BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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MAY, 1943

A., II.—ORGANIC CHEMISTRY

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Offices of the Bureau: 56 Victoria Street, London, S.W.1

Publishers: THE CHEMICAL SOCIETY, Burlington House, Piccadilly, London, W.1

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A., II.—Organic Chemistry

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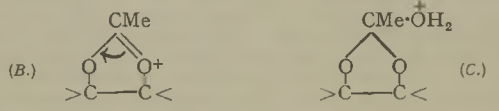
I.—ALIPHATIC.

Double linking isomerisation in the preparation of straight-chained aliphatic olefines of higher mol. wt. F. Asinger (*Ber.*, 1942, **75**, [*B*], 1247—1259).—Al_2O_3 is obtained by pptn. of AlCl$_3$ with aq. NH_3, washing the ppt. until Cl-free, peptisation with HNO_3, heating at 450°, grinding for 5 hr. with 20% HNO_3, and drying for 4 hr. at 450°. For dechlorinations this catalyst is heated in a Jena glass tube at 250° and the chloride, mixed with N_2, is passed over it. α-Chloro-*n*-dodecane gives a dodecene mixture with ~5% of a dark green polymerisate. The mixture is ozonised and then quantitatively oxidised to acids by Ag_2O in alkaline suspension. The acids are separated by very slow fractional distillation. The hydrocarbon mixture contains Δ^{α}- 3·9, Δ^{β}- 17·3, Δ^{γ}- 19·4, Δ^{δ}- 20·3, Δ^{ϵ}- 19·4, and Δ^{ζ}- 19·6 mol.-% -dodecene. Dechlorination of cetyl chloride in like manner gives 25% of polymerides, cyclic compounds, olefines with the group ·CH_2·C(:CH_2)·CH_2· or ·CH_2·CMe:CH·CH_2·, and a mixture of hexadecenes: Δ^{α}- 0·8, Δ^{β}- 4·8, Δ^{γ}- 12·6, Δ^{δ}- 15·5, Δ^{ϵ}- 17·4, Δ^{ζ}- 16·4, Δ^{η}- 16·9, Δ^{θ}- 16·4 mol.-%. ι-Chloroheptadecane yields 25% of polymerisate and the following mol.-% of the heptadecenes: Δ^{α}- 1·0, Δ^{β}- 1·25, Δ^{γ}- 4·2, Δ^{δ}- 9·15, Δ^{ϵ}- 10·8, Δ^{ζ}- 13·7, Δ^{η}- 15·7, Δ^{θ}- 22·4, Δ^{ι}- 23·4. Dehydration of *n*-dodecanol by pure Al_2O_3 at 380° gives 96% of a dodecene mixture containing Δ^{α}- 40·0, Δ^{β}- 40·0, Δ^{γ}- 7·9, Δ^{δ}- 2·0, Δ^{ϵ}- 0·75, Δ^{ζ}- 0·35 mol.-%. With Al_2O_3 activated by HCl the dodecene mixture contains Δ^{α}- 10·7, Δ^{β}- 19·7, Δ^{β}- 16·8, Δ^{δ}- 17·6, Δ^{ϵ}- 17·3, Δ^{ζ}- 19·3 mol.-%. If the catalyst is activated by SiO_2 the dodecene mixture contains Δ^{α}- 10·7, Δ^{β}- 18·3, Δ^{γ}- 24·5, Δ^{δ}- 21·2, Δ^{ϵ}- 13·6, Δ^{ζ}- 11·8 mol.-%. With a very active, pure Al_2O_3 dehydration occurs at 250°, giving a dodecene mixture with Δ^{α}- 40·0, Δ^{β}- 29·0, Δ^{γ}- 11·7, Δ^{δ}- 8·15, Δ^{ϵ}- 6·10, and Δ^{ζ}- 5·10 mol.-%. *n*-Dodecanol (3 mols.) and conc. syrupy H_3PO_4 (3·5 mols.) are slowly heated to 190° and then at 210—220°/600 mm., when the greater part of the olefine mixture distils. It contains Δ^{α}- 8·0, Δ^{β}- 25·2, Δ^{γ}- 25·2, Δ^{δ}- 17·9, Δ^{ϵ}- 13·0, and Δ^{ζ}- 10·6 mol.-% -dodecene. Technical samples of hexa- and octa-decene are shown to be mixtures of isomerides. A nearly homogeneous Δ^{α}-dodecene is obtained by dehydrogenating *n*-dodecanol by stearic acid at 250° and finally at 330—350°/600 mm. The absence of isomerisation is not due to low temp. but to the absence of a catalyst. H. W.

Isomerising action of anhydrous magnesium bromide on complex olefines with terminal double linking. [**Cetene** = Δ^{α}-**hexadecene.**] F. Asinger (*Ber.*, 1942, **75**, [*B*], 1260—1263).—A mixture of Δ^{α}- and Δ^{β}-dodecene (mol. ratio, 97·64 : 2·36) is converted by boiling for 6 hr. with $MgBr_2$ in C_6H_6 into a mixture of Δ^{α}- 83·41, Δ^{β}- 10·0, Δ^{γ}- 4·20, Δ^{δ}- 2·24, Δ^{ϵ}- 0·42 mol.-% -dodecene. The author does not therefore share the view of Suida *et al.* (A., 1943, II, 78) that " it is very unlikely that isomerisations occur during the Grignard synthesis since high temp. are avoided " and does not consider the proof of the homogeneity of cetene to be valid. H. W.

Rôle of neighbouring groups in replacement reactions. I. Retention of configuration in the reaction of dihalides and acetoxyhalides with silver acetate. II. Effects of small amounts of water on the reaction of silver acetate in acetic acid with butene and *cyclo*hexene derivatives. S. Winstein and R. E. Buckles. **III. Retention of configuration in the reaction of γ-bromobutan-β-ols with phosphorus tribromide. IV. Identity of various preparations of 1 : 2-dibromo*cyclo*hexane.** S. Winstein. **V. Effect of the neighbouring acetoxy group on the course of the replacement of the *p*-toluenesulphonate group of *trans*-2-acetoxy*cyclo*hexyl *p*-toluenesulphonate.** S. Winstein, H. V. Hess, and R. E. Buckles (*J. Amer. Chem. Soc.*, 1942, **64**, 2780—2786, 2787—2790, 2791—2792, 2792—2795, 2796—2801).—I. Interaction of *erythro*- or *threo*-CHMeBr·CHMe·OAc, *meso*- or *dl*-$(CHMeBr)_2$, *dl-trans*-2-bromo-1-acetoxy*cyclo*hexane, or *dl-trans*-1 : 2-dibromo*cyclo*hexane (**I**) with AgOAc gives $(CHMe·OAc)_2$ or 1 : 2-diacetoxy*cyclo*hexane (**II**), respectively, with almost complete (>87—98%) retention of configuration. Optically active $(CHMeBr)_2$ and *trans*-2-bromo-1-acetoxy*cyclo*hexane give completely inactive products. The reactions, considered to be of S_Ni type, probably involve a double inversion. The steric results are ascribed to production of intermediates, >C<(Br⁺)>C< (*A*) and (*B*). The scope and results of reactions involving such intermediates are discussed.

II. Addition of H_2O (up to 1—2 mols.) in the above-mentioned reactions leads to increasing amounts of OH·$[CHMe]_2$·OAc and

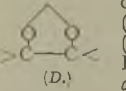


1-hydroxy-2-acetoxy*cyclo*hexane (**III**) (up to 64—72%) and inversion (up to 95—98%). Under the conditions of these reactions the monoacetates are converted to a considerable extent into diacetates but the diacetates are hardly affected. The bromohydrins which might be intermediates do not react similarly and configuration is mainly retained. Thus, the OH is introduced only after the first OAc. The formation of the monoacetate involves (*B*) and thence the orthoacetate (*C*), which then loses a proton and undergoes ring-fission without inversion; the single inversion thus occurs in formation of (*B*). Similar reactions are discussed.

III. *erythro*- and *threo*-CHMeBr·CHMe·OH with PBr_3 give $(CHMeBr)_2$ with 95% and ~90%, respectively, of retention of configuration. Reaction thus proceeds by way of (*A*).

IV. (**I**) obtained from *cyclo*hexene (**IV**) is also obtained from (i) *cyclo*hexene oxide (**V**), 2-bromo*cyclo*hexanol [prep. from (**IV**) or 2-bromo*cyclo*hexanone], 2-bromo*cyclo*hexyl *p*-toluenesulphonate, or *cis*-(**II**) by fuming HBr, (ii) from 2-bromo*cyclo*hexanol [prep. from (**V**)] by PBr_3, or (iii) *cis*- or *trans*-(**II**) by HBr–AcOH. (**I**) is considered to be the *trans*-compound. Formation of (*B*) favours formation of *trans*-dihalide in nucleophilic replacement reactions.

V. *trans*-2-Acetoxy*cyclo*hexyl *p*-toluenesulphonate (**VI**) with KOAc–AcOH gives 93%-pure *trans*-(**II**), but addition of H_2O gives increasing amounts of inversion and *cis*-(**III**). In EtOH containing $CaCO_3$ and a trace of H_2O, (**VI**) gives a product hydrolysed to *cis*-glycol, and in EtOH–KOAc gives *cis*-(**III**). In AcOH (no KOAc), *cis*-(**II**) is formed. Reactions proceed by way of (*B*). Formation of the *cis*-compounds involves (*D*) (R = OEt or OAc).



R. S. C.

Dehydration of alcohols. XIX. *tert*.-Amyl alcohol and the related dimethylneopentylcarbinol. F. C. Whitmore, C. S. Rowland, S. N. Wrenn, and G. W. Kilmer (*J. Amer. Chem. Soc.*, 1942, **64**, 2970—2972; cf. A., 1941, II, 347).—Distillation of CMe_2Et·OH from 15% H_2SO_4 gives a 7 : 1 mixture of $CHMe:CMe_2$ + $CH_2:CMeEt$, but that of CH_2Bu^{γ}·CMe_2·OH gives a 1 : 4·5 mixture of $CHBu^{\gamma}:CMe_2$ + $CH_2:CMe·CH_2Bu^{\gamma}$. The large effect of the Bu^{γ} is noted. Passage of $CHMeBu^{\gamma}$·OH over activated Al_2O_3 gives good yields of $CH_2:CHBu^{\gamma}$, but none if the Al_2O_3 is made even slightly alkaline.

R. S. C.

Autoxidation of oxygen-active acids. VI. Total analyses of the process of autoxidation of the methyl esters of linoleic and linolenic acid and the hexaenoic acid of cod-liver oil by means of magnesium alkyl halides and the nature of mol. multiplication. W. Treibs (*Ber.*, 1942, **75**, [*B*], 1164—1180; cf. A., 1943, II, 80).—OH, CO, and α-oxido-groups react immediately and quantitatively with 1 mol. of MgMeI in each case. CO_2Me of the higher fatty acids reacts somewhat more slowly but the change is invariably complete after 10 min. at 20—25° or 1 min. at 80° and requires 2 MgMeI. Tetrahydronaphthalene, *cyclo*hexene (**I**), and Δ^3-menthene H peroxide behave like OH-ketones, requiring 2 mols. of MgMeI and evolving 1 mol. of CH_4. The second mol. of MgMeI essentially oxidises (**I**) to *cyclo*hexenol. With MgPhBr the main secondary product is Ph_2. With ascaridole the total requirement of MgMeI is invariably ~2 mols. and with rising temp. there is an evolution of CH_4 approaching a limiting val. of 1 mol. In the analysis of the oils the sample is treated with a known excess of MgMeI. CH_4 evolved immediately is measured and after a suitable interval the unchanged reagent is decomposed by a suitable alcohol and the CH_4 evolved is again measured. It is thus shown that the immediately occurring mol. enlargement of elæostearic ester (**II**) is a dimerisation caused by the formation of a perdioxan ring which speedily isomerises to a dihydroxydioxan ring: O·CHR·CH·O / O·CHR·CH·O → O<CR(OH)·CH / CHR·C(OH)>O. The Me esters of linoleic, linolenic, and the hexaenoic acid of cod-liver oil are first converted into a labile, monomeric monoperoxide the O_2H group of which does not directly participate in the following

mol. enlargement of which it is essentially a preliminary. The actual enlargement occurs in precisely the same manner as with (**II**), a labile perdioxan ring being formed which passes spontaneously into a dihydroxydioxan ring. The most important phase of autoxidation, the multiplication of the mol., occurs in the same manner with all O-active acids. The most characteristic difference is that in (**II**) the intermol. directive forces required for the formation of the dimeric peroxide bridge are already present in virtue of the conjugated system whereas in the other esters they must be created by the monomeric monoperoxide stage. H. W.

Lower hydrates of soap. M. J. Buerger, L. B. Smith, A. de Bretteville, jun., and F. V. Ryer (*Proc. Nat. Acad. Sci.*, 1942, **28**, 526—529).—Evidence, which includes *X*-ray powder photographs, is presented which shows that soap forms previously considered to be anhyd. are hydrates of Na stearate with $\frac{1}{2}$ and $\frac{1}{4}$ mol. H_2O per mol. (See also A., 1943, I, 117.) J. L. E.

Alkylation of linseed oil. J. G. Smull and J. S. Saylor (*J. Amer. Chem. Soc.*, 1942, **64**, 3054).—When the Me esters obtained from linseed oil by MeOH are treated with NaOEt–EtOH at 60° and then with EtI, first at room temp. and then at 90°, the product, b.p. 205°/14 mm., is considered to be alkylated (:CH·CHEt·CH:) because of its reduced I val. (average 177·4) and failure to give the fulvene reaction. R. S. C.

Macrocyclic ring systems. I. Preparation and cyclisation of ω-halogenoacylacetic esters. H. Hunsdiecker (*Ber.*, 1942, **75**, [*B*]. 1190—1197).—The action of NaOAlk on RHal·CO·CHAc·CO_2Et (**I**) may follow the courses: (**I**) → RHal·CO·CH_2·CO_2Me and thence → [·R·CO·CH·CO_2Me]$_n$ or $\begin{matrix}R\\|\\CO\end{matrix}$>CH·$CO_2$Me or OMe·R·CO·$CH_2$·$CO_2$Me; (**I**) → OMe·R·CO·CHAc·CO_2Et. The relative probabilities are estimated by measurement of the rates of fission of Et hexoylacetoacetate, of condensation of *n*-C_6H_{13}Br with CHAcNa·CO_2Et, and of ether formation from NaOMe and Bu^{α}Br. The first change is certainly complete within 90 min. whilst in the same time the second and third changes have proceeded to the extent of ~1% and ~3%, respectively. In harmony, the fission of halogenoacylacetoacetates proceeds very smoothly without disturbing side or consequent changes. An exception is furnished by Et δ-bromovalerylacetoacetate, which gives a mixture of ~40% of Et δ-bromovalerate and ~60% of Me *cyclo*hexan-2-one-1-carboxylate. μ-Bromotridecoic acid is converted ($SOCl_2$) into its chloride, which is condensed with CHAcNa·CO_2Et in Et_2O to a product transformed by NaOMe–MeOH at room temp. into *Me β-keto-χ-bromopentadecoate*, m.p. 47° (yield 67%); the corresponding *I*-compound (**II**) has m.p. 56·5°. *Me β-keto-κ-bromoundecoate*, b.p. 158°/1 mm. (*Cu* compound, m.p. 126°), and *Me β-keto-ν-bromotridecoate*, b.p. 185°/4 mm., m.p. 34·5° (corresponding *I*-compound, m.p. 46°), are obtained similarly. Very gradual addition of (**II**) to a boiling suspension of anhyd. K_2CO_3 in boiling COMeEt affords *Me* cyclo*tetradecan*-2-*one*-1-*carboxylate*, b.p. 145°/1·5 mm. (semicarbazone, m.p. 186—188°), converted by 80% H_2SO_4 at room temp. into cyclo*tetradecanone*, m.p. 52° (*semicarbazone*, m.p. 198°). H. W.

Mechanism of the Diels–Alder reaction. R. B. Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 3054—3059).—This reaction occurs by ionisation of the two components (cf. Weiss, A., 1942, II, 229), reversible formation of an intermol. semipolar linking, [A⁺]:[B⁻], and finally irreversible formation of the product. Donor or acceptor mols. [NPhMe$_2$, *s*-$C_6H_3(NO_2)_3$] may be catalytic. R. S. C.

Use of formaldehyde and 2 : 6-dichlorophenol-indophenol in determination of ascorbic and dehydroascorbic acid.—See A., 1943, III, 258.

Determination of ascorbic acid based on use of standardised 2 : 6-dichlorophenol-indophenol in xylene.—See A., 1943, III, 257.

Mercaptals and mercaptols of β-thiolpropionic acid. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**, No. 8, 15 pp.).—*Mercaptals* from SH·[CH_2]$_2$·CO_2H (**I**) and the following aldehydes are described: CH_2O, m.p. 142—143°, MeCHO, m.p. 62—63° (decomp.), EtCHO, m.p. 93—94·5°, CHO·CO_2H, m.p. 131—132°, PhCHO, m.p. 88—89·5°, 4 : 3 : 1-OH·C_6H_3(OMe)·CHO, m.p. 123—124°, 3 : 4 : 1-(OMe)$_2$$C_6H_3$·CHO, m.p. 85—88°, 3 : 4 : 1-CH_2O_2·C_6H_3·CHO, m.p. 104—105°, CH_2Ph·CHO, m.p. 109—110°, Ph·[CH_2]$_2$·CHO, m.p. 72—73°, CHPh:CH·CHO, m.p. 93—95°, and furfuraldehyde, m.p. 87—88°. *Mercaptols* from (**I**) and the following ketones are prepared: $COMe_2$, m.p. 88—89°, COMeEt, m.p. 53—54°, $COEt_2$, m.p. 97—98°, AcO$_2$H, m.p. 147—148° (*semi-mercaptol*, m.p. 91·5—92°, first formed), CH_2Ac·CO_2H, m.p. 129—130° (decomp.) (from CH_2Ac·CO_2Et), Ac·[CH_2]$_2$·CO_2H, m.p. 142—143°, *cyclo*hexanone, m.p. 96—97°, COPhMe, m.p. 111—112°, CH_2Ph·COMe, m.p. 117—118°, $COPh_2$, m.p. 147·5—148·5°, BzO$_2$H, m.p. 161—162° (decomp.). Arabinose did not react. M. H. M. A.

Direct introduction of the chloroformyl (·COCl) group into acid chlorides.—See A., 1943, II, 134.

Condensations. XVIII. Acylation of the anions of certain esters with ethyl carbonate. C. R. Hauser, B. Abramovitch, and J. T. Adams (*J. Amer. Chem. Soc.*, 1942, **64**, 2714—2715; cf. A., 1943, II, 81).—Adding Bu^{γ}OAc and then Et_2CO_3 to NaCPh$_3$–Et_2O–N_2 gives *Et Bu$^{\gamma}$ malonate* (54%), b.p. 93—95°/17 mm. *Bu$^{\gamma}$ propionate* (prep. from Bu^{γ}OH and EtCOCl in NPhMe$_2$; 63% yield), b.p. 118—118·5°, gives similarly *Et Bu$^{\gamma}$ methylmalonate* (72%), b.p. 94—95°, and CH_2Bu^{γ}·CO_2Et gives *Et$_2$* tert.-*butylmalonate* [*Et α-carbethoxy-ββ-dimethyl*-n-*butyrate*] (47%), b.p. 102—104°/11 mm. R. S. C.

Preparation of ethyl ethylmalonate and Δ¹-*cyclo*hexenylmalonate from the corresponding oxaloacetates.—See A., 1943, II, 133.

Dipole moments of diethyl esters of substituted malonic acids, and of glyptals.—See A., 1943, I, 116.

Alkylsuccinic acids. II. *n*-Amyl- and *n*-decyl-succinic acids. S. U. Mehta and K. S. Nargund (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 134—135; cf. A., 1942, II, 278).—*n-Heptane-αaβ-tricarboxylic acid*, m.p. 134—135°, at 190° yields *n-amylsuccinic acid*, m.p. 81—82° (*anhydride*, b.p. 140°/13 mm.; *monoanilide*, m.p. 112—115°; *mono*-p-*toluidide*, m.p. 122—124°). *n-Dodecane-αaβ-tricarboxylic acid*, m.p. 135°, yields *n-decylsuccinic acid*, m.p. 94—95° (*anhydride*, m.p. 70—71°; *monoanilide*, m.p. 103—104°; *Et$_2$* ester, b.p. 175—180°/13 mm.). A. Lt.

Mechanism of photolysis of propaldehyde.—See A., 1943, I, 133.

Keto-ethers. X. α-Methoxyethyl alkyl ketones. W. P. Wallace and H. R. Henze (*J. Amer. Chem. Soc.*, 1942, **64**, 2882; cf. A., 1942, II, 300).—MeOH (1), paraldehyde (1 equiv.), and dry HCl give CHMeCl·OMe (95%), b.p. 70—72°/746 mm., converted in dry Et_2O into OMe·CHMe·CN (36%), b.p. 117—119°/740 mm., which with MgRBr in Et_2O gives 13—63% of Me, b.p. 115—116°/739 mm. (141°), and Et α-methoxyethyl ketone, b.p. 135—136°/750 mm. (120·5°). *OMe·CHMe Pr$^{\alpha}$*, b.p. 154—155°/746 mm. (169°), *Pr$^{\beta}$*, b.p. 57—58°/31 mm. (146°), *Bu$^{\alpha}$*, b.p. 81—82°/36 mm. (154°), *Bu$^{\beta}$*, b.p. 51—52°/9 mm. (145°), sec.-*Bu*, b.p. 76—77°/36 mm. (127°), *Bu$^{\gamma}$*, b.p. 54—64°/34 mm. (121°), n-, b.p. 60—61°/3 mm. (144°), and iso-*amyl ketone*, b.p. 64—65°/6 mm. (154·5°), figures in parentheses being m.p. of the *semicarbazones*. M.p. are corr. R. S. C.

Catalytic interchange of groups in aliphatic amines.—See A., 1943, I, 132.

Preparation of mixed *sec.* aliphatic amines, NHRR′. H. R. Henze and D. D. Humphreys (*J. Amer. Chem. Soc.*, 1942, **64**, 2878—2880).—Condensation of NH_2Bu^{α} with the appropriate ketone or aldehyde and hydrogenation (Raney Ni; 75°/3000 lb.; cf. A., 1940, II, 722) of the crude product gives 31—52% of NHEtBu$^{\alpha}$, b.p. 111—112°/747 mm., NHPr$^{\alpha}$Bu$^{\alpha}$, b.p. 138—139°/745 mm., iso-*propyl*-n-*butylamine*, b.p. 124—125°/748 mm., n-*butyl*-iso*butyl*-, b.p. 150—151°/738 mm., -sec.-*butyl*-, b.p. 149—149·5°/751 mm., -*n*-amyl-, b.p. 180—182°/743 mm., and -*iso*amyl-amine, b.p. 175—177°/745 mm. NH_2Me and Pr$^{\alpha}$CHO lead to NHMeBu$^{\alpha}$ (26%), b.p. 89—91°/750 mm.), and NMeBu$^{\alpha}_2$. CH_2Br·COMe (**I**) and NHBu$^{\alpha}$R (2 mols.) in Et_2O give 41—74% of N-*methyl*-, b.p. 76°/19 mm. (104—104·5°), -*ethyl*-, b.p. 87—88°/17 mm. (126·5—127·5°), -n-, b.p. 90—91°/12 mm. (130·5—131°), and -iso-*propyl*-, b.p. 92—94·5°/13 mm. (151—152°), -N-*butylaminoacetone*, N-n-*butyl*-N-iso-, b.p. 106—107°/14 mm. (139—139·5°), and -sec.-*butyl*-, b.p. 105—106°/12 mm. (172—172·5°), -n-, b.p. 110—111°/6 mm. (107·5—108·5°), and -iso-*amyl*-, b.p. 80—82°/3 mm. (116—117°), *-aminoacetone*, figures in parentheses being m.p. of the *semicarbazones*. Picrates and hydrochlorides were oils. Other physical data of the products are recorded. M.p. and b.p. are corr. R. S. C.

Azides of organic bases. A. Cirulis and M. Straumanis (*J. pr. Chem.*, 1942, [ii], **161**, 65—76).—NH_2Me,HCl, NaN_3, and H_2O containing a little NH_2Me at 100—150°, or 33% aq. NH_2Me and HN_3 (from NaN_3–H_2SO_4), give *methylamine azide*, m.p. 140°. Similarly prepared are *ethyl*-, m.p. 65°, n-*propyl*-, m.p. 85°, n-, m.p. 85°, and iso-*butyl*-, m.p. 115°, *allyl*-, *dimethyl*-, m.p. 74°, *diethyl*-, m.p. 48°, *di*-n-*propyl*-, m.p. 101°, *di*-n-, m.p. 143°, and -iso*butyl*-, m.p. 135°, and *di*-iso*amyl-amine azide*, m.p. 176°; *ethylene*-[(CH_2·NH_3)$_2$](N_3)$_2$, m.p. 172° (decomp.), and *propylene-diamine azide*, m.p. 166° (decomp.); *αγ-diaminopropan-β-ol azide*, m.p. 115°; *guanidine*, m.p. 46°, and *amidoguanidine azide*, m.p. 123°; *benzylamine*, m.p. 157°, *piperidine*, m.p. ~60° (decomp.), *amino*cyclo*hexane*, m.p. 112—113°, *piperazine*, m.p. 180—181°, and "*nitron*" *azide*, decomp. 160°. A. T. P.

Muscarine. II. F. Kögl and H. Veldstra [and, in part, P. J. van der Laan] (*Annalen*, 1942, **552**, 1—36; cf. A., 1931, 1279).—Unsuccessful attempts are described to discriminate between the formulæ OH·CHEt·CH(NMe$_3$·OH)·CHO and OH·NMe$_3$·CHEt·CH(OH)·CHO for muscarine (**I**). Passage of Br vapour through CHMe:CH·CHO in 75% aq. MeOH at <0° gives *α-bromo-β-methoxybutaldehyde* (**II**), b.p. 56·5°/1·8 mm., oxidised by $K_2Cr_2O_7$ and dil. H_2SO_4 to *α-bromo-β-methoxybutyric acid*, m.p. 60°, which is transformed by KOH–EtOH into OMe·CMe:CH·CO_2H, m.p. 128·5°, hydrolysed by dil. H_2SO_4 at 100° to $COMe_2$. $NHMe_2$ in cold Et_2O converts (**I**) into *α-dimethylamino-β-methoxybutaldehyde*, b.p. 34—35°/0·6 mm., which in MeOH gives the *methiodide*, m.p. 160—161°, which reduces Fehling's solution but colours magenta–H_2SO_3 slowly if at all. It is transformed into the corresponding hygroscopic *chloride*, m.p. 130°, softens at 125° (*aurichloride*, m.p.

70—80°), *reineckate*, and *aurichloride*, m.p. 116° (decomp.). $CHEt:CH\cdot CHO$ similarly affords *α-bromo-β-methoxy-*n*-valeraldehyde*, b.p. 58—60°/0·85 mm., and thence *α-dimethylamino-β-methoxy-*n*-valeraldehyde*, b.p. 40—42°/0·4 mm. [*methiodide*, m.p. 186—187° (decomp.); *reineckate*; *aurichloride*, m.p. 148° (decomp.)]. Pharmacologically these compounds are inactive on the isolated frog heart in comparison with (**I**). Gradual addition of HOCl to $CHEt:CH\cdot CO_2H$ in H_2O at 0° leads to *α-chloro-β-hydroxy-*n*-valeric acid* (**II**), b.p. 139°/3 mm., m.p. 66° (*Et* ester, b.p. 92°/2 mm.; *Ac* derivative, m.p. 99°); these substances do not give homogeneous products with NMe_3. (**I**) is converted by NaOH in aq. EtOH into *Na αβ-epoxy-*n*-valerate*, transformed by 33% $NHMe_2$ at 100° into *β-dimethylamino-α-hydroxy-*n*-valeric acid* (**III**), m.p. 200° (decomp.), also obtained from (**II**) and 33% $NHMe_2$–C_6H_6 at 100°. (**III**) is oxidised by $Pb(OAc)_4$ in AcOH to *α-dimethylamino-*n*-butaldehyde*, b.p. 44—45°/18 mm., which strongly reduces Fehling's solution; the corresponding *methiodide*, m.p. 185—186°, reduces warm Fehling's solution but does not give a colour with magenta–H_2SO_3. *Crotonaldehyde Me_2 acetal*, b.p. 116—119°, and HOCl in H_2O at 0° afford *α-chloro-β-hydroxy-*n*-butaldehyde Me_2 acetal*, b.p. 78°/0·6 mm., which with NaI and 33% $NHMe_2$–MeOH at 100° yields *β-dimethylamino-α-hydroxy-*n*-butaldehyde Me_2 acetal*, b.p. 80°/0·5 mm., m.p. ~30°; this gives a non-cryst. methiodide and methochloride (**IV**) (corresponding *aurichloride*, m.p. 90°). (**IV**) is hydrolysed by conc. HCl at room temp. to the non-cryst. aldehyde methochloride (corresponding *aurichloride*, m.p. 195—196°). *α-Bromo-*n*-valeraldehyde Me_2 acetal*, b.p. 94°/30 mm. (corresponding *Et_2 acetal*, b.p. 97°/23 mm.), is converted into *Δ$^{\alpha}$-pentenal Me_2 acetal*, b.p. 68°/45 mm. (*Et_2 acetal*, b.p. 62°/16 mm.), which gives *α-chloro-β-hydroxy-*n*-valeraldehyde Me_2 acetal*, b.p. 71°/0·3 mm. (*Et_2 acetal*, b.p. 88°/0·3 mm.), and thence *β-dimethylamino-α-hydroxy-*n*-valeraldehyde Me_2 acetal* (**V**), b.p. 77°/0·3 mm. [*Et_2 acetal* (**VI**), b.p. 86°/0·3 mm.]. (**V**) gives a non-cryst. methiodide and methochloride (corresponding *aurichloride*, m.p. ~90°) whilst (**VI**) yields a *methiodide*, m.p. 125°, converted into the methochloride (aurichloride, m.p. ~90°). *β*-Dimethylamino-α-hydroxy-*n*-valeraldehyde methochloride reduces Fehling's solution and fairly readily gives a violet colour with magenta–H_2SO_3; the corresponding *reineckate* is cryst. but the m.p. of the *aurichloride*, ~175°, varies with different specimens. Dipropenyl glycol is oxidised by BzO_2H in light petroleum (b.p. 40—60°) to *βγ-ζη-diepoxyoctane-δε-diol* (**VII**), m.p. 138—140°, with some *βγ-epoxyoctane-δεζη-tetraol*, m.p. 178°. (**VII**) is oxidised by $Pb(OAc)_4$ in warm *n*-C_5H_{12} to *βγ-epoxybutanol*, b.p. 87—88°/400 mm., which liberates I from KI in AcOH. It is slowly transformed by 15% $NHMe_2$–H_2O into *β*-dimethylamino-α-hydroxy-*n*-butaldehyde, converted through the non-cryst. methiodide into the *reineckate* and thence into a non-homogeneous aurichloride.

The isolation of (**I**) from toadstool has been improved. In AcOH muscarine chloride has the simple mol. wt. *Muscarine aurichloride* has m.p. 115—117°. H. W.

Glucosamine. α- and β-Glucosamine and penta-acetylglucosamine. O. Westphal and H. Holzmann [with E. Reiche] (*Ber.*, 1942, **75**, [*B*], 1274—1282).—The action of NEt_3 and EtOH on a suspension of powdered glucosamine hydrochloride (**I**) from lobster shells (α-form) for 2 days at as low a temp. as possible followed by 3 or 4 similar treatments with decreasing amounts of NEt_3 gives *α-glucosamine* (**II**), m.p. 88° (corr.), $[\alpha]_D^{20}$ +100° to +47·5° (equilibrium val.) in H_2O in 30 min. The mutarotation is ~50 times as rapid as that of glucose. Similar treatment of (**I**) with $NHEt_2$ leads to *β-glucosamine* (**III**), m.p. 110—111° (corr.), $[\alpha]_D^{20}$ +28° to +47·5° (equilibrium val.) in H_2O in 30 min. Thus obtained (**III**) is not quite homogeneous. In EtOH containing piperidine at 40° and at 60° there is a gradual conversion of (**II**) into (**III**), which itself undergoes chemical alteration. In contact with abs. EtOH at 40° there is a complete conversion of (**II**) into pure (**III**) and by this method (**III**) as obtained above is converted into the homogeneous material, m.p. 120° (corr.), $[\alpha]_D^{20}$ +14° to +47·5° (equilibrium val.) in H_2O in 30 min. (**II**) is transformed by prolonged contact with Ac_2O–C_5H_5N at room temp. into *α*-penta-acetylglucosamine (**IV**), m.p. 139°, $[\alpha]_D^{20}$ +92·0° in $CHCl_3$, whilst under similar conditions (**III**) gives *β*-penta-acetylglucosamine (**V**), m.p. 186°. (**III**) is converted by Ac_2O and C_5H_5N containing a little NEt_3 into a mixture of (**IV**) and (**V**). H. W.

***NN*-Di-*n*-butylhydroxylamine and its oxalate.** V. H. Dermer and O. C. Dermer (*J. Amer. Chem. Soc.*, 1942, **64**, 3057).—Adding NO_2 in Et_2O to well-stirred $MgBu^{\alpha}Br$ in Et_2O gives *NN-di-*n*-butylhydroxylamine*, m.p. 52·5—53° (reduces Ag, Cu^{II}, and Au^{III}), isolated as *oxalate*, m.p. 144—144·5°, which can be titrated as free acid. R. S. C.

Oxidation of geometrically isomeric platinoglycines. A. A. Grünberg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 57—58).—K_2PtCl_6 and *cis*-$(NH_2\cdot CH_2\cdot CO_2)_2Pt$ give yellow crystals of *cis*-$Pt(NH_2\cdot CH_2\cdot CO_2H)_2Cl_2$; the *trans*-form is similarly obtained: the configurations are proved by reduction with $K_2C_2O_4$. F. R. S.

Benzoylation and resolution of alanine. M. Levy and A. H. Palmer (*J. Biol. Chem.*, 1942, **146**, 493—495).—A modification in the prep. of benzoyl-*dl*-alanine by BzCl and NaOH and its resolution by brucine and strychnine are described. The equation $[\alpha]_D = 35{\cdot}2° + 1{\cdot}0c$ (c = concn. in g. per 10 ml.) expresses the optical activity of benzoylalanine in one equiv. of alkali. Alanine in excess of HCl has $[\alpha]_D^{20}$ 14·5°, the sign of the rotation being opposite in sense to the configuration. The equations of Pacsu and Mullen (A., 1941, II, 36) should be discarded. W. McC.

Interaction of formaldehyde with *l*(−)-asparagine. D. C. Carpenter and F. E. Lovelace (*J. Amer. Chem. Soc.*, 1942, **64**, 2899—2902).—Interaction of *l*-asparagine (**I**) + NaOH (1 mol.) with varying amounts of CH_2O is followed by determination of pH, α, and unchanged CH_2O. (**I**) reacts first with 1 mol. of CH_2O to give the CH_2: compound and then with a second mol. to give a compound of unknown structure which readily loses CH_2O. R. S. C.

Oxidation of amino-acids by hydrogen peroxide in formic acid. G. Toennies and R. P. Homiller (*J. Amer. Chem. Soc.*, 1942, **64**, 3054—3056).—H_2O_2 in 88% HCO_2H forms the max. amount of HCO_3H in 1 hr. at room temp. This reagent rapidly oxidises *dl*-methionine (2·05 O consumed; sulphone formed), *dl*-cystine (5·25 O consumed; cysteic acid formed), and *l*-tryptophan (3·05 O consumed; ? product), but only very slowly affects 16 other NH_2-acids. R. S. C.

Synthesis of peptides of *l*-serine. J. S. Fruton (*J. Biol. Chem.*, 1943, **146**, 463—470).—*l*-Serine, $[\alpha]_D^{27}$ +14·8° in 2N-HCl, or its Me ester, and $CH_2Ph\cdot O\cdot COCl$, give *carbobenzyloxy-*l*-serine*, m.p. 121°, $[\alpha]_D^{20}$ +5·6° in AcOH, or its Me ester, and thence *carbobenzyloxy-*l*-serinhydrazide* (**I**), m.p. 181°, and -l-*serinamide* (**II**), m.p. 132—133°, $[\alpha]_D^{20}$ +14·4° in EtOH. (**I**) is converted into the azide (**III**), which in dry EtOAc with $NH_2\cdot CH_2\cdot CO_2CH_2Ph$ in Et_2O at room temp. affords *carbobenzyloxy-*l*-serylglycine CH_2Ph ester*, m.p. 102°, hydrogenated (Pd–C; MeOH) to l-*serylglycine*, $[\alpha]_D^{26}$ +30·2° in N-HCl. The latter is also obtained by hydrogenating *carbobenzyloxy-*l*-serylglycine*, m.p. 131°, prepared from its *Et* ester, m.p. 105—107°, and N-NaOH–MeOH at room temp. (**III**) and *l*-alanine Me ester give, through its *Me* ester, m.p. 113—114°, *carbobenzyloxy-*l*-seryl-*l*-alanine* (+0·5H_2O), m.p. 161—162° after 3 hr. at 100° in vac.; hydrogenation yields l-*seryl-*l*-alanine*, $[\alpha]_D^{20}$ −30·4° in N-HCl. Also prepared from (**III**) are *carbobenzyloxy-*l*-seryl-*l*-serine*, m.p. 169—171° (*Me* ester, m.p. 143—145°), *l*-seryl-*l*-serine, $[\alpha]_D^{25}$ +14·2° in N-HCl, *carbobenzyloxy-*l*-seryl-*l*-glutamic acid*, m.p. 152—153° (*Et_2* ester, m.p. 85—86°), and l-*seryl-*l*-glutamic acid*, $[\alpha]_D^{20}$ −9·4° in N-HCl. Partial hydrolysis of dipeptides containing *l*-serine occurs by aq. extract of swine intestinal mucosa at 40°. (**II**) is hydrolysed by cysteine–papain or by cysteine–ox spleen cathepsin; the hydrolysis follows the kinetics of a first order reaction. (**III**) in EtOAc at 40° gives *4-carbobenzyloxyamino-oxazolid-2-one*, m.p. 171°, converted by 10% HCl into $CH_2Ph\cdot O\cdot CO\cdot NH_2$. A. T. P.

Tetranucleotide of yeast- and thymo-nucleic acid.—See A., 1943, II, 143.

Acrylonitrile. II. Reactions with ketones. H. A. Bruson and T. W. Riener (*J. Amer. Chem. Soc.*, 1942, **64**, 2850—2858; cf. A., 1943, II, 62).—In presence of a little $CH_2Ph\cdot NMe_3\cdot OH$ (**I**) or KOH etc., CH_2:CH·CN (**II**) condenses with COArMe to give $COAr\cdot C([CH_2]_2\cdot CN)_3$ and thence the tricarboxylic acid, with numerous cyclic ketones, all the H adjacent to the CO being substituted, and with $COMe\cdot CH_2R$ to give $COMe\cdot CR([CH_2]_2\cdot CN)_2$ and then some substitution in the Me. Dropping (**II**) into COArMe and a little (**I**) in dioxan or $Bu^{\gamma}OH$ at 25—40° gives *γ-benzoyl-*, m.p. 128—129°, *γ-2-naphthoyl-*, m.p. 122°, *γ-*p*-phenylbenzoyl-*, m.p. 178°, *γ-*p*-anisoyl-*, m.p. 133°, *γ-*p*-toluoyl-*, m.p. 161—162°, *γ-mesitoyl-*, m.p. 126°, *γ-*p*-chlorobenzoyl-*, m.p. 141—142°, and *γ-*p*-bromobenzoyl-*, m.p. 151—152°, *-γ-β′-cyanoethylpimelodinitrile* and thence (boiling aq. KOH) the corresponding *tricarboxylic acids*, m.p. 143—145°, 173—174°, 236—238°, 219°, 226°, —, 225—227°, and 241—243°, respectively. COPhEt and $COPh\cdot CH_2Ph$ give similarly *γ-benzoyl-γ-methyl-*, m.p. 66°, and *-γ-phenyl-pimelodinitrile*, m.p. 149—150°, hydrolysed to the *pimelic acids*, m.p. 166—167° and 172—173°, respectively. The appropriate cyclic ketone in (**I**)–dioxan or –C_6H_6 or 40% aq. KOH–$Bu^{\gamma}OH$ gives 1-*keto*-2 : 2-*di-β-cyanoethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 80°, 2 : 2 : 6-*tri-β-cyanoethyl*-6-*methyl*cyclo*hexanone*, m.p. 69—70°, 2 : 2 : 5 : 5-*tetra-β-cyanoethyl*cyclo*pentanone*, m.p. 175°, 2 : 2 : 6 : 6-*tetra-β-cyanoethyl*-cyclo*hexanone*, m.p. 165°, -4-*methyl-*, m.p. 138°, -4-tert.-*amyl-*, m.p. 145°, -4-*aαγγ-tetramethyl-*n*-butyl-*, m.p. 155—156°, and -4-cyclo*hexyl*-cyclo*hexanone*, m.p. 223—224°, and 4 : 4-*di-β-cyanoethyl*-2 : 2 : 5 : 5-*tetramethyltetrahydrofuran*-3-*one*, m.p. 153°, alkaline hydrolysis then yielding 2 : 2 : 5 : 5-*tetra-β-carboxyethyl*cyclo*pentanone*, +H_2O, m.p. 173°, 2 : 2 : 6 : 6-*tetra-β-carboxyethyl*cyclo*hexanone*, m.p. 179—180°, -4-*methyl-*, m.p. 205—206°, -4-tert.-*amyl-*, m.p. 205°, -4-*aαγγ-tetramethyl-*n*-butyl-*, m.p. 185—186°, and -cyclo*hexyl*-cyclo*hexanone*, m.p. 205—206°, and 4 : 4-*di-β-carboxyethyl*-2 : 2 : 5 : 5-*tetramethyltetrahydrofuran*-3-*one*, m.p. 170—171°. With 1—2 mols. of (**II**), cyclohexanone gives 2-*β-cyanoethyl-*, b.p. 138—142°/10 mm., and 2 : 2- (or 2 : 6-)*di-β-cyanoethyl*-cyclo*hexanone*, m.p. 69°. $CO(CH_2Ph)_2$ gives only a syrup, yielding, by hydrolysis, *γε-diphenyl-γ-β′-carboxyethyl-*n*-heptan-δ-one-γη-dicarboxylic acid*, m.p. 205°; similarly, $COEt_2$ gives only *aη-dicyano-γε-dimethyl-γ-β′-cyanoethyl-*n*-heptan-γ-one*, m.p. 90—91°, and thence

the *tricarboxylic acid*, m.p. 116°. COMeEt and (**II**) in KOH–MeOH–Bu$^{\gamma}$OH give *γ-acetyl-γ-methylpimelodinitrile* (**III**), m.p. 67°, the structure of which is proved by hydrolysis to *γ-acetyl-γ-methylpimelic acid*, m.p. 125°, which with KOCl–NaOH at 60—70° gives $CHCl_3$ and *γ-carboxy-γ-methylpimelic acid*, m.p. 111°. Further reaction of (**III**) with (**II**) gives *αη-dicyano-γ-methyl-γε-di-β′-cyanoethyl*-n-*heptan*-δ-*one*, m.p. 84—85°. COMePr$^{\alpha}$ and (**II**) give *γ-acetyl-γ-ethylpimelodinitrile* (**IV**), m.p. 109°, and *αη-dicyano-γ-ethyl-γ-β′-cyanoethyl*-n-*heptan*-δ-*one*, m.p. 90—91°. Hydrolysis of (**IV**) yields *γ-acetyl-*, m.p. 112—113°, and oxidation gives *γ-carboxy-γ-ethylpimelic acid*, m.p. 172°. Similarly are obtained *γ-acetyl-γ-*iso*propyl-*, m.p. 101°, b.p. 200—205°/2 mm., *-γ-*n-*butyl-*, m.p. 63°, b.p. 205—210°/2 mm., and *γ-*n-*amyl-pimelodinitrile*, m.p. 47°, b.p. 195—200°/1 mm., *γ-acetyl-γ-*iso*propyl-*, m.p. 148°, *-γ-*n-*butyl-*, m.p. 60—61°, and *-γ-*n-*amyl-pimelic acid*, m.p. 73—74°, *γ-carboxy-γ-*iso*propyl-*, m.p. 160—161°, *-γ-*n-*butyl-*, m.p. 125°, and *-γ-*n-*amyl-pimelic acid*, m.p. 114—115°. $COMe_2$ yields *γ-acetyl-γ-β′-cyanoethylpimelodinitrile* (**V**), m.p. 154°, and then *αη-dicyano-γγ-di-β′-cyanoethyl*-n-*heptan*-δ-*one*, m.p. 121—122°, and a resin containing perhaps $(CN\cdot[CH_2]_2)_{5-6}$ compounds. (**V**) yields as above *γ-acetyl-*, m.p. 149—150°, and *γ-carboxy-γ-β′-carboxyethylpimelic acid*, softens 182°, m.p. 192°. $COMe\cdot CH_2Ph$ gives *γ-acetyl-γ-phenylpimelodinitrile*, m.p. 109—110°, *γ-acetyl-*, m.p. 171—172°, and *γ-carboxy-γ-phenylpimelic acid*, m.p. 154°. $CH_2Ac\cdot CO_2R$ gives *γ-acetyl-γ-carbomethoxy-*, m.p. 154°, and *-γ-carbethoxy-pimelodinitrile*, m.p. 82°. Camphor, *iso*phorone, and $COBu^{\beta}_2$ do not react with (**II**). $CH_2{:}CMe\cdot CN$ or $CHMe{:}CH\cdot CN$ cannot replace (**II**). R. S. C.

II.—SUGARS AND GLUCOSIDES.

Phosphorylations and reactions with triphenylmethyl chloride. K. Zeile and W. Kruckenberg (*Ber.*, 1942, **75**, [*B*], 1127—1140).—$NHPh\cdot POCl_2$ and glucose 1 : 2 : 3 : 4-tetra-acetate in C_5H_5N at room temp. with subsequent addition of EtOH afford *Et tetra-acetyl-glucosidoanilino*-N-*phosphonate*, m.p. 116—117°, $[\alpha]_D^{18}$ +25° in C_6H_6. In C_5H_5N $(NHPh)_2POCl$ (**I**) and $(NHPh)_2PO\cdot OH$ give *pyrophosphor-tetra-anilide*, m.p. 222°, also obtained when a solution of (**I**) in C_5H_5N is pptd. by H_2O. Cholesterol and $NPh_2\cdot POCl_2$ (1 : 1) in C_5H_5N at 100° yield *cholesteryl diphenylamine*-N-*phosphonate*, m.p. 173°, whereas the reactants (2 : 1) afford tetracholesteryl pyrophosphate, $C_{106}H_{184}O_8P_2,2H_2O$, m.p. 208°. $NPh_2\cdot POCl_2$ and α-methylglucoside in C_5H_5N at room temp. give 3 : 6-*diphenylamine*-N-*phosphoryl-α-methylglucoside*, m.p. 251°, $[\alpha]_D^{18}$ −18° in C_5H_5N, which is converted by Ac_2O in abs. C_5H_5N at room temp. into the 2 : 4-*diacetate*, m.p. 138°, $[\alpha]_D^{21}$ −80° in C_6H_6, but does not react with CPh_3Cl–C_5H_5N at 100°. Treatment of xylose with CPh_3Cl and C_5H_5N at 100° gives a product which cannot be worked up successfully by crystallisation but is separated chromatographically (Al_2O_3) into *mono-*, m.p. 98°, softens at 80°, and *di-(triphenylmethyl)-xylose*, m.p. 100°, softens at 88°, $[\alpha]_D^{17}$ +4·16° in C_6H_6. Indef. m.p., indistinct cryst. form, and a pronounced tendency to retain solvent make the homogeneity of these compounds very doubtful. Treatment of the crude material with BzCl leads to the isolation of 1 : 5-*di(triphenylmethyl)xylose* **2 : 3**-*dibenzoate* (**I**), m.p. 235°, $[\alpha]_D^{17}$ +31° in C_6H_6. Under similar conditions arabinose yields a *CPh*$_3$ derivative, m.p. 93°, softens at 86°, $[\alpha]_D$ ±0° in C_5H_5N, converted into a *diacetate*, m.p. 73°, softens at 68°, and a *dibenzoate*, m.p. 210°. *Di(triphenylmethyl)*-d-*ribose*, m.p. 211°, and its *diacetate*, m.p. 285°, are described. Fructose affords *tri(triphenylmethyl)*-d-*fructose*, m.p. 100—112°, $[\alpha]_D^{18}$ +39·7° in C_6H_6 (*diacetate*, m.p. 97—99°, $[\alpha]_D^{18}$ +28° in $CHCl_3$). *Tri(triphenylmeithyl)*-l-*sorbose diacetate* has m.p. 100—103°, $[\alpha]_D^{18}$ +17·2° in $CHCl_3$. (**I**) is transformed by HCl–C_6H_6 at room temp. into 1-*triphenylmethyl*-d-*xylose* 2 : 3-*dibenzoate*, m.p. 165°, $[\alpha]_D^{29}$ −4·87° in C_5H_5N, which with *p*-$C_6H_4Me\cdot SO_2Cl$ in C_5H_5N at room temp. yields the 5-p-*toluenesulphonate*, m.p. 171° diminishing to 165° on exposure to air, $[\alpha]_D^{19}$ +14·4° in C_5H_5N. Piperidine and arabinose in abs. EtOH at 40° yield *piperidine*-N-*arabinoside*, m.p. 104°, $[\alpha]_D^{20}$ −15·4° in C_5H_5N, which reverts to its components when exposed to air. The non-cryst. piperidine-*N*-xyloside is characterised as the very hygroscopic *hydrochloride*, m.p. 125°, $[\alpha]_D^{18}$ +9·6° in EtOH. This is converted by CPh_3Cl in abs. C_5H_5N at room temp. into 1-*deoxy*-5-*triphenylmethyl*-1-*piperidino*-d-*xyloketose*, m.p. 68°, $[\alpha]_D^{19}$ −4·8° in EtOH [*hydrochloride* (+0·5H_2O), m.p. 148°, $[\alpha]_D^{19}$ −42·1° in EtOH]. H. W.

Preparation of hexose diphosphate, hexose monophosphate, and phosphoglyceric acid. K. P. DuBois and V. R. Potter (*J. Biol. Chem.*, 1943, **147**, 41—46).—Hexose diphosphate and monophosphate and phosphoglyceric acid are prepared from a single fermenting mixture, and PhMe-treated fresh brewers' yeast is used, instead of the usual Lebedev extract. The rate of formation, and method of isolation, of the P esters from glucose, Na_2HPO_4, NaH_2PO_4, and PhMe at pH 7·0 at 37° are examined (cf. Neuberg *et al.*, A., 1943, II, 83). A. T. P.

Synthesis of 5-*D*-glucosido-*D*-arabinose. N. S. MacDonald and W. L. Evans (*J. Amer. Chem. Soc.*, 1942, **64**, 2731—2733).—Gentiobioseoxime (prep. described), amorphous, with NaOAc–Ac_2O at 105—120° gives *gentiobionitrile octa-acetate* (35%), m.p. 108—109°, $[\alpha]_D^{25}$ +8·60° in $CHCl_3$ (with $AgNO_3$–MeOH–H_2O–NH_3 at room temp. gives quantitatively AgCN), converted by NaOMe–MeOH–$CHCl_3$ at 0°, removal of HCN, and acetylation into 5-D-*glucosido*-D-*arabinose hepta-acetate*, β- (**I**) (32%), m.p. 161—162°, $[\alpha]_D^{25}$ −14·4° in $CHCl_3$, and *α-form* (a little), m.p. 132—133°, $[\alpha]_D^{25}$ +23·1° in $CHCl_3$. NaOMe–MeOH at 0° hydrolyses (**I**) to the hygroscopic, amorphous free sugar, which mutarotates to $[\alpha]_D^{30}$ −31·4° in H_2O, reduces Fehling's solution, gives a *phenylosazone*, m.p. 209—210°, and with NaOMe–MeOH and then boiling dil. HCl gives 100% of pentose (gentiobiose gives none; *D*-arabinose tetra- and *D*-glucose penta-acetate give 100%). M.p. are corr. R. S. C.

Stability of β-methylmaltoside towards hot alkali. T. J. Schoch, E. J. Wilson, jun., and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 2871—2872).—The 1 : 4-α-glucoside linking in β-methylmaltoside and Ca maltobionate and the 1 : 4-β-linking in β-methylcellobioside are stable to hot alkali. Thus, attack on starch by alkali must occur at the terminal CHO (cf. Evans *et al.*, A., 1930, 326). R. S. C.

Constitution of arabo-galactan. IV. Structure of the repeating unit. E. V. White (*J. Amer. Chem. Soc.*, 1942, **64**, 2838—2842; cf. A., 1942, II, 397).—Arabogalactan (**I**) and Me_2SO_4–30% NaOH–N_2 give a Me ether (OMe 44·4%), which by partial hydrolysis (boiling 0·14N-HCl–MeOH) yields products separated into fractions by light petroleum and Et_2O. The monosaccharides are investigated by complete methylation and then methanolysis. (**I**) yields, *inter alia*, 2 : 3 : 5-trimethylmethyl-*l*-arabinoside, octa- and hepta-methyl-6-*d*-galactosidogalactose, and a residue containing mainly 2 : 4-dimethylgalactose anhydride units. The dimethylated units are united more through $C_{(1)}$–$C_{(6)}$ than through $C_{(1)}$–$C_{(3)}$, there being also some $C_{(1)}$–$C_{(3)}$–$C_{(6)}$ linking. A complete structure is tentatively suggested. R. S. C.

Polysaccharides of carragheen moss (*Chondrus crispus*). **I. Linkage of *d*-galactose residues and ethereal sulphate.** J. Buchanan, E. E. Percival, and E. G. V. Percival (*J.C.S.*, 1943, 51—54).—The products of methylation and hydrolysis of extracts of carragheen moss by cold and hot H_2O have been studied. The isolation of β-methylglucoside tetra-acetate, tetramethylglucopyranose, and glucosazone shows that small amounts of glucose are present. Colorimetric determinations on galactose-free syrups indicate ~20% of ketoses. From the isolation of galactosazone, 6-methylgalactosazone, and tetramethyl-*d*-galactopyranoseanilide, it is inferred that 2-methyl- and 2 : 6-dimethyl-galactose are present, and that galactose residues constitute 31% of the cold, 33% of the hot, extract. From the slow removal of SO_4 by NaOH and the fact that the OH groups on $C_{(2)}$ and $C_{(6)}$ are free, it is concluded that the SO_4 residue is attached to $C_{(4)}$, while the galactose residues are joined by positions 1 and 3. A. Li.

Polysaccharides of Iceland moss (*Cetraria islandica*). **I. Hemicelluloses.** H. Granichstadten and E. G. V. Percival (*J.C.S.*, 1943, 54—58).—Hydrolysis of the hemicelluloses extracted from Iceland moss by cold 4% NaOH, after removal of lichenin and lichen acids, yields glucose (89), galactose (8), mannose (3), and a uronic (? glucuronic) acid (5%). Methylation, fractionation, and determinations of η show that the " hemicellulose " is a mixture with mean mol. wt. similar to that of lichenin. Hydrolysis of the fractions produces 2 : 4 : 6- (*anilide*, m.p. 162—166°) and other trimethylglucoses, and shows the presence of galacto- and gluco-pyranose end groups. These results, and investigation of positions 2, 6, and 4 by oxidation and amide formation, production of *p*-$C_6H_4Me\cdot SO_2$ derivative, and effect of methanolysis on [α], respectively, show that the hemicelluloses consist chiefly of β-glucose units linked through positions 1 : 2, 1 : 3, 1 : 4, and 1 : 6. A. Li.

Fractionation of starch by selective precipitation with butanol. T. J. Schoch (*J. Amer. Chem. Soc.*, 1942, **64**, 2957—2961).—Defatted starch (150—450 g.) in H_2O (1 l.) is added with stirring to boiling H_2O–BuOH (14 : 2 l.), autoclaved at 18—20 lb., centrifuged to remove 0·4% of insol. matter, and slowly cooled. The ppt. (~22% for maize or potato starch) is removed by centrifuging (and, if desired, purified by similar repptn.); the filtrate yields the sol. portion. The ppt. is spherocryst. (different for maize and potato starches), has a high alkali no., and is more sol. and more liable to gel and retrograde than the sol. part. Other minor differences are also noted. Part of the sol. fraction of maize starch but all that from potato starch undergoes electromigration. The sol. part of potato starch contains all the P, all of which electromigrates. Waxy maize starch gives no insol. fraction. R. S. C.

Causes of the diversity in acid hydrolysis of starch substances. M. Samec and M. Dermelj (*Gazzetta*, 1942, **72**, 145—150; cf. A., 1930, 416; 1931, 941).—Amylo-amylose (**I**), the first sol from potato starch heated with H_2O at 120°, erythro-amylose (**II**), the sol obtained from later fractions on repeated further heating of the residual gels with H_2O, and erythro-granulose (**III**), from Lintner's acid and β-amylase (**IV**), are hydrolysed (*a*) by 0·5N- and (*b*) by 50% H_2SO_4. In (*a*), the reducing power to $KMnO_4$ increases, at first more rapidly with (**II**) than with (**I**), and then vice versa. In (*b*), the velocity coeff. of (unimol.) hydrolysis of (**I**) is approx. const up

to 65% decomp., then increases; of (**II**), increases up to 65% decomp. and then decreases sharply; of (**III**), increases steadily. This diversity is discussed with reference to the structure of the substances; in (**I**), fission of α-1 : 4 glucosidic linkages precedes that of maltose (more rapid); in (**II**), mols. with branched linkings, more slowly attacked, accumulate during hydrolysis; in (**III**), α-1 : 4 glucosidic linkings have already been attacked by (**IV**), and branched linkings are first hydrolysed. E. W. W.

III.—HOMOCYCLIC.

Properties of synthetic lubricating oils. Cyclic hydrocarbons with 22 carbon atoms per molecule. E. Neyman-Pilat and S. Pilat (*Ind. Eng. Chem.*, 1941, **33**, 1382—1390).—2-*Dodecyl*-p-*cymene*, $C_{22}H_{38}$, b.p. 163—164°/1 mm., and -p-*menthane*, $C_{22}H_{44}$, b.p. 159—160°/1 mm., *α-perhydrocarvacryl-β-diisoamylethane*, $C_{22}H_{44}$, b.p. 150—152°/1 mm., and *-β-(1-decahydronaphthyl)ethane*, $C_{22}H_{40}$, b.p. 165—166°/1 mm., *αβ-dicarvacryl-*, $C_{22}H_{30}$, b.p. 155—156°/1 mm., and *αβ-diperhydrocarvacryl-ethane*, $C_{22}H_{42}$, b.p. 153—154°/1 mm., and 1-*dodecyldecahydronaphthalene*, $C_{22}H_{42}$, b.p. 170—171°/1 mm., are synthesised, and physical consts. are determined. The influence of structure on b.p. is studied. Reduction of the aromatic to the corresponding hydroaromatic rings decreases the b.p. for mono- and di-cyclic uncondensed compounds by 3—4°, and for polycyclic compounds by 50°. Branching of the paraffinic side-chain lowers the b.p. by 7—9°. Splitting the side-chain and alkylation of the rings with shorter chains, and introduction of strongly alkylated rings, *e.g.*, perhydrocarvacryl, lowers the b.p. Introduction of unalkylated rings slightly increases the b.p. for condensed naphthenic rings and uncondensed benzene and *cyclo*hexane rings, and the rise in b.p. is appreciable in the case of condensed polycyclic aromatics. Data obtained by synthesis of pure hydrocarbons may be applied to the determination of the general character of the chemical structure of certain oils. A. T. P.

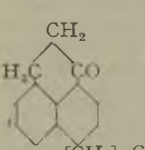
Organic reactions with boron trifluoride. XXVII. Boron trifluoride-catalysed alkylations of halogenobenzenes. G. F. Hennion and V. R. Pieronek (*J. Amer. Chem. Soc.*, 1942, **64**, 2751—2752; cf. A., 1942, II, 84).—Primary or *sec.* alcohols (Pr, Bu, amyl, octyl; *cyclo*hexanol) with PhCl, PhBr, or PhI, BF_3, and P_2O_5 (0·25 mol.) at room temp., raised slowly to 75—85°, give 19·1—66·4% of *p*-halogeno-*sec.*-alkylbenzenes. Yields decrease as the mol. wt. of ROH or halogen increases. Absence of *m*-isomerides is proved by oxidation ($K_2Cr_2O_7$–H_2SO_4–AcOH at 70—75°) to *p*-Hal·C_6H_4·CO_2H only. The *sec.*-alkyl of the product is proved by conversion of C_6H_4Cl·CHMeEt by Na in liquid NH_3 at −34° into *p*-CHMeEt·C_6H_4·NH_2 (10%) and CHPhMeEt (50%). The following (with *n* and *d*) are recorded: *β-p*-chlorophenyl-propane, b.p. 66—72°/11 mm., -butane, b.p. 81—82°/8 mm., *-n*-pentane, b.p. 93—96°/9 mm., and *-n*-octane, b.p. 106—108°/3 mm., *γ-p*-chlorophenyl-*n*-pentane, b.p. 95°/10 mm.; *p*-chlorophenyl*cyclo*hexane, b.p. 145—147°/19 mm.; *β-p*-bromophenyl-propane, b.p. 58—60°/3 mm., -butane, b.p. 96—98°/8 mm., and *-n*-pentane, b.p. 68—72°/3 mm.; *β-p*-iodophenyl-butane, b.p. 92—94°/3 mm., and *-n*-pentane, b.p. 94—97°/3 mm. R. S. C.

Chemical mol. wt. determination of polystyrenes. I. W. Kern and H. Kämmerer (*J. pr. Chem.*, 1942, [ii], **161**, 81—112).—Mol. wt. and Br content of many polystyrenes prepared from styrene and $(p\text{-}C_6H_4Br\text{·}CO)_2O_2$ in absence or presence of Bz_2O_2 are determined, and constitutions are discussed. A. T. P.

Stereoisomeric diphenyloctatetraenes. L. Zechmeister and A. L. LeRosen (*J. Amer. Chem. Soc.*, 1942, **64**, 2755—2759).—Ph·[CH:CH]$_4$·Ph (**I**), m.p. 235—237° (corr.), in boiling C_6H_6 (several hr.), boiling Ph_2O (15 min.), or Ph_2 at 140° (5 hr.) or with I in C_6H_6 at 25° gives partly two isomerides, separated by chromatography (Al_2O_3); irradiation (ultra-violet) in C_6H_6 gives unchanged (**I**) 83% with 12% and 2%, respectively, of the above-named and traces of two further isomerides. All the isomerides regenerate (**I**) when kept in C_6H_6 (proved by change of absorption spectra) or rapidly when solutions are evaporated. Steric interference of the *o*- and γ-H greatly decreases the stability of the *αβ-cis*-forms. Therefore, if (**I**) is the all *trans* form, the commonest isomerides are *trans-cis-trans-trans* and *trans-cis-cis-trans*, respectively. R. S. C.

Arylamine salts as derivatives for identifying aromatic sulphonic acids. O. C. Dermer and V. H. Dermer (*J. Org. Chem.*, 1942, **7**, 581—586).—The alkali sulphonate, a small excess of freshly distilled amine, HCl, and H_2O are heated until dissolution is complete, charcoal is added, and the solution is filtered and cooled. The salts are cryst. from 1% AcOH to minimise hydrolysis. NH_2Ph, *o-* and *p*-C_6H_4Me·NH_2 salts of many aromatic sulphonic acids with their m.p. are listed. Some of the m.p. are inconveniently high and blurred by decomp. and the vals. for isomerides and for homologues and other structurally related compounds often do not vary sufficiently to ensure differentiation but the compounds are exceptionally easy to prepare and crystallise and do not show any tendency to form an oil. Almost none are hydrated. The following appear new: NH_2Ph *salt* of sulphonic acid of 4-*iso*propylnaphthalene-1-, m.p. 190° (decomp.); 2-chlorotoluene-5-, m.p. 229—230·5°; 2-bromotoluene-5-, m.p. 234—236°; *p*-bromobenzene-, m.p. 237—238°; 2-iodotoluene-5-, m.p. 237—239°; 2-chloro-3-nitrotoluene-5-, m.p. 246—248° (decomp.); *p-tert.*-butylbenzene-, m.p. 249—250°; *p*-ethylbenzene-, m.p. 250—251°; 3 : 4-dichlorobenzene-, m.p. 254—255°; *p*-phenoxybenzene-, m.p. 256—258°; 4-bromo-3-nitrobenzene-, m.p. 256—259°; 4-*p*-nitrophenoxybenzene-, decomp. 255—260°; 2 : 4-dinitrobenzene-, m.p. 259—262° (decomp.); 2 : 5-dichlorobenzene-, m.p. 262—263°; diphenyl-4 : 4′-di-, m.p. >330° (decomp.). *o*-Toluidine *salt* of sulphonic acid from: *p*-chlorobenzene-, m.p. 162·5—164°; 3 : 4-dichlorobenzene-, m.p. 170—172°; 2-chlorotoluene-5-, m.p. 173·5—175°; 2-bromotoluene-5-, m.p. 178—180°; *p*-bromobenzene-, m.p. 182—183·5°; 2-iodotoluene-5-, m.p. 190·5—191·5°; *p*-ethylbenzene-, m.p. 192—193°; 4-bromo-3-nitrobenzene-, m.p. 199—200°; *p*-phenoxybenzene-, m.p. 205·5—207°; *p*-4-nitrophenoxybenzene-, m.p. 226—228°; 2-chloro-3-nitrotoluene-5-, m.p. 235—237° (decomp.); 2 : 4-dinitrobenzene-, m.p. 245—246·5° (decomp.); 2 : 5-dichlorobenzene-, m.p. 250—251°; *p-tert.*-butylbenzene-, m.p. 253—254°; diphenyl-4 : 4′-di-, m.p. >330° (decomp.). *p*-Toluidine *salt* of sulphonic acid from: 3 : 4-dichlorobenzene-, m.p. 204—206°; *p*-ethylbenzene-, m.p. 208—209°; *p*-bromobenzene-, m.p. 215—216·5°; 2-chlorotoluene-5-, m.p. 218—220°; 2-iodotoluene-5-, m.p. 220—222°; 2-bromotoluene-5-, m.p. 222—223°; 4-bromo-3-nitrobenzene-, m.p. 235—236° (decomp.); 2-chloro-5-nitrotoluene-, m.p. 238—240° (decomp.); 2 : 4-dinitrobenzene-, m.p. 245—247° (decomp.); 2 : 5-dichlorobenzene-, m.p. 247—248°; diphenyl-4 : 4′-di-, m.p. >330° (decomp.). H. W.

Chloromethylation of naphthalene and the application of 1 : 5-dichloromethylnaphthalene to the syntheses of polycyclic ring systems. I. G. Lock and E. Walter (*Ber.*, 1942, **75**, [*B*], 1158—1163).—Treatment of $C_{10}H_8$ with paraformaldehyde, AcOH, conc. HCl, and H_3PO_4 gives mainly 1-$C_{10}H_7$·CH_2Cl (**I**) with smaller amounts of 1 : 5-$C_{10}H_6(CH_2Cl)_2$ (**II**), m.p. 150° (corr.), and $CH_2(C_{10}H_7\text{-}1)_2$. Under similar conditions 1-$C_{10}H_7$Me yields 48% of 1 : 4-$C_{10}H_6$Me·CH_2Cl (**III**), b.p. 185—189°/17 mm., with viscous material of higher b.p.; if the duration is diminished the yield of (**III**) falls and unchanged 1-$C_{10}H_7$Me is left. By diminishing the relative proportion of $C_{10}H_8$ the yield of (**II**) can be raised to ~20% but (**I**) is usually present to the extent of ~20%. (**III**), KOAc, and boiling AcOH afford 1 : 5-*diacetoxymethylnaphthalene*, m.p. 78°, hydrolysed by KOH–aq. EtOH to 1 : 5-*dihydroxymethylnaphthalene*, m.p. 127° (*bisphenylcarbamate*, m.p. 184°). (**II**) and $CHNa(CO_2Et)_2$ give *Et*$_2$ *di-αα′-carbethoxy-ββ′*-1 : 5-*naphthylenedipropionate*, m.p. 66·5°, hydrolysed to the tetracarboxylic *acid*, which is decarboxylated to 1 : 5-*naphthalenedi-β-propionic acid*, m.p. 258° (corr.), (*Et*$_2$ ester, m.p. 37°). It is converted by HF at room temp. into *Et perinaphthindan*-1-*one*-7-*β-propionate* (**IV**), m.p. 90° (*semicarbazone*, decomp. ~228°). H. W.


(IV.)

Dialkylation of naphthalene. 1 : 4-Di*cyclo*hexylnaphthalene. C. C. Price, H. M. Shafer, M. F. Huber, and C. Bernstein (*J. Org. Chem.*, 1942, **7**, 517—521).—The action of $AlCl_3$ on a mixture of $Bu^{\gamma}Cl$ and $C_{10}H_8$ in CS_2 gives a solid mixture of di-*tert.*-butylnaphthalenes from which varying proportions of an *isomeride* (**I**), m.p. 145—146°, can be separated. This is readily oxidised by CrO_3–AcOH to a *quinone*, m.p. 83—83·5° (*diacetate*, m.p. 139—140°, of the corresponding quinol), but it could not be converted into a picrate. The residue from (**I**) gives a picrate, m.p. 156—156·5°, from which is obtained a hydrocarbon mixture, m.p. 80—82°, separated by fractional crystallisation from EtOH or AcOH into (**I**) and an isomeric *compound*, m.p. 103—104°. Oxidation of these compounds with dil. HNO_3 does not give a naphthalic acid whilst treatment with $HgSO_4$–H_2SO_4 gives only small amounts of *o*-$C_6H_4(CO)_2O$; probably the H_2SO_4 catalyses the elimination of Bu^{γ} during the oxidation. $(CH_2\text{·}CO)_2O$ and *p*-$C_6H_4Bu^{\gamma}_2$ in CS_2 containing $AlCl_3$ at −15° give almost entirely *p-tert.*-butylbenzoylpropionic acid, m.p. 126°, identified further by oxidation ($KMnO_4$) to *p*-$C_6H_4Bu^{\gamma}$·CO_2H. A small quantity of an ill-defined *acid*, m.p. 176—177° (*benzylthiuronium* salt, m.p. 142—143°), also results. The acid is unsaturated towards Br and $KMnO_4$ and is converted by the latter into compounds, m.p. 194—196° and 217—218°, respectively. The only product which could be obtained under similar conditions from *p*-$C_6H_4Bu^{\gamma}_2$ and $(CH\text{·}CO)_2O$ is p-tert.-*butylbenzoylacrylic acid*, plates, m.p. 123°, or needles, m.p. 128°, unsaturated towards Br and oxidised by $KMnO_4$ to *p*-$C_6H_4Bu^{\gamma}$·CO_2H. Passage of BF_3 through a solution of $C_{10}H_8$ in *cyclo*hexanol at room temp. leads to 1 : 4-*dicyclohexylnaphthalene* (**II**), m.p. 83—83·5°, dehydrogenated by Se at 350° to 1 : 4-$C_{10}H_6Ph_2$, m.p. 132—133°. The liquid mixture remaining after removal of (**II**) is similarly dehydrogenated to $C_{10}H_6Ph_2$, m.p. 231°. H. W.

Aromatic hydrocarbons and their derivatives. XXXIII. New synthesis of tetracene. E. Clar (*Ber.*, 1942, **75**, [*B*], 1271—1273).—Gradual addition of $AlCl_3$ to tetrahydronaphthalene and *o*-$C_6H_4(CO)_2O$ in $C_2H_2Cl_4$ gives *o*-5 : 6 : 7 : 8-tetrahydro-β-naphthoylbenzoic acid, which is immediately dissolved in NaOH and reduced

by Zn dust to o-5 : 6 : 7 : 8-*tetrahydro-β-naphthylmethylbenzoic acid*, m.p. 145—147°. It is cyclised by NaCl–$ZnCl_2$ at 300—310° to 5 : 12-dihydrotetracene (**I**), which is dehydrogenated by passage over Cu at 400° or (for small quantities) by chloranil in boiling AcOH to tetracene [2 : 3-benzanthracene] (**II**), m.p. 357° (vac.). (**I**) is best deprived of a yellow colour, due to (**II**), by heating with a little $(CH{\cdot}CO)_2O$ in boiling xylene. The absorption spectrum of (**I**) is essentially that of a simple derivative of $C_{10}H_8$. H. W.

Synthesis of polynuclear hydrocarbons from benzanthrone. N. P. Grechkin and A. E. Arbusov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 50—52).—Benzanthrone and *o*-$C_6H_4Me{\cdot}MgBr$ give 6-o-*tolylbenzanthrone*, m.p. 150·5—153°, which is pyrolysed to 3 : 4 : 6 : 7-*dibenzpyrene*, m.p. 238—239°, in 28% yield. Similarly obtained are 6-(2′-*methyl*-1′-*naphthyl*)*benzanthrone*, m.p. 182—184°, and 6 : 7-*benz*-3 : 4-*naphthopyrene*, m.p. 242—244° (8% yield). F. R. S.

Alkylation of amines. I. J. H. Billman, A. Radike, and B. W. Mundy (*J. Amer. Chem. Soc.*, 1942, **64**, 2977—2978).—NH_2Ph or $C_{10}H_7{\cdot}NH_2$ (3) heated with R_3PO_4 (R = Me, Et, Pr^n, or Bu^n) (2 mols.), followed by boiling 25% NaOH, gives 60—99% of $NArAlk_2$. $Pr^\beta_3PO_4$ gives 80·5% of $NHPhPr^\beta$. *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ decomposes under the conditions of alkylation. R. S. C.

***cyclo*Butane derivatives. I. Degradation of *cis*- and *trans*-*cyclo*butane-1 : 2-dicarboxylic acids to the corresponding diamines.** E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter. **II. Thermal decomposition of *trans*-*cyclo*butane-1 : 2-bistrimethylammonium hydroxide.** E. R. Buchman, M. J. Schlatter, and A. O. Reims (*J. Amer. Chem. Soc.*, 1942, **64**, 2696—2700, 2701—2703).—I. $(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$ at 70—80° with $SOCl_2$ and then Br (later at 100°) and finally MeOH at 0° gives *meso*- (**I**) (70%), m.p. 73·5—74° and *dl*-$(CH_2{\cdot}CHBr{\cdot}CO_2Me)$ (**II**) (~20%), m.p. 11—12°. With boiling KCN–MeOH, (**I**) and (**II**) give comparable yields (~72%) of Me_2 1-*cyano*cyclo*butane*-1 : 2-*dicarboxylates*, m.p. 89·5—90° (**III**) (~28%), and b.p. 119—120°/2 mm. (**IV**) (~72%); a *compound*, $C_{10}H_{12}O_5N_2$ (? related to Me_2 αα′-dicyanoadipate), m.p. 172·5—173·5° (decomp.), is also isolable from old specimens. Hydrolysis (Fuson *et al.*, A., 1929, 794; 1934, 1104) of (**III**) gives cyclo*butane*-1 : 1 : 2-*tricarboxylic acid*, m.p. (+$x H_2O$) 135° (decomp.) or (anhyd.) 91—92° (loses CO_2 at ~130°). Hydrolysis of crude (**IV**) by boiling 6N-HCl, decarboxylation at 170—180°/20 mm., boiling with AcCl, and final distillation gives 81% of *cis*-*cyclo*butane-1 : 2-dicarboxylic anhydride, m.p. 76·5—77°; b.p. 127—130°/2 mm., and thence (boiling H_2O) the *cis*-acid (**V**) (85%), m.p. 139·5—140°, which at 200° gives 51% of *trans*-acid (**VI**), m.p. 130·5—131°. With CH_2N_2, (**V**) gives 94% of *cis*-Me_2 ester (**VII**), b.p. 85°/3 mm., and with boiling HCl–EtOH gives 71% of *cis*-Et_2 ester, b.p. 99—100°/2 mm. Hydrolysis, decarboxylation, and esterification of crude (**IV**) gives 82% of mixed Et_2 esters. (**VII**) is largely isomerised by boiling MeOH–NaOMe; hydrolysis then gives 76% of (**VI**). N_2H_4,H_2O at 130° converts the esters into cis-, *forms*, m.p. (stable) 140—140·5° and 134·5—135°, and trans-cyclo*butane*-1 : 2-*dicarboxydihydrazide*, m.p. 223—223·5°, the latter being readily obtained from the mixed esters and both yielding by hydrolysis their respective acids. Treating the derived *dihydrochlorides* [trans-, m.p. ~200° (decomp.)], with $NaNO_2$–H_2O–Et_2O at 13—16°, evaporating the Et_2O layer diluted with EtOH, and boiling the resultant EtOH solution gives cis-, m.p. 101·5—102° [and a little (?) 4 : 5-*dimethylenedihydrouracil*, m.p. 258·5—259°], and trans-NN′-*dicarbethoxy*-1 : 2-*diamino*cyclo*butane*, m.p. 129·5—130°, which, when boiled with KOH–MeOH and distilled at 170° in steam, give respectively cis- (**VIII**) (77%), b.p. 147°/760 mm., 75°/50 mm., and trans-1 : 2-*diamino*cyclo*butane* (**IX**) (63%), b.p. 151°/760 mm., 74°/50 mm. [*cis*-, sublimes ~150° (decomp.), and *trans*-carbonate, sublimes ~110° (decomp.); cis-, m.p. 145·5—146·5°, and trans-$(PhSO_2)_2$, m.p. 153·5—154°, and cis-, m.p. 204·5—205°, and trans-Bz_2 derivative, m.p. 245·5—246°; cis-, m.p. 255° (decomp.), and trans-*dipicrate*, m.p. 254° (decomp.); trans-*bisphenylcarbamyl* derivative, m.p. 279—280°; trans-*oxalate*, m.p. 268° (decomp.)]. (**VIII**) and (**IX**) are also obtained from (**V**) and (**VI**) respectively by, successively, H_2SO_4–$CHCl_3$–N_3H at 40°, aq. KOH, and steam-distillation at ~160°. Bz_2 with (**VIII**) or (**IX**) gives tetraphenylpyrazine. With $COCl_2$–Et_2O at 0°, (**VIII**) gives the cyclic *carbamide*, m.p. 147—147·5°, but (**IX**) gives an amorphous substance. With CS_2–EtOH, (**VIII**) gives a dithiocarbamate, which sinters at ~152° giving H_2S and 2-*thiol*-4 : 5-*dimethylene*-4 : 5-*dihydroglyoxaline*, m.p. 168·5—169°, formed also by evaporating an aq. solution of the salt. (**IX**) gives a *dithiocarbamate*, $C_5H_{10}N_2S_2$, sinters at 263°. $MeCS{\cdot}NH_2$ and (**VIII**) give exothermally (later at 80°) 2-*methyl*-4 : 5-*dimethylene*-4 : 5-*dihydroglyoxaline*, m.p. 89—90° (picrate, m.p. 150—150·5°); (**IX**) reacts after heating to give a substance whence it is readily regenerated by hydrolysis.

II. The crude dihydrochloride of (**IX**) with boiling 90% HCO_2H–36% CH_2O gives trans-1 : 2-*bisdimethylamino*cyclo*butane* (**X**), b.p. 83°/50 mm. [*dipicrate*, m.p. 244° (decomp.)] [(**VIII**) gives a tar], but with boiling MeI–KOH–MeOH gives 2-*dimethylamino*cyclo*butyltrimethylammonium iodide*, decomp. 218—218·5°, which with MeI–EtOH at 100° gives (**XI**). The *dimethiodide* (**XI**), m.p. 251° (decomp.) [corresponding *dipicrate*, m.p. 288° (decomp.)], of (**X**) with Ag_2O–H_2O gives the dimethohydroxide, which at ~250° or with Pt–asbestos at 350—360° gives *cyclo*butanone, b.p. 98·5—99° [semicarbazone, m.p. 212—212·5°; phenylhydrazone, m.p. 98—98·5°; 2 : 4-dinitrophenylhydrazone, m.p. 147—147·2° (lit. 132—133°)], 2-1′-hydroxy-1′-*cyclo*butyl- and 2-*cyclo*butylidene-*cyclo*butanone, separated by chromatography of the 2 : 4-*dinitrophenylhydrazones*, orange, m.p. 186—187° (decomp.), and red, sinters at 184° (decomp.), respectively, 1 : 5 $NHMe_2$–NMe_3, and (**X**). 1-Dimethylamino-Δ^1-*cyclo*butene is postulated as an unstable intermediate. M.p. are corr. R. S. C.

Acetoacetarylamides.—See B., 1943, II, 108.

***N*-Polyhydroxyalkylarylamines.**—See B., 1943, II, 107.

Derivatives of *N*-phenylarylamines.—See B., 1943, II, 107.

5-Acetamidosaccharin, a derivative of sulphanilamide. O. G. Backeberg and J. L. C. Marais (*J.C.S.*, 1943, 78—79).—*m*-$C_6H_4Me{\cdot}NHAc$ and $ClSO_3H$ at 0° give 3 : 1 : 6-$NHAc{\cdot}C_6H_3Me{\cdot}SO_2Cl$ (**I**), converted into *acet*-m-*toluidide*-6-*sulphonamide* (**II**), m.p. 204°, and -6-*sulphonanilide*, m.p. 155°. (**II**) and Br–AcOH or aq. NaOH–NaOBr give the 4(?)-*Br*-derivative, m.p. 262°, hydrolysed (boiling 10% aq. NaOH) to 4(?)-*bromo*-m-*toluidine*-6-*sulphonamide*, m.p. 185°. (**I**) or (**II**) and boiling 10% aq. NaOH afford 3 : 1 : 6-$NH_2{\cdot}C_6H_3Me{\cdot}SO_3H$ (with Br–H_2O gives 1 : 2 : 4 : 6 : 3-$C_6HMeBr_3{\cdot}NH_2$) or m-*toluidine*-6-*sulphonamide* (**III**), m.p. 172° [2 : 4(?)-Br_2-derivative, m.p. 198°; Bz_2 derivative, m.p. 265°, also prepared from *m*-$C_6H_4Me{\cdot}NHBz$ and $ClSO_3H$, followed by NH_3], respectively. 6 : 1 : 3-$NH_2{\cdot}SO_2{\cdot}C_6H_3Me{\cdot}N_2HSO_4$ [from (**III**) and H_2SO_4–OMe·NO–MeOH] with boiling H_2O gives m-*cresol*-6-*sulphonamide*, m.p. 207°, methylated by Me_2SO_4–aq. NaOH to 3 : 1 : 6-$OMe{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}NH_2$. (**II**) and aq. $KMnO_4$ at 85° give 5-*acetamidosaccharin*, m.p. 299°, but attempted deacetylation gives a non-cryst. syrup. A. T. P.

Sulphanilamide derivatives. VIII. Sulphanilylamidines. E. H. Northey, A. E. Pierce, and D. J. Kertesz (*J. Amer. Chem. Soc.*, 1942, **64**, 2763—2765; cf. A., 1940, II, 304).—$NH_2{\cdot}CMe{:}NH,HCl$, *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$, and 50% NaOH in $COMe_2$ at 10—20° give N^4-*acetylsulphanilylacetamidine*, m.p. 244·2—244·7°, hydrolysed by 7·5N-HCl at 60° to *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (**I**). Sulphanilyl-acet- (**II**), m.p. 151·4—152° (lit. 149°), -iso*hexo*-, m.p. 126—127·2°, -*a*-*phenylacet*-, m.p. 177—179°, -benz-, m.p. 210·2—210·7° (lit. 203°), and -p-*tolu*-*amidine*, m.p. 234·9—235·4°, are prepared from $NH_2{\cdot}CR{:}NH,HCl$ by NaOH–*p*-$NO_2{\cdot}C_6H_4{\cdot}SO_2Cl$ (**III**)–$COMe_2$, followed by Fe dust in dil. HCl at 95—100°, the intermediate NO_2-compounds having m.p. 190·7—191·3°, 247—250° (decomp.), 194·3—195·8°, 180·3—181°, and 149·5—160°, respectively. Disubstitution also occurs in amounts varying with the amount of (**III**) used; *disulphanilyl*-*acet*-, m.p. 191·6—191·8°, -*benz*-, m.p. 206·4—207·6° (decomp.), and -p-*tolu*-*amidine*, m.p. 166·9—167·5°, and the corresponding $(NO_2)_2$-compounds, m.p. 189—190·7°, 241·8—242·6°, and 213·7—214·9°, respectively, sol. in alkali, are described. N^1-Nicotinoyl-*p*-nitrobenzenesulphonamide and PCl_5 in $POCl_3$ at 80—85° give the imide chloride, which with aq. NH_3 gives p-*nitrobenzenesulphonyl*-, m.p. 232·5—233·5°, and thence p-*sulphanilyl*-*nicotinamidine*, m.p. 208·1—208·2°. *p*-$NO_2{\cdot}C_6H_4SO_2{\cdot}N{:}CPhCl$ with aq. NH_2Me, $NHEt_2$– or 2-aminopyridine–$COMe_2$ gives similarly N-p-*nitrobenzenesulphonyl*-N′-*methyl*-, m.p. 181·2° (decomp.), and -N′-2′-*pyridyl*-*benzamidine*, m.p. 180·7° (decomp.), and N-p-*sulphanilyl*-N′-*methyl*-, m.p. 228·1—229·2°, -N′N′-*diethyl*-, m.p. 193·7—194°, and -N′-2′-*pyridyl*-*benzamidine*, m.p. 206·8—207·5°. The sulphanilylamidines are $ArSO_2{\cdot}N{:}CR{\cdot}NH_2$ [since acid or alkaline hydrolysis yields (**I**)] and probably $ArSO_2{\cdot}N{:}CR{\cdot}NH{\cdot}SO_2Ar$ etc. The physiological activity of (**II**) is equal to that of (**I**), but that of the other sulphanilylamidines is low. M.p. are corr. R. S. C.

***p*-Aminobenzenesulphonylguanylguanidine and derivatives.**—See B., 1943, III, 88.

***p*-*cyclo*-Hexylaminodiphenylamine.**—See B., 1943, II, 107.

Nitrophenylallylthiosemicarbazides. Analytical properties. A. W. Scott and J. T. Andrews (*J. Amer. Chem. Soc.*, 1942, **64**, 2873—2874).—$CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NHPh$ (**I**) and its *o*-, m-, m.p. 120°, and p-NO_2-derivative (**II**), m.p. 188° (decomp.), give colours or ppts. with Ag, Hg^I, Hg^{II}, and Cu^{II}. The sensitivity is *p*- ≫ *o*- > *m*-NO_2, (**I**). (**II**) gives a ppt. with solutions containing 1 p.p.m. of Hg^{II} and a slight colour with 1 pt. in 10^7; unsatisfactory quant. results were obtained. R. S. C.

Reversible photochemical processes in rigid media. Dissociation of organic molecules into radicals and ions.—See A., 1943, I, 133.

Initial step in the action of acids on tetra-arylhydrazines. G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1942, **64**, 2808—2810).—Addition of HCl to $(NPh_2)_2$ causes initial formation, even near liquid air temp., of NPh_2^+, spectroscopically identified. Both NPh_2Cl and NPh_2^+ are too unstable to be observed except at very low temp. W. R. A.

5-*tert*.-Amyl-*o*-cresol.—See B., 1943, II, 107.

Long-chain acyl- and alkyl-phenols. K. Paranjpe, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 120—123).—PhOH, RCO_2H, and $ZnCl_2$ yield >70% of *o*-$OH{\cdot}C_6H_4$ undecyl, tridecyl, pentadecyl, new m.p. 58°, and heptadecyl ketone

new m.p. 66—67° [*Me ethers*, b.p. 110°/50 mm., 180—182°/66 mm., and 190°/30 mm. (m.p. 38°), and m.p. 42° (oxidised by $KMnO_4$ in $COMe_2$ to *o*-OMe·C_6H_4·CO_2H), respectively], reduced (Clemmensen) to *o-hydroxydodecyl-*, b.p. 175°/30 mm., *-tetradecyl-*, b.p. 170°/60 mm., *-hexadecyl-*, b.p. 210°/45 mm., and *-octadecyl-benzene*, m.p. 58°, respectively. PhOMe, RCOCl, and $AlCl_3$ in $PhNO_2$ yield >84% of *p-OMe·*C_6H_4 *undecyl*, m.p. 57° (oxime, m.p. 60°), *tridecyl*, m.p. 63° (semicarbazone, m.p. 71°; oxime, m.p. 66°), pentadecyl, and *heptadecyl ketone*, m.p. 75° (oxidised to *p*-OMe·C_6H_4·CO_2H). These are demethylated to the phenols, and reduced (Clemmensen) to *p-methoxy-dodecyl-*, b.p. 180°/50 mm., *-tetradecyl-*, b.p. 210°/60 mm., *-hexadecyl-*, m.p. 54°, and *-octadecyl-benzene*, m.p. 60°, respectively. A. LI.

***p*-Toluenesulphonates of nitro-4-phenylphenols.** S. E. Hazlet, D. A. Stauffer, and H. O. Van Orden (*J. Amer. Chem. Soc.*, 1942, **64**, 3057).—2 : 6-*Di-*, m.p. 186—187°, and 2 : 6 : 4′-*tri-nitro-4-diphenylyl p-toluenesulphonate*, m.p. 219—220°, are prepared from the appropriate NO_2-phenol and *p*-$C_6H_4Me·SO_2Cl$ in C_5H_5N or C_5H_5N–dioxan, respectively. R. S. C.

Structure of Skita's "9 : 10-dihydroxydecahydrophenanthrene." P. Levine (*J. Amer. Chem. Soc.*, 1942, **64**, 3046—3047).—Skita's so-called 9 : 10-dihydroxy-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-deca- (A., 1926, 173; cf. A., 1943, II, 65) is 9 : 10-*dihydroxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octa-hydrophenanthrene* (**I**), since it consumes 1 equiv. of $Pb(OAc)_4$ in C_6H_6 to give the quinone, which with Zn dust and a trace of NEt_3 in Ac_2O gives the diacetate of (**I**). R. S. C.

Phenylethylamines. IV. Dimethoxy- and dihydroxy-phenyl-*n*-propylamines. E. H. Woodruff (*J. Amer. Chem. Soc.*, 1942, **64**, 2859—2862; cf. A., 1940, II, 213).—Hydrolysis and methylation of hydroxy-4-methylcoumarins gives *trans*-$(OMe)_2C_6H_3$·CMe:CH·CO_2H. $(OMe)_2C_6H_3$·COMe gives by the Reformatsky reaction and dehydration at 250—300° etc. 2 : 3-, m.p. 121—122° (Et ester, b.p. 165—175°/8 mm.), 2 : 6-, m.p. 143—144° (*form*, m.p. 185—185·5°, obtained from 6-hydroxy-4-methylcoumarin) (*Et* ester, b.p. 136—138°/0·03 mm.), 3 : 4-, m.p. 138—140° (Et ester, b.p. 200—203°/11 mm.), and 3 : 5-*dimethoxy-β-methylcinnamic acid*, m.p. 123·5—124·5° (Et ester, b.p. 197—203°/11 mm.). Electrolytic reduction of cinnamic acids gives β-2 : 3-, m.p. 77°, b.p. 181—184°/0·15 mm., -2 : 4-, m.p. 104—105°, -2 : 5-, m.p. 78—79°, b.p. 175—185°/0·1 mm., -2 : 6-, m.p. 78·5—79°, b.p. 190—197°/3 mm., -3 : 4-, m.p. 84—85°, and -3 : 5-*dimethoxyphenyl*-n-*butyric acid*, b.p. 184—185°/0·05 mm., and thence the *amides*, m.p. 90—91°, 133—134°, 122° (lit. 121°), 153—155°, 131°, and 92·5—93°, respectively, which with NaOBr give β-2 : 3-, b.p. 150—154°/11 mm. (133·5—134°), β-2 : 4-, b.p. 158—160°/14 mm. (146—147°), β-2 : 5-, b.p. 164—166°/16 mm. (149—150°), β-2 : 6-, b.p. 155—158°/5 mm. (143—145°), β-3 : 4-, b.p. 163—166°/15 mm. (205—206°), and β-3 : 5-*dimethoxyphenyl*-n-*propylamine*, b.p. 179—184°/14 mm. (105—107°), figures in parentheses being m.p. of the *hydrochlorides*. Conc. HCl at 160° then yields the corresponding *β-dihydroxyphenyl*-n-*propylamine hydrochlorides*, m.p. 191—191·5°, 222—223°, 167·5—169·5°, 93—95°, 180—181°, and 164—166°, respectively. 5-Hydroxy-4-methylcoumarin and H_2–Raney Ni in EtOH at 60°/60 lb. give 5-*hydroxy-4-methyl*-3 : 4-*dihydrocoumarin*, m.p. 160°, b.p. 214°/5 mm. R. S. C.

3-Alkoxydiphenyls. See B., 1943, II, 108.

Rôle of neighbouring groups in replacement reactions.—See A., 1943, II, 117.

4-Nitrodiphenyl ether-4′-sulphonyl chloride and -4′-sulphonamide. V. H. Dermer and O. C. Dermer (*J. Amer. Chem. Soc.*, 1942, **64**, 3056—3057).—*p*-NO_2-C_6H_4·OPh and warm conc. H_2SO_4 give 4-$NO_2C_6H_4$·O·C_6H_4·SO_3H-4 (**I**), converted by PCl_5 into 4-*nitrodiphenyl ether-4′-sulphonyl chloride*, m.p. 84—85° (corr.), which is also obtained (m.p. 85·5—86·5°) from *p*-OPh·C_6H_4·SO_2Cl by H_2SO_4–HNO_3–AcOH at 60—70° and yields the *amide*, m.p. 130—131°. The acid of Jones *et al.* (A., 1916, i, 644) was (**I**). R. S. C.

ααβ-Tri-*p*-anisyl-Δ^α-propene and -butene.—See B., 1943, III, 88.

Attempted asymmetric syntheses involving the Grignard reagent in optically active solvents. D. S. Tarbell and M. C. Paulson (*J. Amer. Chem. Soc.*, 1942, **64**, 2842—2844).—CHPhMe·OH is inactive when prepared from MgMeI and PhCHO in *d*-CHMeEt·OMe or bornyldimethylamine (**I**), but in (**I**) a dextrorotatory by-product is formed. In *l*-menthyl Me ether (**II**), b.p. 83°/12 mm., $[\alpha]_D^{25}$ −95·6°, MeI or EtI with Mg gives an insol. product preventing further reaction; MgMeI (Et_2O removed after prep.) and Pr^{α}CHO in (**II**) give Bu^{α}OH and COMePr^α. Heating Mg and PhBr in (**I**) at 130—140° and then adding paraldehyde at 110—120° gives CHPhMe·OH (45—60%), α usually 0. R. S. C.

Phenol–formaldehyde resins. Acetylation of hydroxybenzyl alcohols. R. Barthel (*J. pr. Chem.*, 1942, [ii], **161**, 77—80).—*o*-OH·C_6H_4·CH_2·OH, PhOH, and Ac_2O give PhOAc and *o-acetoxybenzyl acetate*, b.p. 103—104°/1 mm. 1 : 4 : 2 : 6-OH·$C_6H_2Me(CH_2·OH)_3$ similarly affords its *triacetate*, b.p. 157—158°/1 mm. Acetylation (Ac_2O) of the resin obtained when 1 : 4 : 2-OH·$C_6H_3Me·CH_2·OH$ is heated at 150° for a short time gives little of the corresponding *diacetate*, b.p. 122—123°/1 mm., and a product hydrolysed to di-2-hydroxy-5-methylbenzyl ether, m.p. 101—102°. A. T. P.

Formation of phenol–formaldehyde resins. X. Mechanism of "hardening" of resols. "Hardening" of *p*-hydroxymesityl alcohol. E. Adler, H. von Euler, and J. O. Cedwall (*Arkiv Kemi, Min., Geol.*, 1942, **15**, **A**. No. 7, 17 pp.; cf. B., 1942, II, 25).—4 : 3 : 5 : 1-OH·$C_6H_2Me_2·CH_2·OH$ (**I**) (from 2 : 6 : 1-$C_6H_3Me_2$·OH and 40% CH_2O in 5% NaOH for 24 hr.) at 140—155° for 30—60 min. gives 55—57% of unchanged (**I**), CH_2O, 10—13% of (4 : 3 : 5 : 1-OH·$C_6H_2Me_2)_2CH_2$, 1—15% of *di-(4-hydroxy-3 : 5-dimethylbenzyl) ether*, m.p. not given, and 0—5% of 4 : 4′-*dihydroxy*-3 : 5 : 3′ : 5′-*tetramethyl-αβ-diphenylethane* (**II**), m.p. 168—169° {*diacetate*, m.p. 148—149°; *Me*$_1$, m.p. 88—88·5°, insol. in dil. NaOH, and *Me*$_2$ *ether*, m.p. 108—109°). At 170—180° (**I**) gives in good yield (**II**) and 4 : 4′-*dihydroxy*-3 : 5 : 3′ : 5′-*tetramethylstilbene* (**III**), m.p. 233—236° [*diacetate*, m.p. 239—240°, gives a red colour with $C(NO_2)_4$], separated via the insol. (**II**)–C_6H_5N complex. (**III**) is reduced to (**II**) by H_2–PtO_2 in AcOH, but not in EtOAc, and gives with Br–Et_2O the dibromide, m.p. 187° (decomp.), and thence (KOH) (4 : 3 : 5 : 1-O·$C_6H_2Me_2$·$CH)_2$. It is concluded that condensation in PhOH–CH_2O type resins at low temp. takes place by way of ·CH_2·O·CH_2· and ·CH_2· linkings, which are supplemented at high temp. by ·CH_2·CH_2· and ·CH:CH· linkings formed from *p*-quinonemethides. At all temp. condensation occurs primarily *para* to OH, followed by secondary cross-linkings in the *o*-positions. M. H. M. A.

ααββ-Tetraphenylethanol. A. Banchetti (*Gazzetta*, 1942, **72**, 74—77; cf. Wegler, A., 1934, 292).—The best prep. of $CHPh_2·CPh_2·OH$ (**I**) is that of Paternò *et al.* (A., 1909, i, 393). When distilled at atm. pressure, (**I**) gives $(CHPh_2)_2$ (**II**), which may account for the variability of m.p. assigned to (**I**). Using the Kofler microscope, m.p. of (**I**) and (**II**) are 244° and 215°, respectively. E. W. W.

Reaction of magnesium *n*-butyl bromide with aromatic ketones. (Misses) H. M. Crawford, M. E. Saeger, and F. E. Warneke (*J. Amer. Chem. Soc.*, 1942, **64**, 2862—2864).—MgBu^{α}Br (**I**) with COPhMe gives *β-phenyl*-n-*hexan-β-ol* (72—80%), b.p. 123—124°/9 mm., dehydrated by Lucas reagent to *β-phenyl*-Δ^β-n-*hexene*, b.p. 223—226°. $COPh_2$ and (**I**) give $CHPh_2$·OH (17—30%) and $(CHPh_2)_2O$ (5·6%). Bz$_2$ and (**I**) give benzoin (0—13%). *αβ-diphenyl*-n-*hexan-β-ol-α-one* (**II**) (0·5—5·6%), m.p. 124°, and *εζ-diphenyl*-n-*decane-εζ-diol* (0—trace), m.p. 184°. Dehydration (Lucas reagent) of (**II**) gives *αβ-diphenyl-*Δ^β-n-*hexen-α-one*, b.p. 288—290°. COPh·CH_2Ph gives 0—7·4% of $(CHPh·)_2$, 0—traces of $[CH_2Ph·CPh(OH)·]_2$, and 0—traces of the ? *pinacolone*, m.p. 133°. R. S. C.

Action of alkaline reagents on αδ-dihalogeno-αδ-dibenzoylbutanes. R. C. Fuson, H. H. Hully, J. F. McPherson, and F. W. Spangler (*J. Org. Chem.*, 1942, **7**, 462—465; cf. A., 1932, 746; 1940, II, 178).—αδ-Dibromo-αδ-dibenzoylbutane is converted by alkaline reagents, best $NHEt_2$, into 5-bromo-5-benzoyl-1-phenyl-Δ^1-*cyclo*pentene oxide (**I**), m.p. 138—139°, converted by NH_2OH into an *oxime* (**II**), m.p. 178—179° (decomp.), and an unstable compound, m.p. 90—93° (decomp.). (**II**) and $SOCl_2$ in $CHCl_3$ give the corresponding 5-*carboxyanilide*, m.p. 172—173° (decomp.). MgPhBr and (**I**) in Et_2O afford 5-*bromo*-1-*phenyl*-5-α-*hydroxybenzhydryl*-Δ^1-cyclo*pentene oxide*, m.p. 127—129° (decomp.), converted by Zn dust in boiling AcOH into (probably) 1-*phenyl*-5-*benzhydrylidene*-Δ^1-cyclo*pentene oxide*, m.p. 159—160°. (Bz·$[CH_2]_2)_2$ and Cl_2 in hot CCl_4 give αδ-*dichloro-αδ-dibenzoylbutane*, m.p. 177—178°, transformed by $NHEt_2$ in boiling C_6H_6 into 5-*chloro*-5-*benzoyl*-1-*phenyl*-Δ^1-cyclo*pentene oxide* (**III**), m.p. 131—132° (*oxime*, m.p. 168—169°), which does not give a ppt. with boiling $AgNO_3$–EtOH and does not decolorise $KMnO_4$ in $COMe_2$. (**III**) is reduced by Zn and AcOH to (Bz·$[CH_2]_2)_2$. With MgPhBr in Et_2O (**III**) yields 5-*chloro*-1-*phenyl*-5-α-*hydroxybenzhydryl*-Δ^1-cyclo*pentene oxide* (**IV**), m.p. 169·5—170·5°, which is rearranged by HCl in Et_2O to a *compound*, $C_{24}H_{21}O_2Cl$, m.p. 70—80°. Reduction of (**IV**) by Zn dust and boiling AcOH gives 1-*phenyl*-5-α-*hydroxybenzhydryl*-Δ^1-cyclo*pentene oxide*, m.p. 112—113°. H. W.

Autoxidation of hydrocarbons. VI. Indane peroxide. H. Hock and S. Lang (*Ber.*, 1942, **75**, [**B**], 1051—1054).—Freshly distilled indane is treated with dry O_3 while irradiated at 60°, the product is treated with 25% NaOH at −5°, and the resulting Na salts are acidified and extracted with Et_2O; the Et_2O solution is washed with aq. $NaHCO_3$ (the acid removed contains a little homophthalic acid) dried, and distilled, thus giving 1-*indanyl H peroxide* (**I**), b.p. 64—65°/0·01 mm., 74—75°/0·04 mm., violent decomp. 135—140°. (**I**) is catalytically decomposed by aq. $FeSO_4$ at 100° into indan-1-one (**II**) (70%), obtained also in 90% yield by the oxidation of (**I**) by $Pb(OAc)_4$ in AcOH at 15—25°. Reduction of (**I**) by Na_2SO_3–H_2O affords indan-1-ol (**III**), new m.p. 39°. Decomp. of (**I**) with 2N-NaOH at 70° affords (**II**) and (**III**). (**I**) and Me_2SO_4 give 1-*indanyl Me peroxide*, b.p. 43—44°/0·05 mm., vigorous decomp. 140°. H. W.

Characteristics of β-hydroxy-β-2 : 5-dimethoxyphenyl*iso*propylamine hydrochloride. R. Baltzly and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 3040).—The substance, m.p. 176° (decomp.), previously (A., 1940, II, 83) thus named is α-2 : 5-*dimethoxybenzoylethylamine hydrochloride* and is hydrogenated (Pt-black; H_2O) to

β-hydroxy-β-2 : 5-dimethoxyphenyl*iso*propylamine (*hydrochloride*, m.p. 215°; Ac_2 derivative, m.p. 120°). R. S. C.

Hydrogenated acids of chaulmoogra oil. N. P. Buu-Hoi and P. Cagniant (*Ber.*, 1943, **75**, [*B*], 1181—1189).—Catalytic hydrogenation (Raney Ni) of Et hydnocarpate, b.p. 158—161°/0·2 mm., $[\alpha]_D \sim +56°$, and Et chaulmoograte, b.p. 171—172°/0·2 mm., $[\alpha]_D \sim +51°$, gives the H_2-esters, b.p. 198—200°/13 mm., and 216—218°/12 mm., respectively, hydrolysed to dihydrohydnocarpic (**I**), b.p. 180—182°/1·3 mm., m.p. 63·5°, and dihydrochaulmoogric acid (**II**), b.p. 199—201°/1·3 mm., m.p. 73°, respectively. (**I**) is converted by Br and red P at room temp. and then at 100°, followed by aq. H_2SO_3 or EtOH at 0°, into *α-bromodihydrohydnocarpic acid* (**III**), a viscous liquid, or its *Et* ester (**IV**), b.p. 195°/3 mm., which rapidly blackens on exposure to light and air, respectively. (**IV**) and anhyd. $NPhEt_2$ at 215—220° for 72 hr. give *Et ψ-hydnocarpate* [*κ*-cyclo*pentyl*-Δ^{α}-*undecenoate*], b.p. 168—170°/1 mm., hydrolysed to the *acid*, m.p. 57°, which is hydrogenated (PtO_2 in EtOH) to (**I**). *α-Bromodihydrochaulmoogric acid* (**V**), m.p. 56—57° (*Et* ester, b.p. 204—205°/1 mm.), and *ψ-chaulmoogric* [μ-cyclo*pentyl*-Δ^{α}-*tridecenoic*] *acid*, m.p. 72° (*Et* ester, b.p. 190—195°/2·2 mm.), hydrogenated to (**II**), are similarly obtained. *α-Iododihydrochaulmoogric acid*, m.p. 52°, from (**V**) and KI in boiling 96% of EtOH, gives a non-cryst. chloride and an *amide*, m.p. 109°. Aq. KOH and (**III**) at 100° afford *α-hydroxydihydrohydnocarpic acid*, m.p. 75°, in 90% yield. *α-Hydroxydihydrochaulmoogric acid* has m.p. 86°. (**V**) and KCN in boiling aq. EtOH afford *α-cyanodihydrochaulmoogric acid*, m.p. 73°. *α-Anilino-*, m.p. 128—129°, and α-2-*naphthylamino-*, m.p. 142°, *-dihydrohydnocarpic acid* and *α-anilino-*, m.p. 131—132°, and α-2-*naphthylamino-*, m.p. 143—144°, *-dihydrochaulmoogric acid* are prepared by heating the Br-acids with NH_2Ar. (**V**) and NaSH in boiling aq. EtOH give *α-thioldihydrochaulmoogric acid*, m.p. 66° after softening, oxidised by I to the disulphide, m.p. 70°. Distillation of dihydrohydnocarpamide with P_2O_5 under 3 mm. gives *dihydrohydnocarponitrile*, b.p. 164—165°/0·5 mm. *Dihydrochaulmoogronitrile*, b.p. 192—195°/3 mm., is transformed by NH_2OH in boiling EtOH into *dihydrochaulmoogramideoxime*, m.p. 89°. (**V**) and MgMeI (3 mols.) in Et_2O give a complex mixture, b.p. 195—300°/1 mm., with acidic and ketonic properties. H. W.

Mechanism of the Arndt–Eistert reaction. C. Huggett, R. T. Arnold, and T. I. Taylor (*J. Amer. Chem. Soc.*, 1942, **64**, 3043).—Eistert's mechanism (A., 1935, 332) for this reaction is confirmed by conversion of $Ph^{13}CO_2H$ (giving, by decarboxylation by Cu chromite in quinoline, CO_2 containing 2·51% of ^{13}C) into $CH_2Ph{\cdot}^{13}CO_2H$ (giving by similar decarboxylation CO_2 containing 2·53% of ^{13}C). R. S. C.

Modification of Willgerodt's reaction. E. Schwenk and (Miss) E. Bloch (*J. Amer. Chem. Soc.*, 1942, **64**, 3051—3052).—COArMe and S in boiling morpholine give $CH_2Ar{\cdot}CS{\cdot}C_4H_8ON$, hydrolysed (crude, if necessary) by alkali in boiling H_2O or EtOH to $CH_2Ar{\cdot}CO_2H$ (10—75% yield). Halogen or OMe may be present in Ar, but not NO_2, NH_2, OH, or OAc. *Phenyl-*, m.p. 79—80°, *o-*, an oil, and m-*anisyl-*, m.p. 82—84°, *p*-bromo- and 2 : 5-dimethoxy-phenyl-, oils, *β-naphthyl-*, m.p. 108—109°, 2-phenanthryl-, an oil, and o-*benzyloxyphenyl-*, m.p. 118—119°, *-thioacetmorpholide* are thus prepared and hydrolysed. o-*Benzyloxy-acetophenone* (prep. from *o*-$OH{\cdot}C_6H_4{\cdot}COMe$ and CH_2PhCl in boiling 15% NaOH), b.p. 182—184°/11 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 207—209; *semicarbazone*, m.p. 175—177°), and *-phenylacetic acid*, m.p. 97—99°, are described. R. S. C.

Synthesis of derivatives of *s*-diphenylethane related to materials occurring naturally. IV. Stilbene-2-acetic acid. S. Natelson and S. P. Gottfried (*J. Amer. Chem. Soc.*, 1942, **64**, 2962—2963; cf. A., 1941, II, 133).—*o*-$CHPh{:}CH{\cdot}C_6H_4{\cdot}CHO$ (**I**) (improved prep.) and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give 2-*hydroxy-*, m.p. 92—93°, and thence $(SOCl_2)$ 2-*chloro-methylstilbene*, b.p. 170—185°/15 mm., and (NaCN–aq. EtOH) *stilbene*-2-*acetonitrile*, m.p. 81—82°, which in boiling conc. HCl–AcOH gives *stilbene*-2-*acetic acid* (**II**), m.p. 105—106°, and its *amide*, m.p. 152—153° [in conc. HCl–AcOH yields (**II**)]. The oxazolone from (**I**) and hippuric acid with aq. $Ba(OH)_2$ at 85° gives *α-benzamido*-o-*styrylcinnamic acid*, m.p. 199—202°, whence (**II**) is obtained in poor yield by NaOH and then H_2O_2. 4 : 5 : 1 : 2-$(OMe)_2C_6H_2(CO)_2O$, 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CH_2{\cdot}CO_2H$, and NaOAc at 230° give 4 : 5 : 3′ : 4′-*tetramethoxy-α-benzylidenephthalide*, m.p. 179—180°, reduced by Na–Hg in aq. NaOH to 4 : 5 : 3′ : 4′-*tetramethoxybenzylphthalide*, m.p. 146—148°, which, when dissolved in KOH–EtOH, evaporated, and heated at 180° yields 4 : 5 : 3′ : 4′-*tetramethoxystilbene*-2-*carboxylic acid*, m.p. 209—211°. (**II**) does not yield a lactone. R. S. C.

Synthetic anthelmintics. IV. Synthesis of lactones similar to desmotroposantonin. K. Paranjpe, N. L. Phalnikar, and K. S. Nargund. **V. γ-p-Alkoxyphenylbutyrolactones.** J. J. Trivedi and K. S. Nargund (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 124—126, 127—130).—IV. 1-Keto-7-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, Zn, and $CH_2Br{\cdot}CO_2Et$ in PhMe yield *Et* 1-*hydroxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetate*, m.p. 50° (free *acid*, m.p. 127°), which is dehydrated (P_2O_5 in C_6H_6) and then hydrolysed (cold alkali) to 7-*methoxy*-3 : 4-*dihydro*-1-*naphthylacetic acid*, m.p. 141·5°, converted by 60% H_2SO_4 at room temp. into the *lactone*, m.p. 60°, of 2-hydroxy-7-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid, demethylated (HBr–AcOH) to the *OH-lactone*, b.p. 240°/10 mm. 1-*Keto*-5-*methoxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 195°/50 mm. (from 2 : 5 : 1-$OMe{\cdot}C_6H_3Me{\cdot}[CH_2]_3{\cdot}CO_2H$ and P_2O_5 in C_6H_6), similarly yields 1-*hydroxy*-5-*methoxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid*, m.p. 90°, 5-*methoxy*-8-*methyl*-3 : 4-*dihydro*-1-*naphthylacetic acid*, b.p. 192°/50 mm., and 2-*hydroxy*-5-*methoxy-*, b.p. 190°/20 mm., and 2 : 5-*dihydroxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid lactone*, b.p. 180°/40 mm.

V. $(CH_2{\cdot}CO)_2O$, PhOAlk, and $AlCl_3$ in $PhNO_2$ give 80—90% of *γ-keto-γ*-p-*ethoxy-*, -n-*propoxy-*, -n-*butoxy-*, -iso*butoxy-*, -iso*amyloxy-*, and -n-*hexyloxy-phenylbutyric acid*, m.p. (to clear liquids) 137—138°, 118—119°, 112, 131—132°, 120°, and 109°, respectively, turbid liquids being formed 4—5° below these [*semicarbazones*, m.p. 189°, 178—179°, 171—172°, 188—189°, 185°, and 181°, respectively; *Me* esters, m.p. 50—51, 58°, 43—44°, —, —, and —, respectively; *Et* esters, m.p. 52°, —, (b.p.) 240°/20 mm., —, —, and —, respectively], reduced (Na + EtOH) to the *γ-OH-acids*, m.p. —, 101°, 80, 73°, 83—84°, and —, respectively, which yield the *γ*-p-*alkoxyphenylbutyrolactones*, m.p. 73—74°, 64°, 63—64°, (b.p.) 198°/5 mm., 74°, and 66—67°, respectively. The CO-acids are also obtained from *p*-$OH{\cdot}C_6H_4{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2Et$, AlkBr, and K_2CO_3 in $COMe_2$. A. Li.

Mechanism of the reaction between hindered carbonyl compounds and the Grignard reagent. II. R. T. Arnold and R. W. Liggett (*J. Amer. Chem. Soc.*, 1942, **64**, 2875—2877; cf. A., 1942, II, 142).—Cleavage of allyl ethers by, or addition of, Grignard reagents depends on the amount of steric hindrance around the CO. 1-*Bromo*-2 : 3-*dimethylnaphthalene* (prep. from 2 : 3-$C_{10}H_6Me_2$ by Br–$CHCl_3$–CCl_4 at 0°—room temp.), m.p. 63—64°, with Mg–MgEtBr (trace) in Et_2O and then CO_2 gives 2 : 3-*dimethyl*-1-*naphthoic acid* (**I**), m.p. 167—168°, the *allyl* ester (prep., as the allyl esters below, from the Na salt by $CH_2{:}CH{\cdot}CH_2Br$ in xylene), m.p. 33—34°, b.p. 155—160°/2 mm., of which with MgPhBr gives 97% of (**I**) and 82·4% of $CH_2{:}CH{\cdot}CH_2Ph$ (**II**). *Allyl triphenylacetate*, m.p. 85—85·5°, and MgPhBr give 93% of $CPh_3{\cdot}CO_2H$. $CHMeEt{\cdot}CO_2Et$ with $NaCPh_3$ and then CH_2PhBr gives *Et α-benzyl-α-methyl*-n-*butyrate*, b.p. 127—130°/9—10 mm., which affords, by way of the acid (**III**), the *allyl* ester, b.p. 139—140°/8 mm., converted by MgPhBr into (**III**) (87%) and (**II**) (70%). *Allyl αα-diphenylpropionate*, b.p. 175—177°/8 mm., with MgPhBr gives $CPh_2Me{\cdot}CO_2H$ (88%). *Allyl β-ethyl*-n-*hexoate* (prep. from the alcohol and acid chloride in C_5H_5N–$CHCl_3$), b.p. 79—79·5°/8 mm., and MgPhBr give the acid (30%), (**II**) (26%), and impure carbinol (~49%). *Allyl α-ethyl*-n-*butyrate* (25·3 g.), b.p. 165—167°, with MgPhBr gives $CHEt_2{\cdot}CO_2H$ (4·5), (**II**) (9·0), and a carbinol (10·3 g.), b.p. 170—175°/8 mm., converted by HCO_2H into *γ-benzhydrylidene*-n-*pentane*. *Allyl hexahydrobenzoate* (prep. from the acid chloride), b.p. 103—104°/18 mm., and MgPhBr (2 mols.) give only the carbinol, dehydrated by HCO_2H to benzhydrylidene*cyclo*hexane, m.p. 82—83°. Et *cyclo*hexanone-2-carboxylate with NaOEt–EtOH–xylene–$PhSO_3Et$ gives Et 2-ethyl-*cyclo*hexanone-2-carboxylate, b.p. 125—130°/18 mm. (*semicarbazone*, m.p. 156·5—157°), which by successive treatment with H_2–Raney Ni at 175—200°/2000 lb., P_2O_5–C_6H_6, H_2–Raney Ni at 150°/1800 lb. (gives an ester, b.p. 100—110°/10—15 mm.), KOH–MeOH, $SOCl_2$, and esterification gives *allyl* 1-*ethyl*cyclo*hexanecarboxylate*, b.p. 97—98°/8 mm. With MgPhBr this gives only the carbinol. R. S. C.

Preparation of *o*-hydrazinobenzoic acids and indazolones by reduction of diazotised anthranilic acids by sulphurous acid. K. Pfannstiel and J. Janecke (*Ber.*, 1942, **75**, [*B*], 1096—1107).—*o*-$CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2,HCl$, new m.p. 189—190°, is obtained in 84% yield from *o*-$CO_2H{\cdot}C_6H_4{\cdot}N_2Cl$ and aq. SO_2 through which passage of SO_2 is continued; the acid has m.p. 247° (m.p. of the indazolone). The following *-2-hydrazinobenzoic acids* are obtained analogously: 4-*nitro-*, m.p. 237° [*hydrochloride*, m.p. 208—209° (decomp.); *CHPh:* derivative, m.p. 251° (decomp.)]; 5-*nitro-*, m.p. 264—275° (decomp.), darkens greatly at 216° [*hydrochloride*, m.p. as for acid; *CHPh:* derivative, m.p. 253° (decomp.)], also obtained from 5 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}CO_2H$ and N_2H_4,H_2O in boiling abs. EtOH; 6-chloro-, which could not be recryst. [*hydrochloride*, m.p. 227° (decomp.) (sinters 205°)] on account of ready ring closure, transformed by boiling PhCHO into 5-*chloro*-4-*hydroxy*-3-*phenylcinnoline*, m.p. >300°. The indazolones [except (**I**) and (**II**) (below)] are obtained from the *o*-hydrazinobenzoic acids and their hydrochlorides by boiling, very dil. HCl. Thus are obtained indazolone, m.p. 247° (Ac_2 derivative, m.p. 135°), 4-*nitro-* (**I**), also hydrated, m.p. 245° (decomp.), alters >200° [hydrochloride, m.p. 245° (decomp.)], 5-*nitro-*, m.p. 275° (decomp.), darkens at 270, 6-*nitro-*, unstable orange-red needles or stable yellow prisms (+1MeOH), orange-red needles or lemon-yellow, compact crystals (+1AcOH), orange-red hydrated needles, m.p. 244° (for all forms), and 7-*nitro-* (**II**), m.p. 295—305° (hydrochloride), and 4-*chloro-indazolone* (anhyd. and +0·5H_2O), m.p. 263° [hydrochloride, m.p. 231° (decomp.), hydrolysed by H_2O]. Reduction of the appropriate NO_2-compound by $SnCl_2$ and HCl gives 4-*amino-*, m.p. 245° (decomp.), 5-*amino-* (+ H_2O), m.p. 290° (decomp.),

6-*amino*-, m.p. 287° (decomp.), and 7-*amino*-, m.p. 260° (decomp.), becomes discoloured at 230°, *-indazolone dihydrochlorides*. H. W.

Local anæsthetics. II. Alkoxybenzoates of β-monoalkylamino-β-methylpropan-α-ols and β-monoalkylaminobutan-α-ols. J. S. Pierce, J. M. Salsbury, W. W. Haden, and L. H. Willis (*J. Amer. Chem. Soc.*, 1942, **64**, 2884—2885; cf. A., 1942, II, 404).—NH_2·CMe_2·CH_2·OH or NH_2·CHEt·CH_2·OH with AlkBr at 100° gives β-ethyl-, m.p. 72—73°, b.p. 167—170°, *β-n*-propyl-, m.p. 56—57·5°, b.p. 185—188°, *β-n*-amyl-, m.p. 56—59°, b.p. 218—221°, β-n-*hexyl*-, m.p. 62—62·5°, b.p. 235—238°, β-n-*heptyl*-, m.p. 50—52°, b.p. 253—256°, β-n-, m.p. 68—69°, b.p. 202—204°, and *β-iso*-butyl-, m.p. 48—49°, b.p. 184—187°, *β-iso*amyl-, m.p. 73—74°, b.p. 214—217°, *β-allyl*-, b.p. 183—187°, and *β-benzyl*-, m.p. 53—57°, b.p. 277—280°, *-amino-isobutyl alcohol* (cf. Kremer *et al.*, A., 1942, II, 283), *β-ethyl*-, b.p. 177—179°, β-n-*propyl*-, b.p. 192—193°, β-n-, b.p. 210—213°, and *β-iso-butyl*-, b.p. 195—198°, β-n-, b.p. 227—230°, and β-iso-*amyl*-, b.p. 221—224°, β-n-*hexyl*-, b.p. 247—252°, β-n-*heptyl*-, b.p. 263—266°, *β-allyl*-, b.p. 194—197°, and *β-benzyl*-, b.p. 283—285°, *-amino-n-butyl alcohol*. The derived hydrochlorides with RCOCl at, successively, 100°, 130°, and 150° give *β-n-butylamino*isobutyl p-*anisoate hydrochloride*, m.p. 154—155°, *β-n-amyl*-, m.p. 128—129°, and *β-n-hexyl-amino*isobutyl p-*ethoxybenzoate hydrochloride*, m.p. 135—136°, *β-n-butylamino*isobutyl o-, m.p. 118—120°, and m-*ethoxy*-, m.p. 106—108°, p-n-*propoxy*-, m.p. 98—100°, p-, m.p. 125—127°, and o-n-*butoxy*-, m.p. 91—94°, p-n-*amyloxy*-, m.p. 125—126°, p-n-*hexyloxy*-, m.p. 125·5—127°, and p-n-*heptyloxy-benzoate hydrochloride*, m.p. 117—118°, *β-n-amylamino*isobutyl m-*ethoxy*-, m.p. 73—76°, p-n-*propoxy*-, m.p. 103—106°, p-n-*amyloxy*-, m.p. 103—104°, and p-n-*heptyloxy-benzoate hydrochloride*, m.p. 105—106°, *β-n-hexylamino*-isobutyl p-n-*propoxy*-, m.p. 118—120°, p-n-*butoxy*-, m.p. 122—123°, and p-n-*heptyloxy–benzoate hydrochloride*, m.p. 105—107°, *β-n-propyl-amino*isobutyl p-n-*butoxy*-, m.p. 105—107°, p-n-*amyloxy*-, m.p. 112—113°, and p-n-*heptyloxy-benzoate hydrochloride*, m.p. 108—110°, *β-ethyl*-, m.p. 136—138°, and *β-benzyl-amino*isobutyl p-n-*butoxy-benzoate hydrochloride*, m.p. 161—162°, *β-benzylamino*isobutyl p-n-*amyloxybenzoate hydrochloride*, m.p. 139—140°, *β-ethyl*-, m.p. 184—185°, β-n-*butyl*-, m.p. 134—135°, *β-n-hexyl*-, m.p. 135—136°, and *β-benzyl-amino*-n-*butyl* p-*ethoxybenzoate hydrochloride*, m.p. 181—184°, *β-n-butylamino*-n-*butyl* p-n-, m.p. 129—131°, and p-iso-*propoxy*-, m.p. 119—121°, and p-n-*butoxy-benzoate hydrochloride*, m.p. 114—116°, *β-n-hexylaminobutyl* p-n-*propoxybenzoate hydrochloride*, m.p. 112—114°, and *β-n-propylamino*-n-*butyl* p-n-*heptyloxybenzoate hydrochloride*, m.p. 108—109°. B.p. (not m.p.) are corr. R. S. C.

3-Bromosalicylic acid.—See A., 1943, II, 146.

Veratrole and methylenedioxybenzene series. R. T. Arnold and F. Bordwell (*J. Amer. Chem. Soc.*, 1942, **64**, 2983—2986).—p*K* (in 50% EtOH) recorded below show that the structure of the C_6H_6 rings in the veratrole and CH_2O_2:C_6H_4 series is very similar. Me veratrate, m.p. 58—59°, b.p. 165°/15 mm., and HNO_3 (*d* 1·59) in AcOH at 0° give 6 : 3 : 4 : 1-NO_2·$C_6H_2(OMe)_2$·CO_2Me, m.p. 144—145°, hydrogenated (Raney Ni; MeOH; 110°/1000 lb.) to the NH_2-ester, m.p. 128—129° (lit. 133°), which yields (diazo-reaction; $CuSO_4$–H_2SO_4) the 6-OH-ester, m.p. 95—96°, and thence the 6-OH-acid, m.p. 204—205° (decomp.) (lit. 201—202°) (p*K* 4·60). 6 : 3 : 4 : 1-NH_2·$C_6H_2(OMe)_2$·CHO yields 6 : 3 : 4 : 1-OH·$C_6H_2(OMe)_2$·CHO, m.p. 106—107° (p*K* 9·12), the *oxime*, m.p. 146—147°, of which in boiling Ac_2O gives *6-hydroxyveratronitrile*, sinters 120°, m.p. 142—145° (decomp.) (p*K* 8·69). *5-Nitro-4-hydroxyveratrole*, m.p. 142—143° (p*K* 8·33), is obtained from 5 : 1 : 2 : 4-NO_2·$C_6H_2(OMe)_2$·NHAc by hydrolysis and subsequent diazo-reaction. 36% of 3 : 4 : 6 : 1-CH_2O_2:$C_6H_2(OH)$·CO_2Me, m.p. 100—101°, is obtained from the NH_2-ester by a diazo-reaction as above. Similar reactions give *6-hydroxypiperonal* (**I**), m.p. 125—126° (p*K* 8·90), and thence the *oxime*, m.p. 142·5—143·5°, and *6-hydroxypiperonitrile*, m.p. 220—225° (decomp.) (p*K* 8·41). Ac_2O and (**I**) in C_5H_5N at 35—40° give *6-acetoxypiperonal*, m.p. 126—127°, oxidised by $KMnO_4$–$COMe_2$–H_2O to *6-acetoxypiperonylic acid*, m.p. 149—150°, which is obtained only with difficulty from the OH-acid (p*K* 4·58). *2-Nitro-4 : 5-methylenedioxyphenol*, m.p. 82·5—84°, is obtained from the NO_2-amine by a diazo-reaction. 3 : 4 : 1-CMe_2O_2:C_6H_3·NO_2 with H_2–Raney Ni in EtOH and then Ac_2O–NaOAc gives 3 : 4-iso*propylidenedioxyacetanilide*, m.p. 108·5—109·5°. 4 : 5 : 2 : 1-CMe_2O_2:$C_6H_2(NO_2)$·NH_2, m.p. 127—128°, gives (diazo-reaction) a little *2-nitro-4 : 5-isopropylidenedioxyphenol*, m.p. 148—149° (p*K* 8·68 in 67% EtOH). Veratric and piperonylic acid have p*K* 6·21 and 6·19, respectively R. S. C.

Identification of *o*- and *p*-sulphobenzoic acids as their *S*-benzylthiuronium salts. E. Campaigne and C. M. Suter (*J. Amer. Chem. Soc.*, 1942, **64**, 3040—3041).—*p*-SO_3H·C_6H_4·CO_2H, prepared by way of the Ba salt from *p*-C_6H_4Me·SO_3H by alkaline $KMnO_4$, with *S*-benzylthiuronium chloride gives *S-benzylthiuronium H p-sulphobenzoate*, m.p. 212·6—214·4° (corr.). *o*-SO_3H·C_6H_4·CO_2H gives the *dl*-*S-benzylthiuronium* salt, m.p. 205·5—206·5° (corr.). The *m*-acid gives a sol. salt. R. S. C.

Preparation of ethyl ethylmalonate and Δ¹-*cyclo*hexenylmalonate from the corresponding oxaloacetates. P. Galimberti [in part with S. Ponzini] (*Gazzetta*, 1942, **72**, 125—130).—$Et_2C_2O_4$ (**I**), Pr^aCO_2Et, and EtOH–NaOEt (**II**) at 60°, followed by H_2SO_4, give *Et₂ α-oxalobutyrate*, an oil, which at 160° loses CO, giving CHEt(CO_2Et)$_2$. *cyclo*Hexanone, CH_2Br·CO_2Et, and Zn in boiling C_6H_6 give Et 1-hydroxy*cyclo*hexylacetate, which with $KHSO_4$ gives Et Δ¹-*cyclo*hexylacetate. This with (**I**) and (**II**), followed by H_2SO_4, gives *Et₂ Δ¹-cyclohexenyloxaloacetate*, an oil, which at 135—140° loses CO, giving Et_2 *cyclo*hexenylmalonate. CH_2Ph·CO_2Et, (**I**), and (**II**), followed by EtI, give *Et₂ α-oxalo-α-phenylbutyrate*, b.p. 280—285°. E. W. W.

Carboxylation. IV. Direct introduction of the chloroformyl (·COCl) group into alicyclic and aliphatic acid chlorides. M. S. Kharasch, K. Eberly, and M. Kleiman (*J. Amer. Chem. Soc.*, 1942, **64**, 2975—2977; cf. A., 1942, II, 393).—*cyclo*Hexane and $ClCO_2CCl_3$ at 225° give 3% of *cyclo*hexane-1 : 1-dicarboxyl dichloride (**I**), identified by hydrolysis to the acid and conversion into the diamide, m.p. 261° (lit. 237°); absence of hexahydrobenzoyl chloride is due to the fact that this chloride gives similarly 81% of (**I**). Similarly $Pr^\beta COCl$ gives 70% of $CMe_2(COCl)_2$, $CHEt_2$·$COCl$ gives 90% of $CEt_2(COCl)_2$, $CHEtBu^\alpha$·$COCl$ gives 30% of $CEtBu(COCl)_2$, EtCOCl gives 15% of $CHMe(COCl)_2$, and CH_2Ph·$COCl$ gives 2% of $CHPh(COCl)_2$, but AcCl gives no $CH_2(COCl)_2$. The ease of α-substitution is thus CHR_2·$COCl$ > CH_2R·$COCl$ > AcCl. R. S. C.

Characteristic reaction of phenylmethylhydrazones of aromatic aldehydes. R. Ciusa and M. Di Fonzo (*Gazzetta*, 1942, **72**, 166—169).—The reaction (cf., Ciusa *et al.*, A., 1922, i, 474) whereby CHPh:N·NPhMe with HCl–Et_2O gives CHPh:N·NMe·C_6H_4·CHPh·C_6H_4·NMe·NH_2 (which with PhCHO gives its CHPh: derivative) is carried out with substituted compounds. *p*-OMe·C_6H_4·CH:N·NPhMe gives a similar *dimeride*, m.p. 233° (*p-nitrobenzylidene* derivative, m.p. 195°), and 3 : 4 : 1-CH_2O_2:C_6H_3·CH:N·NPhMe yields a *dimeride*, m.p. 178°, which with *p*-NO_2·C_6H_4·CHO gives, by condensation and replacement, *bis-p-nitrobenzaldehyde* p:p''-*piperonylidenebisphenylmethylhydrazone*, m.p. 200°. E. W. W.

Catalytic reduction of *N*-phenylnitrophenylnitrones. A. Gandini (*Gazzetta*, 1942, **72**, 28—37).—With Pt-black in Et_2O, *o*- and *p*-NO_2·C_6H_4·CH:NPh:O with 4 H_2 give orange-coloured resinous products, but with 1—3 H_2 they also give small quantities of N-*phenyl*-o- (**I**), m.p. 133°, and -p-*amino*-, m.p. 136—138°, and -o-, m.p. 132° [mixed m.p. with (**I**), 110—118°], and -p-*hydroxylamino-nitrone*, m.p. 116—117°. *m*-NO_2·C_6H_4·CH:NPh:O with 1 or 2 H_2 gives uncrystallisable products, but with 3 or, better, 4 H_2 gives N-*phenyl*-N-m-*aminobenzylhydroxylamine*, m.p. 122·5—123°. E. W. W.

Bromination of ketones.—See B., 1943, II, 108.

Synthesis of ketones having a diethylstilbœstrol carbon skeleton.—See B., 1943, III, 88.

Acetylphenylcarbinol and benzoylmethylcarbinol. Simultaneous formation starting from β-chloro-α-phenylpropan-α-one or from α-chloro-α-phenylpropan-β-one. Their identification. G. Richard (*Compt. rend.*, 1942, **214**, 673—675; cf. Favorski *et al.*, A., 1935, 622). —With N-NaOH in 50% aq. EtOH, CHPhCl·COMe (**I**) (rapidly at room temp.) or CHMeCl·COPh (slowly at 60°) gives COPh·COMe, b.p. 101—102°/12 mm. (semicarbazone, m.p. 229°), and a mixture of OH·CHPh·COMe (separated as $NaHSO_3$ compound), b.p. 122—123°/12 mm. [semicarbazone, m.p. 18]—182°; benzoate, new m.p. 108—109°; converted by $SOCl_2$ in CCl_4 into (**I**), which with C_6H_6 ($AlCl_3$) yields $CHPh_2$·COMe], and OH·CHMe·COPh, b.p. 128—132°/12 mm. (semicarbazone, m.p. 193°). A. Li.

Condensation of methylsuccinic anhydride with tolyl methyl ethers. B. L. Bhatt and K. S. Nargund (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 131—133).—With methylsuccinic anhydride and $AlCl_3$ in $PhNO_2$ (CS_2 or $C_2H_2Cl_4$ gives the same products in lower yields), *o*-C_6H_4Me·OMe yields *γ-keto-γ-6-methoxy*-m-*tolyl-α-methylbutyric acid*, m.p. 124° [*Ag* salt; *semicarbazone*, m.p. 170° (decomp.); *Me*, b.p. 190—192°/13 mm., and *Et* ester, b.p. 197—198°/10 mm.], oxidised (NaOBr) to 4 : 3 : 1-OMe·C_6H_3Me·CO_2H, *m*-C_6H_4Me·OMe yields *γ-keto-γ-5-methoxy-o-tolyl-α-methylbutyric acid*, m.p. 113° (*semicarbazone*, m.p. 172—173°; *Me*, b.p. 187—189°/12 mm., and *Et* ester, b.p. 193°/11 mm.), oxidised to 4 : 2 : 1-OMe·C_6H_3Me·CO_2H, and *p*-C_6H_4Me·OMe yields *γ-keto-γ-4-methoxy*-m-*tolyl-α-methylbutyric acid*, m.p. 129° (no semicarbazone; *Me*, b.p. 176—180°/9 mm., and *Et* ester, b.p. 160°/3 mm.), oxidised to 2 : 5 : 1-OMe·C_6H_3Me·CO_2H. The CO-acids give pyrylium derivatives with *o*-OH·C_6H_4·CHO and HCl. A. Li.

Factors determining the course and mechanism of Grignard reactions. V. Effect of metallic halides on the reaction of Grignard reagents with phenyl styryl ketone and benzophenone. M. S. Kharasch and D. C. Sayles (*J. Amer. Chem. Soc.*, 1942, **64**, 2972—2975; cf. A., 1942, II, 48).—Metallic chlorides (2—5%) do not affect the ratio of 1 : 2 to 1 : 4 addition of MgMeBr (1·4 mols.) to CHPh:CH·COPh (**I**), but change the nature of the products. In absence of a chloride at 0—5°, CHPhMe·CH_2·COPh (**II**) (59%) and *δ-benzoyl-αγε-triphenyl-Δ$^{\alpha\gamma}$-n-hexadiene* (**III**) (41%), m.p. 176°, are formed; 1 mol.-% of $FeCl_3$ leads to (**II**) (66%), (**III**) (9%), (·CHPh·CH_2·COPh)$_2$, forms (**IV**) (21%), m.p. 197°, and (**V**) (4%),

m.p. 276°; CuCl leads to (**II**) (69%), (**III**) (24%), and (**IV**) (7%); $MnCl_2$ leads to (**II**) (73%) and (**III**) (27%); $CoCl_2$ yields only (**IV**) (82%) and (**V**) (18%). (**III**) is formed by addition of (**I**) to (**II**) under the influence of MgMeBr, and also of C_5H_5N, NMe_3, or NaOEt; its formation is entirely suppressed only if 3 mols. of MgMeBr are used. At 20—25°, MgEtBr and $COPh_2$ with or without $CoCl_2$ give only $CPh_2Et{\cdot}OH$, but at −12° 50% of $(CPh_2{\cdot}OH)_2$ is obtained in presence of 2 mol.-% of $CoCl_2$, showing that the stability of CoEtCl is the determining factor. Metallic halides have little effect on the 1 : 4 addition of MgPhBr to (**I**), but 2—5 mol.-% of $FeCl_3$ or $CoCl_2$ gives 2—5% of (**V**). MgEtBr and (**I**) at 25° give 60% of $COPh{\cdot}CH_2{\cdot}CHPhEt$ (removed by acethydrazidepyridinium chloride) and 40% of *αγ-diphenyl-*Δ^{α}*-n-penten-γ-ol* (**VI**), an oil (cf. Kohler, A., 1907, i, 1050); at −25° somewhat less (**VI**) is formed. (**VI**) is determined by titration by $KMnO_4$. In one experiment using $MnCl_2$ a *substance*, $C_{32}H_{32}O_2$, m.p. 136° (2 : 4-*dinitrophenylhydrazone*), was isolated. R. S. C.

α-Alkylaminoacylophenones.—See B., 1943, II, 108.

Action of phosphoric oxide on phenyl esters. Mechanism of the Fries reaction. A. Schönberg and (Miss) A. Mustafa (*J.C.S.*, 1943, 79—80).—PhOBz and P_2O_5 in $PhNO_2$ at 150° give *p*-$C_6H_4Bz{\cdot}OBz$ and PhOH (converted into Ph phosphates). *m*-Tolyl and α-$C_{10}H_7$ benzoate similarly give 6-benzoyl-*m*-tolyl and 4-benzoyl-1-naphthyl benzoate, respectively. Results support the view of Rosenmund *et al.* (A., 1928, 1010) on the mechanism of the Fries reaction. A. T. P.

Enediols. XI. Vinylogues of ethylene and acetylene glycols. R. C. Fuson, D. J. Byers, and A. I. Rachlin (*J. Amer. Chem. Soc.*, 1942, **64**, 2891—2893; cf. A., 1943, II, 35).—$CH_2{:}CMes{\cdot}COMes$ (**I**) (Mes = mesityl) and Mg + MgI_2 in hot C_6H_6 give *αβεζ-tetramesityl-*$\Delta^{\alpha\varepsilon}$*-n-hexadiene-αζ-diol* (**II**) (94%), m.p. 207—208° (*diacetate*, m.p. 217·5—218·5°), the structure of which is proved by atm. oxidation in $COMe_2$ to $(CH_2{\cdot}COMes)_2$ and MesOH. Boiling HCl–EtOH ketonises (**II**) to *αβεζ-tetramesityl-*n*-hexane-αζ-dione*, m.p. 259—261°, which with MgEtBr in Et_2O–C_6H_6 regenerates (**II**). With $KMnO_4$ in $COMe_2$, (**II**) yields (**I**) and a little yellow *αβεζ-tetramesityl-*$\Delta^{\beta\delta}$*-n-hexadiene-αζ-dione* (**III**), m.p. 282—284°; with $Pb(OAc)_4$ in C_6H_6, (**III**) is the main and (**I**) the subsidiary product. H_2–PtO_2 in C_6H_6 or Zn dust in AcOH at 100° reduces (**III**) to colourless *αβεζ-tetramesityl-*$\Delta^{\alpha\gamma\varepsilon}$*-n-hexatriene-αζ-diol* (**IV**), m.p. 252—253°, unstable [with boiling Ac_2O gives a *diacetate*, m.p. 273—274°, obtained directly from (**III**) by H_2–PtO_2 and a little $ZnCl_2$–HCl in Ac_2O], which with aq. H_2O_2 regenerates (**III**). (**IV**) and *αβεζ-tetramesityl-*Δ^{γ}*-n-hexene-αζ-dione*, m.p. 201°, are interconvertible by HCl–EtOH and MgEtBr. R. S. C.

Velocity of formation of oximes of *cyclo*hexanone and its derivatives.—See A., 1943, I, 132.

New benzyl derivative of 4-methyl*cyclo*hexanone. A. R. Poggi (*Gazzetta*, 1942, **72**, 16—18).—4-Methyl*cyclo*hexanone, CH_2PhCl, and $NaNH_2$ in C_6H_6 give the 2-*CH*$_2$*Ph* derivative, b.p. 169·5—170°/17 mm. [*oxime*, m.p. 129° (softens 125°); *semicarbazone A*, m.p. 196° (softens 160°), *B*, m.p. 174° (softens 169°); 2 : 4-*dinitrophenylhydrazone*, m.p. 146° (softens 141°)]. E. W. W.

Preparation of β-6-keto-2-methyl-Δ^1**-*cyclo*hexenylpropionic acid.** E. Schwenk and (Miss) E. Bloch (*J. Amer. Chem. Soc.*, 1942, **64**, 3050—3051).—Adding $(CH_2O)_3$ to $CH_2Ac{\cdot}CO_2Me$ and piperidine at 60—80°, adding Na_2SO_4 and keeping in the cold, and hydrolysing the product by boiling NaOEt–EtOH gives *Me* 3-*methyl*-Δ^2-cyclo*hexenone*-4-*carboxylate* (**I**) (37%), b.p. 135°/2 mm. (*semicarbazone*, m.p. 168—170°), and some 3-methyl-Δ^2-*cyclo*hexenone, b.p. 70°/2 mm. With NaOMe and $Br{\cdot}[CH_2]_2{\cdot}CO_2Me$ in boiling MeOH, (**I**) gives *Me* β-6-*keto*-3-*carbomethoxy*-2-*methyl*-Δ^1-cyclo*hexenylpropionate* (83%), b.p. 170—180°/1 mm. (*semicarbazone*, m.p. 145—148°). This and the corresponding Et ester, b.p. 184—186°/2 mm. [similarly prepared (70%); 2 : 4-*dinitrophenylhydrazone*, m.p. 120—122°], are converted by boiling 42% HI into β-6-*keto*-2-*methyl*-Δ^1-cyclo*hexenylpropionic acid*, m.p. 79—81°, which could not be cyclised to a hydrindone derivative. R. S. C.

Macrocyclic ring systems. II. Synthesis of *r*-muscone. H. Hunsdiecker (*Ber.*, 1942, **75**, [*B*], 1197—1201).—$CHMe{:}CH{\cdot}CO_2Et$ and $CH_2(COMe)_2$ are condensed (NaOEt in EtOH) to the tricarboxylic ester, which is hydrolysed, decarboxylated, and partly esterified to a mixture (**I**) of Me H β-methylglutarate and β-methylglutaric anhydride. Mixed electrolysis (Pt cathode, Ni anode, MeOH–NaOMe) of (**I**) and *κ-methoxyundecoic acid*, f.p. 32·7°, b.p. 170°/4 mm. (from $Br{\cdot}[CH_2]_{10}{\cdot}CO_2H$), gives Me_2 βε-dimethylhexane-αζ-dicarboxylate, b.p. 115°/1·5 mm., Me *ν*-methoxy-β-methyltetradecoate (**II**), b.p. 146°/1·5 mm. (yield 34·4%), and *αν*-dimethoxyeicosane, b.p. 185—193°/1·5 mm. (**II**) and 40% HBr–AcOH at 150° give *ν-bromo-β-methyltetradecoic acid*, b.p. 207°/3 mm., m.p. 51—52°, transformed ($SOCl_2$) into the chloride, which is condensed with $CHAcNa{\cdot}CO_2Et$ giving a product converted by NaOMe at room temp. into *Me o-bromo-β-keto-δ-methylhexadecoate* (**III**), m.p. 22°. (**III**) is converted into the I-derivative, which is added gradually to a boiling suspension of anhyd. K_2CO_3 in boiling COMeEt, giving Me 2-keto-4-methyl*cyclo*pentadecanecarboxylate, b.p. 162°/1 mm., hydrolysed and decarboxylated by 80% H_2SO_4 at room temp. to *r*-muscone, b.p. 132—134°/0·8 mm. (semicarbazone, m.p. 133—133·5°). H. W.

Fluorenones and diphenic acids. IX. Establishment of authentic 1- and 4-bromofluorenones. E. H. Huntress, K. Pfister, tert., and K. H. T. Pfister (*J. Amer. Chem. Soc.*, 1942, **64**, 2845—2849; cf. A., 1939, II, 370).—Fluorenone-1-carboxyl chloride (**I**) gives the amide (**II**), m.p. 226·5—227°, and thence (KOBr–KOH) 1-aminofluorenone, m.p. 118—118·5° (lit. 110°) (*Ac*, m.p. 138—138·3°, and *Bz* derivative, m.p. 149—149·8°), which afford by diazo-reactions 1-*chloro-*, m.p. 137—137·8°, 1-bromo- (**III**), m.p. 134—134·3° (lit. 135°), 1-*iodo-*, m.p. 146·5—147°, and 1-*cyano-fluorenone* (14%), m.p. 174—174·5° [also obtained (48%) (m.p. 177·2—177·8°) from (**II**) by PCl_5 at 200°; proof of orientation: hydrolysis by hot 50% H_2SO_4 to the acid]. Fluorenone-4-carboxylic acid (prep. from diphenic acid by H_2SO_4 at 140 ± 5°) gives ($SOCl_2$; aq. NH_3) the amide, m.p. 223—224°, and thence (KOBr–KOH) 4-amino-, m.p. 138—139°, and (diazo-reaction) 4-bromo-fluorenone, m.p. 125—126° [depresses the m.p. of (**III**); cf. France *et al.*, A., 1938, II, 437; Miller *et al.*, A., 1936, 335]. The acid, m.p. 227—228°, obtained from 3 : 1 : 2-$C_6H_3Br(CO)_2O$, C_6H_6, and $AlCl_3$ (Stephens, A., 1922, i, 141, m.p. 231·5°), is shown to be 3- (not 6-)*bromo-2-benzoylbenzoic acid*; it gives a *Me* ester, m.p. 136·7—137·5°, acid chloride, m.p. 121—122° (lit. 119—120°), *amide*, m.p. 202—202·5°, and thence 2-*bromo*-6-*aminobenzophenone*, m.p. 84·5—85·5°, which with $NaNO_2$–H_2SO_4 at 0° and later with added Na_2SO_4 at 100° yields (**III**) (25%). Warm NH_2Ph and (**I**) give *fluorenoneanil-1-carboxylanilide*, m.p. 184·7—185°. M.p. are on a Cu block. R. S. C.

Indene derivatives. II. Triketohydrindene. A. Schönberg and R. Moubacher (*J.C.S.*, 1943, 71—72).—*Triketohydrindene* (**I**), m.p. 255° (dark red solid melts to a bluish-green liquid, from which red crystals re-form), is obtained from its hydrate (ninhydrin) (**II**) and $SOCl_2$ at 60—70° (in a vac.), or less readily from (**I**) at 190° in a vac. (**I**) with hot H_2O (1 min.) in absence of direct sunlight gives (**II**), also obtained when the bluish-green solution of (**I**) in C_6H_6 is shaken with H_2O. (**I**) gives a bluish-green solution in hot AcOH, but is almost colourless in cold AcOH owing to the formation of a dissociable additive compound. (**II**) heated in C_6H_6 gives a bluish-green solution containing (**I**), and (**II**) at 190° in a current of O_2 yields *o*-$C_6H_4(CO)_2O$. An inner-salt formula is suggested for (**II**). A. T. P.

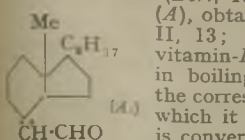
2-Nitro-1-amino-4-acylamidoanthraquinones.—See B., 1943, II, 108.

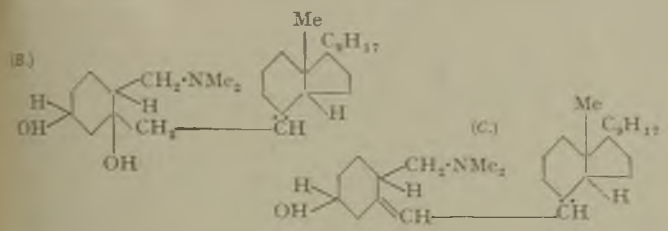
Action of bases on 1-diazoanthraquinone-2-sulphonate and its derivatives. J. I. Lynas-Gray and J. L. Simonsen (*J.C.S.*, 1943, 45—47).—Na 1-diazoanthraquinone-2-sulphonate (**I**) (1 part), its 4-NHPh- (**II**) and 4-Br-derivative (**III**) in Et_2O react with NH_2R (3 parts) and Cu-bronze (0·003 part) at 0°, then at 60°, and the resulting mixtures are separated by chromatographic analysis (EtOH–Al_2O_3); yields of sulphonic acids are calc. as Na salts. (**I**) and NH_2Ph thus give 1-aminoanthraquinone-2-sulphonic acid (**IV**) (100%), whereas (**I**) and aq. NH_3 (no Cu necessary) give (**IV**) (50%) and 1-hydroxyanthraquinone-2-sulphonic acid (50%). (**I**) and NH_2Ph–AcOH at 0°, followed by aq. NaOH until alkaline, give the Na diazoamino-compound, which with aq. H_2SO_4 at 50° affords PhOH, (**IV**), and the *NH*$_2$*Ph* salt, m.p. 248° (darkens at 238°), of 1-diazophenylaminoanthraquinone-2-sulphonic acid. (**II**) and NH_2Ph yield 1-amino-4-anilinoanthraquinone-2-sulphonic acid (**V**) (15%) (p-*toluidine* salt, decomp. 269—270°, sinters 263°), 1-anilinoanthraquinone-3-sulphonic acid (**VI**) (45%) (*Na* salt; p-*toluidine* salt, decomp. ~290°, sinters 286—288°), and 1 : 4-dianilinoanthraquinone-2-sulphonic acid (**VII**) (40%) (*Na* salt; p-*toluidine* salt, decomp. 252°), whereas (**II**) and *p*-$C_6H_4Me{\cdot}NH_2$ or *m*-4-xylidine yield (**V**) (10 or 62%, respectively), (**VI**) (50 or 32%), and 4-anilino-1-*p*-toluidino- (40%) (*Na* salt; p-*toluidine* salt, m.p. 231—232°) or 4-anilino-1-*m*-4-xylidino-anthraquinone-2-sulphonic acid (6%) (*Na* salt; p-*toluidine* salt, decomp. 250°), respectively. Reduction of the respective Na sulphonates with glucose affords 1-*anilino*-4-p-*toluidino-*, m.p. 250°, and -4-m-4′-*xylidino-anthraquinone*, m.p. 232—233°, the latter also being obtained from 1 : 3 : 4-$C_6H_3Me_2Cl$, 1-amino-4-anilinoanthraquinone, Cu, and NaOAc. (**III**) and NH_2Ph yield (**V**) (10%), 4-bromo-1-aminoanthraquinone-2-sulphonic acid (20%) (p-*toluidine* salt, decomp. 252°), (**VI**) (40%), and (**VII**) (30%), but (**III**) and aq. NH_3 at 70—80° give 1 : 4-diaminoanthraquinone-2-sulphonic acid (94%) (*Na* salt) and 5—6% of 4 : 4′-diamino-1 : 1′-dianthraquinolyl-3 : 3′-disulphonic acid (**VIII**) (*Na*$_2$ salt; p-*toluidine* salt, +3H_2O, m.p. 234—235°), also obtained from Na 4-bromo-1-aminoanthraquinone-2-sulphonate and Cu–H_2O (+ a drop of alkali), and reduced (glucose) to 4 : 4′-*diamino*-1 : 1′-*dianthraquinonyl*, m.p. 356—358° [? 3 : 3′-*Br*$_2$-derivative, m.p. 415—416°, from (**VIII**) and Br]. (**III**) and NH_2Me give 100% of *Na* 1-*amino*-4-*methylaminoanthraquinone*-2-*sulphonate*. A. T. P.

IV.—STEROLS AND STEROID SAPOGENINS.

Attempted synthesis of the antirachitic vitamin. XI. Partial synthesis of vitamin-*D*$_2$ and its 3-*epi*-compounds. K. Dimroth and

E. Stockstrom (*Ber.*, 1942, **75**, [*B*], 1263—1270).—The aldehyde (*A*), obtained according to Windaus *et al.* (A., 1943, II, 13; cf. Heilbron *et al.*, A., 1936, 1105) from vitamin-D_2 dinitrobenzoate, is converted by $Al(OPr^{\beta})_3$ in boiling $Pr^{\beta}OH$ followed by NaOH–MeOH into the corresponding primary *alcohol* (**I**), m.p. 71°, from which it is re-formed by oxidation with CrO_3. (**I**) is converted by PBr_3 and C_5H_5N in C_6H_6 followed by Mg in Et_2O into the Grignard reagent, which is treated with the base from 3-acetoxy-6-dimethylaminomethyl*cyclo*hexanone hydrochloride, m.p. 191°; the non-cryst. product is hydrolysed to isomeric *alcohols* (as *B*), m.p. 64° and 145°. Direct treatment of the acetate mixture with PBr_3 followed by solid KOH





gives the unsaturated *alcohols* (as *C*), m.p. 151° and 164°; the former is degraded (Hofmann) to vitamin-D_2 (**I**), m.p. 108—109° (block), 114° (bath), $[\alpha]_D^{20}$ +122° in EtOH [dinitrobenzoate, m.p. 148—149° (bath)], identical chemically and biologically with the natural product. The latter gives a *substance* (**II**), m.p. 179—180°, isomeric with (**I**) which is possibly feebly dextrorotatory. The ultra-violet absorption spectra of (**I**) and (**II**) are practically identical with one another and with that of natural (**I**). H. W.

Partial oxidation of cholic acid. T. F. Gallagher and W. P. Long (*J. Biol. Chem.*, 1943, **147**, 131—134).—The OH groups of cholic acid are oxidised (CrO_3) in the order 7, 12, 3. Me cholate and CrO_3–aq. AcOH at −7° to 0° give products, separated chromatographically after acetylation into *Me* 7-*keto*-3 : 12-*diacetoxycholanate* (**I**) (40%), m.p. 114—117° (corr.), $[\alpha]_D$ +64° in EtOH [*oxime*, m.p. 155·5—157° (corr.)], Me 7 : 12-diketo-3-acetoxycholanate (40%), and Me dehydrocholate (20%). (**I**) and boiling aq. NaOH–EtOH yield 3 : 12-*dihydroxy*-7-*ketocholanic acid*, m.p. 197—199° (corr.) (negligible rotation in EtOH) (*Me* ester, m.p. 152—154°). The *semicarbazone*, m.p. 175—177° (corr.), of (**I**) and N_2H_4,H_2O–NaOEt–EtOH at 200° give a good yield of deoxycholic acid (cf. Haslewood, A., 1942, II, 365). A. T. P.

Preparation of progesterone by oxidising cholesterol with hydrogen peroxide. C. Serono and E. Marchetti (*Gazzetta*, 1942, **72**, 151—154).—Cholesterol dibromide in C_6H_6 with H_2O_2 in presence of Ag_2O and dil. NaOH, at 60—80°, followed by debromination (Zn–AcOH), gives progesterone. E. W. W.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Resistance of cineole derivatives to concentrated acids. G. Cusmano (*Gazzetta*, 1942, **72**, 68—73).—2-Ketocineole (**I**) is fairly stable to conc. HCl (**II**), which slowly gives carvacrol and a product containing Cl; conc. HNO_3 (**III**) has a slow oxidising action. (**II**) or (**III**) may be used to liberate 3-substituted 2-ketocineoles from their semicarbazones, since the velocity of hydrolysis is > that of formation of secondary products. (**I**) is stable to conc. H_2SO_4 (**IV**) at 0°, but at 5° gives "*iso*camphorone." The semicarbazone of (**I**) with (**IV**) at <30° slowly gives, by a new transposition, carvacrylsemicarbazide (**V**) (2-*p*-cymylsemicarbazide; cf. Wheeler *et al.*, A., 1929, 1438), with 8-hydroxycarvotanacetone (**VI**). Either of the two semicarbazones of carvone (**VII**) with (**IV**) gives (**V**) and (**VI**), with some (**VII**). The semicarbazone of (**VI**) gives (**V**) and (**VI**). E. W. W.

Decomposition of pernitrosocamphor. A. Gandini (*Gazzetta*, 1942, **72**, 131—134).—Pernitrosocamphor in paraffin at 100° begins to lose H_2O. At 150—160° decomp. to NO, NO_2, and α-campholenonitrile is soon complete. E. W. W.

Decomposition of ascaridole by heat. M. M. Janot and M. Chaigneau (*Compt. rend.*, 1942, **214**, 746—747).—When ascaridole is heated in air or N_2, or at 320°/0·1 mm., it yields a mixture of C_3H_8, CO, C_3H_6, and C_2H_4 in the approx. ratio 2 : 3 : 1 : 1, together with small amounts of CO_2. At 760 mm. O_2 is unnecessary for the start of the decomp. J. N. A.

Melanthigenin and its identity with hederagenin. (Miss) Z. Mustafa and G. Soliman (*J.C.S.*, 1943, 70—71).—Melanthigenin, $C_{29}H_{47}O_3{\cdot}CO_2H$, m.p. >325°, isolated by hydrolysis of an EtOH extract of the defatted seeds of *Nigella sativa*, L., is hederagin (comparison of the Ac_2 and Bz_2 derivatives and the Me ester and its Ac_2 and Bz_2 derivatives). The position of its one double bond is located by the formation of a diformyl lactone. F. R. S.

VI.—HETEROCYCLIC.

Tetrahydrofurfuryl acetals.—See B., 1943, II, 113.

5-Hydroxycoumarins. I. Chalkones from 5-hydroxy-6-acetyl-4-methylcoumarin. N. M. Shah (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 109—112).—5-Hydroxy-6-acetyl-4-methylcoumarin (**I**) with RCHO and 50% aq. KOH (added slowly with cooling) at room temp. yields 5-*hydroxy*-4-*methyl*-6-*coumarino styryl ketone* (2 forms), m.p. 220—221° (**II**) and 175—176° (**III**), and 5-*hydroxy*-4-*methyl*-6-*coumarino* 3′-*hydroxy*-4′-*methoxy*-, m.p. 163—164°, 2′ : 4′-*dihydroxy*-, m.p. 166—167°, 3′ : 4′-*dihydroxy*-, m.p. 163°, 4′-*methoxy*-, m.p. 243°, and 2′-*hydroxy*-*styryl ketone*, m.p. 233° (decomp.). With dil. NaOH at 100°, (**II**) gives (**III**), whilst (**III**) yields 4-*methylflavanono*-7′ : 8′ : 6 : 5-α-*pyrone*, m.p. 237°. With SeO_2 in $C_5H_{11}{\cdot}OH$, (**III**) yields 4-methylflavono-7′ : 8′ : 6 : 5-α-pyrone. CHPh:CH·CHO gives no cryst. product with (**I**). A. Li.

Aluminium chloride, new reagent for condensation of β-ketonic esters with phenols. VIII. Condensation of resacyl- and gallacylphenones (4-acyl-resorcinol and -pyrogallols) containing long-chain acyl groups. M. C. Chudgar and N. M. Shah (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 113—115).—4-Stearylresorcinol (**I**) and $CH_2Ac{\cdot}CO_2Et$ with $AlCl_3$ in $PhNO_2$ at 110—115° yields 5-*hydroxy*-6-*stearyl*-4-*methylcoumarin* (+0·5H_2O), m.p. 116—117° (red colour with $FeCl_3$; *acetate*, m.p. 98°), which with NaOAc in Ac_2O gives 2′ : 4-*dimethyl*-3′-*hexadecylchromono*-7′ : 8′ : 6 : 5-α-*pyrone*, m.p. 135—136°. (**I**) is reduced (Clemmensen) to 4-octadecylresorcinol, which with $CH_2Ac{\cdot}CO_2Et$ ($POCl_3$) at room temp. yields 7-*hydroxy*-6-*octadecyl*-4-*methylcoumarin*, m.p. 116—117° (*acetate*, m.p. 78—79°). 5-Nitro- and 5-bromo-4-stearylresorcinol and 4-stearylpyrogallol do not undergo this reaction. These results are explained in terms of fixation of the double linking. A. Li.

Reduction of –CH(OH)·CCl_3 group attached to benzo-α-pyrone nucleus. II. M. C. Chudgar and N. M. Shah (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 116—119).—7-Methoxy-4-methyl-3-βββ-trichloro-α-methoxyethyl)coumarin is reduced (Zn–AcOH) to 7-*methoxy*-4-*methyl*-3-α-*chlorovinyl*-, m.p. 160—161°, or (Zn–AcOH–conc. HCl) to -3-ββ-*dichloroethyl*-*coumarin*, m.p. 113—114°. 7-Hydroxy-4-methyl-6-ethyl-3-βββ-trichloro-α-hydroxyethyl- (**I**) is reduced (Zn–AcOH) to -3-α-*chlorovinyl*-, m.p. 138—140° (*acetate*, m.p. 191—192°), or (Zn–AcOH–HCl) to -3-ββ-*dichloroethyl*-*coumarin*, m.p. 253—255° [*acetate* (**II**), m.p. 167°], similarly obtained from the acetate of (**I**). The latter is reduced (Zn–AcOH) to (**II**). 4-Butylresorcinol with $CO_2Et{\cdot}CHAc{\cdot}CH(OH){\cdot}CCl_3$ and $POCl_3$ at room temp. yields 7-*hydroxy*-4-*methyl*-3-βββ-*trichloro*-α-*hydroxyethyl*-6-*butylcoumarin*, m.p. 166—167° (*acetate*, m.p. 123—124°), which undergoes the same reactions as (**I**), giving 7-*hydroxy*-, m.p. 167°, and -*acetoxy*-4-*methyl*-3-α-*chlorovinyl*-6-*butyl*-, m.p. 143°, and 7-*hydroxy*-, m.p. 196—197°, and -*acetoxy*-4-*methyl*-3-ββ-*dichloroethyl*-6-*butylcoumarin*, m.p. 156—157°. A. Li.

Transformation of *o*-nitrobenzoyloxyacetoarones into *o*-hydroxyaroylnitrobenzoylmethanes, and synthesis of nitroflavones. V. V. Virkar (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 136—139; cf. A., 1940, II, 22).—o-3′-*Nitrobenzoyloxyacetophenone*, m.p. 99—100° (from *o*-OH·C_6H_4·COMe and *m*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ in C_5H_5N at 100°), with Na in PhMe at 130° yields 3′-*nitro*-2-*hydroxydibenzoylmethane*, m.p. 157°, cyclised (HBr–AcOH) to 3′-*nitro*-, m.p. 203°, reduced ($SnCl_2$–Sn–HCl) to 3′-amino-flavone. Similarly 1-3′-, m.p. 152°, and 1-4′-*nitrobenzoyloxy*-2-*acetonaphthone*, m.p. 151°, yield respectively 1-*hydroxy*-3′-, m.p. 196°, and -4′-*nitrobenzoyl*-2′-*naphthoylmethane*, m.p. 222°, 3′-, m.p. 262°, and 4′-*nitro*-, m.p. 293°, and 3′-, m.p. >300° (hydrochloride, m.p. >300°), and 4′-*amino*-*flavone*, m.p. 265° (hydrochloride, m.p. >300°). A. Li.

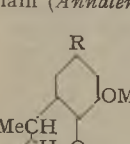
Chromones of the naphthalene series. Transformation of *o*-naphthoyloxyacetoarones into *o*-hydroxydiaroylmethanes. V. V. Virkar and R. C. Shah (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 140—143; cf. A., 1940, II, 22).—o-α-, m.p. 108°, and o-β-*naphthoyloxyacetophenone*, m.p. 119° (from *o*-OH·C_6H_4·COMe and $C_{10}H_7{\cdot}COCl$ in C_5H_5N), with Na in PhMe at 130° yield respectively o-*hydroxybenzoyl*-1′-, m.p. 124°, and -2′-*naphthoylmethane*, m.p. 141°, cyclised by HI in Ac_2O to 2-1′-, m.p. 138—139°, and 2-2′-*naphthylchromone*, m.p. 134°. Similarly 4-*benzoyloxy*-2-2′-*naphthoyloxyacetophenone*, m.p. 103—104°, gives 2-*hydroxy*-4-*benzoyloxybenzoyl*-2′-*naphthoylmethane*, m.p. 167—168°, which yields, with HBr in AcOH, 7-*benzoyloxy*-, m.p. 198°, and with HI in Ac_2O, 7-*hydroxy*-2-2′-*naphthylchromone*, m.p. 288° (*acetate*, m.p. 190°), whilst 2-benzoyloxy-4-methoxyacetophenone gives 2-*hydroxy*-4-*methoxydibenzoylmethane*, m.p. 105°, and 7-methoxyflavone. 4-*Benzoyloxy*-2-1′-*naphthoyloxyacetophenone*, m.p. 104°, with Na in boiling C_6H_6 yields 7-*hydroxy*-2-1′-*naphthylchromone*, m.p. 291° (sintering at 188°) (*acetate*, m.p. 173°; *benzoate*, m.p. 159°). A. Li.

Kostanecki–Robinson reaction. IV. Acetylation, propionylation, and butyrylation of orcpropiophenone. P. L. Trivedi, S. M. Sethna, and R. C. Shah (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 144—150).—2 : 4-*Dihydroxy*-6-*methylpropiophenone* (**I**), m.p. 127—128° (from orcinol, EtCN, $ZnCl_2$, and HCl in Et_2O), with NaOAc in Ac_2O at 180—190° yields the *acetate*, m.p. 122—123°, of 7-*hydroxy*-2 : 3 : 5-

trimethylchromone, m.p. 269—273°, the *Me ether*, m.p. 159°, of which is also obtained by treatment of 2 : 4 : 6 : 1-(OMe)$_2$C$_6$H$_2$Me·COMe (**II**) with EtOAc and Na at 115—120°, methylation (MeI in COMe$_2$), and cyclisation (HBr at room temp.). (**I**) with EtCO$_2$Na and (EtCO)$_2$O at 180—190° yields the *propionate*, m.p. 75°, of 7-*hydroxy*-3 : 5-*dimethyl*-2-*ethylchromone*, m.p. 258—261° (*acetate*, m.p. 107—108°), the *Me ether*, m.p. 130—131°, of which is also obtained from (**II**) by treatment with EtCO$_2$Et and Na at 115—120°, methylation, and cyclisation. (**I**) with PrCO$_2$Na and (PrCO)$_2$O at 180—190° yields a product which with conc. H$_2$SO$_4$ gives 7-*hydroxy*-3 : 5-*dimethyl*-2-*propylchromone*, m.p. 238—241° (*acetate*, m.p. 95°), the *Me ether*, m.p. 91—92°, of which is also obtained from (**II**), PrCO$_2$Et, and Na as above. A. Li.

Dibenzfurans.—See B., 1943, II, 6.

Lignin. LII. Constitution of dehydrodi*iso*eugenol and its significance in the chemistry of lignin. K. Freudenberg and H. Richtzenhain (*Annalen*, 1942, **552**, 126—135; cf. Erdtmann, A., 1933, 390, 818).—Evidence is adduced in favour of the constitution (*A*) (R = CH:CHMe, R′ = H) for dehydrodi*iso*eugenol. Fission of the compound *A* (R = Pr^a, R′ = Me) with K in liquid NH$_3$ followed by methylation (NaOH–Me$_2$SO$_4$) of the product gives α-3 : 4-*dimethoxyphenyl*-β-2 : 3-*dimethoxy*-5-*propylphenylpropane* (**I**), b.p. 145—150°/0·01 mm., demethylated by HBr in boiling AcOH to the corresponding (*OH*)$_4$-compound (**II**), m.p. 131°. 2-Hydroxy-3-methoxy-5-allyl- is hydrogenated (Pd–BaSO$_4$ in AcOH) to 2-*hydroxy*-3-*methoxy*-5-n-*propyl*-*benzaldehyde*, b.p. 155°/10 mm. (2 : 4-dinitrophenylhydrazone, m.p. 223°), the Na salt of which is methylated (NaOH–Me$_2$SO$_4$) to 2 : 3-*dimethoxy*-5-n-*propylbenzaldehyde*, b.p. 155—156°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 202°). This is converted by hippuric acid, anhyd. NaOAc, and Ac$_2$O at 100° into the *azlactone*, C$_{21}$H$_{21}$O$_4$N, m.p. 158—159°, hydrolysed by boiling 10% NaOH to 2 : 3-*dimethoxy*-5-n-*propylphenylpyruvic acid*, m.p. 130—131°, which is oxidised by H$_2$O$_2$ in presence of NaHCO$_3$ at 0° to 2 : 3-*dimethoxy*-5-n-*propylphenylacetic acid*, m.p. 93—94°. This is converted into the chloride, which with veratrole and AlCl$_3$ in CS$_2$ affords 2 : 3-*dimethoxy*-5-n-*propylbenzyl* 3 : 4-*dimethoxyphenyl ketone*, m.p. 87—88°. The ketone is converted into its Na$_4$ derivative, which with MeI in C$_6$H$_6$ at 100° yields α-*keto*-α-3 : 4-*dimethoxyphenyl*-β-2 : 3-*dimethoxy*-5-n-*propylphenylpropane*, m.p. 101°, slowly reduced (Clemmensen) to (**I**), which is hydrolysed to (**II**). Attempted dehydrogenation of coniferyl alcohol (**III**) by FeCl$_3$ leads to an amorphous condensate which after methylation, treatment with hot alkali, renewed methylation, and oxidation yields veratric acid with traces of *iso*hemipinic acid. These acids are obtained from lignin and the coumaronecarboxylic acid (*A*; R = CO$_2$H, R′ = Me) under the same circumstances. Dehydrogenation of (**III**) is therefore in part at any rate similar to that of *iso*eugenol. H. W.



(*A*.)

Furylchromones. G. B. Marini-Bettolo (*Gazzetta*, 1941, **71**, 635—641).—2-Hydroxy-4-methoxy- (**I**) and -3 : 4-dimethoxy-ω-furfurylideneacetophenone (**II**) with SeO$_2$ in boiling C$_5$H$_{11}$·OH (15 hr.) give 7-*methoxy*-, m.p. 160°, and 7 : 8-*dimethoxy*-2-*furylchromone*, m.p. 165°. 2 : 4 : 5 : 1-OH·C$_6$H$_2$(OMe)$_2$·COMe with furfuraldehyde and KOH–EtOH gives 2-*hydroxy*-4 : 5-*dimethoxy*-ω-*furfurylideneacetophenone* (**III**), m.p. 128°, which with SeO$_2$ gives 6 : 7-*dimethoxy*-2-*furylchromone*, m.p. 204°. With hot EtOH–KOH, followed by H$_2$O$_2$, (**I**), (**II**), and (**III**) give respectively 3-*hydroxy*-7-*methoxy*-, m.p. 178°, -7 : 8-*dimethoxy*-, m.p. 244°, and -6 : 7-*dimethoxy*-2-*furylchromone*, m.p. 212°. With dil. HCl in boiling EtOH (30 hr.), (**I**), (**II**), and (**III**) give respectively 2-*hydroxy*-4-*methoxy*-, m.p. 165°, -3 : 4-*dimethoxy*-, m.p. 98°, and -4 : 5-*dimethoxy*-*phenacyl*-*lævulic acid*, m.p. 127, furylchromanones not being formed. E. W. W.

Arylthioisatins.—See B., 1943, II, 109.

Thionaphthen vat dye.—See B., 1942, II, 47.

Phenoxthionins.—See B., 1943, II, 109.

Oxides of phenoxthionins.—See B., 1943, II, 45.

Synthesis of vitamin-B_6.—See B., 1943, III, 21.

Nicotin-*p*-phenetidide.—See B., 1943, III, 41.

Oxidation of adrenaline. F. Bergel and A. L. Morrison (*J.C.S.*, 1943, 48).—Adrenaline (**I**) in 2% AcOH is oxidised (KIO$_3$) to an iodoquinone (**II**), which is reduced (NaHSO$_3$) and acetylated to 2-*iodo*-5 : 6-*diacetoxy*-1-*methylindole*, m.p. 153—155°. Reduction of (**II**) with Zn–Ac$_2$O–NaOAc or Mg–AcOH affords 5 : 6-*diacetoxy*-1-*methylindole* (**III**), m.p. 100—101°. Catalytic oxidation (Pd–C) of (**I**) causes 2 O$_2$ to be absorbed, and although (**II**) cannot be isolated, reduction catalytically or with NaHSO$_3$ gives a substance apparently identical with (**III**). F. R. S.

5-Hydroxyindole. F. Bergel and A. L. Morrison (*J.C.S.*, 1943, 49).—2-*Nitro*-5-*benzyloxytoluene*, m.p. 70—71°, prepared from the OH-compound, with KOEt and Et$_2$C$_2$O$_4$ gives 2-nitro-5-benzyloxypyruvic acid, m.p. ~100—105° (*phenylhydrazone*, m.p. 152—153°), which is reduced (FeSO$_4$–aq. NH$_3$) to 5-*benzyloxyindole*-2-*carboxylic acid*, m.p. 193—194° (*Me* ester, m.p. 150—151°). Reduction (Pd–C–MeOH–H$_2$) of the acid affords 5-*hydroxyindole*-2-*carboxylic acid*, m.p. 246° (decomp.) (*Me* ester, m.p. 146—147°), which is decarboxylated (Cu) in small yield to 5-*hydroxyindole*, m.p. 107—109°. F. R. S.

Mechanism of indole formation from phenacylarylamines. I. A. F. Crowther, F. G. Mann, and (in part) D. Purdie (*J.C.S.*, 1943, 58—68).—The conversion of the phenacyl derivatives of primary arylamines into 2-arylindoles depends on the presence of catalytic impurities (*e.g.*, amine hydrobromides and hydriodides). The theory of the mechanism that the derivative undergoes normal cyclisation to give 3-phenylindole which isomerises to the 2-compound is incorrect since pure phenacylaniline (**I**) is stable but when heated with traces of many hydrobromides and hydriodides and quaternary bromides and iodides is converted readily into 2-phenylindole (**II**). The catalysts are listed according to whether they cause conversion into (**II**), cause partial conversion into diphenylacylaniline, no apparent change, or decomp. to non-cryst. syrups. The alternative theory that a diamine is first formed and cyclises with loss of the original amine is also incorrect. Pure (**I**) and NH$_2$Ph give NN-*di*-(β-*anilino*-α-*phenylvinyl*)*aniline* (**III**), m.p. 205—209°, but in presence of NH$_2$Ph,HBr, (**II**) is obtained. Pure (**I**) and *p*-C$_6$H$_4$Me·NH$_2$ yield NN-*di*-(β-p-*tolylamino*-α-*phenylvinyl*)-p-*toluidine*, m.p. 175—183°, and with a catalyst, 2-phenyl-5-methylindole is obtained. Similarly (**I**), 2 : 4 : 1-C$_6$H$_3$Me$_2$·NH$_2$, and NH$_2$Ph,HBr form 2-phenyl-5 : 7-dimethylindole, isolated as the *picrate*, m.p. 156—157·5°. The following are described: *hydrobromide*, m.p. 183° (decomp.), and *hydriodide*, m.p. 145°, of (**I**), p-*chlorophenacylaniline*, m.p. 113—115° (*Ac* derivative, m.p. 143°), and *di*-(β-*anilino*-α-p-*chlorophenylvinyl*) *ether*, m.p. 192—193° (*Ac*$_2$ derivative, m.p. 232—233°), obtained at the same time; p-*chlorophenacyl*-p-*toluidine*, m.p. 148—150°, and -2 : 4-*dimethylaniline*, m.p. 117°; 2-p-*chlorophenyl*-5-*methylindole*, m.p. 250·5—251·5° [*NO*-derivative, m.p. 277° (decomp.)]; p-*toluenesulphonyl* derivative, m.p. 71°, of *N*-ethyl-*p*-toluidine; 2 : 4-*dimethyl*-, b.p. 229—232°/763 mm., and p-*chloro*-N-*ethylaniline*, b.p. 247—250°/760 mm. (p-*toluenesulphonyl* derivative, m.p. 102·5—104°); 4 : 4′-*diethoxydiphenylamine*, m.p. 94°; *hydrochloride*, m.p. 158°, and *picrate*, m.p. 110°, of phenacyl-*N*-ethylaniline; *phenacyl*-N-*ethyl*-p-*toluidine*, m.p. 110—111°; p-*chlorophenacyl*-N-*ethylaniline*, m.p. 83° (*hydrochloride*, m.p. 169°; *picrate*, m.p. 116—117°), -N-iso*butylaniline*, m.p. 91°, and -N-*ethyl*-p-*toluidine* (**IV**), m.p. 95·5° [*hydrochloride*, m.p. 177—178° (decomp.); *picrate*, m.p. 135—136°]; and p-*chloro*-(p′-*chlorophenacyl*)-N-*ethylaniline*, m.p. 105—106°.

The phenacyl derivatives of *sec.* arylalkylamines behave entirely differently, giving 3-aryl-1-alkylindoles, which (with one exception) could not be isomerised to 2-aryl-1-alkylindoles. When (**IV**) is exposed to air at 100° for 7 hr., appreciable amounts of *p*-C$_6$H$_4$Cl·CO$_2$H are obtained, and with EtOH–ZnCl$_2$ or fused with ZnCl$_2$ it gives 3-p-*chlorophenyl*-5-*methyl*-1-*ethylindole* (**V**), m.p. 92° (*picrate*, m.p. 102·5—103·5°), and some *dimeride*, m.p. 157·5°. Similarly, 3-*phenyl*-1-*ethyl*-, b.p. 188—192°/1·5 mm. (*picrate*, m.p. 83—83·5°), and -5-*methyl*-1-*ethyl*-*indole*, b.p. 220—222°/17 mm. (*picrate*, m.p. 107·5—108°), and 3-p-*chlorophenyl*-1-*methyl*-, m.p. 96° (*picrate*, m.p. 107—107·5°), -1-*ethyl*-, m.p. 81°, and -1-iso*butyl*-*indole*, m.p. 71—72°, are obtained, but phenacyl-*N*-methylaniline with EtOH–ZnCl$_2$ gives 3-phenyl-1-methylindole and with fused ZnCl$_2$ the 2Ph derivative. Phenacyl-*N*-ethylaniline and NH$_2$Ph at 150° for 8 hr. afford NHPhEt and (**III**), whilst (**IV**) similarly yields *p*-chlorophenacylaniline and NN-*di*-(β-*anilino*-α-p-*chlorophenylvinyl*)*aniline*, m.p. 172—180°. *p*-C$_6$H$_4$Me·NHEt and (**IV**) (equimols.) in air at 100° for 7 hr. give much *p*-C$_6$H$_4$Cl·CO$_2$H and 4 : 4′-dichlorobenzil but in a closed vessel at 140—150°, p-*chloro*-(α*β*-*bis*-p-*tolylethylamino*)-*vinylbenzene*, m.p. 123—123·5°, is formed in addition; the latter is the only diamine obtained and it could not be converted into an indole. When (**IV**) is boiled with excess of NHPhEt, NHPhBu^n, or *p*-C$_6$H$_4$Me·NHEt, (**V**) is obtained in each case. An ionic mechanism is put forward to explain the results obtained. The following are also described: p-*chlorophenyl*-N-*ethylnitrosoamine*, m.p. 58—59°; p-*chloroacetophenonephenylhydrazone*, m.p. 112—113°; 2-*phenyl*-, m.p. 84—84·5° (3-*NO*-derivative, m.p. 130—131°), 2-*phenyl*-5-*methyl*-, b.p. 171—173°/0·2 mm., m.p. 70·5° (3-*NO*-derivative, m.p. 161—162°), and 2-p-*chlorophenyl*-1-*ethylindole*, b.p. 171°/0·2 mm., m.p. 86—87° (3-*NO*-derivative, m.p. 138—139°); 2-p-*chlorophenyl*-1-n-*propylindole*, b.p. 222—225°/15 mm., m.p. 54° (3-*NO*-derivative, m.p. 137—138°), -1-iso*butylindole*, b.p. 173—178°/0·3 mm., m.p. 87—87·5° (3-*NO*-derivative, m.p. 93°), and -5-*methyl*-1-*ethylindole*, b.p. 239°/13 mm., m.p. 127—128·5°. The crystallographic measurements of the dimeride of (**V**) are given. F. R. S.

3-Substituted indoles.—See B., 1943, II, 109.

8-Aminoquinaldone. G. Jacini (*Gazzetta*, 1942, **72**, 42—46).—*o*-C$_6$H$_4$(NH$_2$)$_2$ (1 mol.) and CHAc·CO$_2$Et (**I**) (2 mols.) (room temp.) give 2-methylbenziminazole and some *Et*$_2$ o-*phenylenebis*-β-*aminocrotonate*, m.p. 103°, which in paraffin (**II**) at 200—250° gives a *substance*, C$_{14}$H$_{14}$O$_3$N$_2$, decomp. ~350°. *o*-NH$_2$·C$_6$H$_4$·NHAc and (**I**) in boiling EtOH give *Et* β-o-*acetamidoanilinocrotonate*, m.p. 104°, which in (**II**) at 230—240° gives 8-*acetamido*-4-*hydroxy*-2-*methyl*-

quinoline, m.p. 292—293°. This with boiling 10% H_2SO_4 gives *8-amino-4-hydroxy-2-methylquinoline*, decomp. ~300°. E. W. W.

Preparation of 2-hydroxy-4-alkylquinoline-6-sulphonamides. (Signa.) L. Monti and S. Palmieri (*Gazzetta*, 1941, **71**, 662—667).—NHPh·CO·CH_2Ac and SO_2Cl_2 at 80° give a product which with conc. aq. NH_3 gives *2-hydroxy-4-methylquinoline-6-sulphonamide* (**I**), m.p. 316—318° (softens at 310°), also obtained from the quinoline. [The SO_2Cl_2 must be freshly distilled, otherwise the product includes *p*-NH_2·SO_2·C_6H_4·NH·CO·CH_2Ac (also obtained, prep. modified, from CH_2Ac·CO_2Et and *p*-NH_2·C_6H_4·SO_2·NH_2), which does not condense to (**I**), either in conc. H_2SO_4 or in heavy petroleum at 300°.] *o-*, *m-*, and *p*-C_6H_4Me·NH·CO·CH_2Ac similarly treated give *2-hydroxy-4* : 8-, m.p. 310—312° (decomp.), and -4 : 7-*dimethylquinoline-6-sulphonamide*, m.p. 325—326° (decomp.), and 2-hydroxy-4 : 6-dimethylquinoline, respectively. E. W. W.

Quinolines, benzquinolines, and acridines.—See B., 1943, II, 6.

Mechanism of cyclisation reactions. E. Berliner (*J. Amer. Chem. Soc.*, 1942, **64**, 2894—2898).—Ring-closure by acid of *o*-CH_2Ph·C_6H_4·COR to 9-substituted anthracenes, of *o*-NHPh·C_6H_4·COR to 5-substituted acridines, etc. has, as first step, addition of a proton to give *o*-CH_2Ph*·C_6H_4·C+R·OH etc., which then closes the ring by electrophilic attack on the Ph marked *. Acid ring-closure of CAr_3·OH to 9-arylfluorenones occurs by preliminary formation of $^+CAr_3$, which is evidenced by development of colour similar to that of the carbinol in conc. H_2SO_4. *o-a-*, m.p. 96·4—97·2°, and *o-β-naphthylaminoacetophenone* (**I**) [both prepared from $C_{10}H_7Br$, *o*-NH_2·C_6H_4·COMe (**II**), K_2CO_3, and Cu powder in boiling $PhNO_2$], b.p. 195—196°/6 mm., with a little H_2SO_4 in AcOH at 100° give rapidly *5-methyl-1* : 2-, m.p. 111·6—112·2° [sulphate; *picrate*, m.p. 251—255° (decomp.)], and -3 : 4-*benzacridine*, m.p. 145—145·2° [*picrate*, m.p. 245—248° (decomp.), obtained also from (**I**) by boiling with picric acid]. Condensing 9-bromophenanthrene with (**II**) as above and heating the product with H_2SO_4–AcOH gives *5-methyl-1* : 2 : 3 : 4-*dibenzacridine*, m.p. 121·4—122·4° [*picrate*, m.p. 206—208° (decomp.)]. 2-$C_{10}H_7$·COPh [prep. from 2-$C_{10}H_7$·CN by MgPhBr–Et_2O and then HCl–H_2O–$COMe_2$ (later with C_6H_6); 82·5% yield], m.p. 81—82°, and *α*-$C_{10}H_7$·MgBr in Et_2O give, after decomp. by aq. NH_4Cl, *phenyl-α-naphthyl-β-naphthylcarbinol* (**III**), m.p. 168—169°, and +*x*C_6H_6 or *x*EtOH, m.p. 195—205°, which with a few drops of HCl in boiling AcOH gives a green and then a red colour, *9-phenyl-1* : 2 : 5 : 6-*dibenzfluorene* (**IV**), m.p. 219—219·5°, being formed during the second change; (**III**) gives a green ppt. with $AlCl_3$, $AlBr_3$, I, PCl_5, or $SnCl_4$ in C_6H_6 and (**IV**) is formed after ~5 min. at 100°. Phenyldi-*α*, m.p. 169—170°, and *-β-naphthylcarbinol* (similarly prepared), m.p. 216·5—217·5°, give similarly 9-phenyl-3 : 4 : 5 : 6-, m.p. 275°, and -1 : 2 : 7 : 8-*dibenzfluorene*, m.p. 148·5—149·5°, respectively. *o*-C_6H_4Ph·COPh with 34% aq. HBr + AcOH at the b.p. gives 9-phenylfluorenyl acetate and the polymeride (**V**) of 9-fluorenol and with a little H_2SO_4 in Ac_2O at 100° gives mainly (**V**). M.p. are corr. R. S. C.

Sulphonamide derivatives of pyrazole. I. 1-*p*-Sulphonamidophenyl-3-methyl-5-pyrazolone. G. B. Crippa and S. Maffei (*Gazzetta*, 1942, **72**, 97—99).—*p*-NH_2·NH·C_6H_4·SO_2·NH_2 diazotised and reduced gives p-*hydrazinobenzenesulphonamide*, m.p. 155° (*Ac* derivative, m.p. 224°), which with CH_2Ac·CO_2Et (**I**) gives the *sulphonamidophenylhydrazone* (**II**), m.p. 142°, of (**I**). Above its m.p., (**II**) gives 1-p-*sulphonamidophenyl-3-methyl-5-pyrazolone*, m.p. 237°. E. W. W.

Action of copper on ethyl malonate and on 5 : 5-diethylbarbituric acid [exposed to the air]. B. Ciocca and E. Dumontel (*Gazzetta*, 1942, **72**, 197—200).—$CH_2(CO_2Et)_2$ (**I**) exposed to the air with Cu powder at 50—60° gives its *Cu* derivative, $C_7H_{11}O_4Cu$. (**I**) does not react with CuO or Cu_2O. 5 : 5-Diethylbarbituric acid in EtOH similarly gives a *Cu* derivative, $C_7H_{10}O_3N_2Cu_2$. E. W. W.

***cyclo*Heptenylbarbituric acids.**—See B., 1940, III, 42.

Barbituric acids.—See B., 1943, III, 89.

Pyrimidines.—See B., 1943, II, 109.

Sulphanilamidompyrimidines.—See B., 1943, II, 21.

Thioammelines.—See B., 1943, II, 130.

Indigoid dyes of the *cis*-series. II. *NN'*-Ethyleneindigotin. R. Pummerer and E. Stieglitz (*Ber.*, 1942, **75**, [*B*], 1072—1085).—Dehydroindigotin (**I**) and furylethylene in dry PhCl at ~100° yield *NN'-furylethyleneindigotin*, m.p. 213°. Similarly (**I**) and CH_2:CH·CO_2Me in a sealed tube at ~100° afford *Me indigotin-NN'-acrylate*, m.p. 209°, hydrolysed by $NaHCO_3$ in boiling aq. MeOH to *indigotin-NN'-acrylic acid* (*Ag* and *Na* salts), decarboxylated by Cu powder in boiling PhCl under CO_2 to *NN'-ethyleneindigotin* $\left(\begin{matrix}C_6H_4\cdot N\cdot CH_2\cdot\\ CO\text{—}C\end{matrix}\right)_2$ (**II**). This is converted by boiling KOH–EtOH–H_2O into *ethyleneindigotin-yellow*, $C_{18}H_{14}O_3N_2,0{\cdot}5H_2O$. The structure of (**II**) is established by its oxidation (conc. HNO_3 in AcOH) to ethylenedi-isatin, m.p. 279°, transformed by NaOH and H_2O_2 into ethylenedianthranilic acid, m.p. 228°. The experiments do not lead to a particular formula or theory to explain the play of colours of alkyleneindigotins (**III**) in various solvents but show that it is due to mesomerism since (*a*) it cannot be due to *cis–trans*-isomerism because the *trans*-forms of (**III**) are spatially impossible, (*b*) there cannot be a mixture of two isomerides of other type or tautomerides as no evidence therefor can be found in the absorption curves of the extreme red and blue solutions, (*c*) association to double mols. is not causative of the blue solutions, and (*d*) a little dipole solvent is required to cause much displacement towards blue whereas much more of a different solvent is required to produce the reverse effect. H. W.

Absorption spectra of phthalo*cyclo*hydrazides.—See A., 1943, I, 80.

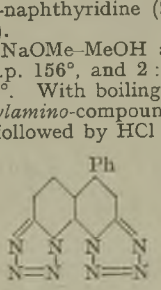
Quinazoline derivatives. I. L. Monti and A. Simonetti. **II.** L. Monti, A. Osti, and S. Piras. **III.** L. Monti (*Gazzetta*, 1941, **71**, 651—653, 654—658, 658—662).—I. 4-Hydroxy-2-methylquinazoline (**I**) heated with *p*-NMe_2·C_6H_4·CHO, with furfuraldehyde, and with chloral, gives respectively *4-hydroxy-2-p-dimethylaminostyryl-*, m.p. 300—302° (decomp. from 290°) (*picrate*, m.p. 214—215°), *-2-β-furylvinyl-*, m.p. 210—212° (darkening 206—208°) (*picrate*, decomp. 224—226°), and *-2-γγγ-trichloropropenyl-quinazoline*, decomp. 194—195°.

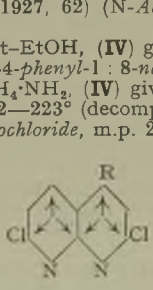
II. 4-Hydroxyquinazoline (**II**) and NHBz·CH_2·OH (**III**) in boiling AcOH give *3-benzamidomethyl-4-quinazolone*; m.p. 180—182°, hydrolysed by boiling dil. HCl to the *dihydrochloride*, m.p. 242—244°, of *3-aminomethyl-4-quinazolone* (**IV**) [*picrate*, m.p. 200—202° (decomp. from 180°)]. Similarly (**I**) and (**III**) in AcOH give *2-methyl-3-benzamidomethyl-4-quinazolone*, m.p. 184—186°, hydrolysed by dil. HCl, followed by dil. aq. NH_3, to *2-methyl-3-aminomethyl-4-quinazolone* (**V**), m.p. 268—270° (decomp.; darkening from 235—240°) [*picrate*, m.p. 210—240° (decomp.)]. The structure assigned to (**IV**) and (**V**) is supported by the non-reactivity of 3-methyl- and 2 : 3-dimethyl-quinazolone [prepared by Me_2SO_4-methylation of (**II**) and (**I**), respectively] with (**III**).

III. In petroleum jelly at 180°, (**I**), NH_4Cl, and paraformaldehyde give (**V**). Using NH_2Me_2Cl, NH_2Et_2Cl, and piperidine hydrochloride, *2-methyl-3-dimethylaminomethyl-*, m.p. 295—296° (darkening 280°) (*picrate* *, darkens 250°), *-3-diethylaminomethyl-*, m.p. 282—284° (darkening 250°) (*picrate* *, darkens 220—225°), and *-3-piperidinomethyl-4-quinazolone*, decomp. 288—290° (darkening 270°) (*picrate* *, darkens 205—210°) are formed. (* These picrates carbonise without melting.) E. W. W.

Naphthyridines. I. Derivatives of 4-phenyl-1 : 8-naphthyridine. II. Reactivity of 2 : 7-dichloro-4-phenyl-1 : 8-naphthyridine. A. Mangini and M. Colonna (*Gazzetta*, 1942, **72**, 183—190, 190—197).—I. 2 : 6-Diaminopyridine (**I**) with $CH_2Bz·CO_2Et$ (**II**) at 140—180° gives *7-amino-2-hydroxy-4-phenyl-1* : 8-*naphthyridine* (**III**), m.p. <345° (*hydrochloride*, m.p. >350°; *picrate*, decomp. 245—254°; *N-Ac* derivative, m.p. <345°). At 100°, or in boiling PhMe, (**I**) and (**II**) give *2-amino-6-benzoylacetamidopyridine*, m.p. 153—154°, which in conc. H_2SO_4 gives (**III**), which can be characterised by diazotisation and decomp. to 2 : 7-*dihydroxy-*, m.p. 272—273°, chlorinated (PCl_5) to 2 : 7-*dichloro-4-phenyl-1* : 8-*naphthyridine* (**IV**), m.p. 158°. With $CH_2Ac·CO_2Et$, (**I**) gives 7-amino-2-hydroxy-4-methyl-1 : 8-naphthyridine (Seide, A., 1927, 62) (*N-Ac* derivative, m.p. <285°).

II. With NaOMe–MeOH and NaOEt–EtOH, (**IV**) gives 2 : 7-*dimethoxy-*, m.p. 156°, and 2 : 7-*diethoxy-4-phenyl-1* : 8-*naphthyridine*, m.p. 87—88°. With boiling *p*-OEt·C_6H_4·NH_2, (**IV**) gives the 2 : 7-*bis*-p-*phenetylamino*-compound, m.p. 222—223° (decomp.), and with N_2H_4,H_2O, followed by HCl the *dihydrochloride*, m.p. 253—254°, of

(**V.**) 



(*A.*)

2 : 7-*bishydrazino-4-phenyl-1* : 8-*naphthyridine* (*bis*-p-*nitrobenzylidene* derivative, m.p. 327—328°), which with $NaNO_2$–HCl gives 1 : 2 : 7 : 8-*ditriazolo-4-phenyl-1* : 2 : 7 : 8-*tetrahydro-1* : 8-*naphthyridine* (**V**), darkens 200—202°, explodes 203°. 2 : 7-Dichloro-4-methyl-1 : 8-naphthyridine (**VI**) (Seide, *loc. cit.*) with NaOMe–MeOH and NaOEt–EtOH gives 2 : 7-*dimethoxy-*, m.p. 102—103°, and 2 : 7-*diethoxy-4-methyl-1* : 8-*naphthyridine*, m.p. 72—73°. The electronic structure of (**IV**) and (**VI**) is discussed, and expressed in formula *A*. E. W. W.

Triazines.—See B., 1943, II, 7.

Spectroscopic studies on porphyrins.—See A., 1943, I, 80.

Bile pigments. XXXVI. Action of yeast and ascorbic acid on hæmins. E. Stier (*Z. physiol. Chem.*, 1942, **275**, 155—165; cf. A., 1943, II, 46).—Acetylhæmatoporphyrin Me_2 ester Fe salt (**I**) or Me_4 hæmatoporphyrin Fe salt in aerated 50% aq. C_5H_5N with yeast (*Saccharomyces cerevisiæ*) at 50° for 30 min. yields the corresponding pyridineverdoparahæmatin (**II**), also obtained from (**I**) with pyrogallol–O_2 (cf. A., 1942, II, 382; Warburg *et al.*, A., 1930, 1199). (**I**) with ascorbic acid–O_2 at 55—60° gives (**II**) and, by

treatment with MeOH–HCl, acetylhæmatoglaucobilin Me_2 ester and a pigment with absorption max. (Et_2O solution) at 532, 500, and <447 mμ. (Zn complex in Et_2O, 630, 536, and <452 mμ.). Ascorbic acid–O_2 readily oxidises phyllohæmin ester to the corresponding pyridineverdoparahæmatin, which with MeOH–HCl affords phyllo-glaucobilin ester. Rhodohæmin Me_2 ester is similarly oxidised to rhodopyridineverdoparahæmatin Me_2 ester which, with MeOH–HCl, yields *rhodoglaucobilin Me_2 ester*, m.p. 226° (sinters at 210°), the first cryst. pigment of the bilitriene type; fluorescence spectra are compared with those of a typical bilidiene derivative. F. O. H.

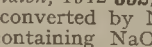
Chlorophyll. CXIV. Transition from the chlorophyll-*b* into the *a*-series. H. Fischer and H. Gibian (*Annalen*, 1942 **552**, 153—166).—Pyrophæophorbide *b* Me ester (**I**) is converted by NaOMe and N_2H_4,H_2O in C_5H_5N and MeOH containing NaOMe at 115—120° into some deoxophyllerythrin Me ester, m.p. 264°, and mainly inactive mesodeoxopyrophæophorbide *a* Me ester (**II**), m.p. 209—211°, thus establishing by direct experiment the intimate connexion of the chlorophyll-*a* and -*b* series. (**I**) is hydrogenated (Pd–100% HCO_2H) to mesodeoxopyrophæophorbide *a* Me ester, dimorphous, m.p. ~186° or 204°, $[\alpha]_{red}^{20}$ −645°±115° in $COMe_2$, identical with that prepared from pyrophæophorbide *a* Me ester, thus establishing the identical steric arrangement of substituents in the two chlorophyll series. Mesopurpurin 3-Me ester, N_2H_4,H_2O, NaOMe–MeOH, and C_5H_5N at 115—120° afford inactive mesophyllochlorin Me ester, m.p. 166—167°, with some phylloporphyrin, m.p. 234°. Pyrophæophorbide *a* is converted by N_2H_4,H_2O at 100° in a sealed tube or in open vessels into optically inactive mesopyrophæophorbide *a* Me ester (**III**), m.p. 205—206° (*Zn* complex salt, m.p. 158°), also obtained similarly from pyrophæophorbide *b* Me ester. The prep. of (**II**) from (**III**) by N_2H_4,H_2O or H_2–Pd–100% HCO_2H is described. The action of Pd and 100% HCO_2H on phæophorbide *a* gives a small amount of (**II**), much decomposed material, and (?) deoxophæoporphyrin a_5 Me_2 ester, m.p. 287°, also obtained from phæophorbide *b*. Reduction of purpurin 7-Me_3 ester, 18-Me ester, and 18-Me ester imide leads to much decomposed material and the spectrum of the corresponding meso-compound. Sucrose and cholesterol are unchanged by N_2H_4,H_2O, NaOMe–MeOH, and C_5H_5N at 100°. H. W.

Constitution of the prosthetic group of cytochrome-*c*. K. Zeile and H. Meyer (*Z. physiol. Chem.*, 1940, **265**, 22; cf. A., 1940, II, 110). —The porphyrin-*c* isolated by the authors was the prosthetic group of cytochrome-*c*, whilst Theorell's product (A., 1939, II, 394) resulted from recombination of products of hydrolysis. W. McC.

Pyrazoleanthrone dyes.—See B., 1943, II, 111.

Nucleic acids. XXI. Tetranucleotide of yeast- and thymo-nucleic acid. H. Bredereck and E. Hoepfner [with I. Jochmann and A. Martini (*Ber.*, 1942, **75**, [*B*], 1086—1095).—Analyses of the deaminated tetranucleotide of thymonucleic acid agree with the formula $C_{39}H_{48}O_{28}N_{12}P_4$. The mol. wt. of thymic acid determined by the diffusion method is 1067 (calc. 992). Yeast-nucleic acid, purified through the Pb salt, is converted by warming with 0·5% NaOH at 50° for 10 min. into the corresponding *tetranucleotide* (**I**). Titration shows the presence of a pentabasic acid and the increase in acidity after fission with alkali corresponds with 3 equivs. Analyses and determinations of mol. wt. support the formula $C_{38}H_{49}O_{28}N_{15}P_4$, which is supported by the determination of guanine and adenine and analyses of the *Mg* salt. Deamination of (**I**) affords xanthine, hypoxanthine, and uracil. Methylation (Me_2SO_4) of (**I**) in feebly alkaline medium gives a product in which fission has not occurred and which is hydrolysed by HCl–MeOH to 1 : N^2-dimethylguanine, 1 : N^6-dimethyladenine, and 1 : N^6-dimethylcytosine. (**I**) is therefore $(OH)_2PO{\cdot}O{\cdot}RB{\cdot}[O{\cdot}PO(OH){\cdot}O{\cdot}RB]_2{\cdot}O{\cdot}PO(OH){\cdot}O{\cdot}RB$ (R = ribose; *B* = base). H. W.

Fulminic synthesis of *iso*oxazole derivatives. III. A. Quilico and L. Panizzi (*Gazzetta*, 1942, **72**, 155—165).—C_2Na_2 in Et_2O with moist CHI:N·OH (**I**) [prep. from $Hg(CH{:}N{\cdot}OH)_2$ and Na–Hg, followed by HI, described], followed by treatment with aq. $Na_2S_2O_3$, gives the *oxime* (**II**), m.p. 147—148°, of iso*oxazole-5-aldehyde*, an oil (p-*nitrophenylhydrazone*, m.p. 210—211°). Oxidation of (**II**) by $K_2Cr_2O_7$–H_2SO_4 gives *iso*oxazole-5-carboxylic acid. C_2PhNa with (**I**) in Et_2O, followed by aq. $Na_2S_2O_3$, gives the *oxime* (**III**), m.p. 150—151°, of 5-*phenyl*iso*oxazole-3-aldehyde*, m.p. 61—62° (p-*nitrophenylhydrazone*, m.p. 225—228°), oxidised by CrO_3–H_2SO_4–AcOH to 5-phenyl*iso*-oxazole-3-carboxylic acid, also obtained from (**III**) and aq. KOH. With nitrous fumes, (**III**) in EtOH gives 3 : 4-(5′ : 5′′-*diphenyl*-3′ : 3′′-di*isooxazolyl*)-1 : 2 : 5-*oxadiazole* 2-*oxide*, m.p. 185—186°. Mechanisms of the two syntheses are discussed. E. W. W.

Heterocyclic syntheses. II. Dichloromethyl*iso*oxazoles and corresponding aldehydes. L. Panizzi (*Gazzetta*, 1942, **72**, 99—108; cf. A., 1942, II, 394).—$CHCl_2{\cdot}CO{\cdot}CH_2Ac$ with NH_2OH,HCl in EtOH gives 5-*methyl*-3-*dichloromethyl*iso*oxazole* (**I**), b.p. 71—72°/5—6 mm., stable to conc. H_2SO_4 and to dil. KOH or KOH–MeOH at the b.p., and *dichloroacetonylacetoxime*, $CHCl_2{\cdot}CO{\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH$ (**II**), m.p. 67·5—69·5°, b.p. 136°/6 mm. (*Ac* derivative, oil). (**II**) resists benzoylation and action of NH_2OH or *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$; in boiling aq. HCl, (**II**) gives 3-*methyl*-5-*dichloromethyl*iso*oxazole* (**III**), m.p. 38—38·5°, b.p. 88—89°/11 mm. With NaOEt–EtOH at 170—180°, (**II**) and (**III**) give 5-*methyl*iso*oxazole*-3- and 3-*methyl*iso*oxazole*-5-*aldehyde* (cf. Quilico *et al.*, A., 1939, II, 523). COPhMe and $CHCl_2{\cdot}CO_2Et$ with NaOMe in Et_2O give *ωω-dichlorobenzoylacetone*, b.p. 170—171°/11 mm. [*Cu* salt, m.p. 196—197° (decomp.)], which with KOH gives COPhMe and $CHCl_2{\cdot}CO_2H$, and with NH_2OH,HCl in aq. EtOH gives *dichloroacetonylbenzaldoxime* (**IV**). m.p. 96—97° (*Ac* derivative, m.p. 82—83°). (**IV**) is unreactive like (**II**), but with conc. HCl gives 3-*phenyl*-5-*dichloromethyl*iso*oxazole*, m.p. 64·5—65°, which with NH_2Ph at 120—130° gives 3-*phenyl*-5-*bis*-(p-*aminophenyl*)*methyl*iso-*oxazole*, m.p. 167—168·5° [Ac_2 derivative, m.p. 156—157° (decomp.)], diazotisable. The possibility that (**II**) and (**IV**) have the *iso*-oxazoline·structure,  , is considered, but the true oxime structure is preferred. E. W. W.

***iso*Oxazole-3 : 5-dicarboxylic acid.** C. Musante (*Gazzetta*, 1942, **72**, 134—142).—$CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$ [*Cu* salt, m.p. 202—203° (decomp.)] and NH_2OH,HCl in boiling EtOH give the *Et* ester (**I**), m.p. 113—113·5° (*dibromide*, m.p. 129°), of 5-*styryl*iso*oxazole*-3-*carboxylic acid* [prep. from (**I**) and conc. HCl], m.p. 193—195° (decomp.) (*Ag* salt; *Me* ester, m.p. 145°), which at 200° gives, with ring-opening, *α′-cyano-α-benzylideneacetone*, m.p. 98—99° [p-*nitrophenylhydrazone* (**II**), m.p. 207—208°], also obtained from $CHPh{:}CH{\cdot}CO_2Et$ and MeCN (Na). On prolonged heating with alkali or acid, (**II**) gives 5-*amino*-1-p-*nitrophenyl*-3-*styrylpyrazole*, m.p. 172—173°. With boiling aq. $K_2Cr_2O_7$–H_2SO_4, (**I**) gives, with BzOH, iso*oxazole*-3 : 5-*dicarboxylic acid* (+H_2O, lost at 110°), m.p. 213° (decomp.) [Na_2 salt, darkens from 260°; Ag_2 salt, decomp. (semi-explosively) ~220°; Me_2 ester, m.p. 101°; *diamide*, darkens from 250°, no m.p. <300°; *dianilide*, m.p. 283° (variable) (decomp.)]. E. W. W.

Thiazolines.—See B., 1943, II, 7.

Synthesis of possible lipophilic chemotherapeuticals of the sulphanilamide group. S. Rajagopalan (*Current Sci.*, 1942, **11**, 394—396).—Condensation (C_5H_5N) of the appropriate acid chlorides and sulphonamides yields the following N^4-acylsulphonamides, having the m.p. given: cyclo*hexoylsulphanilamide*, 238°; n-*butyryl*-, 206°, n-*hexoyl*-, 197°, and n-*heptoyl*-*sulphapyridine*, 193°; n-*butyryl*-, 244—246° (decomp.), n-*hexoyl*-, 198—199°, n-*heptoyl*-, 202—203°, cyclo-*hexoyl*-, 222—223° (decomp.), *palmity* -, 140—147°, and *stearyl-sulphathiazole*, 148—150°, and n-*butyryl*-, 224—225°, n-*hexoyl*-, 181—182°, n-*heptoyl*-, 175—176°, and cyclo*hexoyl-sulphathiazoline*, 220°. N^4-*n*-Hexoylsulphanilamide with the acid chloride in C_5H_5N yields N^4-n-*hexoyl*-N^1-*acetyl*-, 166—169° (decomp.), -n-*butyryl*-, 164—168°, -n-*heptoyl*-, 148—152°, -cyclo*hexoyl*-, 185—187°, -*palmityl*-, 123—126°, and -*stearyl-sulphanilamide*, 127—130°. Sulphanilamide with the acid chloride (2 mols.) in C_5H_5N yields N^4N^1-*di*-n-*hexoyl*-, 164—172°, -*di*-n-*butyryl*-, 217—220°, and -*di*-n-*heptoyl-sulphanilamide*, 131—134°. A. Li.

Thiazole sulphanilamides.—See B., 1943, III, 88.

Preparation of standard samples of] methylene-blue. H. O. Moraw (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 798—799).—Analyses are given. A. A. E.

VII.—ALKALOIDS.

Alkaloids of various plant species within the genus *Nicotiana*. A. A. Shmuk and A. Borozdina (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 62—65).—A method for separating and identifying nicotine (**I**), nornicotine (**II**), and anabasine (**III**) is described. 42 species have been examined and divided into groups in which the main alkaloid is (*a*) (**I**), (*b*) (**II**), (*c*) a mixture of (**I**) and (**II**), (*d*) (**III**). F. R. S.

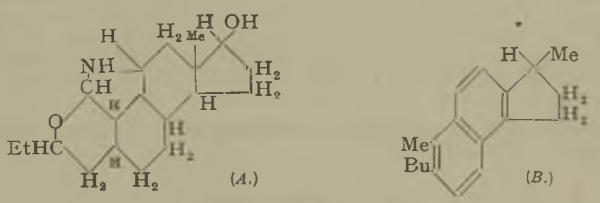
Salts of cinchona alkaloids.—See B., 1943, III, 21.

***Salamander* alkaloids. II. Samandarone and samandaridine, minor alkaloids in poison of fire and alpine salamanders.** C. Schopf and K. Koch (*Annalen*, 1942, **552**, 37—61; cf. A., 1935, 97).—The bulk of the samandarine (**I**) is removed from the total alkaloids as the sparingly sol. hydrochloride or, better, hydrobromide. The residual alkaloids deposit samandarone (+$1H_2O$) (**II**), m.p. 189°, $[\alpha]_D^{21}$ −115·7° in $COMe_2$ [*hydrochloride*, m.p. 355° (decomp.), softens at 350°; double *salt* with $HgCl_2$, m.p. 246° (decomp.); corresponding *salt* from (**I**), m.p. 209° (decomp.)], the isolation of which is completed by its conversion into *N*-benzoylsamandarone and its *semicarbazone*, m.p. 255—257° (decomp.), softens at 253°. *Samandaronesemicarbazone*, has m.p. 308° (decomp.) [*hydrochloride*, m.p. 350—355° (decomp.), softens at 275°]. (**I**) + (**II**) constitute 70—75% of the Et_2O-sol. bases of the alpine salamander. The hydrochlorides remaining after removal of (**I**) contain *samandaridine hydrochloride* (+$2H_2O$ and anhyd.) (**III**), m.p. 343° (decomp.), sparingly sol. in H_2O; the base appears to be present in the male but not in the female alpine salamander. In addition to (**I**) and (**II**) the fire salamander contains at least one primary or *sec.* base without ketonic character and a further ketonic primary or *sec.*

base; one or more *tert.* bases are also present. Treatment of (**III**) with NH_3 affords *samandaridine* (**IV**), $C_{21}H_{31}O_3N$, m.p. 289°, $[\alpha]_D^{21}$ +29·5° in 2N-AcOH [*hydrobromide*, m.p. 346° (decomp.); *hydriodide*, decomp. 315°; *nitrate*, m.p. 255° (decomp.), softens at 253°]. N in (**IV**) is *sec.* since (**IV**) is converted by MeI into *N-methylsamandaridine methiodide*, m.p. 301° (decomp.), by HNO_2 into *N-nitrososamandaridine*, m.p. 278° (decomp.), which does not react with Ac_2O–C_5H_5N, and by Ac_2O–C_5H_5N at room temp. into the non-basic *N-acetylsamandaridine*, m.p. 228—229°, softens at 227°. (**IV**) does not contain OH (Zerevitinov) and the presence of >CO could not be detected with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ or NH_2OH. (**IV**) is transformed by KOH–EtOH into *samandaridic acid*, $C_{21}H_{33}O_4N$, m.p. 284—287°, foams at 279° [*Ag* salt (+$2H_2O$), decomp. 205°]. (**IV**) therefore contains a lactone group but the nature of the third O could not be established. (**IV**) does not contain a double linking since it does not decolorise $KMnO_4$ in hot H_2SO_4, is indifferent towards Br in AcOH, and does not absorb H_2 catalytically. Like (**I**) it appears to be composed of three carbocyclic rings. When exposed to air in conc. HCl (**II**) and (**IV**) do not give the blue-violet colour characteristic of (**I**). H. W.

***Salamander* alkaloids. III. Constitution of samandarine.** C. Schöpf and K. Koch [with W. Contzen] (*Annalen*, 1942, **552**, 62—105; cf. A., 1935, 97).—Hydroxydihydrode-*N*-dimethylsamandarine (**I**), obtained by addition of H_2O to de-*N*-dimethylsamandarine (**II**), contains CO in addition to the new OH since it gives an *oxime*, m.p. 204—206° (slight decomp.; softens at 203°), resinified by Ac_2O–C_5H_5N and a *semicarbazone* (+1EtOH), m.p. 168—169° (decomp.). (**I**) does not appear to be affected by Na–EtOH, $Pb(OAc)_4$ in AcOH at 60°, or HIO_4 in 2N-AcOH at 65°. Hydroxydihydrode-*N*-dimethylsamandarone (**III**), new m.p. 154—155° after softening at 145° (hydriodide, new m.p. 272°), likewise gives an *oxime*. The conversion of the de-bases which contain a double linking and ethereal O into the hydroxydihydrode-bases which contain newly formed CO and OH but no double linking is explicable only on the assumption that they are enol ethers. (**II**) and (**I**) therefore contain the respective arrangements, $\rangle C{\cdot}NMe_2$, $>C{:}CH{\cdot}O{\cdot}CH<$, $>CH(OH)$ and $\rangle C{\cdot}NMe_2$, $>CH{\cdot}CHO$, $OH{\cdot}CH<$, $>CH(OH)$. The de-bases of samandarone (**IV**) and deoxysamandarin (**V**) contain $\rangle C{\cdot}NMe_2$, $>C{:}CH{\cdot}O{\cdot}CH<$, $>CO$ and $\rangle C{\cdot}NMe_2$, $>C{:}CH{\cdot}O{\cdot}CH<$ $>CH_2$. For the corresponding hydroxydihydro-bases the corresponding formulæ are valid, viz., $\rangle C{\cdot}NMe_2$, $>CH{\cdot}CHO$, $OH{\cdot}CH\langle$, $>CO$ and $\rangle C{\cdot}NMe_2$, $>CH{\cdot}CO{\cdot}$, $OH{\cdot}CH<$, $>CH_2$ or the forms $\rangle C{\cdot}NMe_2$, $>CH{\cdot}CH(OR){\cdot}O{\cdot}CH<$, $>CO$ and $\rangle C{\cdot}NMe_2$, $>CH{\cdot}CH(OR){\cdot}O{\cdot}CH<$, $>CH_2$. The H_2-bases obtained by catalytic reduction of (**I**) and de-*N*-dimethylsamandarone correspond with $\rangle C{\cdot}NMe_2$, $>CH{\cdot}CH_2{\cdot}O{\cdot}CH<$, $>CH{\cdot}OH$ and $\rangle C{\cdot}NMe_2$, $>CH{\cdot}CH_2{\cdot}O{\cdot}CH{\cdot}$, $>CO$. Samandarine (**VI**), (**IV**), and (**V**) contain the grouping $>C{\cdot}NH{\cdot}\dot{C}{\cdot}\dot{C}H{\cdot}O{\cdot}C<$ since (**III**) under the influence of boiling Ac_2O suffers partial re-closure of the N ring and re-formation of the O bridge, giving a compound converted by KI into *N-methylsamandarone methiodide* (+$1H_2O$), m.p. 275—276° (decomp.; softens at 274°), and de-*N*-dimethylsamandarone, m.p. 145° (softens at 143°), which is itself indifferent to boiling Ac_2O. (**VI**), (**IV**), and (**V**) therefore receive the partial structures $\rangle C{\cdot}NH{\cdot}CH(CH{:}){\cdot}O{\cdot}CH<$ $>CH{\cdot}OH$, $\rangle C{\cdot}NH{\cdot}CH(CH{:}){\cdot}O{\cdot}CH{:}CO$, and $\rangle C{\cdot}NH{\cdot}CH(CH{:}){\cdot}O{\cdot}CH{:}CH_2$, respectively. This "aldehyde-ammonia" formula of (**VI**) explains the formation of methyl- (**VII**) and phenyl-samandiol (**VIII**) from (**VI**) and the requisite Grignard reagent since (**VI**) may be regarded as containing masked CO. (**VII**) and (**VIII**) contain therefore the arrangement, $\rangle C{\cdot}NH{\cdot}CH(CH{:}){\cdot}R$ in which R = Me or Ph. Further, the newly introduced OH is *sec.* since (**VII**) and (**VIII**) are oxidised to methyl- and phenyl-samandione. The non-reactivity of (**II**) and dihydrode-*N*-dimethylsamandarine is due to the absence of the sufficiently reactive "aldehyde-ammonia" group. The structure also explains the evolution of N_2 in addition to that of N oxides observed when *N*-nitrososamandarine is boiled with 20% HCl, reaction being expressed: $\rangle C{\cdot}N(NO){\cdot}\dot{C}H{\cdot}O{\cdot}CH< \rightarrow OH{\cdot}\dot{C}H{\cdot}O{\cdot}CH<$ + $[\rangle C{\cdot}NH{\cdot}NO] \rightarrow \rangle C{\cdot}OH + N_2$. (**VI**) is very stable towards acid hydrolysis, its hydrochloride being unaffected by H_2O at 140—150° or at 225° for 13 hr. Boiling 10% $HClO_4$ is without considerable action but at 140—150° a strongly unsaturated, amorphous base is obtained. Similarly boiling conc. HCl yields CO_2 and amorphous products. Samandesone (**IX**), new m.p. 194—195°, gives a *methiodide*, m.p. 304—305° (softens after darkening, at 289°), does not condense with *o*-$C_6H_4(NH_2)_2$ in boiling EtOH, and could not be degraded satisfactorily by H_2O_2 in AcOH or alkaline solution. It is reduced by Na and EtOH to samandesol (**X**) in which the presence of a new OH is demonstrated by Zerevitinov's method and by the formation of an *acetate*, m.p. 119—120°. It gives a *hydriodide*, m.p. 272—274° (decomp.), and a *methiodide* (+$1H_2O$), m.p. 297° (decomp.; softens at 294°), and is oxidised by CrO_3 in dil. H_2SO_4 at 100° to (**IX**). *Samandesonic acid* (+$1{\cdot}5H_2O$) is obtained by the action of NH_3 on (**IX**). (**X**) similarly affords samandesolic acid, m.p. 204—205° (decomp.), which contains 3 active H (Zerevitinov). It is re-converted into (**X**) by sublimation in a high vac., by boiling 2N-HCl, by 6% HCl–MeOH at room temp., or by boiling abs. EtOH. (**VI**) is transformed by HBr–AcOH at 65—75° into *bromodeoxysamandarine*, m.p. 159—160°, converted by Zn dust and boiling AcOH into *deoxysamandarine*, m.p. 123° [*hydrochloride* (**XI**), m.p. 305° (decomp.) after softening], obtained also from *N*-benzoylsamandaronesemicarbazone and NaOEt in EtOH at 180—190°. (**XI**) is converted by aq. Na_2CO_3 followed immediately by MeI into *N-methyldeoxysamandarine methiodide*, m.p. 277—279° (decomp.), converted by Ag_2O and subsequent heating at 100—150°/13 mm. into *de-N-dimethyldeoxysamandarine*, m.p. 78°, softens at 76° [*hydriodide*, m.p. 271—272° (decomp.), softens at 268°]. This with 3% H_2SO_4 at 100° yields *hydroxydihydrode-N-methyldeoxysamandarine* (**XII**), m.p. 122—123°, softens at 120° (*hydriodide*, decomp. 277°; softens at 273°; *oxime*, m.p. 168—169°, softens at 166°). (**XII**) is oxidised by CrO_3 and dil. H_2SO_4 at 100° to *deoxosamandesone*, m.p. 99—100°, softens at 98° [*hydriodide* (+ $1H_2O$ and anhyd.), m.p. 258—259° (decomp.), softens at 256°]. *Deoxosamandesonic acid* [*hydrazide*, m.p. 152° (slight decomp.), softens at 149°] has m.p. 156—157° (decomp.).

Dehydrogenation of (**VI**) by Se gives a hydrocarbon (**XIII**), b.p. 85—95° (bath)/0·003 mm., which could not be obtained cryst. and did not give a cryst. picrate. Cryst. products could not be obtained from it by nitration, bromination, or energetic oxidation with $KMnO_4$ (towards which it is saturated at room temp.) or HNO_3. Its homogeneity is not established but, if assumed, analyses and



mol. wt. determinations indicate the formula $C_{19}H_{24}$ as most probable and its formation therefore: $C_{19}H_{31}O_2N \rightarrow C_{19}H_{24} + 2H_2O + NH_3$. As it is not further changed when heated with much Se for 8 hr. at 360—370°, all 6-membered rings are already aromatic and (**XIII**) cannot be a phenanthrene hydrocarbon. Probably it is a $C_{10}H_8$ derivative with a further carbocyclic ring. These observations and considerations of its origin and relationships suggest the constitutions *A* and *B* for (**VI**) and (**XIII**). H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

Preparation of a homologue of methylarsepedine, methyl-*As*-methylarsepedine. E. V. Zappi and L. M. Simonin (*Ciencia*, 1942, **3**, 160—161).—The Grignard compound from $Cl{\cdot}[CH_2]_4{\cdot}CHMeCl$ and $AsMeCl_2$ yields 1 : 2-*dimethylarsepedine*, b.p. 169°/760 mm., 85°/22 mm. [*methiodide*, sublimes (sealed tube) 340°; *methochloride*; *picrate*, m.p. 231° (decomp.)], which oxidises in air and with I in ligroin gives a resin. (Cf. A., 1916, i, 575.) F. R. G.

Amylchlorophosphines.—See B., 1943, I, 152.

Mercuriphenyl salts.—See B., 1943, II, 110.

3-Bromosalicylic acid. C. K. Kanvinde, A. N. Kothare, and V. V. Nadkarny (*Current Sci.*, 1942, **11**, 397).—*o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ and $Hg(NO_3)_2$ at 100° give a Hg derivative which with Br in AcOH yields 2 : 3 : 1-$OH{\cdot}C_6H_3Br{\cdot}CO_2H$ (60%). A. Li.

Organo mercury compounds.—See B., 1943, III, 89.

Mercuration of pyridine. C. K. Kanvinde, R. S. Borkar, A. N. Kothare, and V. V. Nadkarny (*J. Univ. Bombay*, 1942, **11**, **A**, Part 3, 101—104).—C_5H_5N when heated with $Hg(OAc)_2$ at 178—180° and treated with H_2O and NaCl yields *3-chloromercuripyridine* (+H_2O) (**I**), m.p. 184°, and a compound, C_5H_5N,Hg_2Cl_2, decomp. 203—205°. *3-Bromo-* (+H_2O), m.p. 148°, and *3-iodo-mercuripyridine* (+H_2O), m.p. 123°, and the *compounds*, C_5H_5N,Hg_2Br_2, decomp. 223°, and C_5H_5N,Hg_2I_2, decomp. 232—236°, are similarly obtained, using KBr and KI. The filtrate from the pptn. of (**I**) with saturated aq. KI yields pyridine mercuri-tri-iodide, $(C_5H_5NH)HgI_3$, m.p. 152—153°. A. Li.

Effect of metallic chlorides on the reaction of Grignard reagents with phenyl styryl ketone and benzophenone.—See A., 1943, II, 134.

IX.—PROTEINS.

Ferritin. II. *apo*Ferritin of horse spleen. S. Granick and L. Michaelis. (*J. Biol. Chem.*, 1943, **147**, 91—97).—A 3% solution of ferritin (**I**), which contains 20% of Fe, is dialysed with 2 : 2′-dipyridyl (**II**) through a Cellophane membrane against acetate buffer

at pH 4·6 through which N_2 is passed and to which $Na_2S_2O_4$ is added. The pink Fe^{II}–(**II**) complex diffuses through the membrane. Repetition of the procedure produces finally a colourless protein solution which crystallises on addition of $CdSO_4$. The cryst. form of the apo*ferritin* (**III**) is identical with that of the Fe-containing (**I**). The mol. wt. is ~500,000. The only Fe compound which will re-combine with (**III**) to yield the brown (**I**) is the as yet uncharacterised colloidal compound present in the crystallisation liquors of (**I**). P. G. M.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

New stereoisomerides of methylbixin. L. Zechmeister and R. B. Escue (*Science*, 1942, **96**, 229—230).—I catalysis, and melting of crystals, effects *cis–trans* conversion in methylbixin. The resulting mixture is separable into 8 stereoisomerides by chromatographic analysis using $CaCO_3$ and C_6H_6–light petroleum mixtures. E. R. R.

Cativic acid.—See B., 1943, II, 110.

Tutin. S. N. Slater (*J.C.S.*, 1943, 50—51).—An improved method of separation from the leaves and stem of *Coriaria lurida* gives tutin (**I**), $C_{15}H_{18}O_8$, m.p. 209—210° (*Ac* derivative, m.p. 177°), which is reduced (Pd–C–H_2) to the H_2-derivative, m.p. 190—192° [*Br*-derivative, m.p. 257° (decomp.)]. Picrotoxin (**II**) is similarly hydrogenated and brominated (Br–H_2O) to *bromohydropicrotoxinin*, m.p. 255° (decomp.). Bromination (Br–H_2O) of (**I**) affords α-, m.p. 256° (decomp.) (main product), and β-bromotutin, m.p. 237° (decomp.); similar bromination of (**II**) yields a mixture containing β-bromopicrotoxinin, m.p. 282° (decomp.). It is considered that (**I**) is probably not identical with coriarine. F. R. S.

Penicillin *B*, an antibacterial substance from *Penicillium notatum*.—See A., 1943, III, 353.

XI.—ANALYSIS.

Apparatus for small-scale catalytic hydrogenation.—See A., 1943, I, 103.

Determination of methoxyl and ethoxyl groups. L. M. Cooke and H. Hibbert (*Ind. Eng. Chem.* [*Anal.*] 1943, **15**, 24—25).—Total alkoxyl is determined by Vieböck's method. OMe is determined in the Vieböck apparatus by absorbing the MeI and EtI in EtOH–NMe_3 followed by evaporation to dryness and NMe_3EtI separated by extraction with a saturated solution of NMe_4I in abs. EtOH. The residual NMe_4I is determined titrimetrically. J. D. R.

Iodoform micro-test for the higher alcohols and ketones. F. H. Stodola (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 72—73).—CHI_3 is prepared from the alcohol or ketone with KOH–I in MeOH, and recognised by the red colour formed on addition of *m*-$C_6H_4(OH)_2$. J. D. R.

Determination of aliphatic nitrate esters. Colorimetric method. H. Yagoda (*Ind. Eng. Chem.* [*Anal*], 1943, **15**, 27—29).—The blood, urine, or other sample is extracted with Et_2O, the extract washed and evaporated, and the residue dissolved in $COMe_2$ and treated with a solution of *m*-xylenol in $COMe_2$ and 62·5% H_2SO_4. The nitroxylenol formed is steam-distilled, the distillate treated with NaOH, and the yellow colour determined colorimetrically against similar preps. made with standard quantities of KNO_3. The method has been applied to nitroglycerin, erythritol tetranitrate, and pentaerythritol tetranitrate over the range 3·0—0·005 mg. J. D. R.

Adsorption analysis of some triglycerides and fatty acids.—See A., 1943, I, 124.

Quantitative spectral analysis of molecules. P. P. Schorigin (*J. Phys. Chem. Russ.*, 1941, **15**, 1072—1081).—Raman spectra can be used for quant. analysis of liquid mixtures, if the frequency of the exciting light, the width of the spectrograph slit, etc. are standardised. The frequency, intensity, and half-width of the Raman lines must be determined. A mixture of C_6H_6, PhMe, *cyclo*hexane (**I**), methyl*cyclo*hexane (**II**), *cyclo*pentane (**III**), $CH_3Pr^{\beta}Bu^{\gamma}$, and Δ^{α}-heptene, and one containing C_6H_6, PhMe, (**I**), (**II**), (**III**), *cyclo*hexene, and CCl_4 have been analysed in this way; the largest relative error was 15% (*i.e.*, 11·5% instead of 10%). J. J. B.

Iodometric micro-determination of pyruvic acid, glucose, and of a mixture of these two substances. E. Haag and C. Dalphin (*Helv. Chim. Acta*, 1943, **26**, 246—250).—The iodometric determination of $AcCO_2H$ ($AcCO_2H \equiv 6$ I) is only quant. if the amount of acid does not exceed 1·1 mg. Using Kolthoff's technique for glucose (**I**) this requires that at least 17·5 c.c. of 0·01N-$Na_2S_2O_3$ should be required for titrating the excess of I. Prolongation of the time of oxidation from 10 to 90 min. does not affect the iodometric determination of (**I**). The application of the method to the simultaneous determination of (**I**) and $AcCO_2H$ is described. H. W.

Adsorption analysis : experimental arrangement and results with mixtures of glucose and lactose.—See A., 1943, I, 139.

Determination of free and acetylated sulphanilamide. S. Anderson (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 29—30).—Sulphanilamide (**I**) and acetylsulphanilamide (**II**) are determined together in aq. solution by use of a Cenco replica grating spectrograph, using a H_2 arc as the source of ultra-violet light. (**I**) absorbs all light below 310 mμ., and (**II**) absorbs only light below 286 mμ. By use of a fluorescent screen, the unknown solution is balanced against a known solution of (**I**), using filters absorbing below 310 mμ. and also below 286 mμ. The former reading gives free (**I**), the latter total of free (**I**) and (**II**). Modifications are decribed which make the method applicable to blood. J. D. R.

Acriflavine as internal indicator for sulphanilamide–nitrite titrations. H. F. Frost (*Analyst*, 1943, **68**, 51).—Acriflavine gives a colour change from yellow to violet at the end-point in the diazotisation method (A., 1942, II, 388). S. B.

[Determination of] halogens in halogenated fluoresceins. J. H. Jones (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 944—947).—Determinations of Cl and Br by the Vieböck and Zacherl–Krainick methods in 100—200-mg. samples gave results ~98±1% of calc. vals. A. A. E.

Determination of 2-methyl-1 : 4-naphthaquinone and its solution in water. F. Giral and S. Garcia Iglesias (*Ciencia*, 1942, **3**, 157—159).—The method of Novelli (A., 1941, II, 298) permits the determination of 2-methyl-1 : 4-naphthaquinone (**I**) to within 4—5 μg. A solution prepared by adding 100 mg. of (**I**) in 1 c.c. of EtOH to 100 c.c. of 1% Na deoxycholate in H_2O at pH 7·0 is stable for 3—4 days. F. R. G.

Determination of furfuraldehyde. I. J. Duncan (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 162—164).—The plant material is distilled with 18·5—24% HCl, and the furfuraldehyde determined in the distillate by the NH_2Ph–AcOH colorimetric method, which is more accurate and sp. than the titration method. J. D. R.

Fluorescence test for β-indolylacetic acid. J. H. Hamence (*Analyst*, 1943, **68**, 13—14).—When heated with conc. H_2SO_4 at 100° indolyl-3-acetic acid (**I**) gives a yellowish-green, indolyl-3-propionic acid gives a bluish, and indole gives a slight fluorescence. 0·02 mg. of (**I**) may be detected. S. B.

Determination of nicotinic acid and sodium nicotinate. L. E. Harris and B. I. Duis (*J. Amer. Pharm. Assoc.*, 1943, **32**, 31—32).—Determination of nicotinic acid (**I**) and Na nicotinate by pptn. as Cu nicotinate gives good results with solutions or tablets. The $CuSO_4$ reagent does not form a ppt. with aneurin, riboflavin, or Ca pantothenate, but certain combinations and concns. of these substances cause low results in the assay of (**I**), whilst presence of rice bran, liver, or beef extracts causes high results. The method is not entirely satisfactory for determination of nicotinamide after hydrolysis to (**I**), unless hydrolysis is very carefully carried out with HNO_2 and all NH_3 subsequently removed. J. N. A.

[Determination of] 8-hydroxyquinoline sulphate. A. M. Allison (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 796—798).—Duggan's gravimetric procedure using phosphotungstic acid is subject to error arising from the solubility of the ppt. but could probably be improved. A. A. E.

[Determination of] barbituric acid derivatives. L. E. Warren (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 799—808).—Extraction with $CHCl_3$ + Et_2O gave satisfactory collaborative results. Precise procedure is recorded. A. A. E.

Photochemical spectrum of cytochrome oxidase.—See A., 1943, III, 272.

[Determination of] quinine ethylcarbonate. H. G. Underwood (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 824—828).—Acidimetric determination as quinine after extraction gives satisfactory results. A. A. E.

Iodometric semimicro-determination of arsenic in sodium cacodylate and cacodylic acid. V. Levine and W. M. McNabb (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 76—77).—The sample is digested with $KHSO_4$–H_2SO_4, and the resulting solution reduced with NaH_2PO_2 followed by determination of As with I. J. D. R.

Separation and determination of protein-sulphur, sulphide-sulphur, and other sulphur in sodium sulphide dispersions of keratin. E. F. Potter and C. B. Jones (*Ind. Eng. Chem.* [*Anal.*], 1943, **15**, 15—17).—The dispersion is heated with basic Al acetate, the H_2S evolved collected in $Pb(OAc)_2$, and the S determined, giving sulphide-S. The residual protein is collected and ignited with $Mg(NO_3)_2$ and the protein-S determined as $BaSO_4$, and the residual S in the filtrate from the protein is oxidised with NaOBr and determined as $BaSO_4$. J. D. R.

INDEX OF AUTHORS' NAMES, A., II.

MAY, 1943.

ERRATA.

Abstracts A., II, 1943.

Page	Line	
16	32	Delete "(I)" after thioacetone.
18	35	In the formula for umbellatine "C_4" should be "C_{17}."

JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

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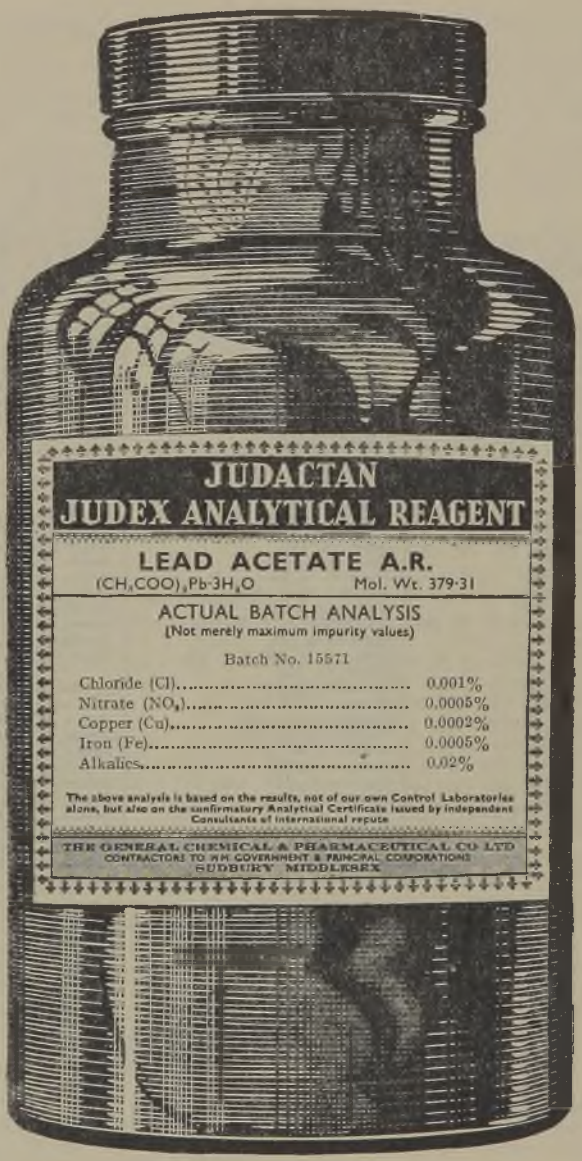
ANALYSIS



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