and 3-bromo-5-iodo-2-aminobenzoic acid. W. C. Sumpter (*J. Amer. Chem. Soc.*, 1941, **63**, 2027—2028).—5-Iodoisatin and Br in boiling EtOH give 7-*bromo*-5-*iodoisatin*, m.p. 247—248°, which with 3% H_2O_2 in alkali gives 3-*bromo*-5-*iodo*-2-*aminobenzoic acid*, m.p. 226—227°, also obtained from 2 : 5 : 1-$NH_2{\cdot}C_6H_3I{\cdot}CO_2H$ by Br–EtOH. 5-Bromoisatin is unaffected by ICl. R. S. C.

Preparation of 1-acyl-1 : 2-dihydroquinoline-2-nitriles and their hydrolysis to aldehydes. J. M. Grosheintz and H. O. L. Fischer (*J. Amer. Chem. Soc.*, 1941, **63**, 2021—2022).—RCOCl, HCN, and quinoline (1 : 1 : 2 mols.) in C_6H_6 at −5° and later room temp. (16 hr.) give usually 64—96% of 2-*cyano*-1-*acetyl*-, m.p. 96—97°, -*propionyl*- (10%), m.p. 49—50°, -benzoyl-, m.p. 154—155°, -cinnamoyl-, m.p. 154—155°, -n-, m.p. 97·5—98°, and -iso-*butyryl*-, m.p. 129—129·5°, -iso*valeryl*-, m.p. 90—90·5°, -o-, m.p. 164—164·5°, and -p-*anisoyl*-, m.p. 120·5—121·5°, -o-, m.p. 165—166°, -m-, m.p. 116—119°, and -p-*chlorobenzoyl*-, m.p. 140—143°, -1 : 2-*dihydroquinoline*, which yield 90% of RCHO and quinoline-2-carboxylic acid when the acid (5—10N-H_2SO_4) solution is distilled in steam. For direct prep. of aldehydes from acids, isolation of RCOCl and the nitrile is unnecessary. $CHR{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$-*p* are reported in which R = Me, m.p. 127·5—128°, Et, m.p. 128—129°, Pr$^\alpha$, m.p. 90—91°, Pr$^\beta$, m.p. 131·5—132°, *o*-, m.p. 208°, and *p*-$OMe{\cdot}C_6H_4$, m.p. 162°, *o*-, m.p. 247—248°, *m*-, m.p. 220°, and *p*-C_6H_4Cl, m.p. 219°, $CHPh{:}CH$, m.p. 169·5—170·5°, and Ph, m.p. 193—194°, and $CHR{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$-2 : 4 in which R = Bu$^\alpha$, m.p. 96—98°, and Bu$^\beta$, m.p. 122—123°. R. S. C.

Condensation of ethylaniline with acetylene in presence of $HgCl_2$. I. F. Kriuk (*J. Gen. Chem. Russ.*, 1940, **10**, 1507—1509).—A solution of NHPhEt and $HgCl_2$ in EtOH, saturated with C_2H_2, yields indole (**I**) and quinaldine (**II**) by the reactions: $NHPhEt + C_2H_2 \rightarrow NPhEt{\cdot}CH{:}CH_2$ (**III**); 2(**III**) → $NPhEt{\cdot}CHMe{\cdot}CH{:}CH{\cdot}NPhEt \rightarrow$ (**I**) + (**II**) + C_2H_6 + $2H_2$. R. T.

Acridine derivatives. VI. S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1941, **18**, 25—28; cf. A., 1939, II, 364).—The hydrochlorides, m.p. 187° and 257°, respectively, of 4 : 2 : 1- or 5 : 2 : 1-$NH_2{\cdot}C_6H_3Cl{\cdot}CO_2H$, and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$–aq. Na_2CO_3 afford 2-*chloro*-4, m.p. 142°, and -5-(p-*acetamidobenzene*)*sulphonamidobenzoic acid*, m.p. 263°, converted by *p*-$NH_2{\cdot}C_6H_4{\cdot}OMe$–$K_2CO_3$–$C_5H_{11}{\cdot}OH$–Cu powder into 4-, m.p. 158—160°, and 5-(p-*acetamidobenzene*)*sulphonamido*-4′-*methoxydiphenylamine*-2-*carboxylic acid*, m.p. 218—220°, and thence by $POCl_3$ at 100° (bath) into 5-*chloro*-2-, m.p. 245—247° (decomp.), and -3-(4′-*acetamidobenzene*)*sulphonamido*-7-*methoxyacridine* (**I**), m.p. 243—244° (decomp.) (hydrolysed by aq. HCl–EtOH to the corresponding 4′-NH_2-compound, m.p. ~180°). Equimols. of 2 : 5-dichloro-7-methoxyacridine and *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NEt_2$, or *p*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$ in PhOH at 110—120°, 120°, or 150—160°, respectively, give N^4-(2-*chloro*-7-*methoxy*)*acridylaminobenzene*-*sulphon*-*amide*, m.p. 286°, -*diethylamide*, m.p. 175° (hydrochloride, m.p. 260—261°), or -*acetamide*, m.p. 248—250°. Similarly prepared are N^4-(7-*methoxy*)*acridylaminobenzene*-*sulphon*-*diethylamide*, m.p. 263—264°, and -*acetamide*, m.p. 143—145°. A. T. P.

Acridine synthesis and reactions. II. Synthesis of proflavine from *m*-phenylenediamine and its derivatives (continued). A. Albert (*J.C.S.*, 1941, 484—487; cf. A., 1941, II, 148).—By interrupting the reaction between *m*-$C_6H_4(NH_2)_2$ (*picrate*, m.p. 184°) and glycerol with $H_2C_2O_4$ or HCO_2H at 140° after 10 min. and neutralising (aq. NH_3) the cooled, diluted melt, 3 : 3′-*diamino*-N-*formyldiphenylamine* (**I**), m.p. 138·5°, N-2′ : 4′-*diamino*-α-*hydroxybenzyl*-m-*phenylenediamine* (**II**), m.p. ~120° (decomp.), and *bis*-2 : 4 : 2′ : 4′-*tetra*-*aminobenzhydryl ether* (**III**), m.p. ~295° (decomp.), are obtained. $NHPh{\cdot}C_6H_4{\cdot}NO_2$-*m*, $ZnCl_2$, and HCO_2H give 3-*nitro*-N-*formyldiphenylamine*, m.p. 77°, reduced to the 3-NH_2-compound, m.p. 131—132° (decomp.); 3 : 3′-*dinitro*-N-*formyldiphenylamine*, m.p. 145—146°, similarly prepared, is reduced to (**I**). By heating *m*-$C_6H_4(NH_2)_2$ with HCO_2H and H_3BO_3 in distilling PhMe, (**II**) is obtained and when this is warmed with HCl in glycerol, a 75% yield of proflavine (**IV**) is formed. $CO[C_6H_3(NH_2)_2$-2 : 4$]_2$ is reduced to 2 : 4 : 2′ : 4′-*tetra*-*aminobenzhydrol*, decomp. 200°, remelts 290°, which is formed when (**III**) is hydrolysed in 50% aq. $COMe_2$ with HCl. It is concluded that the dihydrochloride of (anhydro)-2 : 4 : 2′ : 4′-tetra-aminobenzhydrol is the immediate precursor of (**IV**). F. R. S.

5-4′-Diphenylyl-5-R-hydantoins and 4 : 4′-diphenylylenebis-5:5-R-hydantoins. H. R. Henze and L. M. Long (*J. Amer. Chem. Soc.*, 1941, **63**, 1941—1943).—*p*-$C_6H_4Ph{\cdot}COR$ and KCN in NH_2Ac at 110° give 71—90% of 5-4′-diphenylyl-5-*methyl*-, m.p. 295°, -5-*ethyl*-, m.p. 256°, -5-n-, m.p. 201·5—202·5°, and -5-iso-*propyl*-, m.p. 270—271°, -5-n-, m.p. 199·5°, and -5-iso-*butyl*-, m.p. 224—225°, -5-n-, m.p. 195—196·5°, and -5-iso-*amyl*-, m.p. 232—233°, -5-α-*methyl*-n-*butyl*-, m.p. 262°, -5-α-*ethyl*-n-*propyl*-, m.p. 249—250°, -5-phenyl-, m.p. 242°, and -5-n-*hexyl*-, m.p. 185—186·5°, -*hydantoin*. (*p*-$C_6H_4{\cdot}COR)_2$ gives similarly 53—80% of 4 : 4′-*diphenylene*-*bis*-5-5-*methyl*-, m.p. 360°, -*ethyl*-, m.p. 335°, -n-, m.p. 214°, and -iso-*propyl*-, m.p. 360°, -n-, m.p. 310°, and -iso-*butyl*-, m.p. 295°, -n-, m.p. 312°, and -iso-*amyl*-, m.p. 335°, -n-*hexyl*-, m.p. 284°, and -*phenyl*-, m.p. 282°, -*hydantoin*. M.p. are corr. R. S. C.

Hydantoins. I. A. Novelli (*Anal. Asoc. Quim. Argentina*, 1941, **29**, 83—87).—The following hydantoins, prepared from ketones, KCN, and $(NH_4)_2CO_3$ (cf. Bucherer and Steiner, A., 1934, 1231), are described: 5 : 5-o-*diphenylene*-, decomp. 308—310°, 5 : 5-o-*phenylenetrimethylene*-, m.p. 237·5—239·5° (from α-tetralone), 5 : 5-2′-*methyl*-5′-iso*propyl*cyclo*penta*-*methylene*-, m.p. 217—219°, 5-3′-*phenanthryl*-5-*methyl*-, m.p. 232—235°, 5-2′-*phenanthryl*-5-*ethyl*-, m.p. 315—317°. F. R. G.

Synthesis of *N*-disubstituted 5-phenylethyl-5-aminomethylhydantoins. H. R. Henze and C. B. Holder (*J. Amer. Chem. Soc.*, 1941, **63**, 1943—1945).—α-*Chloro*-δ-*phenylbutan*-β-ol, m.p. 46—47°, b.p. 112—114°/4 mm., and CrO_3 give $Cl{\cdot}[CH_2]_2{\cdot}COPh$, m.p. 40—41° (lit. 84—85°), b.p. 110·5—111·5°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 147·2—147·7°), which with $NHMe_2$,HCl and Na_2CO_3 in aq. $COMe_2$ at <0° or NHR_2 (2 equivs.) in Et_2O or C_6H_6 at 0° gives α-*dimethyl*-, b.p. 106—107°/3·5 mm. (*picrate*, m.p. 118—119°), -*ethyl*-, b.p. 119°/4 mm. (*picrate*, m.p. 104·5—105·5°, -n-*propyl*-, b.p. 136—138°/4 mm. (*picrate*, m.p. 116·5—117·5°), -n-*butyl*-, b.p. 159—160°/5·5 mm. (*picrate*, m.p. 99—100°), and -iso-*amyl*-, b.p. 161—163°/4 mm. (*picrate*, an oil), -*amino*-δ-*phenylbutan*-β-*one* and α-*morpholino*-δ-*phenylbutan*-β-*one*, m.p. 23—24°, b.p. 180—181°/7 mm. (*picrate*, m.p. 136·3—137·3°). With KCN and $(NH_4)_2CO_3$ in 50—65% EtOH at 58—60° these give 5-β-*phenylethyl*-5-*dimethyl*-, m.p. 232·3—233·3°, -*ethyl*-, m.p. 203·3—205·3°, -n-*propyl*-, m.p. 196·5—197·5°, -n-*butyl*-, m.p. 161—163°, and -iso*amyl*-, m.p. 124·7—127·2°, -*aminohydantoin*. 5-β-*Phenylethyl*-5-NN-*phenylethylamino*-, m.p. 176—177·5°, and -5-*morpholino*-*hydantoin*, m.p. 222—223°, are also prepared. M.p. are corr. R. S. C.

Action of diazomethane on lactones and lignins. E. Y. Spencer and G. F. Wright (*J. Amer. Chem. Soc.*, 1941, **63**, 2017—2020).—The so-called phenolic OH content, determined by CH_2N_2, is not characteristic of native lignin as it depends on the method of extraction. *E.g.*, bound phenolic OH is present in Et_2O-sol. birch lignin extracted by Ac_2O; CH_2N_2 raises the OMe from 19·7 to 21·9%, but after hydrolysis by 10% alkali from 23·3 to 34% (some xylosazone is obtained after hydrolysis). Further, CH_2N_2 reacts with lactones; *e.g.*, valerolactone gives $OH{\cdot}[CH_2]_2{\cdot}CO_2Me$, identified as acetate, and coumarin gives *Me* 3-o-*anisylpyrazoline*-4-*carboxylate*, m.p. 94·5°. Lignin probably contains coumarin linkings since the N content is raised from 0 to nearly 1% by treatment with CH_2N_2. R. S. C.

Interaction of organic sulphur compounds with hydrogen peroxide. XXI. Mechanism of desulphurisation of thiopyrine to antipyrine by hydrogen peroxide. II. R. Kitamura and T. Ono (*J. Pharm. Soc. Japan*, 1941, **61**, 17—19; cf. A., 1939, II, 456).—5-Thiopyrine and H_2O_2 (2 mols.) in MeOH give a crude oily dioxide (**I**), converted by distillation into SO_2 and 1-*phenyl*-3-*methylpyrazole*, m.p. 34·5—35·5°, b.p.

143—145°/18 mm., also obtained from 5-chloro-1-phenyl-3-methylpyrazole by P–HI and oxidised by $KMnO_4$–KOH to 1-phenylpyrazole-3-carboxylic acid. 3-Thiopyrine similarly gives 1-*phenyl-5-methylpyrazole*, b.p. 140—143°/20 mm., oxidised to 1-phenylpyrazole-5-carboxylic acid. The reaction mechanism is discussed. R. S. C.

Reaction between organic sulphur compounds and hydrogen peroxide. XXII. Mechanism of the desulphurisation of thiopyrine (→ antipyrine) by hydrogen peroxide. III. Synthesis of tetrabromothiopyrine dioxide and the consideration of the mechanism of desulphurisation. R. Kitamura (*J. Pharm. Soc. Japan*, 1941, **61**, 39—42).—A study of the behaviour of thiopyrine (**I**) towards H_2O_2 followed by Br and towards Br alone or in presence of HBr in aq. and non-aq. medium leads to the following conclusions. (**I**) and its homologues are converted by H_2O_2 into a dioxide (**II**) and then a trioxide (**III**) from which desulphurisation occurs. Desulphurisation at the greatest rate occurs mainly from (**II**); little part is played by (**III**) and the change is rapidly completed. With compounds which react less readily a relatively greater amount of (**III**) is formed and this consequently has a more pronounced function in the desulphurisation. The first type of action is best shown by 1 : 2-diphenyl-3-methyl-5-thiopyrazole with the slowest oscillation and the second type by 1 : 2 : 3-trimethyl-5-pyrazole with its most rapid oscillation. With this compound the trioxide is the main initial material in desulphurisation and the process is therefore incomplete at room temp. (**I**), dithio-, di- and 3-thiopyrine resemble one another and are placed between the two extreme classes; nevertheless with these substances desulphurisation takes place mainly from the dioxide and is generally complete. (**I**) and its hypothetical monoxide are rapidly converted by H_2O_2 into the dioxide. H. W.

Oscillation state and reactivity. Constitution of antipyrine and related compounds. IX. Comparison of 1 : 2-diphenyl-3-methyl-5-thiopyrazole and analogous compounds. X. Products of the reaction of thiopyrine with bromine water. R. Kitamura. **XI. Derivatives of antipyrine.** R. Kitamura and G. Sunagawa (*J. Pharm. Soc. Japan*, 1941, **61**, 8—12, 12—14, 14—17; cf. A., 1941, II, 304).—IX. Relative rates of desulphurisation by H_2O_2–KOH are 1 : 2-*diphenyl-5-methyl-* (**I**) > 1-phenyl-2 : 3-dimethyl- > 1 : 2 : 3-trimethyl-5-thiopyrazole (**II**). 5-Keto-1 : 2-diphenyl-3-methylpyrazole (**III**) and $POCl_3$ give 5-*chloro*-1 : 2-*diphenyl-3-methylpyrazole chloride* (**IV**), m.p. 234—237°, converted by KSH into (**I**), m.p. 185—186°, b.p. 243—244°/0·01 mm., yellow and colourless *forms*. Aq. Cl_2 converts (**I**) into the *trioxide*, decomp. 263—265°, which is better obtained from (**IV**) by Na_2SO_3, is desulphurised faster than is (**I**), and is converted by 2N-KOH into (**III**). (**II**) also exists in yellow and colourless forms and with neutral H_2O_2 gives the trioxide (**V**), decomp. 274—276°, or later 5-keto-1 : 2 : 3-trimethylpyrazole (**VI**), also obtained from (**V**) by boiling KOH. The first step in desulphurisation of (**II**) by alkaline H_2O_2 is formation of the dioxide, which is mainly converted into (**V**) and thence (**VI**) and to a small extent yields (**VI**) directly. The results are explained by means of the oscillation theory.

X. 5-Keto-1-phenyl-2 : 3-dimethylpyrazole absorbs 7—8 Br in H_2O to give the *compound*, $\begin{matrix}NMe\cdot NPhBr\\ |\\ CMe{=}{=}CH\end{matrix}\!\!>\!C\cdot SBr(OBr)_2$, decomp. 112—113° (cf. Komata, *J. Chem. Soc. Japan*, 1938, **59**, 482). In warm H_2O or cold N-Na_2CO_3 or -KOH this gives Br and the trioxide, decomp. ~300°, and yields the Br quantitatively to 0·1N-KOH at 100° in 5 min. or at room temp. in 2 days.

XI. Antipyrine and NaOCl (2 mols.) in 2N-NaOH give 4-chloroantipyrine (**VII**), m.p. 126—127°, and an oil, converted by warm H_2O into (**VII**) (cf. Leulier, A., 1924, i, 875; Komata, *J. Chem. Soc. Japan*, 1937, **58**, 1305). With $POCl_3$, (**VII**) gives 4 : 5-dichloro-1-phenyl-3-methylpyrazole (**VIII**), m.p. 54—55°, and the *methochloride* (**IX**), decomp. 173—178° [yields (**VIII**)], thereof. With conc. aq. KSH, (**IX**) gives 1-phenyl-2 : 3-dimethyl-5-thiopyrazole, converted by H_2O_2–NaOH into (**VIII**). Na_2SO_3 and (**IX**) give 4-chloro-1-phenyl-2 : 3-dimethyl-5-thiopyrazole trioxide, rapidly converted into (**VIII**) by H_2O_2–NaOH or boiling KOH. R. S. C.

Pyrimidines. CLXXII. Hydrogenolysis of 4-iminobarbituric acid. J. C. Ambelang and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 1934—1935; cf. A., 1941, II, 270).—Hydrogenation (PtO_2; ~80°/2·5 atm.; H_2O) of 4-iminobarbituric acid causes fission of the $C_{(4)}$–N linking (giving uracil), which supports the structure assigned to toxoflavine I. 5 : 5-*Dichloro*-2 : 4-*diketo*-2-*ethoxyhexahydropyrimidine*, m.p. 230° (decomp.), is prepared by chlorination in abs. EtOH. R. S. C.

Polarisation in heterocyclic rings with aromatic character. XIV. Syntheses of pyrimidine and dipyrimidyl homologues. M. Yanai and T. Naito (*J. Pharm. Soc. Japan*, 1941, **61**, 46—53).—Et hexoylacetoacetate and NH_3 in cold Et_2O yield Et hexoylacetate (**I**), b.p. 127—130°/20 mm. (*Cu* compound, m.p. 107°), NH_2Ac, and hexoamide, m.p. 100°. (**I**), NaOEt, and $CS(NH_2)_2$ in boiling EtOH yield 6-*amyl*-2-*thiouracil*, m.p. 151—153°, transformed by 0·1N-KOH and 3% H_2O_2 at 20° into 6-*amyluracil*, m.p. 171—173°; this with $POCl_3$ at 120° affords 2 : 4-*dichloro*-6-*amylpyrimidine*, b.p. 130—135°/3 mm., which with H_2–Pd–$CaCO_3$ in MeOH gives 6-*amylpyrimidine*, b.p. 130—135° (bath)/0·05 mm. (*aurichloride*, m.p. 110—112°; *platinichloride*, decomp. 208°). *Valeroamidine hydrochloride* (corresponding *picrate*, m.p. 190°) and $CH_2Ac\cdot CO_2Et$ are converted by 10% KOH–EtOH at room temp. into 4-*hydroxy*-6-*methyl*-2-n-*butylpyrimidine* (**II**), m.p. 120°, transformed by boiling $POCl_3$ into 4-*chloro*- (**III**), b.p. 110—115° (bath)/3 mm., whence are derived 4-*amino*-6-*methyl*-2-n-*butylpyrimidine*, m.p. 97°, and 6-*methyl*-2-n-*butylpyrimidine*, b.p. 130—135° (bath)/5 mm. (*platinichloride*, m.p. 186°). *Et valeroylacetoacetate*, b.p. 115—118°/5 mm. (*Cu* salt, m.p. 55·5°), from $Bu^{\alpha}COCl$, $CH_2Ac\cdot CO_2Et$, and Mg turnings in C_6H_6 at 80—85°, is slowly transformed by boiling H_2O into valeroylacetone (*Cu* salt, m.p. 137°), which condenses with $CO(NH_2)_2$ and conc. HCl in abs. EtOH to *diuramidovaleroylacetone*, m.p. 144°, as main product. (**III**) is converted by Cu-bronze in boiling cumene into 6 : 6′-*dimethyl*-2 : 2′-*di*-n-*butyl*-4 : 4′-*dipyrimidyl*, b.p. 180—185° (bath)/0·01 mm. (*hydrochloride*, m.p. 247°). 4-Chloro-2-benzyl-6-methylpyrimidine and HI (*d* 1·7) at room temp. and then at 50° yield the 4-*I*-compound, m.p. 127°, transformed by Cu-bronze in boiling cumene into 2 : 2′-*dibenzyl*-6 : 6′-*dimethyl*-4 : 4′-*dipyrimidyl*, m.p. 199°. Cu-bronze converts 2-chloro-4-benzyl-6-methylpyrimidine in cumene, tetrahydronaphthalene, or without solvent into an unidentified *compound*, $C_{24}H_{20}N_4Cl_2$, m.p. 226°, and HI transforms it into 4-benzyl-6-methylpyrimidine. (**III**) and HI yield (**II**). 2 : 4-Dichloro- and HI (*d* 1·7) at room temp. afford *chloroiodo-*, m.p. 90°, and 2 : 4-*di-iodo-*, m.p. 161°, -6-*methylpyrimidine*. The last-named reacts with difficulty with Cu-bronze, giving a small proportion of *substance*, m.p. 185—189°, and appears to be unchanged by Na. H. W.

Pyrazine series. III. Amination of 2 : 5-dimethylpyrazine. Synthesis of 3-sulphanilamido-2 : 5-dimethylpyrazine. R. R. Joiner and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1941, **63**, 1929—1930; cf. A., 1940, II, 193).—2 : 5-Dimethylpyrazine and $NaNH_2$ in $NPhMe_2$ at 165° give 35% of the 3-NH_2-derivative, m.p. 111—112°, b.p. 119—122°/10 mm. (cf. Tschitschibabin *et al.*, A., 1931, 100), which with *p*-$NHAc\cdot C_6H_4\cdot SO_2Cl$ in C_5H_5N at <50° gives 3-N′-*acetylsulphanilamido-*, m.p. 238—239°, and thence (6N-HCl; 100°) 3-*sulphanilamido*-2 : 5-*dimethylpyrazine*, m.p. 227—228° (corr.). R. S. C.

Synthesis of substances of probable antimalarial action. I. Structure and pharmacological properties. II. Benzimidazole compounds with a γ-diethylaminopropyl group. V. A. Izmailski and A. M. Simonov (*J. Gen. Chem. Russ.*, 1940, **10**, 1580—1587, 1588—1599).—I. 3-*Amino*-4-*benzamidoanisole* (**I**), m.p. 200—200·5° (prepared by reduction of the corresponding 3-NO_2-compound), condenses with PhCHO to 3-*benzylideneamino*-4-*benzamidoanisole*, m.p. 96—97°. With HNO_2 (**I**) yields 1-*benzoyl*-5-*methoxy*-1 : 2 : 3-*benztriazole*, m.p. 116°. (**I**) with $NEt_2\cdot[CH_2]_3\cdot Cl$ (**II**) (2 hr. at 110—115°, then 3 hr. at 130—135°, then 10 hr. at 150—155°) gives 4-*benzamido*-3-(N-γ-*diethylaminopropyl*)*aminoanisole*, m.p. 143·5—144°, which had no antimalarial properties. 3-*Amino*-4-*benzenesulphonamidoanisole*, m.p. 116·5—117·5°, is prepared by reduction of the corresponding 3-NO_2-compound. Attempts to condense this compound with (**II**) were unsuccessful.

II. 3-Nitro-4-(*p*-toluenesulphonamido)anisole and (**II**) in EtOH, in presence of K_2CO_3 (12 hr. at the b.p.), yield 3-*nitro*-4-(p-*toluenesulphonyl*-γ-*diethylaminopropyl*)*aminoanisole*, m.p. 77·5—78°. This is dissolved in 90% H_2SO_4, and the solution is made neutral with aq. NH_3 after 12 hr., giving 3-*nitro*-4-(γ-*diethylaminopropyl*)*aminoanisole*, b.p. 191·5—193·5°/2·5 mm. (*picrate*, melting at 114—115°, to yield a chromo-isomeride, m.p. 126—127°), reduced by $SnCl_2$ in HCl to 3-*amino*-4-

(*γ-diethylaminopropyl*)*aminoanisole*, b.p. 196—198°/4 mm. This with Ac_2O in HCl (90 min. at the b.p.) yields 5-*methoxy*-2-*methyl*-1-(*γ-diethylaminopropyl*)*benziminazole* (**III**), b.p. 184—185°/2 mm. (*dipicrate*, m.p. 236°). 3-Amino-4-acetamidoanisole (**IV**) and PhCHO in EtOH yield 3-*benzylideneamino*-4-*acetamidoanisole*, m.p. 128—128·5°. (**IV**) and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ yield 2 : 4-*dinitro*-2′-*acetamido*-5-*methoxydiphenylamine*, m.p. 263·5°. (**IV**) condenses with (**II**) in EtOH (3 hr. at 110—115°, then 13 hr. at 135—140°) to 6-*methoxy*-2-*methyl*-1-(*γ-diethylaminopropyl*)*benziminazole* (**V**), b.p. 190·5—191·5°/2 mm. [*dipicrate*, m.p. 218·5—219° (decomp.)]. This with PhCHO (3—4 hr. at 200°) yields 6-*methoxy*-2-*styryl*-1-(*γ-diethylaminopropyl*)*benziminazole* (*dihydrochloride*, m.p. 234—236°). A solution of (**IV**) in AcOH–HCl, heated at the b.p. for 1 hr., yields 5(6)-*methoxy*-2-*methylbenziminazole*, m.p. 141·5—142·5° (*picrate*, m.p. 191·5—192·5°), which with (**II**) (3—4 hr. at 110—115°) gives a mixture of (**III**) and (**V**). None of the above-described products have any antimalarial action. R. T.

Polarisation in heterocyclic rings having aromatic character. XIII. Polarisation in pyrimidine rings. E. Ochiai and M. Yanai (*J. Pharm. Soc. Japan*, 1940, **60**, 192—199; cf. A., 1941, II, 149).—2-Aminopyrimidine and picryl chloride (**I**) in C_6H_6 give 4 : 6-*dinitropyrimidino*-(1′ : 2′-2 : 1)-*benziminazole*, m.p. 196° (decomp.), whereas 4-aminopyrimidine affords picramide and 4-hydroxypyrimidine. 2-Amino- or 2 : 4-diamino-6-methylpyrimidine and (**I**) give 2-*picramido*-6-*methyl*-, m.p. 166—167°, or 2-*picramido*-4-*amino*-6-*methyl*-*pyrimidine*, m.p. 195—196° [4-*acetate* (**II**), m.p. 235°], converted by boiling with PhOH–$PhNO_2$ into 4 : 6-*dinitro*-6′-*methyl*-, m.p. >300°, or 4 : 6-*dinitro*-4′-*amino*-6′-*methyl*-*pyrimidino*-(1′ : 2′-2 : 1)-*benziminazole*, m.p. >330° [*acetate*, m.p. 323—325°, by acetylation or from (**II**)], respectively. 6-Methylpyrimidine (**III**) and $NaNH_2$–Bu$^{\alpha}$Br give 6-amylpyrimidine, b.p. 105—130°/0·01 mm., 135—138°/0·03 mm. (*picrate*, m.p. 126—128°). (**III**) and CH_2PhCl–$NaNH_2$ afford 6-(*dibenzylmethyl*)*pyrimidine*, b.p. 105—110°/0·01 mm. (*hydrochloride*, m.p. 259—260°; *aurichloride*, m.p. 198—200°), and a *compound*, $C_{24}H_{22}N_4$, b.p. 189—190°/0·01 mm., m.p. 120° (*picrate*, m.p. 153—155°), probably formed from 2 mols. of 6-(β-phenylethyl)pyrimidine. 6-Styrylpyrimidine is hydrogenated (Pd) to 6-(*β-phenylethyl*)-*pyrimidine*, m.p. 27—30° (*picrate*, m.p. 123—125°). 4-Hydroxy-2-benzyl-6-methylpyrimidine and $POCl_3$ at 120—130° give the corresponding 4-*Cl*-compound, m.p. 81—83°, converted by Zn–H_2O into 2-*benzyl*-6-*methylpyrimidine*, m.p. 36—37°, b.p. 135—140°/5 mm. (*picrate*, m.p. 126°; *hydrochloride*, m.p. 175—176°). $CH_2Ac{\cdot}CO{\cdot}CH_2Ph$–$CO(NH_2)_2$–HCl–EtOH afford 2-*hydroxy*-6-*benzyl*-, m.p. 61—63° [and a *substance*, $C_{12}H_{12}ON_2$, +H_2O, m.p. 167—169°, converted by boiling H_2O or aq. EtOH into (**III**)], and ($POCl_3$) 2-*chloro*-6-*benzyl*-4-*methylpyrimidine*, m.p. 27—28°, b.p. 170—175°/4 mm., and thence (Zn–H_2O) 6-*benzyl*-4-*methylpyrimidine*, b.p. 140—145°/4 mm. (picrate, m.p. 148°; hydrobromide, m.p. 151—152°). A. T. P.

Quinoline derivatives. VI. D. Das-Gupta and T. N. Ghosh (*J. Indian Chem. Soc.*, 1941, **18**, 120—122).—$[CO_2Et{\cdot}CH(CO{\cdot}NHPh)]_2CO$ with *m*- and *p*-$C_6H_4Me{\cdot}NH_2$ at 160—170° yields αα′-m-, m.p. 206—207° (which does not condense with aldehydes in AcOH), and -p-*tolylcarbamyl*-*acetonedicarboxylic acid dianilide*, m.p. 222—223°, which could not be converted into C_5H_5N derivatives. 2 : 4-Dihydroxy-3-carbethoxy- with NH_2Ph at 170° yields 2 : 4-*dihydroxy*-3-*phenylcarbamyl*-6-*methylpyridine*, m.p. 279—280°, converted by conc. H_2SO_4 at 100° into 2 : 2′-*dihydroxy*-6-*methylpyridino*-3 : 4-(3′ : 4′)-*quinolinedisulphonic acid* (+H_2O), m.p. >300° (*picrate*, turns brown at 217°, black >300°; Ac derivative uncrystallisable), unaffected by aq. NaOAc or boiling conc. HCl. A. Li.

Diquinolyls. VII. Formation of 2 : 3′-diquinolyl by action of selenium on quinoline. K. Ueda (*J. Pharm. Soc. Japan*, 1940, **60**, 210).—Quinoline with Se at 280—300° yields 2 : 3′-diquinolyl. A. Li.

Di*iso*quinolyls. I. Synthesis of 4 : 4′-di*iso*quinolyl. K. Ueda (*J. Pharm. Soc. Japan*, 1940, **60**, 210).—4-Bromo*iso*quinoline with N_2H_4,H_2O in EtOH–KOH in presence of Pd–$CaCO_3$ yields 4 : 4′-di*iso*quinolyl, m.p. 149°. A. Li.

Metallic triazine complexes. F. G. Mann (*Nature*, 1941, **147**, 778—779).—A discussion (cf. A., 1941, II, 93). Hexacovalent Pd^{II} compounds have been described previously (cf. A., 1929, 678). L. S. T.

Chemotherapy of bacterial infections. IV. Synthesis of *N′*-sulphonamide-substituted heterocyclic derivatives of sulphanilamide. K. Ganapathi (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 386—389).—The following compounds have been obtained by standard methods: *sulphanilyl*-, m.p. 188—189°, *acetylsulphanilyl*-, m.p. 266°, N^4-*sulphanilylsulphanilyl*-, m.p. 155—160°, and N^4-*acetylsulphanilylsulphanilyl*-, m.p. 143—145° (decomp.), -*guanidine*; 4-N^1-*sulphanilamidouracil*; 5-N^1-*sulphanilamidobarbituric acid*; 2-N^1-*sulphanilamido*-, m.p. 216—218°, and 2-N^1-*sulphanilamido*-5-*methyl*-, m.p. 190—192°, -1 : 3 : 4-*thiodiazole*; 2-N^1-*sulphanilamido*-, m.p. 240—242°, 2-N^1-*sulphanilamido*-4-*methyl*-, m.p. 236—238°, 2-N^1-*sulphanilamido*-4 : 6-*dimethyl*-, m.p. 235—240°, and 2-N^1-*sulphanilamido*-4 : 6 : 6-*trimethyldihydro*-, m.p. 230—232°, -*pyrimidine*; 7-N^1-*sulphanilamidoalloxazine*. The group $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NR$ is essential for therapeutic activity, the degree and range of which are governed by the nature of R present at the sulphonamide radical. Of R tried, only the heterocyclic compounds the ring structures of which are present in products of vital biochemical functions (as vitamins or co-enzymes) yield sulphanilamide derivatives of outstanding val. Apparently some sp. spatial configuration of the whole mol. is essential for intense therapeutic activity. H. W.

Cobalt compounds of protoporphyrin. H. F. Holden (*Austral. J. Exp. Biol.*, 1941, **19**, 89—92).—The visible and ultraviolet spectra of cobalti- and cobalto-protoporphyrins and their compounds with globin, KCN, and glyoxaline are described. D. M. N.

Pyrrole series. V. Reinvestigation of the configuration of hæmin. A. H. Corwin and R. H. Krieble (*J. Amer. Chem. Soc.*, 1941, **63**, 1829—1834; cf. A., 1940, II, 193).—Rigid proof is provided of the structure of "natural" deuteroporphyrin (**I**) (Fischer *et al.*, A., 1928, 1385), mainly by alternative unambiguous synthesis of intermediates. Et_2 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate and aq. KOH at 160° give 95% of 2 : 4-dimethylpyrrole (**II**), b.p. 72°/25 mm., unstable in air. Addition of $COEt{\cdot}CH_2{\cdot}NH_2$,HCl (prep. *in situ* from $COEt{\cdot}CH{:}N{\cdot}OH$ by mossy Sn–$SnCl_2$–HCl improved) and 1% NaOH (to maintain p_H 6) to $CO_2Et{\cdot}C(ONa){:}CH{\cdot}CO_2Et$ in H_2O at 85° gives 65% of 4-carbethoxy-2 : 3-dimethylpyrrole-5-carboxylic acid, m.p. 210° (decomp.), converted as above into 2 : 3-dimethylpyrrole (**III**), b.p. 72°/25 mm., more stable than (**II**). Passing HCl into (*a*) 5-formyl-2 : 4-dimethylpyrrole (modified prep.; 75% yield), m.p. 91°, and (**III**), or (*b*) 5-formyl-2 : 3-dimethylpyrrole (**IV**), m.p. 127·5—128°, and (**II**) in abs. EtOH gives 95% of the hydrochloride, decomp. 222°, converted (83%) by a little aq. NH_3 into 3 : 5 : 4′ : 5′-dipyrrylmethene (**V**), m.p. 82—83°, unstable. Fischer's m.p. 115° for (**V**) is erroneous, attempts to repeat his experiments exactly giving, in one experiment, only a similar, but mixed, product. HCl, 90% HCO_2H, and (**II**) in EtOH give under defined conditions 50% of the hydrochloride (**VI**), red and blue forms, decomp. 226°, converted as above into 3 : 5 : 3′ : 5′-tetramethyldipyrrylmethene (**VII**), m.p. 116—118°. (**III**), (**IV**), and conc. HCl in EtOH give the hydrochloride (80%), decomp. 212°, of 4 : 5 : 4′ : 5′-tetramethyldipyrrylmethene (**VIII**), m.p. 116°. HCO_2H and (**III**) give only NH_4Cl. (**V**), (**VII**), and (**VIII**) give depressions of m.p. when mixed. Addition of Fe powder to deuterohæmin in HCl–AcOH, pptn. of the porphyrin by H_2O, boiling with dry HCl–AcOH, and purification by chromatography gives "natural" deuteroporphyrin Me_2 ester (**IX**), m.p. 224·5°. Br and (**VI**) in boiling CCl_4–$CHCl_3$ give 4 : 4′-dibromo-3 : 5 : 3′ : 5′-tetramethyldipyrrylmethene hydrobromide (**X**) (>83%). Prep. of 5 : 5′-dibromo-4 : 4′-dimethyldipyrrylmethene-3 : 3′-dipropionic acid hydrobromide (**XI**) from 5-carbethoxy-2 : 4-dimethylpyrrole-3-acrylic acid (hydrogenation: $PdCl_2$–C; aq. NaOH) by way of the 3-propionic acid, m.p. 153°, the 2-bromomethyl-3-propionic acid, and 5 : 5′-dicarboxy-4 : 4′-dimethyldipyrrylmethane-3 : 3′-dipropionic acid is improved. Heating (**X**), (**XI**), and BzOH at 180—182°, esterification of the product, and chromatography gives *deuteroporphyrin* XIII Me_2 ester, m.p. 243—243·5° [depression of m.p. with (**IX**)]. Similarly, but including debromination by hydrogenation (Busch catalyst; C_6H_6), 4 : 3′-dibromo-3 : 5 : 4′ : 5′-tetramethyldipyrrylmethene hydrobromide, (**XI**), and BzOH give deuteroporphyrin IX Me_2 ester, m.p. 223·5—224°, identical with "natural" (**IX**). R. S. C.

Absorption spectra of *ms*-tetraphenylporphine and its metal complex salts.—See A., 1941, I, 397.

Phenolic invert soaps. J. B. Niederl and F. A. Abbruscato (*J. Amer. Chem. Soc.*, 1941, **63**, 2024).—Treatment of *p*-$CH_3Bu^{\gamma}\cdot CMe_2\cdot C_6H_4\cdot OH$ with 30% CH_2O and NHR_2 in MeOH at room temp. and then with MeI gives 4-2′-*hydroxy*-5′-*aαγγ-tetramethyl*-n-*butylbenzylmorpholine*, m.p. 44—45° (*methiodide*, m.p. 176—177·5°), 1-2′-*hydroxy*-5′-*aαγγ-tetramethyl*-n-*butylbenzylpiperidine*, m.p. 92—93° (*methiodide*, m.p. 162—163·5°), 2-*hydroxy*-5-*aαγγ-tetramethyl*-n-*butylbenzyldi-ethyl*-, m.p. 124—125°, -n-*propyl*-, m.p. 135—136·6°, and -n-*butyl*-*ammonium iodide*, m.p. 132—133°. R. S. C.

Synthesis of 3 : 5-diamino-4-morpholinopyridine. E. Ochiai and Y. Ito (*J. Pharm. Soc. Japan*, 1941, **61**, 53—54).—4-Hydroxypyridine is converted by fuming HNO_3 and fuming H_2SO_4 at 140—145° into 3 : 5-*dinitro*-4-*hydroxypyridine*, decomp. 325°, transformed by the successive actions of $POCl_3$ + PCl_5 at 140° and morpholine in boiling abs. EtOH into 3 : 5-*dinitro*-, m.p. 163—164°, reduced (Pd–C in HCl–MeOH) to 3 : 5-*diamino*-4-*morpholinopyridine*, m.p. 231° (*picrate*, m.p. 213°; *Ac*$_2$ derivative, m.p. 216°). H. W.

Thiazolines.—See B., 1941, II, 335.

Polarisation in heterocyclic rings with aromatic character. XII. Polarisation in the thiazole ring. III. F. Nagasawa (*J. Pharm. Soc. Japan*, 1940, **60**, 219—224).—The activity of the $C_{(4)}$ like that of the $C_{(5)}$ position towards electrophilic reagents is slight; it is increased by the presence of substituents with +*M* or +*E* effect at $C_{(2)}$ but not to the extent observed with the activity of $C_{(5)}$. Treatment of 2-*amino*-5-*methylthiazole* (**I**), b.p. 80°/0·01 mm., m.p. 95—96·5°, with H_2SO_4 + HNO_3 causes decomp. without production of NO_2-derivatives. Nitration [H_2SO_4 (*d* 1·84) + HNO_3 (*d* 1·5)] of 2-*acetamido*-5-*methylthiazole*, m.p. 224°, at 0° gives small amounts of a NO_2-derivative, m.p. 249° (*picrate*), and much resin. The respective thiazoles are converted by fuming H_2SO_4 (20% SO_3) and HNO_3 at 160° into 4-*nitro*-2 : 5-*dimethyl*-, m.p. 56·5°, *nitro*-4-*methyl*-, m.p. 57·5°, and 5-*nitro*-2 : 4-*dimethyl*-, b.p. 65°/0·07 mm., -*thiazole*. 2 : 5-Dimethylthiazole is unaffected by fuming H_2SO_4 (20% SO_3) at 100° or 150° but is transformed by prolonged action of the acid at 200° into 2 : 5-*dimethylthiazole*-4-*sulphonic acid*, decomp. 284° [*Ba* salt (+1H_2O), decomp. 353°], in relatively poor yield. 2-*Hydroxy*-5-*methylthiazole*, m.p. 139—141·5°, reacts with fuming H_2SO_4 (20% SO_3) at room temp., 60°, and 100° (best at 60°) giving the non-cryst. -4-*sulphonic acid* [*Ba* salt (+1H_2O)] but reaction occurs less readily than with the -4-Me compound. (**I**) and fuming H_2SO_4 (20% SO_3) at 60° or 100°, but not at 1°, afford a *monosulphonic* acid, decomp. 292° [*Ba* salt (+1H_2O)], which could not be diazotised and is re-converted into (**I**) by conc. HCl at 135°. 2-*Piperidino*-5-*methylthiazole* (**II**), b.p. 128°/4 mm., m.p. 35° (*picrate*, m.p. 144°), is transformed by fuming H_2SO_4 (20% SO_3) at room temp. or 60° into the -4-*sulphonic* acid, decomp. 273° (*Ba* salt). Under similar conditions 2-*piperidino*-4-*methylthiazole* (**III**), b.p. 102—104°/4 mm., m.p. 36° (*picrate*, m.p. 153°; *perchlorate*, m.p. 126·5°), gives 2-*sulphon*-ω-*hydroxyamylamido*-4-*methylthiazole*-5-*sulphonic acid* (*Ba* salt). 2-Hydroxy-5-methylthiazole decolorises Br in $CHCl_3$ and evolves HBr at room temp. but the product is too unstable to permit its isolation; under like conditions (**I**) does not decolorise Br and (**II**) does not yield a Br-derivative, whereas (**III**) is transformed into 5-*bromo*-2-*piperidino*-4-*methylthiazole*, m.p. 39·5° (*perchlorate*, m.p. 158°). 2-Acetamido-4-methylthiazole, H_2SO_4 (*d* 1·84), and HNO_3 (*d* 1·5) give 5-*nitro*-2-*acetamido*-4-*methylthiazole*, decomp. 224°. H. W.

Molecular compounds in the sulphonamide series. II. S. Kuroyanagi and H. Kawai (*J. Pharm. Soc. Japan*, 1940, **60**, 183—184).—M.p. and f.p. curves for combinations of (*a*) *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH_2$ (**I**), *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot SO_2\cdot NMe_2$-*p*, or 2-sulphanilamidopyridine (**II**), and (*b*) 5 : 5-diethylbarbituric acid, dimethylaminoantipyrine (**III**), or 2-phenylquinoline-4-carboxylic acid (**IV**) show that only two combinations, viz., (**I**) (1 mol.) + (**IV**) (2 mols.), and (**II**) (1 mol.) + (**III**) (1 mol.), gave evidence of formation of mol. compounds. Thermal analysis of the systems 2-sulphanilamido-6-methylpyridine and (**III**) or *p*-$NO_2\cdot C_6H_4\cdot OH$ (**V**), and 2-sulphanilamido-4-methylthiazole and (**V**), shows that no mol. compound is formed. A. T. P.

Preparation of γ-diethylaminopropyl derivatives of 1-aminobenzthiazole. K. Tsuda, S. Sakamoto, H. Matsuda, and T. Kanno (*J. Pharm. Soc. Japan*, 1940, **60**, 184—189).—1-Acetamidobenzthiazole (**I**) (1 mol.) in NaOEt (1 mol.)–EtOH [or the K salt of (**I**) in EtOH] and $Br\cdot[CH_2]_3\cdot NEt_2$, HBr (**II**) (1·3 mols.) in NaOEt (1·3 mols.)–EtOH at 100° (bath) afford 1-N-*acetyl*-γ-*diethylaminopropylaminobenzthiazole*, b.p. 185—187°/0·03 mm. (*dipicrate*, m.p. 158°), hydrolysed by 10% aq. HCl at 100° (bath) to γ-*diethylaminopropylaminobenzthiazole*, b.p. 200—210°/0·01 mm. [*dipicrate*, m.p. 197° (or +$COMe_2$, m.p. 168°); meconate, m.p. 179° (decomp.)], also obtained from 1-chlorobenzthiazole and $NH_2\cdot[CH_2]_3\cdot NEt_2$ at 100°. 1-Aminobenzthiazole (**III**) or (**I**) and (**II**) at 130° afford 1-*imino*-2-γ-*diethylaminopropyl*-1 : 2-*dihydrobenzthiazole*, b.p. 170—180°/0·03 mm. [*dipicrate*, m.p. 192° (+H_2O); *meconate*, m.p. 217° (decomp.)] [*acetimino*-derivative, m.p. 57° (*dipicrate*, m.p. 145°)]. The following are prepared: 3-*methoxy*-, m.p. 146° (Ac derivative, m.p. 213°), and 4-*chloro*-1-*aminobenzthiazole*, m.p. 205° (*Ac* derivative, m.p. 291°); 5-*chloro*-, m.p. 62° [*dipicrate*, m.p. 188°; *meconate*, m.p. 165° (decomp.); *Ac* derivative, m.p. 107°], 5-ethoxy- [*meconate*, m.p. 210° (decomp.); *Ac* derivative, m.p. 96°], 5-amino- [*meconate*, m.p. 203° (+1·5$C_7H_4O_7$); *Ac* derivative, m.p. 202°], 3-*chloro*- [*dipicrate*, m.p. 170°; *meconate* (+3H_2O), m.p. 113° (decomp.); *Ac* derivative, b.p. 230°/0·01 mm. (*dipicrate*, m.p. 162°)], and 1-γ-*diethylaminopropylamino*-3-*methoxybenzthiazole*, b.p. 200°/0·01 mm. [*dipicrate*, m.p. 202°; *meconate*, m.p. 154—155° (decomp.); *Ac* derivative, b.p. 210°/0·01 mm. (*dipicrate*, m.p. 153°)]; 5-*nitro*-1-N-*acetyl*-γ-*diethylaminopropylaminobenzthiazole*, m.p. 129°; 5-chloro-, b.p. 190—200°/0·05 mm. [*dipicrate*, m.p. 143° (decomp.); meconate, m.p. 232° (decomp.)], 5-methoxy- [*meconate*, m.p. 217—218° (decomp.)], 3-chloro-, b.p. 200°/0·1 mm. [*dipicrate*, m.p. 190°; *meconate*, m.p. 230° (decomp.)], and 3-*methoxy*-1-*imino*-2-γ-*diethylaminopropylbenzthiazoline*, b.p. 170—200°/0·05 mm. (*dipicrate*, m.p. 196—198°; meconate). (**III**) and $O\cdot CH_2\cdot CH\cdot CH_2\cdot NEt_2$ yield 1-γ-*diethylamino*-β-*hydroxypropyl*)*aminobenzthiazole*, b.p. 230—250°/0·01 mm. (*dipicrate*, m.p. 189°), also obtained from 1-chlorobenzthiazole and $NH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NEt_2$. 2-Acetamido-4-methylthiazole is converted (K salt–MeI; reflux) into the N-*Me* derivative, m.p. 110°, or (MeI at 100°) into 2-*acetimino*-3 : 4-*dimethylthiazole*, m.p. 115° (+H_2O, m.p. 51°). A. T. P.

Heterocyclic sulphonamides. U. P. Basu and S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1941, **18**, 167—168).—2-Chloro-*cyclo*hexanone with $CS(NH_2)_2$ in boiling EtOH yields 2-amino-3 : 4-tetrahydrobenzthiazole (*hydrochloride*, m.p. 243—244°), which with *p*-$NHAc\cdot C_6H_4\cdot SO_2Cl$ (**I**) in C_5H_5N at room temp. yields the *Ac* derivative, m.p. 180° (indef.), of 2-*sulphanilamido*-3 : 4-*tetrahydrobenzthiazole* (**II**), m.p. 150—154° (indef.). 4-Methylthiazole with (**I**) in EtOAc at room temp. and hydrolysis (5% HCl in 50% EtOH at 100°) of the product yields 2-sulphanilamido-4-methylthiazole (Fosbinder *et al.*, A., 1939, II, 525). (**I**) and 4-sulphanilamido-1-phenyl-2 : 3-dimethyl-5-pyrazolone (Roblin *et al.*, A., 1940, II, 359) show no activity against pneumococcal (type I) infections in white mice. A. Li.

Synthesis of methoxy-γ-diethylaminopropyl derivatives of benzthiazole and benziminazole. E. Ochiai and M. Katada (*J. Pharm. Soc. Japan*, 1940, **60**, 211—216).—2-*Amino*-5-, m.p. 154° (*picrate*, decomp. 230—255°) [prepared by treating diazotised 3 : 4 : 1-$NO_2\cdot C_6H_3(NH_2)\cdot OMe$ with KCNS and $Cu_2(CNS)_2$, and reducing ($SnCl_2$ + HCl) the resulting 3-*nitro*-4-*thiocyanoanisole*, m.p. 126°], and -6-methoxy-, m.p. 158° [from *p*-$OMe\cdot C_6H_4\cdot NH\cdot CS\cdot NH_2$ (1 mol.) and Br (3 atoms) in $CHCl_3$ at 50°; cf. Dyson *et al.*, A., 1927, 680; different reaction conditions yield a Br-containing product, decomp. 222°], and 4-amino-6-methoxy-benzthiazole (prepared by the method of Fox *et al.*, A., 1939, II, 524) yield *Ac* derivatives, m.p. 223° (*K* salt, decomp. 265°), 226°, and 157—158°. the Na or K salts of which with $NEt_2\cdot[CH_2]_3\cdot Br$ in EtOH yield the *Ac* derivatives, b.p. —, 195—200° (bath temp.)/0·6 mm. (*picrate*, m.p. 188°), and 195—205° (bath temp.)/0·02 mm. (*perchlorate*, decomp. 186°), respectively, of 2-γ-*diethylaminopropylamino*-5-, b.p. 195—200° (bath temp.)/0·9 mm. (*perchlorate*, decomp. 244—245°), and -6-*methoxy*-, b.p. 200—205° (bath temp.)/0·7 mm. (*picrate*, decomp. 198°; *perchlorate*, decomp. 193°), and 4-γ-*diethylaminopropylamino*-6-*methoxy*-*benzthiazole*, b.p. 215—220° (bath temp.)/0·8 mm. (*picrate*, decomp. 141°). 1 : 3 : 4-$OMe\cdot C_6H_3(NH_2)_2$,2HCl with HCO_2H yields 6-*methoxybenziminazole*, m.p. 123° [*picrate*, m.p. 191°; 1-$NEt_2\cdot[CH_2]_3$

derivative (NEt_2·$[CH_2]_3$·Br in EtOH–NaOEt), b.p. 195—200° (bath temp.)/0·2 mm. (*picrate*, m.p. 174°)], nitration (room temp.) of which yields 5-nitro-, m.p. 244° (*nitrate*, decomp. 204°), reduced (Pd) to 5-amino-6-methoxybenziminazole {*Ac*, m.p. 210°, and NEt_2·$[CH_2]_3$ derivative, b.p. 135—140° (bath temp.)/0·06 mm. (*picrate*, decomp. 206°)}. A. Li.

Sulphanilamides derived from pyridine, quinoline, and thiazole.—See B., 1941, III, 245.

Synthesis of heterocyclic derivatives of diaryl sulphones. I. E. Ochiai and T. Takubo (*J. Pharm. Soc. Japan*, 1941, **61**, 6—7).—2-Chloro-4-methylthiazole with *p*-NO_2·C_6H_4·OH or 2-thiol-4-methylthiazole (**I**) and Zn in anhyd. C_5H_5N at 120—130° gives p-NO_2·C_6H_4 4-*methyl*-2-*thiazolyl*, m.p. 54°, and *di*-4-*methyl*-2-*thiazolyl sulphide*, b.p. 134—135°/16 mm. (*picrate*, m.p. 136°), oxidised by 30% H_2O_2 in AcOH at room temp. to the corresponding *sulphones*, m.p. 171° and 125°, respectively. 2-Chloropyridine and (**I**) similarly yield 2-*pyridyl* 4-*methyl*-2-*thiazolyl sulphide*, b.p. 166—168°/0·05 mm. (*picrate*, m.p. 118°), and *sulphone*, m.p. 121°. R. S. C.

5-Ethinylruban-5-ol and related compounds. G. R. Clemo and E. Hoggarth (*J.C.S.*, 1941, 476—477).—Condensation of 5-ketoruban with C_2H_2 in presence of K in *tert.*-C_5H_{11}·OH gives 5-*ethinylruban*-5-*ol*, m.p. 213°, which is reduced (Pt–H_2) to 5-ethylruban-5-ol. 5-Keto-6 : 9-rubanene with C_2H_2 affords a *compound*, $C_{19}H_{18}ON_2$, m.p. 238°, reduced to the substance obtained by the action of MgEtI on the ketone. Similarly 3-ketoquinuclidine (**I**) and C_2H_2 yield 3-*hydroxy*-3-*ethinylquinuclidine*, m.p. 159—160°, reduced to the -3-*Et* compound, b.p. 98—100°/1 mm. (*picrate*, m.p. 178°), also formed from MgEtI and (**I**). F. R. S.

Constitution of yohimbine. M. J. S. Dewar and F. E. King (*Nature*, 1941, **148**, 25).—Distillation of yohimbic acid with Cu and CuO instead of alkali improves Hahn's prep. of yohimbol (A., 1928, 432). The identity observed between the H_2SO_4 colour transformations of this carboxyl-free *sec.* alcohol and of yohimbine invalidates the evidence which places the CO_2Me at $C_{(f)}$ (A., 1941, II, 176). The structure now proposed has CO_2Me at $C_{(16)}$ and OH at $C_{(19)}$. L. S. T.

Azo compounds of morphine. I. A. C. Roy (*J. Indian Chem. Soc.*, 1941, **18**, 29—32).—When morphine is coupled with ArN_2Cl to give azo dyes, the pharmacological activity is modified but not destroyed. Azo dyes thus prepared are benzene-, m.p. 175° (decomp.) (cryst.); p-*methyl*-, m.p. 210° (decomp.) (amorphous), 2 : 4-*dimethyl*- (this and the following do not melt at 300° and are amorphous), p-*chloro*-, 2 : 4 : 6-*tribromo*-, p-*hydroxy*-, o-*methoxy*-, and o-, m-, and p-*nitrobenzene*-*azomorphine*; α-*naphthaleneazomorphine*; *diphenyl*-4 : 4′-*bisazomorphine*. A. T. P.

Alkaloids of *Rauwolfia canescens* (Linn.). I. (Miss) A. Mookerjee (*J. Indian Chem. Soc.*, 1941, **18**, 33—39).—The air-dried leaves of *R. canescens* are extracted with EtOH (+0·1% AcOH) at room temp., the extract is conc., added to H_2O, extracted with Et_2O, and the aq. solution made alkaline with NH_3 and extracted with Et_2O, and the alkaloid pptd. as the *oxalate*, m.p. 245—246° (decomp.) (+$2H_2O$, lost at 125—130° over P_2O_5), which is decomposed by aq. NH_3 to "*rauwolscine*" (**I**), $C_{21}H_{26}O_3N_2$, m.p. 231—232° (decomp.), $[\alpha]_D^{30}$ −40° in EtOH (contains CO_2Me) [*hydrochloride*, m.p. 278—280° (decomp.), $[\alpha]_D^{30}$ +74° in H_2O; *nitrate*, m.p. 257—258° (decomp.); *sulphate*, m.p. 256—257° (decomp.); *platinichloride*, m.p. 255—257° (decomp.); *picrate*, m.p. 208° (decomp.) (+2EtOH)], which with conc. NH_3 at room temp. in a closed vessel affords *rauwolscinic acid*, m.p. 262—264° (decomp.) [+H_2O, lost at 120—125° (P_2O_5)], reconverted into (**I**) by HCl–MeOH. (**I**) shows similar colour reactions to those of yohimbine, with which it is not identical. Some photomicrographs are shown. A. T. P.

Alkaloids of *Stemona tuberosa*, Loureiro. III. Tuberostemonine. H. Kondo, K. Suzuki, and M. Satomi (*J. Pharm. Soc. Japan*, 1940, **60**, 149—157; cf. A., 1940, II, 237).—Tuberostemonine (**I**) in MeOH or 2N-HCl is slowly hydrogenated in presence of a very large proportion of PtO_2 to hydrotuberostemonine (**II**), m.p. 133° (hydrochloride, m.p. 281°); the "isomeride," m.p. 118—120° (cf. Schild, A., 1936, 350), is separated chromatographically into (**I**) and (**II**). After treatment with Ag_2O (**II**) does not give Ehrlich's reaction for pyrrole; it does not react with MeI although it behaves as a weak base towards mineral acid. Tuberostemonine methohydroxide passes at 145°/vac. into *hydroxy*-N-*methyltuberostemonine* (**III**), $C_{23}H_{37}O_5N$, m.p. 123—125° (*perchlorate*, m.p. 217°), which is stable at 130°/vac. Like its *Ac* derivative, decomp. 213°, (**III**) does not react with MeI in MeOH. (**III**) does not appear to yield an oxime. Me_2SO_4 transforms (**III**) at 120° into an amorphous substance characterised as the *perchlorate*, $C_{23}H_{35}O_5N,HClO_4$, m.p. 210°, with a small proportion of a cryst. *material*, $C_{23}H_{37}O_5N,Me_2SO_4$, m.p. 245°. (**III**) and CNBr in C_6H_6 at room temp. yield an *adduct*, $C_{23}H_{37}O_5N,CNBr$, m.p. 232° (decomp.), which is not affected by boiling 2N-KOH–EtOH or by 20% H_2SO_4 at 120°. (**III**) is dehalogenated by Ag_2O and then transformed by 30% H_2SO_4 or HCl into the *anhydro-base*, $C_{24}H_{36}O_5N_2$, m.p. 210°, which with 30% HCl at 100° gives the *chlorocyanide*, $C_{24}H_{35}O_4N_2Cl$, m.p. 160°. Hydrolysis of (**I**) by 0·5N-KOH–EtOH and treatment of the neutralised solution with CH_2N_2 leads only to the re-formation of (**I**). Similarly successive treatment of (**I**) with KOH–EtOH, Me_2SO_4, and KI gives only tuberostemonine methiodide, m.p. 236—238°, also obtained from K tuberostemonate and MeI. (**I**) does not appear to be changed by Na and EtOH but is converted by Na and boiling *iso*-C_5H_{11}·OH into an amorphous base. (**I**) does not react with solid KOH and *iso*-C_5H_{11}·OH at 100—200°. H. W.

VI.—ORGANO-METALLIC COMPOUNDS.

Asymmetrical analogues of cacodyl oxide. G. Kamai and V. M. Zoroastrova (*J. Gen. Chem. Russ.*, 1940, **10**, 1568—1572).—$AsEtI_2$ and $Pr^{\beta}Br$ with 5N-NaOH in 55% EtOH yield *ethyliso*propyliodoarsine, b.p. 87—88°/13 mm. *Benzylethyliodoarsine*, b.p. 169—170°/15 mm., is prepared similarly from $AsEtI_2$ and CH_2PhBr. AsRR′I and 10N-NaOH at room temp. yield oxides of the type $(AsRR')_2O$ (R = Me, R′ = Et; R = *Et*, R′ = Pr^{β}, b.p. 130—132°/17 mm.; R = *Me*, R′ = *Ph*, b.p. 202—203°/15—16 mm.; R = *Et*, R′ = *Ph*, b.p. 189°/5 mm.; R = *Et*, R′ = CH_2Ph, b.p. 174—175°/16 mm.; R = Ph, R′ = *p*-tolyl). $(AsPhMe)_2O$ is oxidised by atm. O_2 to phenylmethylarsinic acid, m.p. 178—179°, which with CH_2Cl·CO_2Na yields *phenylmethyloxarsylacetic acid*, converted by H_2S into *phenylmethylthioarsylacetic acid* [*phenyl*(*carboxymethyl*)*methylarsine sulphide*], m.p. 132—133°. R. T.

Steric hindrance in Grignard reaction. I. Reaction of magnesium mesityl bromide with ethyl formate and acetate. I. I. Lapkin, V. S. Schklaev, and T. I. Schklaeva (*J. Gen. Chem. Russ.*, 1940, **10**, 1449—1452).—Mg mesityl bromide (**I**) and HCO_2Et in Et_2O react with difficulty at the b.p., yielding mesitol and dimesitylmethane. (**I**) does not react with EtOAc in Et_2O; in PhMe it reacts only very slowly (30 hr. at the b.p.), yielding mesityl acetate and αα-dimesitylethyl acetate. R. T.

Chemotherapy of bacterial infections. II. Chemistry of some organo-selenium compounds related to sulphanilamides. P. L. N. Rao (*J. Indian Chem. Soc.*, 1941, **18**, 1—6; cf. A., 1940, II, 274).—*p*-NHAc·C_6H_4·SeCN (1 part) refluxed with 2·5N-KOH–EtOH (5 parts for 6 hr. or 1·7 parts for ½ hr.) gives p-*amino*- (**II**), m.p. 76—78°, or -*acetamido*-*selenophenol* (**III**), m.p. 160—165°, respectively. (**I**)–$(NH_4)_2S$ yield (**III**) and (*p*-NHAc·C_6H_4)$_2$Se. (**III**) is oxidised (dil. H_2O_2) to *di*-p-*acetamidophenyl diselenide*, m.p. 204—206° (softens from 180—182°), and (**II**) (prepared as above but not isolated) is oxidised by atm. O_2 or H_2O_2 to (*p*-NH_2·C_6H_4)$_2Se_2$ [*sulphate*, m.p. 210—215° (decomp.); *Bz*$_2$ derivative (**IV**), m.p. 265—267° (decomp.); *di*-*hexoyl*, m.p. 175—177°, and -*valeroyl* derivative, m.p. 172—173°]. *p*-NO_2·C_6H_4·SeO_2H, neutralised with NH_3, is oxidised by aq. $KMnO_4$ to *K* 4-*nitrophenylselenonate* (anhyd. or +H_2O, gradually lost at room temp.). (**IV**) and HNO_3 (*d* 1·4) at −6° to −3° afford 4-*benzamidophenylseleninic acid*, m.p. 186° (decomp.) [hydrolysed to the 4-NH_2-compound (*Ba* salt)], and thence *K* 4-*benzamidophenylselenonate*. *Ag* 4-*acetamidophenylselenonate* is prepared in an analogous manner. *p*-NO_2·C_6H_4·SeCN, *p*-C_6H_4Br·NO_2, and aq. K_2CO_3–EtOH (refluxed for 2 days) yield (*p*-NO_2·C_6H_4)$_2$Se (**V**), new m.p. 175°, reduced to 4 : 4′-*diaminodiphenyl selenide*, m.p. 115—117°, which is also obtained by hydrolysis of the corresponding Ac_2 derivative. *p*-$C_6H_4Br(Cl)$·NO_2 and Na_2Se–Se–EtOH give (*p*-NO_2·C_6H_4)$_2Se_2$ and (**V**) (cf. Baker *et al.*, A., 1930, 1302). (**I**) and Br–$CHCl_3$ afford 4-*acetamidophenylselenotribromide*, m.p. 130—132° (decomp.) (softens at 100°), which loses 2 Br in vac. (1 week) to give the -*selenobromide*

(boiling H_2O yields a substance, m.p. 168—169°). *p*-$NO_2{\cdot}C_6H_4{\cdot}SeO_2K$ and PCl_5 afford *p*-$NO_2{\cdot}C_6H_4{\cdot}SeCl$, converted by ice-$H_2O$ or aq. NH_3 into (*p*-$NO_2{\cdot}C_6H_4)_2Se_2$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}SeO_2H$. A. T. P.

VII.—PROTEINS.

Molecular structure of protein fibres. D. J. Lloyd (*J. Soc. Dyers and Col.*, 1941, **57**, 281—287).—Proteins are classified into silk fibroin, myosin–keratin, and collagen types. Their general properties are discussed, special emphasis being laid on the sorption of H_2O and swelling. C. S. W.

Nature of the intramolecular fold in α-keratin and α-myosin. W. T. Astbury and F. O. Bell (*Nature*, 1941, **147**, 696—699).—A basis for an intramol. fold in α-keratin and α-myosin is proposed, illustrated, and discussed. L. S. T.

Action of formaldehyde on gluten [gelatin?]. A. S. Schpitalski, E. A. Emelianova, and S. B. Faerman (*J. Appl. Chem. Russ.*, 1940, **13**, 1642—1648).—The effect of aq. CH_2O on aq. gelatin (**I**) varies according to the concn. of (**I**). When this is low the η increases, and gelation is prevented, whilst when it is high the opposite effects are produced. However, the dimensions of the (**I**) mols. appear to increase in all cases. CH_2O has little effect on hydrolysed (**I**). R. T.

Formation of humins during acid hydrolysis of proteins. V. A. Kaschirskich (*J. Gen. Chem. Russ.*, 1940, **10**, 1495—1500).—Insol. residues formed during hydrolysis of proteins (caseinogen) or NH_2-acids (glycine, alanine, crystine, glutamic acid, tyrosine, tryptophan) in presence of carbohydrates (glucose, fructose, lactose, galactose, arabinose, cellulose) by means of 20% HCl are supposed to originate from condensation of reactive furan compounds derived from the carbohydrates with NH_2-acids, or with each other, to yield nitrogenous or N-free humins, respectively. R. T.

Acyl and sulphonyl derivatives of proteins.—See B., 1941, II, 324.

Humin formation during protein hydrolysis.—See A., 1941, III, 948.

Carrier weights of conjugated proteins. E. E. Broda and C. F. Goodeve (*Nature*, 1941, **148**, 200—201).—Carrier wts., *i.e.*, the no. of g. of protein carrying 1 g.-equiv. of prosthetic group, are tabulated for numerous conjugated proteins. The data show that the Svedberg unit is the lower limit of the carrier wts., and that all sufficiently well-defined compounds have carrier wts. close to simple multiples of the unit. L. S. T.

VIII.—ANALYSIS.

Distilling column head.—See A., 1941, I, 391.

Continuous water remover.—See A., 1941, I, 392.

Simultaneous micro-determination of elements in organic compounds containing alkali. H. Agematsu (*J. Pharm. Soc. Japan*, 1940, **60**, 233—235).—C and H are determined essentially according to Pregl. Na compounds (3—5 mg.) are weighed into a Pt boat and covered with 2—3 times the amount of dry Cr_2O_3. With K salts 1—2 mg. of Cr_2O_3 suffices and an excess must be carefully avoided. The boat is heated gently with a moving burner until the contents are melted and then very strongly after carbonisation is complete. The residue is treated with H_2O and unchanged Cr_2O_3 is removed by an asbestos filter. CrO_4'' is determined in the filtrate gravimetrically as $PbCrO_4$ or iodometrically. N can be determined simultaneously. With explosive substances an addition of CuO is necessary. The process is not applicable in the presence of halogen or S because the metals produce very stable alkali halides and sulphates. H. W.

Micro-determination of nitrogen by oxidative digestion. C. N. B. Rao, M. V. L. Rao, and M. S. Ramaswamy (*Current Sci.*, 1941, **10**, 261—262).—An aq. suspension (1 c.c.) of the material is treated with conc. H_2SO_4 and HgO (~50 mg.) and to the boiling solution 100% chromic acid (0·2—0·3 c.c.) is added. After 5 min. the solution is diluted with H_2O (5—10 c.c.), decolorised with Na_2SO_3, and boiled after adding Zn dust (~10—20 mg.). The NH_3 is distilled from the solution which has been rendered alkaline and determined titrimetrically (colorimetrically when the NH_3 content is <10 μg.). J. L. D.

Adaptation of the micro-Kjeldahl method to determination of nitrogen in organic compounds containing nitro- and azo-groups. R. V. Bhat (*Proc. Indian Acad. Sci.*, 1941, **A**, **13**, 269—272).—A no. of NO_2- [*e.g.*, *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, 3 : 5 : 1-$C_6H_3(NO_2)_2{\cdot}CO_2H$, etc.] and azo-compounds (*e.g.*, azo-dyes from Naphtol AS derivatives and diazotised Fast Red bases) are analysed correctly for N by the micro-Kjeldahl method, using pure cotton cellulose as reducing agent; the substance is heated with H_2SO_4 (*d* 1·84), K_2SO_4, and bleached cotton for ½ hr., $CuSO_4$ and H_2SeO_3 are then added, and heating is continued (1—1½ hr.), NH_3 being determined as usual. Details are given of the method, which is useful in estimating dyes on the fibre. A. T. P.

Determination of sulphur in organic compounds. Oxidation of sulphur of cystine and methionine, combination of Parr oxygen bomb and acidimetric benzidine method, and determination of small amounts of sulphur present as concontaminant in organic materials. T. P. Callan and G. Toennies (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 450—455).—A process for the oxidation of org. S compounds by $KMnO_4$–NaOH prior to S determination is described. Methionine gives no SO_4'' by this procedure, and other wet oxidation processes give variable and incomplete vals. A procedure is detailed in which the substance is burned in a bomb in compressed O_2, and the SO_4'' is determined acidimetrically as benzidine sulphate. The presence of Hg and NaCl, within certain limits, does not interfere in this method, which is accurate to a few hundredths %. J. D. R.

Micro-determination of sulphur. Modified bomb method. J. F. Alicino (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 506).—A modification of the Elek–Hill method (A., 1933, 1063) is described. The Na_2O_2 in the fusion mixture is decreased to 0·35 g., and 0·06 g. of $KClO_3$ is substituted for the sucrose + KNO_3. This reduction in quantity of the fusion mixture permits filtration of the $BaSO_4$ by filter-stick, minimises contamination of the $BaSO_4$ by co-pptn. and adsorption of salts, and eliminates the need for using reagents of special purity. Analyses of typical org. substances show the accuracy of the method. L. S. T.

Determination of iodine in organic compounds with the calorimetric bomb. I, II. B. Longo (*Atti R. Accad. Sci. Torino* [*Cl. Sci. fis. mat. nat.*], 1938, **73**, I, 428—430, 431—433; *Chem. Zentr.*, 1938, ii, 3843).—I. A modification of Garelli and Saladini's method for Cl and Br (cf. A., 1932, 1149) is extended to I. The KIO_3 formed in the bomb is reduced with N_2H_4 and the I determined by Volhard's method.

II. In presence of Cl or Br the solution from the bomb is treated with N_2H_4 and the halogens are determined in separate portions by Volhard's method, and by Gooch's method after treatment with HNO_2. A. J. E. W.

Determination of reactive hydrogen by Grignard's reagents in an atmosphere of carbon dioxide. A. P. Terentiev and K. D. Schtscherbakova (*J. Gen. Chem. Russ.*, 1940, **10**, 2041—2046).—The reactive H content of org. compounds is derived from the vol. of CH_4 evolved when the compound reacts with MgMeI in Et_2O in absence of atm. O_2. Apparatus for this method is described. R. T.

Determination and detection of dienes with conjugated ethylenic linkings. I. V. I. Esafov. **II.** V. I. Esafov and A. V. Schpadi (*J. Appl. Chem. Russ.*, 1941, **14**, 140—147, 148—150).—I. Kaufmann's iodometric method (A., 1937, II, 47) is not applicable to dienes with conjugated double linkings, owing to secondary polymerisation reactions. MacIlhiney's reaction is recommended for detection of dienes.

II. Non-conjugated polyenes react with Br in CCl_4 in the same way as olefines. With conjugated dienes considerable evolution of HBr takes place; this reaction is sp. for such dienes, and can serve for their identification in mixtures with other hydrocarbons. R. T.

Determination of ammonia and carbamide by modification of the Conway diffusion method.—See A., 1941, I, 426.

Gasometric determination of amino-acids.—See A., 1941, III, 947.

Micro-chemical reaction for detection of celandine.—See A., 1941, III, 819.

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