BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MAY, 1942.

I.—ALIPHATIC.

Alkylation of paraffins at low temperatures in the presence of aluminium chloride. H. Pines, A. V. Grosse, and V. N. Ipatieff (*J. Amer. Chem. Soc.*, 1942, **64**, 33—36; cf. U.S.P. 2,112,846, B., 1941, II, 31).—$CHMe_3$ and CH_2:CHEt in presence of $AlCl_3$ at −35° (apparatus described) yield 60% of C_8H_{18} and 12% of $C_{12}H_{26}$. The former are identified by Raman spectra as $CHMeEtBu^{\gamma}$ (a primary reaction product), $CH_2Pr^{\beta}Bu^{\gamma}$ and $(CH_2Pr^{\beta})_2$ (formed by preliminary isomerisation of *n*- to *iso*-C_4H_8), and $CHMePr^{\beta}_2$ (formed by isomerisation of other octanes). $CHMe_3$ and C_3H_6 give similarly 42% of C_7H_{16} and 20% of $C_{10}H_{22}$. The C_7H_{16} are similarly shown to contain $CHMeEtPr^{\beta}$ and some $CH_2Pr^{\beta}_2$. R. S. C.

Production of *iso*paraffins.—See B., 1942, II, 46.

Photolysis of methyl bromide.—See A., 1942, I, 179.

Chlorination of chloroform to carbon tetrachloride in presence of ferric chloride.—See A., 1942, I, 177.

Separation of olefines from mixtures of hydrocarbons.—See B., 1942, II, 47.

Low-temperature polymerisation of *iso*olefines.—See B., 1942, II, 47.

Production of hydrocarbons of high mol. wt. [from *iso*butene].—See B., 1942, II, 47.

Structure and absorption spectra. III. Normal conjugated dienes. R. B. Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 72—75; cf. A., 1941, II, 195).—Absorption max. of normal conjugated dienes (*i.e.*, those in which the ethylenic linkings are not in one ring) are accurately calc. by adding to $\lambda_{max.}$ (217 mμ.) for $(CH_2{:}CH)_2$ 5 mμ. for each substituent and 5 mμ. for each exocyclic ethylenic linking. The substance previously (Booker *et al.*, A., 1940, I, 27) considered to be $\Delta^{3:8(9)}$-normenthadiene probably consists mainly of the $\Delta^{\cdot 2:4(8)}$-compound. R. S. C.

Course of autoxidation reactions in polyisoprenes and allied compounds. II. Hydroperoxidic structure and chain scission in low-molecular polyisoprenes. E. H. Farmer and D. A. Sutton (*J.C.S.*, 1942, 139—148).—Progressive determinations of O_2 intake and peroxidic O content and measurements of I val. show that in the autoxidation of squalene (**I**) (in C_6H_6), dihydrofarnesene (**II**), and dihydromyrcene (**III**), the primary reaction is the production of a hydroperoxide group, which in (**I**) and (**II**) reacts with double linkings giving OH-compounds and (to a small extent) scission products. Low O_2 intake is compatible with advanced oxidation of parts of the mol. Some subsidiary chain scission appears to occur at single linkings. (**II**) does not undergo any saturation during autoxidation. Reduction (Al–Hg + H_2O–Et_2O–EtOH) of the products from (**III**) yields a mixture containing *hydroxy-*, b.p. 90—103°/12 mm., and (mainly 1 : 2)*dihydroxy-dihydromyrcene*, b.p. (?) 115°/1 mm. (Cf. A., 1942, II, 170.) A. Li.

Rubber, polyisoprenes, and allied compounds. I. Synthesis of low-molecular polyisoprenes of the rubber and squalene type. E. H. Farmer and D. A. Sutton (*J.C.S.*, 1942, 116—121).—Geranylacetone with MgEtBr in Et_2O yields *dihydronerolidol* (**I**), b.p. 137—140°/8 mm., dehydrated ($KHSO_4$) to *dihydrofarnesene*, b.p. 129—131°/11 mm. [*trihydrochloride* (**II**), m.p. 52°, also obtained from (**I**) and anhyd. HCl], which with Br in $CHCl_3$ yields an oil, and with O_3 gives $COMe_2$ and its peroxide, MeCHO, and AcOH, but no CH_2O, HCO_2H, or COMeEt. Dehydration ($KHSO_4$) of farnesol, reduction (Na + EtOH) of the product, and treatment with HCl yields a mixture of bisabolene trihydrochloride and (**II**). (**I**) with $MgBr{\cdot}[CH_2]_4{\cdot}MgBr$ in Et_2O yields *dihydroxydihydrosqualene*, b.p. 220—235°/1 mm., which with HCl in Et_2O gives a mixture of the three hydrochlorides obtained similarly from squalene. A. Li.

Separation of divinylacetylene and ethinylbutadiene and purification of the latter.—See B., 1942, II, 47.

Identification of alcohols in aqueous solution. W. N. Lipscomb and R. H. Baker (*J. Amer. Chem. Soc.*, 1942, **64**, 179—180).—Aliphatic alcohols are isolated from aq. solution as 3 : 5-dinitrobenzoates by shaking with the acid chloride, aq. NaOAc, NaOH, and C_6H_6–light petroleum at 0°. R. S. C.

Vapour-phase partial oxidation of ethyl alcohol.—See A., 1942, I, 177.

iso- and *n*-**Butyl alcohols from carbide.**—See B., 1942, II, 45.

Oxychlorides of silicon and corresponding ethyl esters.—See A., 1942, I, 152.

Purification of glycols.—See B., 1942, II, 48.

Chain structure of linear polyesters. Trimethylene glycol series.—See A., 1942, I, 136.

(A) **Structure of ($\alpha\gamma\delta\zeta$-)dibenzylidenedulcitol.** (B) **($\beta\gamma\delta\varepsilon$-)Dibenzylidenedulcitol.** (C) **Second $\beta\gamma\delta\varepsilon$-dibenzylidenedulcitol.** W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 132—136, 136—137, 137—140).—(A) Fischer's dibenzylidenedulcitol (**I**) (modified prep.; A., 1894, 395) is proved to be the $\alpha\gamma\delta\zeta$-compound. $Pb(OAc)_4$–AcOH attacks (**I**) very slowly. With Ac_2O–C_5H_5N or RCOCl–C_5H_5N, (**I**) gives the *βε-diacetate*, decomp. 265°, *-dichloroacetate*, decomp. 228—229°, *-dibenzoate* (**II**), decomp. 285°, and *-di-p-toluenesulphonate* (**III**), m.p. 215° (decomp.). With Ac_2O–AcOH–(drop) H_2SO_4, (**II**) gives *dulcitol βε-dibenzoate αδζ-tetra-acetate*, m.p. 157—158°. In boiling C_5H_5N, (**III**) is unchanged and $\beta\gamma\delta\varepsilon$-di*iso*propylidenedulcitol $\alpha\zeta$-di-*p*-toluenesulphonate (**IV**) gives a $(C_5H_5N)_2$ compound, m.p. 199—200°. NaI–Ac_2O has no effect on (**III**) but converts (**IV**) into the $\alpha\zeta$-di-iodide. In boiling aq. N-HCl-dioxan, (**II**) gives dulcitol $\alpha\zeta$-dibenzoate (**V**) (15), *dl*-galactitol $\alpha\delta$-dibenzoate (29%), and a syrup (56%). With Na and then CH_2PhCl in boiling dioxan, (**I**) gives the *βε-$(CH_2Ph)_2$ ether* (**VI**), decomp. 246—250°, hydrolysed by boiling aq. N-HCl–dioxan to *dulcitol βε-$(CH_2Ph)_2$ ether*, m.p. 168—169°, which consumes 1 HIO_4, giving no CH_2O, and consumes 1 $Pb(OAc)_4$, giving *dl*-glyceraldehyde *β*-CH_2Ph ether (*semicarbazone*, m.p. 132—134°). (**VI**) is accompanied by some *β-CH_2Ph ether*, m.p. 164—165° (*ζ-acetate*, m.p. 204—206°).

(B) Passage of HCl into (**V**) and PhCHO gives *βγδε-dibenzylidenedulcitol αζ-dibenzoate* (**VII**), m.p. 119—120°, converted by Ac_2O–AcOH–H_2SO_4 into dulcitol *βγδε*-tetra-acetate *αζ*-dibenzoate (**VIII**) and by NaOMe–MeOH–$CHCl_3$ at 5° into 2 : 3 : 4 : 5-*dibenzylidenedulcitol* (**IX**), m.p. 149—150°, the *αζ-diacetate* (**X**), m.p. 168—169°, of which (prep. by Ac_2O–C_5H_5N) is also obtained from dulcitol *αζ*-diacetate by HCl–PhCHO.

(C) PhCHO, (**V**), and $ZnCl_2$ (pure) at 23—25° (not 60°) give only 17% of (**VII**) and 67% of a (? *stereo*)*isomeride* (**XI**), m.p. 147—148°. PhCHO–$ZnCl_2$ converts (**XI**) into (**VII**), and Ac_2O–AcOH–H_2SO_4 gives (**VIII**). With NaOMe–MeOH–$CHCl_3$ at 5°, (**XI**) gives a *βγδε-dibenzylidenedulcitol* (**XII**), m.p. 173—174° [*αζ-diacetate*, m.p. 167—168°, converted into (**X**) by PhCHO–$ZnCl_2$ at 60°]. (**VII**) and (**XII**) give *αζ-$(CPh_3)_2$ ethers*, m.p. 184—186° and 240—242°, and *αζ-di-p-toluenesulphonates*, m.p. 167—168° and 175—176°, and thence (NaI–Ac_2O) *αζ-di-iodides*, m.p. 127—128° and 162—163°, respectively. M.p. (all papers) are corr. R. S. C.

Use of Bunte salts in synthesis. III. Preparation of aliphatic disulphides. H. E. Westlake, jun., and G. Dougherty (*J. Amer. Chem. Soc.*, 1942, **64**, 149—150; cf. A., 1941, II, 184).—$NaRS_2O_3$ (prep. *in situ*) with I or H_2O_2 in aq. EtOH give R_2S_2, yields being R = Bu$^{\alpha}$ 57, 56, n-*heptyl* (b.p. 143—147°/5 mm.) 66, 65, n-*octyl* (b.p. 178—183°/5 mm.) 69, 52, n-*dodecyl* 35, ~70, and *n*-octadecyl 49%, —, respectively. R. S. C.

Aliphatic sulphinic acids. I. Analysis and identification. P. Allen, jun. (*J. Org. Chem.*, 1942, **7**, 23—30).—*Mg alkanesulphinates*, $(RSO_2)_2Mg,2H_2O$ (R = Me to $C_{16}H_{33}$ inclusive), are obtained from the requisite Grignard reagent and SO_2. They are insol. in EtOH; the lower members are sparingly sol. in hot H_2O but the higher ones are insol. They are very readily electrified by friction. They are stable in H_2O at room temp. for several days but are quickly oxidised when heated. The Na salts are obtained from the Mg compounds and Na_2CO_3 or NaOH or by neutralising the free sulphinic acid with Na_2CO_3. Owing to their ready oxidisability, they could not be obtained quite pure. Dry Na and Mg salts are stable in air. Titration of the salts with oxidising agents in acid medium leads to only ~80—90% of the theoretical vals. In alkaline solution they can be accurately titrated potentiometrically with $KMnO_4$ or $Ca(OCl)_2$. Another convenient method is to add an excess of $KMnO_4$ to the alkaline solution followed by sufficient As_2O_3 to react with the MnO_2 and extra $KMnO_4$; the solution is acidified and, after disappearance of the MnO_2, is titrated with $KMnO_4$ to the colorimetric or potentiometric end-point. In neutral solution

potentiometric titration gives results almost but not quite so good as those obtained in alkaline solution. The higher Mg salts require a preliminary digestion (40—60 min.) with dil. NaOH without or with an insufficiency of $KMnO_4$, after which the mixture is titrated hot to the potentiometric end-point. The Na salts are transformed by $(CH_2Br)_2$ in boiling EtOH into *αβ-dialkylsulphonylethanes*, $(n\text{-}R{\cdot}SO_2{\cdot}CH_2{\cdot})_2$, in which R = Me, m.p. 190°, Et, m.p. 136—137°, Pr^a, m.p. 159·3—160·3°, Bu^a, m.p. 179·2—180·2, *amyl*, m.p. 183·7—184·2°, *hexyl*, m.p. 177·5—178·5°, *heptyl*, m.p. 176—177·5°, *octyl*, m.p. 172·8—173·5°, *nonyl*, m.p. 172·5—173·5°, *decyl*, m.p. 169·9—170·9°, *undecyl*, m.p. 168·3—169·3°, *dodecyl*, m.p. 165·8—166·8°, *tridecyl*, m.p. 163·4—164·1°, *tetradecyl*, m.p. 160·9—161·9°, *pentadecyl*, m.p. 158·7—159·9°, *hexadecyl*, m.p. 154·6—155·8°. The requisite Na sulphinate and EtI in boiling EtOH afford *Et undecyl*, m.p. 76·5—77·5°, *dodecyl*, m.p. 75·0—76·0°, and *hexadecyl*, m.p. 77·0—79·0°, *sulphone*. H. W.

Manufacture of aliphatic acids and their anhydrides.—See B., 1942, II, 48.

Production of esters.—See B., 1942, II, 49.

Manufacture of β-chloropropionic acid.—See B., 1942, II, 49.

Hexoic acid esters.—See B., 1942, II, 49.

Synthesis of methylated fatty acids. A. K. Schneider and M. A. Spielman (*J. Biol. Chem.*, 1941, **142**, 345—354).—*cyclo*Hexanone and n-$C_{12}H_{25}$·MgBr afford 1-*dodecyl*-Δ^1-cyclo*hexene* (43% yield), b.p. 140—143°/1·5 mm., oxidised by CrO_3–aq. AcOH to ε-ketostearic acid (43% yield), m.p. 86·5—87°, reduced (Clemmensen) to stearic acid. n-$C_{12}H_{25}$·MgBr–$ZnCl_2$–Et_2O and COCl·$[CH_2]_8$·CO_2Et in C_6H_6 (in N_2) yield *ι-ketodocosanoic acid*, m.p. 91·5° (62% yield), converted by Zn–Hg in EtOH nearly saturated with HCl into *n*-docosanoic acid, m.p. 79—80·5° (85% yield). Similarly prepared are *ι-keto-tetracosanoic acid*, m.p. 94—94·5°, and *n*-tetracosanoic acid, m.p. 82·5—83·5°. $CHMe(CO_2Et)_2$–NaOBu^a–n-$C_{16}H_{33}$I afford the Et_2 ester and thence the dicarboxylic acid, decarboxylated at 150—180°/10 mm. to α-methylstearic acid, new m.p. 54·5° (amide, m.p. 104·5°). Similarly prepared are *α-methyl-eicosanoic acid*, m.p. 61·5—62° (*amide*, m.p. 108°), *-docosanoic acid*, m.p. 67—67·5° (*amide*, m.p. 109—109·5°), *-tetracosanoic acid*, m.p. 72—72·5° (*amide*, m.p. 111·5°), and *-hexacosanoic acid*, m.p. 75·5—76° (*amide*, m.p. 113°). Et ι-ketoundecoate, b.p. 153—154°/6 mm., and n-$C_{14}H_{29}$·MgBr–Et_2O (in N_2) at 25° afford, through the resulting ester, a carboxylic acid, dehydrated at 180—210° (+ a trace of I) and then hydrogenated (Pt, or Raney Ni at 175°/160 atm., in EtOH) and hydrolysed, to give *ι-methyltetracosanoic acid*, m.p. 51° (*amide*, m.p. 79—79·5°); *ι-methyl-docosanoic acid*, m.p. 45·5—46° (*amide*, m.p. 78—78·5°), and *-hexacosanoic acid*, m.p. 54—55° (*amide*, 81—81·5°), are also prepared. Morpholine acetate and CHMe:CH·CHO give a mixture of polymerides, which after hydrogenation (Raney Ni) yield only n-C_8H_{17}·OH and n-$C_{12}H_{25}$·OH. A. T. P.

Long-chain acids. III. Bisnoroleic acid. P. C. Mitter and P. N. Bagchi (*J. Indian Chem. Soc.*, 1941, **18**, 461—464; cf. A., 1940, II, 203).—Me oleate and MgMeI give *αα-dimethyl-Δ^4-octadecen-α-ol*, b.p. 167—172°/3 mm., converted by successive treatments with Br–AcOH, CrO_3–AcOH, Zn–AcOH, and MeOH–H_2SO_4 into *Me* Δ^7-*heptadecenoate* (*Me noroleate*), b.p. 159—165°/6 mm., which with MgMeI yields *αα-dimethyl-Δ^6-heptadecen-α-ol*, b.p. 160—164°/4 mm., and thence, by successive stages as above, *Me* Δ^5-*hexadecenoate* (*Me bisnoroleate*), b.p. 150—155°/6 mm. (low yield). A. T. P.

Preparation of α-hydroxycarboxylic acids.—See B., 1942, II, 49.

Influence of halides on oxidation of ascorbic acid.—See A., 1942, III, 329.

Photochemical oxidation of chloral sensitised by bromine.—See A., 1942, I, 179.

Production of unsaturated aliphatic aldehydes.—See B., 1942, II, 50.

Syntheses in the carotenoid series. V. Preparation of higher aliphatic polyenealdehydes. J. Schmitt and A. Obermeit (*Annalen*, 1941, **547**, 285—292).—Self-condensation of crotonaldehyde (I) by piperidine acetate in 70% EtOH [whereby OEt is not introduced (cf. lit.)] at room temp. gives dodecapentaenal (**II**), m.p. 165°. Sorbaldehyde and (I) give *tetradecahexaenal*, m.p. 192°, converted into palmitic acid by way of Me·$[CH{:}CH]_6$·$CH{:}C(CO_2H)_2$ and Me·$[CH{:}CH]_7$·CO_2H. In 70% EtOH, (I) and (II) give hexadecaheptaenal, m.p. 216—217°, but in C_6H_6 some eicosanonaenal is also formed. R. S. C.

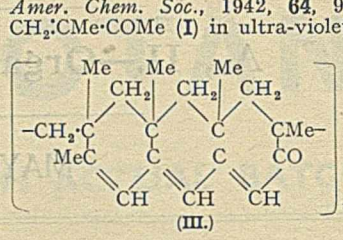
Preparation of glyceraldehyde α-methyl ether.—See B., 1942, II, 50.

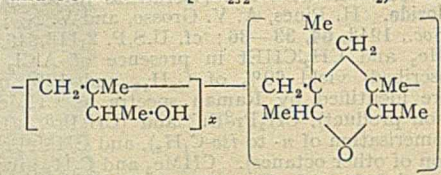
Photolysis of keten in presence of hydrogen and methane.—See A., 1942, I, 179.

Manufacture of unsaturated ketones and ketonic resins.—See B., 1942, II, 51.

Thermal decomposition of acetone catalysed by iodine.—See A., 1942, I, 176.

Structure of vinyl polymerides. XII. Polymeride of methyl *iso*propenyl ketone. C. S. Marvel, E. H. Riddle, and J. O. Corner (*J. Amer. Chem. Soc.*, 1942, **64**, 92—94; cf. A., 1941, II, 83).—$CH_2{:}CMe{\cdot}COMe$ (I) in ultra-violet light or with Bz_2O_2 at 25° gives polymerides, mol. wt. (II) 11,200 and ~36,000, respectively; at 60° in $COMe_2$ it gives a polymeride, mol. wt. ~6000, or without a solvent ~12,000 (cf. Staudinger *et al.*, A., 1936, 1336). The products are obtained solid by adding the $COMe_2$ solution to H_2O (<100 c.c. per g. of polymeride). The head-to-tail structure, $[{\cdot}CH_2{\cdot}CMeAc{\cdot}]_n$, of (**II**) is proved by pyrolysis at 270—300° or 360° to H_2O and a $COMe_2$-sol. *polymeride* (**III**) {and a little (I) and $COMe{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CO{\cdot}CMe{:}CH_2$} with loss of 63% of


(III.)


(IV.)

the O, random ring-closure requiring loss of 68·8%. This structure is confirmed by hydrogenation (Raney Ni; dioxan; 175°/2000 lb.) to the *compound* (**IV**) (86·47% ring-closure), m.p. 195—205°; the structure of (**IV**) is in turn proved by analysis of the *acetate* and *chloroacetate*, (prep. in C_5H_5N). R. S. C.

Structure and absorption spectra. IV. αβ-Unsaturated ketones. R. B. Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 76—77; cf. A., 1942, II, 161).—In calculating absorption max. of *αβ-*, *ββ-*, or *αββ*-substituted *αβ*-unsaturated ketones, each substituent contributes 11 mμ. (not 15) and each exocyclic ethylenic linking an additional 5 mμ. The ketones, m.p. 94° and 37°, obtained from di-Δ^1-*cyclo*hexenylacetylene by HCO_2H are probably 3-pentamethylene-Δ$^{3(a)7(a)}$- and -Δ^7-hexahydroindone, respectively. R. S. C.

Cyclic methyleneimines. IV. Hydrolysis of quaternary compounds. Preparation of secondary amines. J. Graymore (*J.C.S.*, 1942, 29—30).—*NN'N''*-Trimethyltrimethylenetriamine (**I**) with $PhSO_2Cl$ in Et_2O yields *bis*(*benzenesulphonmethylamidomethyl*)*methylamine*, m.p. 122—123°, hydrolysed (dil. HCl or NaOH) to CH_2O, NH_2Me, $PhSO_2{\cdot}NHMe$, and an unstable *product* (**II**), $C_9H_{22}N_4Cl_2,4CH_2O$, m.p. 118—120° (decomp.), hydrolysed to CH_2O and NH_2Me only. (**I**) with p-$C_6H_4Me{\cdot}SO_2Cl$ yields (**II**), p-$C_6H_4Me{\cdot}SO_2{\cdot}NHMe$, and *methylenebis*-p-*toluenesulphonmethylamide*, m.p. 117—118°, hydrolysed to CH_2O and p-$C_6H_4Me{\cdot}SO_2{\cdot}NHMe$. The mechanism of the reaction is discussed. A. Li.

4-Co-ordinated mercuric salts with diamines.—See A., 1942, I, 180.

Amino-derivatives of pentaerythritol. II. Thermal decomposition of the tetrahydrochlorides of tetrakismethylaminomethylmethane and tetrakisdimethylaminomethylmethane. G. M. Gibson, J. Harley-Mason, A. Litherland, and F. G. Mann. **III. Formation and thermal decomposition of some quaternary salts of tetrakisdimethylaminomethylmethane.** G. M. Gibson and F. G. Mann (*J.C.S.*, 1942, 163—175, 175—181; cf. A., 1938, II, 474).—II. The *tetrahydrochloride*, m.p. 264° (decomp.), of tetrakismethylaminomethylmethane {*dihydrate*, b.p. 245—248°; *tetrahydrobromide* [*monohydrate*, m.p. 266° (decomp.)]; $(PhSO_2)_4$ derivative, m.p. 239°} at 275° yields a mixture containing the *dihydrochloride*, m.p. 262—263°, of *αγ-bismethylaminopropane* (+H_2O), b.p. 141—144° (*dipicrate*, m.p. 193—194°) (synthesised from Br·$[CH_2]_3$·Br and aq. EtOH–NH_2Me at 120—130°). *Tetrakisaminomethyl-* (+$4H_2O$), m.p. 100—100·5°, with Me_2SO_4 yields *tetrakisdimethylaminomethyl-methane* (**I**), b.p. 248—249°/769 mm. [also prepared from $C(CH_2Br)_4$ and $NHMe_2$ in EtOH at 170°], the tetrahydrochloride (+$3H_2O$) of which when heated at 232—233° evolves H_2O and CH_2O, giving a mixture containing NH_2Me, $NHMe_2$, and NMe_3 hydrochlorides, and the *dihydrochloride* (**II**), m.p. 260° (decomp.) (unaffected by boiling dil. HCl), of a tert. *amine* (**III**), $C_8H_{18}N_2$, b.p. 150—154° [*dihydrobromide*, m.p. 243° (darkening); *dihydriodide*, m.p. 203—205° (previous softening); *dipicrate*, 185·5—187·5°; *bis*-d-α-*bromocamphor-π-sulphonate* (which could not be resolved), m.p. 170—176°, $[M]_D^{19}$ +556° in H_2O; *dimethiodide* (**IV**), m.p. 216—217° (decomp., preliminary darkening); *dimethochloride* (+H_2O) (**V**), m.p. 184—196° (efferv., resolidifying and remelting at 200°); *diaurichloride*, m.p. 237—238·5° (decomp.); *platinichloride*, m.p. 245° (decomp.); *dimethopicrate*, m.p. 257—257·5° (decomp.); *dimetho*-d-*camphorsulphonate* (which could not be resolved), m.p. 261—263° (slight softening), $[M]_D^{13}$ +101° in H_2O; *dibenzyliodide*, m.p. 168—169°; *dibenzylpicrate*, m.p. 199—201°]. (**II**) in *cyclo*hexane is slowly hydrogenated (PtO_2), rapidly after addition of AcOH. (**III**) in H_2O, or (**IV**) in MeOH, is completely hydrogenated to $CHMe_3$ and $NHMe_2$,HCl (or NMe_3,HCl) (no intermediate product isolable). Oxidation (alkaline $KMnO_4$) or (**V**) yields $H_2C_2O_4$ and CH_2O (no intermediate product isolable). O_3 does not affect (**V**), but decomposes (**III**), no CO-compound being

detected in the product. (**III**) with aq. Br gives only a perbromide (?), but (**II**) with Br in $CHCl_3$ yields the dihydrobromide of (**II**). $CHMe(CH_2Br)_2$ with EtOH–$NHMe_2$ at 130° yields *αγ-bisdimethylamino-β-methylpropane*, b.p. 151—152° (*dihydrochloride*, m.p. 233—234°; *dibenzylpicrate*, m.p. 169—171°), the *dimethiodide*, m.p. 267—268°, of which could not be reduced catalytically. $OH{\cdot}CH(CH_2Cl)_2$ with EtOH–$NHMe_2$ at 115—120° yields *αγ-bisdimethylaminoisopropyl alcohol*, b.p. 80—82°/17 mm. (*dimethiodide*, decomp. 250°), which could not be oxidised to the ketone. $CO(CH_2Cl)_2$ with MgMeBr yields *αγ-dichloro-β-methylisopropyl alcohol*, b.p. 71—72°/18 mm., which with β-$C_{10}H_7{\cdot}ONa$ gives *β-hydroxy-β-methyltrimethylene-αγ-bis-2-naphthyl ether*, m.p. 151—152°, and with EtOH–$NHMe_2$ at 115—125° yields *αγ-bisdimethylamino-β-methylisopropyl alcohol*, b.p. 80—81°/20 mm. [*dihydrochloride*, m.p. 250° (efferv.); *dipicrate*, m.p. 172—173°; *dimethiodide*, m.p. 176—177° (*monohydrate*, m.p. 105—110°)]. This could not be dehydrated, but with $SOCl_2$ in $CHCl_3$ yields *β-chloro-αγ-bisdimethylamino-β-methylpropane*, b.p. 81°/15 mm. (*dipicrate*, m.p. 155—156°). HCl could not be eliminated from this, which with EtOH–KOH yields *αγ-bisdimethylamino-β-ethoxy-β-methylpropane*, b.p. 91—92°/15 mm. [*dimethiodide*, m.p. 140—150° (efferv., previous softening)], but its *dimethiodide*, m.p. 195—196° (decomp.), with MeOH–KOH (1 mol.) affords *αγ-bistrimethylammonium-β-methylpropenylene di-iodide* (**VI**), m.p. 203—204° [corresponding *dimethopicrate*, (**VII**), m.p. 245—246° (decomp.)]. Excess of MeOH–KOH yields NMe_3,HI and a compound giving a 2 : 4-dinitrophenylhydrazone, m.p. 174—177°. (**VI**) is hydrogenated (PtO_2) quantitatively to NMe_3,HI and $CHMe_3$. Oxidation (alkaline $KMnO_4$) of (**VI**) yields $H_2C_2O_4$, also obtained (91%) from $AcCO_2H$. When boiled with H_2O–Ag_2O, (**IV**) or (**V**) yields a solution containing the ion $(^+NMe_3{\cdot}CH{:}CHMe{\cdot}CH_2)_2O$ (**VIII**) [*dipicrate*, m.p. 173—174°; *diaurichloride*, m.p. 201—202°; *platinichloride*, m.p. 206—207° (decomp.)], whilst $CMeCl(CH_2{\cdot}NMe_3I)_2$ or an old specimen of (**V**) yields (**VII**), the former on prolonged boiling with Ag_2O giving (**VIII**). It is concluded that (**IV**) and (**VI**) are geometrical isomerides, and that (**II**) is $NMe_3{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}NMe_2$. *Acetonyltrimethylammonium picrate* (from CH_2AcCl and aq. EtOH–NMe_3) has m.p. 149—150°. Mixed Et_2 *cis-* and *trans*-1-methyl*cyclo*propanedicarboxylate with aq. NH_3 gives the mixed *amide-ammonium* salt, m.p. 167—169° (efferv., previous softening), and with N_2H_4,H_2O yields the mixed *dihydrazide*, m.p. 167—170°, which with HNO_2 affords a small amount of 2 : 3-diamino-1-methyl*cyclo*propane (*Bz_2* derivative, m.p. 197—200°). Trimethyleneimine with MeI in Et_2O at 0° gives its *hydriodide*, m.p. 146·5° [resolidifying and remelting at 240—250° (decomp.)], but with MeOH–KOH, then MeI at 0°, yields *N-methyltrimethyleneimine methiodide*, m.p. 225° (decomp.).

A. Lɪ.

III. Boiling EtI and (**I**) yield the *diethiodide*, m.p. 128°, decomp. by heat into the monohydrated dihydriodide of the Me_3 base. (**I**) and allyl iodide give the *monoallyliodide*, m.p. 145—146° (decomp.) and 207° after re-solidification (*monohydriodide*, m.p. 157—158°), converted by MeI into the *monoallyliodide monomethiodide*, m.p. 114—115° (decomp.), which appears to afford the *tetramethiodide*, m.p. >350°, of (**I**) when heated. In Et_2O (**I**) and CH_2PhI give the *dibenzyliodide monohydrate*, m.p. 128—129° (decomp.), and *monobenzyliodide*, m.p. 146—147° and 190—196° after re-solidifying (*hydriodide*, m.p. 170°). The *monobenzyliodide allyliodide* has m.p. 145—146° (decomp.). Under other conditions the reaction of the base with CH_2PhI causes rupture of the amine mol. with the formation of $NMe_2I(CH_2Ph)_2$ and the dibenzyliodide of the "pyro" base. The thermal decomp. of these products has been studied.

H. W.

Structure of sphingosine. H. E. Carter, F. J. Glick, W. P. Norris, and G. E. Phillips (*J. Biol. Chem.*, 1941, **142**, 449—450).—Sphingosine is n-$C_{12}H_{37}{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}CH_2{\cdot}OH$ (cf. Klenk *et al.*, A., 1931, 829). Sphingosine sulphate and BzCl–aq. NaOH–Et_2O give the *N*-Bz derivative, reduced (PtO_2) to *N*-benzoyldihydrosphingosine (**I**), converted by BzCl–C_5H_5N into the Bz_3 derivative, m.p. 144—146° [hydrolysed by hot aq. alkali to (**I**)]. Since (**I**) is not oxidised by HIO_4, it is probably an *αγ*-glycol, not an *αβ* derivative (*loc. cit.*); (**I**), however, readily affords a cyclic acetal with PhCHO–$ZnCl_2$, a reaction characteristic of either an *αβ*- or *αγ*-glycol.

A. T. P.

Quantitative investigation of amino-acids and peptides. VIII. Solubility and specific rotations of *l*(−)-leucine at 25°. M. P. Stoddard and M. S. Dunn (*J. Biol. Chem.*, 1941, **142**, 329—343).—*l*(−)-Leucine (**I**) of high purity is prepared by decomp. of the recryst. monohydrochloride, obtained from natural leucine, with aq. NH_3 at p_H 7. Solubility of (**I**) is 2·19±0·01 g. per 100 g. H_2O at 25·1±0·03°, and $[\alpha]_D^{25}$ is +15·20±0·04° in 6N-HCl, or −10·57±0·04° in H_2O; ash, H_2O, Cl, NH_3, Fe^{II}, Fe^{III}, and PO_4 content are negligible (<0·004%), methionine content is ~0·1%, and NH_2-acids other than (**I**), ~0·5%.

A. T. P.

Manufacture of acetonitrile.—See B., 1942, II, 52.

II.—SUGARS AND GLUCOSIDES.

β-Form of the Cori ester (*d*-glucopyranose 1-phosphate). M. L. Wolfrom, C. S. Smith, D. E. Fletcher, and A. E. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 23—26).—$(CH_2Ph)_2$ *β-d*-glucopyranose tetra-acetate 1-phosphate (prep. described; 73% yield; cf. Zervas, A., 1939, II, 360) with H_2–PdO in abs. EtOH etc. gives *β-d-glucopyranose dibrucine 1-phosphate* (**I**), m.p. (+10H_2O) 160—165° (decomp.; sinters at 120—122°) and (anhyd.) 162—166° (decomp.), $[\alpha]_{5892\cdot5}^{29}$ (+10H_2O) −20° in H_2O. The isomeric *α*-salt (**II**) has m.p. (+8H_2O) 173—178° (sinters at 165°) and (anhyd.) 182—184° (decomp.), $[\alpha]_{5892\cdot5}^{27}$ (+8H_2O) +0·5° in H_2O. The rotatory dispersions of (**I**) and (**II**) are described. Hydrolysis of (**I**) by N-HCl at 33° is faster than that of (**II**). Derivation of cellulose from *β*- and of starch and glycogen from *α-d*-glucopyranose 1-phosphate makes it probable that the former exists in nature.

R. S. C.

Polymorphism of *d*-galactose diethylmercaptal penta-acetate. L. H. Welsh and G. L. Keenan (*J. Amer. Chem. Soc.*, 1942, **64**, 183—186).—This substance exists in forms of initial m.p. 76·5—77°, 80·5—81°, and 90·5—91°. Photomicrographs are given.

R. S. C.

Structure of N^4-*d*-glucosidosulphanilamide. C. E. Braun, J. L. Towle, and S. H. Nichols, jun. (*J. Org. Chem.*, 1942, **7**, 19—22).—Cautious addition of *β*-acetobromo-*d*-glucose (**I**) in anhyd. $CHCl_3$ to a well-stirred mixture of p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (**II**), Ag_2O, and $CaSO_4$ in anhyd. dioxan gives *d*-glucosidosulphanilamide tetra-acetate, m.p. 191°, $[\alpha]_D^{19}$ −78·4° in anhyd. C_5H_5N, −62·6° in $CHCl_3$, deacetylated to N^4-*d*-glucosidosulphanilamide (**III**), m.p. 204° when very slowly heated, $[\alpha]_D^{23}$ −119·6° in H_2O, $[\alpha]_D^{24}$ +29·7° in 0·1N-HCl, identical with the product of Kuhn and Birkofer (A., 1938, II, 173). The conclusion that the glucose residue is attached to N^4 in (**III**) depends on the fact that it, when compared directly with (**II**) and p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHAc$, fails to yield a picrate, a picramide, a substituted thiocarbamide with α-$C_{10}H_7{\cdot}NC$, and fails to give a positive reaction with Ehrlich's reagent. Its mode of synthesis from (**I**) appears to justify the conclusion that (**III**) is a *β*-glucoside. On an equal wt. basis (**III**) is only about half as active against streptococci as (**II**) and is not less toxic. Even if the difference in mol. wts. is considered (**III**) is still slightly less active than (**II**). However, the greater solubility of (**III**) in H_2O may be advantageous.

H. W.

Acetate, m.p. 172·5—173°, of a pentahydroxychalkone hexoside from *Coreopsis gigantea*.—See A., 1942, III, 360.

Recent progress in the chemistry of pectic materials and plant gums. E. L. Hirst (*J.C.S.*, 1942, 70—78).—A review.

A. Lɪ.

***X*-Ray and electron microscope studies of the processes in the grinding of cellulose.** K. Hess, H. Kiessig, and J. Gundermann (*Z. physikal. Chem.*, 1941, **B**, **49**, 64—82).—Changes in state of cellulose (**I**) fibres by mechanical destruction have been studied. The distribution to primary fibrils of 100—750 A. thickness has been demonstrated. *X*-Ray investigations have shown that the lattice-ordered state of the fibrils disappears but reappears on treatment with H_2O not as (**I**) but as hydrated (**I**). A diminution in viscosity on grinding is attributed to processes which occur inside the primary fibrils. On continued grinding the primary fibrils become curled and matted together in clumps without any discernible fracture of the fibrils. The changes in properties of the product arise not only from surface enlargement but also from changes of state occurring inside the primary fibrils.

W. R. A.

Oxidation of cellulose by nitrogen dioxide. E. C. Yackel and W. O. Kenyon (*J. Amer. Chem. Soc.*, 1942, **64**, 121—127).—Keeping cotton in N_2O_4 or circulating N_2O_4 over it gives oxidised cellulose, which is fluffy, white, non-friable, and has high affinity for basic dyes. If the CO_2H is >15%, the product is indistinguishable from the starting material. If the CO_2H is <15%, some surface hardening and shrinkage occurs. If the CO_2H is >13%, the products are sol. in 2% aq. NaOH, dil. aq. NH_3, Na_2CO_3, warm aq. C_5H_5N, or aq. quaternary NH_4 hydroxides; products containing <13% of CO_2H swell but do not dissolve. Insol. salts are obtained, *e.g.*, the Ba salt, from the hydroxide or by displacement of AcOH from acetates. CO_2H is best determined by a modification of the CO_2-evolution method used for uronic acids; displacement of AcOH from aq. $Ca(OAc)_2$ gives lower results for highly oxidised products, probably owing to incomplete penetration of the reagent or adsorption of AcOH. Interaction with N_2O_4 is at first rapid, but later much slower. Correlation of the ratio of reactants with composition of the product is good.

R. S. C.

Properties of cellulose oxidised by nitrogen dioxide. I. C. C. Unwin and W. O. Kenyon (*J. Amer. Chem. Soc.*, 1942, **64**, 127—131).—Oxidation of cotton by N_2O_4 (see preceding abstract) gives oxidised cellulose (**I**) containing, after sufficiently long interaction, ~25% of CO_2H. Determination of CO_2H by (*a*) dissolution in warm aq. C_5H_5N and later addition of 0·5N-NaOH and (*b*) dissolution in aq. C_5H_5N–0·5N-NaOH, followed in both cases by back-titration, is described. Method (*a*) gives low results, similar to those of the $Ca(OAc)_2$ method; method (*b*) gives results similar to those of the CO_2-evolution method, which is considered best of all. Cu no., determined by the Forest Products Laboratory method, increases to 71·0; the Knecht–Thompson method gives much lower results; reduction of Cu salts is considered to be entirely due to fission of uronic acid units to give CHO during digestion with the

reagents. Acetates are best analysed by a distillation method. Yields of furfuraldehyde are ~60%, comparable with those from alginic and pectic acid. CO_2H and acylable OH account for all the original OH. It is concluded that oxidation by N_2O_4 attacks primary OH without affecting *sec.* OH and in fully oxidised material all CH_2·OH are converted into CO_2H. R. S. C.

New microchemical reaction for cellulose. E. E. Post and J. D. Laudermilk (*Stain Tech.*, 1942, **17**, 21—24).—3 drops of 2% I in 5% KI, diluted with 9 vols. of H_2O containing 0·28% of glycerol, are applied with a glass rod, left for 30 sec., and blotted dry. Then 1 drop of saturated aq. LiCl is added, and the prep. covered and examined. The blue colour reaction for cellulose develops within 5 min. E. E. H.

Relation between the method of preparation, distribution of substituents, and solubility in water or alkali of methyl and ethyl ethers of cellulose. J. F. Mahoney and C. B. Purves (*J. Amer. Chem. Soc.*, 1942, **64**, 15—19).—Five H_2O- or alkali-sol. methyl- and ethylcelluloses are partly esterified with *p*-C_6H_4Me·SO_2Cl in C_5H_5N (heterogeneous mixtures) and the amounts of primary OH determined by conversion of the products into 6-iodides. The amounts of 2 : 3- + 3 : 4-glycol are determined by HIO_4. Alkylation in a quaternary NH_4 base gives products in which OAlk is uniformly distributed along the chain, but the technical heterogeneous alkylation of alkali-cellulose leads to non-uniform distribution; moreover, the ratio of primary to *sec.* OH alkylated is higher in the former than in the latter reaction. Steric effects probably account for this difference. R. S. C.

Methods for investigating the distribution of ethoxy-groups in a technical ethylcellulose. J. F. Mahoney and C. B. Purves (*J. Amer. Chem. Soc.*, 1942, **64**, 9—15).—Oxidation of a technical ethylcellulose (**I**) (2·48 OEt per glucose unit; mol. wt. 232) by $Pb(OAc)_4$ shows presence of 0·01 unit of 2 : 3-glycol. That of the ethylglucopyranosides (obtained by hydrolysis) by HIO_4 shows 0·25—0·29 unit of 2 : 3- + 3 : 4-glycol. That of the derived free sugars by $Pb(OAc)_4$ shows 0·13—0·15 unit of 1 : 2-glycol. Thus, 0·13—0·15 free OH per glucose unit occurs in position 2 and 0·24—0·28 in position 3. Interaction of (**I**) with *p*-C_6H_4Me·SO_2Cl (**II**) in C_5H_5N (homogeneous solution) at 20° is followed for 6 months by determination of S and OEt in the product and periodic conversion thereof into the 6-iodide by NaI in $(CH_2Ac)_2$; this shows 0·124 free primary OH per unit in (**I**). Mathematical analysis of the reaction rate (unimol.) with (**II**) shows rapid esterification of 0·151 OH per unit at $C_{(2)}$ and slower esterification of 0·245 OH at $C_{(3)}$, these estimates being more accurate than those given above. First-order consts. for reaction with (**II**) are 15, 2·3, and 0·07 for OH in positions 6, 2, and 3, respectively. R. S. C.

III.—HOMOCYCLIC.

Oxidation of *cyclo*hexane.—See B., 1942, II, 52.

Synthesis of condensed ring systems. VII. Successful use of ethylene in the Diels–Alder reaction. L. M. Joshel and L. W. Butz (*J. Amer. Chem. Soc.*, 1941, **63**, 3350—3351).—C_2H_4 with $(CH_2{:}CH)_2$ at 200°/4500 lb. gives <18% of *cyclo*hexene, with $(CH_2{:}CMe)_2$ at 200°/6200 lb. gives 50% of 1 : 2-dimethyl*cyclo*hexene, and with *cyclo*pentadiene at 190—200°/5800 lb. gives 74% of bi*cyclo*[2 : 2 : 1]-Δ^2-heptene. R. S. C.

Preparation of $\Delta^{6:8(14)}$-, $\Delta^{7:9(11)}$-, $\Delta^{7:14}$-, and $\Delta^{8:14}$-cholestadienes. J. C. Eck and E. W. Hollingsworth (*J. Amer. Chem. Soc.*, 1942, **64**, 140—144).—Δ^8-Cholesten-7-one and $Al(OPr^\beta)_3$–$Pr^\beta OH$ give Δ^8-*cholesten-7-ol*, m.p. 79—80°, $[\alpha]_D^{24}$ +4·2° in CCl_4, dehydrated by HCl–EtOH to $\Delta^{6:8(14)}$-*cholestadiene*, m.p. 84—85°, $[\alpha]_D^{24}$ +1·1° in CCl_4 (absorption max. ~245 mμ.). Δ^8-Cholestene (**I**) and $Hg(OAc)_2$–EtOH–AcOH give $\Delta^{7:9(11)}$-*cholestadiene*, m.p. 83—84°, $[\alpha]_D^{20}$ +31·3° in $CHCl_3$ (absorption max. 243 mμ.), also obtained by Br–$CHCl_3$ at −75°. With BzO_2H in $CHCl_3$, (**I**) gives $\Delta^{7:14}$-*cholestadiene*, m.p. 82—83°, $[\alpha]_D^{21}$ −93·2° in CCl_4 [absorption max. 242 and 250 mμ.; (:CH·CO)$_2$O *adduct*, m.p. 170—174°]. $\Delta^{8(14)}$-Cholestene (**II**) and BzO_2H give $\Delta^{8:14}$-*cholestadiene*, m.p. 83—84°, $[\alpha]_D^{20}$ −23·0° in CCl_4 (absorption max. 245 mμ.), also obtained by SeO_2 in boiling EtOH (product, $[\alpha]_D^{23}$ −19·7°), Br–MeOH–Et_2O, or CrO_3, giving no (:CH·CO)$_2$O adduct, and hydrogenated (Pd) to (**II**). [α] are compared with those of similar compounds. Br-titrations are discussed. R. S. C.

Catalysts for polymerisation of benzyl chloride.—See A., 1942, I, 177.

***p*-Cymene. VII. Simultaneous nitration and partial dealkylation of *p*-cymene.** T. F. Doumani and K. A. Kobe (*J. Org. Chem.*, 1942, **7**, 1—5; cf. A., 1940, II, 162).—*p*-C_6H_4Me·NO_2, obtained with 1 : 4 : 2-$C_6H_3MePr^\beta$·NO_2 by the mononitration of *p*-$C_6H_4MePr^\beta$, is derived by the replacement of Pr^β by NO_2. The spent mixed acids contain $Pr^\beta OH$ and $COMe_2$, the latter arising by oxidation of a part of the former. H. W.

Preparation and reactions of 4-amyl-*m*-xylenes. D. Nightingale and O. G. Shanholtzer (*J. Org. Chem.*, 1942, **7**, 6—14).—In the reaction between decahydronaphthalene, 4-*neopentyl*-m-*xylene*, b.p. 97—98°/10 mm., and $AlCl_3$, the neopentyl radical is cleaved to form *iso*pentane in 20% yield. This is the first primary alkyl radical to react in this manner. The branched *sec.*-amyl radical gives a larger yield of mixed pentanes in this reaction than do the two straight-chain *sec.*-amyl radicals. 5-*tert.*-Amyl-*m*-xylene (**I**), b.p. 102—103°/14 mm., obtained from *m*-xylene, $AlCl_3$, and *tert.*-$C_5H_{11}Cl$, gives the highest yield of *iso*pentane. 4-tert.-*Amyl*-m-*xylene* (**II**), m.p. 93—95°/14 mm., is derived from *m*-xylene, *tert.*-C_5H_{11}·OH, and H_2SO_4. The following -m-*xylenes* are described: 4-n-*amyl*-, (**III**), b.p. 123—124°/16 mm., 4-iso*amyl* (**IV**), b.p. 116—117°/15 mm.; 4-*β*-*amyl* (**V**), b.p. 102—103°/11 mm., 4-*β*-Δ^β-*pentenyl*-, b.p. 104—113 mm.; 4-*β*-*γ*-*methylbutyl* (**VI**), b.p. 100—102°/13 mm.; 4-*β*-*γ*-*methyl*-Δ^β-*butenyl*-, b.p. 106—110°/16 mm.; 4-*γ*-n-*amyl*- (**VII**), b.p. 105—106°/13 mm.; 4-*γ*-Δ^γ-*pentenyl*-, b.p. 103—105°/16 mm.; 4-*α*-*β*-*methyl*-n-*butyl*-, b.p. 108—111°/13 mm.; 4-*α*-*β*-*methyl*-Δ^α-*butenyl*-, b.p. 107°/10 mm. They are obtained by Clemmensen reduction of the requisite ketones, of which 2 : 4-*dimethyl*isovalerophenone, b.p. 131—132°/12 mm. (*semicarbazone*, m.p. 196°), and 2 : 4-*dimethylpivalophenone*, b.p. 107—109°/6 mm., which does not yield a semicarbazone, are new. The 4-*n*- and 4-*iso*-valeryl ketones give solid *by-products*, $C_{26}H_{38}O_2$, m.p. 146° and 139—140°, respectively. *m*-Xylene is transformed by CH_2O and conc. HCl into 2 : 4-*dimethylbenzyl chloride* (**VIII**), b.p. 92—94°/8 mm.; (**I**), (**II**), and (**III**) are converted similarly into their CH_2Cl derivatives, b.p. 120—128°/3 mm., (**IX**), b.p. 115—123°/4 mm., and b.p. 125—135°/3 mm. (**X**). (**VIII**), (**IX**), and (**X**) are converted by an excess of NH_2Ac at 190—220° into the CH_2·*NHAc* compounds, m.p. 109°, 150°, and 105°, respectively. Nitration, reduction, and subsequent acylation of (**I**)—(**VII**) gives the $(NHAc)_2$- and $(NHBz)_2$-derivatives, m.p. 304° and 302°; — and 308°; 234° and 220°; — and 208°; 234° and 241°; 264° and 234—235°; 279—280° and 252—253°, respectively. H. W.

Poly*cyclo*hexylnaphthalenes.—See B., 1942, II, 52.

9-Vinylphenanthrenes. III. α-9-Phenanthrylstilbene. F. Bergmann (*J. Amer. Chem. Soc.*, 1942, **64**, 69—72).—α-9-Phenanthrylstilbene (**I**), m.p. 167°, prepared from *αβ*-diphenyl-α-9-phenanthrylethyl alcohol (A., 1940, II, 308), is accompanied by a small amount of an *isomeride* (**II**), m.p. 140°. (**I**) and (**II**) are shown to have the Ph in *trans*- and *cis*-positions, respectively. A trace of I in boiling $PhNO_2$ converts (**II**) into (**I**). In Et_2O, (**I**) gives a Li_2 derivative, converted by EtOH into α-9-*phenanthryldibenzyl* (**III**), m.p. 197°, and a little 9-*benzyl*-1a : 4a-*dihydro*-1 : 2 : 3 : 4-*dibenzofluorene* (**IV**), m.p. 236°, or by CO_2 into *αβ*-*diphenyl*-α-9-*phenanthrylsuccinic anhydride* (**V**), m.p. 256—258° (decomp.). In boiling Ac_2O, (**V**) gives *compounds*, $C_{29}H_{18}O_3$, m.p. 276°, and $C_{29}H_{20}O_2$, m.p. 248—249° (with CH_2N_2 gives a ? *Me* ester, m.p. 175—176°, very resistant to HI). The Li_2 derivative of (**II**) with EtOH gives (**III**) and traces of 10-*phenyl*-1 : 2 : 3 : 4-*dibenzophenanthrene* (**VI**), m.p. 185°, but with CO_2 at 0° gives (**VI**) and an amorphous acid, which gives no anhydride but in hot Ac_2O yields 2-*phenyl*-3-9′-*phenanthrylindone*, m.p. 255°, and CO_2. R. S. C.

Hydrogenation of β-iminonitriles. H. Adkins and G. M. Whitman (*J. Amer. Chem. Soc.*, 1942, **64**, 150—154).—CH_2R·CN (R = H, Me, Et, Pr^α, or Ph) gives, by the Thorpe reaction, CH_2R·C(:NH)·CHR·CN or probably CH_2R·$C(NH_2)$:CR·CN. Hydrogenation (Raney Ni) readily gives CH_2R·CH(NH_2)·CHR·CH_2·NH_2 but CH_2R·CH(NH_2)·CHR·CN could not be obtained. Except when R = Ph, a little hydrogenolysis to NH_2·$CH(CH_2R)_2$ (not formed by way of the diamine, which is stable) occurs; if R = Ph, 2% of Ph·$[CH_2]_2$·NH_2 is formed. NH:CBu^α·$CHPr^\alpha$·CN exists as trimeride in freezing and as dimeride in boiling C_6H_6 and as solvate in boiling EtOH. NPh:CMe·CH_2·CN (**I**) (prep. from NH:CMe·CH_2·CN by NH_2Ph–AcOH–H_2O) is dimeric in boiling C_6H_6 and solvated in EtOH. Bu^αCN and β-piperidinocinnamonitrile (**II**) are monomeric in C_6H_6. Hydrogenation of (**I**) gives NH_2Ph (73—84%), NH_2·CHMe·$[CH_2]_2$·NH_2 (8%), and ? NHBu^α·CHMe·$[CH_2]_2$·NH·CHMe·CH_2·CN. Hydrogenation of (**II**) leads only to hydrogenolysis of the piperidino-group. Hydrogenation (Raney Ni; 70—126°/150 atm.) of NO_2·CH_2·CHPh·CH_2·COPh gives *βδ*-*diphenyl*-n-*butylamine*, b.p. 144·5°/1 mm. (3-*nitrophthalimide*, m.p. 129·5°; *phenylthiocarbamide*, m.p. 191—191·5°). Addition of CH_2Ph·CN and then of MeI to $NaNH_2$–Et_2O gives CHPhMe·CN, converted by CH_2Ph·MgCl–Et_2O into CHPhMe·CO·CH_2Ph; with NH_3–H_2–Raney Ni in dioxan at 150°/100 atm., this gives *β*-*amino*-*αγ*-*diphenylbutane*, b.p. 142·5°/51—54 mm. (*hydrochloride*, m.p. 174—175·5°; *picrate*, m.p. 190·5—191·5°; 3-*nitrophthalimide*, m.p. 152—153°; *phenylthiocarbamide*, m.p. 146·5—147°). *αγ*-*Diamino*-*β*-*methyl*-n-*pentane*, b.p. 110°/88 mm. [*platinichloride*, m.p. 237° (decomp.)], *αγ*-*diamino*-*β*-*ethyl*-n-*hexane*, b.p. 99°/17 mm. (*dihydrochloride*, m.p. 153—165°), ε-*amino*-n-*nonane*, b.p. 78°/20 mm. (*hydrochloride*, m.p. 178—180°; *picrate*, m.p. 149·5—150°), ε-*amino*-δ-*methyl*-n-*nonane*, b.p. 87—90°/18 mm. (*picrate*, m.p. 153·5—154·5°), *αγ*-*diamino*-*β*-n-*propyl*-n-*heptane*, b.p. 100°/5 mm. [*dihydrochloride*, m.p. 106—110° (decomp.)], and *αγ*-*diamino*-*βδ*-*diphenylbutane*, b.p. 166—168°/1·5 mm. (*dihydrochloride*, m.p. >280°), are incidentally prepared. R. S. C.

Hydrogenation of primary arylamines.—See B., 1942, II, 95.

Action of chlorine on arylthiocarbimides and reactions of *iso*cyanodichlorides. II. G. M. Dyson and T. Harrington (*J.C.S.*, 1942, 150—153; cf. A., 1940, II, 125).—A modified scheme is proposed for the action of Cl_2 on PhNCS; the unstable additive compound, probably NPh:C(SCl)·NPh·CSCl (cf. *loc. cit.*), is converted by NaOH into 1-anilinobenzthiazole. PhNCS–$NPh{:}CCl_2$–Cl_2 give (mainly) *p*-$C_6H_4Cl{\cdot}N{:}CCl_2$, b.p. 220—226°, converted by NH_2Ph–C_6H_6 (reflux) into s-*diphenyl*-p-*chlorophenylguanidine hydrochloride*, m.p. 256° (some triphenylguanidine hydrochloride is formed). $NPh{:}CCl_2$ and $NHPh_2$ in $C_2H_2Cl_4$ yield *pentaphenylguanidine hydrochloride*, m.p. 227°; *o*-, *m*-, or *p*-$C_6H_4Me{\cdot}N{:}CCl_2$ similarly gives s-*tetraphenyl*-o-, m.p. 172°, -m-, m.p. 174—176°, and -p-*tolylguanidine*, m.p. 175°, respectively. Tertiary amines do not react under the conditions. *p*-$C_6H_4Me{\cdot}N{:}CCl_2$ or *p*-$NO_2{\cdot}C_6H_4{\cdot}N{:}CCl_2$ and EtOH (reflux) give p-*tolyl*-, m.p. 51°, or p-*nitrophenyl-urethane*, m.p. 127°, respectively, in excellent yield, whereas $NPh{:}CCl_2$ or *m*-$NO_2{\cdot}C_6H_4{\cdot}N{:}CCl_2$ yields the respective urethane and NH_2Ph,HCl or *m*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$,HCl, respectively. *m*- or *o*-$C_6H_4Me{\cdot}N{:}CCl_2$ affords the respective urethane and a *hydrochloride*, $C_{20}H_{22}O_2N_2$,HCl, m.p. 270°, or a *substance* (contains N and Cl), m.p. 108°, respectively. $NPh{:}CCl_2$ and PhOH at 150° give *Ph phenylimidocarbonate*, m.p. 136°, and similarly prepared are p-*tolyl phenyl*-, m.p. 110°, *Ph* p-*tolyl*-, m.p. 108°, p-*tolyl* o-*tolyl*-, m.p. 115°, *Ph* p-*bromophenyl*-, m.p. 154°, *Ph* p-*nitrophenyl*-, m.p. 165°, and p-*chlorophenyl* p-*nitrophenyl-imidocarbonate*, m.p. 185°. Interaction of $NPh{:}CCl_2$ with C_6H_6–$AlCl_3$ gives NHPhBz, probably through $NPh{:}CPh{\cdot}OH$. A. T. P.

δ-Substituted semicarbazides. II. Semicarbazones of aldehydes and ketones. R. Barré and L. Piché (*Canad. J. Res.*, 1942, **20, B**, 17—20; cf. A., 1942, II, 88).—δ-*p*-Nitrophenylsemicarbazones are most suitable for determination of aldehydes and ketones, being very rapidly and quantitatively pptd. The following are described: δ-p-*nitrophenyl*-, m.p. 191° (*hydrochloride*, m.p. 215°), δ-2 : 4-*dinitrophenyl*-, m.p. 178°, δ-p-*nitrobenzyl*-, m.p. 164° (*hydrochloride*, m.p. 195—197°), δ-*p*-xenyl- (*hydrochloride*, m.p. 308°), and δ-4′-*nitroxenyl-semicarbazide*, m.p. 178° (*hydrochloride*, m.p. 219°); *glucose*-δ-*phenyl*-, m.p. 161°, -δ-p-*bromophenyl*-, m.p. 168°, *-benzyl*-, m.p. 115°, -p-*xenyl*- (**I**), m.p. 194°, *-nitroxenyl*-, m.p. 172°, and *-xanthyl*- (**II**), m.p. 183°, *-semicarbazone*; *acetone*-2 : 4-*dinitrophenyl*-, m.p. 248°, -p-*nitrobenzyl*-, m.p. 162°, -p-*xenyl*- (**III**), m.p. 228°, and *-nitroxenyl*-, m.p. 261°, *-semicarbazone*; *acetone*-, m.p. 264°, *benzaldehyde*-, m.p. 235—236°, m-*nitrobenzaldehyde*-, m.p. 276°, *vanillin*-, m.p. 261°, *glyoxylic acid*-, m.p. 249°, *pyruvic acid*-, m.p. 261°, and *glucose*-, m.p. 192—193°, -δ-p-*nitrophenylsemicarbazone*. Solubilities of the named and other $COMe_2$ and glucose derivatives are recorded: those of (**I**), (**II**), and (**III**) are very low, but the compounds form gels and it is difficult to dehydrate them. R. S. C.

Direct introduction of the amino- and substituted amino-groups into the aromatic and heterocyclic nucleus. VI. Action of alkali diphenylamides on aromatic nitro-compounds. F. W. Bergstrom, I. M. Granara, and V. Erickson (*J. Org. Chem.*, 1942, **7**, 98—102). —$PhNO_2$ reacts fairly readily with a solution of $NaNPh_2$ or $KNPh_2$ in liquid NH_3 at −33°, giving $NPh_2{\cdot}C_6H_4{\cdot}NO_2$-*p*, m.p. 141·4—142·6°, optimum yields (45%) being secured with an excess of $PhNO_2$. Reaction occurs also in Et_2O but is much less complete in C_6H_6. In liquid NH_3 at room temp. an unidentified product, m.p. 201—212·5°, is also obtained and this is the sole isolable product when an excess of $KNPh_2$ is used under these conditions. $Ba(NPh_2)_2$ resembles $NaNPh_2$ in its action. $NHPh{\cdot}C_6H_4{\cdot}NO_2$-*p*, m.p. 132·5—133·5°, and large amounts of tar result from KNHPh and $PhNO_2$ in liquid NH_3 at −33° whereas an unidentified material, m.p. 157—158°, is derived from KNHPh, $PhNO_2$, and KNO_3 at room temp. *o*-$C_6H_4Me{\cdot}NO_2$ and $NaNPh_2$ give, among other products, (*o*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot})_2$, m.p. 120—121°. Similarly, *p*-$C_6H_4Me{\cdot}NO_2$ gives (*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot})_2$, m.p. 177·5—179°, in very poor yield. $NaNPh_2$ and *m*-$C_6H_4Me{\cdot}NO_2$ in liquid NH_3 at −33° give (?) 4-nitro-2-methyltriphenylamine, m.p. 129·5—130·5°. Definite compounds could not be obtained from $NaNPh_2$ and *o*-$NO_2{\cdot}C_6H_4{\cdot}OMe$ or 1-$C_{10}H_7{\cdot}NO_2$. H. W.

Identification of aromatic sulphonic acids containing an amino-group. C. F. H. Allen and G. F. Frame (*J. Org. Chem.*, 1942, **7**, 15—18).—The customary methods of identifying sulphonic acids are not applicable to those containing NH_2 on account of the sensitiveness of this group towards PCl_5 and its tendency to inner salt formation. If, however, the NH_2 is diazotised and replaced by Cl the resulting Cl-acid is readily transformed into a cryst. sulphonamide. The method is applicable to amino-mono- and -di-sulphonic acids in the C_6H_6 series and to monosulphonic acids in the $C_{10}H_8$ series. (The m.p. of chlorosulphonamides derived from the commoner aminosulphonic acids are tabulated.) In the case of disulphonic acids of the $C_{10}H_8$ series the steps are satisfactory only as far as the formation of the disulphonyl chloride by reason of the high m.p. of the disulphonamides. The disulphonyl chlorides are all solids of convenient m.p. but they do not generally crystallise well and are not suited to qual. org. analysis; 2 : 3 : 6-$C_{10}H_5Cl(SO_2Cl)_2$, m.p. 165°, is exceptional. The corresponding disulphonanilides have suitable m.p. and are readily made. 1 : 4 : 8-, 2 : 3 : 6-, 2 : 4 : 8-, 2 : 5 : 7-, and 2 : 6 : 8-$C_{10}H_5Cl(SO_2{\cdot}NHPh)_2$ have m.p. 233°, 185°, 235°, 206°, and 192°, respectively. 1-*Chloronaphthalene*-3 : 6 : 8-*trisulphonanilide*, m.p. 249°, is described. *Chlorobenzene*-2 : 5-*disulphonamide*, m.p. 229°, and 2-*chlorotoluene*-5-*sulphonamide*, m.p. 131°, are new. H. W.

Interaction of chloramine-*T* and hydrogen sulphide, phosphine, and arsine.—See A., 1942, I, 181.

Structure of N^4-*d*-glucosidosulphanilamide.—See A., 1942, II, 166.

Acid salts of *p*-aminobenzenesulphonylguanidine.—See B., 1942, III, 86.

***p*-Acylaminobenzenesulphonylguanidine.**—See B., 1942, II, 142.

Manufacture of benzidine, tolidine, and dianisidine.—See B., 1942, II, 95.

Kinetic considerations of the thermal decomposition of benzenediazonium chloride in various solvents.—See A., 1942, I, 147.

Direct diazotisation of nitrobenzene. F. W. Bergstrom and J. S. Buehler (*J. Amer. Chem. Soc.*, 1942, **64**, 19—21).—$PhNO_2$ evolves N_2 when treated with $NaNH_2$ or KNH_2 in liquid NH_3 or with $Ca(NH_2)_2$ alone, but products (after hydrolysis) are tars. Addition of $PhNO_2$ to β-$C_{10}H_7{\cdot}OH$ (**I**) and an excess of $NaNH_2$ or KNH_2 in liquid NH_3 gives N_2 and, after hydrolysis, 13—30% of 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}N_2Ph$; O←$NPh(NH_2){\cdot}ONa$ and thence $NPh{:}N{\cdot}ONa$ are probable intermediates. Na benzene*iso*diazotate does not thus react with (**I**)–$NaNH_2$. Some, but not all, other NO_2-compounds evolve N_2 with (**I**)–$NaNH_2$, but the products were not obtained cryst. R. S. C.

Stable diazo-compounds.—See B., 1942, II, 143.

Preparation of tri-*m*-nitrophenyl orthoformate. M. Calvin and J. R. Segesser (*J. Amer. Chem. Soc.*, 1942, **64**, 186).—*m*-$NO_2{\cdot}C_6H_4{\cdot}OH$ and $CCl_3{\cdot}CO_2H$ in conc., aq. KOH at 90° give a small amount of *tri*-m-*nitrophenyl orthoformate*, m.p. 182—183°. R. S. C.

Preparation of aryl acetoacetates.—See B., 1942, II, 95.

Influence of hydroxyl-ion concentration on the autoxidation of quinol.—See A., 1942, I, 176.

Behaviour of rhenium and of the complex thiocyanates of rhenium and molybdenum with toluene-3 : 4-dithiol.—See A., 1942, I, 181.

Course of autoxidation reactions in polyisoprenes and allied compounds. I. Structure and reactive tendencies of the peroxides of simple olefines. E. H. Farmer and A. Sundralingam (*J.C.S.*, 1942, 121—139).—*cyclo*Hexene with O_2 at 30—40° in light from a Hg-vapour lamp for 2—4 hr. yields 30—40% of oxygenated material containing 80% of Δ²-*cyclo*hexenyl H peroxide (**I**), with some Δ²-*cyclo*hexenol (**II**) and *cyclo*hexene epoxide (**III**) [isolated by reduction (Na_2SO_3) of the product immediately the O_2 intake ceases, and fractionation]. Fractionation of the oxidation product at 1 atm. yields some *trans-cyclo*hexane-1 : 2-diol. (**I**) at 70—80° gives chiefly (**II**), with a small amount of " dimeride," approx. $C_6H_{10}O_2$, but no (**III**), and with ultra-violet light at 35° followed by hydrogenation (PtO_2, EtOH) yields *cyclo*hexanol and " dimeric " material, b.p. 110—176°/0·5 mm. (**I**) with *cyclo*hexene yields (**II**), a small amount of (**III**), and polymeric material. (**I**) with N-H_2SO_4 at 40—45° during 1 week gives *cyclo*hexane-1 : 2 : 3-triol, a " dimeric " acidic residue, and small amounts of (**II**) and *cyclo*pentenealdehyde [? from a secondary product in (**I**)]. With H_2O at 110° the same products are formed in different proportions. Hock's observations (A., 1938, II, 360) on the action of dil. NaOH on (**I**) are confirmed. 1-Methyl*cyclo*hexene with O_2 at 35° similarly yields methyl*cyclo*hexenol, 1-methyl*cyclo*hexene-1 : 2-epoxide [hydrolysed (H_2SO_4) to the *trans*-1 : 2-diol], and 2(with some 3)-*methyl*-Δ²-cyclo*hexenyl H peroxide* (**IV**), b.p. 64—67°/0·2 mm. (**IV**) is reduced (Na_2SO_3) to 2(+3)-*methyl*-Δ²-cyclo*hexenol* (*A*) [3 : 5-dinitrobenzoate, an oil (α-$C_{10}H_7{\cdot}NH_2$ *complex*, m.p. 95—96°)], or (H_2, PtO_2, EtOH) to impure 2-methyl*cyclo*hexanol. (**IV**) with N-H_2SO_4 at 45° yields 1-*methyl*-cyclo*hexane*-1 : 2 : 3-*triol*, b.p. 152—154°/1 mm., m.p. 95° (40—50% yield), 1-acetyl*cyclo*pentene (5%), and crude (*A*), but no other CO-compound. (**IV**) with dil. NaOH at room temp., then at 30°, yields (*A*), and small amounts of Ac·$[CH_2]_3{\cdot}CO_2H$ and an *acid*, $C_7H_{10}O_2$, m.p. 207°, unaffected by H_2 (PtO_2), but oxidised ($KMnO_4$) to an acid, (?) $C_7H_{12}O_6$, m.p. 69°. 1 : 2-Dimethyl*cyclo*hexene with O_2 at 23° yields 2 : 3-*dimethyl*-Δ²-cyclo*hexenyl H peroxide* (**V**), b.p. 67—70°/0·5 mm., the 1 : 2-epoxide (hydrolysed to the *trans*-1 : 2-diol), and 2 : 3-*dimethyl*-Δ²-cyclo*hexenol* (**VI**), b.p. 80—82°/13 mm. (α-*naphthylurethane*, m.p. 139—140°), oxidised (CrO_3) to the ketone. With N-H_2SO_4 at 45°, (**V**) yields 1 : 2-*dimethyl*cyclo*hexane*-1 : 2 : 3-*triol*, m.p. 109°, impure (**VI**), some polymeric material, and 2-acetyl-1-methyl-Δ¹-*cyclo*pentene. (**V**) with dil. NaOH at room temp., then at 30—40°, yields (**VI**), Ac·$[CH_2]_3{\cdot}CO_2H$, and an acid, m.p. 196—197°. With Fe^{II} phthalocyanine, (**I**) rapidly decomposes to (**II**), Δ²-*cyclo*hexenone, *cyclo*pentene-1-aldehyde, etc.; (**IV**) yields (*A*) and the corresponding ketones etc., and (**V**) yields (**VI**), the corresponding ketone, a little $(CH_2{\cdot}CH_2Ac)_2$, etc. The " dimeric " products formed with (**I**), (**IV**), and (**V**) contain neutral H_2O-insol., neutral H_2O-sol., and acidic H_2O-sol. material, mostly unsaponifi-

able. The mechanism of autoxidation and reactions of the H peroxides are discussed. A. Li.

Bimolecular reduction of hindered aldehydes. R. C. Fuson, E. C. Horning, M. L. Ward, S. P. Rowland, and J. L. Marsh (*J. Amer. Chem. Soc.*, 1942, **64**, 30—33).—When RCHO is reduced by Mg + MgI_2, the primary product, $(rCHR{\cdot}O{\cdot}MgI)_2$, is oxidised by R′CHO (R = R′ = Ph) to COPh·CHPh·O·MgI, which gives benzoin. This oxidation does not occur if R or R′ is sterically hindered and the products are then $(CHR{\cdot}OH)_2$. Thus, mesitaldehyde [prep. from *s*-$C_6H_3Me_3$ in 82·5% yield by HCl–$Zn(CN)_2$–$AlCl_3$ in $(CHCl_2)_2$ at 70°] (67 g.), m.p. 10·5°, b.p. 124—128°/15 mm., with Mg + MgI_2 in boiling C_6H_6–Et_2O gives *hydromesitoin* (13 g.), m.p. 214—215° (*diacetate*, m.p. 181—182°; also obtained from mesitoin by H_2–Cu chromite in EtOH at 125°/2300 lb.), iso*hydromesitoin* (36 g.), m.p. 160—161° [*diacetate*, m.p. 124—125°; hydrogenated (Cu chromite; abs. EtOH; 250°/2000 lb.) to (2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CH_2)_2$], and *αβ-dimesitylethylene* (1·2 g.), m.p. 132—133°. 2 : 4 : 6-*Triethylbenzaldehyde*, b.p. 146—149°/21 mm. (oxidised by air to the known acid; 2 : 4-*dinitrophenylhydrazone*, m.p. 180—181°; *semicarbazone*, m.p. 155—156°), is obtained as above in 75% yield. 2 : 4 : 6-*Tri*iso*propylbenzaldehyde* (**I**) (prep. as above; 65% yield), b.p. 123—125°/4 mm. (*semicarbazone*, m.p. 150—151°), with Mg + MgI_2 gives 2 : 4 : 6 : 2′ : 4′ : 6′-*tri*iso*propyl-hydrobenzoin* (**II**), m.p. 285—286° (*diacetate*, m.p. 201—202°), -iso*hydrobenzoin* (**III**), m.p. 186—187° (*diacetate*, m.p. 160—161°), and -*stilbene*, m.p. 147—148°. Hydrogenation (Cu chromite; EtOH; 250°/6000 lb.) of (**II**) or (**III**) gives *αβ-di*-2 : 4 : 6-*tri*iso*propylphenylethane* (**IV**), m.p. 160—161° (3 : 3′-Br_2-compound, m.p. 199—200°, prepared by Br–$CHCl_3$). *s*-$C_6H_3Pr^{\beta}_3$ with $CH_2Cl{\cdot}OMe$ and $SnCl_4$ in CS_2 at 0° gives 2 : 4 : 6-*tri*iso*propylbenzyl chloride* (85%), b.p. 129—130°/4 mm., which with MgMeI–Et_2O yields (**IV**). 2 : 3-*Dimethyl*-1-*naphthaldehyde* [*guaialdehyde*] (**V**) (prep. from 2 : 3-$C_{10}H_6Me_2$ as above in 38% yield with other aldehydes), m.p. 77·5—78·5°, b.p. 165—168°/4 mm. [*semicarbazone*, m.p. 265° (decomp.)], with Mg + MgI_2 gives *αβ-di*-2 : 3-*dimethyl*-1-*naphthylethylene glycol* (**VI**), m.p. 162—163·5° (*diacetate*, m.p. 198—199°), and an *isomeride*, m.p. 274—275·5° (*diacetate*, m.p. 290—293°), thereof. With H_2–Raney Ni in EtOH at 150°/1400 lb., followed by Pd–C at 250° on the product, (**V**) gives 1 : 2 : 3-$C_{10}H_5Me_3$, with H_2O_2–AcOH gives 1 : 2 : 3 : 4-O:$C_{10}H_4Me_2$:O [obtained similarly, but impure, from (**VI**)], and with $Al(OPr^{\beta})_3$ in C_6H_6 gives 2 : 3-*dimethyl*-1-*hydroxymethylnaphthalene* [*guaiylcarbinol*], m.p. 114—115°. R. S. C.

Cyclisation of dieninenes. XIII. Methoxy*cyclo*hexenylacetylene derivatives. C. S. Marvel and W. L. Walton (*J. Org. Chem.*, 1942, **7**, 88—97; cf. A., 1941, II, 357).—4-Methoxy*cyclo*hexanone (**I**), b.p. 84—85°/14 mm. (semicarbazone, m.p. 175—176·5°; 2 : 4-dinitrophenylhydrazone, m.p. 150°), is condensed with C_2H_2 in presence of K *tert.*-amyloxide to 4-*methoxy*-1-*acetylenyl*cyclo*hexanol* (**II**), b.p. 121—122°/20 mm. (p-*nitrobenzoate*, m.p. 74·5—75·5°; 3 : 5-*dinitrobenzoate*, m.p. 112—114°), accompanied by (?) 4 : 4′-*dimethoxy*-2-cyclo*hexylidene*cyclo*hexanone*, b.p. 155°/4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 154—155°). (**II**) is reduced (H_2–PtO_2–EtOH) to 4-*methoxy*-1-*ethyl*cyclo*hexanol*, b.p. 114—116°/22 mm. (3 : 5-*dinitrobenzoate*, m.p. 117·5—118°), stereoisomeric with the *alcohol*, b.p. 114—122°/22 mm. (3 : 5-*dinitrobenzoate*, m.p. 117—118°), prepared from (**I**) and MgEtBr. (**II**) is rearranged by conc. H_2SO_4 at room temp. to a ketone (2 : 4-*dinitrophenylhydrazone*, m.p. 163—164°). Treatment of 1-acetylenyl*cyclo*hexanol with MgEtBr and then with (**I**) leads to *αβ*-1 : 1′-*dihydroxy*-4-*methoxydi*cyclo*hexylacetylene* (**III**), *cis–trans* isomerides, b.p. 110°/10^{-5} mm. (3 : 5-*dinitrobenzoate*, m.p. 166—167°), and m.p. 60—62° (3 : 5-*dinitrobenzoate*, m.p. 131—132°). Similar condensation of (**II**) with *cyclo*pentanone gives an (impure) *glycol* (**IV**), b.p. 110°/10^{-5} mm.; an analogous compound (**V**) is obtained from 2-methyl*cyclo*pentanone and a *glycol*, b.p. 110°/10^{-5} mm., from (**I**). Treatment of (**III**), (**IV**), and (**V**) with H_2SO_4 affords respectively Δ1′-cyclo*hexenyl*-, b.p. 135—135·5°/2 mm., Δ1′-cyclo*pentenyl*-, b.p. 174—175°/19 mm., and Δ1′-2-*methyl*cyclo*pentenyl*-, b.p. 137—139°/3 mm., -Δ1-4-*methoxy*cyclo*hexenylacetylene*. The separation of (**III**) into its two components does not simplify the problem of separating the products obtained by the cyclisation reaction. This is evidence that the first step is dehydration which converts either isomeride into the same acetylene. Attempts to dehydrate (**III**) directly give a mixture of cyclic ketones and other products. This mixture is reduced (PtO_2–H_2) and then treated with 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ to give a mixture of cryst. 2 : 4-*dinitrophenylhydrazones*. Two of these, m.p. 190—191° and 173—174°, give analytical data as required by derivatives of the expected cyclic ketone but it is uncertain whether they are stereoisomerides of the phenanthrone or whether one is a phenanthrone and the other a spiranone. The third compound, m.p. 227—228°, is dodecahydrophenanthrone-2 : 4-dinitrophenylhydrazone, proving loss of OMe as MeOH and reduction of the double linking thus developed. When the conditions of cyclisation are made more drastic, the amount of the unsubstituted ketone derivative increases at the expense of one of the methoxylated substances. Loss of OMe occurs after cyclisation since its loss at the acetylene stage would result in the formation of a dihydrobenzene derivative and thence a benzenoid mol. which does not cyclise. Dehydrogenation of the mixed ketones over Pd–C at 330° gives phenanthrene, 3-methoxyphenanthrene, and, apparently, anthracene and a methoxyanthracene. The isolation of the two hydrocarbons is an indication that at least one of the cyclisation products may be a spiran. Oxidation of 3-methoxy-*cyclo*hexanol with H_2SO_4 and $Na_2Cr_2O_7$ at 65—70° gives only Δ2-*cyclo*hexenone, b.p. 63°/14 mm. (semicarbazone, m.p. 160—161°; 2 : 4-*dinitrophenylhydrazone*, m.p. 165—166° from EtOH or 167·5—168° from EtOAc). Δ1-*cyclo*Hexenylacetophenone (2 : 4-*dinitrophenylhydrazone*, m.p. 163—164°) is not affected by cold AcOH–H_2SO_4 or by hot AcOH containing a little H_2SO_4 and is hydrolysed to COPhMe by fairly conc. aq. H_2SO_4. H. W.

Organic sulphur compounds. XXVII. Relation between the constitution of thioethers and thiols and their sensitivity towards alkali. A. Schönberg and Y. Iskander (*J.C.S.*, 1942, 90—95).—p-*Nitrobenzylthiolacetic acid*, m.p. 114°, obtained from $SH{\cdot}CH_2{\cdot}CO_2H$–*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$ in aq. EtOH–$NaHCO_3$ (reflux), is hydrolysed by boiling 5% aq. NaOH for 5 min., through (probably) $ONa{\cdot}NO{:}C_6H_4{:}CH{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, to *p*-azobenzaldehyde (**I**). Similarly prepared is *β*-p-*nitrobenzylthiolpropionic acid*, m.p. 104—105°, hydrolysed to *p*-azoxybenzaldehyde and $(CO_2H{\cdot}[CH_2]_2{\cdot}S{\cdot})_2$ (**II**), with a trace of (**I**). *p*-$NO_2{\cdot}C_6H_4{\cdot}CPh_2Cl$ and $SH{\cdot}CH_2{\cdot}CO_2H$–PhMe give p-*nitrotriphenylmethylthiolacetic acid*, m.p. 153—155°, hydrolysed by 5% aq. NaOH to *p*-$NO_2{\cdot}C_6H_4{\cdot}CHPh_2$ (**III**) [probably through $OH{\cdot}NO(ONa){\cdot}C_6H_4{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H \rightarrow ONa{\cdot}S{\cdot}CH_2{\cdot}CO_2H$ + $OH{\cdot}NO{:}C_6H_4{:}CPh_2 \rightarrow$ (**III**)]. p-*Aminobenzylthiolacetic acid*, m.p. 155—156°, prepared from the NO_2-compound by Sn–HCl, is unchanged after boiling with 5% aq. NaOH for 20 min.; $CH_2Ph{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, $CH_2Ph{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2H$, new m.p. 82—83°, and $CPh_3{\cdot}S{\cdot}CH_2{\cdot}CO_2H$ are affected only slightly or not at all by boiling 5% aq. NaOH. COPh·CHPhCl (**IV**) and NaSH–EtOH at 0° yield *didesyl sulphide*, $(COPh{\cdot}CHPh)_2S$ (**V**), m.p. 168—169° and 128—129° (probably *r*- and *meso*-forms), and *desylthiol*, COPh·CHPh·SH (**VI**), m.p. 42—44° [hydrolysed by 10% aq. NaOH–EtOH to $COPh{\cdot}CH_2Ph$ (**VII**)]. (**IV**)–BzSH–EtOH, or (**VI**)–BzCl–C_5H_5N, afford *desyl thiobenzoate*, m.p. 110—112°, hydrolysed to (**VII**), BzOH, H_2S, and S. (**V**) (either form) also gives (**VII**), with some $OH{\cdot}CPh_2{\cdot}CO_2H$. (**IV**) and $SH{\cdot}[CH_2]_2{\cdot}CO_2H$ at 100° (bath) yield (**II**) and *β-desylthiolpropionic acid*, m.p. 108—109°. Alkaline hydrolysis of the latter is slower than with desylthiolacetic acid, which readily affords (**VII**). (**IV**)–PhSH–NaOEt give COPh·CHPh·SPh, new m.p. 83—84°, only partly decomposed by boiling aq. NaOH–EtOH to PhSH. $COPh{\cdot}CPh_2Cl$ (**VIII**)–BzSK–EtOH afford *α-benzoylbenzhydryl thiobenzoate*, m.p. 129—130°, converted by 10% aq. NaOH–EtOH into *α-benzoylbenzhydrylthiol*, m.p. 98—101° (aq. $FeCl_3$–AcOH gives the corresponding *disulphide*, m.p. 150—154°). (**VIII**) and $SH{\cdot}CH_2{\cdot}CO_2H$ or $SH{\cdot}[CH_2]_2{\cdot}CO_2H$ at 100° (bath) yield $COPh{\cdot}CHPh_2$ and $COPh{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, or (**II**) and *β-(benzoylbenzhydrylthiol)propionic acid*, m.p. 134—136°, respectively; hydrolysis of the respective acid by boiling 7% aq. NaOH yields benzhydrylthiolacetic acid, m.p. 128° (cf. Behaghel *et al.*, A., 1939, II, 374), and *β-(benzhydrylthiol)propionic acid*, m.p. 89—90°. (**VIII**) and PhSH–PhMe (boil) afford *Ph α-benzoylbenzhydryl sulphide*, m.p. 119°, converted by 10% aq. NaOH–EtOH into $CHPh_2{\cdot}SPh$. Mechanisms of the various hydrolysis reactions are discussed. There is no general parallelism between thermolability of thioethers and their sensitivity to alkali, *e.g.*, (**V**) is thermolabile (forms a blue thiobenzil) and is also sensitive to alkali, whilst the thermolabile $CPh_3{\cdot}SPh$ is very stable to alkali. A. T. P.

Vapour-phase esterification of benzoic acid with ethyl alcohol. Effect of oxides on the catalytic activity of silicon carbide and alundum.—See A., 1942, I, 150.

Mechanism of "aromatising" diene reactions in nitrobenzene. F. Bergmann (*J. Amer. Chem. Soc.*, 1942, **64**, 176—177).—Aromatisation during diene reactions can occur when dienolisation is possible. Thus, di*cyclo*hexenyl with $(:CH{\cdot}CO)_2O$ in boiling $PhNO_2$ gives 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene-9 : 10-dicarboxylic anhydride (**I**), m.p. 305°, but with $CHMe{:}CH{\cdot}CO_2H$ or $CHPh{:}CH{\cdot}CO_2H$ gives 9-*methyl*-, m.p. 164°, and 9-phenyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 14-dodecahydrophenanthrene-10-carboxylic acid, respectively. In boiling $PhNO_2$ 3 : 6-diphenyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride gives 3 : 6 : 1 : 2-$C_6H_2Ph_2(CO)_2O$ and in $PhNO_2$ at 170—175° 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 14-dodecahydrophenanthrene-9 : 10-dicarboxylic anhydride gives (**I**), but anthracene*endo*succinic anhydride is unchanged. *meso*-$(CHPh{\cdot}CO_2H)_2$ in hot $PhNO_2$ gives $(:CHPh{\cdot}CO)_2O$, and benzoin gives benzil. *p*-$C_6H_4Br{\cdot}NO_2$, *p*-$C_6H_4Cl{\cdot}NO_2$, or *m*-$C_6H_4(NO_2)_2$ does not cause aromatisation. R. S. C.

Chemotherapeutic comparison of the trypanocidal action of aromatic diamidines. J. N. Ashley, H. J. Barber, A. J. Ewins, G. Newbery, and A. D. H. Self (*J.C.S.*, 1942, 103—116).—Amidines are best obtained by saturating with HCl a solution of the nitrile in EtOH (2·5—3 mols.) and, for sparingly sol. aromatic nitriles, an inert diluent ($CHCl_3$, C_6H_6, $PhNO_2$, or an excess of EtOH) at 0—5°, keeping for 5—7 days at room temp., and treatment of the resulting OEt·CR:NH,HCl (*A*) with 10% NH_3–abs. EtOH. Reaction occurs between OEt·CR:NH and NH_3, but 10 mols. of NH_3 are required

to suppress the decomp., (*A*) + 2EtOH → NH_4Cl + $CR(OEt)_3$. The following are thus prepared: p-*aminophenylacetamidine dihydrochloride*, m.p. 270°; p-*amidinomethylbenzamidine dihydrochloride*, m.p. 280—285° (decomp.); 4 : 4′-diamidino-, *-dimethylamidino-*, *-di-N-diethylamidino-*, *-di-N-phenylamidino-*, and *-diamidinomethyl-diphenyl dihydrochloride*; 4 : 4′-diamidinodiphenylmethane dihydrochloride, -ethane dihydrochloride, +0·5H_2O, and *-propane dihydrochloride*; 4 : 4′-*diamidino-triphenylmethane dihydrochloride*, *-methyldiphenyl dihydrochloride*, *-benzophenone dihydrochloride*, m.p. 300°, *-benzhydrol dihydrochloride*, m.p. 212°, *-benzylideneacetophenone dihydrochloride*, *-deoxybenzoin dihydrochloride*, +1·5H_2O, m.p. 280—282°, -diphenyl ether, m.p. 215—216° (*dihydrochloride*, +2H_2O), *-diphenyl sulphide*, m.p. 209—210° (decomp.), *-diphenylsulphone dihydrochloride*, m.p. 290° (decomp.), -benzylaniline dihydrochloride, +H_2O, m.p. 296°, -dibenzylamine trihydrochloride, *-dibenzyl ether*, m.p. 195° (decomp.) (*dihydrochloride*, +H_2O), -dibenzyl sulphide, m.p. 198—199° (decomp.), *-diphenoxymethane dihydrochloride*, m.p. 249° (decomp.), *-αβ*-diphenoxyethane, m.p. 234—235° (decomp.) (*dihydrochloride*, +H_2O, m.p. 297°), *-αγ*-diphenoxypropane dihydrochloride, m.p. (+H_2O) 292° or (anhyd.) 300°, *-αδ-diphenoxybutane dihydrochloride*, +2H_2O, m.p. 259—261°, *-αε*-diphenoxy-*n*-pentane, m.p. 186° (decomp.) [*dihydrochloride*, +2H_2O, m.p. 233—234° (decomp.); *dimethanesulphonate*], *-αζ-diphenoxy-n-hexane dihydrochloride*, +2H_2O, m.p. 246—247° (decomp.), *-αη-diphenoxy-n-heptane*, m.p. 175—177° (decomp.) [*dihydrochloride*, +2H_2O, m.p. 245—246° (decomp.)] *-aκ*-diphenoxy-*n*-decane dihydrochloride, m.p. 254°, *-azobenzene dihydrochloride*, +H_2O, m.p. >300°, *-benzanilide*, m.p. 245—250° (decomp.), *-benzenesulphonanilide dihydrochloride*, +4H_2O, m.p. 239°, *-β*-phenoxyethylaniline, m.p. 204° (decomp.) (dihydrochloride, +2H_2O, m.p. 296—297°), *-diphenyl disulphide dihydrochloride*, +2H_2O, m.p. >300°, *-diphenylcarbamide dimethanesulphonate*, +H_2O, and *-αδ-diphenylbutadiene dihydrochloride*; *di*-(p-*amidinophenylmethyl*) *ether*, m.p. indefinite (*dihydrochloride*); *4-amidino-2′-cyanodiphenyl*, m.p. 160—161°; 3 : 4′-, m.p. 300°, and 4 : 4′-diamidinostilbene dihydrochloride, +2H_2O, m.p. 300°, and anhyd. (corresponding *dimethanesulphonate*); *4-nitro-*, m.p. 300°, reduced by $SnCl_2$–aq. HCl–AcOH to *4-amino-4′-amidinostilbene dihydrochloride*, m.p. 300°; *4-amidinodiphenyl ether*, m.p. 126—127°; *p*-amidinophenyl *p*-amidinobenzyl ether, m.p. 232—233° (*dihydrochloride*); m-*amidinophenyl* p-*amidinobenzyl ether dihydrochloride*, +0·5H_2O; p-*amidinomethylphenyl* p-*amidinobenzyl ether*, m.p. 182°; p-*amidinophenyl β*-p-*amidinophenylethyl ether dihydrochloride*, +H_2O; *αγ-di*-m-*amidinophenoxypropane dihydrochloride*, m.p. 202—204° (decomp.); *αε-di*-m-*amidinophenoxy-n-pentane dihydrochloride*, +2H_2O; *ωω′-di*-p-*amidinophenoxyxylene dihydrochloride*, +H_2O; and p-*di*-p′-*amidinobenzyloxybenzene dihydrochloride*, +2H_2O. Yields of dinitriles obtained by the Sandmeyer reaction are much improved by sublimation of the crude product at 0·1—1 mm. (apparatus described). Thus are prepared 4 : 4′-*dicyano-triphenylmethane* (5%), m.p. 134—145°, *-benzophenone* (**I**) (60%), m.p. 162° (lit. 204°) (*phenylhydrazone*, m.p. 242—243°), *-benzhydrol* [prep. from (**I**) by Al–Hg in EtOH–NH_3], m.p. 158—159°, *-stilbene* (**II**) (45%), m.p. 282°, *-azobenzene* (45%), m.p. 270°, and *-diphenyl sulphide*, m.p. 133—134°. The di-(imino-ether) from (**II**) with NHPh·NH_2 in abs. EtOH at 50° gives *αβ-di-*(p-*phenylbenzamidrazino*)*ethylene*, m.p. 261—262° (decomp.) (*dihydrochloride*, m.p. >300°). 3 : 4′-Diaminostilbene, m.p. 153°, is obtained from the $(NO_2)_2$-compound by $SnCl_2$–AcOH–aq. HCl, and converted (Sandmeyer) into 3 : 4′-*dicyanostilbene* (26%), m.p. 137—138°. Addition of Ac_2O to *p*-NO_2·C_6H_4·CH_2·CO_2Na and *p*-NO_2·C_6H_4·CH:CH·CHO at 140—150° and heating at 150° and then with more Ac_2O at 160° gives *αδ-di*-p-*nitrophenyl*-$\Delta^{\alpha\gamma}$-*pentadienoic acid*, m.p. 295—300°, reduced by $SnCl_2$–aq. HCl–AcOH to the $(NH_2)_2$-acid, which yields (Sandmeyer) *αδ-di*-p-*cyanophenylbutadiene*, m.p. 260—261° (decomp.). *4-Cyanostilbene*, m.p. 114°, is prepared (Sandmeyer) in 16% yield. *p*-NO_2·C_6H_4·CH_2·CO_2H and *p*-NHAc·C_6H_4·CHO in piperidine at 160° give *4-nitro-4′-acetamido-*, m.p. 255°, hydrolysed (aq. EtOH–HCl) to 4-nitro-4′-amino-, m.p. 245° (lit. 229—230°), which affords *4-nitro-4′-cyano-stilbene* (31%), m.p. 247—249°. $(CH_2$·C_6H_4·CH:N·OH-*p*$)_2$ in boiling Ac_2O gives 70% of (*p*-CN·C_6H_4·$CH_2$$)_2$, other methods giving poor yields. (*p*-NH_2·C_6H_4·N:$)_2$, m.p. 245—246°, is best obtained by reducing the $(NO_2)_2$-compound by Na_2S in boiling aq. EtOH. Distillation of $(CH_2Ph$·$CO_2)_2Ca$ in a steel retort gives 60% of $CO(CH_2Ph)_2$, b.p. 178—182°/10—11 mm., reduced (Clemmensen) to Ph·$[CH_2]_3$·Ph (70%), b.p. 155—160°/9—10 mm., which affords successively *αγ-di*-p-*chloromethyl-*, m.p. 103—104°, *-hydroxymethyl-*, m.p. 118—122°, -aldehydo-, an oil (dioxime, m.p. 125—127°), and *-cyano-phenylpropane*, m.p. 94—95°. *p*-CN·C_6H_4·CHO (**III**), *p*-CN·C_6H_4·COMe, and a little piperidine in boiling, abs. EtOH give 4 : 4′-*dicyanobenzylideneacetophenone*, m.p. 216—217°, obtained less well by other methods and resistant to H_2–Pd. *Di*-p-*cyanophenyl ether*, m.p. 180°, is obtained in 50% yield by the Sandmeyer reaction and in 37% yield from *p*-CN·C_6H_4·ONa (**IV**), *p*-C_6H_4BrCN (**V**), and a little Cu powder at 250—270°. Heating *di*-p-*carbamylphenylsulphone* (prep. from the acid by way of the acid chloride), m.p. >300°, with P_2O_5 gives *di*-p-*cyanophenylsulphone*, m.p. 232—233°, also obtained by the Sandmeyer reaction. Boiling (**V**) with PhOH (excess) and KOH gives *Ph* p-*cyano-*, m.p. 43—45°, and p-*carbamyl-phenyl ether*, m.p. 164—165°. *p*-NH_2·C_6H_4·CN (**VI**), m.p. 82—84°, is best (80%) obtained by boiling crude *p*-NHAc·C_6H_4·CH:N·OH in Ac_2O and hydrolysing (2N-HCl) the product. The Sandmeyer reaction [$KCu(CN)_2$; 90—95°] gives 65—70% of *p*-OH·C_6H_4·CN, b.p. 148°/1 mm., which with NaOEt and then *p*-CN·C_6H_4·CH_2Cl (**VII**) in boiling EtOH gives 90% of p-*cyanophenyl* p-*cyanobenzyl ether*, m.p. 167—168°. With *m*-OH·C_6H_4·CN, *p*-OH·C_6H_4·CH_2·CN, or *p*-·$C_6H_4(OH)_2$, (**VII**) gives similarly m-*cyanophenyl*, m.p. 97—98°, *ω-cyano*-p-*tolyl* p-*cyanobenzyl ether* (and a little amide), m.p. 92°, and 1 : 4-*di*-p-*cyanobenzyloxybenzene*, m.p. 170—171°, respectively. CH_2I_2 or Br·$[CH_2]_n$·Br (*n* = >1) with (**IV**) (prep. by NaOEt– or NaOH–EtOH) in boiling, abs. EtOH gives *di*-p-*cyanophenoxymethane* (30%), m.p. 148°, *αβ-di*-p-*cyanophenoxyethane* (**VIII**) (55%), m.p. 197°, *αγ-di*-p-*cyanophenoxypropane* (83%), m.p. 188°, *αδ-di*-p-*cyanophenoxy*-n-*butane* (60%), m.p. 168—169°, *αε-di*-p-*cyanophenoxy*-n-*pentane* (78%), m.p. 114—114·5°, *αζ-di*-p-*cyanophenoxy*-n-*hexane* (70%), m.p. 147°, *αη-di*-p-*cyanophenoxy*-n-*heptane* (55%), m.p. 107°, and *aκ-di*-p-*cyanophenoxy*-n-*decane* (30%), m.p. 123°; *p*-$C_6H_4(CH_2Br)_2$ gives similarly *ωω′-di*-p-*cyanophenoxyxylene* (60%), m.p. 215—216°; a similar reaction in H_2O gives *β*-p-*cyanophenoxyethyl bromide* [45%; and a little (**VIII**)], m.p. 59°, which with (**VI**) at 130—140° gives 4 : 4′-*dicyano-β-phenoxyethylaniline* (35%), m.p. 163°. Hydrolysis of (**VII**) by aq. Na_2CO_3 gives successively 4-cyano- (**IX**), m.p. 41—42°, b.p. 203°/53 mm. (*phenylurethane*, m.p. 112—113°), and *4-carbamyl-benzyl alcohol*, m.p. 134—135° [believed by Banse (A., 1894, i, 575) to be (**IX**)], but in boiling 33% aq. KOH gives (*p*-CO_2H·C_6H_4·$CH_2$$)_2O$, m.p. 272—274° (and some *p*-OH·CH_2·C_6H_4·CO_2H), converted by PCl_5 into the diacid chloride and thence successively by aq. NH_3 into *di*-p-*carbamyl-*, m.p. 241°, and by P_2O_5 in xylene into *di*-p-*cyano-benzyl ether*, m.p. 97—98°, also obtained from (**VII**), (**IX**), and NaOEt in EtOH at 95—100°. With N_2O_4–$CHCl_3$ at 0° and later room temp., (**IX**) gives (**III**) and a little acid, but with $Cu(NO_3)_2$ gives mixtures. With KCN–EtOH–H_2O, (**III**) gives 4 : 4′-*dicyanodeoxybenzoin* (40%), m.p. 219—220°, and a little acid. p-*Cyanobenzoyl chloride* (prep. by $SOCl_2$; PCl_5 gives too much anhydride), m.p. 65°, with (**VI**) in C_5H_5N gives p-*cyanobenz-p′-cyanoanilide*, m.p. 259—261°; p-*cyanobenzenesulphon-p′-cyanoanilide*, m.p. 201—202°, is similarly prepared. Ph·$[CH_2]_2$·Br (**X**) (prep. simplified; 90% yield) and (**IV**) give p-*cyanophenyl β-phenylethyl ether* (20%), m.p. 64°, which with HNO_3–H_2SO_4 at −5° gives 3 : 4 : 1-NO_2·$C_6H_3(OH)$·CN, m.p. 143°, but with HNO_3 (*d* 1·5) at −10° to 0° gives 2-*nitro*-4-*cyanophenyl β*-(? 4-)*nitrophenylethyl ether*, m.p. 185—186°, hydrolysed by conc. H_2SO_4 at 90° to 3 : 4 : 1-NO_2·$C_6H_3(OH)$·CO_2H (42%). Only traces of ether are obtained from *p*-OH·C_6H_4·CN and *p*-NO_2·C_6H_4·$[CH_2]_2$·Br (**XI**). *β*-p-*Aminophenylethyl bromide hydrochloride*, m.p. 212—213°, is obtained from (**XI**) by H_2–PtO_2 in HCl–EtOH or by $SnCl_2$–HCl at 80—90° and gives (Sandmeyer; 20—30°; in presence of C_6H_6; 40% yield) *β*-p-*cyanophenylethyl bromide*, m.p. 53°, b.p. 135—140°/2 mm., and thence p-*cyanophenyl β*-p-*cyanophenylethyl ether* (10—12%), m.p. 129—130°. *p*-CN·C_6H_4·NHBz and PCl_5 at 120° give N-p-*cyanophenylbenziminochloride* (76%), m.p. 88—89°, b.p. 194—198°/3 mm., which with (**IV**) in Et_2O gives N-p-*cyanophenylbenzimino-p′-cyanophenyl ether* (82%), m.p. 155°, rearranged smoothly at 280—300° into *benzdi*-p-*cyanophenylamide* (**XII**), m.p. 219°. This gives *benzdi*-p-*amidinophenylamide*, +2·5H_2O, m.p. 194° (decomp.), converted, after dehydration (100—110°/1—2 mm.), at 180—200° into NH_2Bz (82%) and *di*-p-*cyanophenylamine* (76%), m.p. 240—246° [obtained by hydrolysis of (**XII**) in $(CH_2$·$OH)_2$, but not from (**V**) and (**VI**)], which yields *di*-p-*amidinophenylamine dihydrochloride*, +H_2O, or its *H sulphate*, *B*,1·5H_2SO_4. R. S. C.

Physico-chemical properties of the chromophoric groups, azomethine (·CH:N·) and azomethinevinylene (·CH:CH·CH:N·).—See A., 1942, I, 164.

Derivatives of *β-o*-anisylpropaldehyde. A. Zaki and H. Fahim (*J.C.S.*, 1942, 182).—*β-o*-Anisylpropaldehyde (prep. from the acid chloride by H_2–Pd in xylene) gives a $NaHSO_3$ compound, m.p. 163—164°, and a p-*nitrophenylhydrazone*, m.p. 126—127°. F. R. S.

Catalytic action of Japanese acid earth. XI. Isomerisation of aldehydes to ketones and the explanation of migration of radicals on the electronic viewpoint (continued). K. Ishimura (*Bull. Chem. Soc. Japan*, 1941, **16**, 252—262; cf. A., 1942, II, 55).—*p*-C_6H_4Me·MgI–CH_2Bz·OH–Et_2O afford di-*p*-tolyl, *p*-C_6H_4MeI, PhMe, and *α-phenyl-α*-p-*tolylethylene glycol* (**I**), m.p. 84·5—85·5° [*monobenzoate*, m.p. 136° (corr.)], oxidised by CrO_3–AcOH to *p*-C_6H_4Me·COPh. (**I**) and dil. H_2SO_4 at 180—185° afford *p*-C_6H_4Me·CHPh·CHO, b.p. 176° (corr.)/7 mm., which, passed over Japanese acid earth at 300—350°, gives C_6H_6, PhMe, and COPh·CH_2·C_6H_4Me-*p* (*p*-C_6H_4Me·CO·CH_2Ph not formed). *p*-Toluoylcarbinol (**II**) and *m*-C_6H_4Me·MgI yield *α*-m-*tolyl-α*-p-*tolylethylene glycol*, m.p. 59—60° [*monobenzoate* (+H_2O), m.p. 173—174° (corr.; decomp.)], oxidised to *m*-tolyl *p*-tolyl ketone (**III**), m.p. 72°, or converted by aq. $H_2C_2O_4$ at 115—120° into *m-tolyl-p-tolylacetaldehyde* (**IV**), b.p. 182° (corr.)/7 mm. [*semicarbazone*, m.p. 179—180° (corr.; decomp.)]. (**IV**) and aq. $AgNO_3$–KOH–EtOH yield *m-tolyl*-p-*tolylacetic acid*, m.p. 93—94°, and (**III**). (**III**) affords isomeric oximes, m.p. 119—121° and m.p. 133—134°, and Beckmann

rearrangement (PCl_5–Et_2O) yields *p*-tolu-*m*- and *m*-tolu-*p*-toluidide, respectively. *m*-$C_6H_4Me{\cdot}CH_2{\cdot}COCl$ and PhMe–$AlCl_3$ yield p-*tolyl* m-*methylbenzyl ketone* (**V**), m.p. 68° [*semicarbazone*, m.p. 192—194° (slight decomp.); *oxime*, m.p. 108—109°]. m-*Tolyl* p-*methylbenzyl ketone* (**VI**), m.p. 40—41° (oxidised on long keeping in air to *m*- + *p*-toluic acid; *oxime*, m.p. 88·5°, rearranged to p-*tolylacet*-m-*toluidide*, m.p. 123—124°), is obtained from *p*-$C_6H_4Me{\cdot}CH_2{\cdot}CN$–*m*-$C_6H_4Me{\cdot}MgI$, or from *p*-$C_6H_4Me{\cdot}CH_2{\cdot}CHO$ (**VII**)–*m*-$C_6H_4Me{\cdot}MgI$, followed by oxidation (CrO_3–AcOH) of the carbinol. (**II**) is hydrogenated (colloidal Pt; aq. AcOH) at 22°/761 mm. to p-*tolylethylene glycol*, m.p. 76·5—77·5°, converted by very dil. HCl at 180—185° into (**VII**). m-*Tolu*-p-*methylbenzylamide* has m.p. 116°. (**IV**) passed over Japanese acid earth at 300—350°/30 mm. (CO_2) yields (**VI**), but not (**V**), *i.e.*, only the *m*-tolyl radical migrates. A. T. P.

Syntheses in the carotenoid series. III. Preparation of a methyl homologue of dehydro-β-cyclocitral. IV. Preparation of ω-phenyl- and ω-furyl-polyenealdehydes. J. Schmitt (*Annalen*, 1941, **547**, 256—270, 270—284; cf. A., 1942, II, 126).—III. *iso*Phorone and MgMeBr give 1 : 1 : 3 : 5-tetramethyl-$\Delta^{2:4}$-*cyclo*hexadiene (**I**), b.p. 155°/760 mm., 52°/20 mm., and a small amount of a *substance*, $C_{19}H_{32}O_2$, m.p. 162·5°. With $(CH{\cdot}CO)_2O$, (**I**) gives an *adduct*, m.p. 101° (derived acid, m.p. 100°), with Br gives 1 : 2 : 3 : 5 : 4 : 6-$C_6Me_4Br_2$, and with SeO_2 in aq. AcOH gives 2 : 2 : 4 : 6-tetramethyl-$\Delta^{3:5}$-*cyclo*hexadienone (**II**), b.p. 90—95°/16 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 234°), *iso*durene, and ? 2 : 2 : 4-*trimethyl*-6-*hydroxymethyl*-$\Delta^{3:5}$-cyclo*hexadienone*, b.p. 86—87°/0·3 mm. (absorption max. 258 ± 1 mμ.; gives a 2 : 4-*dinitrophenylhydrazone*, $C_{16}H_{16}O_4N_4$, m.p. 237°, and *semicarbazone*, $C_{11}H_{15}ON_3$, m.p. 206°, with loss of H_2O). With a drop of H_2SO_4 in Ac_2O, (**II**) gives a red and with $SbCl_3$–$CHCl_3$ a bluish-green colour, with $(CH{\cdot}CO)_2O$ gives an *adduct*, m.p. 152° [derived acid, m.p. 172° (decomp.) (2 : 4-dinitrophenylhydrazone, m.p. 268°)]. $CH_2Br{\cdot}CO_2Et$, (**II**), and Zn in C_6H_6 give *Et* 1 : 5- (or 1 : 3-)*epoxy*-2 : 2 : 4 : 6-*tetramethyl*-Δ^3- (or Δ^5-)cyclo*hexenylacetate*, b.p. 100—105°/0·1 mm., hydrolysed by hot KOH–MeOH to an oily acid, which, when distilled at 12 mm., decomposes to give 2 : 3 : 4 : 4 : 6- or 2 : 2 : 3 : 4 : 6-pentamethyl-Δ^5-*cyclo*hexenone, b.p. 90—95°/12 mm. (*semicarbazone*, m.p. 173°), and a little ? 1 : 3 : 5 : 5-tetramethyl-6-methylene-$\Delta^{1:3}$-*cyclo*hexadiene, b.p. 70—75°/12 mm. (blue, later green, colour with $SbCl_3$–$CHCl_3$, red with a drop of H_2SO_4 in Ac_2O). With $CH_2Cl{\cdot}CO_2Et$ and NaOEt in Et_2O, (**II**) gives *Et* 1 : α-*epoxy*-2 : 2 : 4 : 6-*tetramethyl*-$\Delta^{3:5}$-cyclo*hexadienylacetate*, b.p. 105°/0·1 mm., which yields an oily acid, converted by distillation at 12 mm. into 2 : 2 : 4 : 6-tetramethyl-$\Delta^{4:6}$-*cyclo*hexadiene-1-aldehyde [*semicarbazone*, ? *forms*, m.p. 175° and (after sintering) 207° (absorption max. 307 mμ., log ε 4·27 ± 0·03); 2 : 4-*dinitrophenylhydrazone*, m.p. 200°; blue colour with H_2SO_4–Ac_2O, reddish-brown with H_2SO_4, violet after some min. with $SbCl_3$–$CHCl_3$, yellow with Schiff's reagent; reduces NH_3–$AgNO_3$], and a *substance*, $C_{12}H_{14}O_2$, m.p. 138°.

IV. ω-Phenyl- and ω-furyl-polyenealdehydes, $R{\cdot}[CH{:}CH]_n{\cdot}CHO$ (R = Ph, 2-furyl), are obtained in good yield by condensing aldehydes by piperidine acetate in a solvent (70% EtOH) in which the products are insol.; condensation with crotonaldehyde (**III**) is the easier the more unsaturated is the other reactant. Purification is by recrystallising and sublimation. Thus, $CHPh{:}CH{\cdot}CHO$ and (**III**) give ζ-phenylheptatrienal (50%), m.p. 116° (lit., 96°, 94°, 112·5—113°), and κ-phenylundecapentaenal (**IV**) (20%), m.p. 183°. $Ph{\cdot}[CH{:}CH]_3{\cdot}CHO$ and (**III**) give similar yields of *θ-phenylnonatrienal*, m.p. 144°, and *μ-phenyltridecahexaenal*, m.p. 213°. β-2-Furylacraldehyde and (**III**) give ζ-2-furylheptatrienal, m.p. 111°, and *κ-furylundecapentaenal* (**V**), m.p. 194°. δ-Furylpentadienal and (**III**) give *θ-furylnonatetraenal*, m.p. 155°, and *μ-furyltridecahexaenal*, m.p. 218°. In C_6H_6, (**IV**) and (**III**) give ξ-phenylpentadecaheptaenal (80%), m.p. 232° (lit. 234°). In PhMe, (**V**) and (**III**) give *ξ-furylpentadecaheptaenal* (poor yield), m.p. 230° (decomp.). The pure products are stable. Regularities of the m.p., colour, and colour reactions are noted. The Ph and furyl series are similar in properties. R. S. C.

Prototropic changes of carbonyl compounds.—See A., 1942, I, 149.

Lignin and related compounds. LIX. Aromatic aldehydes from plant materials.—See A., 1942, III, 360.

Structure and absorption spectra. IV. αβ-Unsaturated ketones.—See A., 1942, II, 164.

Application of Fries reaction to esters of quinol. R. Y. Shahane (*Current Sci.*, 1941, **10**, 523—524).—*p*-$C_6H_4(OAc)_2$ is converted by heated $AlCl_3$ into 1 : 2 : 5-$C_6H_3Ac(OH)_2$, m.p. 202°, in 76% yield. Similarly a 42% yield of 1 : 2 : 5-$C_6H_3Bz(OH)_2$ is derived from *p*-$C_6H_4(OBz)_2$. H. W.

Fries migration of the esters of polyhydroxy-phenols. R. D. Desai and C. K. Mavani (*Current Sci.*, 1941, **10**, 524).—*p*-$C_6H_4(OAc)_2$ and *p*-$C_6H_4(OBz)_2$ give good yields of 1 : 2 : 5-$C_6H_3Ac(OH)_2$ and -$C_6H_3Bz(OH)_2$. 1 : 3 : 5-$C_6H_3Me(OAc)_2$ gives 2 : 4-diacetylorcinol, readily de-acetylated to γ-orcacetophenone. 1 : 2 : 3-$C_6H_3(OAc)_3$ gives exclusively gallacetophenone in excellent yield. 1 : 3 : 5-$C_6H_3(OAc)_3$ gives mainly 2 : 4 : 6-triacetyl- or 2 : 4-diacetyl-phloroglucinol according to conditions and phloracetophenone only in traces. H. W.

***p*-Anisyl γ-phenoxypropyl ketone.** W. E. Bachmann and A. L. Wilds (*J. Amer. Chem. Soc.*, 1942, **64**, 186).—This *substance*, m.p. 59—60·5°, is obtained from *p*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ and $OPh{\cdot}[CH_2]_3{\cdot}CN$ in Et_2O by way of the imine hydrochloride. R. S. C.

Application of the Nencki reaction to β-naphthol. R. D. Desai and W. S. Waravdekar (*Current Sci.*, 1941, **10**, 524—525).—Excellent yields of 1-lauryl-, 1-palmityl-, and 1-stearyl-2-naphthol are obtained from β-$C_{10}H_7{\cdot}OH$ and the requisite acid by the Nencki reaction. H. W.

Photochemical decomposition of cyclic ketones.—See A., 1942, I, 151.

Structure of vinyl polymerides.—See A., 1942, II, 164.

Synthesis of an analogue of the sex hormones. W. E Bachmann and D. G. Thomas (*J. Amer. Chem. Soc.*, 1942, **64**, 94—97).—*m*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}OH$ [prep. from *m*-$C_6H_4I{\cdot}OMe$, EtBr, Mg, and $(CH_2)_2O$ in Et_2O–C_6H_6; 85% yield] with PBr_3–C_6H_6 gives the bromide (66%), which with $CHNa(CO_2Et)_2$ etc. gives γ-*m*-anisylbutyric acid. The derived (PCl_5–C_6H_6) chloride with $SnCl_4$–C_6H_6 at 0° gives 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 78—79·5° (lit. 77·5—82°), converted by $Me_2C_2O_4$ etc. at 5—15° into the *Me* 2-*glyoxylate* (95%), m.p. 76·5—77·5°, which with glass powder at 175—185° gives *Me* 1-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoate*, m.p. 88—89·5° after sintering (Pyrex; preheated bath). Subsequent reactions are as described earlier (A., 1941, II, 138). Methylation gives *Me* 1-*keto*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoate* (84%), m.p. 91—92·5°, converted (Reformatsky; dehydration; reduction; esterification) into *Me* 2-*carbomethoxy*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetate*, α-, m.p. 77·5—79°, and β-form, an oil. Hydrolysis gives 2-*carbomethoxy*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid*, α-, m.p. 118·5—120·5°, and *β-form*, m.p. 128—130°, which by Arndt–Eistert–Wolff reactions yield *Me* β-2-*carbomethoxy*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylpropionate*, α-, m.p. 52—53·5° (clear at ~64°), and β-form, an oil. Cyclisation then affords 3′-*keto*-4′-*carbomethoxy*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*cyclo*pentano*-1′ : 2′-1 : 2-*naphthalene*, α-, m.p. 94—96·5°, and *β-form*, m.p. 117—119° (both m.p. after sintering; Pyrex; preheated bath), hydrolysed to 3′-*keto*-6-*methoxy*-, α-, m.p. 38·5—40·5°, and β-*form*, m.p. 112—113·5°, which with AcOH–48% HBr–N_2 gives 3′-*keto*-6-*hydroxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*cyclo*pentano*-1′ : 2′-1 : 2-*naphthalene*, α- (**I**), m.p. 155—156°, and *β-form* (**II**), m.p. 212—214° (vac.). In 5-mg. doses (**I**) is inactive, but (**II**) induces œstrous response (rats). R. S. C.

Action of hydrogen bromide in acetic acid on unsaturated 1 : 4-diketones. M. Couper and R. E. Lutz (*J. Org. Chem.*, 1942, **7**, 79—87; cf. A., 1933, 607).—The reaction between HBr–AcOH and two of four unsaturated αδ-diaryl-βγ-dimethyl-αδ-diketones is essentially reduction, whereas in the other two it is reduction and bromination in a *para* position in Ph. β-$C_{10}H_7{\cdot}OH$ acts as Br acceptor and in its presence the reactions are confined to reduction (and furanisation in two cases). A mechanism of bromination is given. The product of the action of HBr–AcOH on $(CMeBz)_2$ is trans-β-*benzoyl*-γ-p-*bromobenzoylbutane* (**I**), m.p. 125°, also obtained by reduction ($SnCl_2$, AcOH, conc. HCl) of the -Δβ-*butene* (**II**), m.p. 125° (prep. from β-*p*-bromobenzoyl-αβ-dimethylacrylyl chloride, $AlCl_3$, and C_6H_6). Dimethylfumaryl chloride, $AlCl_3$, and PhBr in CS_2 afford trans-βγ-*di*-p-*bromobenzoyl*-Δβ-*butene* (**III**), m.p. 172·5—173°, converted by $SnCl_2$ in boiling AcOH–conc. HCl or by Zn dust and boiling, conc. AcOH into 2 : 5-*di*-p-*bromophenyl*-3 : 4-*dimethylfuran* (**III**), m.p. 181°, also obtained in poor yield from PBr_5 and 2 : 5-diphenyl-3 : 4-dimethylfuran or (**I**). (**IV**) is oxidised by HNO_3 in well-cooled $EtCO_3H$ to cis-βγ-*di*-p-*bromobenzoyl*-Δβ-*butene* (**V**), m.p. 138—139°. (**I**) is scarcely affected by prolonged boiling with KOH–EtOH, is not reduced by Zn–AcOH or catalytically in presence of Pt or Pd–$BaSO_4$, and is oxidised (hot HNO_3 or $KMnO_4$) to *p*-$C_6H_4Br{\cdot}CO_2H$. It cannot readily be furanised. Bromination (Br–HBr–AcOH) of it leads to (**IV**). HBr–AcOH and $(CMeBz)_2$ in presence of β-$C_{10}H_7{\cdot}OH$ afford 2 : 5-diphenyl-3 : 4-dimethylfuran, m.p. 116—117°. (**II**) and HBr–AcOH give (**IV**) and (**I**) (ratio 1 : 4), whereas in presence of β-$C_{10}H_7{\cdot}OH$ the product is (**I**). (**III**) similarly yields (**IV**), also in presence of β-$C_{10}H_7{\cdot}OH$; (**IV**) is also obtained from (**V**). $(CH_2Bz)_2$ and HBr–AcOH give diphenylfuran, m.p. 90—92°. αβ-Dimesitoylethylene, HBr–AcOH, and β-$C_{10}H_7{\cdot}OH$ afford αδ-dimesitylbutane-αδ-dione, m.p. 130—132°. H. W.

Application of the *p*-hydrogen method to some problems of organic constitutions. I.—See A., 1942, I, 166.

Preparation of tetrahydroxybenzoquinone and rhodizonic acid salts from the product of oxidation of inositol by nitric acid. P. W. Preisler and L. Berger (*J. Amer. Chem. Soc.*, 1942, **64**, 67—69).—Prep. of K_2 rhodizonate (**I**) and of 1 : 2 : 3 : 5 : 6 : 4-$O{:}C(OH)_4{:}O$ and its K_2 salt from inositol is improved. The K salts are distinguished by solubilities in H_2O and N-HCl and analysed by potentiometric titration [$Na_2S_2O_4$; $K_3Fe(CN)_6$]. The colour changes during titration of SO_4'' by $Ba^{..}$ are probably due to (**I**). R. S. C.

Dyes related to toluidine-green. C. F. H. Allen, G. F. Frame, and C. V. Wilson (*J. Org. Chem.*, 1942, **7**, 63—67).—Comparison of the absorption spectra of homologues of toluidine-green (**I**) with those of the parent substance shows that the curves of dyes having substituents in the 6 : 7-positions resemble the unsubstituted alizarine-cyanine-green rather than (**I**). Halogen and OH in the α-position have a much greater effect on the absorption curves of this type of dye than the same group in a β-position. The 3′-sulphonic acid resembles the corresponding isomeride in the 1 : 5- (blue) series, the curve falling off in the far red. 3 : 6 : 1 : 2-$C_6H_2Cl_2(CO)_2O$, *o*-$C_6H_4Cl_2$, and $AlCl_3$ at 95—98° yield 3 : 6-*dichloro*-o-3′ : 4′-*dichlorobenzoylbenzoic acid*, m.p. 170—171° after softening at ~164°, cyclised by ~8% oleum at 160° to 1 : 4 : 6 : 7-*tetrachloroanthraquinone* (**II**), m.p. 259—260°, the constitution of which is established by its subsequent reactions. *m*-Hemipinic acid and *p*-$C_6H_4(OH)_2$ give 1 : 4 : 6 : 7-*tetrahydroxyanthraquinone* (**III**) (*tetra-acetate*, m.p. 192—193°). Gradual addition of a mixture of 4 : 5 : 1 : 2-$C_6H_2Br_2(CO)_2O$ and *p*-$C_6H_4(OH)_2$ to $AlCl_3$–NaCl at 200—220° yields 6 : 7-*dibromoquinizarin* (**IV**), m.p. 296—298°. (**III**) is reduced by Sn and HCl in AcOH to the 2 : 3-H_2-compound, converted by *p*-$C_6H_4Me{\cdot}NH_2$ and H_3BO_3 at 100° followed by atm. oxidation into 1 : 4-*di*-p-*toluidino*-6 : 7-*dihydroxyanthraquinone*. Similarly (**IV**) is transformed into its H_2-derivative, m.p. 287—289°, and thence into 6 : 7-*dibromo*-1 : 4-*di*-p-*toluidinoanthraquinone*. (**II**) and *p*-$C_6H_4Me{\cdot}NH_2$ at 165—175° slowly give 6 : 7-*dichloro*-1 : 4-*di*-p-*toluidinoanthraquinone*.

H. W.

Dyes related to toluidine-blue. C. F. H. Allen, C. V. Wilson, and G. F. Frame (*J. Org. Chem.*, 1942, **7**, 68—72).—4 : 8-*Di*-m-*toluidino*- (**I**), -p-*toluidino*-, -p-tert.-*amylanilino*- (**II**), -p-*anisidino*- (**III**), -p-*chloroanilino*- (**IV**), -p-*xenylamino*- (**V**), and -β-*naphthylamino*- (**VI**) -1 : 5-*dihydroxyanthraquinone* are obtained from 4 : 8-dichloroanthrarufin and the requisite base. Addition of H_3BO_3 is essential for the otherwise similar prep. of 4 : 8-*di*-o-*chloroanilino*-1 : 5-*dihydroxyanthraquinone*. The sulphonation of these compounds is described. The dyes from (**I**), (**III**), (**V**), and (**VI**) are much more sol. in H_2O than toluidine-blue (**VII**) and from the S : N ratio it appears that 2 SO_3H are present per N. The absorption curves of these dyes resemble that of the blue dye which results when (**VII**) is treated with fuming H_2SO_4 and has S : N > 1. (**II**) gives a dye resembling (**VII**) but apparently weaker. The dyes from (**V**) and (**VI**) absorb in the violet and are greenish, while that from (**IV**) does not have as high absorption in the far red. It appears that only *p*-alkylated amines can be expected to produce dyes closely resembling (**VII**).

H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

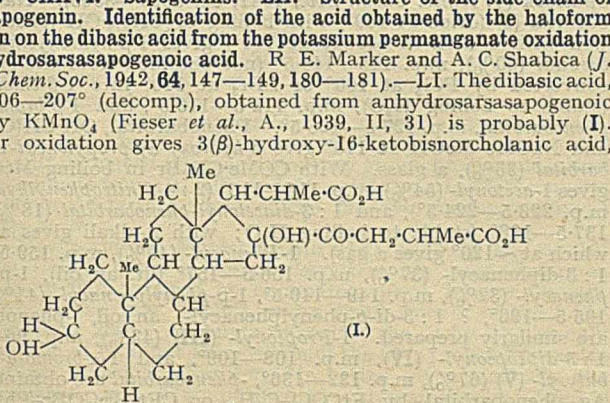
Preparation of $\Delta^{6:8(14)}$-, $\Delta^{7:9(11)}$-, $\Delta^{7:14}$-, and $\Delta^{8:14}$-cholestadienes. A., 1942, II, 167.

Relationship between optical rotatory power and constitution of sterols. II. S. Bernstein, E. J. Wilson, jun., and E. S. Wallis (*J. Org. Chem.*, 1942, **7**, 103—110).—Examination of $[\alpha]_D$ of a no. of sterols and the corresponding acetates, benzoates, and 3 : 5-dinitrobenzoates leads to the equation $[M]_{D\ derivative} = [M]_{D\ sterol}$ + const. The consts. for the acyl groups are quoted and depend on the group itself and on the mode of its union in the mol. Applications are discussed.

H. W.

Synthesis of an analogue of the sex hormones.—See A., 1942, II, 176.

Sterols. CXXV. Sapogenins. LI. Structure of the dibasic acid obtained by permanganate oxidation of anhydrosarsasapogenoic acid. Sterols. CXXVI. Sapogenins. LII. Structure of the side-chain of sarsasapogenin. Identification of the acid obtained by the haloform reaction on the dibasic acid from the potassium permanganate oxidation of anhydrosarsasapogenoic acid. R. E. Marker and A. C. Shabica (*J. Amer. Chem. Soc.*, 1942, **64**, 147—149, 180—181).—LI. The dibasic acid, m.p. 206—207° (decomp.), obtained from anhydrosarsasapogenoic acid by $KMnO_4$ (Fieser *et al.*, A., 1939, II, 31) is probably (**I**). Further oxidation gives 3(β)-hydroxy-16-ketobisnorcholanic acid,



(I.)

and thence by NaOI 3-hydroxy*ætio*bilianic acid (**II**). Oxidation of (**I**) by $KMnO_4$ at room temp. or of its Me ester acetate by CrO_3 and reduction of the product by Na–EtOH or –MeOH gives sarsasapogeninlactone.

LII. NaOI converts (**I**) into (**II**). (**I**) does not reduce $AgNO_3$–aq. NH_3 and is thus not an α-CO-acid (cf. *loc. cit.*).

R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Absorption spectra of terpenoid compounds. II. Irone.—See A., 1942, I, 164.

Vapour-phase thermal isomerisation of α- and β-pinene. L. A. Goldblatt and S. Palkin (*J. Amer. Chem. Soc.*, 1941, **63**, 3517—3522).—Under optimum conditions, pure α-pinene, $[\alpha]_D$ +32·06°, is isomerised at 375° to α-$[(CH{\cdot}CO)_2O$ adduct, m.p. 91—92°] and β-pyronene $[(CH{\cdot}CO)_2O$ adduct, m.p. 163—164°] (α + β 12%), dipentene (~42%), and *allo*cimene (40%), b.p. 88·4°/20 mm. $[(CH{\cdot}CO)_2O$ adduct, m.p. 83—84°]. Pure β-pinene, $[\alpha]_D$ −21·81°, gives similarly myrcene (~67%), *l*-limonene (~13%), and α-camphorene (~9·5%).

R. S. C.

Reactions of β-pinene. I. With selenium dioxide in various solvents. W. D. Stallcup and J. E. Hawkins (*J. Amer. Chem. Soc.*, 1941, **63**, 3339—3341).—SeO_2 and β-pinene give pinocarvone, b.p. 75—78°/3 mm., 221—223°/760 mm., $[\alpha]_D^{30}$ −16·5° [semicarbazone, m.p. 212—213° (corr.); 2 : 4-*dinitrophenylhydrazone*, m.p. 223—223·5° (corr.)], and carvopinone (**I**), b.p. 82—84°/3 mm., $[\alpha]_D^{30}$ +62·7° (polymerises at 140° or when kept to a solid, softens at ~320°, and then melts with decomp.; semicarbazone, m.p. >300°; when distilled with $H_2C_2O_4$ in steam gives carvone and some polymeride). The amount of (**I**) formed depends partly on the solvent and, in general, increases with the time of reaction. The product of Dupont *et al.* (A., 1933, 1166) was a mixture.

R. S. C.

Diethylamides and some derivatives of camphor. M. Herold and E. Jirát (*Časopis Českoslov. Lék.*, 1938, **18**, 165—171).—Camphor-10-sulphonyl chloride, m.p. 67° (from the acid and PCl_5), with $NHEt_2$ gives the sulphondiethylamide, m.p. 50°. Camphoryl chloride (from the acid and PCl_5) similarly yields the di(diethylamide), m.p. 130°. Camphoric anhydride and $NHEt_2$ yield *NN*-diethyl-α-camphoramic acid, m.p. 166°. The pharmacological action of these diethylamides and that of camphor-3-carboxydiethylamide are studied in comparison with that of *o*-$C_6H_4(CO{\cdot}NEt_2)_2$. They show weak analeptic properties or little solubility in usable solvents.

F. R.

Camphorylidenesulphanilamides.—See B., 1942, III, 114.

American musk. I. Chemical constitution of the musk of the Louisiana muskrat. P. G. Stevens and J. L. E. Erickson (*J. Amer. Chem. Soc.*, 1942, **64**, 144—147).—The volatile oil (2·1%) from the scent glands of the Louisiana muskrat (*Ondatra zibethicus rivalicius*) contains dihydrocivetol (58), normuscol (40), and the derived odorous ketones (2%). The following data appear new. *cyclo*-Heptadecane, m.p. 66·0—66·2° (lit. 65°). Dihydrocivet-oxime, m.p. 63—64°, and -2 : 4-*dinitrophenylhydrazone*, m.p. 84·5—86° after sintering. Normusc-2 : 4-dinitrophenylhydrazone, m.p. 108—109°, and -l-*menthylhydrazone*, m.p. 138·5—139·5°. Cryoscopic consts. of civetone and *cyclo*heptadecene are 39 and 20·2, respectively, the high val. of the former being probably due to intramol. conjugation of the CO and C:C.

R. S. C.

VI.—HETEROCYCLIC.

Tetrahydrofuran compounds. II. Preparation of γ-chloro-α-2-tetrahydrofurfurylbutane. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 3539; cf. A., 1941, II, 266).—Furfurylideneacetone and H_2–NiO in EtOH at 125°/100 atm. (initial) give α-2-tetrahydrofurfuryl-*n*-butan-γ-ol (63%), a liquid, which with $SOCl_2$ at C_5H_5N at >50° gives γ-*chloro*-α-2-*tetrahydrofurfuryl*-n-*butane*, b.p. 58—60°/3 mm.

R. S. C.

Preparation of ω-furylpolyenealdehydes.—See A., 1942, II, 175.

Oxime of furfurylideneacetone. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 3538).—*Furfurylideneacetoxime*, m.p. 88—90°, is prepared.

R. S. C.

Synthesis of 4-aminocoumarone-1 : 2-dicarboxylic acid *cyclo*hydrazide, a heterocyclic analogue of 4-aminophthalhydrazide. E. H. Huntress and W. M. Hearon (*J. Amer. Chem. Soc.*, 1942, **64**, 86—90).—Benzfuran-1 : 2-dicarboxylic acid and HNO_3 (1 conc. + 1 *d* 1·5) at 100° give the 4-NO_2-*acid* (**I**) (75%), m.p. 282—284°, which with $KMnO_4$–NaOH gives 2 : 5 : 1-$OH{\cdot}C_6H_3(NO_2){\cdot}CO_2H$ (proof of structure), but gives no anhydride. Its Me_2 ester (**II**) (CH_2N_2), m.p. 150—151°, gives no hydrazide, but evaporation of the acid with aq. N_2H_4 and heating the residue at 160—170° and then 195±5° gives 4-*nitrobenzfuran*-1 : 2-*dicarboxyl*cyclo*hydrazide* (**III**), m.p. 335—336° (*Ac*$_1$ derivative, m.p. 241—243°), also obtained by nitrating the unsaturated *cyclo*hydrazide. With $FeSO_4$–aq. NH_3, (**III**) gives 4-*aminobenzfuran*-1 : 2-*dicarboxyl*cyclo*hydrazide* (**IV**) (40%), decomp. ~330°. Hydrogenation (PtO_2) of (**II**) in AcOH gives Me_2 4-*aminobenzfuran*-1 : 2-*dicarboxylate*, m.p. 137—138°, and thence (**IV**). Hydrogenation of (**I**) gives the 4-NH_2-*acid*, m.p. >400°, which with CH_2N_2 gives Me_2 4-dimethylaminobenzfuran-1 : 2-dicarboxylate, m.p. 65—67°; the Ag salt is unchanged by MeI in xylene. Oxidation of (**IV**) gives less luminescence than does that of 4-aminophthalhydrazide.

R. S. C.

New reactions of 2-keto-1-benzylidenebenzfuran. I. T. B. Panse, R. C. Shah, and T. S. Wheeler (*J. Indian Chem. Soc.*, 1941, **18**, 453—456).—2-Keto-1-*p*-anisylidenebenzfuran (**I**) (reacts similarly to chalkones) and Br–$CHCl_3$ afford 1-*bromo*-2-*keto*-1-(ω-*bromo*-p-*methoxybenzyl*)*benzfuran*, m.p. 148°, converted by boiling MeOH or EtOH into 1-*bromo*-2-*keto*-1-(ω : p-*dimethoxy*-, m.p. 137°, or -(p-*methoxy*-ω-*ethoxy*-*benzyl*)*benzfuran*, m.p. 145°, respectively, or by 0·1N-KOH into 4′-methoxyflavonol. (**I**) and *cyclo*hexanone in boiling EtOH–aq. NaOH yield 2-*keto*-1-[ω-(2′-*keto*-1′-cyclo*hexyl*)-p-*methoxybenzyl*]*benzfuran*, m.p. 278°, and (**I**) and CH_2PhBz (b.p.) or $CH_2Ac{\cdot}CO_2Et$–EtOH–NaOEt (reflux) afford 2-*keto*-1-(β-*benzoyl*-β-*phenyl*-α-p-*anisylethyl*)*benzfuran*, m.p. 243°, or *Et* 5-p-*anisylbenzfurano*-1′ : 2′ : 3 : 4-Δ²-cyclo*hexen*-1-*one*-6-*carboxylate* (**II**), m.p. 159° [*semicarbazone*, m.p. 253—255°; *oxime*, m.p. 183° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 209—210° (decomp.); *Cu* salt, m.p. 210°], respectively. (**II**) and 10% HCl at 160° give 5-p-*anisylbenzfurano*-1′ : 2′ : 3 : 4-Δ²-cyclo*hexen*-1-*one*, m.p. 152°.

A. T. P.

Isolation of a physiologically active tetrahydrocannabinol from *Cannabis sativa* resin. H. J. Wollner, J. R. Matchett, J. Levine, and S. Loewe (*J. Amer. Chem. Soc.*, 1942, **64**, 26—29).—The EtOH-extract (30%) of Indian charas is successively acetylated, fractionated at 0·001 mm., and subjected to chromatography. Fractionation at 0·015 mm. of a fraction, $[\alpha]_D^{21}$ −205° in EtOH, free from cannabidiol diacetate, and later chromatography gives a *tetrahydrocannabinol acetate* (**I**), $[\alpha]_D^{21}$ −214° in EtOH. (**I**) is unaffected by further fractionation or chromatography, has a potency 14·6 (±7·2%) relative to the 7 : 8 : 9 : 10-H_4-compound, is dehydrogenated by S at 225° or chloranil in xylene to cannabinol acetate, is hydrogenated to a H_6-compound, $[\alpha]_D^{21}$ −119° in EtOH, has absorption max. at 2745 (log ε 3·52) and 2805 A. (log ε 3·53), and with (*a*) acid–EtOH or NH_3–PhMe gives a *tetrahydrocannabinol*, (*a*) $[\alpha]_D^{21}$ −216° in EtOH, relative potency 8·04 (±22%), (*b*) absorption max. at 2760 (log ε 3·42) and 2820 A. (log ε 3·43), $[\alpha]_D^{22}$ ~−193° in EtOH.

R. S. C.

Osage orange pigments. VIII. Oxidation. M. L. Wolfrom and A. S. Gregory (*J. Amer. Chem. Soc.*, 1941, **63**, 3356—3358; cf. A., 1941, II, 267).—Pomiferin Me_3 or tetrahydropomiferin Me_3 or *iso*pomiferin Me_2 ether with H_2O_2 and a little KOH in aq. $COMe_2$ give 2 : 3-*epoxides* (yields: 80, 10, and 82%, respectively), m.p. 159·5°, 150—151°, and 200°, respectively (liberate I from hot, but not cold, KI–AcOH), yielding 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CO_2H$ by more prolonged action in more conc. alkali. No epoxide was isolated from osajin, but *iso*osajin Me_2 ether gives a 2 : 3-*epoxide*, m.p. 199·5—200°, and thence *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$. These and known reactions prove that the *iso*flavone nucleus is not reduced in the H_4-derivatives and that neither the 2 : 3-ethylenic linking nor the OH of the 3-aryl nucleus is affected by the acid isomerisation, and fixes the positions of all but one OH.

R. S. C.

Anthochlor pigments of *Coreopsis gigantea*.—See A., 1942, III, 360.

Structure of glycollaldehyde dimeride. R. K. Summerbell and L. K. Rochen (*J. Amer. Chem. Soc.*, 1941, **63**, 3241—3244).—The dimeride (**I**) of $OH{\cdot}CH_2{\cdot}CHO$ is proved to be 2 : 5-dihydroxy-1 : 4-dioxan (cf. E. Fischer, A., 1895, i, 437). Dioxadiene and HBr–$CHCl_3$ at 0° give 2 : 5-dibromo-1 : 4-dioxan (**II**), darkens at 104—106°, decomp. 134°, converted by *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$,HCl (**III**) in 25% AcOH at 100° into $(\cdot CH{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\text{-}p)_2$ (**IV**) and by AgOAc in PhMe at room temp. into 2 : 5-diacetoxy-1 : 4-dioxan (**V**), m.p. 157—158°. (**II**) and (**V**) are identical with the products obtained from (**I**) (H. O. L. Fischer *et al.*, A., 1927, 857). (*p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CH{\cdot}CH_2)_2O$ could not be obtained by ozonolysis etc. of 2 : 5-dihydrofuran, only (**IV**) being isolated. Hydration of dioxene by boiling, very dil. HCl and then treatment with aq. (**III**) gives the p-*nitrophenylhydrazone*, m.p. 142°, of $OH{\cdot}[CH_2]_2{\cdot}O{\cdot}CH_2{\cdot}CHO$ (2 : 4-*dinitrophenylhydrazone*, m.p. 136°). This is converted into (**IV**) by boiling 25% AcOH [with or without addition of (**III**)] or boiling very dil. HCl, but is stable in boiling H_2O.

R. S. C.

2-Vinylthiophen. R. Kuhn and O. Dann (*Annalen*, 1941, **547**, 293—299).—2-Acetylthiophen and $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$–N_2 at 108° give α-2-*thienylethyl alcohol* (**I**) (47%), b.p. 90·5°/11 mm. [5-HgCl derivative, m.p. 157° (block); *phenylurethane*, m.p. 85° (block)], with some 2-*thienylethyl Pr*$^{\beta}$ *ether*, b.p. 75°/12 mm., 154° (decomp.)/755 mm. [hydrolysed by H_3PO_4; 5-HgCl derivative, m.p. 112—113° (block)], and *di*-α-2-*thienylethyl ether* (**II**), b.p. 121—122°/3 mm. [5 : 5′-(*HgCl*)$_3$ derivative, m.p. 196—198° (block)]; more prolonged reaction gives more of the ethers; in C_6H_6, (**I**) is accompanied by (**II**) and 2-*vinylthiophen* (**III**), b.p. 62—63°/50 mm. (**III**) is best obtained by boiling (**I**) with a little quinol; it can be titrated with *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ or $(CNS)_2$ but consumes 2 Cl; its colour reactions and absorption spectrum (max. 272 mμ.) are described; it polymerises when heated or kept, rapidly in O_2.

R. S. C.

9-Thiolphenanthrene and some of its derivatives. P. C. Dutta (*J. Indian Chem. Soc.*, 1941, **18**, 469—471).—K 9-phenanthrenesulphonate and PCl_5–$POCl_3$ at 140° give the chloride, converted by Zn–aq. H_2SO_4 at 100° (bath) into 9-*thiolphenanthrene* (**I**), m.p. 67°, and thence by I–EtOH into *diphenanthrenyl* 9 : 9′-*disulphide*, m.p. 149° (shrinks at 137°). (**I**) and AcCl (water-bath), or BzCl at 150—160°, or Me_2SO_4–aq. NaOH, yield 9-*acetyl*-, m.p. 93° (shrinks at 85°), 9-*benzoyl*-, m.p. 109° (shrinks at 95°), or 9-*methyl-thiolphenanthrene*, m.p. 75°, respectively. (**I**) and $(COCl)_2$ at room temp., followed by $AlCl_3$–CS_2 at room temp., then reflux, afford 4 : 5-*diketo*-4 : 5-*dihydrophenanthro*-9′ : 10′-2 : 3-*thiophen*, m.p. 245° (shrinks at 227°).

A. T. P.

5-Iodo-4 : 6-diketo-2-methyltetrahydropyridine-1-acetic acid.—See B., 1942, III, 114.

Isomeride of dimethylethylpyridine. R. H. Siddiqui (*J. Indian Chem. Soc.*, 1941, **18**, 505—506).—K_2 2 : 6-dimethyl-4-ethylpyridine-3 : 5-dicarboxylate (A., 1940, II, 53) is decarboxylated by short treatment with soda-lime, and after 4 months' contact the product gave no 2 : 6-dimethyl-4-ethylpyridine, but mainly an isomeride (+1·25H_2O), b.p. 195—196°, and a little of a base, b.p. 217—220°. The former base affords a *hydrochloride*, m.p. 197°, hydriodide, m.p. 155°, ethiodide, m.p. 185°, *platinichloride*, m.p. 222°, aurichloride, m.p. 180°, and *picrate*, m.p. 167° (anhyd. or +0·5H_2O).

A. T. P.

Structure of hydroxymethylene-methyl ethyl ketone and -methyl β-phenylethyl ketone. S. N. Joshi, R. Kaushal, and S. S. Deshapande (*J. Indian Chem. Soc.*, 1941, **18**, 479—484).—The $OH{\cdot}CH_2$ derivative (**I**) of COMeEt is $OH{\cdot}CH{:}CMe{\cdot}COMe$, whereas that of $Ph{\cdot}[CH_2]_2{\cdot}COMe$ is $Ph{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$. (**I**) can be distilled without decomp. at 250 mm.; the titre of alkali against (**I**) in EtOH remains const. after 1 week, whereas that of (**II**) diminishes to nearly half of the val. (**I**) and $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ in EtOH–piperidine (water-bath) give 5-*cyano*-6-*hydroxy*-2 : 3-*dimethylpyridine*, m.p. 270°, converted by 50% H_2SO_4 at 150° into 6-*hydroxy*-2 : 3-*dimethylpyridine*-5-*carboxylic acid*, m.p. >280°, decarboxylated by distilling with a little Cu powder to 6-*hydroxy*-2 : 3-*dimethylpyridine*, m.p. 205° (distilled with Zn in H_2, it yields 2 : 3-dimethylpyridine). By similar reactions, (**II**) [*Cu* salt, m.p. 176° (decomp.)] affords 5-*cyano*-6-*hydroxy*-2-β-*phenylethylpyridine*, m.p. 198° (decomp.), and thence the -5-*carboxylic acid*, m.p. 211—212°, 6-*hydroxy*-2-β-*phenylethylpyridine*, m.p. 152°, and 2-β-phenylethylpyridine (platinichloride, m.p. 185°, blackens at 160°) [oxidised by aq. $KMnO_4$ to BzOH and picolinic acid (*Cu* salt, +2H_2O)].

A. T. P.

3 : 3-Di-(4′-hydroxy-2′-methyl-5′-*iso*propylphenyl)oxindole and some derivatives. E. Bureš and J. Kužel (*Časopis Československ. Lék.*, 1938, **18**, 199—208).—Condensation of thymol and isatin with $ZnCl_2$ at 120° yields the α-*isomeride* (**I**), m.p. 284° (decomp.), and condensation with conc. H_2SO_4, the β-*isomeride* (**II**), m.p. 284° (decomp.), of 3 : 3-*di*-(4′-*hydroxy*-2′-*methyl*-5′-iso*propylphenyl*)*oxindole*, differing probably according to whether attachment is made on the α- or β-CO of the isatin mol. (**I**) gives a Hg^{II} salt with $Hg(OAc)_2$ and Br_3-, m.p. 255° (decomp.), Ac_2, m.p. 168°, Ac_3, m.p. 144°, and Bz_2, m.p. 148°, derivatives. (**II**) gives a Hg^{II} salt with $Hg(OAc)_2$ and Br_3-, m.p. 248°, Cl_8-, m.p. 209°, Ac_2, m.p. 159°, Ac_3, m.p. 145°, and Bz_2, m.p. 147°, derivatives and 3 : 3-*di*-(4′-*methoxy*-2′-*methyl*-5′-iso*propylphenyl*)*oxindole*, m.p. 129°.

F. R.

2-Aminoacridine-7-sulphonamide. E. Aarons and A. Albert (*J.C.S.*, 1942, 183).—2-*Aminoacridine*-7-*sulphonamide*, m.p. 253° (decomp.), is prepared by reduction (Na–Hg–EtOH) of the 2-nitroacridone derivative. 2-Aminoacridine-7-sulphonic acid is similarly prepared using Al–Hg.

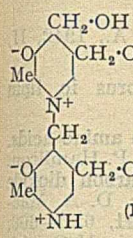
F. R. S.

***N*-Substituted derivatives of phenobarbital.** H. R. Henze and J. J. Spurlock (*J. Amer. Chem. Soc.*, 1941, **63**, 3360—3363).—Na phenobarbital (**I**) (dried at 140°) with boiling $Cl{\cdot}[CH_2]_2{\cdot}OH$ (excess; less well with 1 mol. in MeOH at 110°) gives 1-β-*hydroxyethylphenobarbital* (60%), m.p. 145—145·5° (not obtained from the Ag salt), converted by PCl_5 at 100° or PBr_3 at 110° into 1-β-*chloro*- (**II**) (stable to boiling H_2O), m.p. 112·5—113·5°, and 1-β-*bromo-ethylphenobarbital*, m.p. 127·5—128·5°. Phenobarbital, $OH{\cdot}CH(CH_2Br)_2$, and NaOMe–MeOH at 110° give β-*hydroxy*-αγ-*propylenedi*-1-*phenobarbital* (33%), a glass. With $COMe{\cdot}CH_2Br$ in boiling MeOH, (**I**) gives 1-*acetonyl*- (54%), m.p. 115—116° (2 : 4-*dinitrophenylhydrazone*, m.p. 223·5—224·5°), and 1 : 3-*diacetonyl-phenobarbital* (18%), m.p. 137·5—138° (stable to boiling H_2O; with N-alkali gives an acid, which at ~120° gives a gas). 1-*Phenacyl*- (49%), m.p. 159·5—160°, 1 : 3-diphenacyl- (37%), m.p. 156·5—157° (lit. an oil), 1-p-*bromophenacyl*- (32%), m.p. 149—149·5°, 1-p-*phenylphenacyl*- (44%), m.p. 195·5—196°, ? 1 : 3-di-*p*-phenylphenacyl-, an oil, -phenobarbital are similarly prepared. 1-*Propionyl*- (**III**) (43%), m.p. 96—96·5°, 1 : 3-*dipropionyl*- (**IV**), m.p. 108—109°, and 1-α-*bromo*-α-*ethyl*-n-*butyryl*- (**V**) (67%), m.p. 132—136°, -*phenobarbital* are obtained from Ag phenobarbital by EtCOCl–C_6H_6 or $CEt_2Br{\cdot}COBr$–PhMe, respectively. M.p. are corr. The products have little or no hypnotic effect, but some, notably (**II**)—(**V**), are anticonvulsants.

R. S. C.

Chemistry of vitamin-B_6. IV. Reactions in solutions at elevated temperatures. S. A. Harris (*J. Amer. Chem. Soc.*, 1941, **63**, 3363—3367; cf. A., 1942, II, 30).—Vitamin-B_6 in H_2O at 120° and p_H

6·5 (*i.e.*, conditions of sterilisation) gives the insol. *dimeride* (I) (6·4%), m.p. 205—209°, and later a gelatinous *polymeride*, $C_{24}H_{29}O_7N_3$. (I) is formed from the betaine form of -B_6 (A., 1941, II, 268); its structure is proved as follows. With MeI–C_6H_6–MeOH it gives only a (mono)*methiodide hydriodide* (II), m.p. 197—198°, and with 48% HBr gives the $(CH_2Br)_3$ compound *dihydrobromide*, sublimes >230° (decomp.); -B_6 polymerises only in neutral solution, but its *N*-Me betaine and the 4-Me compound do not polymerise at all. The 4-Me ether at 120° gives a gelatinous polymeride with loss of OMe; in boiling $CH_2Ph{\cdot}OH$, (I) gives the 4-*CH_2Ph ether* (III), m.p. 217—218°. In a borate buffer, (I) gives a faint dichloroquinonechloroimide test and a good colour in a veronal buffer, but (II) gives none. In boiling $CH_2Ph{\cdot}OH$, -B_6 gives its 4-*CH_2Ph ether* (IV), m.p. 166·5° (*hydrochloride*, m.p. 144—145°), and (III). The structure of (IV) is shown by its positive $FeCl_3$ and dichloroquinonechloroimide test (borate buffer). In $Bu^{\alpha}OH$, -B_6 gives the 4-*Bu^{α} ether hydrochloride* (V), m.p. 127—128° (cf. Scudi, A., 1941, III, 685). Relative curative doses are -B_6 1, (I) 40, (IV) ~20, (V) <20. R. S. C.

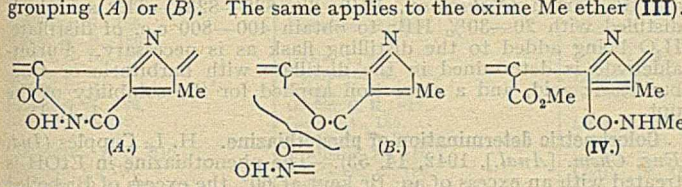


(I.)

Bisbenzimidazoles. (A) M. A. Phillips. (B) R. L. Shriner and R. W. Upson (*J. Amer. Chem. Soc.*, 1942, **64**, 187, 187—188).—Re priority. R. S. C.

Chlorophylls. CVI. Derivatives of purpurin-18. H. Fischer and H. Gibian. **CVII. Chloro-derivatives of chlorophyllporphyrins, phorbides, and chlorins.** H. Fischer and E. Dietl (*Annalen*, 1941, **547**, 216—233, 234—256; cf. A., 1942, II, 152).—Structures given below are supported by, and often deduced from, absorption spectra, which are detailed.

CVI. The absorption spectrum of the so-called oxime (I) (Zn salt) (Dietz *et al.*, A., 1934, 308) of purpurin-18 Me ester (II) (modified prep.) shows a shift towards blue; (I) thus probably contains the grouping (*A*) or (*B*). The same applies to the oxime Me ether (III).



(*A.*) (*B.*) (IV.)

The intermediate H hydroxylamide could not be isolated. Hydrolysis of (I) or (III) to chlorin-p_6 or a derivative thereof failed and the N·OMe of (III) is also unaffected. NaOMe or KOH–$Pr^{\alpha}OH$ gives only unstable, green metal salts. N_2H_4 and (II) similarly give an unstable, green H hydrazide, which yields the "*hydrazone*," sinters at 264°, $[\alpha]^{20}$ +930±200° in $COMe_2$ (white light) (Zn salt), analogous to (I) and also resistant to hydrolysis. Increase in basicity of the reagent permits isolation of the intermediate product. Thus NH_2Me and purpurin-18 in $COMe_2$ at room temp. give an acidic product, converted by esterification into *chlorin-*p_6*-carboxylmethylamide* Me_2 ester (IV), sinters at ~155° (Zn salt), which in conc. H_2SO_4 slowly, in alkali instantaneously, or with NaOH–C_5H_5N, NH_2OH, N_2H_4, or NH_2Me loses MeOH and gives the cyclic "*methylimide*" (V), m.p. >300° (Zn salt), analogous to (I). Piperidine and (II) at room temp. give a H piperidide (VI), converted by esterification into *chlorin-*p_6*-carboxylpiperidide* Me_2 ester (VII) [analogous to (IV)], m.p. 199° (*Zn* salt, sinters at ~280°, m.p. >300°), which cannot yield a cyclic product; (VI), obtained as above, is rapidly hydrolysed to (II) by dil. HCl, but if prepared by hydrolysis (NaOMe) or (VII), resists the action of acid. With NH_3–MeOH, (II) gives chlorin-p_6, but with semicarbazide gives a cyclic product analogous to (I). Mesopurpurin-18 [prep. by hydrogenation (Pd; dioxan) of the *Zn* salt, m.p. >300°, of (II)] gives analogously the cyclic *mesopurpurin-18 Me* ester "*oxime*," m.p. >260° (*Zn* salt; *Me ether*, sinters at ~245°, m.p. 260—280°), "*hydrazone*," m.p. >300° (Zn salt), and "methylimide" (Zn salt), and mesochlorin-p_6-carboxyl-methylimide and -piperidide Me_2 ester (Zn salts). The $CHN_2{\cdot}CO_2Et$ adduct of (II) reacts similarly giving products identical with the adducts from (I), (IV), and (V). HI–AcOH at 50° converts the cyclic products into those of the rhodopurpurin-γ-carboxylic anhydride series.

CVII. Phylloerythrin Me ester with H_2O_2 in 20% HCl at 10° and later CH_2N_2 gives 1-*chlorophylloerythrin Me* ester, sinters at 241°, m.p. >300° (purified by chromatography; impure Cu salt, m.p. 275°; *oxime*, m.p. >340°), and a small amount of the ? Cl_2-ester, sinters at 220°. Attempts to replace the Cl by CN led only to elimination of HCl, but the position of the Cl is proved by spectra and analogy. Phæoporphyrin-a_5 Me_2 ester gives similarly the 10-*Cl*-derivative, m.p. 272° (purified by chromatography; impure Cu salt, m.p. 205°). Mesomethylphæophorbide-*a* gives *chlorohydroxymesomethylphæophorbide*-a (VIII), m.p. 196°, $[\alpha]^{20}$ +438° in $COMe_2$ (white light) (oxime), converted by KOH–PrOH–Et_2O–C_5H_5N (little) at room temp. and then CH_2N_2 into *chlorohydroxymesopurpurin-7 Me_3* ester, m.p. 176°, $[\alpha]^{20}$ +1700° in $COMe_2$ (white light) (also obtained from mesopurpurin-7 Me_3 ester); this gives the *Cu*, $[\alpha]^{20}$ +1250° in $COMe_2$ (white light), and *FeCl* derivative, m.p. 256°, $[\alpha]^{20}$ +4000° in $COMe_2$ (white light), of dihydroxymesopurpurin-7 Me_3 ester, which could not itself be obtained cryst. *Nitromesopurpurin-7 Me_3* ester, m.p. 128°, is obtained by $NaNO_2$ in AcOH at 10°. Short treatment of (VIII) with hot KOH–MeOH–C_5H_5N and then CH_2N_2 gives dihydroxymesochlorin-e_6 Me_3 ester, m.p. 123°, cyclised by NaOH in boiling C_5H_5N. Mesorhodochlorin Me_2 ester gives a *product*, $C_{34}H_{38}O_5N_4Cl_2$, m.p. 150°, $[\alpha]^{20}$ +3250° in $COMe_2$ (white light), and later possibly a Cl_3-derivative. Purpurin-7 Me_3 ester gives a *product*, $C_{37}H_{38}O_7N_4Cl_2$, m.p. 151°. R. S. C.

Application of the *p*-hydrogen method to some problems of organic constitutions. I.—See A., 1942, I, 166.

Thiazoles. Synthesis of 2-phthalimidomethyl-4-diethylaminomethylthiazole. Y. F. Chi and S. Y. Tshin (*J. Amer. Chem. Soc.*, 1942, **64**, 90—91).—$CH_2Cl{\cdot}CN$ (prep. in 71% yield by heating the amide and P_2O_5 at 120—150° and then distilling at 200 mm.) and *o*-$C_6H_4(CO)_2NK$ at 120—130° give *phthalimidoacetonitrile* (77%), m.p. 118—120°, which with H_2S and a little $N([CH_2]_2{\cdot}OH)_3$ in hot EtOH gives *phthalimidoacet-thioamide* (59%), sinters at 155°, m.p. 168—170°. With $CO(CH_2Cl)_2$ in hot abs. EtOH this gives 4-*chloromethyl-2-phthalimidomethylthiazole* (32%), m.p. 133—134·5°, converted by $NHEt_2$ in hot abs. EtOH into 2-*phthalimidomethyl-4-diethylaminomethylthiazole* (46%), m.p. 92—93°. R. S. C.

Thiazole sulphonamides.—See B., 1942, III, 115.

Azine dyes derived from 2 : 3-diketo-4 : 5 : 9′ : 10′-phenanthrathiophen. P. C. Dutta and R. M. Sinha (*J. Indian Chem. Soc.*, 1941, **18**, 477—478).—4 : 5-Diketo-4 : 5-dihydrophenanthra-9′ : 10′-2 : 3-thiophen and the respective *o*-diamine in AcOH yield 4 : 5 : 9′ : 10′-*phenanthrathiopheno*-2 : 3-*phenazine* [*phenanthra*-9″ : 10″-2′ : 3′-*thiopheno*-4′ : 5′ : 2 : 3-*quinoxaline*] (I), m.p. 255°, -2 : 3-2″-*chloro*-4″ : 5″-*tolazine*, m.p. 271° (shrinks at 265°), -2″ : 3″-*phenazine-azine*, m.p. 290°, and -*quinoxaline-azine*, m.p. 233—234°, respectively. A. T. P.

Thiazinocyanines. I. Carbocyanines containing the 2 : 4-benzthiazine nucleus. B. Beilenson and (Miss) F. M. Hamer (*J.C.S.*, 1942, 98—102).—3-Methyl-2 : 4-benzthiazine in C_5H_5N with 2-β-acetanilidovinylbenzoxazole ethiodide gives *trimethin*[2-(3-*ethyldihydrobenzoxazole*)][3-(2 : 4-*benzthiazine*)] (I), m.p. 138°, with the -6 : 7-benzbenzoxazole affords the -6 : 7-*benzbenzoxazole* derivative, m.p. 163°, and with the -benzthiazole (II) yields the -*benzthiazole* derivative (III), m.p. 199—200°; the -4 : 5-*benzthiazole*, m.p. 196°, and -*benzselenazole* derivatives, m.p. 212°, are similarly obtained. *p*-$C_6H_4Me{\cdot}SO_2Et$ and (I) followed by KI give [2-(3-*ethylbenzoxazole*)]-[3-(4-*ethyl*-2 : 4-*benzthiazine*)]*trimethincyanine iodide*, m.p. 237° (decomp.), and (III) similarly affords the -*benzthiazole* compound, m.p. 231—232° (decomp.). 3-Amino-2 : 4-benzthiazine and (II) yield γ-*azatrimethin*-[2-(3-*ethyldihydrobenzthiazole*)][3-(2 : 4-*benzthiazine*)], m.p. 145° (decomp.), and 3-*amino*-2 : 4-*benzthiazine ethiodide*, m.p. 220° (decomp.), and (II) afford [2-(3-*ethylbenzthiazole*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]-γ-*azatrimethincyanine iodide*, m.p. 240° (decomp.). Absorption max. of the various dyes have been compared. The effect of replacing the benzthiazole by the 2 : 4-benzthiazine nucleus in carbocyanine is to produce a hypochromic shift. F. R. S.

VII.—ALKALOIDS.

Azeotropism in the system nicotine–water. Separation of nicotine from related alkaloids by aqueous distillation. C. R. Smith (*Ind. Eng. Chem.*, 1942, **34**, 251—252).—An azeotropic mixture of nicotine (I) and H_2O (2·5 g. per 100 ml.) exhibits a b.p. lowering of 0·012°. (I) can be satisfactorily separated from nornicotine and anabasine by distilling with H_2O, making the distillate alkaline, and redistilling. C. R. H.

Alkaloids of *Rauwolfia canescens* (Linn.). II. (Miss) A. Mookerjee (*J. Indian Chem. Soc.*, 1941, **18**, 485—488; cf. A., 1941, II, 341). —"Rauwolscine" (I) [Me ester of (II)] and 10% aq. KOH at 100° (bath) give "rauwolscinic acid" (II), $[\alpha]_D^{23}$ +136·8° in H_2O [*hydrochloride*, m.p. 255·5—257·5° (decomp.) (+2·5H_2O or anhyd.); *picrate*, +EtOH, m.p. 232—234° (decomp.); *Et* ester, m.p. 234—236° (decomp.) {*hydrochloride*, m.p. 262—264° (decomp.); *picrate*, m.p. 179·5—181·5° (decomp.)}; Pr^{α} ester, m.p. 206—208° (decomp.) {*hydrochloride*, m.p. 264—266° (decomp.)}; Bu^{α} ester, m.p. 181—182·5° (decomp.), after frothing at 105—106° {*hydrochloride*, m.p. 251—253° (decomp.)}]. Absorption curves of the hydrochlorides of yohimbine and (I) are very similar. A. T. P.

Isolation of a new alkaloid from perennial ryegrass. J. Melville and R. E. R. Grimmett (*Nature*, 1941, **148**, 782).—*Perloline* (I), $C_{36}H_{22}O_3N_4(OMe)_4$, has been isolated from *Lolium perenne*, L. (I) is sol. in EtOH and $CHCl_3$, slightly sol. in $COMe_2$, Et_2O, and H_2O. Dil. solutions in $CHCl_3$ are golden-yellow with a green fluorescence that can be detected in ordinary light at a concn. of 1 in 5×10^6. (I) is reduced by $TiCl_3$ to a colourless material, which can be oxidised quantitatively by $Fe(CN)_6'''$. The grass may contain from 3 μg. to 1 mg. per g. dry wt. Other alkaloids have been found in ryegrass. L. S. T.

Alkaloid nicotinates.—See B., 1942, III, 86.

VIII.—ORGANO-METALLIC COMPOUNDS.

Metallation of triphenylarsine. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1941, **63**, 3532—3533).—$AsPh_3$ and $LiBu^a$ in Et_2O give the 3-Li derivative (**I**), which with CO_2 gives a gummy acid, converted by $KMnO_4$ into *diphenyl-m-carboxyphenylarsine oxide* (**II**), m.p. 215°. *m*-$C_6H_4Me{\cdot}MgBr$ and $AsPh_2Cl$ in Et_2O give *diphenyl-m-tolylarsine* (72%), m.p. 170—173° [$HgCl_2$ derivative, m.p. 201—202°; also obtained (2·7%) from (**I**) by Me_2SO_4], slowly oxidised to (**II**) by aq. $KMnO_4$ at 60°. R. S. C.

Relative reactivities of organo-metallic compounds. XLIII. Introduction of aminoaryl groups by the halogen–metal interconversion reaction. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1941, **63**, 2844—2855; cf. A., 1942, II, 41).—*p*-$C_6H_4Br{\cdot}NH_2$ and $LiBu^a$ in Et_2O at −60° give [max. (≯68%) in 9 min.] *p*-$Li{\cdot}C_6H_4{\cdot}NH_2$ (**I**), as judged by the yield of acid obtained. With $AsPhCl_2$ in Et_2O at, successively, −45°, room temp., and the b.p., (**I**) gives 63% (over-all) of *As Ph di-p-aminophenyl* [4 : 4′-*diaminotriphenylarsine*], m.p. 69°, which with *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$–$C_5H_5N$ and later hydrolysis by aq. NaOH gives *As Ph di-p-sulphanilamidophenyl* (**I**), m.p. 198° ($N^4N^{4\prime}$-Ac_2 derivative, m.p. 184°). $PPhCl_2$ similarly gives 64% of *P Ph di-p-aminophenyl*, an oil (Ac_2 derivative, m.p. 169°), and *di-p-sulphanilamidophenyl*, m.p. 202—204° [does not depress the m.p. of (**I**); Ac_2 derivative, m.p. 186—187°]. R. S. C.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Hydrolytic derivatives of lignin volatile compounds. A. Bailey (*J. Amer. Chem. Soc.*, 1942, **64**, 22—23).—The volatile products (27·5%) obtained from BuOH-lignin of Western hemlock by HCl–BuOH–H_2O at 160° contain $COMe_2$ 1·9, Pr^aCHO 1·6, MeOH 2·5, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ 2·5, Pr^aOH 4·8, HCO_2H (as Bu ester) 11·4, and $CHEt{:}CMe{\cdot}CHO$ 2·8%. A non-volatile C_6H_6-sol. and a resinous alkali-sol. fraction were also formed. R. S. C.

Mechanism of chlorination of lignin. E. V. White, J. N. Swartz, Q. P. Peniston, H. Schwartz, J. L. McCarthy, and H. Hibbert (*Paper Trade J.*, 1941, **113**, *TAPPI Sect.*, 299—309).—The reactions involved in the chlorination of lignin (**I**) and of unbleached wood pulp by aq. Cl_2 are discussed. With isolated alkali-(**I**), treatment with aq. Cl_2 results in almost equiv. chlorination and demethoxylation to a degree which increases with increase in the % of Cl added and also with the acidity of the reaction mixture. It is believed that chlorination takes place at either the 6- or the 5-positions of the guaiacyl nuclei of (**I**), depending on whether the *p*-OH groups of these nuclei are free or not. Furthermore, the presence of such Cl atoms induces instability in the OMe groups, which then split off with the formation of quinone or diketo-structures which may then undergo further fission to yield acidic groups in the (**I**). The rate of Cl_2 consumption by ligninsulphonic acid can be accounted for by assuming that the process involves two main reactions, the initial one rapid, and the second slow (second order). The former is one of chlorination and demethoxylation as evidenced by the correlation found to exist between the rate of Cl_2 consumption and the rate of introduction of Cl and accompanying loss of OMe by the (**I**). The latter appears to be essentially an oxidation process in view of its similarity to the second-order internal oxidation reaction involved in the self-decomp. of aq. Cl_2. During aq. acidic chlorination of unbleached pulp little (**I**) is removed, but it is made potentially sol. in alkali, presumably as a result of the formation of CO_2H groups at points from which OMe was split. The removal of chlorinated (**I**) from pulp is shown to be largely a physical process in which such factors as temp. and time of treatment control the degree of dissolution of the (**I**) by the alkaline medium. H. A. H.

XI.—ANALYSIS.

Improved distilling column head.—See A., 1942, I, 188.

Immersion still-head for low-pressure distillation of organic mixtures.—See A., 1942, I, 188.

Chromatography of solutions containing a single solute.—See A., 1942, I, 159.

Modifications in the Dumas micro-method for nitrogen. Automatic apparatus for combustion micro-methods. G. L. Royer, A. R. Norton, and F. J. Foster (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 79—82).—Combustion furnaces, auxiliary control equipment, and procedure are described. Tank CO_2 is used, and gives a const. blank of 0·010 c.c. per determination. The automatic combustion method gives results that are as accurate as, and more reproducible and quicker than, those given the standard Pregl procedure. A single determination requires 40 min. L. S. T.

Aliphatic sulphinic acids. I. Analysis and identification.—See A., 1942, II, 162.

Identification of alcohols in aqueous solution.—See A., 1942, II, 161.

Electrophotometric microdetermination of phosphorus in lipin extracts.—See A., 1942, III, 428.

Gasometric determination of carboxyl groups in free amino-acids. Determination of free amino-acids by titration of carbon dioxide formed in reaction with ninhydrin. D. D. Van Slyke, D. A. MacFadyen, and P. Hamilton (*J. Biol. Chem.*, 1941, **141**, 627—669, 671—680; cf. A., 1938, II, 211).—α-NH_2-acids boiled in H_2O with an excess of ninhydrin (**I**) (chloramine-*T* is less satisfactory) at p_H 1—5 evolve the CO_2 of their CO_2H groups quantitatively in a few min.; details and apparatus are described. Proline and hydroxyproline yield their carboxylic CO_2 similarly. Structures which react are $NH_2{\cdot}CHR{\cdot}CO_2H$ and $CH_2R'{\cdot}NH{\cdot}CHR{\cdot}CO_2H$. When NH_2 is in β or γ position, reactivity of the CO_2H is diminished. Under the conditions used the following give no CO_2: peptides, except where $\cdot C(NH_2){\cdot}CO_2H$ is present, *e.g.*, glutathione; acetylated and benzoylated NH_2-acids; derivatives with no H on NH_2-N; acid esters (*e.g.*, glycine ester) or amides; simple org. acids, *e.g.*, AcOH; OH-acids, *e.g.*, lactic, citric; keto-acids, *e.g.*, $AcCO_2H$. Glutamic acid evolves CO_2 from 1 CO_2H only; creatinine and (**I**) in H_2O react only slightly at p_H 2·5, but CO_2 is evolved in boiling AcOH. The property of aspartic acid (like cystine) to evolve 2 mols. of CO_2 with (**I**) permits its determination in mixtures containing most of the other NH_2-acids (not lysine or proline) yielded by protein hydrolysis. In digestion of casein to peptides by cryst. trypsin no free NH_2-acid is liberated (cf. 20% liberation with crude trypsin). CO_2 is determined by distilling in vac. into $Ba(OH)_2$, and excess of the latter is titrated. A. T. P.

Determination of pentoses with hydrobromic acid. G. Jayme and P. Sarten (*Naturwiss.*, 1940, 28, 822—823).—The sample is distilled with 20—30% HBr to obtain 400—800 c.c. of distillate, H_2O being added to the distilling flask as is necessary. Furfuraldehyde is determined in the distillate with barbituric or thiobarbituric acid, and a correction applied for the solubility of the ppt. J. L. D.

Colorimetric determination of phenothiazine. H. L. Cupples (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 53).—The phenothiazine in EtOH is treated with an excess of aq. Br kept at 60°, the excess of Br boiled off, the solution filtered, and the red colour determined photometrically. The accuracy is ±6%. J. D. R.

Colour reactions of reducing pyrimidines. E. B. Knott (*J.S.C.I.*, 1941, **60**, 313—314).—Aq. solutions of reducing pyrimidines give characteristic colour changes when treated with 0·1N-KI–I, then 1 drop of aq. NH_3 (dil.) followed by EtOH and HCl. A table is given showing how the compounds fall into four groups according to the no. and position of the NH_2-groups in the 4-, 5-, or 6-positions. The test can be adapted for micro-identification. W. C. J. R.

Iodosulphate microchemical identification tests for cinchona alkaloids. C. C. Fulton (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 848—850).—Three reagents are described, all consisting of varying proportions of I–KI in aq. AcOH–H_2SO_4. These reagents give with quinine, quinidine, cinchonine, and cinchonidine characteristic cryst. ppts., readily identified under the microscope. Numerous photomicrographs are reproduced. J. D. R.

Reactivity of porphyrindin in presence of denatured proteins. J. P. Greenstein and W. V. Jenrette (*J. Biol. Chem.*, 1942, **142**, 175—180).—The advantages and disadvantages of the method of determination of SH groups in native and denatured proteins by titration with porphyrindin (**I**) are discussed. The method has been improved by the use of Na nitroprusside as an outside indicator, by standardising the (**I**) solutions against cysteine during the course of the titration with protein, and by modifying the method so as to provide a stepwise and rapid determination of the protein SH groups. When cysteine is added in varying amounts to denatured proteins, it is nearly quantitatively recovered by subsequent titration of the mixtures with (**I**), and there is little, if any, interference by other reducing groups of the proteins, as these react too slowly under the conditions of the method. Data on the SH group content of denatured tobacco mosaic virus protein and of ovalbumin, obtained by the use of various oxidants and sol. denaturing agents, which show good agreement, are compared and discussed. J. N. A.

Determination of hydroxylysine in proteins. D. D. Van Slyke, A. Hiller, and D. A. MacFadyen (*J. Biol. Chem.*, 1941, **141**, 681—705).—Hydroxylysine (**I**) is pptd. from protein hydrolysates with other diamino-acids by phosphotungstic acid, and is determined by the NH_3 liberated from the group $\cdot CH(OH){\cdot}CH(NH_2)\cdot$ with $NaIO_4$. Other NH_2-acids, *e.g.*, serine, threonine, also give quant. yields of NH_3, and these are separated from (**I**) by crystallising the phosphotungstates. In only gelatin and collagen of the proteins analysed did the amount of (**I**) approach 1% of the total protein-N. A. T. P.

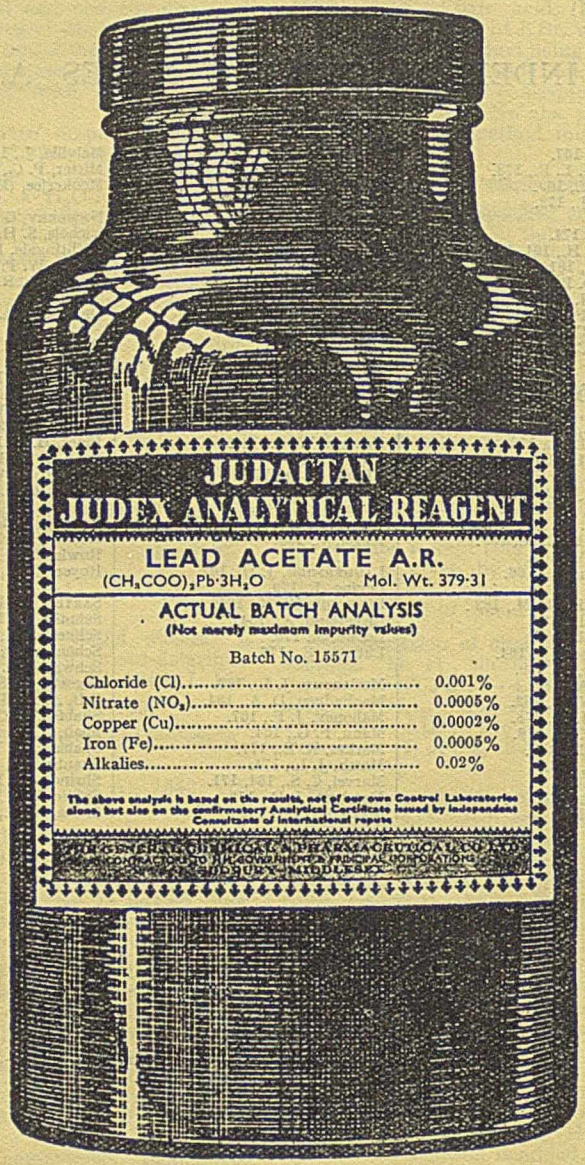
JUDACTAN

ANALYTICAL REAGENTS WITH ACTUAL BATCH ANALYSIS

ACTUAL

BATCH

ANALYSIS



Each Batch subjected to INDEPENDENT ANALYSIS before label is printed

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

THE GENERAL CHEMICAL & PHARMACEUTICAL CO. LTD.

Chemical Manufacturers, Judex Works, Sudbury, Middlesex

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