BRITIS CHEMICAL AND PHYSIOGICAL ABSTRACTS

ISSUED BY THE

Bureau hemical and Physiological Abstracts

[Supported by the l Society, the Society of Chemical Industry, the Physiological Society, the Biochen ciety, and the Anatomical Society of Great Britain and Ireland]

JANUARY, 1943

A II.—ORGANIC CHEMISTRY

CONTENTS

Offices of the Bureau: CLIFTON HOUSE, EUSTON ROAD, LONDON, N.W.1

Publishers: THE CHEMICAL SOCIETY, BURLINGTON HOUSE, PICCADILLY, LONDON, W.1.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JANUARY, 1943.

I.—ALIPHATIC.

Preparation of derivatives of ψ-butylene. V. S. Batalin and P. G. Ugniumov (*Sintet. Kautschuk*, 1936, No. 6, 8—16; cf. A., 1936, 62).—Direct chlorination of ψ-butylene at −10° yields $(CHMeCl)_2$. Cl·$[CHMe]_2$·OH and NaOH afford ψ-butylene oxide, whence $(CHMe·OH)_2$, COMeEt, mono-, di-, and tri-butanolamines were obtained. CH. ABS. (*c*)

Preparation of alkyl halides.—See B., 1942, II, 355.

Manufacture of methyl bromide.—See B., 1942, II, 354.

Preparation of ethyl chloride.—See B., 1942, II, 354.

Mechanism of additions to double bonds. XIV. Nature of the activated complex in bimolecular diene syntheses.—See A., 1943, I, 19.

Raman effect and problems of constitution. XVIII. Hexachlorobutadiene and octachloro*cyclo*pentene.—See A., 1942, I, 387.

Production of additive products of acetylene and alcohols.—See B., 1942, II, 357.

Acidic and basic catalysis in urethane formation.—See A., 1943, I, 20.

Anhydrides of mannitol. S. Müller (*Magyar Biol. Kutató Intézet Munkái*, 1935—6, **8**, 405—413).—Mannitol dibenzoate tri-*p*-toluenesulphonate can be disproportionated into mannitol dibenzoate tetra-*p*-toluenesulphonate and anhydromannitol dibenzoate di-*p*-toluenesulphonate, which is stable to alkali. The varying stability of compounds of the group is explained by at. models. CH. ABS. (*c*)

Stabilisation of ethers.—See B., 1942, II, 357.

Production of ethylene glycol monoethyl ether.—See B., 1942, II, 353.

Synthesis of dimethyl ethers of the two enantiomorphic α-butyrins and their hydrolysis by lipases. E. Baer and H. O. L. Fischer (*J. Biol. Chem.*, 1942, **145**, 61—68).—Serum-lipase of rats and guinea-pigs and liver-lipase of rabbits hydrolyse the *Me*$_2$ *ethers* of d(+)- (**I**) and l(−)- (**II**) -α-butyrylglycerol with a considerable difference in velocity. Tri*iso*propylidenemannitol is hydrolysed to γδ-iso*propylidene*-, m.p. 85—86·5°, $[\alpha]_D$ −29·6° in H_2O, which with Ag_2O and MeI yields *αβεζ-tetramethyl-γδ-*iso*propylidene*-, m.p. 132—134°, $[\alpha]_D^{20}$ −39·0° in H_2O, and thence *αβεζ-tetramethyl*-, b.p. 152—157°/9—10 mm., $[\alpha]_D$ +13·2° in H_2O, -l-*mannitol*. This is transformed by $Pb(OAc)_4$ in C_6H_6 at room temp. into *dimethyl*-l-*glyceraldehyde*, b.p. 37—42°/8—10 mm., immediately reduced (H_2–Raney Ni in EtOAc saturated with H_2O) to l-*αβ-dimethylglycerol*, b.p. 65—66°/7 mm., $[\alpha]_D$ +4·8° in substance, −6·7° in H_2O, which with Pr^{a}COCl in quinoline at room temp. affords (**I**), b.p. 94·5—95·5°/8 mm., $[\alpha]_D$ +5·9°. Similarly obtained are *dimethyl*-d-*glyceraldehyde*, b.p. 38·5—39·0°/8 mm., $[\alpha]_D$ +98·0° in C_6H_6, d-*αβ-dimethylglycerol*, b.p. 67·2—67·4°/8 mm., $[\alpha]_D$ −4·75° in substance, +6·8° in H_2O, and (**II**), b.p. 93·5—94°/8 mm., $[\alpha]_D$ −6·0°. H. W.

Manufacture of crystalline glycollic acid.—See B., 1942, II, 357.

Photosensitised oxidation of ethylenic double bonds.—See A., 1943, I, 22.

Preparation of maleic acid.—See B., 1942, II, 357.

Production of succinic acid.—See B., 1942, II, 358.

Chain photolysis of acetaldehyde in intermittent light.—See A., 1943, I, 22.

3 : 2 Compound, m.p. 146—148°, of propaldehyde with acetaldehyde.—See A., 1942, III, 901.

Hydration of unsaturated compounds. XI. Acraldehyde and acrylic acid.—See A., 1943, I, 20.

Manufacture of keten.—See B., 1942, II, 358.

Counting of free alkyl radicals. Application to the photolysis of acetone.—See A., 1943, I, 22.

Production of methyl vinyl ketone.—See B., 1942, II, 388.

Production of Δ$^{\alpha\gamma}$-hexadien-ε-one.—See B., 1942, II, 358.

Formaldehyde–urea condensation products. IV. Methylolureas. V. The methylene linkage. H. Kadowaki (*Rep. Imp. Ind. Res. Inst., Osaka*, 1933, **14**, No. 6, 1—82; 1934, **14**, No. 11, 1—87; cf. A., 1936, 868).—IV. The prep. of NH_2·CO·NH·CH_2·OH (**I**) [which is converted by aq. NH_3 into $CO(NH_2)_2$ and $(CH_2)_6N_4$] and $CO(NH·CH_2·OH)_2$ from $CO(NH_2)_2$ and CH_2O in aq. solution is described.

V. The following *ethers* are described: of (**I**), *Me*, m.p. 91°, *Et*, m.p. 111°; of dihydroxymethylcarbamide, *Me*$_2$, m.p. 101°, *Et*$_2$, m.p. 124°, *Pr*$_2$, m.p. 95°, *Bu*$_2$, m.p. 84°, (*CH*$_2$*Ph*)$_2$, m.p. 112°, and the *Et*$_2$ *thioether*, m.p. 108·5°; of methylenedihydroxymethylcarbamide, *Me*$_2$, m.p. 240°, *Et*$_2$; of dimethyltrimethylenetetracarbamide, *Me*$_2$. The last is hydrolysed to *mono-* and *di-*(*hydroxymethyl*)-*trimethylenetetracarbamide*. *Peroxides* of (**I**), m.p. 153° (decomp.), and hydroxymethylcarbamide and a related compound, *hexahydroxymethyltricarbamide*, m.p. 170° (decomp.), are described and the classification of the group as acetals is proposed. CH. ABS. (*c*)

Manufacture of diamides of unsaturated carboxylic acids.—See B., 1942, II, 359.

Halogenation of unsaturated compounds in the allyl position. K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann (*Annalen*, 1942, **551**, 80—119).—$(CH_2·CO)_2NBr$ (**I**) is very suitable for the conversion of ·CH_2·CH:CH· into ·CHBr·CH:CH. *o*-$C_6H_4(CO)_2NBr$ and a large excess of boiling *cyclo*hexene (**II**) give 50% of 1-bromo-Δ^2-*cyclo*hexene (**III**) and 20% of *phthal*-2-*bromo*cyclo*hexylimide*, m.p. 132—133°. The reaction is greatly retarded when CCl_4 is used as diluent. *o*-$C_6H_4(CO)_2NCl$ and (**II**) scarcely react in boiling CCl_4 or C_6H_6; at 140° 1-chloro-Δ^2-*cyclo*hexene (**IV**) results in 12·3% yield but the chief product consists of more highly chlorinated substances with a little additive compound. Halogenated sulphon-amides and -imides are unsuitable. Dichloramine *T* immediately loses half its active halogen in contact with (**II**) and the remainder reacts slowly in boiling solution, giving little *p*-$C_6H_4Me·SO_2·NH_2$ and (**IV**) but mainly a non-cryst. oil. N-*Chloro*-N-*benzoyl*-p-*toluenesulphonamide*, m.p. 59—63°, obtained by the action of $Ca(OCl)_2$ on *p*-$C_6H_4Me·SO_2·NHBz$ in CCl_4–H_2O at 0° and (**II**) give essentially resins. Similar results are obtained with *di*-p-*toluenesuplhonchloroimide*, m.p. 100—102°, obtained by the chlorination of di-*p*-toluenesulphonimide, m.p. 168·5°, derived from *p*-$C_6H_4·SO_2·NHNa$ and *p*-$C_6H_4Me·SO_2Cl$ in *o*-$C_6H_4Cl_2$ at 200°. *N*-Chlorosaccharin gives (**IV**) in 28·3% yield, saccharin, and N-2-*chloro*cyclo*hexylsaccharin*, m.p. 169°. In the presence of $COMe_2$ the main product is *cyclo*hexene chlorohydrin. N-*Bromosaccharin*, from Ag saccharin and Br in CCl_4, affords N-2-*bromo*cyclo*hexylsaccharin*, m.p. 128°, but (**III**) could not be isolated. CCl_3·CO·NHCl and (**II**) in boiling CCl_4 slowly give (**IV**) in 14·3% yield and *trichloroacet-2-chloro*cyclo*hexylamide*, m.p. 84°. *N*-Chloroacylanilides are very useful provided that they are not readily isomerised to nuclear-substituted products. 2 : 4 : 1-$C_6H_3Cl_2$·NAcCl, 2 : 4 : 1-$C_6H_3Cl_2$·NBzCl, 2 : 4 : 1-C_6H_3ClBr·NAcCl, 2 : 4 : 1-C_6H_3ClBr·NBzCl, 4 : 1-C_6H_4Cl·NAcCl, and 4 : 1-NO_2·C_6H_4·NAcCl (**V**) give ~70—90% of (**IV**) and ~90% of halogen-free acylanilide. The change does not appear to be influenced by steric hindrance but to be subject to polarisation effects. Steric influences do not appear to control addition. Certain chloroacylanilides such as (**V**) appear particularly prone to di-substitution. 2 : 4-$C_6H_3Cl_2$·NCl·SO_2·C_6H_4Me loses its active H fairly readily but gives >50% substitution. To work economically it is necessary to carry out series experiments in which the non-chlorinated excess of substrate is removed and worked up again. Diethylbarbituric acid is transformed by $Ca(OCl)_2$ in AcOH into the *NN′-Cl*$_2$-derivative, m.p. 127·5°, which gives 28·3% of (**IV**) from (**II**). *NN′N″*-Trichlorocyanuric acid and (**II**) in boiling CCl_4 give cyanuric acid, (**IV**) in 29·2% yield, and a non-volatile, resinous residue. The use of NHBzCl, NHAcCl, O:C_6H_4:NCl, and (·CO·NClMe)$_2$ is described. Bromination by (**I**) is usually effected in boiling CCl_4 (3—4 times the vol. of olefine). Simple olefines of not too small mol. wt. are brominated within 15—60 min., if they contain at least 1 CH_2 vicinal to the double linking. With equiv. amounts the yields are 50—60% and attain 80% in presence of a (recoverable) excess of olefine. The products are homologues of allyl bromide and in suitable cases are homogeneous. The no. of possibilities is limited by the fact that CH_2 reacts with

(**I**) almost invariably more rapidly than Me. The following are thus obtained: monobromides from (**II**), CMe_2:CHMe, b.p. 34—40°/15 mm., *β-methyl-*Δ^{β}*-hexene*, b.p. 54°/12 mm.; Δ^{β}-octene, b.p. 69°/11 mm., di*iso*butylene, b.p. 53°/11 mm.; Δ^{δ}*-nonene*, b.p. 99—112°/1 mm., *dodecene*, b.p. 87°/0·3 mm., and pinene, b.p. 101—109°/12 mm.; CHPh:CH·CH_2Br, b.p. 84—85°/0·8 mm., from CHPh:CHMe; *γγ-diphenylallyl bromide*, b.p. 96—98°/0·5 mm., from CPh_2:CHMe; *γ-bromo-αα-diphenyl-*Δ^{α}*-butene*, m.p. 82°, from CPh_2:CHEt (from MgPhBr and $Pr^{\alpha}CO_2Et$). All the Br-compounds give a spontaneous, vigorous reaction when mixed with the double vol. of *cyclo*hexylamine; the change is typical of allyl bromides and is never observed with simple saturated Br-compounds or with homologous vinyl bromides. Substitution at the C:C linking can occur only to a very limited extent and is not generally observed since Br is quantitatively yielded to boiling $AgNO_3$–EtOH. The allyl bromides are usually readily converted into diolefines by boiling quinoline or collidine, thus further confirming the allyl position of Br. The products contain ~93% of conjugated diene but their constitution is not invariably well defined. $\Delta^{1:3}$*-cyclo*Hexadiene (**VI**), *β-methyl-*$\Delta^{\beta\delta}$*-hexadiene*, b.p. 107°/760 mm., $\Delta^{\beta\delta}$- (or $\Delta^{\delta\zeta}$-)*nonadiene*, b.p. 85—88°/100 mm., and (?) $\Delta^{\alpha\gamma}$*-dodecadiene* (**VII**), b.p. 101°/13 mm., m.p. −52°, are thus obtained. (**VI**) and (**VII**) are highly resistant to (**I**); in course of time active halogen disappears and $(CH_2{\cdot}CO)_2NH$ is formed but Br_1-dienes could not be isolated in appreciable amount. CH_2 in alliance with an open conjugated system is much less reactive than when vicinal to a single unsaturated linking; diolefines are not polymerised in contact with (**I**). Diolefines with isolated double linking behave normally towards (**I**); thus *βι-*dimethyl-$\Delta^{\beta\theta}$-decadiene, b.p. 88°/12 mm. [from *βι-dimethyldecane-βι-diol*, m.p. 74° (*hydrate*, m.p. 53°), through *β-chloro-βι-dimethyldecan-ι-ol*, m.p. 66°, to *βι-dichloro-βι-dimethyldecane*, m.p. 26°, which is dehalogenated by boiling quinoline], affords a *dibromide* which could not be converted satisfactorily into the corresponding tetraene. Polybromination of mono-olefines can be achieved by using a larger proportion of (**I**) or preferably by the action of (**I**) on the purified Br_1-derivative. 1 : 4-Dibromo-Δ^{2}-*cyclo*hexene, m.p. 108°, and (?) *aδ*-dibromo-Δ^{β}-dodecene, b.p. 86°/0·0002 mm., are thus obtained; the last compound is transformed by quinoline into a *dodecatriene*, b.p. 100—108°/10 mm., m.p. −34°, hydrogenated (Pd–$BaSO_4$) to dodecane, m.p. −12°. Bromination of (**II**) in CCl_4 containing dry BzOH gives little (**III**) but the presence of CO_2H appears sometimes immaterial. Acid anhydrides are permissible and ether groups are not essentially harmful particularly if reaction with highly active CH_2 is accomplished in Et_2O. *cyclo*Hexenyl Et ether behaves obscurely since Br enters in part in place of H neighbouring to OEt. *cyclo*Hexenyl acetate readily affords 4-*bromocyclohexenyl acetate*, b.p. 116—118°/12 mm. Cholesterol is very rapidly substituted. Et undecenoate gives an unidentified Br_1-derivative, b.p. 120—126°/0·8 mm., in 46·4% yield. Et oleate yields a reactive Br_1-compound which could not be distilled or smoothly transformed into a diene ester. CHMe:CH·CO_2Me reacts slowly under standard conditions, more rapidly with excess of the boiling ester, to yield *Me γ-bromocrotonate*, b.p. 83—85°/13 mm., hydrolysed to the acid, m.p. 73·5°, which with an excess of alkali gives $O(CH_2{\cdot}CH{:}CH{\cdot}CO_2H)_2$ m.p. 195°. CMe_2:CH·CO_2Me is much more easily transformed into *Me γ-bromo-β-methylcrotonate*, b.p. 84—89°/12 mm. CHMe:CH·CHO gives black decomp. products but its acetal appears to be brominated. H. W.

α-Bromopropionylmethionine, m.p. 111·5—112·5° (corr.).—See A., 1942, III, 906.

(A) **Polymerisation of acrylonitrile and polyacrylonitrile.** (B) **Polymerisation of methacrylonitrile and polymethylacrylonitrile.** W. Kern and H. Fernow (*J. pr. Chem.*, 1942, [ii], **160**, 281—295, 296—314).—(A) Catalytic polymerisation of CH_2:CH·CN with 1% of Bz_2O_2 is examined, and the reaction mechanism is discussed. Under certain conditions of temp. and $[Bz_2O_2]$, there is some loss of HCN and formation of C_5H_5N. Polyacrylonitrile (**I**), decomp. ~350° (99% C_5H_5N + 1% Bz_2O_2), and 40% aq. NaOH afford polyacrylic acid. Polymerisation of a mixture of CH_2:CH·OAc, CHPh:CH_2, and CH_2:CMe·CO_2Me is effected in presence of 5% of H_2O-free HCN and 1% of Bz_2O_2 at 50° for 120 hr.

(B) CH_2:CMe·CN is polymerised in presence of 1—5% of Bz_2O_2 at 60° (cf. A., 1936, 1238). The physical properties of polymethylacrylonitrile (**II**), decomp. ~200° (softens at 115°), are given; warm 40% aq. NaOH converts it into polymethylacrylic acid. Although no pure product is obtained by thermal decomp. of (**I**), (**II**) at 250° affords CH_2:CMe·CN. A. T. P.

Absorption spectra and *X*-ray examination of isomeric gluconononitriles.—See A., 1942, I, 386.

II.—SUGARS AND GLUCOSIDES.

Effect of temperature on the validity of Hudson's rules of isorotation.—See A., 1942, I, 388.

So-called "*iso*sucrose." A. Georg (*Annalen*, 1942, **551**, 272—276; cf. A., 1935, 69; Irvine *et al.*, *ibid.*, 1226).—In reply to Schlubach *et al.* (A., 1942, II, 279) the author maintains the correctness of his hypothesis that *iso*sucrose (**I**) is *β-d*-glucopyranosido-*α-d*-fructofuranoside and not an *iso*turanose. Account is thereby rendered of the products of hydrolysis, the ease of hydrolysis, and the stability towards Weidenhagen's invertase. Reasons are advanced for considering the reducing power of (**I**) to differ from that of "normal" reducing dissacharides. H. W.

Synthesis of 3-*β-d*-glucosidoprotocatechualdehyde and its enzymic fission. B. Helferich and P. Papalambrou (*Annalen*, 1942, **551**, 242—248).—3 : 4 : 1-(OAc)C_6H_3(OH)·CHO and $MeSO_2Cl$ in C_5H_5N at 0° yield 4-*methanesulphonyl-3-acetylprotocatechualdehyde*, m.p. 97°, converted by short warming with C_5H_5N and N-HCl into 4-*methanesulphonylprotocatechualdehyde* (**I**), m.p. 127° (p-*nitrophenylhydrazone*, m.p. 235°), methylated to *methanesulphonylvanillin*, m.p. 89°, also obtained directly from vanillin and $MeSO_2Cl$. (**I**) is transformed by acetobromoglucose and N-NaOH in $COMe_2$ into 4-*methanesulphonyl-3-β-*d*-glucosidoprotocatechualdehyde tetra-acetate*, m.p. 172°, $[\alpha]_D^{25}$ −58° in $CHCl_3$ (3-*methanesulphonyl-4-β-*d*-glucosidoprotocatechualdehyde tetra-acetate* has m.p. 125°, $[\alpha]_D^{22}$ −40·7° in $CHCl_3$). This is transformed by controlled alkaline hydrolysis followed by acetylation (Ac_2O in C_5H_5N at room temp.) into 3-*β-*d*-glucosidoprotocatechualdehyde penta-acetate*, m.p. 134—135·5°, $[\alpha]_D^{18}$ −21·4° in $CHCl_3$ (the isomeric *penta-acetate* has m.p. 120·5°, $[\alpha]_D^{21}$ −28·8° in $CHCl_3$), which is hydrolysed to 3-*β-*d*-glucosidoprotocatechualdehyde*, softens at 125°, m.p. 142—145°, $[\alpha]_D^{21}$ −103° in acetate buffer (p-*nitrophenylhydrazone*, m.p. 235°). This is less readily hydrolysed than the isomeric 4-compound by emulsin of sweet almonds. H. W.

Crystalline cardiac glucoside from *Adonis vernalis*. H. Rosenmund and T. Reichstein (*Pharm. Acta Helv.*, 1942, **17**, 176—184).—From 45 g. of the commercial drug prep. "Adovern" there was obtained 18 g. of a H_2O-sol. resin. From this was obtained 6·1 g. of fraction *B* by partition with $CHCl_3$–96% EtOH, whilst the neutral aq. fraction contained 11·5 g. of fraction *C*. Acetylation of *B* (C_5H_5N–Ac_2O) and chromatography of the crude product yielded an *acetate* of the active cardiac glucoside, m.p. 146—148°, $[\alpha]_D^{16}$ −56·5°±2° in $CHCl_3$ [free *glucoside*, m.p. 263—265° (decomp.), $[\alpha]_D^{16}$ −27° in MeOH], and an *acetate*, m.p. 237—238° (decomp.), $[\alpha]_D^{14}$ +30·4°±3° in $CHCl_3$, hydrolysed to a *substance*, m.p. 238—240° (decomp.), $[\alpha]_D^{15}$ +53±2° in EtOH, the lower biological activity of which corresponded more with that of a genin. Chromatography of the crude product of acetylation of *C* yielded *acetate* 1, m.p. 122—124°, *acetate* 2, m.p. 59—60°, $[\alpha]_D^{16}$ +147°±3° in $COMe_2$, from which a cryst. compound could not be isolated by hydrolysis with $Ba(OH)_2$–MeOH, and an amorphous fraction from which adonitol, m.p. 102—104°, was isolated after hydrolysis with $KHCO_3$ in aq. MeOH. P. G. M.

Composition of the eriodictyol glycoside. A. Mager (*Z. physiol. Chem.*, 1942, **274**, 109—115).—The eriodictyol glycoside, m.p. 184—186° (much decomp.), $[\alpha]_D^{20}$ −51·53° in C_5H_5N, is isolated from citrin by chromatography over Al_2O_3. It is hydrolysed by 1% H_2SO_4 to eriodictyol, m.p. 258—260° (decomp.), and rhamnose, identified as the phenylosazone, m.p. 186—187° (decomp.). H. W.

Hemicelluloses and pectic material from cottonwood.—See A., 1942, III, 950.

III.—HOMOCYCLIC.

Chlorination of benzene.—See B., 1942, II, 359.

Binary systems composed of titanium tetrachloride and nitrocompounds. N. A. Pushin, L. Nikolić, A. Radojčin, and T. Uoroponova (*Annalen*, 1942, **551**, 259—271).—The m.p. diagrams show that $TiCl_4$ forms well-defined equimol. *compounds* with $PhNO_2$, *m-* and *p*-$C_6H_4Cl{\cdot}NO_2$, *m*-$C_6H_4Br{\cdot}NO_2$, *o-*, *m-*, and *p*-$C_6H_4Me{\cdot}NO_2$, and 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ with respective crystallisation temp. 75°, 61°, 54·5°, 72°, 62·5°, 75°, 72·3°, and 64°. $TiCl_4$ and *m*-$C_6H_4(NO_2)_2$ give a 1 : 1 and probably a 2 : 1 *compound*; with 1 : 3 : 5-$C_6H_3Me(NO_2)_2$ the corresponding 1 : 1 and 2 : 1 *substances* crystallise at 43° and 46°, respectively. $TiCl_4$ and 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ do not form a compound and do not always mix completely in the liquid phase. H. W.

Mechanism of the thermal polymerisation of styrene.—See A., 1943, I, 19.

Occurrence of free radicals in chemical reactions. X. Aromatic diacyl peroxides and triphenylmethyl. H. Wieland and A. Meyer (*Annalen*, 1942, **551**, 249—258; cf. A., 1937, II, 498).—Evidence is adduced in favour of the view that the fourth Ph of CPh_4 obtained in small proportion by the interaction if Bz_2O_2 and CPh_3 in C_6H_6 is derived from the solvent. Gradual introduction of 4N-NaOH into the solution obtained by addition of *p*-$C_6H_4Me{\cdot}COCl$ in $COMe_2$ to a mixture of 30% H_2O_2 and $COMe_2$ gives *di*-p-*tolyl peroxide* (**I**), m.p. 143—144° (much decomp.), which with CPh_3 in PhMe affords *CPh*$_3$ p-*toluate*, m.p. 187—189° (obtained also from *p*-$C_6H_4Me{\cdot}CO_2Ag$ and CPh_3Cl), and *triphenyl*-p-*tolylmethane* (**II**), m.p. 163°. (**I**) and CPh_3 in PhCl yield *chlorotetraphenylmethane*, m.p. 194°, and in MeOBz give *Me tetraphenylmethane*-p-*carboxylate*, m.p. 135°. (**II**)

is oxidised by SeO_2 at 220° and then at 320° to *tetraphenylmethane-p-carboxylic acid*, m.p. 214°, decarboxylated to CPh_4, m.p. 274—275°. $(p\text{-}OMe\cdot C_6H_4)_2O_2$ and CPh_3 in C_6H_6 afford CPh_4, with $p\text{-}OMe\text{-}C_6H_4\cdot CO_2H$ and $CPh_2\cdot OH$ which result from the ready hydrolysis of *CPh₃ anisate*, m.p. 164°. $(p\text{-}C_6H_4Me)_2O_2$ and $C(C_6H_4Me\text{-}p)_3$ in PhMe afford *tetra-p-tolylmethane*, m.p. 130°. cyclo*Hexyltriphenylmethane*, m.p. 143—145°, is derived from Bz_2O_2 and CPh_3 in *cyclo*hexane. H. W.

Tri-*o*-tolylmethane. P. D. Bartlett and J. E. Jones (*J. Amer. Chem. Soc.*, 1942, **64**, 1837—1842).—*Tri-o-tolylmethane* (**I**), m.p. 130·5—131·5° after sintering at ~126°, differs from its homologues in giving with $CPhMe_2K$ in Et_2O–N_2 at room temp. in absence of light an insol. K_3 salt, $CH(C_6H_4\cdot CH_2K\text{-}o)_3$, converted by CO_2 into *tri-(o-carboxymethylphenyl)methane* (**II**) (98·3%), m.p. 265—295° (decomp.; block; gradual heating), <310° (later decomp.; block; immediate), and $PhPr^{\beta}$ (86%). The structure of (**II**) is proved by formation of a *Et₃* ester, m.p. 196·5—197·5°, by HCl–EtOH and by stability in conc. H_2SO_4 at 100°. Homologues form salts, CAr_3K, but $CHPh(C_6H_4Me\text{-}o)_2$ (**III**) is intermediate, giving with 0·059N-$CPhMe_2K$ and later CO_2 86% of *phenyldi-o-tolylacetic*, m.p. 184—185° (in H_2SO_4 at 100° gives CO), and 8·6% of *phenyl-o-tolyl-o-carboxymethylphenylacetic acid* (**IV**), m.p. 265—257° (decomp.) (*Me₂* ester, m.p. 105—106°, prepared by MeOH–HCl; gives no CO in H_2SO_4); 0·107N-(**III**) and 0·083N-$CPhMe_2K$ give 39% of (**IV**). Explanations of the differences by means of damped resonance and steric hindrance are discussed. Di-*o*-tolylphthalide [prep. from $o\text{-}C_6H_4(CO)_2O$ and $o\text{-}C_6H_4Me\cdot MgBr$ in Et_2O–C_6H_6; 61·5% yield] and H_2–Cu chromite at 235—250°/2325 lb. give 2 : 2′-*dimethyltriphenylmethane-2″-carboxylic acid* (70—83%), m.p. 241—242° (in one experiment in dioxan, 51% with 2·8% of a neutral substance, m.p. 145·4—146°), converted by PCl_5–C_6H_6 and then NH_2Ph into the *anilide*, m.p. 164·0—164·7°. With PCl_5–PhMe at room temp. and later 100° and then $SnCl_2$–HCl–Et_2O at 0° this gives *di-o-tolyl-o′-aldehydophenylmethane* (44%), sinters at 131°, m.p. 134·5—135° (*oxime*, m.p. 174·8—175·2°; impure *semicarbazone*, m.p. 208·5—209·5°), which with NaOEt–EtOH–85% N_2H_4,H_2O (no hydrazone isolated) at 200—210° gives 83% of (**I**). The m.p. of (**I**) is much depressed by impurities. Interaction of $o\text{-}C_6H_4Me\cdot MgBr$ with $COPh_2$ in C_6H_6–Et_2O, decomp. by dil. H_2SO_4, and heating the product with 85% HCO_2H gives $CHPh_2\cdot C_6H_4Me\text{-}o$ (**V**) (53%), m.p. 81—83°; use of EtOBz instead of $COPh_2$ gives similarly (**III**) (45%), m.p. 102—104°. With $CPhMe_2K$, (**V**) gives 98·7% of $o\text{-}C_6H_4Me\cdot CPh_2\cdot CO_2H$, m.p. 228—229° or 190—200° (block; decomp.), converted in conc. H_2SO_4 at 50° into CO and $o\text{-}C_6H_4Me\cdot CPh_2\cdot OH$ (82·5%), m.p. 98—99° (lit. 98°). $(p\text{-}C_6H_4Me)_3CH$, b.p. 232°/11 mm., gives similarly 73·5% of $(p\text{-}C_6H_4Me)_3C\cdot CO_2H$ and thence $(p\text{-}C_6H_4Me)_3C\cdot OH$. M.p. <230° are corr. R. S. C.

"Tervalent" carbon. XVI. A much discussed radical-chemical problem and its final solution. K. Ziegler (*Annalen*, 1942, **551**, 127—149).—Evidence is adduced from the literature against Hückel's dictum that a dimeride has never been certainly obtained from radicals in which one substituent is of aliphatic nature and that these radicals become altered largely at any rate in another manner. All evidence points in the same direction that substituted ethanes of this type exist which can dissociate spontaneously into radicals. Further it is shown that the rate of autoxidation in presence of pyrogallol of many not exclusively aromatic-substituted ethanes [tetraphenyl-dimethyl- (**I**), -diethyl- (**II**), -dipropyl-, -di*iso*propyl- (**III**), -di-*n*-butyl-, -di*tert.*-butyl-, -di-*n*-amyl-, and -di*cyclo*hexyl-ethane] follows exactly the same laws as that of C_2Ph_6; hence it must be assumed that these compounds behave similarly to C_2Ph_6 and therefore decompose spntaneously into radicals. The only exceptional compound is di-9-phenylfluorenyl. Additional evidence in the same direction is afforded by the isolation of $CPh_2Me\cdot O_2H$ and $CPh_2Et\cdot O_2H$ in the cryst. condition by the autoxidation of $(CPh_2Me)_2$ and $(CPh_2Et)_2$ with O_2 in presence of pyrogallol. Autoxidation of C_2Ph_6 in presence of foreign O_2-acceptors may be accompanied by chain reactions in which CPh_3 functions as a very efficient O_2-carrier. This phenomenon can be utilised for the detection of very slight dissociation since it causes great multiplication of what, in absence of acceptor, may be a very small O_2 absorption. The reaction is strongly positive with all the ethanes described above and since these are employed solely in the colourless, cryst. ethane forms their true radical dissociation is established. Observation of the disproportionating decomp. of (**I**), (**II**), and (**III**) shows that this takes place with certainty through radicals and is caused by two radicals in contact exchanging a H atom between one another; with (**I**), (**II**), and (**III**) respectively this takes place 10, 100, and ~3500 times more slowly than radical formation. Hence with these ethanes in absence of O_2 the dissociation equilibria must be established almost without hindrance. It is remarkable that no marked colour of the solution is observable with these and similar compounds at temp. at which the decomp. consts. are similar to those of C_2Ph_6. This may be due to a much greater rate of re-association or to the feeble colour of the radicals. Tetra*cyclo*hexyldiphenylethane is obtained as a colourless cryst. compound which towards O_2 and pyrogallol behaves in the same manner as C_2Ph_6; O_2 is gradually absorbed as the ethane decomposes and the criteria of "indirect" oxidation through a radical (change of the first order independent of O_2 pressure) are fulfilled. The existence of di*cyclo*hexylphenylmethyl H peroxide is rendered probable and the autoxidation of unsaturated acceptors (*cyclo*hexadiene and styrene) is shown to be greatly accelerated by the ethane. There is no evidence of the particularly marked retardation of the association of di*cyclo*hexylphenylmethyl as postulated by Hückel. Complete hydrogenation of 2 Ph groups of C_2Ph_6 diminishes the rate of dissociation in the ratio 170 : 1 whilst complete hydrogenation of 2 additional Ph groups does not cause much further change. An explanation of the causes of radical dissociation is sought in a combination of Hückel's theory with the author's hypothesis of the dilatation of the central linking by *cyclo*hexyl. H. W.

"Tervalent" carbon. XVII. Kinetics and energetics of radical dissociations. K. Ziegler, A. Seib, K. Knoevenagel, P. Herte, and F. Andreas (*Annalen*, 1942, **551**, 150—186).—Improved methods have been devised for the measurement of the rate of absorption of O_2 by solutions of substituted ethanes or their radicals. An essential for the application of the method is an adequate concn. of pyrogallol and as great a dilution of the ethane as is possible. The correctness of conditions is recognised by the independence of the reaction const. on the O_2 pressure and the strict fulfilment of the requirements for a change of the first order. The absorption of O_2 by C_2Ph_6 in a wide variety of solvents has been measured; the consts. thus obtained agree well with those recorded for absorption of NO and those determined with I in $CHCl_3$ (cf. Ziegler *et al.*, A., 1933, 943). The influence of solvent on the const. is remarkably small. Comparison of the rates of dissociation of C_2Ph_6, diphenyltetradiphenylyl- and tetraphenyldidiphenylyl-ethane in $CH_2(CO_2Et)_2$ shows that the influence of the *p*-Ph group is not particularly marked. Decomp. consts. (K), half life periods (τ), energy of activation (E), and temp.-controlled factors (α) are measured for many tetraphenyldialkylethanes in PhBr over an interval of 40°. In these respects $(CPh_2Me)_2$ is much more closely allied to C_2Ph_6 than to its higher homologues. The latter containing *n*-alkyl groups form a class by themselves with characteristic E and α and possibly without a marked influence of the length of the alkyl chain. Those containing *iso*alkyl residues also form a well-marked group which dissociate much less rapidly than the *n*-alkyl class due mainly to much smaller vals. of α. Dimethyl-, diethyl-, di-*n*-propyl-, and di-*n*-butyl-dixanthyl have almost the same vals. of E and α and form a well-marked group in which the first named compound does not occupy a unique position. In general, the authors' results are not in harmony with the theoretical considerations of Polanyi *et al.* (A., 1929, 404), the apparent agreement noted by Salomon (A., 1934, 44) being fortuitous. From the viewpoint of energy of activation the di-*n*-alkyldixanthyls and $(CPh_2Me)_2$ are equiv., the strongly polarising entry of the 2 oxido-O atoms into the aromatic nucleus having no apparent effect on the firmness of the C–C linking. Comparison of the higher tetraphenyldialkylethanes with the dixanthyls shows that the 2 O cause a distinct increase in the firmness of the central linking. *sec.* Substituents cause a weakening of the attachment of substituted methyls, shown by a lowering of the activation energy by ~2 kg.-cal. The absorption of O_2 by di-9-phenylfluorenyl is a change of the first order but the reaction const. is greatly dependent on the O_2 pressure; in presence of pyrogallol the rate of the total reaction is somewhat diminished but its dependence on the pressure of O_2 is scarcely affected. This unique behaviour is attributed to an increased tendency towards association. Diphenyltetra(diphenylyl)ethane is best prepared by the reduction by $CrCl_2$ of phenyldidiphenylylcarbinol in $COMe_2$ containing HCl. *Diphenyl-*n*-propylcarbinol Me ether*, m.p. 90°, is converted by Na–K followed by $(CMe_2Br)_2$ into *tetraphenyldi-*n*-propylethane*, m.p. 70° (under N_2). $Bu^{\alpha}CO_2Et$ and MgPhBr yield *diphenyl-*n*-butylcarbinol*, b.p. 135—140°/0·2 mm., transformed through the *Me ether*, m.p. 47°, into *tetraphenyldi-*n*-butylethane*, m.p. 62—63° (under air), 68—70° (under N_2). Similarly obtained are *diphenyl-*n*-amylcarbinol*, m.p. 46—47°, its *Me ether*, m.p. 55—57°, and *tetraphenyldi-*n*-amylethane*, which could not be caused to crystallise. *Tetraphenyldiisopropylethane* has m.p. 140—141° (under N_2). *Diphenyltert.-butylcarbinol Me ether*, b.p. 172—173°/13 mm., m.p. 45°, is described. *cyclo*Pentyldiphenylcarbinol (**I**), m.p. 44° (lit. 112°), obtained from Me *cyclo*pentanecarboxylate and MgPhBr or from $COPh_2$, *cyclo*pentyl bromide, and Na, gives a *Me ether*, b.p. 100—105°/0·001 mm., and thence *dicyclopentyltetraphenylethane*, m.p. 117—119° (under N_2), 87—89° (under air). The following are described incidentally: cyclo*pentyldiphenylacetic acid*, m.p. 161—162°, from the K compound and CO_2; cyclo*pentyldiphenylmethane*, b.p. 126°/15 mm., m.p. 32—33°, from the K compound and H_2O or by dehydration (AcOH–H_2SO_4) of (**I**) to cyclo*pentylidenediphenylmethane*, m.p. 62—63°, which is hydrogenated. H. W.

"Tervalent" carbon. XVIII. Mechanism of a disproportionation. K. Ziegler, R. B. Whitney, and P. Herte (*Annalen*, 1942, **551**, 187—205).—The "disproportionating" decomp. of $(CPh_2Me)_2$, $(CPh_2Et)_2$, and $(CPh_2Pr^{\beta})_2$ occurs more slowly than the radical dissociation. Attempts to measure the rate of decomp. by titration of the unsaturated compounds produced by means of Br or ICl are

not sufficiently accurate and the process is followed interferometrically in PhBr at various temp. The reaction is of the first order, thus excluding the possibility that the ethane is in dissociation–association equilibrium with the radicals one of which stabilises itself by unimol. loss of active H which is absorbed by the other radical with immeasurable rapidity. The remaining possibilities are (*A*) that the ethane is in equilibrium with the radical and that disproportionation occurs in true interaction of two radicals, and (*B*) that the ethane is in equilibrium with the radical but the products of disproportionation are formed by a direct decomp. of the ethane portion and, also, a (small) proportion of the radical becomes disproportioned through the ethane. Decision in favour of (*A*) is reached by a study of the autoxidation of $(CPh_2Me)_2$ in very dil. solution in PhCl containing pyrogallol. $CPh_2{:}CH_2$ in the product is transformed by $CPhMe_2K$ into $CPh_2K{\cdot}CH_2{\cdot}CPhMe_2$, which is converted by CO_2 into the non-volatile $CO_2H{\cdot}CPh_2{\cdot}CH_2{\cdot}CPhMe_2$, leaving CHPhMe as the only possible volatile compound. This can be readily detected by slow reaction with $CPhMe_2K$ to CPh_2MeK and thence to $CPh_2Me{\cdot}CO_2H$. It cannot, however, be found thus in the reaction products. Disproportionation therefore is caused by the direct exchange of H between two radicals in contact and an independent direct disproportionating decomp. of tetraphenyldialkylethanes is not encountered. H. W.

" Tervalent " carbon. XIX. Radical hydrogen peroxides ; pyrogallol as antioxidant. K. Ziegler and P. Herte (*Annalen*, 1942, **551**, 206—212).—Gradual addition of solid $(CPh_2Me)_2$ to PhCl containing pyrogallol (**I**) through which O_2 is passing at 80° gives *αα-diphenylethyl H peroxide* (**II**), m.p. 86°, in 70% yield. (**II**) can be sublimed unchanged at 70—75°/high vac. and is stable at its m.p. but commences to decompose at 160° in a complex manner. It sometimes inflames when brought in contact with conc. H_2SO_4, is stable towards warm alkali hydroxide, and liberates I from KI particularly rapidly in presence of AcOH. With boiling H_2O it affords H_2O_2 and $CPh_2Me{\cdot}OH$, also obtained by treating (**II**) with excess of MgPhBr. The free H of (**II**) has no marked acidic properties but (**II**) is converted by CPh_3Cl and alkali into *CPh_3 αα-diphenylethyl peroxide*, m.p. 126—127°. *αα-Diphenylpropyl H peroxide*, m.p. 81—82°, is obtained similarly from $(CPh_2Et)_2$. Loss of H converts (**I**) into complex, sparingly sol. and difficultly volatile substances. H. W.

" Tervalent " carbon. XX. Radicals as catalysts as autoxidation. K. Ziegler and K. Gänicke (*Annalen*, 1942, **551**, 213—221 ; cf. A., 1933, 943).—Further purification of benzodimethylfulvene (**I**) has not led to the formation of reaction chains with >55,000 members in autoxidations catalysed by CPh_3, possibly owing to the formation of compounds between CPh_3 and the unsaturated acceptor. The difference in the activity of $(CPh_2Me)_2$ and $(CPh_2Et)_2$ towards the absorption of O_2 by (**I**) is exactly as would be expected from the great difference in their half-life periods (6600 : 1). Di*cyclo*hexyltetraphenylethane (**II**) is a potent O_2-carrier giving a chain with ~2000 links and thus comparable with that of C_2Ph_6 and (**I**) which has not been purified with particular care. The catalytic activity of (**II**) in $CHCl_3$ is practically non-existent after 143 hr. at 20°. The catalytic activity of dimethyl-, diethyl-, and dibutyl- (**III**) -dixanthyl is < that of (**II**); (**III**) is the most active of the three compounds. Free substituted-methyl radicals can function universally as autoxidation catalysts. Conversely in doubtful cases the incidence of catalytic activity may be regarded as a proof of radical dissociation. In presence of (**I**) and CPh_3 and under conditions which cause ~1200—1500 links in the reaction chain of the undisturbed system there is a reduction to ~500 links in the presence of M./50,000 pyrogallol (**IV**) and to ~15 links when (**I**) and (**IV**) are in equiv. proportions. Amongst compounds which can yield H (**IV**) is by far the most active. PhOH, m-$C_6H_4(OH)_2$, and α-$C_{10}H_7{\cdot}OH$ have approx. equal activity whereas guaiacol and β-$C_{10}H_7{\cdot}OH$ are less potent. Freshly distilled pyrrole is not an inhibitor and does not function as O_2-acceptor. If preserved for a few hr. under N_2 it becomes slightly yellow and then behaves as a powerful antioxidant. PhSH behaves by itself and in conjunction with CPh_3 as a powerful catalyst of autoxidation Ph_2S_2 does not accelerate the autoxidation of (**I**) with or without CPh_3 and does not influence the chain reactions. It is not therefore causative of the action of PhSH. H. W.

Purification of anthracene, phenanthrene, and carbazole.—See B., 1942, II, 359.

Simplified preparation of rubrene. G. Wittig and D. Waldi (*J. pr. Chem.*, 1942, **160**, [ii], 242—244).—CHPh:CHBr and LiPh in Et_2O (N_2), followed by $COPh_2$–Et_2O, afford *αα'γ-triphenyl-Δ$^{\beta}$-propinen-α-ol*, m.p. 81—82°, converted by $SOCl_2$ at −10° into the corresponding chloride, which with 2% of quinoline at 120° in vac. yields rubrene, m.p. 332°. A. T. P.

H. Wieland's work on nitrogenous substances. F. Klages (*Naturwiss.*, 1942, **30**, 351—359).—A review. F. O. H.

Organo-boron–nitrogen compounds. II. Reaction of boron chloride with *p*-toluidine. C. R. Kinney and M. J. Kolbezen (*J. Amer. Chem. Soc.*, 1942, **64**, 1584—1585 ; cf. A., 1939, II, 460).—Addition of p-$C_6H_4Me{\cdot}NH_2$ (**I**) in C_6H_6 to BCl_3–C_6H_6 at 0° gives the 1 : 1 *salt* (95·4%) (**II**), m.p. 159—160° (loses HCl), which in boiling C_6H_6 (or at the m.p.) gives 2 HCl and *" trichloro-p-tolylboron nitride "* (**III**), $NX<^{BCl{\cdot}NX}_{BCl{\cdot}NX}>BCl$ (X = *p*-tolyl), $+C_6H_6$, softens at 304°, m.p. 308—309° (darkens). In cold H_2O, (**III**) gives p-$C_6H_4Me{\cdot}NH_2$,HCl and H_3BO_3. BCl_3 and an excess of (**I**) in C_6H_6 at 110° (bath) give *B tri-p-toluidide* (35%), $B(NH{\cdot}C_6H_4Me\text{-}p)_3$, m.p. 165—166°, unstable in air or H_2O, and reconverted by HCl–C_6H_6 into (**II**) and $C_6H_4Me{\cdot}NH_2$,HCl. R. S. C.

Associating effect of the hydrogen atom. XI. Hydrogen bonds involving the sulphur atom. The S–H–N bond. G. Hopkins and L. Hunter (*J.C.S.*, 1942, 638—642 ; cf. A., 1942, II, 63).—Thioamides possessing the group –NH·CS– are associated by virtue of intermol. S–H–N linkings. Replacement of imino-H, or its engagement in chelate ring formation, prevents association by rendering such bonds impossible. Although CSMe·NHPh (**I**) shows a high degree of association, *thioacet-o-nitroanilide*, m.p. 109°, *Me thioacetanthranilate*, m.p. 110—111°, and *2-thioacetamido-5 : 4'-dimethylazobenzene*, m.p. 137—139°, are substantially unimol., since intramol. co-ordination of the anilido-H renders it non-available for intermol. co-ordination. Isomerides or analogues of these compounds with *m-* or *p*-substituents, *i.e.*, donor groups too far removed to involve anilido-H chelation, are as highly associated as (**I**). Mol. wt. measurements show that 2-thiolbenzthiazole, m.p. 179°, is highly associated (the cyclic S probably plays no part in association), whereas 2-methylthiolbenzthiazole, m.p. 49°, is unimol. 2-Methylbenzthiazole is completely unassociated, as there is no tautomeric H available; 2-anilinobenzthiazole is strongly associated, due to amidine association (*loc. cit.*). The unimol. state of thiodiphenylamine (does not form a S–H–N bond) supports the view that only H capable of tautomeric transfer will take part in S–H–N linkings. Thioacridone shows high association in $PhNO_2$, whereas its *S*-Me and *S*-Bz derivatives are unassociated (in $C_{10}H_8$). Thioacridone is considered to have a chain-polymeric structure in which the mol. units are joined by S–H–N linkings between CS and NH of adjacent mols. Derivatives of $HCS{\cdot}NH_2$ show abnormal association not necessarily dependent on H bonds. $HCS{\cdot}NMe_2$ is highly associated in C_6H_6 solution. The following are prepared from RCO·NHR' and P_2S_5 in boiling xylene : *thioacet*-m-, m.p. 98°, and -p-*nitroanilide*, m.p. 175°, -m-, m.p. 64°, and -p-*toluidide*, m.p. 52—53° (*o*-isomeride has m.p. 66°), *-ethylanilide*, m.p. 49°, and *-benzylanilide*, m.p. 82—83°; *thiobenzbenzylanilide*, m.p. 119—120°; *Et* p-*thioacetamidobenzoate*, m.p. 98°; p-*thioacetamidoazobenzene*, m.p. 143—144°. A. T. P.

Maleanils.—See B., 1942, II, 422.

***N*-Diphenylyloxamic acids.**—See B., 1942, II, 423.

Sulphanilamides and experimental tuberculosis. B. Sjögren (*Nature*, 1942, **150**, 431—432).—*2-Sulphanilamido-1 : 4-naphthaquinone*, m.p. 227°, *1-sulphanilamido-2-methylnaphthalene*, m.p. 248°, and *4-sulphanilamido-2-methyl-1-naphthol*, m.p. 209° (decomp.), have been prepared. They are all more or less sol. in fat solvents and insol. in water. (Cf. A., 1943, III, 49.) E. R. S.

Mechanism of the diazo-coupling reaction. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1942, **58**, 228—231).—For all coupling reactions, whether in acid, neutral, or alkaline media, the condensation of undissociated but polarised (cationoid) NAr:NX (X = OH, OAc, Cl, HSO_4, etc.) with amines or phenols (anionoid) at a polarised C–H linking is the most probable explanation of the known data. Other mechanisms (lit.) are criticised. A. T. P.

Masking of phenolic hydroxyl groups by esterification with methanesulphonic acid. B. Helferich and P. Papalambrou (*Annalen*, 1942, **551**, 235—241).—Phenols are transformed by $MeSO_2Cl$ (**I**) into methanesulphonates which, even when sol. in H_2O, are scarcely affected by prolonged boiling with conc. HCl but are hydrolysed by N-alkali in aq. $COMe_2$ at room temp. With completely esterified polyhydric phenols the removal of 1 $MeSO_2$ is still more easily effected but more drastic treatment is required for removal of the remainder. $MeSO_2Ph$, m.p. 59—61°, is obtained from PhOH and (**I**) in anhyd. C_5H_5N at room temp., or by dropwise addition of (**I**) (alone or in C_6H_6) to PhOH in aq. KOH at 0°. The following are new : *β-$C_{10}H_7$ methanesulphonate*, m.p. 105°; *dimethanesulphonates* of *o-*, *m-*, and *p*-$C_6H_4(OH)_2$, m.p. 104—105°, 87°, and 167°, respectively; *trimethanesulphonates* of 1 : 3 : 5-, 1 : 2 : 3-, and 1 : 2 : 4-$C_6H_3(OH)_3$, m.p. 149·5°, 159°, and 115°, respectively; *alizarin dimethanesulphonate*, m.p. 210°; *quinol monomethanesulphonate*, m.p. 76°; *phloroglucinol mono-* and *di-methanesulphonate*, m.p. 130·5° and 118°, respectively. H. W.

Phosphoric acid esters of substituted quinols.—See B., 1942, III, 277.

Synthetic, highly active œstrogens. W. Salzer (*Z. physiol. Chem.*, 1942, **274**, 39—47).—*p*-OMe·$C_6H_4{\cdot}CH_2Ac$ (**I**), *m*-OMe·$C_6H_4{\cdot}[CH_2]_2{\cdot}Br$ (**II**), and $NaNH_2$ in boiling Et_2O afford *α-p-anisyl-γ-m-anisylpropyl* Me ketone, b.p. 175°/0·5 mm., cyclised by 80% H_2SO_4 at 60—70° to *6-methoxy-2-p-anisyl-1-methyl-3 : 4-dihydronaphthalene*, m.p. 136°;

this is demethylated by KOH–EtOH at 200° to (?) 6-*hydroxy*-2-p-*hydroxyphenyl*-1-*methyl*-3 : 4-*dihydronaphthalene* (**III**), m.p. 193°, accompanied by (?) 6-*methoxy*-2-p-*hydroxyphenyl*-1-*methylnaphthalene*, m.p. 215°, and by MgMeI at 180° solely to (**III**). Similarly, (**I**), *m*-OMe·C_6H_4·CH_2Cl, and powdered $NaNH_2$ in boiling Et_2O yield *α-p*-anisyl-*β-m*-anisylethyl Me ketone, b.p. 175°/0·5 mm., cyclised to 5-*methoxy*-2-p-*anisyl*-1-*methylindene*, m.p. 110°, which is demethylated (KOH–MeOH at 200°) to the 5-hydroxy-2-*p*-hydroxyphenyl derivative (**IV**), identified as its diacetate, m.p. 131°. Hydrogenation of (**IV**) gives a non-cryst. phenolic product (**V**) which does not yield cryst. derivatives. (**III**) and (**IV**) are physiologically active in doses of 0·3—0·5 μg. whereas (**V**) is inactive in a dose of 200 μg. 2-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene, Ph·$[CH_2]_2$·Br, and $NaNH_2$ in boiling Et_2O give 2-keto-1-*β*-phenylethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 210°/6 mm., cyclised (conc. H_2SO_4 at 0—10°) to 5 : 6 : 11 : 12-*tetrahydrochrysene*, m.p. 105°. 6-Methoxy-3 : 4-dihydronaphthalene and BzO_2H in CH_2Cl_2 at ≯10° yield 2-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 135°/0·8 mm. (semicarbazone, m.p. 159°), transformed by (**II**) and $NaNH_2$ into its 1-*β-m*-anisylethyl derivative, b.p. 200—205°/0·2 mm., which is cyclised (80% H_2SO_4 at 70°) to 3 : 9-*dimethoxy*-5 : 6 : 11 : 12-*tetrahydrochrysene*, m.p. 164°. This is demethylated by MgMeI at 180° to the 3 : 9-$(OH)_2$-compound (*diacetate*, m.p. 187°) and by KOH–EtOH to a phenol which results from a disproportionation of the tetrahydrochrysene ring and is physiologically active only in large doses. The OH-compounds show high œstrogenic activity when a " stilbenoid " double linking occurs between the two aromatic rings in these tri- and tetra-cyclic compounds. Disappearance of the double linking causes great loss of physiological activity.

H. W.

***N*-Alkyl- and *N*-Δ$^{\beta}$-alkenylidene-aminophenols.**—See B., 1942, II, 422.

Alkyl–oxygen fission in carboxylic esters. II. Derivatives of *p*-methoxybenzhydrol. M. P. Balfe, M. A. Doughty, J. Kenyon, and R. Poplett (*J.C.S.*, 1942, 605—611; cf. A., 1942, II, 391).—*p*-OMe·C_6H_4·CHPh·OH, its esters, and ethers undergo a variety of interconversions when treated with excess of various carboxylic acids or alcohols. Alkyl–O fission of the hydrol and many derivatives is shown by the constitution of the reaction products or by racemisation of an optically active reactant. *dl-p*-Methoxybenzhydrol (**I**), *o*-$C_6H_4(CO)_2O$, and C_5H_5N (essential) at 55—60° give dl-p-*methoxybenzhydryl H phthalate*, m.p. 102—103° (decomp.), and thence the (+)-*H phthalate* (**II**), m.p. 103—103·5°, $[\alpha]_{5893}^{19}$ +71·2° in CS_2 [from its cinchonidine salt, m.p. 143—144° (decomp.)]. (**II**) and NaOH–EtOH (+2% of H_2O) afford (+)-*p*-methoxybenzhydrol (**III**), m.p. 58—59°, $[\alpha]_{5893}^{13.5}$ +47·85° in CS_2; unless the H_2O content of the NaOH–EtOH is kept low, racemisation occurs. Similar results are obtained with the (−)-H phthalate (**IV**). (**III**), $[\alpha]_{5893}$ +46·8° in CS_2, and *o*-$C_6H_4(CO)_2O$ in C_5H_5N (essential) at 50—60° yield (**II**), $[\alpha]_{5893}$ +38·4° in C_6H_6 (little racemisation). (**III**) is completely racemised in H_2O at 100° (bath) after 30 hr. Racemisation of (**II**) occurs in EtOH (2 months), AcOH (24 hr.), MeOH (288 hr.), $MeNO_2$ (19 hr.), or C_6H_6 (nearly complete after 1656 hr.) at room temp. dl-p-*Methoxybenzhydryl acetate*, b.p. 182—183°/4 mm., is prepared from (**I**) and Ac_2O or AcCl in C_5H_5N, and the *benzoate*, m.p. 57—58°, from (**I**) and BzCl–C_5H_5N at 50—60°, or from the chloride and aq. NaOBz–$COMe_2$. When (**I**) is distilled at 196—198°/11 mm., a residue (~12%) of di-*p*-methoxybenzhydryl ether (**V**), m.p. 120°, is obtained; this is unaffected by Br–CCl_4, BzCl–C_5H_5N, Ac_2O, H_2O, or MeOH, but is converted into (**VI**) (below) with MeOH–H_2SO_4. Distillation of a solution of (**IV**), $[\alpha]_{5893}$ −2·4° in C_6H_6, in dry MeOH during 2·5 hr. gives dl-p-*methoxybenzhydryl Me ether* (**VI**), b.p. 195°/17 mm., m.p. 29° (racemisation indicates alkyl–O fission), also obtained from di-*dl-p*-methoxybenzhydryl phthalate and MeOH in air (20 days), or by slow distillation of a 5% solution of (**I**) in MeOH (*o*-methoxybenzhydrol and anisyl-α-naphthylcarbinol do not similarly react). Trituration of (**III**) or (**IV**) with conc. HCl gives *dl-p*-methoxybenzhydryl chloride (**VII**), also obtained similarly from (**V**), (**VI**), or (**I**) and its H phthalate, acetate, or benzoate. (**VII**) is also obtained from AcCl and (**III**), (**V**), or (**I**) (or acetate), and from (**III**), $SOCl_2$, and C_5H_5N. (**VII**) with cold H_2O yields (**V**) [and a little (**I**)], also obtained from (**I**), (**VII**), and a little C_5H_5N in Et_2O. With 3N-NaOH or K H phthalate in $COMe_2$, (**VII**) affords (**I**) or its H phthalate, respectively. (**IV**) in aq. NaOH (freshly dissolved; not if kept for 10 min.) or (**VII**) in $COMe_2$ with aq. *p*-$C_6H_4Me·SO_2Na$ (**VIII**) gives dl-p-*tolyl* p-*methoxybenzhydryl sulphone*, m.p. 160°; the reaction with (**IV**) involves alkyl–O fission, and racemisation of the resulting *p*-methoxybenzhydryl cation. The H phthalates of *m*-methoxybenzhydrol, anisyl alcohol, CHMe:CH·CHMe·OH, CHPhMe·OH, CPhMeEt·OH, or octan-*β*-ol do not react with (**VIII**); *o*-methoxybenzhydryl H phthalate reacts slowly. (−)-Anisylmethylcarbinyl H phthalate, $[\alpha]_{5893}$ −18° in EtOH, and (**VIII**) in aq. NaOH at room temp. yield dl-p-*tolyl α-anisylethyl sulphone*, m.p. 119—120°, and benzhydryl H phthalate gives (when heated) p-*tolyl benzhydryl sulphone*, m.p. 190—191°. (**II**) and 0·15N-NaOH (18 hr.) afford *o*-$C_6H_4(CO_2H)_2$, (**III**), $[\alpha]_{5893}$ +3·4° in CS_2, and di-*p*-methoxybenzhydryl phthalate, hydrolysed by aq. NaOH–EtOH to (**III**), m.p. 62—63°, $[\alpha]_{5893}$ +19·0° in CS_2. (**IV**) $[\alpha]$ −15·7° in C_6H_6, and K H phthalate–aq. NaOH at room temp. give (**I**), and neutral ester, hydrolysed to (**I**). The *dl*-H phthalate and NaOBz–3N-NaOH yield di-*p*-methoxybenzhydryl phthalate, and BzOH is recovered. (**IV**), $[\alpha]_{5893}$ −15·7°, and dil. NaOH in presence of (+)-*β*-octyl H phthalate (**IX**) give an ester, hydrolysed by NaOH–EtOH to (**I**); (**IX**) is recovered. (**II**) and (**IX**) also lead to (**I**). Benzhydryl, new m.p. 157—158°, phenylmethylcarbinyl, and γ-phenyl-α-methylallyl H phthalates show little change with aq. NaOH (1 mol.) at room temp., but when heated give the alcohols. Some aspects of the mechanism of the formation of the neutral ester remain obscure.

A. T. P.

Restricted rotation in arylolefines. IV. Preparation and resolution of *β*-chloro-*β*-3-chloro-6-methoxy-2 : 4-dimethylphenyl-α-methylacrylic and the corresponding acrylic acid. R. Adams and W. J. Gross. **V. *β*-Bromo-*β*-2-alkoxy-1-naphthyl-α-alkylacrylic acids.** R. Adams, L. O. Binder, and F. C. McGrew. **VI. Substituted *β*-2 : 7-dimethoxy-1-naphthyl-α-methylacrylic acids.** R. Adams, M. W. Miller, F. C. McGrew, and A. W. Anderson (*J. Amer. Chem. Soc.*, 1942, **64**, 1786—1790, 1791—1794, 1795—1801; cf. A., 1942, II, 93).—IV. *o*-Me has a greater steric effect than has *o*-OMe. 1 : 3 : 5-$C_6H_3Me_2$·OMe, $(EtCO)_2O$, and $AlCl_3$ in boiling CS_2 give 2-*methoxy*- (**I**) (75%), b.p. 120—122°/2 mm., and some 2-*hydroxy*-4 : 6-*dimethylpropiophenone*, m.p. 78° [converted into (**I**) by Me_2SO_4–aq. NaOH at 100°]. Et_2O–MgEtBr and then CO_2 at 0°/2—3 atm. and later room temp. convert (**I**) into α-2-*methoxy*-4 : 6-*dimethylbenzoylpropionic acid* (30%), m.p. 88—89°, which with PCl_5–$POCl_3$ at 70° gives a mixture of small amounts of *β-chloro-β*-2-*methoxy*-4 : 6-*dimethyl*-, m.p. 163—164°, and -*β*-3-*chloro*-6-*methoxy*-2 : 4-*dimethyl*- (**II**), m.p. 178—179°, -*phenyl*-α-*methylacrylic acid*. 3 : 5 : 4 : 1-$C_6H_2Me_2Cl$·OH and Me_2SO_4 in boiling aq. NaOH give 2-*chloro*-m-5-*xylenol Me ether* (80%), b.p. 94—96°/6 mm., which yields, as above, 3-*chloro*-6-*methoxy*-2 : 4-*dimethylpropiophenone* (55%), m.p. 66·5—67·5°, α-3-*chloro*-6-*methoxy*-2 : 4-*dimethylbenzoylpropionic acid* (50%), m.p. 118°, and (**II**) (50%). With quinine in warm $COMe_2$, (**II**) gives the *salt*, $[\alpha]_D^{20}$ −30·0° in C_6H_6, and thence the *d*-acid, m.p. 177°, $[\alpha]_D^{20}$ +22·5° in Bu$^{\alpha}$OH, having a half-life period 173 min. in Bu$^{\alpha}$OH at 44° and very short at the b.p. With Ac_2O–$AlCl_3$–CS_2, 3 : 5 : 4 : 1-$C_6H_2Me_2Cl$·OMe gives 3-*chloro*-6-*methoxy*-2 : 4-*dimethylacetophenone* (70%), m.p. 76—77°, b.p. 134—136°/3 mm., and thence, as above, *β-keto-β*-3-*chloro*-6-*methoxy*-2 : 4-*dimethylphenylpropionic acid* (45%), m.p. 113°, dl-, m.p. 181—182°, and d-*β-chloro-β*-3-*chloro*-6-*methoxy*-2 : 4-*dimethylphenylacrylic acid*, m.p. 180°, $[\alpha]_D^{20}$ +12·5° in Bu$^{\alpha}$OH, half-life period 9 min. in Bu$^{\alpha}$OH at 20° (*quinine* salt, $[\alpha]_D^{20}$ −25·0° in C_6H_6). Similarly are prepared 2-*chloro*-m-5-*xylenol Et ether*, 3-*chloro*-6-*ethoxy*-2 : 4-*dimethyl-propio*-, m.p. 53—54°, b.p. 155—156°/7 mm., and -*aceto-phenone*, m.p. 74°, b.p. 145—147°/7 mm., α-3-*chloro*-6-*ethoxy*-2 : 4-*dimethylbenzoylpropionic*, m.p. 115·5—116·5°, *β-keto-β*-3-*chloro*-6-*ethoxy*-2 : 4-*dimethylphenylpropionic*, m.p. 103—104°, *β-chloro-β*-3-*chloro*-6-*ethoxy*-2 : 4-*dimethylphenyl*-α-*methylacrylic*, m.p. 141—142°, and -*acrylic acid*, m.p. 176—177°. These acrylic acids do not give cryst. alkaloidal salts.

V. The smaller steric effect of the *peri*-CH of a $C_{10}H_8$ nucleus compared with an *o*-Me is confirmed. 2 : 1-OMe·$C_{10}H_6$·CHO, $EtCO_2Na$, and $(EtCO)_2O$ at 170° give trans-*β*-2-*methoxy*-1-*naphthyl*-α-*methylacrylic acid* (**III**) (62%) (here and below *trans* and *cis* refer to the CO_2H and aryl nucleus), m.p. 155—156°, converted by Br–$CHCl_3$ in the dark into the *β-Br-acid* (**IV**) (38%), m.p. 208° (oxidised by $KMnO_4$ to 2 : 1-OMe·$C_{10}H_6$·CO_2H; hence structure). 2 : 1-OH·$C_{10}H_6$·CHO, $EtCO_2Na$, and $(EtCO)_2O$ at 170° give 3-*methylnaphtha*-1′ : 2′-5 : 6-2-*pyrone* [" 2-*methyl*-4 : 3-*β*-*naphthopyrone* "] (60%), m.p. 156°, which with aq. KOH at 90° and then warm aq. Me_2SO_4–alkali gives (**III**) or occasionally its cis-*isomeride*, m.p. 167°, converted by Br–$CHCl_3$ into a little (**IV**) and non-acidic material, m.p. 93°. 2 : 1-OEt·$C_{10}H_6$·CHO gives similarly *β*-2-*ethoxy*-1-*naphthyl*- (43%), m.p. 130°, and *β-bromo-β*-2-*ethoxy*-1-*naphthyl*- (**V**) (29%), m.p. 172°, -α-*methylacrylic acid*. In boiling 48% aq. HBr–AcOH, (**IV**) gives 4-*bromo*-3-*methylnaphtha*-1′ : 2′-5 : 6-2-*pyrone* (56%), m.p. 186°, which by hydrolysis and subsequent methylation yields the cis-*isomeride* (**VI**), m.p. 187°, of (**IV**). Perkin reactions using Pr$^{\alpha}$$CO_2K$ and $(Pr^{\alpha}CO)_2O$ and subsequent treatment as above give trans- (**VII**) (40%), m.p. 110°, and cis-*β*-2-*methoxy*-1-*naphthyl*-α-*ethylacrylic acid* (**VIII**), m.p. 120°, and 3-*ethylnaphtha*-1′ : 2′-5 : 6-2-*pyrone* (**IX**), m.p. 111°. With Br–$CHCl_3$, (**VII**) or (**VIII**) gives the 4-*Br*-derivative, m.p. 137°, of (**IX**) and thence (boiling KOH–EtOH; then aq. KOH–Me_2SO_4) *β-bromo-β*-2-*methoxy*-1-*naphthyl*-α-*ethylacrylic acid* (**X**), m.p. 138°. (**IV**), (**VI**), (**V**), and (**X**) give single cryst. salts, which do not mutarotate and regenerate the *dl*-acids.

VI. 2 : 7-$C_{10}H_6(OH)_2$, $Zn(CN)_2$, and HCl in Et_2O give 2 : 7 : 1-$(OH)_2C_{10}H_5$·CHO (**XI**), m.p. 159—160°, converted by Me_2SO_4 in 25% aq. KOH into 2-*hydroxy*-7-*methoxy*-1-*naphthaldehyde* (**XII**) (60%), m.p. 128—129°, which with $EtCO_2K$–$(EtCO)_2O$ at 175—180° gives 7′-*methoxy*-3-*methylnaphtha*-1′ : 2′-5 : 6-2-*pyrone* (**XIII**), m.p. 186·5—187·5°. The Perkin reaction with (**XI**) yields the 7′-*propionoxy*-, m.p. 161—162°, and thence the 7′-*OH-pyrone*, m.p. 263—266° (block), which affords (**XIII**). With HNO_3 (*d* 1·42) in AcOH, (**XIII**) gives its 8′-NO_2-, m.p. 276—278°, and with Br–$CHCl_3$ at 0° its 8′-*Br*-derivative (**XIV**), m.p. 218—219°. With Br–CCl_4, (**XII**) gives 8-*bromo*-2-*hydroxy*-7-*methoxy*-1-*naphthaldehyde* (57%), m.p. 97—99°, and thence (Perkin) (**XIV**). Hot KOH–EtOH, then Me_2SO_4

in 5% aq. KOH at room temp., and finally boiling 20% aq. KOH convert (**XIII**) and (**XIV**) into β-2 : 7-*dimethoxy-* (**XV**), *form*, m.p. 158—159°, and β-*bromo*-β-2 : 7-*dimethoxy*-1-*naphthyl*-α-*methylacrylic acid* (**XVI**), *form*, m.p. 166° (decomp.) (*quinine* salt, m.p. 98—99°, does not mutarotate). Methylation of (**XI**) also affords 2 : 7-*dimethoxy*-1-*naphthaldehyde* (**XVII**) (69%), m.p. 99—100° [*semicarbazone*, m.p. 247° (block)], which yields (Perkin) a *form* (**XVIII**), m.p. 153°, of (**XV**), which is converted thereinto by illumination in EtOH. Br and (**XVIII**) in $CHCl_3$ give a *form*, m.p. 190°, of (**XVI**); this gives *quinine*, m.p. 183—184°, $[\alpha]_D^{28}$ −77·4° in EtOH, and *brucine* salts, m.p. 208—210° (decomp.), $[\alpha]_D^{28}$ −52·5° in EtOAc, which do not mutarotate and regenerate the *dl*-acid; it resists further bromination. With HNO_3 (*d* 1·2) in AcOH, (**XVIII**) gives its 8-NO_2-derivative, m.p. 197—198°, irresolvable by way of its *quinine* salt, m.p. 156°, $[\alpha]_D^0$ −34·3° in C_5H_5N. 2 : 7-$C_{10}H_6(OMe)_2$ and Br in $CHCl_3$ give 1-*bromo*-2 : 7-*dimethoxynaphthalene*, m.p. 88—89°, converted by LiBu in Et_2O and then solid CO_2 into 2 : 7-*dimethoxy*-1-*naphthoic acid*, m.p. 112—113°, which is also obtained from (**XVII**) (proof of structure) in poor yield by $KMnO_4$ in aq. Na_2CO_3 at room temp. With HNO_3 (*d* 1·42) in AcOH, (**XVII**) gives 8-*nitro*-2 : 7-*dimethoxy*-1-*naphthaldehyde*, m.p. 190°, which is also obtained from 2 : 7 : 1-$(OMe)_2C_{10}H_5{\cdot}NO_2$ by $Zn(CN)_2$–$AlCl_3$–HCl–C_6H_6 and does not undergo the Perkin reaction. (**XVII**) gives an *oxime*, m.p. 181—182°, and thence (boiling Ac_2O) 2 : 7-*dimethoxy*-1-*naphthonitrile*, m.p. 129°, which resists hydrolysis. M.p. (all parts) are corr. R. S. C.

Influence of substrate structure on kinetics of carboxypolypeptidase action. M. Bergmann and J. S. Fruton (*J. Biol. Chem.*, 1942, **145**, 247—252).—See A., 1943, III, 57. Carbobenzyloxy-*l*-alanyl chloride and *l*-phenylalanine Et ester in Et_2O afford *carbobenzyloxy*-l-*alanyl*-l-*phenylalanine Et ester*, m.p. 97—98°, hydrolysed to *carbobenzyloxy*-l-*alanyl*-l-*phenylalanine*, m.p. 56—58°. *Carbobenzyloxy*-l-*alanyl*-l-*tyrosine*, m.p. 149—150°, and its *Et* ester, m.p. 138—139°, are obtained similarly. H. W.

Multiple specificity of chymotrypsin. J. S. Fruton and M. Bergmann (*J. Biol. Chem.*, 1942, **145**, 253—265).—See A., 1943, III, 57. Carbobenzyloxyglycyl-*l*-tyrosine Et ester is converted by NH_2 in MeOH into *carbobenzyloxyglycyl*-l-*tyrosinamide*, m.p. 170°, hydrogenated in presence of MeOH and AcOH to *glycyl*-l-*tyrosinamide acetate*, $[\alpha]_D^{22}$ +28·0° in H_2O. *Carbobenzyloxyglycyl*-l-*phenylalaninamide*, m.p. 130°, and *glycyl*-l-*phenylalaninamide acetate*, $[\alpha]_D^{28}$ +28·8° in H_2O, are obtained similarly. Analogous series of changes yield the following: *carbobenzyloxy*-l-*phenylalaninamide*, m.p. 167°, and l-*phenylalaninamide acetate*, m.p. 119—120°; l-*tyrosylglycinamide acetate*; *carbobenzyloxy*-l-*phenylalanylglycinamide*, m.p. 134°, and l-*phenylalanylglycinamide acetate*; *carbobenzyloxy*-l-*tyrosyl*-l-*tyrosinamide*, m.p. 187—189°, and l-*tyrosyl*-l-*tyrosinamide acetate*; N-*carbobenzyloxy*-O-*acetyl*-l-*tyrosyl*-l-*phenylalanine Et ester*, m.p. 170°, and *carbobenzyloxy*-l-*tyrosyl*-l-*phenylalaninamide*, m.p. ·220°; *carbobenzyloxy*-l-*phenylalanyl*-l-*tyrosine Et ester*, m.p. 162°, *carbobenzyloxy*-l-*phenylalanyl*-l-*tyrosinamide*, m.p. 221°, and l-*phenylalanyl*-l-*tyrosinamide*, m.p. 180°; *carbobenzyloxy*-l-*phenylalanyl*-l-*phenylalanine Et ester*, m.p. 140°, *carbobenzyloxy*-l-*phenylalanyl*-l-*phenylalaninamide*, m.p. 230°, and l-*phenylalanyl*-l-*phenylalaninamide*, m.p. 138°; *carbobenzyloxyglycylglycinamide*, m.p. 179—181°, and *glycylglycinamide acetate*. Carbobenzyloxyphenylalanylglycine Et ester is hydrolysed to *carbobenzyloxy*-l-*phenylalanylglycine*, m.p. 152°, and converted by NH_3 in MeOH at 0° into 5-*benzylhydantoin*-3-*acetamide*, m.p. 216—218° (corresponding acid, m.p. 185—186°). H. W.

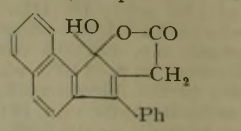
Halogenation of unsaturated compounds.—See A., 1943, II, 2.

Identification of amides through the mercury derivatives. J. W. Williams, W. T. Rainey, jun., and R. S. Leopold (*J. Amer. Chem. Soc.*, 1942, **64**, 1738—1739).—Amides and HgO at the m.p. or, in some cases, in boiling 95% EtOH give derivatives, $Hg(NHAcyl)_2$. *Compounds* in which Acyl = Ac, m.p. 196—197°, *EtCO*, m.p. 201°, *PrCO*, m.p. 222—224°, *Bz*, m.p. 222°, m-, m.p. 245°, and *p*-$C_6H_4Cl{\cdot}CO$, m.p. 258°, o-, m.p. 242°, m-, m.p. 235°, and p-$C_6H_4Br{\cdot}CO$, m.p. 266°, o-, m.p. 196°, m-, m.p. 200°, and p-$C_6H_4Me{\cdot}CO$, m.p. 260°, o-, m.p. 241°, and p-*anisoyl*, m.p. 222°, and o-$OH{\cdot}C_6H_4{\cdot}CO$, m.p. 190°, are described. R. S. C.

Solvent effects in association equilibria.—See A., 1943, I, 15.

Dialkylaminoalkyl fluorene-9-carboxylates [antispasmodic agents].—See B., 1942, III, 277.

Condensation of aromatic ketones with ethyl succinate. C. L. Hewett (*J.C.S.*, 1942, 585—587).—$CHPh{:}CPh{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$ (Stobbe *et al.*, A., 1899, i, 902) is reduced by Na–Hg in aq. NaOH to two isomeric γδ-*diphenylbutane*-αβ-*dicarboxylic acids*, m.p. 188—189° and 138° (slightly impure), both of which with conc. H_2SO_4 (1 min. at 100°) give mixtures of two stereoisomeric 3 : 10-*diketo*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-*benzanthracenes*, m.p. 210—211° (probably *trans*-) and 132—133° (*cis*-, converted into *trans*- during an attempted Clemmensen reduction). $(CH_2{\cdot}CO_2Et)_2$ (**I**), 2-$C_{10}H_7{\cdot}COPh$, and NaOEt in Et_2O–EtOH afford γ-*phenyl*-γ-*naphthylitaconic acid*, m.p. 173·5—174·5° (*Me*$_2$ *ester*, m.p. 94—95°), reduced (Na–Hg) to α-(*phenylnaphthylmethyl*)*succinic acid* (**II**), m.p. 130—131°, and cyclised by conc. H_2SO_4 at room temp. to the *lactone*, $C_{21}H_{14}O_3$ (*A* or *B*), m.p. 166·5—167·5°. The anhydride (prep. by

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

AcCl) of (**II**) with $AlCl_3$ in $PhNO_2$ at 0° gives 4-*keto*-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*phenanthroic acid*, m.p. 243—245° (sinters at 240°). (**I**) and 6-benzoyl-1 : 2 : 3 : 4-tetrahydronaphthalene give two γ-*phenyl*-γ-6-*tetrahydronaphthylitaconic acids*, m.p. 183—185° (**III**) and 188—189°, only slightly affected by Na–Hg. With conc. H_2SO_4 at room temp. (1 min.) (**III**) affords (probably) 3-*phenyl*-5 : 6-*tetramethyleneindone*-2-*acetic acid*, m.p. 165—166°. A. T. P.

Production of benzaldehyde by oxidation of toluene.—See B., 1942, II, 417.

3-β-*d*-Glucosidoprotocatechualdehyde.—See A., 1943, II, 4.

Chromatography of *cis*- and *trans*-benzoin- and -anisoin-oximes with application of the brush method. L. Zechmeister, W. H. McNealy, and G. Sólyom (*J. Amer. Chem. Soc.*, 1942, **64**, 1922—1924).—*cis*- and *trans*-Benzoin- and -anisoin-oximes are separated by adsorption on Neutral Filtrol (+ a filter aid), extruding the column, and painting a streak by aq. $CuSO_4$–NH_3 down the column. The *trans*- and *cis*-oxime zones give green and brown colours, respectively. Isomerisation on the column is <5%. 1—2% of one form can be detected in the other. R. S. C.

Indeno-2′ : 3′ : 2 : 3-benzanthrone. G. Swain and A. R. Todd (*J.C.S.*, 1942, 626—628).—Methyleneanthrone (**I**) and indene in boiling $PhNO_2$ give *indeno*- (**II**), m.p. 218—219°, and a *dihydroindeno*-2′ : 3′ : 2 : 3-*benzanthrone* (**III**), m.p. 252—253°; in C_6H_6 or xylene only (**III**) results. Dehydrogenation of (**III**) to (**II**) is effected by Pd–C at 270—310° (inert atm.) or (partly) by boiling $PhNO_2$. (**II**) or (**III**) and SeO_2–H_2O at 230° afford 1′-*ketoindeno*-2′ : 3′ : 2 : 3-*benzanthrone* (**IV**), m.p. 336—338°. (**I**), Et cinnamate, and $PhNO_2$ give *Et* 3-*phenylbenzanthrone*-2-*carboxylate*, m.p. 155—156°, with a little of (probably) a *dimorph*, m.p. 190—210°, both hydrolysed by aq. KOH–EtOH to the 2-*carboxylic acid* (**V**), m.p. 284—286°, converted by quinoline–Cu-bronze into 3-phenylbenzanthrone, m.p. 182—183°. (**V**) and H_2SO_4 at 100° (bath) give (**IV**). (**II**) and (**IV**) show tumour-inhibitory properties of a moderate order. A. T. P.

Synthesis of emodin and of fumigatin. T. Posternak, J. P. Jacob, and H. Ruelius (*Arch. Sci. phys. nat.*, 1941, [v], **23**, *Suppl.*, 223—225).—3 : 5 : 1-$(OMe)_2C_6H_3{\cdot}CO_2Me$ and 2 : 4 : 5 : 1-$OMe{\cdot}C_6H_2MeBr{\cdot}COCl$ afford (Friedel–Crafts) Me 5′-bromo-2 : 4 : 2′-trimethoxy-4′-methylbenzophenone-6-carboxylate; the free acid is cyclised and partly demethylated by oleum to 1-bromoemodin Me_2 ether, converted (methods: Jacobson *et al.*, A., 1924, i, 752) into emodin [4 : 5 : 7-trihydroxy-2-methylanthraquinone]. 3 : 5 : 4 : 1-$(OH)_2C_6H_2(OMe){\cdot}CHO$ is reduced (H_2, Pd-black, AcOH) to 3 : 5 : 1 : 4-$(OH)_2C_6H_2Me{\cdot}OMe$, the 2-NO-derivative (prep. by $C_5H_{11}{\cdot}O{\cdot}NO$) of which is reduced to the 2-NH_2-compound. This is oxidised ($FeCl_3$) to fumigatin [3-hydroxy-4-methoxy-2 : 5-toluquinone]. C. S.

IV.—STEROLS AND STEROID SAPOGENINS.

H. Wieland's work on sterols. E. Dane (*Naturwiss.*, 1942, **30** 333—342).—A review. F. O. H.

Bio-reduction of steroids.—See A., 1942, III, 915.

Seeds of *Alangium lamarckii*. I. A. Lakshminarasimhaiah, B. L. Manjunath, and B. S. Nagaraj (*J. Mysore Univ.*, 1942, **3**, **B**, 113—116).—The light petroleum (b.p. 40—70°) extract of the seeds contains a *sterol* ("*alengol*"), $C_{30}H_{48\,(or\,50)}O_3$, m.p. 302—307° (slight decomp.), having 4 double linkings and 3 active H [*mono*-(Ac_2O), m.p. 262—265°, and *di*-*acetate* (HCl in AcOH), m.p. 330—334° (decomp.)]. A. Li.

Colour reaction between ergosterol and methyldichloroarsine. P. M. Baranger and J. M. Mercier (*Biochem. J.*, 1942, **36**, 703—705).—$AsMeCl_2$ gives a golden-yellow coloration with a freshly prepared solution of ergosterol in $CHCl_3$; the max. extinction coeff. ∝ [$AsMeCl_2$]. The substances used must be pure and dry. H. G. R.

7-Dehydrocampesterol, a new provitamin-*D*. W. L. Ruigh (*J. Amer. Chem. Soc.*, 1942, **64**, 1900—1902).—Campesteryl acetate and CrO_3–AcOH give 7-*ketocampesteryl acetate*, m.p. 177—178°, $[\alpha]_D^{24}$ −88·6° in $CHCl_3$, reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ to 7(α)-hydroxycampesterol, the *dibenzoate*, m.p. 176·5—177·5°, $[\alpha]_D^{23}$ +96·6° in $CHCl_3$, of which with NaOMe–MeOH at room temp. yields 7(α)-*benzoyloxycampesterol*, m.p. 143—145° (sinters at 126—130°), $[\alpha]_D^{26}$ +115·0° in $CHCl_3$. In boiling $NPhMe_2$ this gives, by way of the digitonide and after benzoylation, 7-*dehydrocampesteryl benzoate*,

m.p. 156—157° (clear at 164°; vac.), and thence (boiling 5% KOH–MeOH) 7-*dehydrocampesterol* (**I**), m.p. 164—165° (vac.), $[\alpha]_D^{25}$ −109·0° in $CHCl_3$ [absorption max. at 272 and 282 mμ. (ε 10,600)]. By comparison with ergosterol, irradiation of (**I**) gives a product the antirachitic potency of which is 4,100,000 i.u. per g. R. S. C.

Minor sterols of yeast. X. Relationships between lanosterol and cryptosterol. H. Wieland and W. Benend [with, in part, E. Joust] (*Z. physiol. Chem.*, 1942, **274**, 215—222).—Lanosterol (**I**) and cryptosterol (**II**) differ from one another solely in the position of the difficultly reactive double linking and are otherwise identical in structure and configuration. Ozonisation of (**I**) or (**II**) gives $COMe_2$ identified as the 2 : 4-dinitrophenylhydrazone, m.p. 128°, in 40% and >50% yield whereas dihydro-lanosterol (**III**) and -cryptosterol (**IV**) yield only CH_2O in small amount. The active double linking in (**I**) and (**II**) is therefore in the group >C:CMe_2. Cryptosteryl acetate is converted by successive treatments with OsO_4 in Et_2O and Na_2SO_3 into *cryptostenetriol acetate*, m.p. 177—179°, hydrolysed to the *triol* (**V**), m.p. 178—180°, $[\alpha]_D^{20}$ +50·50° in $CHCl_3$, also obtained by treating (**II**) with OsO_4 in Et_2O–C_5H_5N and the product with alkaline mannitol. (**V**) and $Pb(OAc)_4$ in C_6H_6 give $COMe_2$ in 80% yield but no CH_2O. Dihydrocryptosteryl acetate (**VI**), (**III**), (**VII**) (below), and α-cholestenol are resistant to OsO_4 whereas dihydrozymosterol gives an almost quant. yield of ester. (**IV**) is converted by HCl in boiling $CHCl_3$ into *iso*dihydrocryptosterol (**VII**), m.p. 135—136°, $[\alpha]_D^{20}$ +40·5° in $CHCl_3$, which could not be hydrogenated (PtO_2 in AcOH). (**VI**) is similarly isomerised to *iso*dihydrocryptosteryl acetate, m.p. 130°, $[\alpha]_D^{20}$ +44·5° in $CHCl_3$. The corresponding benzoate has m.p. 197—198°, $[\alpha]_D^{20}$ +61° in $CHCl_3$. The double linking of (**VI**) does not absorb Br. *iso*Dihydrolanosterol, m.p. 135—136°, $[\alpha]_D^{20}$ +38° (acetate, m.p. 129—130°, $[\alpha]_D^{20}$ +43·6°, benzoate, m.p. 197—198°, $[\alpha]_D^{20}$ +60·3°), is prepared. H. W.

Action of lead tetra-acetate on sterol derivatives. A. Windaus and U. Riemann (*Z. physiol. Chem.*, 1942, **274**, 206—214).—Ergosteryl acetate is converted by $Pb(OAc)_4$ in $CHCl_3$–AcOH at 20° into $\Delta^{7:22}$-ergostadiene-3 : 5 : 6-triol diacetate, m.p. 181—182°, hydrolysed (KOH–EtOH) to the triol, m.p. 241—242°. Under similar conditions 7-dehydrocholesteryl acetate affords Δ^7-*cholestene*-3 : 5 : 6-*triol diacetate*,, m.p. 195°, hydrolysed to the *triol*, m.p. 238—239°. Vitamin-D_2 3 : 5-dinitrobenzoate and $Pb(OAc)_4$ give 5 : 6-*dihydroxydihydrovitamin*-D_2 3 : 5-*dinitrobenzoate*, m.p. 174°, hydrolysed (KOH–MeOH) to 5 : 6-*dihydroxydihydrovitamin*-D_2 (**I**), m.p. 157°, $[\alpha]_D^{20}$ +50° in $CHCl_3$, in which the absence of a conjugated double linking is established spectroscopically. The structure of (**I**) is confirmed by oxidation [$Pb(OAc)_4$] to the aldehyde, new m.p. 59°, of Heilbron *et al.* (A., 1936, 1105). Hydrogenation (Pt-sponge in EtOAc) of (**I**) gives a mixture of products from which (?) dihydroxytetrahydrovitamin-D_2 (**II**), m.p. 199—202°, $[\alpha]_D$ +60° in $CHCl_3$ (3 : 5-*dinitrobenzoate*, m.p. 191°), is isolable; it appears to contain the double linking between $C_{(7)}$ and $C_{(8)}$ intact since it is oxidised [$Pb(OAc)_4$ in $CHCl_3$–AcOH] to an aldehyde (*semicarbazone*, $C_{22}H_{39}ON_3$, m.p. 242°). Further hydrogenation (Pt-sponge in AcOH) of (**II**) yields *dihydroxyhexahydrovitamin*-D_2, m.p. 103°, $[\alpha]_D$ +24·8° in $CHCl_3$ (*dibenzoate*, m.p. 211°). Vitamin-D_3 3 : 5-dinitrobenzoate is converted by $Pb(OAc)_4$ into a non-cryst. ester, hydrolysed to *dihydroxydihydrovitamin*-D_3, m.p. 156°, which with AcOH–$CHCl_3$–conc. H_2SO_4 gives the same colour reaction as (**I**). H. W.

Autoxidation of sterols in colloidal aqueous solution. III. Quantitative studies on cholesterol. IV. Influence of esterification and of constitutional factors. S. Bergström and O. Wintersteiner (*J. Biol. Chem.*, 1942, **145**, 309—326, 327—333).—III. 7-Ketocholesterol (**I**) has been determined by ultra-violet absorption measurements and the 7-hydroxycholesterols (**II**) by the Lifschütz reagent in the products of the autoxidation of aq. cholesterol sols. The rate of reaction is primarily dependent on temp. whilst concn., pH, O_2 pressure, and the nature of the detergent exert comparatively little influence. At 85° the reaction invariably comes to a standstill after a few hr. with ~40% of (**I**) and 20% of (**II**) formed. Autoxidation is limited to these levels by accumulation of the reaction products. Both types of these participate in bringing about this inhibition but each of them more specifically hinders the formation of its own kind. Small quantities of CN′ completely stop the autoxidation. With still smaller concns. of CN′ the reaction is merely delayed and then proceeds until normal levels are reached. The CN′-inhibited system can be reactivated by Cu$^{\cdot\cdot}$. Fe$^{\cdot\cdot}$ and Zn$^{\cdot\cdot}$ moderately accelerate the spontaneous reaction but do not effect a greater conversion. Mn$^{\cdot\cdot}$ causes a very marked inhibition whilst PhOH, salicylaldoxime, and hæmin completely prevent the reaction. Whenever inhibition occurs the formation of both (**I**) and (**II**) is retarded or entirely suppressed. A reaction mechanism involving the intermediate formation of a cholesterol 7-peroxide is discussed.

IV. Study of the course of the autoxidation of cholesteryl acetate, palmitate, and oleate in aq. colloidal solution at 85° shows that esterification greatly diminishes the susceptibility to attack by O_2. Compounds of the cholesterol type [stigmasterol, campesterol, fucosterol, and Me 3(β)-hydroxy-Δ^5-cholenate] are oxidised in the typical manner to 7-ketones and chromogens. The reaction curves resemble those obtained with cholesterol except that the final levels of ketone and chromogens are lower in all cases. *allo*Cholesterol and Δ^5-cholestene-3 : 4-diol do not appear to be autoxidised under these conditions. α-Spinasterol does not yield any Lifschütz-positive products but the absorption spectra indicate that two ketones with max. at 245 and 253 mμ. have been formed. H. W.

Sterol ketones.—See B., 1942, III, 277.

Sterols. CXLIX. Hypoiodite oxidation of pregnan- and pregnenolones. R. E. Marker and R. B. Wagner (*J. Amer. Chem. Soc.*, 1942, **64**, 1842—1843).—3(β)-Acetoxy-pregnan-, -Δ^{16}-pregnen-, -Δ^5-pregnen-, and -$\Delta^{5:16}$-pregnadien-20-one with I–KI–KOH–H_2O–dioxan first at room temp. and then at 80° (then aq. KOH at 100°) give 3(β)-hydroxy-ætiocholanic (**I**), m.p. 224—226° (Me ester, m.p. 128°), -Δ^{16}-*ætiocholenic* (**II**), m.p. 254—256° (*Me* ester, m.p. 150—152°), -Δ^5-*ætiocholenic*, m.p. 273—274°, and -$\Delta^{5:16}$-*ætiocholadienic acid*, m.p. 255—257°, respectively. H_2–PtO_2 reduces (**II**) in AcOH at 3 atm. to (**I**). R. S. C.

Sterols. CL. Sapogenins. LXIII. Position of the hydroxyl groups in digitogenin. R. E. Marker, D. L. Turner, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1942, **64**, 1843—1847).—The second OH of digitogenin (**I**) is not at $C_{(6)}$ and may be at $C_{(15)}$. Cholestane-3 : 6-diol and CrO_3 in AcOH at 70° give 6-*ketocholestane*-2 : 3-*diacid* (**II**), m.p. 228—230° (gas), which with Zn–Hg–conc. HCl–EtOH and then KOH–EtOH gives cholestane-2 : 3-diacid. H_2–PtO_2 in AcOH at 40 lb. reduces (**II**) to a *lactone-acid*, $C_{27}H_{44}O_4$, m.p. 188—190°, but digitogenic or digitoic acid in MeOH to a *dicarboxylic acid*, $C_{27}H_{42}O_7$, m.p. 285—290° (decomp.). $KHSO_4$ at 200—210°/high vac. converts chlorogenin into 3 : 5-dehydrodeoxytigogenin, but has no effect on (**I**). 6-Ketotigogenone (prep. from diosgenin by CrO_3; =chlorogenone) and CrO_3–AcOH at <30° or, better, Kiliani's acid give chlorogenonic acid, m.p. (anhyd.) 232—234° or +AcOH. Digitogenin triacetate and CrO_3–AcOH at 100° give digitogenin lactone triacetate and $CO_2H{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$. Boiling HCl–EtOH has no effect on (**I**), which thus has the *iso*-configuration. (**I**) is unaffected by Zn–Hg–HCl–EtOH or Ac_2O at 200°, whereas other sapogenins give H_4- and ψ-compounds, respectively. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Synthetic menthols. W. E. Huggett (*Quart. J. Pharm.*, 1942, **15**, 218—227).—Mainly a review of the 12 menthols dealing with physical consts., physiological, pharmacodynamic, and pharmacological properties. When 1 g. of H_3PO_4 (*d* 1·75) is mixed with 4·25 g. of synthetic menthol previously dried by boiling, a mixture which has a well-defined setting point and m.p. is obtained. A setting point of 60° or m.p. of 61° is obtained when the *dl*-menthol is free from isomerides; lower vals. indicate their presence. The method is applicable to optically active, inactive, or partly active material, and when the impurity is *iso*menthol an estimate of the amount to within 1% for any mixture containing 0—40% can easily be obtained. The composition of any mixture of isomerides is not readily determined. *dl*-Menthol has m.p. 38° and 27—28° (2 cryst. forms). J. N. A.

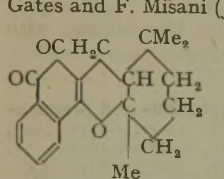
Separation of diastereoisomerides by selective adsorption on optically inactive material. (Miss) M. M. Jamison and E. E. Turner (*J.C.S.*, 1942, 611—612).—*l*-Menthyl *d*- and *l*-mandelates are adsorbed selectively on Al_2O_3. F. R. S.

Constituents of the volatile oil of catnip. II. Neutral components. Nepetalic anhydride. S. M. McElvain, P. M. Walters, and R. D. Bright (*J. Amer. Chem. Soc.*, 1942, **64**, 1828—1831; cf. A., 1942, II, 124).—The part (10%) of the oil insol. in 10% NaOH at 60°/15 min. is resolved by fractionation into β-caryophyllene (**I**) (14%), nepetalactone (**II**) (42%), an *ether*, $C_{14}H_{24}O$ (3%), b.p. 85—87°/0·03 mm., an *ester*, $(C_9H_{14}O_2)_x$ (x = ? 2) (2%), b.p. 115—117°/1 mm., and *nepetalic anhydride* (**III**), $(Me{\cdot}C_5H_7\langle^{CO-O}_{CHMe}\rangle CH)_2O$ (36%), m.p. 139—140°, b.p. 200—210°/1 mm., $[\alpha]_D^{25}$ +136° in $CHCl_3$. All the (**I**) and part of the (**II**) are obtained as a 7 : 3 azeotrope, b.p. 59—61°/0·03 mm. Lack of oxidisable or acid groups and hydrolysis by boiling, dil. HCl to nepetalic acid (**IV**) proves the formula of (**III**). Only the acetate is obtained from (**IV**) by Ac_2O, but AcCl in CCl_4 at room temp. gives also ~50% of (**III**). When kept, (**IV**) gives slowly (**III**). Distilling (**IV**) at 0·2 mm. gives 30% of (**III**), but at 1 atm. gives only (**II**), which is also obtained with H_2O by distilling (**III**) at 1 atm. Of the ingredients only (**II**) has the excitant action on cats and lions characteristic of the oil. R. S. C.

Saponins and sterols. VIII. Saponin of *Dioscorea tokoro*, Makino. K. Fujii and T. Matsukawa (*J. Pharm. Soc. Japan*, 1936, **56**, 408—414; cf. A., 1939, II, 161).—*Dioscorea* saponin is hydrolysed (5% H_2SO_4) to the *sapogenin*, $C_{27}H_{40-42}O_3$, m.p. 198—200° (*monoacetate*, m.p. 190°; *monobenzoate*, m.p. 237°; *dibromide*, m.p. 127°), catalytically reduced and acetylated to *dihydrodioscoreasapogenin acetate*, m.p. 102°, yielding *dihydrodioscoreasapogenin*, m.p. 190°, which is reduced (Pd–Mg) to epi*dihydrodioscoreasapogenin*, m.p. 205° (*monoacetate*, m.p. 206°). Ch. Abs. (*c*)

VI.—HETEROCYCLIC.

Condensation of β-*cyclo*geraniol with leuco*iso*naphthazarin. M. D. Gates and F. Misani (*J. Amer. Chem. Soc.*, 1942, **64**, 1979—1980).—

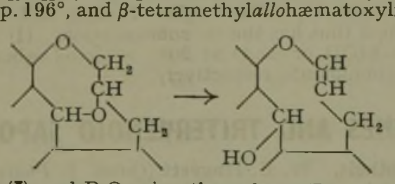


(I.)

1 : 2 : 3 : 4-$C_{10}H_4(OH)_4$ (improved prep.), β-*cyclo*geraniol, and $H_2C_2O_4$ in dioxan–N_2 at 65—70° in the dark give 2-*hydroxy*-3-β-*cyclo*-*geranyl*-1 : 4-*naphthaquinone* (poor yield), m.p. 135—135·5° (corr.), cyclised by conc. H_2SO_4 to β-*cyclogeranolapachone* (**I**), m.p. 232—233·3° (corr.), identical with the so-called " β-geranolapachone " obtained (A., 1942, II, 149) from 2-hydroxy-3-geranyl-1 : 4-naphtha-quinone. R. S. C.

Cannabis indica. **XI. Alkali-soluble portion of American hemp resin.** (Mrs.) A. Madinaveitia, P. B. Russell, and A. R. Todd (*J.C.S.*, 1942, 628—630).—The alkali-sol. resin from American wild hemp has two components; one (I-RAB) is and the other (I-NRAB) is not extracted from alkaline solution with Et_2O (cf. Fulton, A., 1942, III, 771). These materials, with boiling MeOH, or with alkali, yield alkali-insol. resins, from which cannabidiol (**I**) and cannabinol (**II**) respectively have been isolated. The alkali-sol. portion of the resin may contain esters of (**I**) and (**II**) with a phenolic acid, which undergo fission with MeOH. This conclusion is supported by the properties of *cannabinol* p-*carbomethoxybenzoate*, m.p. 195°, and *cannabidiol bis*-p-*carbomethoxybenzoate*, b.p. ~130—150°/10^{-3} mm. F. R. S.

Reduction of tetramethylhæmatoxylone. P. Pfeiffer and W. Christeleit (*J. pr. Chem.*, 1942, [ii], **160**, 315—322; cf. A., 1928, 426; 1938, II, 199).—Chromatographic analysis of the reduction product of tetramethylhæmatoxylone gives tetramethylhæmatoxylonol, $C_{20}H_{22}O_7$, m.p. 188°, α-tetramethyl*iso*hæmatoxylin, $C_{20}H_{22}O_6$, m.p. 196°, and β-tetramethyl*allo*hæmatoxylin (**I**), $C_{20}H_{22}O_6$,



(I.) (II.)

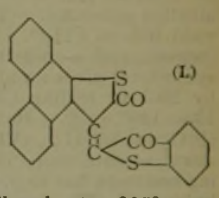
m.p. 150°. (**I**) and P_2O_5 give the α-form (**II**), m.p. 166°, which is acetylated and reduced by Ac_2O–NaOAc, giving a *substance*, $C_{22}H_{26}O_7$, m.p. 181—185°. Tetramethylhæmatoxylin can be characterised (PhNCO at 100°) as the *phenylcarbamate*, $C_{27}H_{27}O_7N$, m.p. 203·5—206·5°. A. T. P.

Active principles of leguminous fish-poison plants. VII. Reduction of elliptone. VIII. Synthesis of dehydrotetrahydroelliptone and of dehydrotetrahydromalaccol. IX. Synthesis of furano*iso*flavones related to rotenone. S. H. Harper (*J.C.S.*, 1942, 587—593, 593—595, 595—598).—VIII. Reduction of *l*-elliptone (*solvate* with $CHCl_2{\cdot}CO_2H$, m.p. 108°) in AcOH over PtO_2 with H_2 gives successively l-*dihydroelliptone* (**I**), m.p. 191°, $[\alpha]_D^{18}$ −132° in C_6H_6 (*oxime*, m.p. 250°; *monoacetate*, m.p. 208°), l-*dihydrodeoxyelliptone* (**II**), m.p. 170°, *octahydrodeoxyelliptone*, m.p. 160° and 139°, $[\alpha]_D^{18}$ −8° in C_6H_6, and perhydroelliptone. Similar reduction of *dl*-elliptone affords dl-*dihydroelliptone* (**III**) (*solvate*, $+0{\cdot}5C_6H_6$, m.p. 188°) and dl-*dihydrodeoxyelliptone*, m.p. 157—159°. (**II**) has been previously characterised as *l*-dihydroelliptone. Addition of I to (**I**) or (**III**) in EtOH–NaOAc yields *dehydrodihydroelliptone* (**IV**), m.p. 264°. Dehydroelliptone with Zn–KOH–EtOH leads to elliptic acid (**V**) (*Et* ester, m.p. 142°) and *elliptol*, m.p. 163° (*Me ether*, m.p. 137°). Cyclisation of (**V**) with NaOAc–Ac_2O gives *Et acetylelliptate*, m.p. 151—153°, and reduction (PtO_2–H_2) of it affords *dihydroelliptic acid* (**VI**), m.p. 200° (*Me*, m.p. 149°, and *Et* ester, m.p. 147°), which is cyclised to a dimorph of (**IV**), m.p. 248—250°. Zn–KOH with (**IV**) forms (**VI**) and *dihydroelliptol*, m.p. 190°. *l*- or *dl*-Tetrahydroelliptone with NaOAc–I gives *dehydrotetrahydroelliptone* (**VII**), m.p. 260° (decomp.), which with Zn–KOH leads to *tetrahydroelliptic acid* (**VIII**), m.p. 202° (*Me* ester *Me ether*, m.p. 123°), and *tetrahydroelliptol* (+ solvent, EtOH–H_2O), m.p. 225°. *l*-Elliptone with AcOH–$C_5H_{11}{\cdot}O{\cdot}NO$ affords *elliptonone*, m.p. 325°, which can be prepared from elliptol with $Me_2C_2O_4$ and NaOAc. Reduction (PtO_2–H_2) of *l-iso*rotenone (cf. Butenandt *et al.*, A., 1930, 477) gives an impure product, m.p. 168°, containing unreduced material, which is oxidised (I–NaOAc–EtOH) to dehydro*iso*rotenone and l-*dihydrodeoxy*iso*rotenone*, m.p. 158°. Biological trials have shown that *l*-elliptone is, next to rotenone, the most toxic insecticidal substance to be isolated from *Derris* resin in an optically active form.

VIII. Condensation of Me 4 : 5-dimethoxy-2-cyanomethylphenoxyacetate, 2-ethylresorcinol, and $ZnCl_2$ (Hoesch) gives *Me tetrahydroelliptate*, m.p. 185°, hydrolysed to (**VIII**), which is cyclised (NaOAc–Ac_2O) to (**VII**) and its O-*Ac* derivative, m.p. 253°. This confirms the structure assigned to elliptone. By the same condensation, using ethylphloroglucinol, *Me tetrahydromalaccolate*, m.p. 184°, is obtained, hydrolysed to the *acid*, m.p. 225°, which is cyclised to *dehydrotetrahydromalaccol*, m.p. 240° (decomp.), and its O-Ac_2 derivative, m.p. 194—196°. It has not proved possible to compare these substances with those derived from natural sources.

IX. Derritol Me ether, Na, and HCO_2Et give *derritol* iso*flavone* (**IX**), m.p. 215°, $[\alpha]_D^{17}$ −37° in $CHCl_3$, hydrolysed (NaOH) to the ether and HCO_2H, and isomerised (AcOH–H_2SO_4) to iso*derritol* iso*flavone*, m.p. 160°, $]\alpha]_D$ ±0° in $CHCl_3$, which is hydrolysed to iso*derritol Me ether*, m.p. 125°. This latter substance may be used for the synthesis of the *iso*flavone. Reduction (H_2–Pd–$BaSO_4$) of (**IX**) leads to *dihydroderritol* iso*flavone*, m.p. 193°, $[\alpha]_D^{21}$ −52° in $CHCl_3$. Elliptol Me ether is similarly converted into *elliptol* iso-*flavanonol*, m.p. 165°, which with AcOH yields the *-flavone*, m.p. 185°, indicating that an intermediate OH-compound is formed in the *iso*flavone synthesis. These *iso*flavones are remarkable in giving a positive Durham test, previously regarded as sp. for the rotenoids. A method has been devised for the detection of the HCO_2H formed in their hydrolysis. This method has been applied to the " toxicarol *iso*flavone " isolated from crude toxicarol to establish conclusively its *iso*flavone nature and hence to support the formula previously assigned (cf. A., 1940, II, 356). F. R. S.

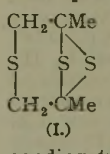
Indigoid dyes. X. P. C. Dutta and R. M. Sinha (*J. Indian Chem. Soc.*, 1942, **19**, 239—240; cf. A., 1936, 1518).—Phenanthra-9′ : 10′-4 : 5-thiophen-2 : 3-dione and 2-hydroxythionaphthen in AcOH (CO_2 passed through) when boiled, with addition of HCl, give phenanthra-9′ : 10′-4 : 5-thiophen-3 : 1″-thionaphthenindigo (**I**), m.p. 290°. Similarly prepared are the 6″ : 7″-, 4″ : 5″-, and 5″ : 6″-*benz*-derivatives of (**I**); all melt at >295°.



(I.)

A. T. P.

Dimeric thioketones. H. Böhme, H. Pfeifer, and E. Schneider (*Ber.*, 1942, **75**, [*B*], 900—909).—Dimeric thioacetone (**I**) could not be obtained by the action of P_2S_3 on $COMe_2$ or from P_2S_5 and $COMe_2$ in boiling PhMe. Trithioacetone, b.p. 116—117°/15 mm., m.p. 24°, best obtained by passing H_2S into a well-cooled mixture of $COMe_2$ and $ZnCl_2$, passes at 215° into $Pr^{\beta}SH$, identified as 2 : 4-dinitrophenyl Pr^{β} sulphide, m.p. 95°. Successive passage of HCl and H_2S into a well-cooled solution of CH_2ClAc in EtOH leads to



(I.)

2 : 6-*dimethyl*-[2 : 6-endo*sulphido*]*dithian* (**I**), b.p. 116—118°/14 mm., m.p. 50—51° (additive *compound* with $HgCl_2$, incipient decomp. 110°). (**I**) does not give an oxime, phenylhydrazone, or *p*-nitrophenylhydrazone and does not react with CH_2N_2, Grignard reagents, Na–Hg in EtOH, or Na in Et_2O. It is oxidised by $KMnO_4$ in acid solution to a mixture of the corresponding *trisulphone*, decomp. >255°, and an unidentified *substance*, $C_6H_{10}O_4S_2$, m.p. 227°. The structure of (**I**) is confirmed by comparison of its absorption spectrum in EtOH and $CHCl_3$ with that of *diacetonyl sulphide*, b.p. 126°/14 mm., m.p. 49°, obtained from CH_2ClAc and $Na_2S,9H_2O$ in boiling $COMe_2$. CHPhClAc and HCl, then H_2S in well-cooled EtOH, afford 2 : 5-diphenyl-[1 : 4-dithien], m.p. 118—119° (Grote, A., 1924, i, 1322). 2 : 5-*Diphenylthiophen*, m.p. 155—156°, is obtained from $(CH_2Bz)_2S$ and P_2S_5 at 170°. H. W.

Nicotin-*p*-toluenesulphonamide.—See B., 1942, III, 246.

Action of acid anhydrides on acenaphthenone. II. Experiments in pyridine solution. E. Ghigi (*Ber.*, 1942, **75**, [*B*], 764—778; cf. A., 1940, II, 179).—Prolonged action of Ac_2O in C_5H_5N on acenaphthenone in the dark affords 7-*acetoxy*-8-4′-*pyridylacenaphthylene* (**I**), m.p. 245—247° after softening, 1 : 8-$C_{10}H_6(CO_2H)_2$, 7-hydroxy-8-1′-acetyl-1′-pyridinoacenaphthylene (**II**), m.p. 145—147°, 7-hydroxy-8-acetylacenaphthylene (**III**), 1 : 8-$C_{10}H_6(CO)_2O$ (**IV**), and MeCHO. The greater is the yield of (**I**), the smaller is the yield of (**II**). Prolonged contact of (**III**) with Ac_2O and C_5H_5N in the dark gives unchanged material and (**IV**). Under similar conditions 7-acetoxy-8-acetylacenaphthylene yields (**III**) and the acetate of (**II**) affords (**I**). (**I**) is transformed by boiling EtOH containing HCl into 7-*hydroxy*-8-4′-*pyridylacenaphthylene hydrochloride*, m.p. 262°, and by boiling 10% NaOH into 7-*hydroxy*-8-4′-*pyridylacenaphthylene*, colourless *form* (**V**), m.p. 185—192°, red *variety* (**VI**), m.p. 126—127° (also obtained directly by hydrolysis with boiling 95% EtOH). AcCl converts (**VI**) into (**I**) and (**V**) into resinous, non-cryst. products. At 130—140° and then at 200° (**VI**) passes into 8-4′-*picolinoylnaphthalene*-1-*carboxylic acid* (**VII**), m.p. 228—231°, identified as the picrate. A *picrate*, m.p. ~170°, of (**VI**) and a *picrate* ($+1H_2O$), m.p. 191°, and *phenylhydrazone*, m.p. 240°, of (**V**) are described. Distillation of (**I**) with Zn dust gives acenaphthene and 8 : 4′-pyridylacenaphthylene, identified as the *picrate*, m.p. 264—265°, and *aurichloride*, m.p. 205—210°. Alkaline $KMnO_4$ oxidises (**I**) to (**VII**) [*picrate*, m.p. 235—240° (decomp.); corresponding *hydroxamic* acid, reddens at ~140°, m.p. 184—185°; *N-oxide*, m.p. 251—255°], converted by KOH at 160° into C_5H_5N, 1-$C_{10}H_7{\cdot}CO_2H$, and *iso*nicotinic acid (**VIII**). Decarboxylation of (**VII**) by Cu-bronze in boiling tetrahydronaphthalene leads to 1-*naphthyl* 4-*pyridyl ketone* (**IX**), m.p. 50—51° [*picrate*, m.p. 168—169°; *phenylhydrazone*, red leaflets, m.p. 100° (decomp.), and pale yellow needles, m.p. 232°; *oxime*, m.p. 195—196°], reduced (Cu and boiling 10%

HCl) to 1-*naphthyl*-4-*pyridylcarbinol*, m.p. 174—175° (*picrate*, m.p. 200°). KOH at 160° converts (**IX**) into 1-$C_{10}H_7$·CO_2H and (**VIII**). CrO_3 in AcOH oxidises (**I**) to (**VII**). (**I**) and KOH at 160° give C_5H_5N, $C_{10}H_8$, and AcOH. $AlCl_3$ and (**I**) at 140° yield (**III**). Acenaphthenone does not give a ppt. after prolonged contact with Bz_2O in C_5H_5N in the dark and is converted by $(EtCO)_2O$ under the same conditions into 7-*propionoxy*-8-4′-*pyridylacenaphthylene*, m.p. 220° (with a little diacenaphthylidenedione), hydrolysed by 10% NaOH to (**VI**). H. W.

Formation of pyrimidine rings. II. Z. Földi, G. von Fodor, I. Demjén, H. Szekeres, and I. Halmos (*Ber.*, 1942, **75**, [*B*], 755—763).—Traube's procedure (A., 1923, i, 1135) can frequently be improved by replacing the nitrile by the corresponding imino-ether. Gradual addition of NaOEt–EtOH to a solution of acetamidine hydrochloride (**I**) and CO_2Et·CH_2·C(OEt):NH,HCl in EtOH gives 4-amino-6-hydroxy-2-methylpyrimidine (**II**), m.p. 293—294° (*Ag* salt), converted by boiling $POCl_3$ into 6-*chloro*-4-*amino*-2-*methylpyrimidine*, m.p. 189° (*picrate*, m.p. ~200°). This is unchanged by Zn powder in boiling EtOH–H_2O and loses Cl only partly in presence of HCl; it is readily dehalogenated by H_2 in presence of Pd–C and HCl to 4-amino-2-methylpyrimidine, m.p. 205° (*hydrochloride*, m.p. 230°). A *substance*, $C_7H_{13}O_2N_2$, softens at 178°, m.p. 185—188°, is obtained as by-product in the prep. of (**II**) and is the main product from CN·CH_2·CO_2Et and (**I**). It appears to contain OEt which is not exactly determinable by Zeisel's method. It is neutral and unchanged by HCl or NH_3. Attempts to convert CO_2Et·C(CN):CH·OEt, CO_2Et·CH(CN)·CH_2·OMe, and OEt·CH:C(CN)$_2$ into their imino-ether hydrochlorides were unsuccessful. (**I**), CO_2Et·CH(CN)·CH_2·CO_2Et (**III**), and NaOEt–EtOH afford *Et* 4-*amino*-6-*hydroxy*-2-*methylpyrimidyl*-5-*acetate*, m.p. >285°. (**III**) is transformed by HCl in abs. EtOH into the imino-ether hydrochloride, which is immediately condensed with (**I**) to 6 : 8-*dihydroxy*-2-*methylpyrimazole* (**IV**), m.p. >360°. It is converted by boiling $POCl_3$ into 6 : 8-*dichloro*-2-*methylpyrimazole*, m.p. 247—247·5°, which is unchanged by boiling 10% NaOH but transformed by 20% HCl at 100° into 4-*amino*-6-*hydroxy*-2-*methylpyrimidine*-5-*acetic acid* (*hydrochloride*), also obtained by the alkaline hydrolysis of (**IV**). The imino-ether bases from CN·CH_2·CO_2Et, m.p. 35—36°, and (**III**) [possibly *Et* 5-*keto*-2-*ethoxy*-Δ^1-*pyrroline*-3-*carboxylate*], an oil, b.p. 100—118°/1 mm., are described. H. W.

1 : 9-Pyrazoleanthrone-6 : 5-(*N*)-benzacridone.—See B., 1942, II, 397.

***N*-Arylmorpholones.**—See B., 1942, II, 396.

Thiazoles.—See B., 1942, II, 397.

Preparation and reactions of 2-methylhexahydrobenzthiazole. W. Dieterle (*Ber.*, 1942, **75**, [*B*], 853—857).—2-Amino*cyclo*hexanol is converted by Ac_2O into its Ac_2 derivative, m.p. 115°, transformed by P_2S_5 at 140° into 2-methylhexahydrobenzthiazole, b.p. 88—90°/9 mm. [*ethiodide* (**I**), m.p. 117—119°; *methiodide*, m.p. 167°]. Me of the quaternary salts is extremely reactive and undergoes condensation by the methods used for polymethine dyes. Those containing the hexahydrobenzthiazole ring are spectroscopically similar to those with the thiazoline ring. (**I**) and anilo-1-tetrahydroquinolylmethane are converted by cautious treatment with Ac_2O into 2-β-*tetrahydroquinolylvinylhexahydrobenzthiazole ethiodide*, m.p. 182°, transformed by warm NaOH into tetrahydroquinoline and 2-*aldehydomethylene*-3-*ethyloctahydrobenzthiazole*, in which CHO is unusually reactive. H. W.

VII.—ALKALOIDS.

High-boiling bases of *Anabasis aphylla*, L. E. Späth, F. Galinovsky, and M. Mayer (*Ber.*, 1942, **75**, [*B*], 805—813; cf. Orekhov *et al.*, A., 1935, 97, 227).—The brown technical sulphate solution of the total bases is treated with conc. $NaHCO_3$ and Et_2O, whereby mainly the bases (**I**) of high b.p. are removed; the residual aq. solution is made strongly alkaline with NaOH and extracted with Et_2O, thereby giving chiefly anabasine and lupinine. Chromatographic separation (Al_2O_3) of (**I**) gives aphyllidine (**II**) and aphylline (**III**). (**II**) has m.p. 112—112·5°, $[\alpha]_D^{18}$ +5·57° in MeOH, gives a *methiodide*, m.p. 225—227° (decomp.), and is hydrogenated (PtO_2 in N-HCl at 14°) to non-cryst. dihydroaphyllidine (**IV**). (**II**) is converted by successive treatments with boiling 5% HCl and HCl–EtOH into *Et aphyllate* (**V**), b.p. 150° (bath)/high vac., which gives a cryst. *monohydrate*, m.p. 76—77°, $[\alpha]_D^{18}$ +25·30° in MeOH (*platinichloride*, $C_{17}H_{30}O_2N_2,H_2PtCl_6$; corresponding *Me ester monohydrate*, m.p. 82—83°). (**V**) is hydrolysed to *aphyllic acid*, m.p. 218—221° (vac.; decomp.), which at 140—150°/high vac. passes into (**III**), $[\alpha]_D^{18}$ +10·08° in MeOH, which could not be caused to crystallise; it gives a picrolonate, m.p. 233—234° (decomp.), and a methiodide, m.p. 219—221° (decomp.). Treatment of (**IV**) with boiling 3% HCl followed by esterification gives (**V**). (**II**) suffers ring-opening when boiled with 5% HCl but the esterified product is non-cryst. and becomes resinified in light petroleum within a few days. (**V**) is also obtained from the residues left after removal of (**II**) and (**III**) from the sulphate liquor. H. W.

Ergot alkaloids.—See B., 1942, III, 278.

***Strychnos* alkaloids. CXVI. Brucine-9-acetic acid and -9-nitrile.** H. Leuchs and H. J. Teuber (*Ber.*, 1942, **75**, [*B*], 920—924).—ψ-Brucine (**I**) is converted by $CH_2(CO_2H)_2$ in hot AcOH into *brucine*-9-*acetic acid* (**II**), m.p. 245—247° (vac.; slight decomp.), $[\alpha]_D^{15}$ −64° in H_2O [*perchlorate* (**III**), (anhyd.) m.p. 240—250° (vac.), (hydrate) softens at 190° and foams and becomes discoloured at 220°; *Me ester perchlorate*, m.p. 191—194° (vac.; decomp.)]. Oxidation of (**III**) by 5N-HNO_3 at 0° gives a red quinone solution reduced by SO_2 to the quinol, $C_{23}H_{24}O_6N_2$ (*perchlorate*), and oxidised by $HClO_4$ at 50° to the nitroquinone, $C_{23}H_{23}O_9N_3$ (*perchlorate*), reduced to the nitroquinol, $C_{23}H_{25}O_9N_3$ (*perchlorate*). (**II**) is reduced (PtO_2 in H_2O) to dihydrobrucineacetic acid, m.p. 282—284°. (**III**) and PhCHO in boiling NaOMe–MeOH afford benzylidenebrucineacetic acid [*perchlorate monohydrate*, becomes discoloured at 240° and gives a resin at 305° (vac.)]. When heated at its m.p. (**II**) yields CO_2 and 9-methylbrucine [*perchlorate*, m.p. 260—300° (decomp.)]. (**I**) and KCN in AcOH at 20° and subsequently at 100° afford *brucine*-9-*nitrile* (**IV**), m.p. 228—232° (vac.) (*hydrochloride*; *perchlorate*), which is not hydrolysed by boiling 2N-NaOH or 2N-$HClO_4$. It is not greatly attacked by Zn–Hg in 6N-HCl but is reduced by H_2 in presence of Pt and N-HCl to 9-*aminomethyldihydrobrucine*, m.p. (hydrated) 120—123° (vac.), (anhyd.) foams at 120—140° and becomes transparent at 160° [*diperchlorate*, m.p. 220—265°; *Ac* derivative, softens at 250°, m.p. 257—260° (vac.)]. (**IV**) is oxidised by $KMnO_4$ in $COMe_2$ to *brucinononitrile*, softens at 260°, m.p. 275—280° (vac.; decomp.). (**IV**) is converted by 2N-$HClO_4$ and 5N-HNO_3 followed by SO_2 at 20° into the quinol, $C_{22}H_{21}O_4N_3$ (*perchlorate*); if the solution is heated to 50° and then reduced the product is the nitroquinol hydrate, $C_{22}H_{22}O_7N_4$ (*perchlorate*). H. W.

Alkaloid of *Berberis umbellata*, Wall. II. R. Chatterjee (*J. Indian Chem. Soc.*, 1942, **19**, 233—238; cf. A., 1941, II, 23).—Umbellatine (**I**), $C_4H_8(OH)_2(CH_2O_2)(NMe)(OMe)_2(OH)_2$ [*nitrate*, m.p. >250°; *sulphate*, m.p. 274° (decomp.); *picrate*, m.p. 232° (decomp.); Ac_2 derivative, m.p. 193° (decomp.) (shrinks at 187°); does not form an oxime or semicarbazone], occurs in the Himalayan *Berberis* sp., and is probably related to berberine in structure. A comparison of the absorption curves and properties of the two compounds indicates close similarity. (**I**) probably possesses a methylenedioxytetrahydro*iso*quinoline skeleton; it contains an imino-Me, and 4 active H (probably from 4 OH). Hydrogenation (Pd–C in MeOH) affords *dihydro-*, chars without melting, and *tetrahydro-umbellatine*, m.p. 213—215° (decomp.). MeI converts (**I**) into a methiodide, but Me_2SO_4–aq. KOH yields the *Me ether*, m.p. 265°. A. T. P.

Alkaloids of the fruit of *Solanum xanthocarpum*. B. L. Manjunath and M. Shadaksharaswamy (*J. Mysore Univ.*, 1942, **3**, **B**, 117—121; cf. A., 1937, II, 435; 1938, II, 35, 299).—From the EtOH extract of the defatted dried fruits of *S. xanthocarpum* have been isolated glucose, rhamnose, galactose, and solanine-*s*, m.p. 279° (shrinks at 273°, decomp. 290°) [*platinichloride*, m.p. 155° (decomp.)], hydrolysed (H_2SO_4) to solanidine, m.p. 197·5°, $[\alpha]_D^{32}$ +113·5° in $CHCl_3$ (Bz_3 derivative, m.p. 227°; *Me*$_3$ *ether methiodide*, m.p. 233—234°), which contains neither OMe nor NMe groups. A. Li.

H. Wieland's work on natural nitrogenous substances (alkaloids and pterins). C. Schöpf (*Naturwiss.*, 1942, **30**, 359—373).—A review. F. O. H.

VIII.—ORGANO-METALLIC COMPOUNDS.

Oxidation of *n*-butylboron.—See A., 1942, I, 400.

Mercurated aliphatic ketones.—See B., 1942, III, 223.

Mercuriphenyl derivative.—See B., 1942, III, 224, 246.

Mercurated 3-nitro-6-alkylphenols.—See B., 1942, III, 223.

IX.—PROTEINS.

Determination of mol. wt. and particle form of some breakdown products of gelatin by precipitation-titration. B. Jirgensons (*J. pr. Chem.*, 1942, [ii], **160**, 21—32).—Mol. wts. of 1000—30,000 have been found by pptn.-titration in agreement with other methods for breakdown products of gelatin. The dependence of precipitability on concn. indicates a long chain form for the particles. F. J. G.

Application of acidic and basic alumina columns to analysis of protein hydrolysates. T. Wieland (*Naturwiss.*, 1942, **30**, 374—376).—The method is based on the adsorption of only aminodicarboxylic acids by acidic (HCl-treated) Al_2O_3 and of only diaminocarboxylic acids by untreated Al_2O_3, neutral NH_2-acids and histidine being unadsorbed. The Na salts of NH_2-acids in 80% EtOH are adsorbed on the acidic Al_2O_3 and can be separated from glucose,

which is not adsorbed under similar conditions. The application of the method to the hydrolysates of caseinogen and other proteins yielded by boiling with 20% H_2SO_4 for 20 hr. or with conc. HCl for 12 hr. is described. Tryptophan is partly degraded during the hydrolysis, whilst the yield of hydroxyglutamic acid (from caseinogen) is greater with the HCl hydrolysis than with the longer H_2SO_4 hydrolysis. F. O. H.

Preparation and properties of protein sols. II. Sols with *l*-histidine, *d*-arginine, *l*-proline, and *l*-hydroxyproline.—See A., 1943, I, 15.

Histidine content of hæmoglobin.—See A., 1942, III, 874.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

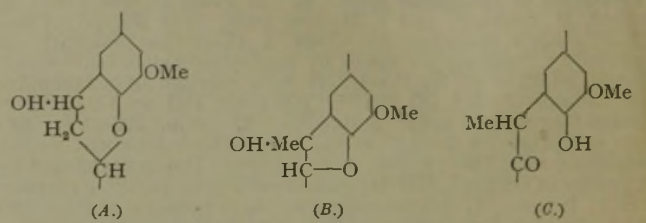
Isolation of three new bitter principles from neem oil. S. Siddiqui (*Current Sci.*, 1942, **11**, 278—279).—Fractionation by solvent methods yielded *nimbin*, $C_7H_{10}O$, m.p. 205° (0·1% of the oil), *nimbinin*, m.p. 192° (0·01%), and *nimbidin*, m.p. 90—100° (1·1%), all neutral, H_2O-insol., and bitter-tasting in aq.-EtOH suspension. R. L. E.

***Primula* saponin.** A. Margot and T. Reichstein (*Pharm. Acta Helv.*, 1942, **17**, 113—140).—The extraction is described of a saponin (as Na salt) from defatted powdered primula root; the yield is 4·1% from *P. officinalis*, and 2·3% from *P. elatior*. The free saponin has m.p. 235—237° (decomp.), $[\alpha]_D^{19}$ −34·8° in MeOH (*P. officinalis*), or m.p. 240—241° (decomp.), $[\alpha]_D^{17}$ −31·8° (*P. elatior*). The yield of *Me* ester (with CH_2N_2 in Et_2O), ? $C_{49}H_{80}O_{19}$, m.p. 314—315° (decomp.), $[\alpha]_D^{14}$ −35·3°, from the latter is >3 times that from the former. The *Me* ester *acetate* has m.p. 205—209°, $[\alpha]_D$ −16·4° to −17·6°. Hydrolysis of both saponins yields: *genin* A, m.p. 248—250°, $[\alpha]_D^{15}$ +16·6° [*diacetate* (**I**), m.p. 220—221°, $[\alpha]_D^{15}$ −31·2° in $CHCl_3$; *triacetate*, m.p. 153—156°, $[\alpha]_D^{23}$ −8·4° in $COMe_2$]; *genin* B, m.p. 248—255°, $[\alpha]_D^{15}$ +62·4° in EtOH [*diacetate* (**II**), m.p. 216—218° (decomp.), $[\alpha]_D$ +64·9° in $CHCl_3$; no triacetate formed]. *Diacetylgenin* C (**III**), m.p. 267—271°, $[\alpha]_D^{15}$ +5·5° in $CHCl_3$, is separated by fractional dissolution from the acetylation products of the genin; it yields by alkaline hydrolysis genin *A*. Oxidation (CrO_3 in AcOH) of (**I**) yields a *compound*, $C_{34}H_{50}O_6$, m.p. 262—265°, $[\alpha]_D$ −3·1° in $CHCl_3$. Similarly (**II**) yields a *substance*, $C_{36}H_{54}O_7$, m.p. 285—293° (decomp.), and (**III**) two substances, m.p. 168—172° and 265—271°. Oxidation (Br) of the $COMe_2$-sol. carbohydrate portion yields *d*-galactose and *d*-glucose. From the products of aq.-EtOH–H_2SO_4 hydrolysis of the saponin an EtOH-insol. Ba salt of a uronic acid was obtained; oxidation (Br) of the free acid yielded two fractions, one which gave a sparingly sol. K salt, and the other a *quinine* salt, m.p. 181—183° (decomp.), which could not be identified. P. G. M.

Constituents of hinokiol. VIII. Synthesis of matairesinol dimethyl ether from hinokinin. S. Keimatsu and T. Ishiguro (*J. Pharm. Soc. Japan*, 1936, **56**, 399—404; cf. A., 1937, II, 21).—Hinokinin with KOH–MeOH at 175—180° for 6—7 hr. gave a *compound*, m.p. 114—116°, and a *phenol* (**I**), acetylation and/or methylation of which gave matairesinol Me_2 ether, identified by m.p., $(NO_2)_2$- and Br_2-compounds. Ethylation (Et_2SO_4) and hydrolysis (KOH) of (**I**) gave *αβ*-bis-(3 : 4-diethoxybenzyl)butyrolactone. Ch. Abs. (*c*)

Claviformin (? $C_9H_{10}O_5$), m.p. 110°.—See A., 1942, III, 937.

Lignin. L. Acetic acid-lignin. K. Freudenberg and E. Plankenhorn (*Ber.*, 1942, **75**, [*B*], 857—867).—Repeated treatment of pine wood with a boiling mixture of AcOH and aq. $MgCl_2$ removes the whole of the lignin as "acetic acid-lignin" (**I**), freely sol. in aq. alkali hydroxide, $COMe_2$, AcOH, C_5H_5N, and undiluted N_2H_4,H_2O, insol. in H_2O and carbonate, scarcely sol. in abs. EtOH, and partly sol. in aq. EtOH. Alkali removes 10% of Ac leaving a product sol. in aq. alkali hydroxide, AcOH, and C_5H_5N but insol. in H_2O and carbonate, almost insol. in aq. EtOH or anhyd. $COMe_2$. The characteristic solubilities are therefore proper to the fundamental Ac-free product. Isolated cuproxam-lignin (**II**) (insol. in alkali) is transformed by AcOH–aq. $MgCl_2$ into (**I**) with the same properties. These, however, are foreign to the native lignin since hydrolysed (**I**) from wood or (**II**) cannot be changed by hot 1% H_2SO_4 into an alkali-insol. product resembling (**II**). (**II**) appears to be more closely related than the alkali- or organosolve- (**III**) -lignin to native lignin. It is brought into solution by HSO_3' and is followed in this respect by laboratory "HCl-lignin" (**IV**) and Tornesch lignin which are dissolved with difficulty or not at all. Technical (**IV**) has been further changed and is partly sol. in alkali owing to partial demethylation. The alkali- and organosolve-lignins are little affected by HSO_3' even after pre-treatment with SO_3''. Lignin in wood and (**III**) have thermoplasticity in common but this property is not shown by (**II**); it appears to depend on the slight degree of condensation of lignin in wood. Determination of phenolic OH in lignin cannot be effected potentiometrically and the regulated Ac elimination from (**I**) gives difficultly interpretable results. Some information is derived from analysis of the Na salts obtained by the action of NaOAlk on hydrolysed (**I**) in an org. medium but the most satisfactory process consists of the treatment of the toluenesulphonates with anhyd. N_2H_4. The increase of phenolic OH from 0·7% in (**II**) to 3·3% in deacetylated (**I**) does not correspond with



(*A.*) (*B.*) (*C.*)

an increase in total OH and is accounted for on the hypothesis that units of type *A* are unchanged by AcOH–$MgCl_2$ followed by hydrolysis whereas units of type *B* pass into those of type *C*. Very little vanillin is obtained by oxidation of (**I**) with $PhNO_2$ and even in presence of $Co(OH)_2$ the yield is ≪ that from untreated lignin. This is ascribed to the inability of *C* and ability of *B* to yield the CHO roup. H. W.

XI.—ANALYSIS.

Gas-fired furnace for semi-micro-determination of carbon and hydrogen. H. A. Paget (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 764—766).—The novel features of the furnace are Ag sleeves, for distribution of heat, on the combustion tube sections, and screens for the sections to prevent premature volatilisation of the test substance. J. D. R.

Isothermal diffusion method of preparing highly purified microchemical reagents.—See A., 1943, I, 26.

Lower aliphatic alcohols. Application of the Zerevitinov determination. W. Hollyday and D. L. Cottle (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 774—775).—Apparatus for determination of lower aliphatic alcohols by the Zerevitinov method is described in detail. *iso*Amyl ether is used as solvent for the alcohol and the Grignard reagent. The concn. of the alcohol in the solvent should be such that no appreciable ppt. of Mg alkoxyiodide is formed. J. D. R.

Determination of alkoxyl groups in cellulose ethers. E. P. Samsell and J. A. McHard (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 750—754).—A detailed description is given of the construction and operation of a modified Zeisel apparatus for the Viebock determination of OEt and OMe in cellulose ethers. The use of a solvent in addition to the HI is not advisable except in the cases of very resistant substances, when PhOH or $(EtCO)_2O$ may be used. J. D. R.

New reaction for the investigation of amino-acids. A. Barreto (*Rev. Quim. Ind.*, 1942, **11**, 275).—1 c.c. of a neutral solution containing NH_2-acids (**I**) with 1 c.c. of 15—20% neutral C_6Cl_5·ONa and 1 c.c. of neutral 40% CH_2O gives a white ppt. of C_6Cl_5·OH. (**I**) may be determined as C_6Cl_5·OH in 1 c.c. of 0·5—1·0% solution by adding 2 c.c. of neutral 20% C_6Cl_5·ONa and 2 c.c. of neutral 40% CH_2O. F. R. G.

Step-photometric determination of œstrogenic stilbenes. E. Huf and G. Widmann (*Z. physiol. Chem.*, 1942, **274**, 88—95).—4 : 4′-Dihydroxy-*αβ*-diethylstilbene gives a yellow-red colour with *p*-SO_3H·C_6H_4·N_2Cl in borate-buffered solution (pH 12) which, under defined conditions, can readily be used for its determination with an accuracy of ±10%. The process can be extended to esters (oil- or H_2O-sol.) if they are hydrolysed before addition of the reagent. Directions are also given for the determination of œstrogenic stilbenes in oil or tablets, from which they are extracted by MeOH. H. W.

Wing pigments of butterflies. XIII. Detection and determination of leucopterin. P. Decker (*Z. physiol. Chem.*, 1942, **274**, 223—230).—Leucopterin (**I**) is detected and approx. determined by measurement of its blue fluorescence in alkaline solution. It could not be detected in human urine, snake excrement, or guano, in which the respective limits of sensitiveness are <1 mg. per l., <0·02%, and <0·3%. The grub of the clothes moth contains 0·01% of (**I**). (**I**) is sol. in ~10^6 parts of H_2O at 20°. H. W.

Determination of protein by biuret and Greenberg methods.—See A., 1943, III, 76.

INDEX OF AUTHORS' NAMES, A., II.

JANUARY, 1943.

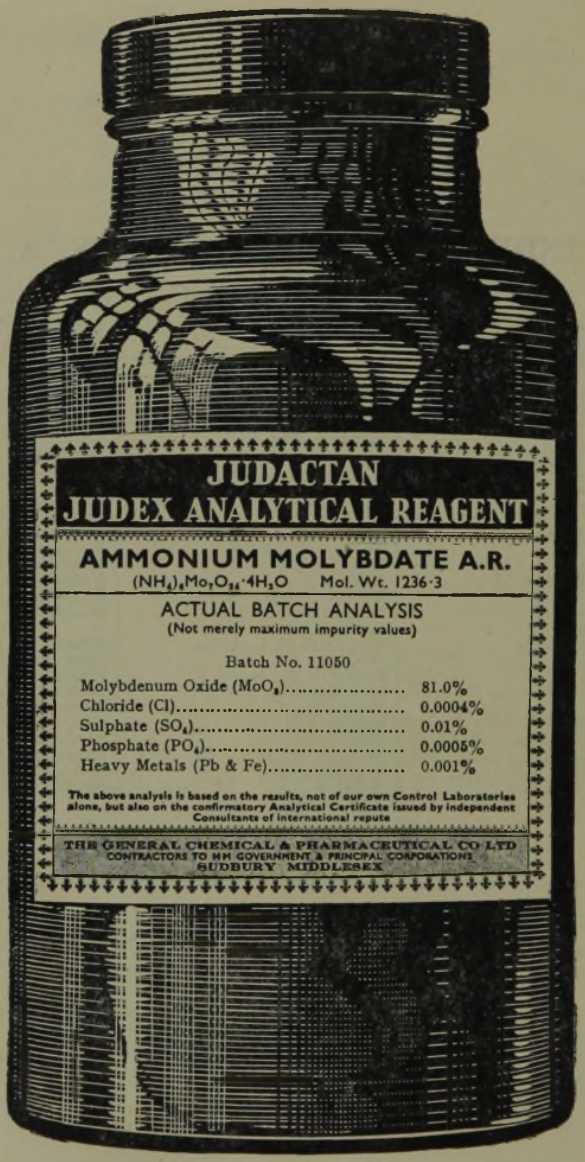
JUDACTAN

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

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD., BUNGAY, SUFFOLK.