BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

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MARCH, 1943

A., II.—ORGANIC CHEMISTRY

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A., II.—Organic Chemistry

MARCH, 1943.

I.—ALIPHATIC.

Reaction of hydrogen atoms with *iso*butane. W. H. White, C. A. Winkler, and B. J. Kenalty (*Canad. J. Res.*, 1942, **20**, B, 255—264).—The reaction of H atoms with *iso*-C_4H_{10} has been investigated by the Wood–Bonhoeffer discharge tube method at 50—250°; the activation energy of the reaction is 10·5±1·5 kg.-cal. The nature of the products at a given temp. depends on the concn. of H atoms present. With low at. concn. (5—9%) CH_4 is essentially the only product at <170°. At 250° the yield of C_2H_6 is ∼ half that of CH_4. With higher at. concn. (14—24%) C_2H_6 is formed in appreciable quantities at 140—170° and exceeds the CH_4 content at 250°. Small amounts of C_3H_8 are formed at the higher temp. The results at low temp. appear to be explained satisfactorily by assuming a primary dehydrogenation reaction, *iso*-$C_4H_{10} + H \rightarrow C_4H_9 + H_2$, followed by a series of "atomic cracking" reactions. To account for the behaviour at higher temp., additional secondary reactions, involving decomp. of radicals and their reaction with mol. H_2, are assumed. H. W.

Reactions of alkyl halides with hydrogen halides.—See A., 1943, I, 65.

Hydrogenation of disubstituted acetylenes. K. W. Greenlee and W. C. Fernelius (*J. Amer. Chem. Soc.*, 1942, **64**, 2505).—*trans*-Hydrogenation of acetylenes (Campbell *et al.*, A., 1941, II, 81) is explained by the mechanism: $Na \rightleftharpoons Na^+ + e^-$; $CR{:}CR + e^- \rightarrow C^-R{:}CR\cdot \rightarrow (+ e^-)$ $(:C^-R)_2$; $(:C^-R)_2 + 2NH_3 \rightarrow (:CHR)_2 + 2NH_2^-$. R. S. C.

Addition of hydrogen fluoride to the triple linking. A. V. Grosse and C. B. Linn (*J. Amer. Chem. Soc.*, 1942, **64**, 2289—2292).—HF and C_2H_2 do not react at −70° to 300°/1 atm. but at room temp./13 atm. give a 35 : 65 mixture of $CH_2{:}CHF$ and $CHMeF_2$ with much polymeride. Other acetylenes react similarly with HF (excess) at −70° to −55°/1 atm. Thus $CH{:}CMe$ gives CMe_2F_2 (61%), m.p. −104·8°, b.p. −0·1°, and some polymeric *product*, $C_6H_{13}F$. $CH{:}CEt$ or $(CMe{:})_2$ gives $CMeEtF_2$, m.p. −116·9°, b.p. 30·4—30·6°/747 mm. $CH{:}CPr^{\alpha}$ gives $CMePr^{\alpha}F_2$, b.p. 58·2—58·8°/749 mm. $CH{:}CBu^{\alpha}$ and $(CEt{:})_2$ give *ββ*-, b.p. 86·0—86·2°/750 mm., and *γγ-difluoro*-n-*hexane* (76%), b.p. 86°/742 mm., respectively. $CH{:}C{\cdot}C_5H_{11}$-*n* gives *ββ-difluoro*-n-*heptane*, b.p. 111·7—111·9°/749 mm. R. S. C.

Constitution of pirylene.—See A., 1943, I, 54.

Structure of co-polymerides of vinyl chloride and vinyl acetate. C. S. Marvel, G. D. Jones, T. W. Mastin, and G. L. Schertz (*J. Amer. Chem. Soc.*, 1942, **64**, 2356—2362).—$CH_2{:}CHCl$ (**I**) and $CH_2{:}CH{\cdot}OAc$ co-polymerise to mixed chains, but those formed initially preferentially remove the (**I**). Thus, after complete polymerisation, the product is heterogeneous. Hydrolysis of the polymeride by HCl–H_2O–EtOH gives a chlorohydrin, unaffected by HIO_4, indicating head-to-tail union. This union is less clearly shown by dehalogenation, which is quantitatively rather erratic and may give *cyclo*propane units since the products decolorise Br–CCl_4 but not $KMnO_4$–$COMe_2$. R. S. C.

Polyene series. VI. Preparation of ethinylcarbinols from *αβ*-unsaturated aldehydes. E. R. H. Jones and J. T. McCrombie (*J.C.S.*, 1942, 733—735).—C_2H_2 is passed into liquid NH_3 and Na added gradually; addition of PhCHO–Et_2O, with continuous introduction of C_2H_2 (3 hr.), gives (cf. Campbell *et al.*, A., 1939, II, 46) $CH{:}C{\cdot}CHPh{\cdot}OH$, m.p. 22°, b.p. 115—116°/16 mm. (82·5% yield) [*phenyl-*, m.p. 81—82°, p-*nitrophenyl-*, m.p. 132°, and *β-naphthyl-urethane*, m.p. 120°; *H phthalate*, m.p. 98—99°; *acetate* (Ac_2O at 100—115°), b.p. 124°/18 mm.]. $CHMe{:}CH{\cdot}CHO$ similarly affords $CH{:}C{\cdot}CH(OH){\cdot}CH{:}CHMe$ (50—65%), b.p. 154—156°, 75°/24 mm. (Hg compound, m.p. >360°; *phenyl-*, m.p. 65°, and *β-naphthyl-urethane*, m.p. 89°; *acetate*, b.p. 110—112°/100 mm.), hydrogenated (Pd–C in MeOH) to $CHEtPr{\cdot}OH$ (*phenylurethane*, m.p. 49—50°), oxidised to COEtPr (2 : 4-dinitrophenylhydrazone, new m.p. 134—135°). $CH_2{:}CH{\cdot}CHO$ gives $CH{:}C{\cdot}CH(OH){\cdot}CH{:}CH_2$ (36%), b.p. 83·5—84·5°/150 mm. (*phenyl-*, m.p. 37°, and *α-naphthyl-urethane*, m.p. 127·5—128·5°; *acetate*, b.p. 87—88°/100 mm.), reduced by H_2–PtO_2–Et_2O to $CHEt_2{\cdot}OH$ [α-naphthylurethane, m.p. 90—91° (lit. 71—72°)]. $CMe_2{:}CH{\cdot}CHO$ yields *isobutenylacetylenylcarbinol* (50%), b.p. 110—113°/100 mm. (*phenyl-*, m.p. 58—59°, and *β-naphthyl-urethane*, m.p. 76°), reduced (H_2–PtO_2–AcOH) to $CHEtBu^{\beta}{\cdot}OH$. $CHPr{:}CEt{\cdot}CHO$ gives $CH{:}C{\cdot}CH(OH){\cdot}CEt{:}CHPr$ (80%), b.p. 96·5—97°/14 mm. (*α-naphthylurethane*, m.p. 57—58°). Tiglic aldehyde ($CHMe{:}CMe{\cdot}CHO$) yields *δ-methylhex-Δ^δ-en-Δ^α-inen-γ-ol* (75%), b.p. 96—97°/50 mm. (*α-naphthylurethane*, m.p. 105°). Furfuraldehyde or $CHPh{:}CH{\cdot}CHO$ gives 2-furyl- (65%), b.p. 83—85°/2 mm., or *styryl-acetylenylcarbinol* (2%), m.p. 66—67°, respectively. Light absorption data are recorded and active H (Zerevitinov) determined (a temp. of 90° is needed before reaction with acetylenic H is complete). A. T. P.

Polyene series. VII. Carbinols from propargyl acetal. I. M. Heilbron, E. R. H. Jones, and H. P. Koch (*J.C.S.*, 1942, 735—737; cf. preceding abstract).—$CH{:}C{\cdot}CH(OEt)_2$ and MgEtBr–Et_2O, followed by EtCHO at 20°, give *ζζ*-diethoxy-Δ^δ-hexinen-*γ*-ol (**I**) (40%), b.p. 107°/3 mm., the *γ*-Me derivative (**II**), b.p. 88°/3 mm., of which is similarly prepared using COMeEt. $CH_2Ph{\cdot}COMe$ gives *εε*-diethoxy-*α*-phenyl-*β*-methyl-Δ^γ-pentinen-*β*-ol (**III**). (**I**), (**II**), and (**III**) contain 1 active H and are characterised by treatment with $NH_2{\cdot}CO_2Et$ in dil. HCl, thus affording the *diurethano*-derivatives [*i.e.*, $(NH{\cdot}CO_2Et)_2$ replacing $(OEt)_2$], m.p. 143°, 111°, and 130°, respectively. (**II**), H_2 (1 mol.), and Pd–$CaCO_3$ in MeOH afford a complex mixture, from which EtOH and 2-*ethoxy*-5-*methyl*-5-*ethyl*-2 : 5-*dihydrofuran* (**IV**), b.p. 151°, 46°/19 mm., and a *substance*, $C_{14}H_{21}O_2{\cdot}OEt$, b.p. 110°/4 mm., are isolated. (**IV**) and 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ in HCl–EtOH yield the 2 : 4-*dinitrophenylhydrazone*, m.p. 194°, of *γ*-methylsorbaldehyde, formed by simultaneous hydrolysis and dehydration; semicarbazide acetate in hot H_2O converts (**IV**) into the *semicarbazone*, m.p. 169° (small yield), of $OH{\cdot}CMeEt{\cdot}CH{:}CH{\cdot}CHO$. Semihydrogenation of (**III**) also gives a poor yield of a dihydrofuran. A. T. P.

Electrical properties of polymethyl acrylate, methacrylate, and α-chloroacrylate, and polychlorethyl methacrylate.—See A., 1943, I, 51.

Fats containing fatty acids with odd numbers of carbon atoms. II—IV.—See A., 1943, III, 46, 131.

Antioxidants and autoxidation of fats. XIV. Isolation of new antioxidants from vegetable fats. C. Golumbic (*J. Amer. Chem. Soc.*, 1942, **64**, 2337—2340; cf. B., 1941, II, 348).—When autoxidation of cottonseed, soya-bean, or mixed hydrogenated vegetable fats has proceeded until tocopherols are all destroyed, there remains a different type of antioxidant. The latter can be conc. by chromatography, best using activated Al_2O_3 and the Et esters (prep. by HCl–EtOH) in light petroleum. The absorption spectra (max. at 560—570 mμ.), inactivation by reductive acetylation to stable, colourless oils, decolorisation to readily oxidisable products, ready reaction with *o*-$C_6H_4(NH_2)_2$ to fluorescent (ultra-violet) products, instability to alkali, red colour, and lack of vitamin-*E* activity resemble the properties of chroman-5 : 6-quinones. These red compounds are formed from colourless phenolic precursors in the fats. R. S. C.

Diastereoisomerism of the *θιλ*-trihydroxystearic acids. Geometric configurations of ricinoleic and ricinelaidic acids. J. P. Kass and S. B. Radlove (*J. Amer. Chem. Soc.*, 1942, **64**, 2253—2257).—Structures assigned below follow established rules (cf. A., 1939, II, 297) and confirm the *cis*-configuration of ricinoleic (**I**) and *trans*-configuration of ricinelaidic acid (**II**). Many data in the literature are corr. Configurations +++ etc. refer to C_λ, C_ι, and C_θ, respectively. (**I**) (prep. from castor oil modified; best by way of Me esters) with $KMnO_4$–KOH–H_2O at 0° gives *θλ*-trihydroxystearic acid, *α*-, m.p. 109·6—112·4°, $[\alpha]_D^{23}$ −2·9° in EtOH, −6·6° in AcOH, and *β*-form, m.p. 137·6—138·2°, $[\alpha]_D^{23}$ −3·9° in EtOH, −11·6° in AcOH, which are the +−− and −−+ acids or vice versa; (**II**) gives similarly *θλ-trihydroxystearic acid*, *γ*-, m.p. 86·8—87·4°, $[\alpha]_D^{23}$ +19·1° in EtOH, +21·8° in AcOH, and δ-form, m.p. 109·4—110·4°, $[\alpha]_D^{23}$ −26·6° in EtOH, −38·7° in AcOH, which are +++ and −−− acids, respectively. Conversely, H_2O_2–AcOH converts (**I**) into the *γ*- and δ-acids and (**II**) into the *α*- and *β*-acids. R. S. C.

Organic acids of leaves of *Bryophyllum calycinum*. Identity of "crassulacean malic acid" with *iso*citric acid.—See A., 1943, III, 150.

Reaction of ninhydrin with ascorbic acid and other endiol compounds. Decarboxylation of dehydroascorbic acid. E. S. West and R. E. Rinehart (*J. Biol. Chem.*, 1943, **146**, 105—108).—Ninhydrin

(**I**) (2 mols.) and ascorbic acid (**II**) (1 mol.) at room temp., or more quickly on warming, give hydrindantin (**III**), $C_{18}H_{10}O_6$, also obtained from (**I**) and H_2S (cf. Ruhemann, *J.C.S.*, 1911, **99**, 792, 1306). Reductone or dihydroxymaleic acid gives a similar ppt. Oxidation of (**II**) by (**I**) apparently stops at the stage of dehydroascorbic acid (**IV**); (**IV**) and (**I**) do not give (**III**). CO_2 formed in the reaction (**I**) + (**II**) is probably due to decarboxylation of (**IV**), possibly involving hydrolysis of the lactone bridge, with formation of *l*-xylosone. At least part of the metabolism of (**II**) in the body may involve oxidation to (**IV**), followed by decarboxylation. A. T. P.

Photometric method for determining ascorbic acid.—See A., 1943, III, 191.

Photochemical decomposition of methyl *n*-butyl ketone.—See A., 1943, I, 66.

Synthesis of α-amino-acids from substituted acetoacetic esters. K. E. Hamlin, jun., and W. H. Hartung (*J. Biol. Chem.*, 1942, **145**, 349—359).—The synthesis of α-NH_2-acids by nitrosating the respective substituted acetoacetic ester in 85% H_2SO_4 with BuO·NO at −5° to 0°, followed by hydrolysis by aq. NaOH of the α-oximino-ester to the acid, and then hydrogenation at room temp./10 atm., using Pd–C (2 mol. equiv. of HCl in EtOH), is described; the method is general. The α-oximino-ester can be similarly reduced, followed by hydrolysis of the NH_2-acid ester. Alanine, α-amino-butyric acid, norvaline (Bz derivative, m.p. 153·5°), nor- and *iso*-leucine, aspartic acid, glutamic acid, phenylalanine, and *O*-methyl-tyrosine (HCl at 180° gives tyrosine) are prepared. The following are described: α-oximino-acids, R·C(:N·OH)·CO_2H [R = Me, m.p. 182° (decomp.); Et, m.p. 155° (decomp.); Pr, m.p. 145° (decomp.); Bu, m.p. 137° (decomp.); CHMeEt, m.p. 145° (decomp.); CH_2Ph, m.p. 168° (decomp.); *p*-OMe·C_6H_4·CH_2, m.p. 157° (decomp.)], and -esters, R·C(:N·OH)·CO_2Et [R = Me, m.p. 96°; CH_2·CO_2Et, an oil; $[CH_2]_2$·CO_2Et, m.p. 82°]. Photomicrographs of the NH_2-acids are reproduced. A. T. P.

Poly-condensation of α-amino-acid esters. Poly-condensation of (I) glycine esters, (II) alanine ethyl ester. M. Frankel and E. Katchalski (*J. Amer. Chem. Soc.*, 1942, **64**, 2264—2268, 2268—2271).—I. Average degrees of polymerisation are denoted by numerical prefixes. Passage of N_2 or H_2 through NH_2·CH_2·CO_2Et (**I**) at room temp. gives a 20-*polymeride*, decomp. ~280—300°, quantitatively hydrolysed by boiling 10% H_2SO_4 to glycine; subsequent contact with air gives a 25-*polymeride*; use of O_2 gives a 16-*polymeride*. In xylene at room temp. (3 months), (**I**) gives a 12-*polymeride* or, at the b.p. (8 hr.) and then room temp. (2 months), a 13-*polymeride*. In C_6H_6 at room temp. (70 days), (**I**) gives a 1 : 1 mixture of 4-polymeride and anhydride, but at the b.p. (7 hr.) and then room temp. (70 days) gives a 17-*polymeride* (quantitatively hydrolysed by 25% HCl). Similar experiments with NH_2·CH_2·CO_2Me (modified prep.) give 18-, 30-, 27-, and 35-*polymerides*. NH_2·CH_2·CO_2Bu$^\beta$ gives a 10-*polymeride*. Subsequent heating at 130° gives still higher polymerides, *e.g.*, the 20- and 16-polymeric Et esters give up to a 42-*polymeride* and the 30-polymeric Me ester gives a 110-*polymeride*. The polymerides are isolated by removing impurities in hot H_2O (picric acid and biuret tests on washings negative); the chain-length is determined by the OMe content.

II. NH_2·CHMe·CO_2Et at room temp./15 mm. gives after 5 months a *tetrapeptide* (hygroscopic *hydrochloride*), *alanine anhydride*, and a 10-polymeric *Et ester*; at 40° it gives a 16-*polymeride*, at 80° a 14-*polymeride*, converted at 150° gradually into a 23-*polymeride* and quantitatively hydrolysed by HCl. Unlike the glycine polymerides, these polymerides are sol. in H_2O and are isolated as residues after " mol." sublimation of other products. R. S. C.

Sodium bismuth triglycollamate. R. A. Lehman and R. C. Sproull (*J. Amer. Pharm. Assoc.*, 1942, **31**, 190—192).—CH_2Cl·CO_2H is converted into triglycollamic acid in 60% yield; this gives *Bi H triglycollamate*, $C_6H_{10}O_8NBi$, and a hydrated double *salt*, $C_{12}H_{22}O_{17}N_2Na_3Bi$, of Na Bi triglycollamate with Na_2 triglycollamate. P. G. M.

Crystal structure of β-glycylglycine.—See A., 1943, I, 54.

Raman spectra of betaine.—See A., 1943, I, 50.

Lysine and ornithine. H. D. Dakin (*J. Biol. Chem.*, 1943, **146**, 237—240).—Varying amounts (~5—10% of total present) of lysine (**I**) and ornithine (**II**) may be pptd. by alternate use of excess of 15% aq. $AgNO_3$ and N- or 2N-NaOH, until a brown ppt. of Ag_2O appears; the ppt. is decomposed by HCl. Formation of hydantoins by ring-closure of the PhNCO derivatives of (**I**) and (**II**) with HCl is accompanied by progressive racemisation; the latter is limited by adding EtOH, which gives quick dissolution and reaction (2·5 min.). Thus prepared are optically homogeneous *hydantoin* derivatives of *d*-lysine, m.p. 200—202°, $[\alpha]_D^{20}$ −62·5° in C_5H_5N (from aq. AcOH), and *d*-ornithine, m.p. 208—209°, $[\alpha]_D^{20}$ −48·0° in C_5H_5N; derivatives from inactive (**I**) or (**II**) melt at 190—191° and 191—192°, respectively. A partly racemised hydantoin can be completely racemised by 0·5N-NaOH in 24 hr. A. T. P.

Preparation of asparagine.—See A., 1943, III, 74.

Action of enzymes on αα′-iminodicarboxylic acids. P. Karrer and R. Appenzeller [with, in part, A. Kugler] (*Helv. Chim. Acta*, 1942, **25**, 1149—1154; cf. A., 1942, II, 278).—*dl*-Leucine and *dl*-CHMeBr·CO_2H (**I**) in N-NaOH at 37° give r-*αα′-iminopropionic-hexoic acid*, m.p. 239°. *l*-Leucine (**II**) and *l*-CHMeBr·CO_2H afford (+)-*αα′-iminopropionichexoic acid*, m.p. 214°, $[\alpha]_D^{18}$ +16°, whilst *αα′-iminopropionic-l-hexoic acid*, m.p. 233° (decomp.), $[\alpha]_D$ ±0° in H_2O, is derived from (**II**) and *d*-CHMeBr·CO_2H. dl-*αα′-Imino-aceticpropionic acid*, m.p. 217° (decomp.), is derived from (**I**) and glycine. These acids are not affected by *d*-amino-acid oxidase (**III**) or by the *l*-amino-acid oxidase and other enzymes present in fresh liver and kidney tissue. The observed oxidative deamination of *dl*-methylalanine by (**III**) is confirmed (cf. Keilin *et al.*, A., 1936, 241) but this behaviour is not general for *sec.* amines since it is not shown by *N*-butyl-*dl*-alanine. H. W.

Behaviour of polyamides on heating. R. Brill (*J. pr. Chem.*, 1942, [ii], **161**, 49—64).—*X*-Ray diagrams of threads of the condensate (**I**) of adipic acid and $(CH_2)_6N_4$, and of ε-aminohexoic acid (**II**), were obtained at various temp. In the case of (**I**) the symmetry increases with rise of temp., the monoclinic lattice becoming hexagonal. The transformation temp. is ~161°, but there is considerable hysteresis. In the presence of H_2O vapour, however, the hysteresis is much diminished and the transformation occurs at 140°. The results for (**II**) show minor differences from those for (**I**). In agreement with Fuller *et al.* (A., 1941, I, 103), it is found that at high temp. segments of the polyamide mol. execute rotational vibrations. In the case of (**I**) the orientation achieved mechanically at the beginning of the work is decreased as the temp. rises, whilst for (**II**) the orientation is increased with rise of temp. A. J. M.

II.—SUGARS AND GLUCOSIDES.

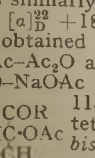
Reactions relating to carbohydrates and polysaccharides. LXVII. Synthesis of methylated glucose derivatives. T. H. Evans, I. Levi, W. L. Hawkins, and H. Hibbert (*Canad. J. Res.*, 1942, **20. B**, 175—184).—α-Methylglucoside (from glucose, MeOH, and HCl) with PhCHO (anhyd. $ZnCl_2$) yields 4 : 6-benzylidene-α-methylglucoside, new m.p. 163—164°, methylated (Me_2SO_4–NaOH in N_2) and hydrolysed (0·275N-H_2SO_4 in N_2) to 2 : 3-dimethyl-α-methylglucoside, m.p. 81·5—83°. 2 : 3-*Dimethylgluconophenylhydrazide*, from the gluconic acid and NHPh·NH_2 in boiling Et_2O, has m.p. 166·5—167°. 2 : 3-Dimethyl-β-methylglucoside is prepared either from β-methylglucoside via the 4 : 6-CHPh derivative, or from 2 : 3-dimethylglucose via the Bz_3 compound. 2 : 3 : 4-Trimethyl-*l*-glucosan on methylation and hydrolysis (as above) yields 2 : 3 : 4-trimethylglucose, which with MeOH–HCl gives 2 : 3 : 4-trimethyl-α- and -β-methylglucosides, the former methylated (as above) to 2 : 3 : 4 : 6-tetramethyl-α-methylglucoside, hydrolysed (5% H_2SO_4) to 2 : 3 : 4 : 6-tetramethylglucose. A. Li.

Rates of reaction of di*iso*propylidene-glucose, -galactose, and -sorbose with *p*-toluenesulphonyl chloride in pyridine solution. R. C. Hockett and M. L. Downing (*J. Amer. Chem. Soc.*, 1942, **64**, 2463—2464).—Reaction of *p*-C_6H_4Me·SO_2Cl (**I**) (8 mols.) with 1 : 2·5 : 6-di*iso*propylidene-*D*-glucose, 2 : 3·4 : 6-di*iso*propylidene-*L*-sorbose, or 1 : 2·3 : 4-di*iso*propylidene-*D*-galactose (1 mol.) in C_5H_5N at 23° is found polarimetrically to be pseudounimol. and have half-change times in the ratio 74·2 : 2·1 : 1. The selectivity of (**I**) for primary or *sec.* OH thus closely resembles that of CPh_3Cl (cf. A., 1942, II, 6). R. S. C.

Agar-agar. III. Isolation of hepta-acetyl-*dl*-galactose from 3 : 6-anhydro-β-methyl-*d*-galactoside. T. L. Cottrell and E. G. V. Percival. **IV.** E. G. V. Percival and T. G. H. Thomson (*J.C.S.*, 1942, 749—750, 750—755).—III. 3 : 6-Anhydro-β-methyl-*d*-galactoside with Ac_2O–H_2SO_4 at 37° yields *dl*-galactose hepta-acetate, similarly obtained (Pirie, A., 1936, 593) from agar, which probably therefore contains 3 : 6-anhydro-*l*-galactose units.

IV. Washed, methylated agar with AcBr in $CHCl_3$ yields *Me$_5$ methyl*-d-*galactonate* (**I**), m.p. 46°, $[\alpha]_D^{14}$ +20° in H_2O, and a mixture of methylated disaccharide esters hydrolysed (5% H_2SO_4) to 2 : 5-*dimethyl*-3 : 6-*anhydro*-l-*galactonic acid*, m.p. 160°, $[\alpha]_D^{15}$ −65° in H_2O (the amide, m.p. 171°, gives a negative Weerman reaction), tetramethyl-*d*-galactopyranose (isolated as anilide), and 2 : 4 : 5 : 6-*tetramethyl*-d-*galactonic acid* (syrup), $[\alpha]_D^{14}$ −3° in H_2O, the *Me* ester, b.p. 110—135°/0·07 mm., $[\alpha]_D^{15}$ +11° in H_2O, of which with MeOH–NH_3 yields an amide (syrup) giving a negative Weerman reaction, and with MeI and Ag_2O gives (**I**). Hydrolysis (MeOH–HCl) of methylated agar gives no tetramethyl-*d*-galactopyranose (cf. A., 1937, II, 445), but the production of dimethylmethyl-galactosides is confirmed, and a small amount of substance is formed which when methylated, hydrolysed, and treated with NH_2Ph yields *tetramethyl*-l-*galactoseanilide*, m.p. 197°, $[\alpha]_{15}^{20}$ +70° in $COMe_2$. Hydrolysis (H_2O at 130° under pressure) of agar yields a gel, " δ," and a H_2O-sol. fraction, " λ." These have been acetylated, methylated, and hydrolysed, and the relative mol. wts. of the products determined (η and I val.), but the results do not explain the differences in properties of " δ " and " λ." A. Li.

Action of diazomethane on acyclic sugar derivatives. III. Synthesis of ketoses and of their open-chain (keto) acetates. M. L. Wolfrom, S. W. Waisbrot, and R. L. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 2329—2331; cf. A., 1942, II, 395).—1-Diazo-1-deoxy*keto*-*d*-fructose tetra-acetate in boiling AcOH gives *keto*-*d*-fructose penta-acetate (Hudson *et al.*, A., 1916, i, 116), thus proving the nature of the reaction. 1-Diazo-1-deoxy*keto*-*d*-glucoheptulose penta-acetate gives similarly keto-d-*glucoheptulose hexa-acetate* (70%), m.p. 104—105°, $[\alpha]_D^{22}$ +18·7° in $CHCl_3$ [absorption max. at 2830 A. (log ε 1·60)], also obtained from 1-bromo*keto*-*d*-glucoheptulose penta-acetate by KOAc–Ac_2O at 70° and converted by NH_3–MeOH at 0° and then Ac_2O–NaOAc at 100° into the cyclic hexa-acetate, m.p. 114·5—115·5°, $[\alpha]_D^{23}$ +86° in $CHCl_3$ (cf. lit.). Mucyl dichloride tetra-acetate with CH_2N_2 in Et_2O at <0° gives "1 : 8-*bisdiazomucyldimethane*" *tetra-acetate* (*A*; R = CHN_2), m.p. 179—180° (decomp.), which with HCl–Et_2O or boiling AcOH gives "1 : 8-*dichloromucyldimethane*" *tetra-acetate* (*A*; R = CH_2Cl), m.p. 174—175°, and "1 : 8-*dihydroxymucyldimethane*" *hexa-acetate* (*A*; R = CH_2·OAc), m.p. 193—195° (decomp.), respectively.


(*A*.)

R. S. C.

Fructosan from *Yucca mohavensis*, Sarg. K. P. Dimick and B. E. Christensen (*J. Amer. Chem. Soc.*, 1942, **64**, 2501—1502).—The fat-free stem of this plant yields to 70% EtOH 42% of a *fructosan* (*Ba* salt; *acetate*), possibly a fructopyranose and similar to that from rye flour (A., 1935, 69). R. S. C.

Optical rotatory power of crocin in true and in colloidal solution. R. Kuhn and I. Löw (*Kolloid.-Z.*, 1942, **100**, 136—137).—The extremely high optical activity shown by crocin in aq. (colloidal) solution (cf. A., 1939, II, 246) becomes negligibly small when the substance is in true solution in MeOH, AcOH, C_5H_5N, or 10% aq. C_5H_5N. F. L. U.

Structure of the dextrins isolated from maize syrup. M. Levine, J. F. Foster, and R. M. Hixon (*J. Amer. Chem. Soc.*, 1942, **64**, 2331—2337).—Prep. of dextrins from maize syrup, essentially by MeOH, is described. Fractional pptn. from H_2O by MeOH gives fractions containing 2—26 (average) glucose units, the higher fractions being free from maltose or glucose. I–KOH yields K dextrinates, the K content of which agrees with the mol. wt. calc. from the I-reducing power and with [α]. Methylation is smoothly effected by Na–MeI in liquid NH_3; determination, after hydrolysis, of tetramethylglucose shows absence of branching (confirmed by absence of dimethylglucose) and non-reducing fractions (confirmed by [α]). The smaller dextrins give quantitatively unstable compounds of phenylhydrazide type; the larger dextrins (<6 units) absorb NHPh·NH_2; a stereochemical explanation is offered. R. S. C.

Action of aqueous sodium hydroxide on starch. Strengthening of intramolecular linkings. C. Dumazert and R. Michel (*Compt. rend.*, 1942, **214**, 645—647; cf. A., 1939, II, 470).—If starch is pretreated with aq. NaOH, degradation by H_2SO_4–EtOH is arrested and hydrolysis by pancreatic amylase is much slower, thus suggesting a greater stability of certain intramol. linkings. A. T. P.

Investigation of the constitution of starch from the action on it of starch-splitting enzymes. K. Myrbäck (*Tekn. Samfund. Handl.*, 1941, 79—129).—The action of dextrinogen amylase (**I**) on starch (**II**) gives ~21% of "limit" dextrin (**III**) having 6, 4, and, especially, 3 glucose residues per mol. Taka-amylase gives ~20% of (**III**) (6 residues per mol.), and small quantities of tetra- and tri-saccharides. Pancreatic or salivary amylases, however, produce chiefly tetrasaccharides and ~25 and 27% of (**III**), respectively, since the enzymes which decompose (**III**) specifically are absent. If (**I**) contains no PO_4''' the whole of the P_2O_5 of (**II**) is to be found in (**III**), especially in those of high mol. wt.; PO_4''' has no influence on the rate of decrease of (**III**) formation Presence of reducing groups (*e.g.*, ·CHO) in the substrate is (contrary to K. Meyer's theory) without important influence on the saccharoamylase activity. J. G.

Starch studies: preparation and properties of starch triesters. J. W. Mullen and E. Pacsu (*Ind. Eng. Chem.*, 1942, **34**, 1209—1217; cf. B., 1942, III, 214).—Methods for the prep. of starch esters are critically reviewed and a preferred method is described involving gelatinisation of starch in azeotropic C_5H_5N–H_2O, and acylation in presence of C_5H_5N as catalyst. The triacetates, tripropionates, and tributyrates have been prepared from 5 varieties of starch and their physical properties studied. Special discussion is devoted to the results for η. The acetates from different starches differ mainly in their mol. wt., due to different contents of amylose and amylopectin; the degree of branching is of secondary importance. The behaviour of starch acetate agrees with the assumption that it forms approx. spheroidal mols. I. A. P.

Physico-chemical characteristics of glycogen. W. B. Bridgman (*J. Amer. Chem. Soc.*, 1942, **64**, 2349—2356).—Glycogen, prepared by acid or base, is non-homogeneous. It lies mainly in the range of sedimentation const. 20—120*S*. The max. (S_{20} = 70*S*) corresponds to a mol. wt. 2 × 10^6 if the particle is spherical or 4 × 10^6 if frictional resistance is evaluated by the measured diffusion const. This mol. wt. may be that of an aggregate or chemical mol. Interpretation of results on non-homogeneous systems is discussed. R. S. C.

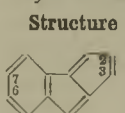
Determination of the mol. wt. of cellulose by an end-group method. E. Husemann and O. H. Weber (*J. pr. Chem.*, 1942, [ii], **161**, 1—19).—Practical details of a method already outlined (A., 1943, I, 8) are given. A. J. M.

Connexion between carboxyl content and degree of polymerisation of celluloses and the ripening of viscose and its bleaching by chlorine. O. H. Weber and E. Husemann (*J. pr. Chem.*, 1942, [ii], **161**, 20—29).—The oxidation of cellulose has been investigated by finding the ·CO_2H content by the reversible methylene-blue method, and the η in Schweitzer's reagent, and calculation from the latter of the degree of polymerisation by Staudinger's method. Under the action of atm. O_2 on Na-cellulose, a splitting of the cellulose chain takes place with formation of 1 CO_2H for each broken linking. The effect of Cl_2 on cellulose in the bleaching process is investigated for solutions of different pH. From comparison of degrees of polymerisation and monose nos. it is clear that in acid solutions (pH 0·9) there is considerable breakdown of the mol. In addition to monocarboxylic acids, mols. containing no CO_2H are formed. At pH 5·5, the breakdown does not proceed so far and is oxidative. On the alkaline side autoxidation occurs. A. J. M.

III.—HOMOCYCLIC.

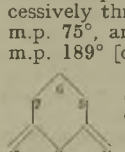
***iso*Butyl*cyclo*butane and di*cyclo*butylmethane.** B. A. Kazanski and V. P. Golmov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **34**, 196—198).—Pasage of *cyclo*butanecarboxylic acid (**I**) and $Pr^{\beta}CO_2H$ over ZnO–MnO at 400—403° gives *iso*butyrone, cyclo*butyl Pr*$^{\beta}$ *ketone* (**II**), b.p. 162—164° (yield 37%), and *dicyclobutyl ketone* (**III**), b.p. 201°/731 mm., 104°/30 mm. (*semicarbazone*, m.p. 129—130°), better obtained under identical conditions from (**I**) alone. (**II**) gives *semicarbazones*, prisms, m.p. 137—138°, and needles, m.p. 114—115°, and with $N_2H_4.H_2O$ affords the *hydrazone* (**IV**), b.p. 89—90°/6 mm., and mainly the *azine*, b.p. 140—141°/6 mm. *iso*Butyl*cyclobutane*, b.p. 119—119·5°/743 mm., is prepared by distillation of (**IV**) with solid KOH and Pt–C. (**III**) and $N_2H_4.H_2O$ give the corresponding *azine*, b.p. 187—188°/7 mm., and (mainly) the *hydrazone*, b.p. 117—118°/25 mm., converted as above into *dicyclobutylmethane*, b.p. 160·8—161°/743 mm. H. W.

Structure of "diphenylene." W. Baker (*Nature*, 1942, **150**, 210—211).—"Diphenylene," $C_{12}H_8$, prepared by Lothrop's method (A., 1941, II, 247) does not readily yield Ph_2 on hydrogenation, neither does it show the properties of an acetylene or an allene. The annexed formula is proposed. A. A. E.



Structure of "diphenylene." C. A. Coulson (*Nature*, 1942, **150**, 577—578).—Baker's *cyclo*pentindene formula for the compound $C_{12}H_8$ (see above) is supported by the fact that the bond strain energy is only a few kg.-cal., whilst that in the diphenyl formula is large, possibly ~100 kg.-cal., although the mobile electrons in the latter are more stable than those in the former. A. A. E.

New type of aromatic hydrocarbon. Acephenalane and its derivatives. Buu-Hoï and P. Cagniant (*Compt. rend.*, 1942, **214**, 493—495).—5-Bromoacenaphthene is converted by successive treatments with Mg in presence of EtBr and $(CH_2)_2O$ into β-5-*acenaphthylethyl alcohol*, b.p. 180°/0·9 mm. (*phenylurethane*, m.p. 161°), transformed successively through the corresponding *bromide* (**I**), b.p. 171°/0·8 mm., m.p. 75°, and *nitrile*, m.p. 83°, into β-5-*acenaphthylpropionic acid*, m.p. 189° [corresponding *chloride* (**II**), m.p. 104°, and *amide*, m.p. 149°]. (**I**) and $CHNa(CO_2Et)_2$ afford *Et*$_2$ β-5-*acenaphthylethylmalonate*, b.p. 220—230°/1·3 mm., hydrolysed and decarboxylated to γ-5-acenaphthylbutyric acid, m.p. 148° (amide, m.p. 182°). $AlCl_3$ and (**II**) in $PhNO_2$ at room temp. give 7-*ketoacephenalane*, m.p. 194° (*oxime*, m.p. 240°; *semicarbazone*, decomp. 235—245°), which is reduced (Clemmensen) to *acephenalane* (**III**), b.p. 168—170°/1·3 mm., m.p. 122° [additive *compound*, m.p. 116°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$]. 7-*Ketoacephenalene* forms yellow needles, m.p. 177—178°. H. W.


(**III**.)

Chaulmoogryl quaternary salts. R. Baltzly, W. S. Ide, and J. S. Buck (*J. Amer. Chem. Soc.*, 1942, **64**, 2514—2515).—Chaulmoogryl bromide and 33% $NHMe_2$–MeOH at 105—110° give chaulmoogryldimethylamine, m.p. >0°, b.p. 170°/0·5 mm. [*methiodide*, m.p. >170° (decomp.); *benzyliodide*, dimorphic, m.p. 99°]. *Trimethyl-*, mp. 227—230° (decomp.), and *benzyldimethyl-octadecylammonium iodide*, m.p. 93°, are also described. R. S. C.

***cyclo*Hexylsulphamic acid.**—See B., 1943, II, 44.

***p*-Aminodimethylaniline. II. *o*-Chloro- and -nitro-derivatives.** E. E. Ayling, J. H. Gorvin, and L. E. Hinkel (*J.C.S.*, 1942, 755—758; cf. A., 1941, II, 359).—*p*-NMe_2·C_6H_4·NHAc (**I**) affords (method: Pinnow *et al.*, A., 1894, i, 281) 1 : 2 : 4-NMe_2·$C_6H_3(NO_2)$·NHAc (90%) (**II**), m.p. 132° and 122—123 (dimorphs), and *N-nitroso*-4-*acetamidomethylaniline* (6%), m.p. 146° (cf. Hodgson *et al.*, A., 1934, 884).

p-NH_2·C_6H_4·NMe_2 and HNO_3 (*d* 1·5; 2 mols.) in AcOH–H_2SO_4 at 0° give 2 : 6 : 4 : 1-$(NO_2)_2C_6H_2(NH_2)$·NMe_2. NMe_2Ph–HNO_3–AcOH and a little $NaNO_2$ at <15° afford 2 : 4 : 1-$(NO_2)_2C_6H_3$·NMe_2, reduced by $SnCl_2$ in EtOH–HCl to 2 : 4 : 1-NH_2·$C_6H_3(NO_2)$·NMe_2 (**III**), m.p. 63° (*Ac*, m.p. 163°, and *CHPh:* derivative, m.p. 128°). (**I**) and Cl_2–$CHCl_3$ at room temp. yield 2-*chloro*-4-*acetamidodimethylaniline* (**IV**), m.p. 119—120°, also obtained from (**II**)–$Na_2S_2O_4$–aq. EtOH, followed by diazotisation and treatment with Cu_2Cl_2. Diazotised (**III**) with Cu-bronze, boiling MeOH, or HNO_3–Cu-bronze or –Cu_2O, gives *p*-NO_2·C_6H_4·NMe_2 (**V**). 4 : 2 : 1-NO_2·C_6H_3Cl·NMe_2, m.p. 78° [from (**V**) and Cl_2–$CHCl_3$ or from (**III**) by the diazo-reaction], is reduced by $SnCl_2$–HCl to 2-*chloro*-4-*aminodimethylaniline*, m.p. 61·5—63° (*stannichloride*), also obtained by hydrolysis (conc. HCl) of (**IV**). (**II**) and HNO_3 (*d* 1·42) in AcOH afford 4 : 2 : 6 : 1-NHAc·$C_6H_2(NO_2)_2$·NMe·NO or in HCl-NHAc·$C_6H_2(NO_2)_2$·NMe_2. (**IV**) in AcOH or HCl similarly gives 2-*chloro*-6-*nitro*-N-*nitroso*-4-*acetamidomethylaniline* (**VI**), m.p. 132—133°, or 2-*chloro*-6-*nitro*-4-*acetamidodimethylaniline* (**VII**), m.p. 165—166° (attempted hydrolysis causes decomp.), respectively. (**VI**) is oxidised by HNO_3 (*d* 1·5) at 0°, then at room temp., to 2-*chloro*-6 : N-*dinitro*-4-*acetamidomethyaniline* (**VIII**), m.p. 152—153°. (**II**) or (**IV**) and Cl_2–$CHCl_3$ yield (**VII**) or 2 : 6-*dichloro*-4-*acetamidodimethylaniline* (**IX**), m.p. 153—154° (*amine*, m.p. 90—91°), respectively. (**VII**) and aq. $Na_2S_2O_4$–EtOH give the 6-NH_2-compound, m.p. 152°, converted (diazo-reaction) into (**IX**). Boiling PhOH and (**VI**) or (**VIII**) give 2-*chloro*-6-*nitro*-4-*acetamidomethylaniline*, m.p. 208—209°, also obtained from (**VII**) and Br–$CHCl_3$. 4 : 2 : 6 : 1-NHAc·$C_6H_2(NO_2)_2$·NMe_2 and Br–$CHCl_3$ give 4 : 2 : 6 : 1-NHAc·$C_6H_2(NO_2)_2$·NHMe. A. T. P.

Preparation of symmetrical azo-compounds, the positional influence of the nitro-group on the decomposition of nitronaphthalenediazonium sulphates by cuprous hydroxide, and an improved method for the production of 2-nitronaphthalene. H. H. Hodgson, E. Leigh, and G. Turner (*J.C.S.*, 1942, 744—746; cf. A., 1942, II, 52). Decomp. of ArN_2HSO_4 (**I**) with CuOH at room temp. depends on the positivity of the C to which N_2 is attached. When this is very great, as in 2 : 1-NO_2·$C_{10}H_6$·N_2HSO_4, ArH results, and 85% of 2-$C_{10}H_7$·NO_2 is obtained. Gradations in positivity are shown in the decomp. of NO_2·$C_{10}H_6$·N_2HSO_4, with variations of the predominating product, viz., $(NO_2$·$C_{10}H_6$·$N:)_2$ or $(NO_2$·$C_{10}H_6$·$)_2$, indicating min. or medium positivity, respectively. The respective % yields of $(:NAr)_2$, ArOH, and ArH obtained from various (**I**) and CuOH are quoted in parentheses: Ar = Ph (33; 26·5; 27·5); *o*- (80; trace; trace), *m*- (0; 28; trace; +35% of 3 : 3′-dichlorodiphenyl), and *p*-C_6H_4Cl (70; 31; trace); *o*- (35; trace; 39·5), *m*- (mainly 3 : 3′-dinitro-azobenzene + -diphenyl; 13% of $PhNO_2$), and *p*-NO_2·C_6H_4 (35; 13; 8); β-$C_{10}H_7$ (54; trace; 34); 2 : 1- (65; trace; 25), 1 : 2- (87·5; trace; trace) and 4 : 1-$C_{10}H_6Cl$ (78·3; trace; trace); 1 : 2- (0; trace; 10; +1 : 1′-dinitro-2 : 2′-dinaphthyl), 4 : 1- (trace; 32·5; 31), and 5 : 1-NO_2·$C_{10}H_6$ (40·5; 15; 42). Mechanisms of reaction are discussed. 2 : 2′-*Dichloro*-1 : 1′-, m.p. 173—174°, and 1 : 1′-*dichloro*-2 : 2′-*azonaphthalene*, m.p. 170—171°, are prepared from $C_{10}H_6Cl$·N_2Cl, NaOAc, and aq. Na_2SO_3 at room temp., then at 60°. 5 : 5′-*Dinitro*-1 : 1′-*azonaphthalene* (**I**), m.p. 322—323°, is obtained similarly. 5 : 1-$C_{10}H_6I$·NO_2 and Cu-bronze at 220—230° yield 5 : 5′-dinitro-1 : 1′-dinaphthyl, m.p. 228—229°. 5 : 1-NO_2·$C_{10}H_6$·N_2HSO_4 and Cu paste or Cu-bronze give 1-$C_{10}H_7$·NO_2, 5 : 1-NO_2·$C_{10}H_6$·OH (trace), and (**I**) (mainly); Cu-bronze in EtOH affords 1-$C_{10}H_7$·NO_2. A. T. P.

Action of cuprous oxide on diazotised amines in ethyl-alcoholic acid solution. H. H. Hodgson and H. S. Turner (*J.C.S.*, 1942, 748—749).—NH_2Ar are efficiently deaminated when ArN_2HSO_4 (prep. by NO·SO_4H–AcOH) are added to finely divided Cu_2O in EtOH; % yields of ArH are: Ar = *p*-C_6H_4Me (45); *o*- (89), *m*- (78), and *p*-NO_2·C_6H_4 (97); *o*-CO_2H·C_6H_4 (65); 2 : 5 : 1-$C_6H_3Cl_2$ (57); 3 : 5 : 1 : 4-$(NO_2)_2C_6H_2Me$ (40); $(·C_6H_4$-*p*$)_2$ (49); β-$C_{10}H_7$ (60); 1 : 2- (70) and 2 : 1-NO_2·$C_{10}H_6$ (79); 2 : 4 : 1-NO_2·$C_{10}H_5Cl$ (94); 4 : 2 : 1-NO_2·$C_{10}H_5I$ (80); 2 : 4 : 1-$(NO_2)_2C_{10}H_5$ (65); 1- (75) and 2-anthraquinonyl (70%). A. T. P.

Influence of *p*-substituents on the decomposition of zinc chloride double salts of diazonium chlorides by acetic anhydride. H. H. Hodgson and C. K. Foster (*J.C.S.*, 1942, 747—748; cf. A., 1942, II, 401).—(*p*-C_6H_4R·$N_2)_2ZnCl_4$ (**I**) with hot Ac_2O gives (mainly) *p*-C_6H_4R·OAc (**II**) and *p*-C_6H_4RCl. The comparative influence of R towards OAc replacement is in the decreasing order of the negative (−*I*) effect, viz., Cl > OMe > Me; OH is anomalous. (β-$C_{10}H_7$·$N_2Cl)_2$,$ZnCl_2$ and Ac_2O at 60—95° give β-$C_{10}H_7$·OAc (48%; part hydrolysed to β-$C_{10}H_7$·OH) and 2-$C_{10}H_7Cl$ (23·5%); (**I**) (R = OH) (at ~110°) yields *p*-$C_6H_4(OAc)_2$ (70%) and *p*-C_6H_4Cl·OH (18·8%). (**II**) (R = Cl, Me, and OMe) are determined as *p*-C_6H_4R·OH (49, 38·6%) and *p*-C_6H_4R·OMe (39%), respectively. A. T. P.

Mutual influence of chromophoric groups in systems with closed π electron groups.—See A., 1943, I, 49.

***C*-Alkylation of phenols.**—See B., 1943, II, 43.

Bromination of 4-diphenylyl chloroacetate. S. E. Hazlet, L. C. Hensley, and H. Jass (*J. Amer. Chem. Soc.*, 1942, **64**, 2449—2450).—*4-Diphenylyl chloroacetate* (prep. by CH_2Cl·COCl–C_5H_5N–dioxan), m.p. 116—117°, b.p. 185°/3 mm., with Br and a trace of Fe powder in CCl_4 at 70—80° gives 26% or in CH_2Cl·$CHCl_2$ gives 60% of *4′-bromo-4-diphenylyl chloroacetate*, m.p. 141—142·8° (also obtained from *p*-C_6H_4Br·C_6H_4·OH-*p* and hydrolysed thereinto), but in AcOH gives, according to the grade of AcOH and conditions, *p*-C_6H_4Ph·OH + 4 : 2 : 6 : 1-$C_6H_2PhBr_2$·OH, CH_2Cl·CO_2H + *p*-C_6H_4Ph·OAc, or *4-diphenylyl bromoacetate*, b.p. 185°/3 mm., m.p. 112—112·5°. 2-*Bromo*- and 2 : 6-*dibromo*-4-*diphenylyl chloroacetate* have m.p. 60·5—62° and 83—84°, respectively. R. S. C.

Esters of *sec.*-hydroxyaralkylalkylamines. J. S. Buck and R. Baltzly (*J. Amer. Chem. Soc.*, 1942, **64**, 2263—2264).—*p*-OMe·C_6H_4·$[CH_2]_2$·NH·CH_2Ph with CH_2O (1·1 mol.) and HCO_2H (5 mols.) etc. gives *benzyl-β-p-anisylethylmethylamine hydrochloride* (**I**), m.p. 170°, but the 3 : 4-$(OMe)_2$-compound was not thus methylated. With conc. HCl–CO_2 at 170°, (**I**) gives *benzyl-β-p-hydroxyphenylethylmethylamine hydrochloride*, m.p. 198° [*O-acetate*, m.p. 211°, *-benzoate*, m.p. 191°, and *-CO_2Et*-derivative (prep. by $ClCO_2Et$–NaOH–N_2), m.p. 128—129°, *hydrochlorides*]. Hydrogenation (Pd–C) of the appropriate salts in 80% AcOH gives PhMe and *β-p-acetoxy-*, m.p. 194°, *β-p-benzoyloxy-*, m.p. 198°, and *β-p-carbethoxyoxyphenylethylmethylamine hydrochloride*, m.p. 138·5—139°. 3 : 4 : 1-$[OMe)_2C_6H_3$·$[CH_2]_2$·NHMe and CH_2PhCl–EtOH at room temp. give *benzyl-β-homoveratrylmethylamine hydrochloride* (30%), m.p. 205°, and thence, as above, *benzyl-β-3 : 4-dihydroxy-*, m.p. 153° (*diacetate*, m.p. 174—175°; *dibenzoate*, m.p. 131—132°), and *β-3 : 4-diacetoxy-*, m.p. 142—143°, *-dibenzoyloxy-*, m.p. 163—164°, and *-di(carbethoxyoxy)-*, m.p. 115°, *-phenylethylmethylamine hydrochloride*. R. S. C.

Mixed aromatic phosphates.—See B., 1943, II, 44.

Use of deuterium as a tracer in the Claisen rearrangement. G. B. Kistiakowsky and R. L. Tichenor (*J. Amer. Chem. Soc.*, 1942, **64**, 2302—2304).—When nuclear-deuterated Ph allyl ethers rearrange, the D displaced migrates entirely to the O. 2 : 4 : 6 : 1-$C_6H_2D_3$·OH and 4 : 2 : 6 : 1-$C_6H_2DMe_2$·OH, prepared from the phenol by D_2O–HCl at 100°, with CH_2:CH·CH_2Br–NaOH–H_2O–$COMe_2$ at the b.p. give the allyl ethers, which are rearranged at 230—240° and 190—200°, respectively. The products are treated with AcCl, and the DCl–HCl mixture evolved is collected in HCl and analysed for D by infra-red absorption. Migration of D does not occur when 2 : 4 : 6 : 1-CH_2:CH·CH_2·$C_6H_2D_2$·OH is heated at 210—230°. 2 : 6-Dimethyl-4-allylphenol, m.p. 26—27° (phenylurethane, m.p. 137—139°), gives an *acetate*, b.p. 105—110°/2 mm. R. S. C.

α-Bromo-αββ-tri-*p*-anisylethylene [synthetic œstrogenic agent].—See B., 1943, III, 41.

Nuclear alkylation of alkylaminophenols.—See B., 1943, II, 43.

Synthesis of *p*-hydroxyphenyl amyl sulphide. E. Miller, F. S. Crossley, and M. L. Moore (*J. Amer. Chem. Soc.*, 1942, **64**, 2322—2323).—*p*-OH·C_6H_4·N_2Cl and *n*-C_5H_{11}·SH (**I**) in aq. NaOH at 10° and then 60° give *p*-OH·C_6H_4·S·C_5H_{11}-*n* (25—30%), m.p. 62—62·5°, and (*n*-C_5H_{11}·S)$_2$, b.p. 89—91°/1 mm., reduced by Na–EtOH to (**I**) and obtained also from *n*-$C_5H_{11}Br$ by Na_2S_2–EtOH or from (**I**) by I–NaOH–$H_{II}O$. *p*-OH·C_6H_4·S·C_5H_{11}-*iso* is similarly prepared. R. S. C.

Polyene series. V. Employment of γ-2 : 6 : 6-trimethyl-Δ¹-*cyclo*hexenyl-α-methylcrotonaldehyde for the synthesis of vitamin-*A* and analogues. I. M. Heilbron, A. W. Johnson, E. R. H. Jones, and A. Spinks (*J.C.S.*, 1942, 727—733; cf. A., 1939, II, 548).—The synthesis of vitamin-*A* described by Kuhn *et al.* (A., 1937, II, 288) could not be repeated. NaOMe (added slowly), β-ionone, b.p. 82°/10^{-2} mm. (regenerated from the semicarbazone), and CH_2Cl·CO_2Et in light petroleum (b.p. 40—60°) in N_2 first at −60°, then at 20° (18 hr.), and finally at the b.p. (6 hr.), give *Et αβ-oxido*-δ-2 : 6 : 6-*trimethyl*-Δ¹-cyclo*hexenyl-β-methyl*-Δ$^{\gamma}$-*pentenoate*, b.p. 55° (bath)/10^{-3} mm., hydrolysed (10% KOH–EtOH at 20°; then 4N-H_3PO_4) to the corresponding *acid* (**I**), m.p. 132° (decomp.) (poor yield) [*Me* ester, b.p. 70—80° (bath)/10^{-4} mm.], stable only in N_2 in the dark. There is no evidence that (**I**) or its esters exist in the isomeric CO-form. There is a marked difference in the intensities of absorption at 2860 A. between the Et ester and (**I**) or its Me ester, and a variation in η is noted in the case of the esters; similar variations occur with the esters (below) from mesityl oxide, and are ascribed to the existence of stereoisomeric forms of the glycide acid. α-Ionone, (reaction in Et_2O) similarly affords *Et αβ-oxido*-δ-2 : 6 : 6-*trimethyl*-Δ²-cyclo*hexenyl-β-methyl*-Δ$^{\gamma}$-*pentenoate*, b.p. 135—145°/0·2 mm., 70° (bath)/10^{-4} mm.; the derived acid (**II**) did not crystallise. Mesityl oxide and CH_2Cl·CO_2Et–NaOMe–Et_2O give a mixture of *Et*, b.p. 65°/1 mm., and *Me αβ-oxido-ββ-dimethyl*-Δ$^{\gamma}$-*hexenoate*, b.p. 60°/1 mm., hydrolysed to the *acid* (**III**), m.p. 72°. The oxido-group in the above esters largely resembles an ethylenic linking in absorption properties. Crude (**I**) and Cu at 130°/15 mm. (1·5 hr.) afford a non-ketonic fraction, b.p. 80—90°/0·1 mm., and γ-2 : 6 : 6-*trimethyl*-Δ¹-cyclo*hexenyl-α-methylcrotonaldehyde* (**IV**), b.p. 45° (bath)/10^{-4} mm. (*phenylsemicarbazone*, m.p. 182°; 2 : 4-*dinitrophenylhydrazone*, m.p. 164·5°), purified by regeneration from the *thiosemicarbazone*, m.p. 192°, by steam-distillation in presence of *o*-$C_6H_4(CO)_2O$ in N_2. The αβ-unsaturated nature is shown by its absorption spectrum (cf. Ishikawa *et al.*, A., 1937, II, 426). (**II**) is decarboxylated

similarly to *γ*-2 : 6 : 6-*trimethyl*-Δ^2-cyclo*hexenyl*-*α*-*methylcrotonaldehyde*, b.p. 45° (bath)/10^{-4} mm. (regenerated from the *thiosemicarbazone*, m.p. 158—159°; *phenylsemicarbazone*, m.p. 123—124°; 2 : 4-*dinitrophenylhydrazone*, m.p. 148·5—149·5°), with light absorption data analogous to those of (**IV**). The two aldehydes described by Ishikawa *et al.* (*loc. cit.*) are probably identical, being derived from *α*-ionone. (**III**) and Cu at 145°/760 mm. give a mixture, b.p. 125—135°, which affords, through the *semicarbazone*, m.p. 184°, (mainly) *αγ*-*dimethyl*-Δ^α-*pentenaldehyde*, $CHPh^{\beta}$:CMe·CHO, b.p. 130—135° (*phenylsemicarbazone*, m.p. 178°; 2 : 4-*dinitrophenylhydrazone*, m.p. 164—165°). (**IV**), $COMe_2$, and $Al(OBu^{\gamma})_3$ in C_6H_6 and N_2 give *η*-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-*ε*-*methyl*-$\Delta^{\nu\varepsilon}$-*heptadien*-*β*-*one*, b.p. 75—80° (bath)/10^{-4} mm. [*semicarbazone*, m.p. 189—190° (decomp.)], converted by MgEtBr into *θ*-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-*γζ*-*dimethyl*-$\Delta^{\delta\zeta}$-*octadien*-*γ*-*ol*, b.p. 70—80° (bath)/10^{-4} mm. CH:CNa [from C_2H_2 and Na (not $NaNH_2$) in liquid NH_3] and citral in Et_2O give *α*-*acetylenylgeraniol* (**V**), CMe_2:CH·$[CH_2]_2$·CMe:CH·$CH(OH)$·C:CH, b.p. 88°/0·02 mm., which with Ac_2O–C_5H_5N at 100° in N_2 affords the *acetate*, b.p. 92—95°/0·5 mm. (absorption spectrum similar to that of the carbinol); prolonged treatment of (**V**) with Ac_2O at 110° gives (mainly) *ει*-dimethyldeca-$\Delta^{\nu\varepsilon\theta}$-triene-$\Delta^\alpha$-inene. (**IV**) similarly yields *ζ*-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-*δ*-*methylhex*-Δ^δ-*ene*-Δ^α-*inen*-*γ*-*ol*, b.p. 115—120°/10^{-3} mm.; the *acetate*, b.p. 130—135°/0·1 mm., shows light absorption data indicating some migration of a double linking. A. T. P.

Polyene series. VI. Preparation of ethinylcarbinols from *αβ*-unsaturated aldehydes. VII. Carbinols from propargyl acetal.—See A., 1943, II, 53, 54.

Physiologically active phenylethylamines containing a *tert.* hydroxyl. C. M. Suter and A. W. Weston (*J. Amer. Chem. Soc.*, 1942, **64**, 2451—2452).—The appropriate Grignard reagent and COPh·CHR·NHR′,HCl give *β*-hydroxy-*β*-phenyl-*n*-butyl-, m.p. 180—181° (lit. 183·5°, 184—186°), and -*n*-hexyl-amine hydrochloride, m.p. 151—152°, *β*-amino-*γ*-phenyl-*n*-butan-, m.p. 239—239·5° (decomp.) (lit. 244°), -*n*-*pentan*-, m.p. 220·5—222° (decomp.), -*n*-*heptan*-, m.p. 213—216° (decomp.), and -*n*-*nonan*-, m.p. 193—200° (decomp.), -*γ*-*ol hydrochloride*, *β*-*amino*-*α*-cyclo*hexyl*-*α*-*phenylpropan*-*α*-*ol hydrochloride*, $+2H_2O$, m.p. 261—263° (decomp.), *β*-methylamino-*γ*-phenyl-*n*-butan-, m.p. 234—235° (lit. 245—248°), -*n*-pentan-, m.p. 197·5—198·5° (decomp.) (lit. 192°), -*n*-*hexan*-, m.p. 182·5—183·5° (decomp.), -*n*-*heptan*-, m.p. 149—150°, and -Δ^ε-*n*-*hexen*-, m.p. 166·5—167·8°, -*γ*-*ol hydrochloride*. M.p. are corr. Alk in the grouping CAlk·C·NH has little effect on the pressor activity but reduces the toxicity. Some of the products are irritant (rabbits' cornea). R. S. C.

Hexamethylene *O*-acylmandelates.—See B., 1943, III, 41.

Preparation of phenylpropiolic acid. M. Reimer (*J. Amer. Chem. Soc.*, 1942, **64**, 2510).—Prep. of CPh:C·CO_2H from $CHPh$:CH·CO_2H by way of the dibromide (prep. in boiling CCl_4) is improved to 76% over-all yield. R. S. C.

Nitration of 4-diphenylyl benzoate. S. E. Hazlet and H. O. Van Orden (*J. Amer. Chem. Soc.*, 1942, **64**, 2505—2506).—*p*-C_6H_4Ph·OBz with fuming + conc. HNO_3 in AcOH at room temp. gives 4′-*nitro*-4-*diphenylyl benzoate*, m.p. 209—210°, also obtained from *p*-NO_2·C_6H_4·C_6H_4·OH-*p*. 2-Nitro-, m.p. 111°, 2 : 6-, m.p. 157—158°, and 2 : 4′-*dinitro*-, m.p. 151—152°, and 2 : 6 : 4′-*trinitro*-4-*diphenylyl benzoate*, m.p. 168°, are described. R. S. C.

Chemical constitution and the tanning effect I. Simple esters and polyesters of gallic acid. A. Russell and W. G. Tebbens, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2274—2276).—Gallic acid and ROH–HCl give n-*amyl* (**I**), m.p. 127°, and n-*hexyl gallate* (**II**), m.p. 92°. 3 : 4 : 5 : 1-$(OAc)_3C_6H_2$·$COCl$ and *d*-arabitol in quinoline–$CHCl_3$ at room temp. give d-*arabityl pentatriacetylgallate*, m.p. 72° after sintering, hydrolysed by NaOH–H_2O–$COMe_2$–N_2 at 0° to d-*arabityl pentagallate* (**III**), m.p. 83° after sintering. Relative tanning properties are: very good, gallotannin; fair, (**III**), *dl*-erithrityl tetragallate, mannityl and *sorbityl hexagallate*, m.p. 76° after sintering; poor, ethylene glycol di- and glyceryl tri-gallate; none, gallic acid, Me, Et, Pr^{α}, Pr^{β}, and Bu^{α} gallate, (**I**), (**II**). $(CH_2·OH)_2$, glycerol, *dl*-erythritol, *d*-arabitol, sorbitol. R. S. C.

Condensation of phenylglyoxylic acid with phenylacetonitrile. M. Cordier and J. Moreau (*Compt. rend.*, 1942, **214**, 621—623; cf. A., 1935, 975).—$COPh$·CO_2H and CH_2Ph·CN condense with difficulty in presence of aq. alcoholic alkali, but in piperidine (~2 mols.) alone, *α*-*hydroxy*-*β*-*cyano*-*αβ*-*diphenylpropionic acid*, decomp. slowly >180° or more rapidly ~210°, is obtained (40% yield). It is converted by HCl–AcOH at 100° into $(CPh·CO)_2O$. A. T. P.

Symmetrical cyanostilbenes. J. B. Niederl and A. Ziering (*J. Amer. Chem. Soc.*, 1942, **64**, 2486—2487).—CH_2Ar·CN with I–NaOMe–MeOH–Et_2O gives ~35% of *αβ*-*dicyano*-4 : 4′-*dimethoxy*-, m.p. 187°, -3 : 4 : 3′ : 4′-*dimethylenedioxy*-, m.p. 235°, and -*tetramethoxy*-*stilbene*, m.p. 205°. 4 : 4′-*Dihydroxy*-*αβ*-*dicyanostilbene*, m.p. 287° (*diacetate*, m.p. 217°), obtained (diazo-method) from the $(NH_2)_2$-derivative shows some œstrogenic activity. $CHArEt$·CN with I–$NaNH_2$ in Et_2O gives ~25% of *γδ*-*dicyano*-*γδ*-*diphenyl*-, m.p. 175°, and -*di*-3 : 4-*methylenedioxyphenyl*-n-*hexane*, m.p. 213°. *p*-NO_2·C_6H_4·$CHEt$·CN (prep. from $CHPhEt$·CN by fuming HNO_3 at 0°), b.p. 165°/3 mm., with I–NaOMe gives *γδ*-*dicyano*-*γδ*-*di*-p-*nitro*-, m.p. 225°, and thence -p-*amino*-, m.p. 205°, and -p-*hydroxy*-, m.p. 218°, -*phenyl*-n-*hexane*. Reactions, CH_2R·CN (R = 3 : 4-CH_2O_2:C_6H_3) + Et_2CO_3–Na–C_6H_6 (60°) → CN·CHR·CO_2Et, b.p. 161°/3 mm. → (+EtI–NaOEt–EtOH) → CN·$CEtR$·CO_2Et, m.p. 72° → (cold alkali) CN·$CEtR$·CO_2H, m.p. 110° → (180°) $CHEtR$·CN, b.p. 174°/5 mm., are reported. R. S. C.

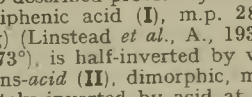
Acrylonitrile. I. Cyanoethylation of active methylene groups. H. A. Bruson (*J. Amer. Chem. Soc.*, 1942, **64**, 2457—2461).—In presence of strong bases, CH_2:CH·CN (**I**) adds to reactive $>CH_2$ giving $>CH$·$[CH_2]_2$·CN and then $>C([CH_2]_2·CN)_2$. 40% aq. CH_2Ph·NMe_3·OH (**II**) is an excellent catalyst; solvents (dioxan, $Bu^{\gamma}OH$) and cooling are advisable to control the reaction. Fluorene thus affords 9 : 9-*di*-*β*-*cyanoethylfluorene* (74%), m.p. 121°. Indene gives 1 : 1-*di*-, b.p. 210—220°/2 mm., and much 1 : 1 : 3-*tri*-*β*-*cyanoethylindene*, m.p. 65°, b.p. 280—290°/1 mm. Anthrone gives 9 : 9-*di*-*β*-*cyanoethylanthr*-10-*one*, m.p. 215°. 2-Nitrofluorene gives 2-*nitro*-9 : 9-*di*-*β*-*cyanoethylfluorene* (~100%), m.p. 236—237°. In absence of a base, *cyclo*pentadiene (**III**) and (**I**) give (Diels–Alder) exothermally 2 : 5-endo*methylene*-Δ^3-*tetrahydrobenzonitrile*, b.p. 80—85°/11 mm., but in presence of (**II**)–dioxan at 20—25° give *hexa*-*β*-*cyanoethyl*cyclo*pentadiene*, m.p. 203°, and liquids, b.p. 100—280°/1 mm. Similarly, dimethylfulvene and (**I**) alone give 2 : 5-endo-Δ^α-iso*butenylidene*-Δ^3-*tetrahydrobenzonitrile*, m.p. 87°, b.p. 95—100°/1 mm., but in presence of (**II**) give impure *β*-cyanoethyl derivatives. *ωω*-Dimethylbenzofulvene with (**I**) and (**II**) in dioxan at 25—35° gives a *β*-*cyanoethyl* derivative, m.p. 121°, but Diels–Adler products are resinous. Alkaline hydrolysis converts the products into 9 : 9-*di*-*β*-*carboxyethylfluorene*, m.p. 273—274°, 1 : 1 : 3-*tri*-*β*-*carboxyethylindene*, m.p. 161—162°, 9 : 9-*di*-*β*-*carboxyethylanthr*-10-*one*, sinters 220°, decomp. 230°, and *hexa*-*β*-*carboxyethyl*cyclo*pentadiene*, m.p. 180—181°. CH_2:CH·CO_2R (R = Me or Et) does not replace (**I**), but with (**III**) undergoes Diels–Alder reaction giving *Me*, b.p. 71—73°/8 mm., or *Et* 2 : 5-endo*methylene*-Δ^3-*tetrahydrobenzoate*, b.p. 84—85°/10 mm. $CHMe$:CH·CN with (**II**) and indene or (**III**) gives resinous products, but with fluorene gives 9-*β*-*cyano*isopropylfluorene, m.p. 92—93°. R. S. C.

Preparation of aromatic dinitriles.—See B., 1943, II, 45.

Esters of Δ^4-tetrahydrophthalic acid.—See B., 1943, II, 44.

Stereochemistry of catalytic hydrogenation. I. Stereochemistry of the hydrogenation of aromatic rings. R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone. **II. Preparation of the six inactive perhydrodiphenic acids. III. Optically active perhydrodiphenic acids. Proof of the configuration of the backbone.** R. P. Linstead, W. E. Doering, and (in part) F. H. Slinger. **IV. Hexahydrodiphenic acids.** R. P. Linstead and S. B. Davis. **V. Assignment of *cis* and *trans* configurations.** R. P. Linstead, S. B. Davis, and R. R. Whetstone. **VI. Hydrogenation of 9-phenanthrol and related substances. Identification of three of the possible stereoisomeric forms of the perhydrophenanthrene ring.** R. P. Linstead, R. R. Whetstone, and P. Levine. **VII. Complete hydrogenation of phenanthraquinone.** R. P. Linstead and P. Levine (*J. Amer. Chem. Soc.*, 1942, **64**, 1985—1991, 1991—2003, 2003—2006, 2006—2009, 2009—2014, 2014—2022, 2022—2026).—I. Theoretical. Nomenclature and structural representation are those previously proposed [A., 1939, II, 307; cf. (**I**) and (**V**) below]. For, *e.g.*, hydrogenated 9-phenanthrones and Me H diphenates etc. the configuration of the C_6-ring adjacent to the CO, CO_2Me, etc. is named first. In work described below (9 cases) and in the literature (reviewed), complete hydrogenation of mono-, di-, and tri-cyclic aromatic hydrocarbons, OH-compounds, acids, and derivatives of acids in presence of PtO_2 at room temp. gives mainly *cis*- and *syn*-derivatives, *e.g.*, (**I**). This unilateral addition of H_2 is due to (*a*) complete hydrogenation occurring during a single period of adsorption on the catalyst, (*b*) "catalyst hindrance" (see below), and (*c*) diphenic acid etc. being hydrogenated in the coiled phase, *i.e.*, with the CO_2R contiguous. Catalyst hindrance occurs when the configuration of the reactant–catalyst adsorption complex is such that the surface of the catalyst prevents access of the reagent to some portion of the reactant; it is shown diagrammatically to reduce *trans* and *anti* addition of H in the phenanthrene and diphenic acid series.

II. Configurations assigned below are proved in later work. The six possible dodecahydrodiphenic acids are prepared; three other acids so described previously are accounted for. *cis*-*syn*-*cis*-Dodecahydrodiphenic acid (**I**), m.p. 287—289° (varies with the rate of heating) (Linstead *et al.*, A., 1939, II, 322; Vocke, A., 1934, 189; m.p. 273°), is half-inverted by way of the Me H ester to the cis-syn-trans-*acid* (**II**), dimorphic, m.p. 199—200° and 173—175°, and completely inverted by acid at high temp. to the *trans*-*syn*-*trans*-

(I.)  (V.)

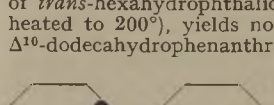
acid (**III**), m.p. 221—223° (*loc. cit.*, 200°). Similarly, the cis-anti-cis-*acid* (**IV**), m.p. 197—198·5°, gives the cis-anti-trans- (**V**), m.p.

205·5—206·5°, and *trans-anti-trans*-acid (**VI**), sinters at 237°, m.p. 246—248° (*loc. cit.*, 244°). When *cis*-Me H (or Me_2) esters are hydrolysed by KOH–MeOH, inversion to the more stable *trans*-form occurs only at the C adjacent to CO_2Me. Diphenic acid (**VII**) (modified prep.; *Me H* ester, m.p. 110—111°) with H_2–PtO_2 in AcOH at 60 lb. gives (**I**) (53%), (**IV**) (10%), (**II**) (7%), *cis*-1 : 2 : 3 : 4 : 5 : 6-hexahydrodiphenic acid (**VIII**) (10%), m.p. 241—242° (bath initially at 235°) (cf. *loc. cit.*), and unchanged (**VII**) (20%); the by-products are separated by fractional acidification of the Na salts in H_2O at the b.p., followed by orthodox methods. Hydrogenation in EtOH is slower but also gives mainly (**I**). The anhydride, new m.p. 146—147°, of (**I**) with NaOMe–MeOH at room temp. gives the cis-syn-cis-*Me H* ester (**IX**) (76·5%), m.p. 128·5—129·5°, and with boiling MeOH + a drop of 15% oleum gives (**IX**) (30%) and the *cis-syn-cis*-Me_2 ester (**X**), m.p. 73—74°. In boiling MeOH + 2% of 15% oleum, (**I**) gives 95% of (**X**) and 2·5% of (**IX**), with CH_2N_2 (excess) in dioxan gives (**X**) (89%), or with CH_2N_2–EtOH (1 equiv.) gives also some (**IX**). CH_2N_2–Et_2O converts (**IX**) into (**X**). Boiling conc. HCl–AcOH hydrolyses (**IX**) or (**X**), without inversion, to (**I**); aq. 20% NaOH also hydrolyses (**IX**) to (**I**). Boiling NaOMe–MeOH followed by a little H_2O partly inverts and then hydrolyses (**IX**), yielding (**II**). KOH in boiling commercial MeOH causes complete inversion of (**X**), yielding (**III**). NaOMe in boiling, freshly dried MeOH converts (**IX**) by half-inversion without hydrolysis into the trans-syn-cis-*Me H* ester (**XI**), m.p. 97—99°; this change is very facile, for MeOH distilled from BaO may contain enough alkali to convert the anhydride of (**I**) into (**XI**). CH_2N_2 (excess) converts (**II**) or (**XI**) into the *trans-syn-cis*-Me_2 ester (**XII**), m.p. 12·5—14·5°, hydrolysed by boiling conc. HCl–AcOH to (**II**) and the cis-syn-trans-*Me H* ester, m.p. 101·5—102·5°. Boiling Ac_2O converts (**II**) into the *cis-syn-trans*-anhydride, m.p. 104—104·5° (cf. Marvel *et al.*, A., 1941, II, 15), and some oily polymeride, both reconverted into (**II**) by boiling aq. alkali. CH_2N_2 converts (**III**) into the trans-syn-trans-Me_2 ester (**XIII**), m.p. 56—57·5°, reconverted into (**III**) by boiling HCl–AcOH. The *trans-syn-trans*-anhydride [prep. from (**III**) by Ac_2O], m.p. 105—106·5°, in boiling dry MeOH gives the trans-syn-trans-*Me H* ester, m.p. 115·5—117·5°, converted by acid or (poor yield) alkali into (**III**), and by CH_2N_2 into (**XIII**). Boiling NaOMe–MeOH completely inverts (**X**), without hydrolysis, yielding (**XIII**), which is also obtained by partial inversion and hydrolysis of the *cis-syn-trans*-Me H ester by KOH–MeOH. With boiling Ac_2O, (**IV**) gives the cis-anti-cis-*anhydride*, *forms*, m.p. 95—96° and 99—100°, and thence (MeOH) the cis-anti-cis-*Me H* ester (**XIV**), m.p. 97·5—99°, converted by CH_2N_2 [as is (**IV**)] into the cis-anti-cis-Me_2 ester (**XV**), m.p. 43—44·5°; both esters are hydrolysed by HCl–AcOH to (**IV**). KOH–MeOH converts (**XIV**) (inversion) into (**V**) (*anhydride*, m.p. 91·5—93°) and (**XV**) into (**VI**) (Me_2 ester, m.p. 84·5—86°). The acid, m.p. 213°, of Vocke (*loc. cit.*) is probably impure (**III**). The acid, m.p. 174°, of Marvel *et al.* (*loc. cit.*) is a dimorph of (**II**). The acid, m.p. 203°, of Linstead *et al.* (*loc. cit.*) is *dodecahydrodiphenyl*-1 : 2′-*dicarboxylic acid*; its predecessors, the unsaturated ketones, m.p. 94° and 39°, have the spiran structures proposed by Woodward (A., 1942, II, 164), and the saturated ketones are the cis- and trans-*forms* of the *perhydrospirans*.

III. In the *syn*-series of dodecahydrodiphenic acids only the intermediate *cis-trans*-form is resolvable; in the *anti*-series all three forms are resolvable. Prep. of active forms of (**II**), (**IV**), and (**VI**), and resistance of (**I**) and (**III**) to resolution prove the configurations assigned above to (**I**)—(**VI**). Five alkaloidal salts of (**I**) were cryst. but regenerated inactive acids. Its Me H ester (**IX**) is, however, resolved by cinchonidine into the l- and d-*Me H* esters, m.p. 133·5—134·5°, $[\alpha]_D^{27}$ −10·7±0·3°, +10·3±0·3° in 95% EtOH. The *l*-ester is hydrolysed by conc. HCl–AcOH to (**I**), α 0, and with CH_2N_2 gives (**X**), α 0, thus conclusively proving the *meso*-nature of (**I**). With NaOMe–MeOH at room temp. (later a little H_2O is added), the *l*- and *d*-esters give, by partial inversion and hydrolysis, the *d*-, m.p. 170—174°, $[\alpha]_D^{29}$ +75°, and *l*-, m.p. 171—174°, $[\alpha]_D^{28}$ −75° in EtOH, *-cis-syn-trans*-acids, respectively. (**III**) (brucine salt, cryst.) resists resolution. Cinchonidine yields the *l*-, m.p. 239—241°, $[\alpha]_D^{26}$ −45±1° (cinchonidine salt, m.p. 204·5—205·5°), and *d-cis-anti-cis*-acid (**XVI**), m.p. 238·5—240·5°, $[\alpha]_D^{27}$ +43±1° in 95% EtOH. The Me_2 ester (CH_2N_2), m.p. 26—28°, $[\alpha]_D^{25}$ +69±1° in 95% EtOH, of (**XVI**) is inverted by boiling KOH–MeOH, yielding the *l*-form, m.p. 257—258·5°, $[\alpha]_D^{26}$ −79·5±5° in 95% EtOH, of the *trans-anti-trans*-acid; the *d*-form, m.p. 257·5—259°, $[\alpha]_D^{20}$ +77·5° in EtOH, is prepared by way of the ephedrine salt of the acid and with the *l*-form regenerates (**VI**).

IV. Absorption of 3 H_2 by (**VII**) in presence of PtO_2 in AcOH yields (**I**) (25%), (**VIII**) (25%), and unchanged (**VII**) (40%). H_2–PtO_2 in AcOH converts (**VIII**) into (**I**) (77%), reaction being again homogeneously *cis-syn* in contrast to the results of Vocke (*loc. cit.*) using Ni. The presence of an aromatic ring in (**VIII**) is proved by prep. of a NO_2-derivative, dimorphic, m.p. 201—202° and 218—219° (yields an amine which diazotises and couples with β-$C_{10}H_7$·OH). In boiling Ac_2O, (**VIII**) yields an oily anhydride, regenerating (**VIII**) by hydrolysis (boiling dil. HCl). At the m.p., (**VIII**) is isomerised to the *trans*-hexahydrodiphenic acid (**XVII**), m.p. 220—221·5° (NO_2-derivative, forms, m.p. 218—219° and 224—225°) (cf. Vocke, *loc. cit.*), best purified by way of the *anhydride* (**XVIII**), m.p. 115—116°. At 243±3° (**XVIII**) is equilibrated with the *cis*-form, but 70% of (**XVIII**) is recovered; some CO_2 is evolved. Hydrogenation of (**XVII**) yields homogeneously (<84%) (**II**).

V. The following and known reactions prove the *cis*-configuration of (**VIII**), (**I**), and (**IV**), and the *trans*-configuration of (**XVII**), (**III**), and (**VI**), and correlate the 9-keto-*as*-octahydrophenanthrenes with the hexahydrodiphenic acids. Oxidation of (**VIII**) by HNO_3 or $KMnO_4$ was unsuccessful, but by O_3 in AcOH (later H_2O_2) gives *cis*-hexahydrophthalic [-*cyclo*hexane-1 : 2-dicarboxylic] acid, separated from unchanged (**VIII**) by partial acidification of the salt and identified by conversion into the dianilide, m.p. 237·5—238° (lit. 234°), and phenylimide, m.p. 132°; the dianilide, m.p. 317—318°, of *trans*-hexahydrophthalic acid (**XIX**), new m.p. 227—229° (pre-heated to 200°), yields no phenylimide. The structure of 9-keto-Δ^{10}-dodecahydrophenanthrene and its precursors (Rapson *et al.*, A., 1935, 1498) is proved by ozonisation in AcOH to give *trans*-2-ketodi*cyclo*hexyl-2′-carboxylic acid, an oil (*oxime*, m.p. 162—163°), converted by Ac_2O into the oily *lactone* (**XX**), which with $KMnO_4$–$NaHCO_3$–$COMe_2$–H_2O gives (**XIX**), m.p. 227—229° (bath initially at 200°) (cf. lit.).



(**XX.**)

The liquid *cis*-9-keto-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (**XXI**) (Cook *et al.*, A., 1936, 334; 1939, II, 103) gives, according to the conditions, a $(NO_2)_2$-, m.p. 95—96·5°, or $(NO_2)_3$-derivative, m.p. 151·5—152°, the latter product being accompanied by the NO_2-derivative (above) of (**VIII**) (proof of structure). *trans*-9-Keto-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (**XXII**) gives a $(NO_2)_3$-derivative, m.p. 182·5—183·5°, and the NO_2-derivative of (**XVII**).

VI. Pt-hydrogenation of phenanthrene hydrocarbons, alcohols, and ketones is substantially *cis-syn*. 9-Phenanthrol (**XXIII**) (modified prep.) with H_2–PtO_2 in AcOH gives a hydrocarbon, b.p. 121°/3 mm., cis-syn-cis-*tetradecahydro*-9-*phenanthrol* (**XXIV**), m.p. 110·5—111°, and a small amount of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-9-phenanthrol (**XXV**), m.p. 134·5—135°; H_2–Raney Ni in EtOH at 120°/123 atm. gives mainly (**XXV**) (best method of prep.) (cf. von Braun *et al.*, A., 1926, 172; m.p. 133°), which is obtained also with difficulty from Na *s*-octahydrophenanthrene-9-sulphonate and KOH at 290—300°. (**XXIV**) is converted into (**I**) by HNO_3 at 100° and thus has the configuration stated; configuration at $C_{(9)}$ is uncertain, but on the hypothesis of catalyst hindrance is as shown. 2-Phenyl*cyclo*hexanone (**XXVI**) and CH_2Br·CO_2Et give the OH-ester (80%), and thence (PCl_5–C_6H_6) an unsaturated ester (77%), b.p. 146—153°/3 mm., and 2-phenyl-Δ^1-*cyclo*hexenylacetic acid (93%), m.p. 92—93°, hydrogenated (Pd–AcOH) to *cis*-2-phenyl*cyclo*hexylacetic acid (**XXVII**), m.p. 168—170°, and some of the trans-*isomeride*, m.p. 113·5—114·5° (**XXVIII**) (not isolated); in H_2SO_4, pure (**XXVII**) gives (**XXI**); the mother-liquors from (**XXVII**) give (**XXII**) (cf. Cook *et al.*, *loc. cit.*). 1-Hydroxy-2-phenyl*cyclo*hexylacetic acid (prep. by hydrolysis of the ester; 75%), m.p. 128—129°, with Ac_2O (cf. *loc. cit.*) gives 17% but with boiling $(Pr^aCO)_2O$ gives 35% of 2-phenyl*cyclo*hexylideneacetic acid, m.p. 168—170° [with $KMnO_4$ gives (**XXVI**); equilibration by alkali gives mainly the $\Delta^{\beta\gamma}$-acid]; hydrogenation thereof is usually *cis*, giving (**XXVII**), but in presence of Pd in C_6H_6 gives 33% of (**XXVIII**) (best method of prep.) with 57% of (**XXVII**). With 1 H_2 in presence of EtOH, (**XXI**) gives 93% of *cis*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-9-phenanthrol (**XXIX**), m.p. 115—116° (*loc. cit.*, m.p. 114—115°), which probably (catalyst hindrance) has the structure shown;

(**XXIV.**)

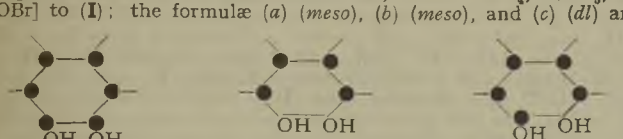
(**XXIX.**)

(**XXXII.**)

however, (**XXII**) gives varying amounts of $C_{(9)}$-epimeric trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-9-*phenanthrols*, m.p. 90—91° and 100—101°. Na–EtOH reduces (**XXI**) to a mixture, including (**XXIX**); $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ gives an inseparable mixture; H_2 (1·95 mols.)–Pd in EtOH gives mainly (?) *cis*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene, b.p. 121—122°/4—5 mm. (lit. 129°/6 mm.), and a little (**XXIX**). Perhydrogenation of (**XXI**) or (**XXIX**) often leads to elimination of O; *e.g.*, with H_2–PtO_2 in EtOH + (little) AcOH it gives a hydrocarbon, b.p. 109—111°/4 mm., with a little (**XXIV**). With H_2 (3·4 mols.) and PtO_2 in EtOH, (**XXI**) gives (**XXIV**), (**XXIX**), an *epimeride* (**XXX**), m.p. 132·5—133·5°, of (**XXIX**), and a mixture (*A*), m.p. 85—87°, which yields (**XXIV**) (10%), (**XXIX**) (10%), and (**XXX**) (30%); similar perhydrogenation of (**XXIX**) gives (**XXIV**) (47%) and (*A*) (10%). CrO_3–AcOH at 0° (later room temp.) oxidises (**XXIV**) to cis-syn-cis-9-*ketotetradeca-hydrophenanthrene* (**XXXI**), m.p. 43—44°, but at 100° gives the trans-syn-cis-*isomeride* (**XXXII**), m.p. 56·5—57·5° [*oxime*, m.p. 224—225°, regenerates (**XXXII**)]; $Al(OBu^{\gamma})_3$–$COMe_2$–C_6H_6 gives a mixture. Structures are proved by oxidation (HNO_3) of (**XXXI**)

to (**I**) and of (**XXXII**) to (**II**). Relations of (**XXXI**) and (**XXXII**) parallel those of the 1-ketodecahydronaphthalenes: boiling NaOEt–EtOH effects the change, (**XXXI**) → (**XXXII**); (**XXXI**) gives an *oxime*, m.p. 150—151°, unstable in hot EtOH, but gives directly the 2 : 4-dinitrophenylhydrazone, m.p. 236—238° (decomp.), of (**XXXII**). H_2–PtO_2 in EtOH reduces (**XXXII**) to trans-syn-cis-*tetradecahydro-9-phenanthrol*, m.p. 88—89°. The ketone, m.p. 57°, of Marvel *et al.* (A., 1941, II, 15, 357) was (**XXXII**), but its precursor, the alcohol, m.p. 67°, is of uncertain structure. $CN{\cdot}CH_2{\cdot}CO_2Et$, (**XXVI**), and NH_4OAc in C_6H_6–AcOH at 140—160° give crude *Et 2-phenylcyclohexylidenecyanoacetate* (54%), b.p. 174°/4 mm. [by reduction (H_2–PtO_2–EtOH or Al–Hg–Et_2O) and then hydrolysis gives (**XXVII**)], containing some 10-*cyano*-1 : 2 : 3 : 4-*tetrahydro-9-phenanthrol* (8%), m.p. 230—231° [*benzoate*, m.p. 183—184°; *picrate*, m.p. 185—190° (decomp.); Na salt, formed by aq. Na_2CO_3; resists hydrolysis]; the latter product is obtained from the former by heating at 200—220°.

VII. Hydrogenation (Pt; Ni) of phenanthraquinone (modified prep. and purification) gives mainly *cis-syn* compounds. H_2–PtO_2 in AcOH at 4 atm. gives slowly α-cis-syn-cis-*tetradecahydrophenanthrene*-9 : 10-*diol* (**XXXIII**), m.p. 173·9—174·4° (*dibenzoate*, m.p. 153·5—154°, prep. in C_5H_5N). In presence of Raney Ni in EtOH at 110°/80 atm., 6 mols. of H_2 are absorbed (cf. von Braun *et al.*, *loc. cit.*), but at 160°/170 atm. 8 mols. are absorbed, yielding, from 26 g., β- (7·54 g.), m.p. 173·9—174·4° [depresses the m.p. of (**XXXIII**)] (*dibenzoate*, m.p. 115·5—116°), and γ-cis-syn-cis- (**XXXIV**) (3·96 g.), m.p. 154·5—155·5° (*dibenzoate*, m.p. 114·2—115°), and α-cis-syn-trans-*tetradecahydrophenanthrene*-9 : 10-*diol* (**XXXV**) (0·138 g.), m.p. 184—184·5°. By H_2–Raney Ni in EtOH at 120°, 9 : 10-dihydroxy-*s*-decahydrophenanthrene, m.p. 135—136° (diacetate, m.p. 160—161°) (cf. Skita, A., 1926, 173), is obtained. All the diols give Criegee's test for 1 : 2-diols. The structures of the *cis-syn-cis*-diosl are proved by oxidation [$Pb(OAc)_4$–C_6H_6, KIO_4, CrO_3–AcOH, or AcO_2H; less well, Beckmann's mixture; not $KMnO_4$, HNO_3, or KOBr] to (**I**); the formulæ (*a*) (*meso*), (*b*) (*meso*), and (*c*) (*dl*) are



(*a*) (*b*) (*c*)

available for the α-, β-, and γ-diols, but the precise allocation thereof is unknown. Similar oxidation to (**II**) proves the *cis-syn-trans* structure of (**XXXV**), for which four formulæ (all *dl*), differing at $C_{(9)-(10)}$, are available. Dehydration of the diols by activated or pptd. Al_2O_3 gives only a trace of ketone; (**XXXIV**) with $KHSO_4$ at 150—160° gives a *compound*, $(C_{14}H_{22}O)_x$ (*x* may be 1), m.p. 202—203°, and a substance giving a crude oxime, m.p. 190—200°. M.p. (all parts) are corr. R. S. C.

Dehydration of αβ-distyryl[ethylene] glycol by sulphuric acid. Formation of γ-phenyl-α-styryl-Δ$^{\alpha}$-butenaldehyde by a hydrobenzoin change followed by displacement of a double linking. Y. Deux (*Compt. rend.*, 1942, **214**, 269—271).—[CHPh:CH·CH(OH)·]$_2$, m.p. 158° (? di-*p*-nitrobenzoate, m.p. 186°), obtained by reduction of CHPh:CH·CHO with Zn–Cu in aq. EtOH, is converted by boiling 20% H_2SO_4 into γ-phenyl-α-styryl-Δ$^{\alpha}$-butenaldehyde (**I**), b.p. 158—160°/5 mm. (semicarbazone, m.p. 210—211°; oxime, m.p. 135—136°). (**I**) is oxidised ($KMnO_4$) to BzOH and $CH_2Ph{\cdot}CO_2H$, and hydrogenated (Raney Ni) to $(Ph{\cdot}[CH_2]_2)_2CH{\cdot}CHO$ (semicarbazone, m.p. 155—156°; oxime, m.p. 98—99°), which is oxidised (Ag_2O) to the corresponding acid, b.p. 210—212°/4 mm. (amide, m.p. 165°; anilide, m.p. 150°), also obtained by decarboxylation of $(Ph{\cdot}[CH_2]_2)_2C(CO_2H)_2$. J. E. P.

***ortho*-Alkylation and -arylation of mesityl aryl ketones.** R. C. Fuson and S. B. Speck (*J. Amer. Chem. Soc.*, 1942, **64**, 2446—2448).—The OMe of *o*-methoxyaryl mesityl ketones is replaced by R by treatment with MgRHal. 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}COCl$ (**I**), the appropriate aryl compound, and $AlCl_3$ in CS_2 at room temp. give 4-*methoxy*-m-*tolyl* (**II**), m.p. 103°, 2-*methoxy*-1-*naphthyl* (**III**), m.p. 109—110°, and m-*anisyl mesityl ketone* (**IV**), m.p. 76°. *o*-*Anisyl mesityl ketone* (**V**), m.p. 112—113°, is obtained from *o*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ and (**I**) in Et_2O. With Et_2O–C_6H_6–MgPhBr at 30° or 60°, (**V**) gives *o*-diphenylyl (**VI**) (35%), m.p. 89° (cf. A., 1942, II, 315), or 2 : 6-*diphenylphenyl mesityl ketone* (**VII**) (20%), m.p. 162°, respectively; 2·5% and traces of (**VII**) are obtained from MgPhBr with 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CO{\cdot}C_6H_4Br$-*o* and (**VI**), respectively. The product (A., 1942, II, 311) from (**V**) and *o*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ is 2-*methoxy*-2′-*mesitoyldiphenyl*. With MgPhBr, (**II**) affords 4-*phenyl*- (18%), m.p. 73°, and 2 : 4-*diphenyl*- (20%), m.p. 131°, and with MgEtBr gives 4-*ethyl*- (28%), m.p. 58°, -m-*tolyl mesityl ketone*. MgRHal and (**III**) give 2-*phenyl*- (59%), m.p. 136°, 2-α-naphthyl- (76%), m.p. 181°, 2-*methyl*- (56%), m.p. 67° (also obtained from 2 : 1-$C_{10}H_6Me{\cdot}COCl$ by $C_6H_3Me_3$–$AlCl_3$ or $C_6H_2Me_3{\cdot}MgBr$), 2-*ethyl*- (80%), m.p. 90°, and 2-n-*butyl*-1-*naphthyl mesityl ketone* (55%), m.p. 73°. MgPhBr and (**IV**) give a little (?) *mesityl* 4-*methoxy*-2-*diphenylyl ketone*, m.p. 194—195° (corr.). R. S. C.

Effect of methoxyl toward stabilising ene-diols. R. P. Barnes and W. M. Lucas (*J. Amer. Chem. Soc.*, 1942, **64**, 2258—2259).—*p*-OMe has a greater stabilising effect on benzoin and the enediol than has *o*-OMe. 2 : 2′-Dimethoxybenzoin (**I**) with Ac_2O–KOAc at 100° gives the *acetate*, m.p. 102°, converted by further boiling into a little *αβ-diacetoxy-αβ-di-o-anisylethylene* (**II**), m.p. 149°, stable to boiling KOAc–AcOH, but hydrolysed by boiling H_2SO_4–aq. EtOH (not conc. H_2SO_4–N_2 at 0°) to (**I**). However, 4 : 4′-dimethoxybenzoin gives an *acetate*, m.p. 93·5°, not convertible into the Ac_2 compound. *αβ-Diacetoxy-αβ-di-p-anisylethylene* [prep. from (*p*-$OMe{\cdot}C_6H_4{\cdot}CO)_2$ (**III**) by H_2–PtO_2–$ZnCl_2$–Ac_2O; (**II**) is similarly obtained], m.p. 121—124°, is converted by conc. H_2SO_4 at room temp., by hydrolysis and oxidation, into (**III**). R. S. C.

Preparation and properties of an ene-diol. β-Mesitoyl-α-*o*-anisylacetylene glycol. R. P. Barnes and W. M. Lucas (*J. Amer. Chem. Soc.*, 1942, **64**, 2260—2261).—*o*-OMe stabilises an ene-diol. *Mesityl o-methoxystyryl ketone* (prep. from *o*-$OMe{\cdot}C_6H_4{\cdot}CHO$ and 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}COMe$ in NaOH–H_2O–EtOH), m.p. 95°, with warm H_2O_2–NaOH–H_2O–EtOH gives the *oxide*, m.p. 73—74°, converted by NaOH in boiling aq. EtOH into *mesityl α-hydroxy-o-methoxystyryl ketone*, m.p. 137° [red $FeCl_3$ colour; 98% enolic (Kurt Meyer)]. With Br–$CaCO_3$ in CCl_4 this gives HBr and *α-bromo-βγ-diketo-α-o-anisyl-γ-mesitylpropane* (**I**), m.p. 84° (non-enolic), converted by boiling KOAc–AcOH into *mesityl α-hydroxy-β-acetoxy-o-methoxystyryl ketone* (**II**), m.p. 94° (red $FeCl_3$ colour; 84% enolic). The *αβ-diacetate* (**III**), m.p. 103—104°, is obtained from (**II**) by AcCl or from (**I**) and Ac_2O–KOAc. Conc. H_2SO_4 at 0° hydrolyses (**II**) or (**III**) to *mesityl αβ-dihydroxy-o-methoxystyryl ketone*, m.p. 105°, which gives a bluish-green $FeCl_3$ colour, decolorises I and 2 : 6-dichlorobenzenone-indophenol, giving in all cases (slowly in air) *o-anisyl mesityl diketone*, m.p. 132°, which with H_2O_2–alkali yields *o*-anisic and mesitoic acids (proof of structure). R. S. C.

Properties of *o*-anisoylmesitoylmethane. R. P. Barnes and C. C. Cochrane (*J. Amer. Chem. Soc.*, 1942, **64**, 2262).—*o-Anisyl* 2 : 4 : 6-*trimethylstyryl ketone*, m.p. 118°, gives a *dibromide*, m.p. 135°, converted by boiling NaOMe–MeOH into *o-anisyl β-methoxy*-2 : 4 : 6-*trimethylstyryl ketone*, m.p. 87°, which with boiling conc. HCl–MeOH gives the *β-OH*-derivative [= *mesityl β-hydroxy-o-methoxystyryl ketone*] (**I**), m.p. 105°. 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe$-*o* gives similarly its *dibromide*, m.p. 86°, *mesityl β* : *o-dimethoxystyryl ketone*, m.p. 85°, and (**I**). (**I**) gives a red $FeCl_3$ colour, is 100% enolic, but is unaffected by CH_2N_2, Ac_2O–H_2SO_4, or AcOH. This and its dual mode of formation indicate its existence as a chelate compound. R. S. C.

Stereoisomeric unsaturated bromo-αδ-dimesityl αδ-diketones. R. E. Lutz and D. H. Terry (*J. Amer. Chem. Soc.*, 1942, **64**, 2426—2430).—Yellow *trans*-$COR{\cdot}CBr{:}CH{\cdot}COR$ (**I**) (R = mesityl here and below) (best prep.: A., 1925, i, 681) is obtained from $(COR{\cdot}CHBr)_2$ by boiling NaOBz–EtOH or AgOBz–Pr^{β}_2O and is converted by illumination in EtOH into a colourless cis-*form*, m.p. 88—89°, whence it is regenerated by illumination in $CHCl_3$–I. Both forms are converted by KI–AcOH into *trans*-$(COR{\cdot}CH{:})_2$ (**II**), by boiling KOH–70% EtOH into $COR{\cdot}C(OH){:}CH{\cdot}COR$, and by NaOMe–MeOH at room temp. into *cis*-$COR{\cdot}C(OMe){:}CH{\cdot}COR$, and are unchanged by Ac_2O–H_2SO_4 at 100°. Boiling HCl–AcOH–H_2O does not affect (**I**). $PhICl_2$ and (**II**) in $CHCl_3$ at room temp. give $(COR{\cdot}CHCl)_2$ (39%), m.p. 209° (decomp.) (cf. A., 1927, 58), which in boiling EtOH gives $COR{\cdot}CCl{:}CH{\cdot}COR$, also obtained from $[COR{\cdot}CH(OH){\cdot}]_2$ by PCl_5–$CHCl_3$. $PhICl_2$ and (**II**) in boiling $CHCl_3$ give a nuclear-chlorinated, unsaturated *diketone*, $C_{22}H_{22}O_2Cl_2$, m.p. 209·5—210°, converted by Zn dust–AcOH into a Cl-containing compound, m.p. 166—167°. *trans*-$COR{\cdot}CMe{:}CH{\cdot}COR$ (**III**) (improved prep.; stable to light in MeOH) with Br–$CHCl_3$ at −10° gives slowly HBr and small amounts of cis-*β-bromo-αδ-dimesityl-γ-methyl-Δβ-butene-αδ-dione* (**IV**), m.p. 143·5—144°, *ββγ-tribromo-αδ-dimesityl-γ-methylbutane-αδ-dione* (**V**), m.p. 188°, and *αδ-dimesityl-β-methylbutane-αδ-dione* (**VI**), m.p. 60·5°. Removal of HBr by $NaHCO_3$ during bromination at 0° leads to 77·7% of (**IV**). With boiling NaOBz- or NaOAc–EtOH, AgOBz–Pr^{β}_2O, or 1 : 1 C_5H_5N–H_2O, (**IV**) gives the trans-*isomeride* (**VII**), m.p. 171—171·5°. (**VI**) is obtained from (**III**) by $SnCl_2$–HCl–AcOH or H_2–Pt or from (**VII**) by Zn dust–AcOH at room temp.; it could not be cyclised. In AcCl + a trace of H_2SO_4, (**III**) gives 4-*acetoxy*-2 : 5-*dimesityl*-3-*methylfuran*, m.p. 88°. R. S. C.

Preparation and alkylation of αδ-dimesityl-γ-methylbutane-αβδ-trione enol. R. E. Lutz and D. H. Terry (*J. Amer. Chem. Soc.*, 1942, **64**, 2423—2426).—*cis*-$COR{\cdot}CBr{:}CMe{\cdot}COR$ (**I**) (R = mesityl here and below) with NaOH in boiling 90% MeOH gives β-hydroxy-αδ-dimesityl-γ-methyl-Δβ-butene-αδ-dione (**II**) (64%), m.p. 124·5—125° (sol. Na and insol., unstable Ag salt; no CO derivative; maroon colour with $FeCl_3$–EtOH; sol. in aq. Na_2CO_3) (cf. A., 1942, II, 408), but in 80% MeOH gives largely non-cryst. material with 30% of a Br-free *compound*, m.p. 234°. With CH_2N_2–Et_2O, (**II**) gives the cis-β- (**III**) (44%), m.p. 134·5—135°, and trans-β-*Me ether* (**IV**) (9%), m.p. 156·5—157°, trans-δ- (**V**) (30%), m.p. 119·5—120°, and cis-δ-*Me ether* (**VI**) (15%), m.p. 142°. (**II**) is also obtained from $COR{\cdot}C(OAg){:}CH{\cdot}COR$ by MeI in boiling Pr^{β}_2O (7% yield),

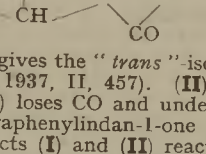
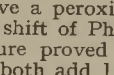
from (**III**) or (**IV**) by HCl–AcOH–H_2O at room temp., or from (**V**) or (**VI**) at the b.p. The Ag salt of (**II**) with MeI–MeOH–H_2O at

(**III.**) COR·C·OMe / COR·CMe ‖ COR·CO·CMe / OMe·CR (**V.**)

0—60° gives 65% of (**V**) and 37% of *αδ-dimesityl-ββ-dimethylbutane-αγδ-trione*, m.p. 132·5—133°, unaffected by boiling HCl–AcOH–H_2O or NH_2OH–MeOH. With NaOMe–MeOH at room temp., (**I**) gives 58% of (**III**) and 12% of (**IV**). Boiling HCl–MeOH converts (**III**) first into (**IV**) and then into (**II**). I–$CHCl_3$–sunlight or boiling NaOAc–EtOH has no effect on (**III**), but illumination in MeOH converts (**IV**) into (**III**) (~100%) or (**V**) into (**VI**). KOH–MeOH and light–$CHCl_3$–I are without effect on (**VI**), as are KOH–MeOH and HCl–MeOH (room temp.) on (**V**). R. S. C.

Constituents of pyrethrum flowers. XV. Presence of the cumulated system in the pyrethrolone side-chain. F. B. LaForge and F. Acree, jun. (*J. Org. Chem.*, 1942, **7**, 416—418).—The structure OH·CH—CO / CH_2·CMe ‖ C·CH_2·CH:C:CHMe for pyrethrolone is confirmed by the similar behaviour of pyrethrone and *α-cyclo*hexyl-$\Delta^{\beta\gamma}$-pentadiene towards halogen addition and subsequent reduction and by their similar absorption spectra. H. W.

Behaviour of carbonyl bridge compounds with alkaline hydrogen peroxide. C. F. H. Allen and J. W. Gates, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2439—2442).—"*cis*"-4 : 7-*endo*Keto-2 : 3 : 5 : 6-tetraphenyl-4 : 7 : 3*a* : 7*a*-tetrahydroinden-1-one (**I**) with aq. H_2O_2–NaOH at <30° absorbs 4 O, giving a *peroxide*, softens ~80°, decomp. up to 200°, which with KI– or HBr–AcOH regenerates (**I**) but in

(**I.**)  (**II.**) 

boiling AcOH gives the "*trans*"-isomeride (**II**), m.p. variable, 215°, of (**I**) (cf. A., 1937, II, 457). (**II**) does not give a peroxide. At 260—270°, (**II**) loses CO and undergoes a 1 : 2 shift of Ph, giving 3 : 3 : 5 : 6-tetraphenylindan-1-one (**III**) (structure proved below). In other respects (**I**) and (**II**) react similarly: both add 1 MgMeI and show 1 active H, with KOH–EtOH give 2 : 3 : 5 : 6-tetraphenyl-4 : 7 : 3*a* : 7*a*-tetrahydroinden-1-one-7-carboxylic acid, and with MgPhBr give the same carbinol etc. 3 : 3 : 5 : 6-Tetraphenylindane-1 : 2-dione (**IV**) [prep. from (**III**) by SeO_2 (cf. *loc. cit.*)] gives a *quinoxaline* derivative and with H_2O_2–NaOH–H_2O–EtOH gives 4 : 5-*diphenyl-2-benzhydrylbenzoic acid* (**V**) (61%), m.p. 258—259° (*Me* ester, m.p. 165°), which with $CuCO_3$ at 260—265° gives 3 : 4-*diphenyl-1-benzhydrylbenzene* [4-*benzhydryl-o-terphenyl*] (30%), m.p. 143° (also prepared from 3 : 4 : 1-$C_6H_3Ph_2$·COPh and MgPhBr and subsequent reduction by Zn–AcOH), and *αα* : 4 : 5-*tetraphenylphthalide* (**VI**) (20%), m.p. 180° (also prepared from 2 : 4 : 5 : 1-CO_2H·$C_6H_2Ph_2$·COPh and MgPhBr). (**VI**) is unaffected by Br, AcCl, or CrO_3, and with Zn–AcOH gives (**V**). 2 : 2-Dibromo-3 : 3 : 5 : 6-tetraphenylindanone with MgPhBr gives first the 2-Br_1-compound and then (**III**). MgRBr and (**III**) give 1 : 3 : 3 : 5 : 6-*pentaphenylindan*-1-*ol*, m.p. 233—234° (decomp.) (dehydrated by boiling 2% H_2SO_4–AcOH to 1 : 1 : 3 : 5 : 6-*pentaphenylindene*, m.p. 227°), 1 : 1 : 5 : 6-*tetraphenyl-3-methyl-*, m.p. 180°, and -3-*α-naphthyl-indene*, m.p. 244°. MgPhBr and (**IV**) in Bu_2O at 100° give 1 : 2 : 3 : 3 : 5 : 6-*hexaphenylindane*-1 : 2-*diol*, m.p. 159°. R. S. C.

General method for synthesis of acenaphthenequinones. Buu-Hoï and P. Cagniant (*Compt. rend.*, 1942, **214**, 315—317).—Acenaphthenone (**I**), NO·C_6H_4·NMe_2, and aq. 10% Na_2CO_3 in EtOH at >40° give *acenaphthenequinonedimethylaminoanil*, m.p. 200—202°, readily hydrolysed (dil. H_2SO_4) to the quinone. 2 : 1-$C_{10}H_6$Me·CH_2Cl and aq. EtOH–KCN afford the nitrile, b.p. 155°/0·5 mm., m.p. 79°, and thence 2 : 1-$C_{10}H_6$Me·CH_2·CO_2H [*chloride* (**II**), b.p. 148—150°/0·5 mm.; *amide*, m.p. 178°]; (**II**) with $AlCl_3$ in C_6H_6 or $PhNO_2$ gives 1-*methylacenaphthen-7-one*, b.p. 158°/21 mm., m.p. 120° (*semicarbazone*, m.p. 213—215°), converted [as for (**I**)] into 1-methylacenaphthenequinone, m.p. 200° [8-*dimethylaminoanil*, m.p. 137° (**III**); *quinoxaline* from *o*-$C_6H_4(NH_2)_2$, m.p. 198°]. (**III**) is accompanied by a little of the corresponding *bismethylacenaphthylidenedione*, m.p. 254° (cf. Sircar *et al.*, A., 1933, 505). 4 : 1-$C_{10}H_6$Me·CH_2Cl, b.p. 124—126°/2·1 mm., similarly yields 4-*methyl*-1-*naphthylacetic acid*, m.p. 148° [nitrile, b.p. 154—156°/0·5 mm.; chloride, b.p. 148°/0·5 mm., cyclised less readily than (**II**); *amide*, m.p. 209°], 3-*methylacenaphthen-7-one*, m.p. 92° [semicarbazone, m.p. 240° (decomp.)], and 3-*methylacenaphthenequinone*, m.p. 178° (8-*dimethylaminoanil*, m.p. 189°; *quinoxaline*, m.p. 262—263°). J. E. P.

1-Nitro-5-aminoanthraquinone.—See B., 1943, II, 45.

IV.—STEROLS AND STEROID SAPOGENINS.

Sterols of alfalfa [lucerne] seed oil. II. Isolation of β- and δ-spinasterol. L. C. King and C. D. Ball (*J. Amer. Chem. Soc.*, 1942, **64**, 2488—2492; cf. A., 1940, III, 83).—This oil yields sterols, giving insol. acetates, which by hydrolysis and then fractionation by 85% EtOH yield *α*- (**I**), m.p. 168·5—169°, $[\alpha]_D^{27}$ −2·7° (acetate, m.p. 180—182°, $[\alpha]_D^{21}$ −6·4°; benzoate, m.p. 196—199°, $[\alpha]_D^{19}$ +2·1°), and *β*-spinasterol, +0·5H_2O, m.p. 148—150° (H_2O lost at 110—125°), $[\alpha]_D^{20}$ +5·9°, and anhyd., m.p. 148—150° [digitonide; *acetate* (**II**), m.p. 153—155°, $[\alpha]_D^{19}$ +5·1°; *benzoate*, m.p. 181—183°, $[\alpha]_D^{19}$ +7·5°]. The sol. acetates yield *δ-spinasterol*, +0·5H_2O, m.p. 143—144°, $[\alpha]_D^{19}$ +6·2° [digitonide; *acetate* (**III**), m.p. 132—133·5°, $[\alpha]_D^{16}$ +0·8°; *benzoate*, m.p. 165—168°, $[\alpha]_D^{19}$ +11·1°]. [α] are in $CHCl_3$. Hydrogenation of (**II**) or (**III**) gives *α*-stigmastenyl acetate. Bessisterol (**IV**) (Kuwada *et al.*, A., 1941, II, 321) differs from (**I**) in [α]. The formulæ of Fernholz *et al.* (A., 1940, II, 373) for (**I**) may apply to (**IV**). R. S. C.

Epimeric 7-hydroxycholesterols. O. Wintersteiner and W. L. Ruigh (*J. Amer. Chem. Soc.*, 1942, **64**, 2453—2457).—7-Ketocholesteryl acetate with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ and later 2% KOH gives crude 7(*α*)-hydroxycholesterol (**I**), m.p. ~176° (Windaus *et al.*, A., 1935, 1363), *di-*$\Delta^{4:6}$-*cholestadien-3-yl* or -$\Delta^{3:5}$-*cholestadien-7-yl ether*, m.p. 158—160°, $[\alpha]_D$ +90·6° in $CHCl_3$ (absorption max. at 243 mμ., ε 54,000 in Et_2O), and $\Delta^{4:6}$-cholestadien-3-one. (**I**) contains up to 20% of 7(*β*)-hydroxycholesterol, m.p. (+MeOH) 186° or (solvent-free) 154—157°, $[\alpha]_D^{23}$ (+MeOH) −87·6° in $CHCl_3$. Partial hydrolysis of the 3 : 7(*β*)-, m.p. 151—152·5° (lit. 155—157°), $[\alpha]_D^{23}$ −107·5° in $CHCl_3$, or 3 : 7(*α*)-dibenzoate gives the 7-monobenzoates. The 3 : 7(*α*)-*diacetate*, m.p. 106—107°, $[\alpha]_D^{27}$ +51·8° in $CHCl_3$, and 7(*β*)-*benzoate* (**II**), m.p. 145—146°, $[\alpha]_D^{26}$ −201° in $CHCl_3$ (3 : 5-*dinitrobenzoate*, m.p. 178·5—179·5°, $[\alpha]_D^{23}$ −88·2° in $CHCl_3$; *H succinate*, m.p. 150—151°), are prepared. Pyrolysis of (**II**) gives little 7-dehydrosterol. R. S. C.

Cholesteryl oxides. P. N. Chakravorty and R. H. Levin (*J. Amer. Chem. Soc.*, 1942, **64**, 2317—2322).—Cholesteryl acetate and *o*-CO_2H·C_6H_4·CO_3H in boiling Et_2O give the *β*- (**I**) (58%), m.p. 111—112°, $[\alpha]_D^{25}$ −21·8°, and *α*-oxide (**II**) (15%), new m.p. 101—103°, $[\alpha]_D^{25}$ −44·6°. Cholesteryl benzoate gives only (50%) its *α*-oxide (**III**), m.p. 164—166°, $[\alpha]_D^{25}$ −28·0°. Cholesterol gives its *α*- (**IV**) (61%), m.p. 141—143°, $[\alpha]_D^{25}$ −44·5° [also obtained from (**II**) by KOH–MeOH], and a small amount of *β*-oxide (**V**), m.p. 105—107°, $[\alpha]_D^{25}$ −12·7° [also obtained from (**I**)]. NH_2·CO·NH·NH_2,HCl and (**I**) in C_5H_5N at 100° give 6-*chloro-5-hydroxy-3-acetoxycholestane* (**VI**), m.p. 187·5—189·5°, unchanged by Ac_2O and also obtained from (**I**) by boiling $FeCl_3$–EtOH, BzCl–CCl_4, or BzCl–C_5H_5N at room temp. and then 100°, or C_5H_5N,HCl in boiling EtOH. C_5H_5N,HCl in EtOH converts (**III**) into 6-*chloro-5-hydroxy-3-benzoyloxycholestane* (**VII**), m.p. 196—198° (unchanged by Ac_2O), (**II**) into (**VI**), and (**IV**) or (**V**) into unstable Cl-compounds which are characterised by conversion into (**VII**) but which in MeOH–$COMe_2$ yield a halogen-free compound, m.p. 99—105°. BzCl with (**II**) gives a product, m.p. 160—170°, converted by Ac_2O into (**VI**), with (**III**) or (**IV**) gives (**VII**), and with (**V**) gives (**VII**) and another *substance*, m.p. 197—198°. With boiling Na_2CO_3–EtOH–H_2O, (**VI**) gives (**IV**), which is also obtained from (**VII**) by KOH–MeOH. The stereochemistry of the reactions is briefly discussed. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Strophanthin. E. Rabald and J. Kraus (*Z. physiol. Chem.*, 1940 **265**, 39—51).—Reduction of strophanthidin (**I**) by Al–Hg or $Al(OPr^{\beta})_3$ gives *strophanthidol* (**II**), m.p. ~180° (softens at 150°) and m.p. 222—223° (corr.) after resolidifying at 180—190°, $[\alpha]_D^{12}$ +37·1° in MeOH [*diacetate*, m.p. 193—195° (corr.)]. (**II**) cannot be hydrogenated completely in presence of Pd-black and with Pd–C or PdO absorbs 1 H_2 with formation of a product, m.p. 180—185°, and, if PdO is used, a substance, m.p. 205—206° (corr.) after melting and resolidifying at ~190°; in presence of PtO_2 (**II**) affords *dihydrostrophanthidol*, melts incompletely at 170—180°, resolidifies and melts at 207—208° (corr.), $[\alpha]_D^{15}$ +35·5° in MeOH, identical with the compound obtained similarly from (**I**). *K*-Strophanthin-*γ* hepta-acetate is reduced [Al–Hg or $Al(OPr^{\beta})_3$] to *K-strophanthol-γ hepta-acetate*, m.p. 172—173° (corr.), $[\alpha]_D^{21}$ −84° in C_6H_6, hydrolysed by $Ba(OMe)_2$ in MeOH to *K-strophanthol-γ* (**III**), softens at 190°, decomp. 195—200°, $[\alpha]_D^{14}$ +8·6° in MeOH [*octa-acetate* (**IV**), softens at 148°, m.p. 153—155° (corr.), $[\alpha]_D^{17}$ +7·1° in C_6H_6], (**III**) is hydrolysed by acid to (**II**) and strophanthotriose, m.p. 225° (corr.; decomp.), $[\alpha]_D$ +7·34° in H_2O. $Ba(OMe)_2$–MeOH and (**IV**) yield *K-strophanthol-γ* 18-*acetate*, m.p. 190—195° (decomp.), $[\alpha]_D^{14}$ +9·85° in MeOH, which is hydrolysed to an acetylated genin. The nomenclature *K*-strophanthin-*α*, -*β*, and -*γ* is suggested for strophanthidin-cymarose (cymarin), strophanthidin-cymarose-glucose, and strophanthidin-cymarose-glucose-glucose respectively. H. W.

Sapogenins. XVII. Position of the carboxyl group in oleanolic and glycyrrhetic acids. G. A. R. Kon and W. C. J. Ross (*J.C.S.*, 1942, 741—744).—Me acetyldehydro-oleanolate (**I**) with SeO_2 in boiling AcOH gives a *diketodehydro-ester* (**II**), $C_{33}H_{46}O_6$, m.p. 247—248°. $[\alpha]_D$ −144° in $CHCl_3$ (cf. Ruzicka *et al.*, A., 1939, II, 331), which is saponified to a neutral substance (**III**), m.p. 286—289°, $[\alpha]_D$ +204° in C_5H_5N (cf. Jacobs *et al.*, A., 1932, 749), and an acid,

m.p. 262—264°, which forms a *pyridazine* derivative, m.p. 263—265°. Oxidation (H_2CrO_4) of (**III**) yields a *triketone*, $C_{19}H_{40}O_3$, m.p. >300° (decomp.). Acetyldeoxoglycyrrhetic ester (**IV**) similarly gives a *diketo-dehydro-ester*, m.p. 236—237°, isomeric with (**II**), and is hydrolysed to the *acid*, m.p. 248—249°, $[\alpha]_D$ −39° in $CHCl_3$, converted into the same hydroxy-diketone. Bromination of Me acetylglycyrrhetate affords a *Br_2-ester*, decomp. 215—220°, $[\alpha]_D$ +521° in $CHCl_3$, and a dehydro-ester, m.p. 241—242°, $[\alpha]_D$ +321° in $CHCl_3$, which is reduced (Zn–Hg–AcOH) to an *ester*, $C_{33}H_{52}O_4$, m.p. 258—259°, $[\alpha]_D$ +127° in $CHCl_3$. (**I**) and (**IV**) are therefore β-ketonic esters and support is thus afforded to the formulæ assigned to the parent acids (Bilham *et al.*, A., 1942, II, 418). F. R. S.

VI.—HETEROCYCLIC.

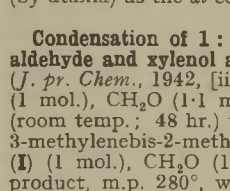
Analogues of synthetic tetrahydrocannabinol. G. A. Alles, R. N. Icke, and G. A. Feigen (*J. Amer. Chem. Soc.*, 1942, **64**, 2031—2035). —*m*-OMe·C_6H_4·CHO (**I**) and $MgBu^aCl$ in Et_2O give α-m-*anisyl*-n-*amyl alcohol* (92%), b.p. 128·5—129°/5 mm., dehydrated by $KHSO_4$ at 135—160° to *m*-OMe·C_6H_4·CH:CHPr^a, b.p. 92—99°/1 mm., which with H_2–PdO in EtOH at 3 atm. gives m-n-*amylanisole* (**II**) (81·5%), b.p. 97—98°/3 mm. *m*-OMe·C_6H_4·CH_2·OH [prep. from (**I**) by H_2–Raney Ni at 90°/90 atm.] with conc. HCl–$CaCl_2$ gives the chloride, b.p. 75°/2 mm., which with $MgBu^aCl$ gives (**II**). 30% aq. HBr–AcOH at 100° converts (**II**) into m-n-*amylphenol*, b.p. 99—100°/1 mm. (3 : 5-*dinitrobenzoate*, m.p. 70°), condensation of which with Et *cyclo*hexanone-2-carboxylate (**III**) by H_2SO_4 at <25° gives 5″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenz*-2-*pyrone*, b.p. 180—185° (bath)/10 μ., and thence (MgMeI in PhOMe at 100°) 2 : 2-*dimethyl*-5″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzpyran* (99%), b.p. 140—145° (bath)/0·5 μ. Similarly are prepared 4′-*methyl*-5″-n-*amyl*-, 5″-*methyl*-, and 4′ : 5″-*dimethyl*-, m.p. 105—106°, -3′ : 4′ : 5′ : 6′-*tetrahydrodibenz*-2-*pyrone*, 2 : 2 : 4′-*trimethyl*-5″-n-*amyl*-, b.p. 155—160° (bath)/2 μ., 2 : 2 : 5″-*trimethyl*-, and 2 : 2 : 4′ : 5″-*tetramethyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzpyran*. *m*-OH·C_6H_4·OBu^a and (**III**) in $POCl_3$–C_6H_6 give 5″-n-*butoxy*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenz*-2-*pyrone* (65%), m.p. 87—88°, b.p. 240—243°/3 mm., also obtained from the 5″-hydroxypyrone by $Bu^a_2SO_4$–2N-NaOH at 90—110° and converted by MgMeI–PhOMe at 100° into 2 : 2-*dimethyl*-5″-n-*butoxy*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzpyran*, b.p. 133—134° (bath)/1 μ. 2 : 2 : 4′-*Trimethyl*-5″-n-*butoxy*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzpyran*, b.p. 162—168°/5 μ., is prepared from the 5-hydroxypyran by $Bu^a_2SO_4$–2N-NaOH at 90—100°. 2 : 2-*Di*- and 2 : 2 : 4′-*tri-methyl*-5″-*ethoxy*-3′ : 4′ : 5′ : 6-*tetrahydrodibenzpyran*, liquids, are similarly prepared. $(PrCO)_2O$ and a drop of H_2SO_4 convert the 5″-hydroxypyrans into 5″-n-*butyroxy*-2 : 2-*di*- and -2 : 2 : 4′-*tri-methyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzpyran*, liquid; the corresponding 5″-acetoxypyrans, m.p. 65—66° and 59—60°, respectively, are prepared by Ac_2O–C_5H_5N. The above-named pyrans produce no ataxia in dogs (doses: 50—100 mg. per kg.) or corneal anæsthesia in rabbits (doses: 10—20 mg. per kg.) (cf. Ghosh *et al*, A., 1941, II, 145). Synthetic tetrahydrocannabinol produces ataxia (8 mg. per kg.) but no corneal anæsthesia (doses up to 32 mg. per kg.) (cf. *loc. cit.*). R. S. C.

Constitution of hibiscetin. P. S. Rao (*Current Sci.*, 1942, **11**, 360; cf. A., 1942, II, 327).—2 : 4 : 3 : 6 : 1-$(OH)_2C_6H(OMe)_2$·CO·CH_2·OMe with [3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CO]$_2O$ and $(OMe)_3C_6H_2$·CO_2Na gives 7-hydroxy-3 : 5 : 8 : 3′ : 4′ : 5′-hexa-, methylated to 3 : 5 : 7 : 8 : 3′ : 4′ : 5′-hepta-methoxyflavone (hibiscetin Me_7 ether). F. R. G.

Products of the reaction of flavonols with boric acid and organic acids and its significance for the anchoring of boron in plant organs. K. Taubock (*Naturwiss.*, 1942, **30**, 439).—Evaporation of solutions or suspensions of flavonols (**I**), H_3BO_3, and $H_2C_2O_4$ in $COMe_2$ gives an Et_2O-sol., intensely yellow pigment (**II**) with marked yellow-green fluorescence very suitable for the detection and determination of traces of (**I**). (**II**) is not very stable and on repeated evaporation passes into an Et_2O-insol., non-fluorescent pigment similar to that obtained with citric and other acids; in dry Et_2O it can be kept for several hr. The most suitable mol. proportions are (**I**) : H_3BO_3 : $H_2C_2O_4$ = 1 : 1 : 4. $H_2C_2O_4$ can be replaced by $CH_2(CO_2H)_2$ but succinic, fumaric, and adipic acid etc. are unsuitable. The presence of OH increases the reactivity. Polybasic CO-acids are unsuitable. Monobasic NH_2-acids give non-fluorescent, Et_2O-insol. pigments but dibasic NH_2-acids give some (**II**). Naringenin, campherol, quercitin, morin, quercetagenin, myricetin and its hexa-acetate show the reaction, which is not exhibited by genistein, daidzein, flavone, or hesperitin. Anthocyanins and anthocyanidins give intensely coloured but non-fluorescent substances; this is true also of *l*-catechin, *dl-epi*catechin, curcumin, and phloretin. Evidence is adduced in favour of the view that B is partly immobilised in many plant organs by combination with (**I**). H. W.

Optically active tetrahydrocannabinols. XIV. *d*- and *l*-3″-Hydroxy-2 : 2 : 4′-trimethyl-5″-*n*-amyl-3′ : 4′ : 5′ : 6′-tetrahydrodibenzpyran. R. Adam, C. M. Smith, and S. Loewe (*J. Amer. Chem. Soc.*, 1942, **64**, 2087—2089; cf. A., 1942, II, 236).—*dl*- is resolved by *l*-menth-hydrazide in EtOH, giving l-3-*methyl*cyclo*hexanone*, b.p. 164—168° (*semicarbazone*, m.p. 181°, $[\alpha]_D^{27}$ +20·8° in EtOH; l-*menth-hydrazone*, m.p. 146°, $[\alpha]_D^{25}$ −31·3° in EtOH). This and the *d*-ketone (prep. from pulegone; l-*menth-hydrazone*, softens at 126—130°, m.p. 130—136°) with $Et_2C_2O_4$–NaOEt at 3—5° (later room temp.) give *Et* d- and l-5-*methyl*cyclo*hexanone*-2-*carboxylate*, b.p. 122—124°/15 mm., $[\alpha]_D^{20}$ +90·5° (→ +73° by keto–enol equilibration), −84·6°, and thence d- and l-3″-*hydroxy*-4′-*methyl*-5″-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenz*-2-*pyrone*, m.p. 177°, $[\alpha]_D^{25}$ +137° in $CHCl_3$, $[\alpha]_D^{27}$ +133°, −127° in EtOH, and d- and l-3″-*hydroxy*-2 : 2 : 4′-*trimethyl*-5″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzpyran*, b.p. 175—185°/0·1 mm., $[\alpha]_D^{25}$ +147·5° in $CHCl_3$, +147° in EtOH, $[\alpha]_D^{26}$ −114° in EtOH. The *d*- and *l*-pyrans are 0·38 and 1·66 times, respectively, as potent (by ataxia) as the *dl*-compound (cf. Leaf *et al.*, A., 1942, II, 202). R. S. C.

Condensation of 1 : 4-dihydroxy-2-methylnaphthalene with formaldehyde and xylenol alcohol. H. von Euler and S. von Kispeczy (*J. pr. Chem.*, 1942, [ii], **160**, 195—202).—2 : 1 : 4-$C_{10}H_5Me(OH)_2$ (**I**) (1 mol.), CH_2O (1·1 mols.), and NaOH (2 mols. as 10% solution) (room temp.; 48 hr.) yield a yellow *compound*, $C_{23}H_{16}O_4$ (probably 3-methylenebis-2-methylnaphthaquinone), and colourless material. (**I**) (1 mol.), CH_2O (1·1 mol.), and conc. HCl (0·1 mol.) afford a product, m.p. 280°, which with Ac_2O–C_5H_5N (100°; 2 hr.) yields a *compound*, $C_{27}H_{22}O_6$, m.p. 305—306° (probably di-1-acetoxy-2-methylnaphthapyran), and a *compound*, $C_{31}H_{28}O_8$, m.p. 238° (probable 3-methylenebis-1 : 4-diacetoxy-2-methylnaphthalene). *m*-4-Xylenol (1 mol.), (**I**) (2·5 mols.), and 96% HCl–EtOH (15 min.; 100°) yield a *compound*, $C_{28}H_{26}O_3$, m.p. 204° [probably (**II**)] (acetate, m.p. 230—231°). W. C. J. R.



(II.)

Thionaphthen-indigotins.—See B., 1943, II, 47.

Phenoxthionins.—See B., 1943, II, 45.

Reaction products from α-chloroketones and potassium cyanide. III. Cyanoacetonylacetone and a new method of preparing acetonylacetone. R. Justoni (*Gazzetta*, 1941, **71**, 375—388).—5-Hydroxy-2 : 4-dicyano-2 : 5-dimethyltetrahydrofuran (**I**) (A., 1942, II, 326) with aq. NaOH gives α′-*cyanoacetonylacetone cyanohydrin*, COMe·CH(CN)·CH_2·CMe(OH)·CN, a syrup, which when distilled gives α′-cyanoacetonylacetone (**II**) (*loc. cit.*) ($FeCl_3$ reaction; *Cu* salt), from which it is also obtained by action of HCN and KOH. With boiling conc. HCl, (**II**) gives 3-*cyano*-2 : 5-*dimethylfuran* (**III**), b.p. 183—183·5°, hydrolysed by 20% KOH in aq. EtOH to the *amide*, m.p. 125°, of 2 : 5-dimethylfuran-3-carboxylic acid. With boiling aq. NH_3 (or solid NH_4 carbonate, or NH_4OAc–AcOH), (**II**) gives 3-*cyano*-2 : 5-*dimethylpyrrole*, m.p. 89—90° (also obtained from COMe·CHNa·CN, CH_2Cl·COMe, and aq. NH_3), which with 50% aq. KOH gives the *amide*, m.p. 160—161°, of 2 : 5-dimethylpyrrole-3-carboxylic acid. With P_2S_3 or P_2S_5 at 85—90°, (**II**) gives (**III**) and some 3-*cyano*-2 : 5-*dimethylthiophen*, b.p. 225—233° (decomp.) (also obtained from 2 : 5-dimethylthiophen and BrCN–$AlCl_3$), which is hydrolysed to the corresponding amide. At 70°, (**I**) and dil. H_2SO_4 give γ-*cyano*-α-*aceto*-γ-*valerolactone* (**IV**) (cf. Obregia, A., 1892, 324), which in aq. NaOH gives acetonylacetone [50% yield from (**I**)]. With RN_2Cl, (**IV**) gives the *phenylhydrazone* (**V**), m.p. 208°, and p-*nitrophenylhydrazone* (**VI**), m.p. 227°, of γ-cyano-α-keto-γ-valerolactone. (Similarly α-aceto-β-ethylidenepropio-γ-lactone gives the corresponding α-phenylhydrazone.) With EtOH–HCl, (**V**) gives α-keto-γ-carbethoxy-γ-valerolactone phenylhydrazone. With boiling 5% NaOH, (**V**) gives 1-phenyl-5-methylpyrazole-3-carboxylic acid. Similarly (**VI**) gives 1-*p*-nitrophenyl-5-methylpyrazole-3-carboxylic acid, new m.p. 219—220° (decomp.), of which the *Me* ester, m.p. 174—175°, is obtained from COMe·CH_2·CO·CO_2Me and *p*-NO_2·C_6H_4·NH·NH_2. E. W. W.

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

4-δ-Diethylaminoamylamino-6-methoxy-, b.p. 210—212°/1·5—2 mm., 5 : 6 : 7-trimethoxy-2-methyl-, b.p. 142°/2 mm. (8-nitro-, m.p. 115°, and 8-amino-derivative, b.p. 153°/2 mm.), and 8-γ-dimethylaminobutylamino-6-hydroxy-quinoline, m.p. 118° (*O*-acetyl derivative, b.p. 195—200°/1 mm.).—See A., 1943, III, 136.

Synthetic application of *o*-β-bromoethylbenzyl bromide. I. Sulphanilamide derivatives of 1 : 2 : 3 : 4-tetrahydroisoquinoline. F. G. Holliman and F. G. Mann (*J.C.S.*, 1942, 737—741).—The prep. of *o*-Br·$[CH_2]_2$·C_6H_4·CH_2Br (**I**) is improved by treating *o*-C_6H_4Br·CH_2Br with NaOEt to give *o-bromobenzyl Et ether*, b.p. 119—120°/18 mm., which under special conditions with EtBr undergoes the Grignard reaction in combination with $(CH_2)_2O$ to form *o*-OH·$[CH_2]_2$·C_6H_4·CH_2·OEt, converted by HBr–AcOH into (**I**). *p*-C_6H_4Me·SO_2·NH_2 and (**I**) with K_2CO_3 yield 2-p-*toluenesulphonyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 142°. Similarly, (**I**) and *p*-NHAc·C_6H_4·SO_2·NH_2 give 2-p-*acetamidobenzenesulphonyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 175—176°, hydrolysed (HCl) to the NH_2-compound, m.p. 174°, also obtained by direct condensation, along with 2-[p-(2′-1′ : 2′ : 3′ : 4′-*tetrahydro*isoquinolyl)-*benzenesulphonyl*]-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 157—157·5°.

p-NH_2·C_6H_4·SO_3Na, Na_2CO_3, and (**I**) afford, after acidification, p-[2-1 : 2 : 3 : 4-*tetrahydroisoquinolyl*)*benzenesulphonic acid* (+0·5H_2O), m.p. 236—237° (efferv.), which with PCl_5–NH_3 gives in small yield the-*sulphonamide*, m.p. 163°, remelts 182—184°. 1-Amino-1 : 2 : 3 : 4-tetrahydroquinoline sulphate and *p*-NHAc·C_6H_4·SO_2Cl with NaOH form p-*acetamidobenzenesulphon*-1-(1 : 2 : 3 : 4-*tetrahydroquinolyl*)-*amide*, m.p. 203° (decomp.), which could not be hydrolysed. *p*-NHAc·C_6H_4·SO_2·NH·NH_2 and *p*-NHAc·C_6H_4·SO_2Cl in C_5H_5N give s-*di*-p-*acetamidobenzenesulphonhydrazide*, m.p. >300°, hydrolysed (HCl) to the NH_2-compound (+H_2O), m.p. 203° (decomp.). The bactericidal properties of the compounds are recorded. F. R. S.

Quinoline derivatives of sulphanilamide. O. G. Backeberg and J. L. C. Marais (*J.C.S.*, 1942, 758).—By condensing sulphanilamide with the appropriate chloro-lepidine and -quinaldine derivatives in AcOH, the following have been prepared: N⁴-(2′-*lepidyl*)-, m.p. 258°, N⁴-(6′-*methoxy*-, m.p. 249°, and N⁴-(6′-*ethoxy*-2′-*lepidyl*)-, m.p. 278°; N⁴-(4′-*quinaldyl*)-, m.p. 280° (decomp.); N⁴-(6′-*methoxy*-, m.p. 301° (decomp.), -(8′-*methoxy*-, m.p. 293° (decomp.), -(6′-*ethoxy*-, m.p. 308° (decomp.), and -(8′-*ethoxy*-4′-*quinaldyl*)-*sulphanilamide*, m.p. 277° (decomp.). F. R. S.

New synthesis of heterocyclic compounds. I. 2 : 3-Dialkylquinolines. V. A. Petrow (*J.C.S.*, 1942, 693—696).—By treating the anil, R·CO·CHR·CH:NAr, prepared by condensing equiv. amounts of CHO·CHMe·COMe or formyl*cyclo*hexanone and the appropriate amine in EtOH, with the amine hydrochloride and $ZnCl_2$ in EtOH, the following have been obtained: 2 : 3-*dimethyl*-5 : 6-*benzoquinoline*, m.p. 124—125° [*picrate*, m.p. 260—261° (decomp.)], from γ-(β′-*naphthyl*-, m.p. 171—172°, and γ-(α′-*naphthyliminomethyl*)-*butan*-β-*one*, m.p. 110—111°; 6 : 7 : 8 : 9-*tetrahydro*-1 : 2-*benzacridine*, m.p. 96·5—97·5° [*picrate*, m.p. 210·5—211·5° (decomp.)], from 1-(α-*naphthyliminomethyl*)cyclo*hexan*-2-*one*, m.p. 118—119°; 1-(β-*naphthyliminomethyl*)cyclo*hexan*-2-*one*, m.p. 181—182°; 9-, m.p. 77—78° [*picrate*, m.p. 215—216° (decomp.)], and 8-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 100—101° [*picrate*, m.p. 189—190° (decomp.)], prepared from 1-(m-*tolyliminomethyl*)cyclo*hexan*-2-*one*, m.p. 152—153°, and dehydrogenated to 2-methylacridine, m.p. 129—130° (lit. 125—126°) [*picrate*, m.p. 225—226° (decomp.)]; 7-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 61—62° [*picrate*, m.p. 189·5—190·5° (decomp.)], prepared from 1-(p-*tolyliminomethyl*)cyclo*hexan*-2-*one*, m.p. 163—164°; *picrate*, m.p. 184—185° (decomp.), of 2-methyl-1 : 2 : 3 : 4-tetrahydroacridine; 1-*anilomethyl*-4-*methyl*cyclo*hexan*-2-*one*, m.p. 161—162°; 6 : 9-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 38—39° [*picrate*, m.p. 187—188° (decomp.)], from 1-(p-*xylyliminomethyl*)cyclo*hexan*-2-*one*, m.p. 100—101°; 7-*phenyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 130° [*picrate*, m.p. 246—247° (decomp.)], from 1-(*diphenylyl*-4′-*iminomethyl*)cyclo*hexan*-2-*one*, m.p. 201—202°, and dehydrogenated to 3-*phenylacridine*, m.p. 127—128° [*picrate*, m.p. 244—245° (decomp.)]; 9-, m.p. 94·5—95·5° [*picrate*, m.p. 197—198° (decomp.)], and 6(or 8)-*chloro*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 92° [*picrate*, m.p. 204—205° (decomp.)], from 1-(m-*chloroanilomethyl*)cyclo*hexan*-2-*one*, m.p. 148—150°; 7-*chloro*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 95—96° [*picrate*, m.p. 188—189° (decomp.)], from 1-(p-*chloroanilomethyl*)cyclo*hexan*-2-*one*, m.p. 169—170°; 9-, m.p. 79—80° [*picrate*, m.p. 191—192° (decomp.)], and 6(or 8)-*bromo*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 86—87° [*picrate*, m.p. 213·5—214·5° (decomp.)], from 1-(m-*bromoanilomethyl*)cyclo*hexan*-2-*one*, m.p. 155—156°; 1-(p-*bromoanilomethyl*)cyclo*hexan*-2-*one*, m.p. 175—176°; 7-*iodo*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 86·5—87·5° [*picrate*, m.p. 219·5—220·8° (decomp.)], from 1-(p-*iodoanilomethyl*)cyclo*hexan*-2-*one*, m.p. 168—169°; 6(or 8)-*carbethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 63—64° [*picrate*, m.p. 161° (decomp.)], from 1-(m-*carbethoxyanilomethyl*)-cyclo*hexan*-2-*one*, m.p. 143—144°; 7-*carbethoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 94·5—95·5° [*picrate*, m.p. 197—198° (decomp.)], from 1-(p-*carbethoxyanilomethyl*)cyclo*hexan*-2-*one*, m.p. 181—182°, and hydrolysed to 1 : 2 : 3 : 4-*tetrahydroacridine*-7-*carboxylic acid*, m.p. 290—291°; 1-(o-*carboxy*-, m.p. 199—200°, and 1-(o-*carbomethoxy*-*anilomethyl*)cyclo*hexan*-2-*one*, m.p. 134·5—135·5°, which do not give acridine derivatives; 7-*hydroxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 290—291° [*picrate*, m.p. 229·5—230·5° (decomp.)], from 1-(p-*hydroxyanilomethyl*)cyclo*hexan*-2-*one*, m.p. 154—155°; 7-*nitro*-, m.p. 170·5—171·5° [*picrate*, m.p. 204·5° (decomp.)], from 1-(p-*nitroanilomethyl*)cyclo*hexan*-2-*one*, m.p. 244—245°, reduced to 7-*amino*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 141° (*Ac* derivative, m.p. 218·5—219·5°); 1-(m-*nitroanilomethyl*)cyclo*hexan*-2-*one*, m.p. 171—172°, which does not form an acridine derivative; 9-*methoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 121·5—122·5° [*picrate*, m.p. 206·5—207·5° (decomp.)], from 1-(o-*methoxyanilomethyl*)cyclo*hexan*-2-*one*, m.p. 131—132°; 7-*methoxy*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 90—91° (*picrate*, m.p. 223·5—224·5° (decomp.)], from 1-(p-*methoxyanilomethyl*)cyclo*hexan*-2-*one*, m.p. 149—150°; 6(or 8)-*acetyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 131—132° [*picrate*, m.p. 211—212° (decomp.)], from 1-(m-*acetylanilomethyl*)cyclo*hexan*-2-*one*, m.p. 139—140°; and 7-*anilino*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 173° [*picrate*, m.p. 251—252° (decomp.)], from 1-(p-*anilinoanilomethyl*)cyclo*hexan*-2-*one*, m.p. 144—145°. A mechanism for the reaction is suggested. F. R. S.

Sulphanilamide derivatives of histidine. M. Amorosa (*Gazzetta*, 1941, **71**, 343—350).—Histidine hydrochloride in aq. NaOH with *p*-SO_2Cl·C_6H_4·NHAc gives the N-*Ac* derivative (**I**), m.p. (+3H_2O) 122—132°, (anhyd.) decomp. 242—243° (*quinine* salt, m.p. 135°), of p-*aminobenzenesulphonylhistidine* (**II**), m.p. 263—264° (decomp.) [p-*carbamido*-derivative, m.p. 229—231° (decomp.)]. With MeOH–HCl, (**I**) or (**II**) gives the *Me ester dihydrochloride* (**III**), m.p. 218—225° (decomp.), of (**II**). Diazotisation of (**II**) and (**III**) and coupling with β-$C_{10}H_7$·OH gives *products*, m.p. 255—257°, and 165—170°, respectively. E. W. W.

***N*-Substituted barbituric acids.** J. S. Buck, W. S. Ide, and R. Baltzly (*J. Amer. Chem. Soc.*, 1942, **64**, 2233).—1-Phenyl- yields 1-*p*-nitrophenyl-, m.p. 188°, and thence 1-p-*aminophenyl*-5-*ethyl*-5-iso*butylbarbituric acid*, m.p. 153°. The appropriate carbamides and malonic esters yields 1-o-*phenetyl*-, m.p. 193·5°, 1-p-*ethylphenyl*-5-*ethyl*-5-n-*butyl*-, m.p. 107°, and 5 : 5-*diethyl*-1-n-*hexyl*-, m.p. 41°, -*barbituric acid*. R. S. C.

Barbituric acids.—See B., 1943, III, 42.

Lysine and ornithine.—See A., 1943, II, 55.

Convenient synthesis of *dl*-methionine. H. R. Snyder, J. H. Andreen, G. W. Cannon, and C. F. Peters (*J. Amer. Chem. Soc.*, 1942, **64**, 2082—2084).—Hydrogenation (Raney Ni) of α-keto-γ-butyrolactonephenylhydrazone in EtOH at 100—150°/1700 lb. gives 3 : 6-diketo-2 : 5-di-β-hydroxyethylpiperazine (**I**) (54%), m.p. 178—180°, but in Ac_2O at 125°/2000 lb. gives α-*acetamido*- (30%), m.p. 82—84°, b.p. 175—178°, hydrolysed to α-amino-γ-butyrolactone (40%) (hydrochloride, m.p. 200—201°). H_2–Pd–C in MeOH converts α-oximino-γ-butyrolactone (prep. by OEt·NO–MeOH), m.p. 183—185°, in MeOH into (**I**) (55—60%), m.p. 186° (decomp.). $SOCl_2$ at 0° to —5° (later warm) and (**I**) give 3 : 6-*diketo*-2 : 5-*di*-β-*chloroethylpiperazine*, m.p. 230—231°, which with NaSMe (2·2 mols.) in EtOH gives 3 : 6-*diketo*-2 : 5-*di*-β-*methylthiolethylpiperazine*, m.p. 231—232°, converted by conc. HCl into *dl*-methionine (85—95%). R. S. C.

Glyoxalines. II. Interaction of benzamidine with phenylglyoxal. R. C. Waugh, J. B. Ekeley, and A. R. Ronzio (*J. Amer. Chem. Soc.*, 1942, **64**, 2028—2031; cf. A., 1942, II, 379).—Data of Kunckell *et al.* (A., 1901, i, 758) are erroneous. Adding conc., aq. KOH to BzCHO,H_2O (**I**) and NH_2·CPh:NH in EtOH gives α-*hydroxyphenacylbenzamidine* (**II**) (40%), OH·CHBz·NH·CPh:NH, +0·5EtOAc, m.p. 112—115° (decomp.). Adding a little 50% aq. KOH to (**I**) and NH_2·CPh:NH_2Cl (**III**) in warm H_2O and then boiling gives 4-*hydroxy*-3 : 4-*diphenylglyoxaline* [? 5-*keto*-2 : 4-*diphenyl*-4 : 5-*dihydroglyoxaline*] (**IV**) (64%), +0·5 dioxan, m.p. 251—252° (*acetate*, m.p. 174°), also obtained by adding acid to (**II**) in hot alkali. In boiling AcOH, (**I**) and (**III**) give 4 : 5-*dihydroxy*-2 : 4-*diphenyl*-4 : 5-*dihydroglyoxaline hydrochloride* (62%), darkens at 260°, m.p. 282° (*diacetate*, m.p. 181°, of the free base), which is also obtained by adding an excess of conc. HCl to (**II**) or (**IV**) in alkali and in absence of acid rapidly gives (**IV**). In EtOH containing a trace of alkali, (**IV**) gives (?) a *polymeride*, darkens at 250°, m.p. 262°, whence it is regenerated by hot alkali. In aq. NaOAc at room temp., (**I**) and (**III**) give 4 : 5-*dihydroxy*-2 : 5-*diphenyl*-1-α-*hydroxyphenacyl*-4 : 5-*dihydroglyoxaline* (87%), m.p. 73—80°, which in EtOH yields (**IV**). In boiling H_2O, (**I**) and (**III**) give NH_3 and a *substance* (<1%), $C_{22}H_{16}N_2$, m.p. 170—172°. Absorption spectra of the products are recorded. R. S. C.

Pyrazole compounds. I. Reaction product of phenylhydrazine and ethyl cyanoacetate. A. Weissberger and H. D. Porter (*J. Amer. Chem. Soc.*, 1942, **64**, 2133—2136).—Contrary to Conrad *et al.* (A., 1906, i, 608), CN·CH_2·CO_2Et, NHPh·NH_2, and NaOEt (2 mols. essential) in EtOH give 3-*amino*-1-*phenyl*-5-*pyrazolone* (**I**) (43%), m.p. 218—220° {N-*Bz*, m.p. 220—221°, N-CO_2Et- (**II**), m.p. 198—199°, (?) $(CO_2Et)_2$-, m.p. 106—108° [with a little piperidine in boiling EtOH gives (**II**)], and N-NH_2·*CO*-derivative, m.p. 235—236°}. With AcCl in dioxan, (**I**) gives the 3-*Ac* derivative (**III**), m.p. 218—220°, but with boiling Ac_2O gives the ON-Ac_2 derivative, m.p. 144—145°, hydrolysed to (**III**) by cold 2% NaOH. NHPh·N:C(CO_2Et)·CH_2·CO_2Et in boiling AcOH–C_6H_6 gives Et 1-phenyl-5-pyrazolone-3-carboxylate (80%; less under other conditions), m.p. 185—186°, converted by 28% aq. NH_3 at room temp. into the *amide* (57%), m.p. 233—235° (decomp.), and by 42% aq. $N_2H_4.H_2O$ at room temp. into the *hydrazide* (86%), m.p. 235—237° (decomp.). With HCl–aq. EtOH–$NaNO_2$ at 5° this gives the azide (62%), deflagrates at 140°, and thence (boiling EtOH) (**II**) and (10% NaOH at 100°) (**I**) (proof of structure). R. S. C.

Pyrrole series. IX. Determination of the bridge structure of dipyrrylmethanes. Estimation of active hydrogen. A. H. Corwin and R. C. Ellingson. **X. Rearrangements of pyrrole rings in the oxidation of dipyrrylmethanes.** A. H. Corwin and K. J. Brunings (*J. Amer. Chem. Soc.*, 1942, **64**, 2098—2106, 2106—2115; cf. A., 1942, II, 380).—IX. NH in pyrroles (9 examples) and dipyrrylmethanes (12 examples) is determined by titration with $NaCPh_3$ in Et_2O–C_6H_6– or –dioxan–N_2, the indicator being the colour of the reagent. Blanks on solvents are necessary. Technique and apparatus are

detailed. C-Substitution by Me, CO_2Et, or Br does not interfere, but COMe consumes additional reagent. $NaCPh_3$ reacts with substances which are indifferent to molten Na or K. The reaction mechanism can be checked by hydrolysis to the starting material or conversion by Me_2SO_4 into the *N*-Me compound; dimethylation is thus possible. 3 : 5-Dicarbethoxy-2 : 4-dimethylpyrrole thus gives the 1 : 2 : 4-Me_3 compound. 3 : 5 : 3′ : 5′-Tetracarbethoxy-4 : 4′-dimethyldipyrrylmethane with 1 or 2 $NaCPh_3$ and then Me_2SO_4 gives the 1 : 4 : 4′-Me_3 and 1 : 4 : 1′ : 4′-Me_4 (**I**) compound, respectively. (**I**) gives a red Na salt (*N*-Na salts are colourless), in which the Na is probably in the bridge CH_2, since the salt cannot be methylated and by hydrolysis regenerates (**I**). 4 : 4′-Dicarbethoxy-3 : 5 : 3′ : 5′-tetramethyldipyrrylmethane with 2 $NaCPh_3$ and then Me_2SO_4 gives the 1 : 3 : 5 : 1′ : 3′ : 5′-Me_6 compound (**II**); use of 1 mol. of $NaCPh_3$ gives a mixture of (**II**) and 1 : 3 : 5 : 3′ : 5′-*Me*$_5$ compound, m.p. 176° (decomp.) [converted into (**II**) by further treatment]. 1 $NaCPh_3$ reacts with the more acidic NH of 4 : 3′ : 5′-tricarbethoxy-3 : 5 : 4′-trimethyldipyrrylmethane, yielding with Me_2SO_4 the 3 : 5 : 1′ : 4′-Me_4 compound (**III**); when the Na_2 salt reacts with 1 mol. of Me_2SO_4 the more basic NNa reacts, yielding the 1 : 3 : 5 : 4′-*Me*$_4$ compound, m.p. 97° [also obtained from 3 : 5-dicarbethoxy-4-methyl-2-chloromethylpyrrole and 3-carbethoxy-1 : 2 : 4-trimethylpyrrole (**V**) in boiling MeOH]; the Na_2 salt and 2 mols. of Me_2SO_4 give the 1 : 3 : 5 : 1′ : 4′-*Me*$_5$ compound (**VI**), m.p. 129°, also obtained from 3 : 5-dicarbethoxy-1 : 4-dimethyl-2-chloromethylpyrrole and (**V**) in boiling MeOH and from (**IV**) by $NaCPh_3$ and then Me_2SO_4. $NaCPh_3$ and (**III**) in dioxan give a blue-fluorescent, red, later violet, solution, whence H_2O or Me_2SO_4 yields a *compound*, $C_{20}H_{24}O_5N_2$, m.p. 203—204°, but in C_6H_6 gives a colourless Na salt, which, as usual, with H_2O regenerates (**III**) and with Me_2SO_4 gives (**VI**).

X. 4 : 4′-Dicarbethoxy-1 : 3 : 5 : 3′ : 5′-pentamethyldipyrrylmethane (**VII**) [prep. from 3-carbethoxy-2 : 4-dimethylpyrrole and (**V**) in CH_2O–aq. MeOH at 45°], m.p. 178—179°, with 1 mol. of Br in CCl_4 gives HBr, 4 : 4′-dicarbethoxy-3 : 5 : 3′ : 5′-tetramethyldipyrrylmethene (**VIII**) (58%), m.p. 189—190° (decomp.), and 4-carbethoxy-1 : 3 : 5-trimethylpyrrole (**IX**) and with 0·5 mol. of Br gives HBr, 96% of (**VIII**), and 4 : 4′-dicarbethoxy-1 : 3 : 5 : 1′ : 3′ : 5′-hexamethyldipyrrylmethane (**X**). (**VIII**) is also obtained from (**VII**) by HCO_2H–HBr or Cl_2–CCl_4, but not by neutral or basic oxidising agents. (**VIII**) and (**X**) absorb Br equally rapidly, (**VII**) more slowly. Cl_2 is absorbed very rapidly by (**VII**), but pptn. of (**VIII**) is then slow. 3-Carbethoxy-2 : 4-dimethylpyrrole with aq. HBr and HCO_2H at 65° (not room temp.) gives (**VIII**). Neutral $KMnO_4$ oxidises 4 : 4′-dicarbethoxy-3 : 5 : 3′ : 5′-tetramethyldipyrrylmethane (**XI**), but not (**VII**), to (**VIII**). (**VII**) is unaffected by CH_2O–HBr. Br converts (**VII**) and (**X**) into (**VIII**) (85·4%) and the 1 : 3 : 5 : 1′ : 3′ : 5′-Me_6-methene. (**VII**) and (**X**) with HBr–CCl_4 give 95% of (**VIII**). 4 : 4′ : 4″-Tricarbethoxy-1 : 3 : 5 : 3′ : 5′ : 3″ : 5″-heptamethyltripyrrylmethane and HBr–CCl_4 give (**XI**) (90%) and (**V**). 3 : 5-Dicarbethoxy-4-methyl-2-dichloromethylpyrrole and (**VII**) in dioxan–HCl give (**VIII**). Br–CCl_4 converts 4 : 3′ : 5′-tricarbethoxy-3 : 5 : 4′-trimethyldipyrrylmethane into 4 : 3′ : 5′-tricarbethoxy-3 : 5 : 4′-trimethyldipyrrylmethene (83%), m.p. 125° (decomp.), but converts 3 : 5 : 4′-tricarbethoxy-1 : 4 : 3′ : 5′-tetramethyldipyrrylmethane into (**VIII**) [and, presumably, 2 : 4 : 2′ : 4′-tetracarbethoxy-1 : 3 : 1′ : 3′-tetramethyldipyrrylmethane (not isolated)]. " Disproportionation " of (**VII**) by Br is thus shown to be due to fission of C·CH_2 and not of NMe; reaction mechanisms involving 2-$CHBr_2$- and 2-H monopyrrole derivatives are discussed. R. S. C.

Methoxyglaucobilins, a new type of bilirubinoid pigment ; Gmelin's reaction. H. Fischer and H. Reinecke (*Z. physiol. Chem.*, 1940, **265**, 9—21).—Bilirubin is dehydrogenated by *p*-O:C_6H_4:O in AcOH to biliverdin, converted by $FeCl_3$ into the *compound*, $C_{33}H_{35}O_6N_4Cl_4Fe$; this is converted by NaOH followed by AcOH and then by CH_2N_2 into *biliverdin Me*$_2$ ester, m.p. 213°, which gives the *compound*, $C_{35}H_{39}O_6N_4Cl_4Fe$, m.p. 257°. Formylneoxanthobilirubic acid is condensed with vinylneoxanthobilirubic acid (**I**) to *Me*$_2$ 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 8-*tetramethyl*-7-*ethyl*-2-*vinyl*-2′α-4′-ms-*bilitriene*-4 : 5-*dipropionate*, m.p. 225° (corresponding *ferrobilin*, m.p. 262°). The *ferrobilin*, m.p. 262°, and *Zn* complex salt of *Me*$_2$ 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 7-*tetramethyl*-8-*ethyl*-2-*vinyl*-2′α-4′-ms-*bilitriene*-4 : 5-*dipropionate* are described. (**I**) and 3 : 3′-dimethyl-5 : 5′-dibromomethylpyrromethene-4 : 4′-dipropionic acid hydrobromide afford *Me*$_4$ 1′ : 12′-*dihydroxy*-1 : 3 : 6 : 7 : 10 : 12-*hexamethyl*-2 : 11-*divinylhexapyrrene*-4 : 5 : 8 : 9-*tetrapropionate*, m.p. 242°. The *Zn* complex salt is dehydrogenated to *dimethoxyætioglaucobilin*, m.p. 193° (corresponding *Cu* complex). Glaucobilin IX α-Me_2 ester affords a *Zn* complex $C_{35}H_{40}O_6N_4Zn$, m.p. 305°, converted into the *dimethoxyglaucobilin ester*, $C_{37}H_{48}O_8R_4$, m.p. 160—162°. Glaucobilin XIII*a* gives a $(OMe)_2$-compound, $C_{37}H_{48}O_8N_4$ (*Cu* complex). Me 6′-bromo-1′-hydroxy- is converted into *Me* 1′ : 6′-*dihydroxy*-2 : 3 : 6-*trimethyl*-1 : 5-*diethyltripyrrene*-4-*propionate*. It is shown that the violet stage of the Gmelin reaction is not explicable by the formation of dihydroxytripyrrenes. H. W.

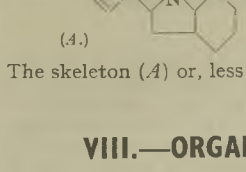
Isomerisation of chlorophylls *a* and *b*. H. H. Strain and W. M. Manning (*J. Biol. Chem.*, 1943, **146**, 275—276).—Chromatographic adsorption (dry powdered sugar; light petroleum) of plant extracts shows that chlorophylls *a* (**I**) and *b* (**II**) are accompanied by small amounts of two other green pigments, *chlorophylls* a′ (**III**) and b′ (**IV**). The adsorption column is washed with light petroleum containing 0·5% of $Pr^{\alpha}OH$ and 0·5% of $NPhMe_2$; (**III**) forms the lowest green band, and (**IV**) separates between (**I**) and (**II**). Higher plants and green algæ extracted at or > room temp. yield (**III**) and (**IV**), but only traces are obtained by extraction at −80°. Plants not containing (**II**) do not yield (**IV**). (**I**) and (**III**), and (**II**) and (**IV**), are interconvertible, rapidly in $Pr^{\alpha}OH$ at 95—100°, to give equilibrium mixtures containing 20% of the new isomeride. Thus it is not certain whether (**III**) and (**IV**) are natural plant constituents. Different phæophytins are obtained from (**I**) and (**III**), suggesting a difference in the org. portion of the mol. With KOH–EtOH, (**I**) and (**III**) afford spectroscopically similar phæopurpurins; (**III**) probably does not correspond with the hypothetical chlorophyll a_2 of Conant *et al.* (A., 1933, 403). A. T. P.

***iso*Oxazole group. X. Nitro-, amino-, and diazo-derivatives of *iso*oxazole.** A. Quilico and C. Musante (*Gazzetta*, 1941, **71**, 327—342).—5-Methyl*iso*oxazole with HNO_3 (*d* 1·51) in H_2SO_4–SO_3 at 60—80° gives 4-*nitro*-, b.p. 187—189°, reduced by $SnCl_2$–HCl to the *hydrochloride*, m.p. 149° (decomp.; darkens from 130°), of 4-*amino*-5-*methyliso*oxazole (**I**), b.p. 130°/25—27 mm. (*Ac*, m.p. 87°, *Bz*, m.p. 140°, *CHPh*:, m.p. 96—97°, *CHPh*:*CH*·*CH*:, m.p. 101°, and m-NO_2·C_6H_4·*CH*:, m.p. 136—137°, derivatives). 3-Methyl*iso*oxazole similarly gives 4-*nitro*-, b.p. 103—107°/25—27 mm., and 4-*amino*-3-*methyliso*oxazole (**II**), m.p. 43°, b.p. 118—120°/25 mm. [*hydrochloride*, m.p. 184° (decomp.); *Ac*, m.p. 90—91°, *Bz*, m.p. 148—149°, and *CHPh*:, m.p. 114°, derivatives]. The diazo-compounds from (**I**) and (**II**) are labile, but the diazonium chloride from 4-amino-3 : 5-dimethyl*iso*oxazole (obtained as above; cf. Morgan *et al.*, *J.C.S.*, 1921, **119**, 700) with boiling aq. $CuSO_4$–H_2SO_4 gives CO_2, Ac_2 (which is also obtained by similar treatment of $COAc_2$, the presumed intermediate product), and 5-*acetyl*-4-*methyl*-2 : 1 : 3-*triazole*, m.p. 173—174° (*Ag* salt; *oxime*, m.p. 202°; p-*nitrophenylhydrazone*, m.p. 253—255°) (which with $K_2Cr_2O_7$–H_2SO_4 is oxidised to 4-methyl-2 : 1 : 3-triazole-5-carboxylic acid), and with boiling dil. H_2SO_4 gives 4-chloro-3 : 5-dimethyl*iso*oxazole, b.p. 151—152° (cf. A., 1939, II, 90) [p-*nitrophenylhydrazone*, m.p. 235° (decomp.)], and $CHClAc_2$, with a *substance*, $C_{10}H_{14}O_3N_4$ (?) [*oxime*, m.p. 196—197° (*Bz* derivative, m.p. 207°); p-*nitrophenylhydrazone*, m.p. +315° (darkens from 300°)]. E. W. W.

Substituted sulphonamides. J. P. English, D. Chappell, P. H. Bell, and R. O. Roblin, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2516).—*p*-NO_2·C_6H_4·SO_2·NH_2 and CH_2Cl·COCl in 4·4% NaOH at 5° give N^1-*chloroacetyl*-p-*nitro*-, m.p. 172—173°, reduced by $SnCl_2$–conc. HCl at 35° to N^1-*chloroacetyl*-p-*amino-benzenesulphonamide*, m.p. 157—158°. 2-*Benzenesulphonamido-pyridine*, m.p. 171—172°, -*pyrimidine*, m.p. 229—230°, -4-*methylpyrimidine*, m.p. 193—194°, -*thiazole*, m.p. 171—172°, and -1 : 3 : 4-*thiadiazole*, m.p. 188—189°, are prepared in C_5H_5N. M.p. are corr. R. S. C.

VII.—ALKALOIDS.

Erythrina alkaloids. XIII. Constitution of erythraline, erythramine, and erythratine. K. Folkers, F. Koniuszy, and J. Shavel, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 2146—2151; cf. A., 1943, II, 49).—Indole is obtained from erythraline (**I**) or erythratine (**II**) by fusion with KOH. (**II**) gives an O-*benzoate*, +2H_2O, m.p. 248—249°, O-*acetate*, m.p. 128—129° [hydrolysed by HCl–EtOH–H_2O to (**II**)], *methiodide*, +0·5H_2O, m.p. 121—125°, $[\alpha]_D^{25}$ +109·7° in H_2O, and anhyd., m.p. 135—136°, $[\alpha]_D$ +110·4° in H_2O, and thence the N-*methyl-methine*, $C_{19}H_{23}O_4N$, solid, which with Zn dust gives a gum. H_2–PtO_2 in H_2O + a little HBr reduces (**II**) to *dihydroerythratine hydrobromide* (**III**), m.p. 249°, unstable at 25°. Absorption spectra are recorded for erythramine (**IV**), (**I**), (**II**), (**III**), dihydroerythramine hydrobromide, 6 : 7-methylenedioxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline hydrobromide, and hydrocotarnine. (**I**), (**II**), and (**IV**) contain one CH_2O_2, OMe, *tert.* N common to two nuclei, and 2, 1, and 1 C:C, respectively; (**II**) contains also a non-phenolic OH; four fused nuclei, of which three are aromatic and common to the three alkaloids and one is variously hydrogenated and oxygenated, are probably present. The skeleton (*A*) or, less probably, its linear analogue, is suggested.


(*A*.)

R. S. C.

VIII.—ORGANO-METALLIC COMPOUNDS.

Bivalent and tervalent rhodium. III. Compounds of rhodic halides with tertiary arsines. F. P. Dwyer and R. S. Nyholm (*J. Proc. Roy. Soc. New South Wales*, 1941, **75**, 140—143).—RhX_3 with AsR_3 in HCl–EtOH gives a sol. form (**I**) and an insol. form (**II**), converted by boiling C_6H_6 into (**I**). It is suggested that (**I**) is $[RhX_3,3AsR_3]$ whilst (**II**) is $(Rh(AsR_3)_6,RhX_6]'''$. The following were prepared : *diphenylmethylarsinerhodic chloride*, m.p. 122—124°

and 176—178°, *bromide*, m.p. 116° and 191°, and *iodide*, m.p. not recorded and 200°; *p-tolyldimethylarsinerhodic chloride*, m.p. (form I) 86—88°, *bromide*, m.p. (form I) 109°, and *iodide*, m.p. 85—86° and 200°. F. R. G.

IX.—PROTEINS.

Present status of mol. wts. of proteins. A. Rothen (*Ann. New York Acad. Sci.*, 1942, **43**, 229—241).—A general survey. N. M. B.

Amino-acid analysis and the structure of proteins. A. C. Chibnall (*Proc. Roy. Soc.*, 1942, **B**, **131**, 136—160).—A lecture. The recent speculations of Bergmann and Niemann on protein structure are reviewed in the light of new analytical data for certain proteins. The mol. of edestin appears to be a system of 6 similar peptide chains of mol. wt. 50,000, the constituent residues of which conform to the Bergmann–Niemann rule. Lactoglobulin is a system of 8—9 peptide chains, not all of like composition, ovalbumin a similar system of 4 chains. The two latter proteins contradict the rule but the component peptide chains may conform to it. Insulin appears to be a system of 18 peptide chains in agreement with Bernal's deductions from crystallographic data. The conclusion that these protein mols. are systems of peptide chains is based in part on titration data and in part on determinations of free NH_2-N; the method of linkage of these chains is discussed. J. H. B.

Structure of silk fibroin. E. Abderhalden (*Z. physiol. Chem.*, 1940, **265**, 23—30).—In addition to polypeptide chains, silk fibroin contains large amounts of 2 : 5-diketopiperazines (**I**) or ring structures closely related thereto. A secondary formation of the isolated (**I**) from poly- or di-peptides is excluded. Glycylalanine, glycyltyrosine, and alanylserine anhydride have been isolated. H. W.

Heats of organic reactions. Digestion of β-lactoglobulin by pepsin.—See A., 1943, I, 63.

Oxidative conversion of casein into protein free of methionine and tryptophan. G. Toennies (*J. Biol. Chem.*, 1942, **145**, 667—670).—Oxidation of casein in HCO_2H solution with H_2O_2 converts methionine and probably tryptophan into biologically inactive products and cystine is partly destroyed. Threonine, serine, and probably other NH_2-acids are unaffected. R. L. E.

Carbon suboxide and proteins. VII. Malonylpepsin. A. H. Tracy and W. F. Ross (*J. Biol. Chem.*, 1943, **146**, 63—68; cf. A., 1942, II, 241).—Malonylation of the free NH_2 and phenolic OH of pepsin inactivates the enzyme. Gentle hydrolysis of the O–malonyl linking causes partial reactivation, indicating intimate association between phenolic OH and activity. The specificity of pepsin is unaltered by the presence of CO_2H groups in positions normally occupied by the basic lysyl residues in pepsin; these residues are thus unessential for activity and are without influence on the specificity of the enzyme. Malonylation of serum-albumin increases the no. of peptide linkings subject to the action of pepsin. A. T. P.

Brain kephalin, a mixture of phosphatides; separation from it of phosphatidyl-serine and -ethanolamine, and a fraction containing an inositol phosphatide. J. Folch (*J. Biol. Chem.*, 1943, **146**, 35—44; cf. A., 1941, III, 743).—Brain kephalin (modified method of isolation from fresh ox brain) in $CHCl_3$ is fractionated by adding to EtOH; fractions are freed from H_2O-sol. impurities by dialysis. Thus obtained are (*a*) *phosphatidylethanolamine* (**I**), sol. in EtOH, which has the composition originally attributed to the whole kephalin, and is hydrolysed to glycerophosphoric acid (**II**) and $NH_2{\cdot}[CH_2]_2{\cdot}OH$, (*b*) phosphatidylserine (**III**), and (*c*) a mixture of phosphatides, one or more of which contains inositol, and which also probably contains some (**III**); hydrolysis yields inositol, serine, and (**II**). With the exception of (**I**), the phosphatides in the kephalin fraction of brain lipins are strongly acidic and are isolated from brain as K or Na salts when treatment with mineral acid is avoided in isolation. A. T. P.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Colour test for citrinin. Its preparation. H. Tauber, S. Laufer, and M. Goll (*J. Amer. Chem. Soc.*, 1942, **64**, 2228—2229).—Prep. of citrinin from *P. citrinum* is outlined. With H_2O_2–EtOH–H_2O it becomes yellow, changed to red by NaOH. The yellow–red change is reversible by H_2SO_4–NaOH. Cultures give the same reaction; penicillin does not. Exposure in dioxan causes a similar, but in EtOH a different, change. R. S. C.

Notatin: an anti-bacterial glucose-aerodehydrogenase from *Penicillium notatum*, Westling.—See A., 1943, III, 143.

XI.—ANALYSIS.

Use of concentrated sulphuric acid instead of lead dioxide for the absorption of oxides of nitrogen in micro-C–H determinations. K. Burger (*Angew. Chem.*, 1942, **55**, 260—261).—H_2O is absorbed in $Mg(ClO_4)_2$, then N oxides in H_2SO_4, and then CO_2 as usually. The H_2SO_4 may be reactivated by passing O_2 through it at 150°. J. W. S.

Quantitative decomposition of organic bromine and iodine compounds by the lime fusion method. W. M. MacNevin and G. H. Brown (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 908).—The method previously described for determination of Cl (A., 1940, II, 263) can be applied to org. Br and I compounds. J. D. R.

Steam-distillation apparatus for micro-Kjeldahl analysis.—See A., 1943, III, 76.

Reduction of unsaturated hydrocarbons at the dropping mercury electrode.—See A., 1943, I, 64.

Determination of inulin.—See A., 1943, III, 152.

Dissociation constants of diphenylselenium dibromide and diiodide.—See A., 1943, I, 61.

Potentiometric studies in oxidation-reduction reactions. XI. Quantitative potentiometric determination of aromatic amines. B. Singh and A. Rehmann (*J. Indian Chem. Soc.*, 1942, **19**, 349—353).—By the use of a bright Pt electrode in the titration liquid, in conjunction with a calomel electrode, *o*- and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, 1 : 2 : 4-$OH{\cdot}C_6H_3(NH_2)_2$, *o*- and *p*-$NH_2C_6H_4{\cdot}OH$, *o*-$C_6H_4(NH_2)_2$, and $NHPh_2$ can be accurately determined potentiometrically. The first three are titrated in aq. HCl against standard KIO_3, and the others are titrated in (usually) aq. H_2SO_4 with standard $NaNO_2$. F. L. U.

Microbiological method for determination of *p*-aminobenzoic acid. M. Landy and D. M. Dicken (*J. Biol. Chem.*, 1943, **146**, 109—114).—The method is based on the growth response of *Acetobacter suboxydans* to *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (**I**); turbidity is measured with a photo-electric colorimeter. No growth occurs in the basal medium in absence of (**I**). Materials insol. in H_2O are first finely-divided, extracted with 10—20 vols. of H_2O for 30 min. at 15 lb., centrifuged, and filtered. The inhibitory action of blood, c.s.f., etc. on the test organism is overcome by autoclaving. (**I**) is widely distributed, *e.g.*, in brewer's yeast, liver extract, fresh liver, and meat extract, and probably in most body tissues. The activity of other compounds similar to (**I**), viz., *p*-amino-phenylacetic acid, -ethyl benzoate, -phenylglycine, etc., is not comparable with that of (**I**), and thus the method has high specificity. A. T. P.

Determination of the tocopherols and tocopherylquinones by the colorimetric oxidation–reduction method. J. V. Scudi and R. P. Buhs (*J. Biol. Chem.*, 1943, **146**, 1—6; cf. A., 1941, III, 685; 1942, III, 702).—The sample containing tocopherols (**I**) is dissolved in BuOH, $AuCl_3$ added, and the mixture kept in the dark at room temp. for 30 min.; aq. technical hexane is added; the org. layer is washed and conc. in vac. under N_2. Reduction is effected using Raney Ni in BuOH with phenosafranine (**II**) as indicator, and the solution is pumped into standard 2 : 6-dichlorophenol-indophenol (**III**). Vitamin-*K* quinol reduces (**III**) immediately, but tocopherylquinones (**IV**) act more slowly (40—60 min.) and are estimated by difference. The specificity of the method can be increased by preliminary reductive treatment with Claisen's alkali. Substances to be tested must be oil-sol. and non-reducing, and with $AuCl_3$ give new substances capable of reversible reduction and oxidation, which have an oxidation–reduction potential > that of (**II**) but < that of (**III**), and which must reduce (**III**) slowly. Carotenoids and vitamin-*A* do not interfere. (**I**) and (**IV**) in the same sample are best determined by two analyses, although this is not essential, as (**I**) can be recovered by light petroleum after determining (**IV**), and then oxidised further. Results are given for wheat-germ oil, refined cottonseed oil, dog plasma, and whole human blood [(**IV**) not observed previously]. The difference in biological activity between α- and β- + γ-tocopherols is discussed, and a method of differentiating suggested, viz., β- and γ- with HNO_2 give (probably) *o*-quinones, whereas α- apparently does not react. A. T. P.

Determination of lanthionine. W. C. Hess and M. X. Sullivan (*J. Biol. Chem.*, 1943, **146**, 15—18).—Lanthionine (**I**) is converted into cysteine (**II**) by colourless 57% HI containing 1% of KH_2PO_2 at 135—140° (in N_2). Neither cystine nor methionine interferes with the determination of (**I**). (**I**) formed by dil. alkali treatment of a protein such as wool or lactalbumin can be determined colorimetrically by first hydrolysing the (**I**)-containing protein with HCl; (**I**) does not react in the Sullivan cystine or cysteine reactions. Then total (**II**) is measured after hydrolysis of the protein with HI. The difference between the two hydrolysates gives amount of (**II**) derived from (**I**), which multiplied by 1·72 gives amount of (**I**). A. T. P.

INDEX OF AUTHORS' NAMES, A., II.

MARCH, 1943.

JUDACTAN

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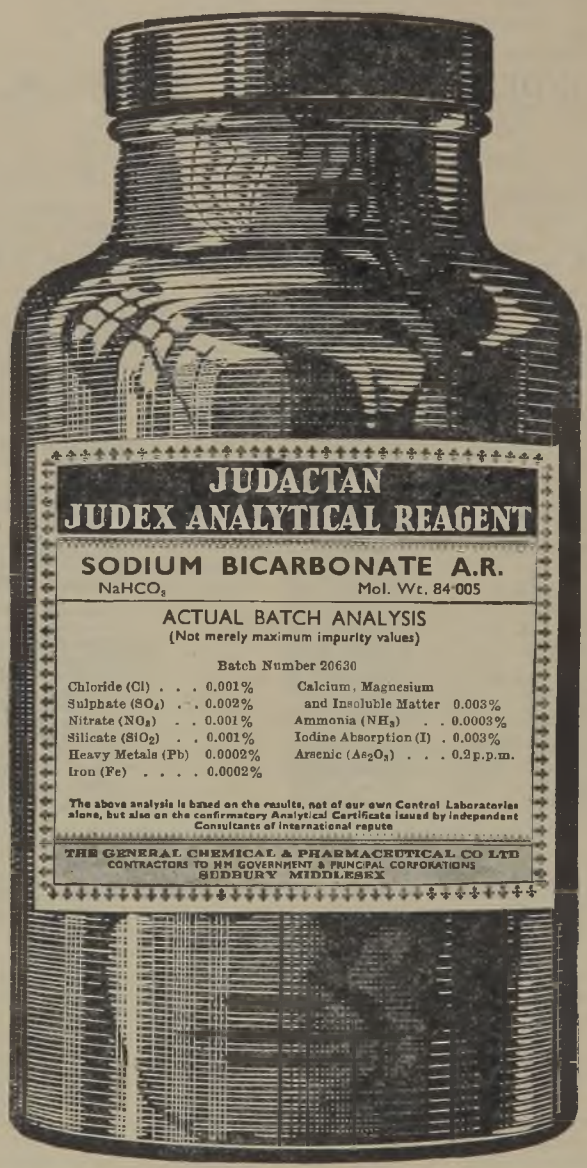
ACTUAL

BATCH

ANALYSIS



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