BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

JUNE, 1944

A II—ORGANIC CHEMISTRY

CONTENTS

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A II—Organic Chemistry.

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I.—ALIPHATIC.

Fluorinated derivatives of propane. V. A. L. Henne and J. V. Flanagan (*J. Amer. Chem. Soc.*, 1943, **65**, 2362—2363; cf. A., 1942, II, 126).—HgO–HF (apparatus: C., 1944, Part 3) replaces Cl by F in C_3H_8 derivatives, including those containing H. In CCl_2RR' gradual change of R = Me to R = CCl_3 progressively hinders and finally prevents the changes, $CCl_2 \rightarrow CClF \rightarrow CF_2$. A central CF_2 usually has little effect on the ease of fluorination of an adjacent CCl_3. 1 mol. of HgO suffices to introduce 2 F. 10—12 mols. of HF are used, the excess acting as solvent. The reactants, precooled to −78°, are mixed at −78° and left to warm up or heated for reaction. Recovery of Hg, best as HgO, is described. Yields may be up to 86%. $CH_2Cl{\cdot}CMeCl_2$ at room temp. gives 51% of $CH_2Cl{\cdot}CMeF_2$. $CCl_2(CH_2Cl)_2$ at 125° (6 hr.) gives *αβγ-trichloro-β-fluoro-*, m.p. −67·8°, b.p. 130·80°, and then *αγ-dichloro-ββ-difluoropropane* (I), m.p. −30·04°, b.p. 96·69°, structures being proved by chlorination of (I) in light to *aaγ-trichloro-ββ-difluoropropane*, m.p. −60·80°, b.p. 127·27°, and then $CCl_3{\cdot}CF_2{\cdot}CH_2Cl$, m.p. −17·13°, b.p. 151·18°, and $CF_2(CCl_3)_2$. $CH_2Cl{\cdot}CCl_2{\cdot}CHCl_2$ gives with decomp. a little monofluoride (not purified) and (?) $CHClF{\cdot}CClF{\cdot}CH_2Cl$, a glass. $CCl_3{\cdot}CMeCl_2$ (II) [a commercial product, erroneously stated to be $CHCl(CHCl_2)_2$] at 100° gives a solid solution of $CCl_3{\cdot}CMeClF$, m.p. 102·4°, b.p. 138·2—138·6°, with a little $CCl_2F{\cdot}CMeCl_2$; further fluorination of (II) gives *aaβ-trichloro-αβ-difluoropropane*, m.p. 27·6°, b.p. 97·7°, which is also obtained from $CCl_3{\cdot}CMeClF$ and with Cl_2 in light gives *aaβγγγ-hexachloro-αβ-difluoropropane*, m.p. −55°, b.p. 196·0°. $CCl_3{\cdot}CMeF_2$ yields very readily 86% of *α-chloro-aaββ-tetrafluoropropane*, m.p. −74·72°, b.p. 19·93°, which is very slowly chlorinated to $CCl_3{\cdot}CF_2{\cdot}CClF_2$ (III), m.p. −92·78°, b.p. 113·95°. $CCl_3{\cdot}CF_2{\cdot}CH_2Cl$ yields at 135° (6—8 hr.) 50% of $CClF_2{\cdot}CF_2{\cdot}CH_2Cl$, m.p. −75·0°, b.p. 68·2°, readily converted into (III). $CCl_2F{\cdot}CF_2{\cdot}CH_2Cl$, m.p. −79·8°, b.p. 109·5°, and $CCl_3{\cdot}CHCl{\cdot}CH_2Cl$, b.p. 192·5—193°, are also reported. R. S. C.

Use of semi-micro-technique in elementary organic chemistry. II. N. D. Cheronis, P. G. Arvan, and H. Teifeld (*J. Chem. Educ.*, 1943, **20**, 431—437; cf. A., 1939, II, 192).—Apparatus for ordinary, fractional, and steam distillations is described. The semi-micro-prep. of decane, *cyclo*hexene, and $Bu^{\alpha}Br$ is given. L. S. T.

Ozonisation of terminal groups of saturated hydrocarbons of the aliphatic series.—See A., 1944, I, 131.

Photochemical chlorination and photochemical oxidation of tetrachloroethylene sensitised by chlorine.—See A., 1944, I, 132.

Unique polyene pigment of the marine diatom *Navicula torquatum*.—See A., 1944, III, 370.

Conjugated systems. XX. Reaction of chloroprene with iodine chloride. XXI. Reaction of αβ-dichlorobutadiene with hypobromous acid and alkyl hypoiodites. Synthesis and properties of dichlorovinylethylene oxide and αβ-dichloro-γ-alkoxybutadienes. XXII. Order of addition of bromine to bromoprene. Synthesis and properties of αβ-dibromo-$\Delta^{\alpha\gamma}$-butadiene. A. A. Petrov (*J. Gen. Chem. Russ.*, 1943, **13**, 155—158, 230—236, 237—241).—XX. Chloroprene and ICl in $CHCl_3$ at −5° yield chiefly $CHCl{:}CH{\cdot}CHCl{\cdot}CH_2I$.

XXI. $CH_2{:}CH{\cdot}CCl{:}CHCl$ (I) and aq. NHBrAc in 1% H_2SO_4 yield *αβ-dichloro-δ-bromo-Δ^{α}-buten-γ-ol*, b.p. 100—106°/10 mm. (*acetate*, b.p. 109—112°/10 mm.), from which *αβ-dichloro-γδ-oxido-Δ^{α}-butene*, b.p. 94—95·5°/85 mm., is obtained by distillation at 150° from 80% KOH. This with 50% H_2SO_4 at 60° yields *αβ-dichloro-Δ^{α}-butene-αδ-diol*, b.p. 135—136°/10 mm. (*diacetate*, b.p. 128·5—129°/10 mm.). (I) and I in MeOH or EtOH in presence of HgO afford *αβ-dichloro-δ-iodo-γ-methoxy-*, b.p. 90—91·5°/5 mm., or *-γ-ethoxy-Δ^{α}-butene*, b.p. 94·5—95°/5 mm. (decomp.). These ethers are converted by heating with 20% KOH in EtOH into *αβ-dichloro-γ-methoxy-*, b.p. 90·5—91·5°/85 mm., or *-γ-ethoxy-$\Delta^{\alpha\gamma}$-butadiene*, b.p. 103·5—105°/85 mm., from which *Me αβ-dichlorovinyl ketone*, b.p. 61·5—62°/30 mm., is obtained by hydrolysis with 5% H_2SO_4 at 40°.

XXII. Bromoprene and Br in $CHCl_3$ at 10—15° yield *αβδ-tribromo-Δ^{β}-butene*, b.p. 121—122°/10 mm. This with KOH in EtOH at 0° gives *αβ-dibromo-$\Delta^{\alpha\gamma}$-butadiene*, b.p. 46—46·5°/10 mm.; when the reaction is conducted in boiling solution $(CH{:}C)_2$ is also produced. R. T.

Raman spectra of two forms of *allo*ocimene.—See A., 1944, I, 118.

Sesquiterpenes. LXI. Synthesis of an aliphatic sesquiterpene alcohol with irregular isoprene chain. H. Schinz and P. H. Müller (*Helv. Chim. Acta*, 1944, **27**, 57—60; cf. A., 1943, II, 181, 182).—Geranylacetone, b.p. 126—130°/11 mm., condenses with 33% CH_2O and $Ba(OH)_2,2H_2O$ in EtOH at 60° to *α-hydroxymethylgeranylacetone* (I), b.p. 122°/0·15 mm. [*allophanate*, m.p. 99—100°, from which (I) is not readily regenerated; non-cryst. semicarbazone], converted by MgMeI into *βζκ-trimethyl-ι-hydroxymethyl-$\Delta^{\beta\zeta}$-undecadien-κ-ol*, b.p. 134—137°/0·07 mm. This is dehydrated by o-$C_6H_4(CO)_2O$ at 180° with a short period at 190° to *βζκ-trimethyl-ι-hydroxymethyl-$\Delta^{\beta\zeta\kappa}$-undecatriene*, b.p. 88°/0·02 mm., 154°/12 mm., which absorbs 3 mols. of H_2 and has an odour reembling that of farnesol. H. W.

Interaction of hydroxy-compounds and phosphorus and thionyl halides in the absence and presence of tertiary bases. I. Optically active β-octanol, ethyl mandelate, and phenylmethylcarbinol. W. Gerrard (*J.C.S.*, 1944, 85—90).—Addition of PCl_3 to (+)-β-octanol (I) and to (−)-OH·CHPh·CO_2Et (II) gives the chloride, RCl, and the H phosphite, $P(OR)_2{\cdot}OH$. Reversed order of mixing gives the chlorophosphite, $PCl_2{\cdot}OR$, which did not decompose to RCl. PCl_3 mixed with (−)-CHPhMe·OH (III) in either order gives (+)-CHPhMeCl (IV) without chlorophosphite. (−)-*Tri-β-octyl phosphite* and PCl_3 give an equilibrium mixture of the two chlorophosphites $PCl_2{\cdot}OR$ and $PCl(OR)_2$ and PCl_3. $SOCl_2$ mixed in either order with (I) and (II) gives an equilibrium mixture of the chlorosulphinate OR·SOCl (V), the sulphite R_2SO_3 (VI), and $SOCl_2$. $SOCl_2$ and (III) give only (IV). With C_5H_5N in Et_2O (I), (II), and (III) on addition of PCl_3 give the corresponding phosphites; with $SOCl_2$ (same conditions) (I) and (II) give the corresponding sulphites but (III) gives (IV) and no sulphite. (III) with Et chlorosulphinate gives (−)-*α-phenylethyl Et sulphite*, which with $SOCl_2$ gives the non-inverted CHPhMeCl. $SOCl_2$ and (+)-di-β-octyl sulphite give an equilibrium mixture of (V), (VI), and $SOCl_2$. Mechanisms depending on oriented collisions on the "front" or on the "back" of the asymmetric C are discussed. Compounds described include: (−)-*β-octyloxyphosphorus dichloride*, b.p. 83—84°/2 mm. 118—119°/17 mm., α_D^{18} −34·5°; (+)-*di-β-octyloxyphosphorus chloride*, b.p. 135—140°/2 mm., α_D^{18} +0·7°; (+)-*β-octyl H_2 phosphite*, α_D^{16} +7·0°; (+)-*di-β-octyl H phosphite*, b.p. 138—140°/2 mm., α_D^{18} +15·8°; (−)-*tri-β-octyl phosphite*, b.p. 162—164°/2 mm., α_D^{20} −0·8°; (−)-*α-carbethoxybenzyloxyphosphorus dichloride*, b.p. 105—108°/2 mm., α_D^{16} −122·9°; (+)-*bis-α-carbethoxybenzyl sulphite*, b.p. 218—221°/2 mm., α_D^{22} +124·1; (−)-*α-phenylethyl Et sulphite*, b.p. 93°/2—3 mm., α_D^{20} −94·5°. (Vals. of α are for l = 10 cm.). D. G.

Stabilisation of polysulphones towards heat. C. S. Marvel and W. H. Sharkey (*J. Org. Chem.*, 1944, **9**, 113—116).—Polysulphones made from olefines containing a trace of $CH_2{:}CH{\cdot}CH_2Br$ (I) are much more stable towards heat than polysulphones made from pure olefines. The preformed polysulphone can also be treated with (I) to cause some stabilisation but the effect is less marked. The effect appears sp. for (I) and is not shown by $CH_2{:}CH{\cdot}CH_2Cl$, EtBr, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}Br$, camphene, α-bromoheptene, undecylenyl bromide, CHPh:CHBr, $CH_2{:}CH{\cdot}CO_2Et$, COEt·CH_2Cl, $CHCl_3$, $C_7H_{15}{\cdot}SH$, CCl_4, p-$C_6H_4Br{\cdot}CH_2Cl$, CH_2PhCl, $CH_2Ph{\cdot}OH$, furfuryl alcohol, furfurylacrylic acid, and chloro*iso*durene. Heat-treatment of polysulphones appears to remove some of the readily decomposable material so that the residue is more stable towards heat. Dissolution and repptn. also improves the thermal stability to some extent. Presence of peroxides in polysulphones increases the amount of decomp. which occurs when they are heated. H. W.

Use of phenyl esters in the Reformatsky reaction.—See A., 1944, II, 162.

Union of gaseous oxygen with methyl oleate at 20° and 120°. D. Atherton and T. P. Hilditch (*J.C.S.*, 1944, 105—107).—The products of autoxidation in O_2 of Me oleate are partly separated by adsorption on SiO_2 gel, and then oxidised ($KMnO_4$ in $COMe_2$) and the scission products examined. At 20° the main products are suberic (I), octoic (II), azelaic (III), and nonoic acids (IV), confirming peroxidation at the $\cdot CH_2\cdot$ groups adjacent to the double linking (cf. Farmer, A., 1943, I, 151). At 120°, only (III) and (IV) and a trace of (I) were isolated, with no (II), as well as more complex products, suggesting action at the double linking. D. G.

Normal aliphatic β-hydroxy- and α-keto-acids. F. Adickes and G. Andresen (*Annalen*, 1943, **555**, 41—56).—The prep. of β-OH-acids by diazotisation of β-NH_2-acids could not be successfully accomplished and ozonisation of allylalkylcarbinols gives only poor yields. Condensation of the aldehydes with 2 fewer C atoms with $CH_2Br{\cdot}CO_2Et$ (Reformatzky) and hydrolysis of the esters gives the OH-acids in 10—12% yield. The following are described: β-hydroxy-valeric, m.p. 43—44° (*Et* ester, b.p. 83—85°/10 mm.); -hexoic, m.p. 13°; *-heptoic*, m.p. 40—41° (*Et* ester, b.p. 94—96°/5 mm.); *-octoic*, m.p. 38—38·5° (*Et* ester, b.p. 101—104°/5 mm.); -nonoic; -decoic, m.p. 56—56·5°; *-undecoic*, m.p. 73—73·5°, softens at 72°; *-lauric acid*, m.p. 70—70·5°, softens at 69°. α-CO-acids up to C_{10} are obtained by prolonged condensation at room temp. (shortened by boiling under a reflux condenser) of the requisite ester with $Et_2C_2O_4$ and NaOEt in Et_2O. For esters of higher mol. wt. KOEt in C_5H_5N is used as condensing agent. The esters are hydrolysed and decarboxylated by boiling HCl. Thus are obtained: α-ketovaleric, m.p. 6—7°, softens at 5° (*Ba* salt; *Et α-ketovalerate* 2 : 4-*dinitrophenylhydrazone*, m.p. 116—116·5°, softens at 115°); *-hexoic*, b.p. 101—102°/20 mm., m.p. 7—8° [*Ba* salt; oxime, m.p. 132—133° (decomp.), softens at 129°; *phenylhydrazone*, m.p. 84—86°, softens at 80°; *Et α-ketohexoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 117—118°, softens at 114°]; *-iso*hexoic, b.p. 92—94°/20 mm.; *-heptoic*, m.p. 29—30° (*Ba* salt; *oxime*, m.p. 126—127°, softens at 125°; *phenylhydrazone*, m.p. 102—103°; *Et* ester, b.p. 87—88°/8 mm., and its 2 : 4-*dinitrophenylhydrazone*, m.p. 102—103°); -octoic, m.p. 32—33°, b.p. 118—123°/13 mm., 104°/6 mm.; -nonoic, m.p. 43—44°, softens at 42° (*Na* salt; oxime, m.p. 98—98·5°, softens at 97°; *Et α-ketononoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°, softens at 85°); -decoic, m.p. 46—47°, b.p. 148—151°/18 mm. (oxime, m.p. 85—86°, softens at 80°; 2 : 4-dinitrophenylhydrazone, m.p. 134°, softens at 132°); *-undecoic*, m.p. 55°, softens at 52° (*oxime*, m.p. 85—86°, softens at 83°; *Et α-ketoundecoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 86°, softens at 85°); *-lauric*, m.p. 56·5—57°, softens at 56° (*oxime*, m.p. 80—81°, softens at 77°; *Et α-ketolaurate* 2 : 4-*dinitrophenylhydrazone*, m.p. 86°, softens at 83°); *-tridecoic*, m.p. 62—62·5° (*oxime*, m.p. 86—86·5°, softens at 84°; *phenylhydrazone*, m.p. 91—92°, softens at 88°; *Et α-ketotridecoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 84—84·5°, softens at 83°); *-pentadecoic acid*, m.p. 68—68·5°, softens at 66° (*oxime*, m.p. 88—88·5°, softens at 87°; *Et α-ketopentadecoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°, softens at 84°). The following are incidental: *Et₂ α-oxalbutyrate*, b.p. 84—85°/0·7 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 98—99°, softens at 96°); *Et₂ α-oxalvalerate* 2 : 4-*dinitrophenylhydrazone*, m.p. 85—86°; *Et₂ α-oxalhexoate*, b.p. 118—122°/mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 84—85°); *Et₂ α-oxalheptoate*, b.p. 135—140°/1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 82—83°); *Et₂ α-oxaloctoate* 2 : 4-*dinitrophenylhydrazone*, m.p. 62—63°, softens at 61°; *Et₂ α-oxalnonoate* 2 : 4-*diphenylhydrazone*, m.p. 65—66°, softens at 64°; *Et₂ α-oxalmyristate* 2 : 4-*dinitrophenylhydrazone*, m.p. 74—75°. H. W.

Monocrotalic acid.—See A., 1944, II, 147.

α-Alkylthiol-aliphatic acids. A. J. Hill and E. W. Fager (*J. Amer. Chem. Soc.*, 1943, **65**, 2300—2301).—Adding a trace of cryst. KI and then, dropwise, $CHRBr{\cdot}CO_2H$ (I) in 50% EtOH to KOH (I) and R'SH (1 mol.) in boiling EtOH–N_2 gives 70—80% (crude) of α-n-*dodecylthiol-n-undecoic*, m.p. 46—48°, α-n-*tetradecylthiol*-n-*butyric*, m.p. 38—39°, and α-n-*hexadecylthiol-acetic*, m.p. 73·5—74°, *-propionic*, m.p. 58—59°, -n-*valeric*, m.p. 47·5—49°, -n-*hexoic*, m.p. 48·5—49·5°, -n-*decoic*, m.p. 42—43°, -n-*undecoic*, m.p. 47—49°, -n-*dodecoic*, m.p. 46—48°, -n-*tetradecoic*, m.p. 46—48°, and *-palmitic acid*, m.p. 46—48°. When R = H—Bu, the products crystallise from light petroleum, but the higher SH-acids gelatinise and are purified by way of the *Ba* salts. R. S. C.

Derivatives of ω-hydroxybutanal. R. Paul (*Compt. rend.*, 1942, **215**, 303—305).—Pentane-αβε-triol (I) is converted into αβ-iso*propylidenedioxypentan-ε-ol*, b.p. 117—118°/12 mm., transformed by $NaNH_2$ into the Na derivative, which with CH_2PhCl in boiling PhMe affords *ε-benzyloxy-αβ-iso*propylidenedioxypentane, b.p. 170—171°/11 mm. This is hydrolysed by 0·25N-H_2SO_4 at 40° to *ε-benzyloxypentane-αβ-diol*, b.p. 188—190°/5 mm., which is readily oxidised by $Pb(OAc)_4$ at room temp. to *γ-benzyloxybutanal*, b.p. 143°/10 mm. (p-*nitro-*, m.p. 88°, and 2 : 4-*dinitro-phenylhydrazone*, m.p. 94—95°). It is oxidised by Ag_2O to *Ag γ-benzyloxybutyrate*, m.p. 200°. *γ-Chlorobutanal*, b.p. 50—51°/13 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 134—135°), is obtained by oxidising [$Pb(OAc)_4$ or $NaIO_4$] the mixture of ε-chloropentane-αβ-diol and β-chloropentane-αε-diol prepared by the action of AcCl on αδ-epoxypentan-ε-ol. It appears to be polymerised readily by heat. Its *oxime*, m.p. 74·5°, is isomerised by Raney Ni at ~100° to *γ-chlorobutyramide*, m.p. 99—100°. (I) in anhyd. Et_2O is readily oxidised by $Pb(OAc)_4$ to $OH{\cdot}[CH_2]_3{\cdot}CHO$, b.p. 65—68°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 104°; *oxime*, b.p. 147°/12 mm.). It is reduced by Na–Hg to $OH{\cdot}[CH_2]_4{\cdot}OH$ and oxidised by excess of Ag_2O at room temp. to *Ag γ-hydroxybutyrate*, m.p. 178—180°. It is converted by 1% HCl–MeOH into 2-*methoxytetrahydrofuran*, b.p. 105—107°/760 mm., in very poor yield. H. W.

Solubilities of normal aliphatic primary amines of high mol. wt.—See A., 1944, I, 123.

Amino-alcohols. XIII. Synthesis of aliphatic amino-alcohols of pharmacological interest. I. W. C. Gakenheimer and W. H. Hartung (*J. Org. Chem.*, 1944, **9**, 85—88).—Electrolytic reduction of NO_2-alkanols (I) gives good yields of the corresponding NH_2-alkanols (II). Raney Ni in presence of CO_2 or AcOH catalyses the hydrogenation of (I) to (II). If reduction is effected in a neutral solvent (I) undergoes fission of the alkane chain with the formation of primary and *sec.* amines. Evidence indicates that fission takes place with some partly hydrogenated product. The following are reported: γ-nitroheptan-δ-ol, b.p. 122—123°/18 mm.; β-nitro-β-methylhexan-γ-ol, b.p. 122—123°/21 mm.; ε-nitro-octan-δ-ol, b.p. 123—124°/13 mm.; *α-nitro-γ-ethylpentan-β-ol*, b.p. 109—111°/26 mm.; *β-nitro-δ-ethylhexan-γ-ol*, b.p. 118—120°/22 mm.; *α-nitroheptan-β-ol*, b.p. 118—120°/24 mm.; *β-nitro-octan-γ-ol*, b.p. 133—134°/22 mm.; *γ-nitrononan-δ-ol*, b.p. 142—143°/23 mm.; *α-nitro-octan-β-ol*, b.p. 130—132°/24 mm.; β-nitrononan-γ-ol, b.p. 134—136°/23 mm.; *β-amino-δ-ethylhexan-γ-ol*, b.p. 110—112°/27 mm. (*Bz* derivative, m.p. 151°); *γ-aminoheptan-δ-ol*, b.p. 98—99°/20 mm. (*Bz* derivative, m.p. 145°); *α-amino-octan-β-ol*, b.p. 130—132°/26 mm. (*Bz* derivative, m.p. 158°); *ε-amino-octan-δ-ol*, b.p. 118—119°/26 mm. (*Bz* derivative, m.p. 149—150°); *γ-aminononan-δ-ol*, b.p. 116—118°/27 mm. (*Bz* derivative, m.p. 161°). H. W.

Amino-acids. II. Alanine. J. H. Billman and E. E. Parker (*J. Amer. Chem. Soc.*, 1943, **65**, 2455—2456; cf. A., 1943, II, 253).—$NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}OH$ affords a phthalimide derivative only with difficulty, but, when treated with BzCl in presence of Na_2CO_3 in C_6H_6 at ≯10° and then kept at 0°, gives *β-benzamido-n-propyl alcohol* (90—91%), m.p. 107—108°, which (crude) with $KMnO_4$ in aq. NaOH at ≯40° gives $NHBz{\cdot}CHMe{\cdot}CO_2H$ (65—70%), m.p. 166°, and thence (boiling 18% HCl) alanine (70—71%). R. S. C.

Solubilities of normal aliphatic nitriles of high mol. wt.—See A., 1944, I, 122.

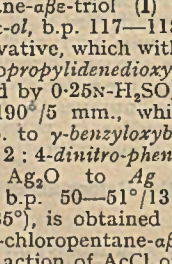
Preparation of malononitrile. A. R. Surrey (*J. Amer. Chem. Soc.*, 1943, **65**, 2471—2472).—70—72% yields are obtained by boiling $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ (1260 g.), $POCl_3$, (800 ml.), and NaCl (1 kg.) in $(CH_2Cl)_2$ (5 l.) for 8 hr. R. S. C.

II.—SUGARS AND GLUCOSIDES.

Theory of a method for comparing the structures of certain compound sugars. Probable relationship of turanose to maltose. C. S. Hudson (*J. Org. Chem.*, 1944, **9**, 117—120).—The keypoint of the method is the symmetry about the central point of mannitol, threitol, the active tartaric acids, and iditol. From this viewpoint are discussed the correlation of natural gentiobiose with synthetic 1-β-*D*-glucopyranosido-*D*-fructose, the probable relationship of turanose to maltose, and the possible relationship of laminaribiose to cellobiose. H. W.

Separation of methylated sugars by chromatographic adsorption of their azobenzene-4-carboxylates. J. K. Mertzweiler, D. M. Carney, and F. F. Farley (*J. Amer. Chem. Soc.*, 1943, **65**, 2367—2368).—*p*-$PhN_2{\cdot}C_6H_4{\cdot}CO$ esters of methylated sugars are prepared in C_5H_5N at, successively, 0° (3 days), 30° (2 days), and 0° (3 days) and are purified by dissolution in $CHCl_3$ and then filtration through a 4—5-cm. column of Al_2O_3 (to remove *p*-$PhN_2{\cdot}C_6H_4{\cdot}CO_2H$), and finally crystallisation from $CHCl_3$–EtOH or EtOH. Yields are ≮95%. Mixed esters are separated by chromatography (? from $CHCl_3$–C_6H_6–light petroleum) on SiO_2 (prep. described); elution is by 1 : 4 EtOH–$CHCl_3$; the solutions obtained are examined colorimetrically as they contain colloidal SiO_2. Excellent results are described for mixed esters of (i) 2 : 3 : 4 : 6-tetramethyl- (I) and 3-methyl-glucose and (ii) (I), 2 : 3 : 6-tri- and 2 : 3-di-methylglucose. R. S. C.

Constitution and configuration of digitalose. O. T. Schmidt, W. Mayer, and A. Distelmaier [with, in part, E. Fürst] (*Annalen*, 1943, **555**, 26—41, and *Naturwiss.*, 1943, **31**, 247—248; cf. Kiliani, A., 1931, 1273).—Digitalose (I) is 3-*methyl*-d-*fucose* (*A*). Digitalin is hydrolysed and the product is largely freed from glucose by fermentation with brewer's yeast. The resulting (I) after crystallisation from EtOH is 80% pure according to OMe content and with $NHPh{\cdot}NH_2$ in aq. AcOH at 100° gives *digitalosephenylosazone*, m.p. 179—180°, $[\alpha]_D^{20}$ +0·5° to +18° (final val.) in C_5H_5N–EtOH (2 : 3). OMe in (I) cannot therefore be attached to $C_{(2)}$. Attachment at $C_{(5)}$ is also excluded since digitalonic acid is oxidised by HNO_3 to a trihydroxyglutaric acid which contains the first 5 C atoms of (I) and also OMe. Since digitalonolactone, m.p. 137—138°, $[\alpha]_D^{20}$ −92·5° to −74·9° in H_2O in 16 days, has the γ structure OMe is not united to $C_{(5)}$ and only $C_{(3)}$ remains. α-Methyl-*l*-fucoside is converted by 10N-NaOH and Me_2SO_4 into 2 : 3 : 4-*trimethyl-α-methyl-l-fucoside*, b.p. 84—88°/1 mm., m.p. 97—98°, $[\alpha]_D^{20}$ −209°±1° in H_2O. 2 : 3 : 4-*Trimethyl-β-methyl-l-fucoside*, b.p. 82—84°/1 mm., m.p. 101·5—102·5°, $[\alpha]_D^{20}$ −21·1°±1° in H_2O, is obtained analogously. These are hydrolysed



by N-H_2SO_4 at 85° to 2 : 3 : 4-*trimethyl-α-l-fucose* (II), m.p. 36—37°, $[\alpha]_D^{20}$ −130°±1·3° (final val.) in H_2O {*monohydrate*, m.p. 65°, $[\alpha]_D^{20}$ −169°±2° to −118°±2° (final val.) in H_2O}. (I) is transformed by HCl–MeOH into a mixture of α- and β-methyldigitaloside, further methylated by K and MeI in liquid NH_3 to a mixture of trimethylmethyldigitalosides. This is hydrolysed by N-H_2SO_4 at 85° and the product is distilled and finally crystallised from Et_2O–light petroleum, thus giving 2 : 3 : 4-*trimethyl-α-d-fucose monohydrate*, m.p. 65°, $[\alpha]_D^{20}$ +168·6°±2° to +118°±2° (final val. after 24 hr.) in H_2O; this is the optical antipode of (II). β-Methyl-*l*-fucoside is converted by $COMe_2$ containing conc. H_2SO_4 into 3 : 4-iso*propylidene-β-methyl*-l-*fucoside* (+1H_2O), m.p. (indef.) 89—97°, transformed by Na and MeI in Et_2O into 2-*methyl*-3 : 4-iso*propylidene-β-methyl*-l-*fucoside* (+1H_2O), m.p. 88—92°, $[\alpha]_D^{20}$ −10·9°±1° in MeOH. *l*-Fucose, from *Fucus vesiculosus*, is converted by $CH_2Ph{\cdot}SH$ and saturated HCl at −15° into l-*fucose dibenzyl mercaptal*, m.p. 184°, $[\alpha]_D^{20}$ +27·8° in C_5H_5N. *l*-Fuconamide, m.p. 182°, is converted by NaOCl and NaOH into *l*-lyxomethylose, isolated as the *phenylbenzylhydrazone*, m.p. 100·5—101°, $[\alpha]_D^{20}$ −36·4° in C_5H_5N. H. W.

Photolysis of the *d*-glycosides : α-benzylfructofuranoside, β-benzylfructopyranoside, and α- and β-phenyl-, -benzyl-, and β-phenylethylglucosides ; and the bearing of the data on the transfer of energy between molecules.—See A., 1944, I, 132.

β-β′β′β′-Trichloroethylgentiobioside, m.p. 204—206° (decomp.), $[\alpha]_D^{25}$ −41·2° in H_2O.—See A., 1944, III, 384.

Polysaccharide hydroxylation by means of *p*-toluenesulphonyl chloride and triphenylchloromethane. W. Low and E. V. White (*J. Amer. Chem. Soc.*, 1943, **65**, 2430—2432).—The arabogalactan (I) from *Larix occidentalis* with *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at 55—90° (1–38 hr.) and then NaI–$COMe_2$ at 100° gives a product in which, independently of the *p*-$C_6H_4Me{\cdot}SO_2$ content (4·7—13·1 units), 3·08—3·21 $C_6H_4Me{\cdot}SO_2$ are replaced and 2·93—3·22 I are introduced. With CPh_3Cl in C_5H_5N at 50° (I) gives a product containing 2·80 CPh_3, into which Ac_2O–C_5H_5N introduces 15·6 Ac (CPh_3 : Ac = 3 : 17·2). Thus (I) is proved to contain 3 primary OH. R. S. C.

Structure of pyrodextrins. B. Brimhall (*Ind. Eng. Chem.*, 1944, **36**, 72—75).—A roasted maize-starch product of British gum type yielded 70% of a fraction (*F*), sol. in 30% and insol. in 70% MeOH, which behaved towards HIO_4 similarly to starch and contained no linear mols. of sufficient length to give a blue I colour, though the average mol. size was ~66 glucose units. Solubility relationships indicated a structure different from that of acid-produced amylodextrins (*A*), whilst *F* was degraded only to the extent of 22% by β-amylase and gave no Schardinger dextrins with *B. macerans*. End-group assay in conjunction with mol. size indicated for *F* a mol. with 4—5 branches with ~5 glucose units in each. Dextrination of amylopectin, amylose, *A*, and other starch products, followed by changes in solubility, reducing power, and β-amylase digestibility, shows that heating causes linear portions of starch mols. to become branched, and the probable mechanism of this change is discussed. I. A. P.

Cellulose triphenylmethyl ether. W. M. Hearson, G. D. Hiatt, and C. R. Fordyce (*J. Amer. Chem. Soc.*, 1943, **65**, 2449—2452).—Cellulose (best, regenerated from the acetate) and CPh_3Cl in C_5H_5N give an ether [1·03 CPh_3 (in this and similar cases per glucose unit)], which with PhNCO–C_5H_5N gives a CPh_3 ether phenylcarbamate (1·03 CPh_3, 1·97 NHPh·CO). HCl–dioxan removes all the CPh_3, giving an ester (1·97 NHPh·CO), which with *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N yields a mixed ester (1·97 NHPh·CO, 0·95 *p*-$C_6H_4Me{\cdot}SO_2$), converted by NaI in $COMe_2$ into a product containing 1·97 NHPh·CO, 0·90 I, and 0·05 *p*-$C_6H_4Me{\cdot}SO_2$. Thus, of the 1·03 CPh_3 introduced, 0·90 were attached to primary and 0·13 to *sec.* OH; the relative reactivities are thence calc. to be 13·8 : 1. The optimum conditions for the reactions described are reported. R. S. C.

III.—HOMOCYCLIC.

Transformations of hydrocarbons at a vanadium contact. III. Ethyl*cyclo*pentane. A. F. Plate and O. G. Sterligov (*J. Gen. Chem. Russ.*, 1943, **13**, 202—212).—Ethyl*cyclo*pentane passed over 1 : 10 V_2O_5–Al_2O_3 catalyst at 440—500° yields gaseous (H_2, C_nH_{2n+2}, C_nH_{2n}, CO, CO_2) and liquid products (methyl*cyclo*pentadiene, *cyclo*pentadiene, PhMe). The catalyst is gradually inactivated by a layer of soot; it may be reactivated by passing air at 500°. R. T.

Semicyclic ethylenic linkings. Effect of certain reagents capable of addition to ethylenic linkings on *cyclo*hexylidene derivatives. D. N. Kursanov and A. S. Kursanova (*J. Gen. Chem. Russ.*, 1943, **13**, 184—188).—The C:C linking of *cyclo*hexylideneacetic acid (I) does not react with *cyclo*pentadiene under the conditions of the Diels–Alder diene reaction. The Me ester (II) of (I) with MgMeI yields γ-cyclo*hexylidene-β-methyl-*Δ^{α}-*propene*, b.p. 103—103·5°/62 mm., which does not react with $CH_2{:}CH{\cdot}CHO$. (II) does not react with CH_2N_2 or with $CHN_2{\cdot}CO_2Et$. It is concluded that the reactivity of semicyclic C:C linkings is < of those in other positions. R. T.

New type of carotene pigment from red yeast (*Torula rubra*).—See A., 1944, III, 369.

3-Chloro-1-α-chlorovinyl-Δ^3-*cyclo*hexene and 1 : 5-dichloro-$\Delta^{1:5}$-*cyclo*octadiene. J. G. T. Brown, J. D. Rose, and J. L. Simonsen (*J.C.S.*, 1944, 101—103).—The two dimerides formed when chloroprene is kept (cf. Carothers *et al.*, B., 1932, 156; A., 1933, 371) are shown to be 3-*chloro*-1-α-*chlorovinyl*-Δ^3-cyclo*hexene* (I), b.p. 66—67°/4 mm., 105°/20 mm., and 1 : 5-*dichloro*-$\Delta^{1:5}$-cyclo*octadiene* (II), b.p. 84—85°/2 mm., 126°/18 mm., by the reactions below. With Br (I) gives a *tetrabromide*, m.p. 146—147°. (I) on hydrogenation gives ethyl*cyclo*hexane, and on ozonolysis gives β-α′-*chlorovinyladipic acid* (III), m.p. 152—154° (*di*-p-*phenylphenacyl ester*, m.p. 54—55°). (III) on ozonolysis gives butane-αβδ-tricarboxylic acid, m.p. 121—122°. Hydrogenation of (III) (Pd catalyst) gives β-*ethyladipic acid* (IV), m.p. 47—49° (*di*-p-*phenylphenacyl ester*, m.p. 100—101°). Reduction of *Et* 1-*ethyl*cyclo*pentan*-2-*one*-1-*carboxylate*, b.p. 115°/13 mm. (from Et sodio*cyclo*pentan-2-one-1-carboxylate and EtI), gives *Et* α-*ethyladipate* (V), b.p. 133°/13 mm. (V) gives α-ethyladipic acid, m.p. 47—49° (*di*-p-*phenylphenacyl ester*, m.p. 118—120°), not identical with (IV). Hydrogenation of (II) (PtO_2 catalyst) gives *cyclo*octane, which yields suberic acid, m.p. 140—141°, on oxidation. Ozonolysis of (II) gives $(CH_2{\cdot}CO_2H)_2$ and a CHO-acid, probably δ-*chloro*-η-*carboxy*-Δ^{δ}-*heptenal*, isolated as its 2 : 4-dinitrophenylhydrazone, m.p. 119°. D. G.

Cyclic compounds containing sulphur. M. Mousseron (*Compt. rend.*, 1942, **215**, 357—359).—Na_2S and 2-chloro*cyclo*hexanol at ~70° yield *di*-2-*hydroxy*cyclo*hexyl sulphide* (I), b.p. 215°/20 mm., m.p. 71—72° (*diacetate*, m.p. 61—62°), whereas under the same conditions or in the cold epoxy*cyclo*hexane affords (I) with a small proportion of an *isomeride* (II), m.p. 89°. (I) and (II) are regarded as *dl*- and *meso*-forms. *cis*-2-Chloro*cyclo*hexanol gives the cis-cis-*di*-2-*hydroxy*cyclo*hexyl sulphide*, m.p. 103—104°. *Di*-2-*hydroxy*cyclo*pentyl*, b.p. 205°/20 mm., m.p. 44°, -cyclo*heptyl*, b.p. 225°/20 mm., m.p. 88°, *di*-3-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthyl*, m.p. 151°, and *di*-3-*hydroxy*-2 : 3-*dihydro*-2-*indenyl*, m.p. 135°, *sulphide* are described. A similar change does not appear to occur with 4-chloro*cyclo*hexanol. The action of NaCNS and anhyd. $CuSO_4$ on cyclenes affords 1 : 2-dithiocyano-2-methyl-, m.p. 60°, -*ethyl*-, m.p. 82°, -*propyl*-, m.p. 86°, and -4-*methyl*-, m.p. 81°, -cyclo*hexane*, 1-*thiocyano*-2-*thiocyanomethyl*cyclo*hexane*, m.p. 63°, 2 : 3-*dithiocyano*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 113°, and 2 : 3-*dithiocyanodecahydronaphthalene*, m.p. 74°. Optically active 1-methyl-Δ^3-*cyclo*hexene adds NH_4HSO_3 to give NH_4 3-methyl*cyclo*hexanesulphonate, characterised by the *Ba* salt, $[\alpha]_{5461}$ +4·38° in H_2O, and the optically inactive *NH_4 4-methyl*cyclo*hexanesulphonate*. 2-Chloro*cyclo*hexanone and NaSEt in anhyd. Et_2O afford cyclo*pentanethiocarboxylic acid*, b.p. 103°/15 mm., m.p. 92—93°. H. W.

Reductions with nickel–aluminium alloy and aqueous alkali. II. Displacement of groups by hydrogen. E. Schwenk, D. Papa, B. Whitman, and H. Ginsberg (*J. Org. Chem.*, 1944, **9**, 1—8; cf. A., 1943, II, 93).—When treated with Ni–Al alloy and aq. alkali halogens and SO_3H are displaced by H, the reaction being apparently independent of their no. or position or of the presence of other groups {substances tested are PhBr, *m*-$C_6H_4Cl{\cdot}CO_2H$, *p*-$C_6H_4Cl{\cdot}NO_2$, *p*-$C_6H_4Cl{\cdot}CHO$, 2 : 5 : 1-$OH{\cdot}C_6H_3Cl{\cdot}CHO$, *p*-$C_6H_4Br{\cdot}COMe$, *p*-$C_6H_4Cl{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$, $PhSO_3H$, *o*- and *m*-$SO_3H{\cdot}C_6H_4{\cdot}CO_2H$, 2-$C_{10}H_7{\cdot}SO_3H$, 2 : 6-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$, and 2 : 3 : 6-$OH{\cdot}C_6H_5(SO_3H)_2$}. All halogen compounds exchange halogen for H quantitatively. Arsanilic acid and HgPh·OAc yield NH_2Ph and Ph_2 respectively. Only halogen and SO_3H are displaced by H from monosubstituted derivatives of C_6H_6. *o*-$NH_2{\cdot}C_6H_4{\cdot}OMe$ and *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}OMe$ are unchanged, but when the *o*–*p*-directive Me or NH_2 of these compounds is replaced by *m*-directive CO_2H quant. replacement of OMe occurs from *o*- and *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ whereas *m*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ remains unaffected. The displacement of OMe from the *m*-position has not yet been observed. A similar displacement of OMe ocurs with other *m*-directive groups such as NO_2, CHO, and Ac. These groups are themselves reducible to the *o*–*p*-orienting NH_2 or Alk. Elimination of OMe can occur only before these groups are reduced. Therefore *p*-$NO_2{\cdot}C_6H_4{\cdot}OMe$ gives NH_2Ph as first change and *p*-$NH_2{\cdot}C_6H_4{\cdot}OMe$ as product of reaction after reduction of NO_2 to NH_2. The two possible reduction products are also obtained from *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ and *o*- and *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ with in some cases BzOH, probably resulting from a Cannizzaro change in the alkaline medium. Similar loss of alkoxy-groups occurs with *p*-$OEt{\cdot}C_6H_4{\cdot}CHO$, *p*-$OEt{\cdot}C_6H_4{\cdot}CO_2H$, *p*-$OPr^{\alpha}{\cdot}C_6H_4{\cdot}CO_2H$, *p*-$OPr^{\beta}{\cdot}C_6H_4{\cdot}CO_2H$, and *p*-$OBu{\cdot}C_6H_4{\cdot}CO_2H$. *o*-$CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$ affords PhMe and *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ but *o*-$SMe{\cdot}C_6H_4{\cdot}CO_2H$ gives only BzOH. Introduction of OH or OMe as third group in the disubstituted derivatives of C_6H_6 alters considerably the course of the displacement since in many cases removal of *m*-orienting groups is observed. In the trisubstituted products 4 : 1 : 3-$OH{\cdot}C_6H_3R{\cdot}OMe$ (R = $\cdot CH_2{\cdot}OH$, CHO, or Ac), 3 : 2 : 1- and 3 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CHO$, 3 : 2 : 1-, 4 : 3 : 1-, and 4 : 2 : 1-$(OMe)_2C_6H_3{\cdot}CHO$ displacement of CHO by H occurs; the only products isolated are *o*-$OH{\cdot}C_6H_4{\cdot}OMe$ or $C_6H_4(OMe)_2$. 4 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2H$ is recovered unchanged whereas 3 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2H$ affords *m*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ if a greatly

increased proportion of alloy and alkali is used. OMe is not displaced from 3 : 2 : 1-, 4 : 3 : 1-, or 4 : 2 : 1-$(OMe)_2C_6H_3\cdot CO_2H$. 3 : 4 : 1-$(OMe)_2C_6H_3\cdot CO\cdot[CH_2]_2\cdot CO_2H$ (I) does not lose 4-OMe although p-$OMe\cdot C_6H_4\cdot CO\cdot[CH_2]\cdot CO_2H$ gives $Ph\cdot[CH_2]_2\cdot CO_2H$ in 65% yield; (I) affords γ-3 : 4-dimethoxyphenylbutyrolactone in 70% yield with a small amount of intractable oil. Neither CO_2H nor OMe is displaced from 3 : 4 : 5 : 1-$(OMe)_3C_6H_2\cdot CO_2H$. H. W.

Polymorphic and isomorphic phenomena with trinitrotoluene etc. —See A., 1944, I, 100.

Ethylation of benzene. Course of the reaction. E. M. Marks, J. M. Almand, and E. E. Reid (*J. Org. Chem.*, 1944, **9**, 13—20).—The proportions of the products obtained by the action of C_2H_4 on C_6H_6 in the presence of $AlCl_3$ depend greatly on the rate of passage of the gas, the temp., the rate of stirring, and the amount of catalyst. A portion of the C_6H_6 appears to be transformed into C_6Et_6, which is then dealkylated to a type of equilibrium mixture containing much s-$C_6H_3Et_3$. H. W.

Poly*iso*propylbenzenes. III. Sulphonyl and nitrosulphonyl chlorides. A. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 2439—2441).—Susceptibility to replacement of Pr^β on treatment of poly*iso*propylbenzenes with $ClSO_3H$ (3 equivs.) in CCl_4 at 30—32° (rising to 45—55°) is sometimes more marked than in nitration. m-$C_6H_4Pr^\beta_2$ gives 1 : 3 : 4-$C_6H_3Pr^\beta_2\cdot SO_2Cl$ (I), m.p. 35—40° (derived *amide*, m.p. 144·2—144·9°, and *anilide*, m.p. 113·9—114·5°). p-$C_6H_4Pr^\beta_2$ gives p-*diiso*propylbenzene-2-*sulphonyl chloride* (II), m.p. 52·5—53° (derived *amide*, m.p. 110·2—110·8°, and *anilide*, m.p. 124·1—125°). 1 : 2 : 4-$C_6H_3Pr^\beta_3$ gives 1 : 2 : 4-*tri*iso*propylbenzene*-5-*sulphonyl chloride* (III), m.p. 141·5—142·2° (derived *amide*, m.p. 154·8—155·7°, and *anilide*, m.p. 187·8—188·8°). s-$C_6H_3Pr^\beta_3$ gives 1 : 3 : 5-*tri*iso*propylbenzene*-2-*sulphonyl chloride* (IV), m.p. 97·2—98·4° (derived *amide*, m.p. 119·0—129·6°, and *anilide*, m.p. 163·6—164·2°). 1 : 2 : 4 : 5-$C_6H_2Pr^\beta_4$ gives (III) (incorrectly described by Huntress *et al.*, A., 1942, II, 136, as 1 : 2 : 4 : 5 : 3-$C_6HPr^\beta_4\cdot SO_2Cl$). With an excess of 96% HNO_3, (I) or (III) gives 6-*nitro*-1 : 3-*diiso*propylbenzene-4-*sulphonyl chloride*, m.p. 102·1—103° (derived *amide*, m.p. 192·4—192·8°, and *anilide*, m.p. 169·8—170·6°), (II) gives 4-*nitro*-1-iso*propylbenzene*-2-*sulphonyl chloride*, m.p. 101·6—102·1° (derived *amide*, m.p. 172·5—173·5°, and *anilide*, m.p. 192·8—193·7°), and (IV) gives 4-*nitro*-1 : 3 : 5-*tri*iso*propylbenzene*-2-*sulphonyl chloride* (V), m.p. 157·5—158° (derived *amide*, m.p. 165·9—166·3°, and *anilide*, m.p. 182·4—183·3°); these NO_2-products can be purified only by chromatography (Al_2O_3); 4% of a *dinitrohexa*iso*propyldiphenyl sulphone*, m.p. 150·2—151·1°, is isolated from crude (V). R. S. C.

Nitration of halogenodiphenyls. II. Di- and tetra-nitro-derivatives of 2 : 2′-dichlorodiphenyl. F. H. Case and R. U. Schock, jun. **III. Nitro-derivatives of 2-chloro- and 2-bromodiphenyl.** F. H. Case (*J. Amer. Chem. Soc.*, 1943, **65**, 2086—2088, 2137—2140; cf. A., 1943, II, 26).—II. $(o\text{-}C_6H_4Cl)_2$ (I) with conc. HNO_3–H_2SO_4 at <40° and then 100° gives 2 : 2′-dichloro-5 : 5′- (II), m.p. 202—203° [also obtained (m.p. 203—204°) from 5 : 2 : 1-$NO_2\cdot C_6H_4Cl$ (III) by Cu], with a small amount of 2 : 2′-*dichloro*-3 : 3′-(? 3 : 5′-)*dinitrodiphenyl* (IV), m.p. 128—129° (cf. Mascarelli *et al.*, A., 1934, 62). With HNO_3 (d 1·6)–H_2SO_4 at 100°, (I), (II), or (IV) gives 2 : 2′-*dichloro*-3 : 3′ : 5 : 5′-*tetranitrodiphenyl* (V), m.p. 304—305°, which loses its Cl to $NaNO_2$ in 50% aq. dioxan (to give a non-phenolic product) (cf. van Alphen, A., 1932, 729). 2-*Chloro*-1-*iodo*-4 : 6-*dinitrobenzene* [prep. from 4 : 6 : 2 : 1-$(NO_2)_2C_6H_2Cl\cdot NH_2$], m.p. 117—118°, with Cu at 240° gives 2 : 2′-*dichloro*-4 : 4′ : 6 : 6′-*tetranitrodiphenyl*, m.p. 159—160°. 2 : 1 : 4-$C_6H_3ClI\cdot NO_2$ and Cu give 2 : 2′-*dichloro*-4 : 4′-*di*-, m.p. 107—108°, and thence 2 : 2′-*dichloro*-4 : 5 : 4′ : 5′-*tetranitrodiphenyl* (VI), m.p. 201—202°. With H_2SO_4–HNO_3 (d 1·6) at 100° (III) gives 2-*chloro*-1-*iodo*-4 : 5-*dinitrobenzene*, m.p. 98—99°, which with Cu powder in boiling $PhNO_2$ gives (VI). 2-*Iodo*-4 : 6-*dinitroanisole* (prep. from the phenol by CH_2N_2), m.p. 69—70°, with Cu powder in boiling $PhNO_2$ gives $[2:3:5:1\text{-}OMe\cdot C_6H_2(NO_2)_2]_2$, m.p. 186—187° [also obtained from $(o\text{-}OMe\cdot C_6H_4)_2$], and thence by hydrolysis $[2:3:5:1\text{-}OH\cdot C_6H_3(NO_2)_2]_2$ (VII), m.p. 245—246° (lit. 249—250°) (cf. Diels *et al.*, A., 1902, i, 219; Borsche *et al.*, A., 1917, i, 390). The structure of (V) is proved by conversion into (VII) by $NaNO_2$ in boiling aq. dioxan.

III. The structure of o-$C_6H_4Cl\cdot C_6H_4\cdot NO_2$-$p$ (VIII), m.p. 74—75°, of Mascarelli *et al.* (*loc. cit.*) is confirmed by prep. from p-$NO_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$-$o$ by a Sandmeyer reaction, but the compound, m.p. 159—160°, supposed (*loc. cit.*) to be o-$C_6H_4Cl\cdot C_6H_3(NO_2)_2$-1 : 3 : 4, is 2-*chloro*-4′ : 5-*dinitrodiphenyl* (IX). (IX) is obtained by nitrating (VIII) (proof of the 4′-NO_2), is unchanged by boiling CrO_3–V_2O_5–AcOH, and is destroyed by reduction. 5 : 2 : 1-$NO_2\cdot C_6H_4Cl\cdot N_2Cl$ in 1 : 1 conc. HCl–H_2O with C_6H_6 and 5N-NaOH gives 2-*chloro*-5-*nitrodiphenyl*, m.p. 59—60°, which with HNO_3 (d 1·5) at 100° gives (IX) (proof of the 5-NO_2). By Schoutissen's method 2 : 4 : 1-$NH_2\cdot C_6H_3(NO_2)\cdot C_6H_4\cdot NO_2$-$p$ gives 2-*chloro*-4 : 4′-*dinitrodiphenyl*, m.p. 153—154°. o-C_6H_4PhBr with, best, $OEt\cdot NO_2$ in conc. H_2SO_4 at <2° and then 25° gives 2-bromo-4′ : 5- (X), m.p. 165—166° (Finzi *et al.*, A., 1938, II, 225), and some -2′ : 5-*dinitrodiphenyl* (XI), m.p. 139—140° [also obtained (m.p. 140—141°) similarly from o-$C_6H_4Br\cdot C_6H_4\cdot NO_2$-$o$]. 5 : 1 : 2-$NO_2\cdot C_6H_3Ph\cdot NH_2$ (prep. from the p-$C_6H_4Me\cdot SO_2$ derivative by boiling 1 : 1 H_2SO_4), m.p. 125—126°, in AcOH with $NaNO_2$–H_2SO_4 at <40° and then CuBr in H_2O–HBr gives 1 : 2 : 5-$C_6H_3PhBr\cdot NO_2$ (XII) and thence (HNO_3–H_2SO_4) (X). 2-*Bromo*-4 : 4′-*dinitrodiphenyl*, m.p. 148—149°, is similarly prepared. o-$C_6H_4Br\cdot C_6H_4\cdot NH_2$-$p$ with KNO_3 in H_2SO_4–oleum at <6° and then Ac_2O gives 2-*bromo*-5-*nitro*-4′-*acetamido*-, m.p. 186—187°, hydrolysed by boiling H_2SO_4–H_2O to 2-*bromo*-5-*nitro*-4′-*amino*-*diphenyl* (XIII), m.p. 111—112°, which with $NaNO_2$ in EtOH–dil. H_2SO_4 gives (XII). KNO_3–H_2SO_4–oleum converts (XIII) into 2-*bromo*-2′ : 5-*dinitro*-4′-*aminodiphenyl*, m.p. 149—150° (isolated as *Ac* derivative, m.p. 246—247°), whence (XI) is obtained by deamination. HNO_3 (d 1·59) at 100° converts (X) or (XI) into 2-*bromo*-5 : 2′ : 4′-*trinitrodiphenyl*, m.p. 140—141°. o-$C_6H_4Br\cdot C_6H_4\cdot NHAc$-$p$ and HNO_3 (d 1·5) in Ac_2O–AcOH at 70° give 2-*bromo*-3′-*nitro*-4′-*acetamido*-, m.p. 135—136° and thence -4′-*amino*-*diphenyl*, m.p. 145—146°, which with $NaNO_2$–H_2SO_4–H_2O–EtOH gives o-$C_6H_4Br\cdot C_6H_4\cdot NO_2$-$m$, m.p. 79—80°. With $OEt\cdot NO_2$ this gives 2-*bromo*-5 : 3′-*dinitrodiphenyl* (XIV), m.p. 165—166°, which with boiling $SnCl_2$–EtOH and then Ac_2O gives 2-*bromo*-5 : 3′-*diacetamidodiphenyl* (XV), m.p. 265—266°. m-$NO_2\cdot C_6H_4\cdot C_6H_4\cdot NHAc$-$m$ with Br in AcOH–NaOAc gives 2-*bromo*-3′-*nitro*-5-*acetamidodiphenyl* (XVI), m.p. 193—194°, and thence the 5-NH_2-compound, m.p. 112—113°, which yields, as above, 2 : 5-*dibromo*-3′-*nitrodiphenyl*, m.p. 97—98°, converted by $SnCl_2$–EtOH and then CrO_3–AcOH into 2 : 5 : 1-$C_6H_3Br_2\cdot CO_2H$. $SnCl_2$–EtOH reduces (XVI) to (XV). 5 : 2 : 1-$NO_2\cdot C_6H_3Br\cdot N_2\cdot HSO_4$ in AcOH–H_2SO_4 is converted by KI–NaOAc–H_2O at 0° into 4-*bromo*-3-*iodo*-1-*nitrobenzene*, m.p. 97—98°, which with 1 : 3 : 4-$C_6H_3I(NO_2)_2$ and Cu gives 2-*bromo*-5 : 3′ : 4′-*trinitrodiphenyl*, m.p. 222—223°, also obtained from (XIV) by HNO_3 (d 1·59) and oxidised by CrO_3–V_2O_5–AcOH to 5 : 2 : 1-$NO_2\cdot C_6H_3Br\cdot CO_2H$. R. S. C.

Use of semi-micro-technique in elementary organic chemistry. IV. Semi-micro-chlorination of organic compounds. N. D. Cheronis (*J. Chem. Educ.*, 1943, **20**, 611—614, 621).—Apparatus for, and results obtained in, the semi-micro-chlorination of C_6H_6, PhMe, $C_{10}H_8$, and *cyclo*hexane are described. L. S. T.

Xanthhydrol as a reagent for the identification of sulphonamides. R. F. Phillips and V. S. Frank (*J. Org. Chem.*, 1944, **9**, 9—12).—Unsubstituted sulphonamides condense with xanthhydrol in AcOH at room temp. to N-*xanthylsulphonamides*, $SO_2R\cdot NH\cdot CH(C_6H_4)_2O$, which are dried at room temp. and crystallised from dioxan–H_2O (3 : 1). Thus are obtained *benzenesulphonxanthylamide*, m.p. 200—200·5° (block), and the following derivatives: o-*Me*, m.p. 182—183·5°, p-*Me*, m.p. 197—197·5°, p-*Et*, m.p. 195·5—197°, p-Pr^a, m.p. 199—200·5°; p-Bu^a, m.p. 185—186·5°, p-n-*amyl*, m.p. 164·5—165°; 3 : 4-Me_2, m.p. 189—190°, 2 : 4-Me_2, m.p. 187—188·5°; 2 : 5-Me_2, m.p. 175—176°; 2 : 4 : 6-Me_3, m.p. 203—204°; p-NH_2-, m.p. 207—208°, and *saccharin*-, m.p. 198—199°. Xanthyl derivatives are not obtained from 2 : 4 : 6 : 1-$C_6H_2Et_3\cdot SO_2\cdot NH_2$, *p-tert.*-butyl-, *p-tert.*-amyl-, and the p-cymene-benzenesulphonamides and p-$C_6H_4Me\cdot NEt\cdot SO_2H$. *p-sec.*-Butyl- and 2-methyl-4-*iso*propylbenzenesulphonamides give very poor yields of products. Branched alkyl groups appear to inhibit the reaction and larger N-alkyl groups retard its rate. (See also C., 1944, 86.) H. W.

Organic reactions with boron fluoride. XXIX. Sulphonation of naphthalene derivatives in presence of boron trifluoride. G. F. Hennion and C. J. Schmidle (*J. Amer. Chem. Soc.*, 1943, **65**, 2468—2469; cf. A., 1944, II, 10).—BF_3 acts in sulphonation reactions only as a powerful dehydrating agent and has no orienting influence. Passing BF_3 into α-$C_{10}H_7\cdot NH_2$ in H_2SO_4 at 75—80° gives 86% of $NH_2\cdot C_{10}H_6\cdot SO_3H$, the yield being 60% in absence of BF_3. Similarly, at 50—55° β-$C_{10}H_7\cdot NH_2$ gives 95% of acids containing 52% of 2 : 5- and 48% of 2 : 8-$NH_2\cdot C_{10}H_7\cdot SO_3H$; at 20° these proportions are 44 : 56 and at 80° are 67 : 33; in absence of BF_3 only 57% sulphonation occurs. Passing BF_3 into β-$C_{10}H_7\cdot OH$ (29 g.) in H_2SO_4 (previously saturated with BF_3 at room temp.) at 80—90° gives 22 g. of acid, mainly 2 : 3 : 6-$OH\cdot C_{10}H_5(SO_3H)_2$. R. S. C.

Poly*iso*propylbenzenes. II. Nitro- and amino-derivatives. A. Newton (*J. Amer. Chem. Soc.*, 1943, **65**, 2434—2439; cf. A., 1943, II, 222).—Nitration of poly*iso*propylbenzenes usually, but not always, involves partial replacement of Pr^β by NO_2 when all the orienting groups favour entry of NO_2 at this position. In absence of this condition, no such replacement occurs. In experiments recorded below, hydrocarbons were nitrated by 96% HNO_3 (1·24—2·05 mols.) in AcOH–Ac_2O at 45—50° and then usually kept at room temp. for 24 hr.; NO_2-compounds (2·5 g.) were oxidised by 70% HNO_3 (20 ml.) and H_2O (12 ml.) at 180° (H_2), yields of crude acids being 50—60% for NO_2- and 13% for $(NO_2)_2$-compounds; NO_2-compounds were reduced to amines by H_2–Raney Ni in 99% $Pr^\beta OH$ at 100°/1200 lb.; amines were nitrated in H_2SO_4 by 70% HNO_3 (1·1 mols.) at 5—10°. m-$C_6H_4Pr^\beta_2$ gives a 95% yield of 2- (25%) and 4-*nitro*-m-*diiso*propylbenzene (74%) (and traces of polynitro-compounds), oxidised to 2 : 1 : 3- and 4 : 1 : 3-$NO_2\cdot C_6H_3(CO_2H)_2$, respectively, and reduced to 2-, an oil (*Bz*, m.p. 106—106·7°, and ? Ac_2 derivative, an oil), and 4-*amino*-m-*diiso*propylbenzene (I) (*Ac*, m.p. 108·3—109°, and *Bz* derivative, m.p.

162·8—163·4°), respectively. With 96% HNO_3 (3·17 mols.) in H_2SO_4 at 70°, *m*-$C_6H_4Pr^{\beta}_2$ gives 4 : 6-*dinitro*-m-*diiso*propylbenzene, m.p. 76·9—77·7°, oxidised to 4 : 6 : 1 : 3-$(NO_2)_2C_6H_2(CO_2H)_2$ (Et_2 ester, new m.p. 124·5—125·2°) and reduced (one NO_2 at room temp., the other at 60°) to 4 : 6-*diamino*-m-*diiso*propylbenzene (II), m.p. 72·6—72·9° [Ac_2 derivative, m.p. 320·5—321·5° (uncorr.)]. (I) gives 6-*nitro*-4-*amino*-m-*diiso*propylbenzene (III), m.p. 75·3—76·1° (*Ac* derivative, m.p. 116·2—117°), and thence (II). By the general method, *p*-$C_6H_4Pr^{\beta}_2$ gives *p*-$C_6H_4Pr^{\beta}\cdot NO_2$ (49·7%) and 2-*nitro*-p-*diiso*propylbenzene (33·7%), yields being 65·0 and 13·6%, respectively, when 70% HNO_3 (~2 mols.) in H_2SO_4 at 0—6° is used. Reduction then affords *p*-$C_6H_4Pr^{\beta}\cdot NH_2$ (*hydrochloride*; Ac, new m.p. 105·8—106·6°, and Bz derivative, m.p. 161·4—162°), and 2-*amino*- (*hydrochloride*; *Ac*, m.p. 80·8—81·5°, and *Bz* derivative, m.p. 124·6—125°), and thence 6-*nitro*-2-*amino*-, m.p. 95·2—96·3°; and 2 : 6-*diamino*-p-*diiso*propylbenzene, m.p. 77·9—78·3°. 1 : 2 : 4-$C_6H_3Pr^{\beta}_3$ gives 5-*nitro*- and thence 5-*amino*-1 : 2 : 4-*tri*iso*propylbenzene*-A (IV) (*Ac*, m.p. 141·9—142·5°, and *Bz* derivative, m.p. 159·2—159·8°). Nitration of (IV) gives (III). *s*-$C_6H_3Pr^{\beta}_3$ gives the 2-NO_2-derivative, m.p. 74·6—75·5°, which with 96% HNO_3 in H_2SO_4 at 35—53° and finally 100° gives the 2 : 4 : 6-$(NO_2)_3$-derivative, m.p. 190·8—191·6°. Reduction etc. affords 2-*amino*- [*hydrochloride*; *Ac*, m.p. 177·3—178·1°, and *Bz* derivative, m.p. 286·5—287·2° (uncorr.)], 4-*nitro*-2-*amino*-, m.p. 75·9—76·5° (*Ac* derivative, m.p. 157·1—157·9°), and 2 : 4-*diamino*-1 : 3 : 5-*tri*iso*propylbenzene*, m.p. 71·9—72·7° ($Ac_{(2)}$ derivative, m.p. >360°). Adding 96% HNO_3 (1·76 mols.) to 1 : 2 : 4 : 5-$C_6H_2Pr^{\beta}_4$ in AcOH–Ac_2O at 30—45° and then keeping at 0° gives 3-*nitro*-1 : 2 : 4 : 5-*tetra*- (V) (15·1%), m.p. 192·6—193·8°, and 5-*nitro*-1 : 2 : 4-*tri*-iso*propylbenzene*-B (VI), m.p. 40·9—41·9°, and -C (? a mixture of -*A* and -*B*). Reduction of the -*B* or -*C* forms (VI etc.) gives (IV). Reduction of (V) gives 3-*amino*-1 : 2 : 4 : 5-*tetra*iso*propylbenzene*, m.p. 150·5—151·3°, oxidised by $K_2Cr_2O_7$ in H_2SO_4–$COMe_2$–H_2O at 30° to *tetra*iso*propyl*-p-*benzoquinone* (92·3%), m.p. 159·5—160·4°. Physical data are recorded for the oily products. M.p. are corr. except where stated. R. S. C.

New method of nuclear methylation of aromatic amines. (Miss) M. G. Barclay, A. Burawoy, and G. H. Thomson (*J.C.S.*, 1944, 109—112).—Dry distillation (temp. >300°) of anhydro-*p*-aminobenzyl alcohol gives a 1 : 1 mixture (<25%) of NH_2Ph and *p*-toluidine (I), small amounts of *p*-$C_6H_4Me\cdot NHMe$, amines of higher b.p., and NH_3, and much resin. In presence of alkali [*e.g.*, Na_2CO_3; $Ca(OH)_2$] 35—40% of (I) and negligible amounts of by-products are obtained. Anhydro-4-amino-3-methylbenzyl alcohol (from *o*-$C_6H_4Me\cdot NH_2$,HCl and aq. CH_2O) in presence of $Ca(OH)_2$ affords *m*-4-xylidine and some (4 : 3 : 1-$NH_2\cdot C_6H_3Me)_2CH_2$. Anhydro-4-amino-2 : 3-dimethylbenzyl alcohol (from *o*-3-xylidine) gives 4-*amino*-1 : 2 : 3-*trimethylbenzene*, b.p. 238—240°, m.p. 24° (*Ac* derivative, m.p. 140°). Anhydro-4-amino-2 : 5-dimethylbenzyl alcohol (from *p*-xylidine) affords *ψ*-cumidine and some (4 : 2 : 5 : 1-$NH_2\cdot C_6H_2Me_2)_2CH_2$, whilst anhydro-4-amino-3-methoxybenzyl alcohol (from *o*-anisidine) gives a moderate yield of 4 : 1 : 3-$NH_2\cdot C_6H_3Me\cdot OMe$; anhydro-4-amino-1-hydroxymethylnaphthalene (from α-$C_{10}H_7\cdot NH_2$) affords α-$C_{10}H_7\cdot NH_2$ and 4 : 1-$C_{10}H_6Me\cdot NH_2$. (*p*-$NH_2\cdot C_6H_4)_2CH_2$ at 400°/18 hr. yields NH_2Ph and (I). It is suggested that the first-formed radicals ·NH·[$C_6H_4\cdot CH_2\cdot NH]_n\cdot C_6H_4\cdot CH_2$· undergo disproportionation to, *e.g.*, $NH_2\cdot[C_6H_4\cdot CH_2\cdot NH]_n\cdot C_6H_4Me$ or (I) + ·NH·[$C_6H_4\cdot CH_2\cdot NH]_{n-1}\cdot C_6H_4\cdot CH_2$·. The reaction can be extended to anhydro-4-aminoaryl alcohols derived from, *e.g.*, NHPhMe. D. G.

Synthesis of *p*-chloroacetanilide. L. Blas and L. Arimany (*Anal. Fis. Quim.*, 1942, 38, 71—82).—NHPhAc in $(CHCl_2)_2$ at 100—115° with a slow stream of Cl_2, and at 140—150° with a rapid stream of Cl_2, yields exclusively *p*-$C_6H_4Cl\cdot NHAc$ and 2 : 4 : 1-$C_6H_3Cl_2\cdot NHAc$ respectively. F. R. G.

Derivatives of chloral with aromatic amines. W. T. Sumerford and D. N. Dalton (*J. Org. Chem.*, 1944, 9, 81—84).—Additive [$CCl_3\cdot CH(OH)\cdot NHAr$ (I)] or condensation [$CCl_3\cdot CH(NHAr)_2$ (II)] compounds are obtained by shaking a solution of the amine or its salts in AcOH with $CCl_3\cdot CH(OH)_2$ dissolved in H_2O containing NaOAc at room temp. Thus are obtained *βββ-trichloro-αα-diarylaminoethanes* in which Ar = o-$C_6H_4\cdot COEt$, m.p. 160°, p-$C_6H_4\cdot CO_2Et$, m.p. 91·5°, p-$C_6H_4\cdot CO_2Me$, m.p. 104°, *β*-$C_{10}H_7$, m.p. 116—118° m-*tolyl*, m.p. 103·5°, o-C_6H_4Cl, m.p. 104°, p-$C_6H_4\cdot OEt$, m.p. 91°, and *Bz*, m.p. 116°, and *βββ-trichloro-α-arylaminoethanols* in which Ar = o-$C_6H_4\cdot CO_2Me$, m.p. 105°, 2 : 4-$OH\cdot C_6H_3\cdot CO_2Me$, m.p. 93°, and p-$C_6H_4\cdot COMe$, m.p. 93°. When heated at 75° 2 mols. of (I) lose 1 mol. of $CCl_3\cdot CH(OH)_2$ and yield (II). In no instance was it possible to cause (I) to lose the elements of H_2O with production of the Schiff's base. M.p. are corr. H. W.

Relations between chemical activity and absorption in the ultraviolet of organic molecules. VI. Action of nitrosyl chloride on substituted amides of acetoacetic acid. K. G. Naik, R. K. Trivedi, and B. N. Mankad (*J. Indian Chem. Soc.*, 1943, 20, 384—388).—$CH_2Ac\cdot CO\cdot NHPh$ (in anhyd. C_6H_6) saturated with gaseous NOCl at ~0° and then heated at 100° (bath) gives NHPh·CO·CAc:N·OH. Similarly the following are obtained: *oximinoacetoacet*-o-, m.p. 130°, and -p-*toluidide*, m.p. 92°, -m-4-*xylidide*, m.p. 145°, -α-, m.p. 138°, and -*β-naphthalide*, m.p. 152°. Contrary to expectation no structural or stereo-isomerides can be isolated. $CH_2Ac\cdot CO\cdot NHAr$ with SO_2Cl_2 in Et_2O gives chloroacetoacet-anilide, m.p. 138°, -m-4-*xylidide*, m.p. 114°, and -*α-naphthalide*, m.p. 135°. (Cf. A., 1944, I, 116.) H. M. C.

Activity of halogen derivatives of substituted amides of malonic acid. I. Action of Grignard's reagent on the chloro-derivatives of substituted amides of malonic acid. II. Velocity of replacement of chlorine atom of the group ·CHCl· in monochloro-derivatives of substituted amides of malonic acid. K. G. Naik, R. K. Trivedi, and S. M. Mehta (*J. Indian Chem. Soc.*, 1943, 20, 345—348, 355—357).—I. Grignard's reagents (MgPhBr and $CH_2Ph\cdot MgCl$) with $CCl_2(CO\cdot NHAr)_2$ give $CHCl(CO\cdot NHAr)_2$ and no di*tert.*-alcohol. A reaction mechanism is suggested. The second Cl cannot be removed in this way. *Chloromalondi-anilide*, m.p. 176°, -p-, m.p. 212°, and -o-*toluidide*, m.p. 179°, and -m-4-*xylidide*, m.p. 202°, are described.

II. The Cl of $CHCl(CO\cdot NHAr)_2$ (Ar = Ph, *o*- and *p*-tolyl, *m*-4-xylyl) is replaced by H on treatment with HI. The velocity of replacement is influenced by the position of the substituents in the C_6H_6 rings and the mol. wts. of the residues attached to the CO-groups. D. G.

Preparation and properties of *N*-substituted sulphamic acids. L. F. Audrieth and M. Sveda (*J. Org. Chem.*, 1944, 9, 89—101).—$NHR\cdot SO_3H$ and $NRR'\cdot SO_3H$ are obtained (*a*) by the gradual addition of $ClSO_3H$ to 3 equivs. of the amine in dry $CHCl_3$ at ≯0°: $3NHRR' + ClSO_3H \rightarrow NRR'\cdot SO_3H,NHRR' + NHRR',HCl$, (*b*) by reduction of the NO_2-compound by $Na_2S_2O_4$ in presence of Na_3PO_4 (to prevent the solution from becoming acid): $ArNO_2 + Na_2S_2O_4 + H_2O \rightarrow NHAr\cdot OH + SO_2 + Na_2SO_4$; $NHAr\cdot OH + SO_2 + Na^+ \rightarrow NHAr\cdot SO_3Na + H^+$; the method suffers from the disadvantage of involving large quantities of H_2O-sol. salts which render difficult the isolation of the sulphamates: (*c*) by treatment of the C_5H_5N,SO_3 additive compound (I) with ~2·5 mols. of the requisite amine in a 3-fold vol. of H_2O at 0° followed by addition of a slight excess of the requisite metallic hydroxide; a disadvantage is the relative instability of (I): (*d*) by interaction of amine and $ClSO_3Na$ which occurs thus: $2NH_2R + ClSO_3Na \rightarrow NHR\cdot SO_3H,NH_2R + NaCl$; the addition of NaOH is therefore not avoided and the method has the further disadvantage that technical $ClSO_3Na$ contains 30% of NaCl. The following are described: *Na phenyl-*, *Na* p-*phenetyl-*, *Na* p-*tolyl-*, *Na* N-*phenyl*-N-*methyl-*, *Na benzyl-*, *Na β-phenylethyl-*, *Na γ-phenylpropyl-*, *Na* n-*hexyl-*, cyclo*hexylammonium*, *Na*, *Ba*, NH_4, m.p. >220°, softens at ~208°, and *Ag* cyclo*hexyl-*, *Na di*cyclo*hexyl-*, *Na* N-cyclo*hexyl*-N-*ethyl-*, *Na* N-cyclo*hexyl*-N-*methyl-*, *Na* 2-*methyl*-cyclo*hexyl-*, and *Na* 1 : 2 : 3 : 4-*tetrahydronaphthyl-sulphamates*. cyclo*Hexyl-*, m.p. 169—170°, and *di*cyclo*hexyl-*, m.p. 161°, *-sulphamic acid* have been prepared. The antipyretic action of these compounds is discussed. The extraordinary sweetness of certain *N*-substituted sulphamic acids is thus far limited to those containing as a substituent (*a*) a *cyclo*hexyl ring which may or may not be substituted and (*b*) a free H on the N, viz., $NHR\cdot SO_3X$, where X is almost any salt-forming group. H. W.

Sulphanilamide derivatives.—See B., 1944, III, 73.

Sulphanilylalkylguanidines.—See B., 1944, III, 73.

***p*-Aminoarylsulphonamidoaryl-*o*-sulphonic acids and their salts.**—See B., 1944, III, 73.

Carbon rings. XXXIV. *cyclo*Decane and its derivatives and the two 9 : 10-diaminodecahydronaphthalenes. P. A. Plattner and J. Hulstkamp (*Helv. Chim. Acta*, 1944, 27, 220—230).—Largely a repetition and extension of the work of Hückel *et al.* (A., 1930, 76; 1933, 494). Reduction of *cyclo*decane-1 : 6-dionedioxime (corresponding *monoxime*, m.p. 155°) gives varying amount of mono- and di-amines and neutral products. Treatment with Na and EtOH gives ~60% of basic components relatively poor in *cyclo*decane derivatives. Replacement of EtOH by amyl alcohol gives nearly 100% of bases, essentially a mixture of α- (I) and β- (II) -1 : 6-diamino*cyclo*decane with cis- (III) and trans- (IV) -9 : 10-*diaminodecahydronaphthalene*. The reaction product is distilled and dissolved in EtOH which is saturated with CO_2, causing the pptn. of the sparingly sol. carbamates of (I) and (II). The bases regenerated therefrom are purified through their hydrochlorides. Thus are obtained (I), b.p. 145°/12 mm., m.p. 43—46° (yield 40%), probably the *trans*-compound and identical with Hückel's base, m.p. 50° (Ac_2 derivative, m.p. 296°; *dipicrate*, decomp. 280—285°; *dihydrochloride*, slow decomp. >200°), and (II) (yield 20%), b.p. 145°/12 mm., m.p. 8—10° [*dihydrochloride* (+$2H_2O$), gradual decomp. >200°; Ac_2 derivative, m.p. 253°; mono-, decomp. 200—210°, and *di-picrate*, decomp. 247—252°]. The portion of the basic mixture which gives EtOH-sol. carbamates or does not give a carbamate consists mainly of (III), b.p. 121°/12 mm., m.p. 41° [*dihydrate*; *dihydrochloride* (+$1H_2O$); Ac_2 derivative, m.p. 242°; *mono-*, m.p. 236° (decomp.), and *di-picrate*, decomp. 242—247°]. (IV) is present to the extent of ~3% and is identified by comparison with the product of the reduction of *trans*-9 : 10-dinitrodecahydronaphthalene; it has m.p. 70°, b.p. ~120°/12 mm., and gives a *dipicrate*, decomp. 262—264°, and an Ac_2 derivative, m.p. >360°.

The constitution of (**III**) and (**IV**) is established by conversion by HNO_2 into 2-*spirocyclo*pentano*cyclo*hexanone. The basic mixture appears to contain further cryst. compounds partly of hydroazulene structure. (**I**) is transformed by MeI and 5N-KOH–MeOH into *α-di*-1 : 6-*dimethylamino*cyclo*decane dimethiodide*, decomp. 305—320°, converted by Ag_2O into the quaternary base, which when decomposed thermally yields cyclo*decadiene*, b.p. 69°/12 mm., hydrogenated (Adams) to *cyclo*decane (**V**), b.p. 75°/12 mm., m.p. 9·5°. Analogously (**II**) affords *β-di*-1 : 6-*dimethylamino*cyclo*decane dimethiodide*, decomp. 310—330°, which is converted into (**V**), m.p. 9·4°. (**II**) is transformed by MeI and KOH–MeOH into bisdimethylaminodecahydronaphthalene dihydriodide (corresponding *base*, m.p. 86°). H. W.

1 : 4-Diamino-2-methylnaphthalene.—See B., 1944, II, 129.

Relations between chemical activity and absorption in the ultraviolet of organic molecules. IV. Interaction of phenylhydrazine with the chloro-derivatives of substituted amides of malonic acid. K. G. Naik, R. K. Trivedi, and C. M. Mehta (*J. Indian Chem. Soc.*, 1943, **20**, 369—371; cf. A., 1944, I, 116).—$CCl_2(CO{\cdot}NHAr)_2$ with $NHPh{\cdot}NH_2$ (**I**) in boiling EtOH gives $NHPh{\cdot}N{:}C(CO{\cdot}NHAr)_2$; in the cold $NHPh{\cdot}NH{\cdot}CCl(CO{\cdot}NHAr)_2$ results. The following are described: *mesoxal-dianilide*-, m.p. 175°, *-di*-m-*chlorotoluidide*-, m.p. 196°, *-di*-p-, m.p. 185°, and *-di*-o-*toluidide*-, m.p. 148°, *-di*-m-4-*xylidide*-, m.p. 172°, *-mono*-p-*toluidide*-, m.p. 195°, and *-mono-chloroanilide-phenylhydrazone*, m.p. 189—190°; *α-chloro-α-phenylhydrazinomalondi-anilide*, m.p. 179°, -p-, m.p. 210—211°, and -o-*toluidide*, m.p. 158°, -m-*chlorotoluidide*, m.p. 218—219°, and -m-4-*xylidide*, m.p. 206°. $CH_2Cl{\cdot}CCl(CO{\cdot}NH{\cdot}C_6H_4Me)_2$ and (**I**) give almost quant. yields of $\begin{matrix}NHPh{\cdot}N\\ CH_2\end{matrix}\!\!>\!C(CO{\cdot}NH{\cdot}C_6H_4Me)_2$; 1-*anilino*-2 : 2-*di*-o-, m.p. 145°, and -p-*tolylcarbamylaziridine*, m.p. 190°, are described. H. M. C.

Action of cuprous oxide on diazotised amines. III. Action in sulphuric acid–glacial acetic acid. H. H. Hodgson, S. Birtwell, and E. Marsden (*J.C.S.*, 1944, 112—113; cf. A., 1943, II, 158).—Deamination by Cu_2O in H_2SO_4–AcOH attains >70% efficiency for amines of the $C_{10}H_8$ series, but is <40% for those of the C_6H_6 series. Efficiency ∝ the positivity of the C atom to which the diazo-group is attached. D. G.

Manufacture of phenols.—See B., 1944, II, 129.

Hydrogen bonding. Nitrocresols. Nitrodihydroxybenzenes.—See A., 1944, I, 129.

Iodination of 4-hydroxydiphenyl. J. C. Colbert, H. W. Houghton, H. R. Schmidt, and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1944, **66**, 122—124).—With 1 mol. of I in KI, *p*-$C_6H_4Ph{\cdot}OH$ (**I**) in aq. NH_3 (91·1% yield) or, less well, in NaOH or with ICl in AcOH gives 3-*iodo*-4-*hydroxydiphenyl*, m.p. 115—116°, which in C_5H_5N yields a *benzoate*, m.p. 99·5—100°, and with conc. HNO_3 in AcOH gives a (?5-)NO_2-derivative, m.p. 95—100° (decomp.). Attempts to diiodinate (**I**) in NaOH by I–KI give a *compound*, $C_{24}H_{16}O_2I_2$, m.p. 170—171° (decomp.), but I–KI in aq. NH_3 or ICl–AcOH yields 3 : 5-*di-iodo*-4-*hydroxydiphenyl*, m.p. 95—97° (86—87°) (*benzoate*, m.p. 159—160°). Tri-iodination could not be achieved. R. S. C.

Phosphoric acid esters of phenols. F. L. Breusch and H. Keskin (*Rev. Fac. Sci. Istanbul*, 1942, **7**, 182—189).—$POCl_3$ and the corresponding phenol gave on warming *tri*-m-*tolyl* (**I**), b.p. 258—263°/4 mm., m.p. 25—26°, *tri*-p-*xylyl*, m.p. 77°, *tri*-2 : 4 : 6-*trichlorophenyl*, m.p. 200—201°, and *di*-o-*chlorophenyl phosphate*, m.p. 121·5° (separated from the tri-ester by solubility of the latter in PhMe). Br and (**I**) give *tri*-6-*bromo*-m-*tolyl phosphate*, m.p. 90°. Br and $(p\text{-}C_6H_4Me)_3PO_4$ give *tri*-3 : 5-*dibromo*-p-*tolyl phosphate*, m.p. 178°, hydrolysed to 2 : 6 : 4 : 1-$C_6H_2Br_2Me{\cdot}OH$. Triaryl phosphates are hydrolysed by alkali (curves given) but are stable towards acid reagents. Solubility data are also given. D. G.

Anomalous oxidation of an ethylene derivative by perbenzoic acid. C. K. Bradsher (*J. Amer. Chem. Soc.*, 1944, **66**, 45—46).—*o*-$C_6H_4Ph{\cdot}MgI$ (**I**) with an excess of PhCHO in boiling C_6H_6 gives *o*-$C_6H_4Ph{\cdot}COPh$ (69·5%), m.p. 86—87°, which with MgMeI and then $KHSO_4$ gives *o*-$C_6H_4Ph{\cdot}CPh{:}CH_2$ (**II**) (56—73%), m.p. 59—61°, b.p. 201—202·5°/12 mm., obtained much less well from (**I**) and COPhMe. With BzO_2H in Et_2O at room temp., (**II**) gives a "*dioxide*," $C_{20}H_{16}O_2$ (46%), m.p. 111—112°, converted by boiling 34% aq. HBr–AcOH, $KHSO_4$ at 170—180°, or conc. H_2SO_4 at 100° (2 min.) into 10-phenyl-9-phenanthrol. R. S. C.

Diphenylyl β-methylallyl ethers.—See B., 1944, II, 129.

α-Bromo-αββ-tri-p-anisylethylene.—See B., 1944, II, 130.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1944, III, 74.

Synthesis and chemical properties of diasone [disodium formaldehydesulphoxylate-diaminodiphenyl sulphone].—See A., 1944, III, 427.

Preparation of *cyclo*hexanols by catalytic reduction of phenols. H. E. Ungnade and A. D. McLaren (*J. Amer. Chem. Soc.*, 1944, **66**, 118—122).—In presence of Raney Ni at, usually, 100—300 atm. phenols are reduced in excellent yield to *cyclo*hexanols, substitution having little effect unless two *o*-substituents are present; 2 : 6 : 1-$C_6H_3Pr^{\alpha}_2{\cdot}OH$ (**I**) is unaffected at 360°, but 4 : 2 : 6 : 1-$C_6H_2MeEt_2{\cdot}OH$ (**II**) gives 1-*methyl*-3 : 5-*diethyl*cyclo*hexane*, b.p. 175—176·5°. Presence of a small amount of 40% NaOH slightly lowers the temp. required for reduction (normally 125—200°) and permits reduction of (**I**) to *cis-cis*-2 : 6-di-*n*-propyl*cyclo*hexanol, m.p. 109—110°, b.p. 241—242° (phenyl-, m.p. 145·5—146·5°, and *α-naphthyl-urethane*, m.p. 137—138°) (cf. Vavon *et al.*, A., 1937, II, 287), and of (**II**) to mixed 4-methyl-2 : 6-diethyl*cyclo*hexanols [90% including a *form*, m.p. 86—87°, b.p. 219—220° (*α-naphthylurethane*, m.p. 143·5—144°)]. In general only one stereoisomeride is formed, but 4 : 2 : 1-$C_6H_3MeBu^{\gamma}{\cdot}OH$ gives only 4-*methyl*-2-tert.-*butyl*cyclo*hexanol* (91%), b.p. 215—216° (*α-naphthylurethane*, m.p. 130—131°), in absence of NaOH (at 160—190°) but in its presence (at 195—220°) yields also 27% of a *form*, m.p. 112—113° (*α-naphthylurethane*, m.p. 130·5—131·5°) (both forms yield the same *cyclo*hexanone). At 110—125°/1200 lb. *p*-$C_6H_4Ph{\cdot}OH$ gives 4-*cyclo*hexyl*cyclo*hexanol (59·2%), *p-cyclo*hexylphenol (25·7%), and 4-phenyl*cyclo*hexanol (7·4%), but in presence of NaOH at 95—115° gives more rapidly 43·2, 16·6, and 30·3%, respectively. Hydrogenation of *o*-allyl-, *o*-propenyl-, or 2 : 6-diallyl-phenol gives the alkylphenol very rapidly at 50° and then the alkyl*cyclo*hexanol at 140—160°; alkali catalyses both reactions. Acylphenols in EtOH at ~110° give good yields of alkylphenols and then at 180° (usually *cis*-)alkyl*cyclo*hexanols, isolation of the alkylphenol being unnecessary; in presence of alkali at 45—65° mixtures of alkylphenols and hydroxyalkyl*cyclo*hexanols are obtained; at 110° mixtures of alkyl- and hydroxyalkyl-*cyclo*hexanols are formed; some hydrogenolysis of the OH of the hydroxyalkyl*cyclo*hexanols occurs during this second stage, but it cannot be completed even at 220° and is thus probably catalysed by the Na phenoxide. Incidentally are described *trans*-4-methyl-, b.p. 167—170° (3 : 5-dinitrobenzoate, m.p. 137·2—138·7°; phenyl-, m.p. 124—124·5°, and *α-naphthyl-urethane*, m.p. 156·5—157·5°), *cis*-2-ethyl-, b.p. 180—182° (phenyl-, m.p. 99—99·8°, and *α-naphthyl-urethane*, m.p. 151—153·5°), 3-*ethyl*-, b.p. 191·5—192° (*α-naphthyl-urethane*, m.p. 98·5—99·5°), 4-ethyl-, b.p. 191—192° (phenyl-, m.p. 114—115°, and *α-naphthyl-urethane*, m.p. 139·5—140·5°), *cis*-2-*n*-propyl-, b.p. 201·5—202° (phenyl-, m.p. 94—95°, and *α-naphthyl-urethane*, m.p. 103—104°), (?*cis-trans*-)2 : 4-, b.p. 176·5—177·5° (phenyl-, m.p. 95—96°, and *α-naphthyl-urethane*, m.p. 152·5—153·5°), *cis-trans*-2 : 5-, b.p. 179—180·5° (phenyl-, m.p. 116—117°, and *α-naphthyl-urethane*, m.p. 172—173·5°), 3 : 4-, b.p. 188—189·5° (phenyl-, m.p. 96—97°, and *α-naphthyl-urethane*, m.p. 162—163°), and *cis-cis*-3 : 5-dimethyl-, m.p. 8—9·8°, b.p. 181—183° (phenyl-, m.p. 106—107·5°, and *α-naphthyl-urethane*, m.p. 141—143°), 2 : 3 : 5-, b.p. 196—197° (*α-naphthylurethane*, m.p. 148—149°), and 2 : 4 : 6-*trimethyl*-, m.p. 70·5—71°, b.p. 182—184° (*α-naphthylurethane*, m.p. 197·5—198°), 4-*α-hydroxyethyl*-, m.p. 91—92·2° (*di*-3 : 5-*dinitrobenzoate*, m.p. 210—212°), and 2-*α-hydroxy*-n-*propyl*-, b.p. 256—259° (*di*-3 : 5-*dinitrobenzoate*, m.p. 162·5—164°), -cyclo*hexanol*. R. S. C.

4 : 4′-Dihydroxy-3 : 3 : 5′ : 5′-tetra(hydroxymethyl)diphenylmethane. F. Seebach (*Ber.*, 1940, **73**, [*B*], 1338—1346).—The compound regarded previously as 1 : 2 : 6-$OH{\cdot}C_6H_3(CH_2{\cdot}OH)_2$ (A., 1939, II, 476) is shown to be 4 : 4′-*dihydroxy*-3 : 5 : 3′ : 5′-*tetra(hydroxymethyl)diphenylmethane* (**I**). The Mg, *Cu*, Li_2, Na_2, *Ca*, and (*FeOH*) compounds are described. The triacetate (*loc. cit.*) is the *hexa-acetate* of (**I**). (**I**) is converted by CH_2N_2 (not Me_2SO_4 or MeI) into 4 : 4′-*dimethoxy*-3 : 3′ : 5 : 5′-*tetra(hydroxymethyl)diphenylmethane*, m.p. 115°, oxidised by $KMnO_4$ at 95° to 4 : 4′-*dimethoxybenzophenone*-3 : 5 : 3′ : 5′-*tetracarboxylic acid* (+AcOH) (**II**), m.p. 216° (*oxime*, m.p. 265°; *Me*$_4$ ester, m.p. 158°), hydrolysed by HI to 4 : 4′-*dihydroxybenzophenone*-3 : 5 : 3′ : 5′-*tetracarboxylic acid*, m.p. 310° (*Mg H* salt). This is transformed by KOH at 310° into 4 : 1 : 3 : 5-$OH{\cdot}C_6H_2(CO_2H)_3$, m.p. 306°, and 2 : 1 : 3-$OH{\cdot}C_6H_3(CO_2H)_2$, m.p. 241°. (**II**) is decarboxylated in boiling quinoline to $CO(C_6H_4{\cdot}OH\text{-}p)_2$, m.p. 206°, methylated to $CO(C_6H_4{\cdot}OMe\text{-}p)_2$, m.p. 141°. H. W.

4-Phenyl-2-methyl*cyclo*hexylacetic acid and related compounds. C. K. Chuang, J. H. Chu, and Y. S. Kao (*Ber.*, 1940, **73**, [*B*], 1347—1353).—Et 1-hydroxy-2-methyl*cyclo*hexylacetate is converted by $SOCl_2$ and C_5H_5N into a mixture of Et 2-methyl-Δ^1-*cyclo*hexenylacetate and Et 2-methyl*cyclo*hexylideneacetate, transformed by C_6H_6 and $AlCl_3$ (2 mols.) at room temp. into a *product*, b.p. 165—167°/2 mm. (saturated towards Br in CCl_4 and alkaline $KMnO_4$), hydrolysed by alkali to a mixture (**I**) from which 4-phenyl-2-methyl*cyclo*hexylacetic acid (**II**), m.p. 126—128° (*amide*, m.p. 183—184°), is isolated. 2-Phenyl-2-methyl*cyclo*hexylacetic acid cannot be present in (**I**), which is not cyclised to the corresponding hexahydrophenanthrone by 85% H_2SO_4 or anhyd. $ZnCl_2$. (**II**) is esterified (EtOH–H_2SO_4), dehydrogenated (S at 220—230°), and hydrolysed (KOH–EtOH) to 3-*methyldiphenyl*-4-*acetic acid*, m.p. 145°. Et 4-phenyl-2-methyl*cyclo*hexylacetate and MgPhBr give the non-cryst. diphenylcarbinol, which is oxidised by CrO_3 in AcOH to 4-*phenyl*-2-*methyl*cyclo*hexanecarboxylic acid*, m.p. 140—141° (amide, m.p.

176—177°), dehydrogenated and decarboxylated by Se at 330—340° to 3-methyldiphenyl, identified by oxidation to diphenyl-3-carboxylic acid, m.p. 165—166°. Me 4-phenyl-2-methyl*cyclo*hexanecarboxylate is dehydrogenated by S at 220—240° and then hydrolysed to 3-methyldiphenyl-4-carboxylic acid (Me ester, m.p. 62—63°). H. W.

Synthesis of coumarins from *o*-hydroxyaryl alkyl ketones. IV. Formation of *o*-coumaric acids from *o*-hydroxyaldehydes. D. Chakravarti and S. A. Momen (*J. Indian Chem. Soc.*, 1943, **20**, 338—340).—2 : 5 : 1-OMe·C_6H_3Me·CHO, 2 : 4 : 1-$(OMe)_2C_6H_3$·CHO, and 2 : 1-OMe·$C_{10}H_6$·CHO condensed with $CH_2Br·CO_2Et$ and CHMeBr·CO_2Et gave OH-esters, which on dehydration and hydrolysis gave *trans-o*-coumaric acids. *o*-OMe-aldehydes always give *trans-o*-methoxycinnamic acids by Perkin's, Chakravarti and Majumdar's, and $CH_2(CO_2H)_2$ condensations. The following appear new: trans-2-*methoxy-5-methyl-*, m.p. 145—146° (*Et* ester, b.p. 165°/7 mm.), trans-2-*methoxy-α* : 5-*dimethyl-*, m.p. 109—110° (*Et* ester, b.p. 160°/5 mm.), and trans-2 : 4-*dimethoxy-α-methyl-cinnamic acid*, m.p. 130° (*Et* ester, b.p. 200°/6 mm.); *β*-2-*methoxy*-1-*naphthyl-*, m.p. 153—154° (*Et* ester, b.p. 210—212°/4 mm.), and *β*-2-*methoxy*-1-*naphthyl-α-methyl-acrylic acid*, m.p. 138—139° (*Et* ester, b.p. 220—225°/5 mm.). Et *β*-hydroxy-*β*-4-methoxy-*m*-tolylpropionate has b.p. 200°/12 mm. D. G.

Transamination reaction. Effect of various nuclear substituted α-amino-α-phenylacetic acids on the course of the reaction. E. K. Harvill and R. M. Herbst (*J. Org. Chem.*, 1944, **9**, 21—30).—The reaction between $AcCO_2H$ and various NH_2-acids is followed by the determination of CO_2 evolved after definite intervals of time and the characterisation of volatile and non-volatile aldehydes produced. In the reaction between $AcCO_2H$ and *p*-OH·C_6H_4·CH(NH_2)·CO_2H, new m.p. 240—241° (decomp.), sublimes at 229°, *p*-OMe·C_6H_4·CH(NH_2)·CO_2H, decomp. 248—285°, sublimes at 230°, and *α-amino-α*-o-*anisylacetic acid* (+H_2O), m.p. 161—162° [*Cu* salt (+$2H_2O$)], both MeCHO and an aromatic aldehyde are formed with alanine (I) and CO_2 whereas in the change between $AcCO_2H$ and *α-amino-α*-p-*chlorophenyl-*, m.p. 261—262° (decomp.), -o-*chlorophenyl-*, m.p. 219·5°, and -o-*hydroxyphenyl-*, m.p. 194—195° (decomp.), -*acetic acid* only an aromatic aldehyde is produced with (I) and CO_2. In the system, $CO_2H·CH(C_6H_4Y)·N{:}CMe·CO_2H \rightarrow C_6H_4Y·CH{:}N·CHMe·CO_2H + CO_2$, the rate of formation of CO_2 increases with increasing dipole moment of C_6H_4Y. The effect of the same group is enhanced by shifting it from the *p*- to the *o*-position. In their effect on the rate of formation of CO_2 the groups studied fall into the order: *o*-Cl > *o*-OMe > *o*-OH > *p*-Cl > *p*-OMe > *p*-OH. *α-Amino-α*-2-*furylacetic acid* has m.p. 212—213° (decomp.). The NH_2-acids are obtained by hydrolysis with $Ba(OH)_2$ of the 5-*arylhydantoins*, $\begin{matrix}CHR·NH\\CO—NH\end{matrix}>CO$, prepared from the appropriate aldehyde, KCN, and $(NH_4)_2CO_3$ in aq. EtOH. Compounds are described in which R = *p*-anisyl, m.p. 195° (lit. 191·5°), *o*-anisyl (II), m.p. 189° (lit. 186—187°), p-C_6H_4Cl·, m.p. 191°, *o*-C_6H_4Cl·, m.p. 175—176°, *p*-OH·C_6H_4·, m.p. 269—270° (decomp.) [lit. 263° (decomp.)], o-*OH·C_6H_4*· (III), m.p. 240—244° (decomp.), and *furyl*, two forms, m.p. 101° and 147°. (III) could not be obtained by the general procedure but results from the hydrolysis of (II) by HI (*d* 1·5). The NH_2-acids and PhNCO in alkaline solution give *α-phenylcarbamido-α-arylacetic acids*, in which Ar = p-*anisyl*, m.p. 196° (decomp.), o-*anisyl*, m.p. 186·2°, p-C_6H_4Cl·, m.p. 185·5°, o-C_6H_4Cl·, m.p. 177—179°, *p*-OH·C_6H_4·, m.p. 192° (decomp.), and 2-furyl, m.p. 147° (decomp.). These are converted by boiling HCl into 3-*phenyl-5-arylhydantoins*, $\begin{matrix}CHR·NH\\CO—NPh\end{matrix}>CO$, in which R = p-*anisyl*, m.p. 179°, o-*anisyl*, m.p. 134°, *p*-C_6H_4Cl·, m.p. 167—168° o-C_6H_4Cl·, m.p. 187·5°, p-*OH·C_6H_4*·, m.p. 171° and 201° after resolidification, and o-*OH·C_6H_4*·, m.p. 224—225°. M.p. are corr. H. W.

Dialkyl phenyl- and phenylalkyl-malonates.—See B., 1944, II, 130.

9 : 9-Di-β-carbamylethylfluorene.—See B., 1944, II, 129.

[Attempted] synthesis of caryophyllenic acid. M. D. Owen (*J. Indian Chem. Soc.*, 1943, **20**, 343—344).—The condensation product of $CMe_2{:}CO$ and *cyclo*pentadiene was oxidised ($COMe_2$–$KMnO_4$ at 4°) to 4-*keto-2-carboxy*-3 : 3-*dimethyl*cyclo*butylacetic acid* (?) (I), m.p. 124—125°. Attempts to reduce (I) to caryophyllenic acid have so far been unsuccessful. D. G.

Amidine salts.—See B., 1944, II, 129.

Lignin. XLII. Vanillincarboxylic acid and related acids. K. Freudenberg and F. Klink (*Ber.*, 1940, **73**, [*B*], 1369—1376).—Me 2-hydroxy-3-methoxy-5-allylbenzoate is not isomerised by KOH in boiling C_5H_{11}·OH or by KOH–MeOH at 135° but is converted by KOH at 220—235° into 2-*hydroxy-3-methoxy-5-propenylbenzoic acid* (I), m.p. 157° (*Me* ester, m.p. 73·5°; *acetate*, m.p. 141°), which when ozonised in EtOAc and then hydrogenated (Pd–C in EtOAc) affords 2-hydroxy-5-aldehydo-3-methoxybenzoic (vanillin-5-carboxylic) acid, m.p. 255° (decomp.). (I) is converted by Me_2SO_4 and NaOH at room temp. into 2 : 3-*dimethoxy-5-propenylbenzoic acid*, m.p. 101°, ozonised and hydrogenated to 5-*aldehydo*-2 : 3-*dimethoxybenzoic acid*, m.p. 152°, and oxidised by $KMnO_4$–$NaHCO_3$ to *iso*hemipinic acid (II), m.p. 255°. (I) is treated with $PhSO_2Cl$ in C_5H_5N and then oxidised ($KMnO_4$–$NaHCO_3$) and hydrolysed (NaOH) to 4-*hydroxy-5-methoxy*iso*phthalic acid*, m.p. 276°. 4 : 5 : 1 : 3-OH·C_6H_2(OMe)$(CHO)_2$ is methylated to 4 : 5 : 1 : 3-$(OMe)_2C_6H_2(CHO)_2$, m.p. 125°, oxidised to (II), which is converted by boiling AcOH–48% HBr into 4 : 5 : 1 : 3-$(OH)_2C_6H_2(CO_2H)_2$ (III), m.p. 291° [Me_2 ester, (IV), m.p. 139°]. Partial esterification of (III) by MeOH–H_2SO_4 gives 1-*Me H* 4 : 5-*dihydroxy*iso*phthalate*, m.p. 216°. (IV) is transformed by successive treatment with MeOH–NaOMe and –CH_2I_2 at 140° into Me_2 4 : 5-*methylenedioxy*iso*phthalate*, m.p. 145—146°, hydrolysed (KOH–MeOH) to the *acid*, m.p. 293—294° (decomp.). Guaiacoldialdehyde is demethylated to 4 : 5-*dihydroxy*iso*phthalaldehyde*, m.p. 200° (*bisphenylhydrazone*, m.p. 249°), which yields 4 : 5-*methylenedioxy*iso*phthalaldehyde*, m.p. 153—154°. H. W.

***o*-Aldehydocarboxylic acids. IV. Synthesis of 5 : 6-methylenedioxyphthalaldehydic acid.** S. N. Chakravarti (*J. Indian Chem. Soc.*, 1943, **30**, 382—383).—5 : 6-Methylenedioxyhomophthalic acid (modified prep.; cf. Haworth *et al.*, A., 1926, 951) was oxidised (SeO_2 in boiling xylene) to 5 : 6-methylenedioxyphthalonic acid, converted through its $NaHSO_3$ compound into 5 : 6-*methylenedioxyphthalaldehydic acid*, m.p. 155°, which was reduced (Na–Hg; dil. NaOH) to 5 : 6-*methylenedioxyphthalide*, m.p. 227°. H. M. C.

Lignin and related compounds. LXXIV. Relation of wood ethanolysis products to the Hibbert series of plant respiratory catalysts. Allylic and dismutation rearrangements of γ-chloro-α-3 : 4-dimethoxyphenylpropan-β-one and α-bromo-3 : 4-dimethoxyphenylpropan-β-one. A. M. Eastham, H. E. Fisher, M. Kulka, and H. Hibbert (*J. Amer. Chem. Soc.*, 1944, **66**, 26—32; cf. A., 1944, II, 115).—The ease with which rearrangements, $CH_2Ar·CO·CH_2X \rightleftharpoons CHArX·COMe \rightleftharpoons COAr·CHMeX$, occur supports Hibbert's view that the C_6—C_3 products isolated after ethanolysis of wood are stabilised end-products formed from progenitors of the coniferyl alcohol type. 3 : 4 : 1-$(OMe)_2C_6H_3$·CH:CMe·NO_2 with $FeCl_3$, Fe dust, and HCl gives the oxime, which by hydrolysis yields *veratryl Me ketone* (I) (70%), b.p. 118°/0·2 mm., which with Br and a trace of Bz_2O_2 in $CHCl_3$ gives *α-bromoveratryl Me ketone* (II) (58%), m.p. 87—88° (*semicarbazone*, m.p. 201·5—202·5°). With 5% KOAc at 100° (II) gives *α-hydroxyveratryl Me ketone* (III) (55%), m.p. 76—77° (*semicarbazone*, m.p. 155—156°), which is unchanged by 5% KOAc at 100° (CO_2) and with AcCl–C_5H_5N yields the oily *α-acetate* (89%) (2 : 4-*dinitrophenylhydrazone*, m.p. 149—150°), also obtained from (I) by $Pb(OAc)_4$–AcOH at 88°. 3 : 4 : 1-$(OMe)_2C_6H_3$·CHCl·CO·NH_2 and HI in AcOH at room temp. give 3 : 4 : 1-$(OMe)_2C_6H_3$·CH_2·CO·NH_2 and thence, successively, the acid, acid chloride, CHN_2 ketone (IV), and *veratryl CH_2Br ketone* (80%), m.p. 44—45°. In boiling AcOH, (IV) gives *veratryl CH_2·OAc ketone* (85%), m.p. 55—56° (*semicarbazone*, m.p. 128—129°). $CuSO_4$ oxidises (III) or 3 : 4 : 1-$(OMe)_2C_6H_3$Cl·CHMe·OH (V) (*semicarbazone*, m.p. 154—155°) in aq. C_5H_5N at 100° to α-3 : 4-*dimethylphenylpropane-αβ-dione* (VI), m.p. 69—70°. With AgOAc in boiling EtOH–CO_2 (II) or 3 : 4 : 1-$(OMe)_2C_6H_3$·CH_2·CO·CH_2Cl (VII) gives 3 : 4 : 1-$(OMe)_2C_6H_3$·CH(OEt)·COMe (VIII). 2% HCl–EtOH–CO_2 converts (III) into (VIII) and 3 : 4 : 1-$(OMe)_2C_6H_3$·CO·CHMe·OEt. With boiling 5% KOAc, (VII) gives (III) and (V) [?(VI)], but with KOAc–AcOH at 90—100° gives 3 : 4 : 1-$(OMe)_2C_6H_3$·CO·CHMe·OAc. 5% H_2SO_4 at 70—80° has no effect on (III), nor has boiling 5% KOAc on (V). NaOMe–MeOH or KOH–MeOH converts (VII) at room temp. into (?) *α-methoxy-α-veratrylethylene oxide*, m.p. 40—41°; the (?) *α-ethoxy*-analogue, b.p. 104°/0·04 mm., is similarly obtained by NaOEt or KOH–EtOH. R. S. C.

Use of phenyl esters in the Reformatsky reaction. M. S. Bloom and C. R. Hauser (*J. Amer. Chem. Soc.*, 1944, **66**, 152—153).—RCO_2Ph and CR′R″Br·CO_2Et undergo the Reformatsky reaction in boiling PhMe–C_6H_6 satisfactorily if neither component has H on $C_{(\alpha)}$; $CMe_2Br·CO_2Et$ with PhOBz gives 52% of $CMe_2Bz·CO_2Et$, with *p*-C_6H_4Ph·OAc gives 11% of $CMe_2Ac·CO_2Et$, and does not condense with EtOBz; very low yields of *β*-CO-ester are obtained from $CH_2Br·CO_2Et$ by PhOBz or $EtCO_2$·C_6H_4Ph-*p*. All the Zn is nevertheless used when the reaction fails; probably condensation of the Ph esters (with H at $C_{(\alpha)}$) and enolisation of the *β*-CO-ester are caused by the Zn alkyl halide. R. S. C.

***cyclo*Alkenyl methyl ketones.**—See B., 1944, II, 130.

Absorption spectra and structure of pyrethrins I and II.—See A., 1944, I, 97.

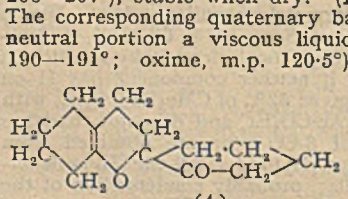
Preparation of *cyclo*pentenones from lactones. R. L. Frank, P. G. Arvan, J. W. Richter, and C. R. Vanneman (*J. Amer. Chem. Soc.*, 1944, **66**, 4—6).—Et lævulate (prep. in 81% yield by distilling a solution of the acid and a little conc. H_2SO_4 in EtOH–C_6H_6), b.p. 93—94°/18 mm., with *n*-C_6H_{13}·MgCl in boiling Et_2O–C_6H_6 gives *γ-methyl-γ*-n-*decolactone* (28%; C_6H_{13}·MgBr gives 31%), b.p. 120—125°/4—5 mm., which with P_2O_5 gives 50% of dihydrojasmone and with Br in CCl_4 at room temp. and then 70—75° (ultra-violet light) gives (?) C_6H_{13}·CMeBr·CH_2·CHBr·CO_2H, converted by distillation into *α-bromo-γ-methyl-γ*-n-*decolactone*, b.p. 121—122°/1 mm. With NaOMe–MeOH at room temp. this gives *α-methoxy-γ-methyl-γ*-n-*decolactone* (65%), b.p. 107—108°/3 mm. (and a *substance*, $C_{12}H_{22}O_3$,

b.p. 151—170°/3—4 mm.), which with P_2O_5 gives a hydrocarbon, b.p. 74—82°/3—5 mm., and (?) *β-methyl-γ-n-nonolactone*, b.p. 112—115°/3—5 mm. R. S. C.

1 : 3-Rearrangement of a phenyl group. C. F. H. Allen and J. Van Allan (*J. Amer. Chem. Soc.*, 1944, **66**, 7—8).—1 : 3-Migration of Ph is proved (cf. A., 1943, II, 325). 2 : 5-Diphenyl-3 : 4-di-*p*-bromophenyl*cyclo*pentadienone and MgPhBr give 1 : 2 : 5-*triphenyl*-3 : 4-*di*-p-*bromophenyl*-$\Delta^{2:4}$-cyclo*pentadienol* (I), m.p. 195°, which gives a red colour in H_2SO_4, shows one active H but does not add MgMeI, and with $(CH{\cdot}CO)_2O$ at 200° gives 3 : 6-*diphenyl*-4 : 5-*di*-p-*bromophenyl*-3 : 6-endo-*α-hydroxybenzylidene*-Δ^4-*tetrahydrophthalic anhydride*, m.p. 222°. At 260—265°/14 mm., (I) rearranges to 2 : 3 : 5-*triphenyl*-3 : 4-*di*-p-*bromophenyl*-Δ^4-cyclo*pentenone*, m.p. 178°, which gives a yellow colour in H_2SO_4, adds 1 MgMeI but shows no active H, and with CrO_3–AcOH gives *p*-$C_6H_4Br{\cdot}COPh$ (53·5%) (2 : 4-*dinitrophenylhydrazone*, m.p. 207—209°), BzOH (63%), and *p*-$C_6H_4Br{\cdot}CO_2H$ (32%). R. S. C.

2 : 3-Disubstituted indones. R. L. Frank, H. Eklund, J. W. Richter, C. R. Vanneman, and A. N. Wennerberg (*J. Amer. Chem. Soc.*, 1944, **66**, 1—4).—Adding 2-phenylindane-1 : 3-dione, m.p. 144—145°, in much C_6H_6 or PhMe to 3—4 mols. of MgRHal in C_6H_6 gives 2-*phenyl*-3-*methyl*- (40%), m.p. 67—68° (*phenylhydrazone*, m.p. 120°), -3-*ethyl*- (I) (42%), m.p. 97—98° (*phenyl*-, m.p. 96—97°, and 2 : 4-*dinitrophenyl-hydrazone*, m.p. 206—207°), and -3-cyclo*hexyl-indone* (10%), m.p. 163—164° (*phenylhydrazone*, m.p. 166—167°), and 2 : 3-diphenylindone (48%), m.p. 152—153°. Phthalide, ArCHO, and NaOEt–EtOH give 2-anisyl- (34·6%), m.p. 153—154°, and 2-3′ : 4′-*dimethoxyphenyl-indane*-1 : 3-*dione* (33·4%), m.p. 188—190°, and thence, as above, 2-*anisyl*-3-*ethyl*- (42%), m.p. 119—120° (*phenylhydrazone*, m.p. 156—157°), and -3-iso*propyl*- (23%), m.p. 138—139°, b.p. 198—203°/2 mm. (*phenylhydrazone*, m.p. 166—168°), and 2-3′ : 4′-*dimethoxyphenyl*-3-*ethyl*- (27%), m.p. 111—112°, b.p. 192—195°/4 mm. (*phenylhydrazone*, m.p. 188—190°), -*indone*. $CHEtBr{\cdot}CO_2Et$, $COPh_2$, and Zn in C_6H_6 give $OH{\cdot}CPh_2{\cdot}CHEt{\cdot}CO_2Et$, cyclised by conc. H_2SO_4 at room temp. to 3-phenyl-2-ethylindone (22%), m.p. 92—93° (oxime, m.p. 179—180°). $CHPr^aBr{\cdot}CO_2Et$, b.p. 93—94°/25 mm., with $COPh_2$ and Zn in C_6H_6 gives a *substance*, m.p. 112—113°, cyclised by H_2SO_4 to 3-*phenyl*-2-n-*propylindone*, m.p. 72·5—73° (*phenylhydrazone*, m.p. 107—108°). With O_3 and then Zn in AcOH, (I) gives the *ozonide* (II), m.p. 92—93°, and 2-*propionylbenzil*, m.p. 93°. 83% of (II) is obtained in $CHCl_3$ at 0°. (II) is very stable, does not explode when heated, and is unaffected by H_2–PtO_2 in EtOH; with 10% KOH–EtOH it gives BzOH (0·95 mol.). With NH_2OH,HCl in boiling C_5H_5N–EtOH, (II) gives 1-keto-4-ethyl-2 : 3 : 1-benzoxazine, $o\text{-}C_6H_4<^{CEt:N}_{CO-O}$ (58%), m.p. 117—119°, and with $NHPh{\cdot}NH_2$ at 230—235° gives 3-phenyl-1-ethylphthalazone (2·5%), m.p. 110—112° (Gottlieb, A., 1899, i, 511, m.p. 102°), also obtained in aq. KOH by NH_2OH or $NHPh{\cdot}NH_2$, respectively, from *o*-$COEt{\cdot}C_6H_4{\cdot}CO_2H$ [prep. from *o*-$C_6H_4(CO)_2O$, $EtCO_2H$, and $EtCO_2Na$ at 170°], m.p. 96—97°. The structure of (I) is also confirmed by its absorption spectrum [max. at 255 mμ. (log ε 4·765) in 95% EtOH]. R. S. C.

2-Methylene*cyclo*hexanone. K. Dimroth, K. Resin, and H. Zetzsch (*Ber.*, 1940, **73**, [*B*], 1399—1409).—In accordance with Mannich *et al.* (A., 1920, i, 850) *cyclo*hexanone (I), CH_2O, and $NHMe_2$,HCl condense smoothly to 2-dimethylaminomethyl*cyclo*hexanone, b.p. 93—94°/11·5 mm. (86% yield), which contrary to these authors gives a *methiodide* (II), m.p. 136—137° (2 : 4-*dinitrophenylhydrazone*, m.p. 206—207°), stable when dry. (II) decomposes gradually in H_2O. The corresponding quaternary base gives under all conditions as neutral portion a viscous liquid, $C_{14}H_{20}O_2$ (semicarbazone, m.p. 190—191°; oxime, m.p. 120·5°), which is not 2-methylene*cyclo*hexanone, is termed provisionally "dimeric ketone" (III), and is possibly (*A*). (III) appears identical with the compound obtained by Mannich *et al.* (A., 1928, 300) from 2-piperidinomethyl*cyclo*hexanone (IV). Condensation of (I) with CH_2O and NH_2Me,HCl proceeds very heterogeneously, giving a most volatile fraction [semicarbazone (V), m.p. 195°] which, contrary to Mannich *et al.*, does not consist of 2-methylene*cyclo*hexanone but is 2-methyl*cyclo*hexanone; the less volatile fractions contain some (III). The ability of (V) to decolorise Br is not evidence of unsaturation but is a general property of the semicarbazones of *cyclo*hexanones and is accompanied by the separation of $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HBr. Decomp. of (IV), its hydrochloride, or *oxalate*, m.p. 136—137°, under the mildest possible conditions gives only (III) and it is improbable that the monomeric ketone can be obtained from such ammonium salts. Energetic dehydrating agents transform 2-hydroxymethyl*cyclo*hexanone (VI) into compounds of high mol. wt. Passage over Al_2O_3 (Brockmann) and treatment with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl and KOAc leads to a compound, $C_{14}H_{22}O_3$ (VII), m.p. 148°, obtained previously by Mannich (*loc. cit.*) and then regarded as a symmetrical ether of (VI) but now (unpublished work) considered as allied closely to (III). Al_2O_3 in boiling abs. C_6H_6 transforms (VI) into (III) whilst (VII) is obtained from (VI) and BzCl in C_5H_5N. Direct condensation of *cyclo*hexanone with CH_2O in dil. aq. alkali gives unchanged material and a viscous yellow oil of high b.p. H. W.



(*A*.)

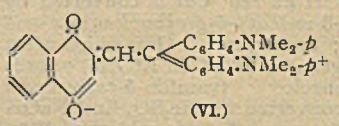
Interaction of diazomethane with 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. R. B. Thompson (*J. Amer. Chem. Soc.*, 1944, **66**, 156).—1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene, CH_2N_2, and Na_2CO_3 in EtOH at 10—15° give 7—8% of non-ketonic material, b.p. 93—96°/0·7 mm., and 6—7% of 3 : 4-*benz*-Δ^3-cyclo*octenone*, m.p. 73—75°, b.p. 103—106°/0·7 mm. (*oximes*, m.p. 164—165° and 89—90°), probably by way of 3 : 4-benz-Δ^3-*cyclo*heptenone which reacts as fast as it is formed. R. S. C.

2-Methyl*meso*benzanthrone and derivatives. D. H. Hey, R. J. Nicholls, and C. W. Pritchett (*J.C.S.*, 1944, 97—100).—$CH_2{:}CMe{\cdot}CHO$ (*oxime*, b.p. 65°/14 mm.) (new methods of prep. given) in dioxan with anthrone in AcOH–H_2SO_4 (*d* 1·53) at 80° gave 2-methyl*meso*benzanthrone (I), oxidised (CrO_3) to anthraquinone-1-carboxylic acid (II). With MnO_2 and H_2SO_4 (I) gave 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl (III) and 3-*hydroxy*-2-*methyl*meso*benzanthrone*, m.p. 206—208 (decomp.) [*Me ether*, m.p. 142°; also prepared from $CH_2{:}CMe{\cdot}CO_2Me$ and anthrone, and from 3-*amino*-2-*methyl*meso*benzanthrone* (IV), m.p. 232°, by diazotisation and heating]. With KOH–EtOH at 120—130° (III) gave 16 : 17-*dimethyldibenzanthrone* (V). KOH fusion of (I) in presence of glucose or KOAc–$C_{10}H_8$–MnO_2 gave (V). With dichloramine-T in AcOH, (I) gave 3-*chloro*-2-*methyl*meso*benzanthrone* (VI), m.p. 227—228°; 3-*nitro*- (VII), m.p. 218—219° [from (I) and 88% HNO_3 in $PhNO_2$ at 40—50°; oxidised (CrO_3) to (II)], and 3-*bromo*-2-*methyl*meso*benzanthrone* [from (I) and from (IV)], m.p. 225°, are described. (VII) is reduced (Na_2S) to (IV). (VI) with KOH–EtOH at 150—155° gave 6 : 15-*dimethyl*iso*dibenzanthrone* (VIII). (VI) with Se, $Ca(OH)_2$, and Cu-bronze in EtOH at 200° gave 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl selenide, m.p. 310—315°, which gave (VIII) with KOH–EtOH at 120—130°. (V) in boiling $PhNO_2$ (preferably in presence of BaO) gives a product for which the structure

is suggested. D. G.

Synthesis of 2-methyl-1 : 4-naphthaquinone (vitamin-*K*) from benzene and citric or *d*-tartaric acid. P. P. T. Sah and W. Brüll (*Ber.*, 1940, **73**, [*B*], 1430—1432).—The scheme is: citric or tartaric acid $\rightarrow CO_2H{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H \rightarrow$ $<^{CHMe{\cdot}CO}_{CH_2-CO}>O \rightarrow$ $CH_2Bz{\cdot}CHMe{\cdot}CO_2H \rightarrow Ph{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CO_2H \rightarrow$ $Ph{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}COCl \rightarrow C_6H_4<^{CH_2{\cdot}CH_2}_{CO-CHMe} \rightarrow C_6H_4<^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CHMe} \rightarrow$ 2-$C_{10}H_7Me \rightarrow$ 2-methyl-1 : 4-naphthaquinone. H. W.

Condensation of naphthaquinones with polar ethylenes. M. Gates (*J. Amer. Chem. Soc.*, 1944, **66**, 124—130).—Condensation readily occurs between $CAr_2{:}CH_2$ and naphthaquinones owing to their electron-donating and -accepting capacities, respectively. The reaction is not catalysed by acids or bases and does not occur in AcOH, in accordance with this explanation. $(p\text{-}NMe_2{\cdot}C_6H_4)_2C{:}CH_2$ (I) (1 mol.) and 1 : 4-$O{:}C_{10}H_6{:}O$ (II) (2 mols.) condense in C_6H_6, $COMe_2$, or dioxan at room temp. or, best (59% yield), dioxan at 70° (24 hr.) to 2-*ββ-di*-p-*dimethylaminophenylvinyl*-1 : 4-*naphthaquinone* (III), purple, m.p. 272—273·5°, and 1 : 4-$C_{10}H_6(OH)_2$ (95%). With Zn dust in Ac_2O–C_5H_5N, (III) gives the *quinol diacetate*, yellow, m.p. 230—231° (decomp.). 1 : 2-$O{:}C_{10}H_6{:}O$ (IV) condenses very rapidly with (I) in warm MeOH, giving 4-*ββ-di*-p-*dimethylaminophenylvinyl*-1 : 2-*naphthaquinone* (83·7%), blue-black, m.p. 199—201° (decomp.) [yellow *quinol diacetate*, m.p. 105·6—106·8°; red *azine*, m.p. 246—247·5°, from *o*-$C_6H_4(NH_2)_2$]. Naphthazarin in C_6H_6 at the b.p. and then 74° or its diacetate in dioxan at 78° with (I) gives similarly 5 : 8-*dihydroxy*- (V), black, m.p. 306—308° (uncorr.), or 5 : 8-*diacetoxy*-2-*ββ-di*-p-*dimethylaminophenylvinyl*-1 : 4-*naphthaquinone*, blue-black, amorphous, m.p. 261—264° [by hydrolysis gives (V), m.p. 307—308° (uncorr.)], respectively, but 1 : 2 : 4-$O{:}C_{10}H_6Me{:}O$ gives a *substance*, $C_{40}H_{40}O_4N_2$, m.p. 298—300° (block; uncorr.). $(p\text{-}OMe{\cdot}C_6H_4)_2C{:}CH_2$, being less polar than (I), condenses less readily; with (II) in boiling MeOH it gives slowly 2-*ββ-di*-p-*anisylvinyl*-1 : 4-*naphthaquinone*, orange-red, m.p. 211·8—212·3°, but with (IV) gives 1 : 2 : 4-$O{:}C_{10}H_5(OMe){:}O$ (8%) and 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxy*-1 : 1′-*dinaphthyl* (43%), pink, m.p. 277·5—278·8° after slight decomp. (derived amorphous *quinone*, m.p. 260—262°), which gives the known $(OMe)_4$-compound. Dissolution (reversible) of the highly coloured products in 3N-HCl gives much paler solutions; this is due to resonance of the free quinones, *e.g.*, (III) with the form (VI), which



(VI.)

is suppressed by salt-formation. Unless otherwise stated, m.p. are corr. R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Separation of *trans*-œstradiol.—See B., 1944, III, 74.

16-Substituted steroids. I. *iso*Œstriol-*A*. M. N. Huffman and H. H. Darby (*J. Amer. Chem. Soc.*, 1944, **66**, 150—152).—Œstrone benzoate and *iso*-C_5H_{11}·O·NO in KOBu$^{\gamma}$–Bu$^{\gamma}$OH–N_2 at room temp. followed by 0·5N-KOH at room temp. give 16-*oximino-œstrone* (81%), m.p. 214—215° (decomp.), reduced by Zn dust in AcOH–H_2O at AcOH–H_2O at 40—45° and then 120—125° to an impure α-ketol, which with H_2–PtO_2 in 0·5N-NaOH gives *iso*œ*striol*-A (I), m.p. 267—269°, $[\alpha]_D^{20\cdot5}$ +88° in EtOH. (I) has the same absorption as theelol [œstriol] but is less sol. With Me_2SO_4–NaOH, (I) gives a *Me*$_1$ *ether*, m.p. 141—142°, but with Ac_2O–C_5H_5N at 100° gives a *triacetate*, m.p. 152°. R. S. C.

Oxidation of sterols.—See B., 1944, III, 74.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Hydrocarbon polymerisation and method of determining catalyst activity.—See A., 1944, I, 131.

Reactions of atoms and free radicals in solution. V. Non-coplanar free 1-*apo*camphyl radical. M. S. Kharasch, F. Engelmann, and W. H. Urry (*J. Amer. Chem. Soc.*, 1943, **65**, 2428—2429; cf. A., 1943, II, 150).—*apo*Camphane-1-carboxyl chloride, Na_2O_2, and a little H_2O in Et_2O at −5° to 10° give a relatively stable, cryst. peroxide (I), which in CCl_4 at the b.p. (20 hr.) gives 1-chloro*apo*camphane (36%), m.p. 170—171° (Bartlett *et al.*, A., 1940, II, 17, m.p. 154—156°), *apo*camphanyl *apo*camphane-1-carboxylate (50%) [hydrolysed by KOH in $(CH_2{\cdot}OH)_2$], *di-1-camphyl* (9%), m.p. 216—217°, *apo*camphane-1-carboxylic acid (II) (5%), and C_2Cl_6 [removed from (II) by KOH–$(CH_2{\cdot}OH)_2$]. Decomp. of (I) yields R· (R = *apo*camphyl) and RCO_2·, and, by interaction of R· with CCl_4, gives CCl_3·; R· is more reactive than CCl_3·. R. S. C.

Triterpenes. LXXXVI. Birch-tar oil. L. Ruzicka, A. G. Boer, and E. Rey (*Helv. Chim. Acta*, 1944, **27**, 183—186).—Technical birch-tar oil is extracted successively with dil. HCl, Na_2CO_3, NaOH, and H_2O, boiled with 10% NaOH–EtOH, and distilled. A fraction b.p. 110—160°/12 mm., is dehydrogenated by S at 180—250° and converted through a series of picrates into additive compounds with s-$C_6H_3(NO_2)_3$, thus leading to the recognition of the presence of 2 : 7-$C_{10}H_6Me_2$, 1 : 2 : 7-$C_{10}H_5Me_3$, and 1 : 2 : 5 : 6-$C_{10}H_4Me_4$. It thus appears that the portions of birch-tar oil which can be dehydrogenated to the methylnaphthalenes are not sesquiterpenes but products of the pyrolysis of betulin. H. W.

Scandol, $C_{30}H_{50}O$, m.p. 161—163°, $[\alpha]_D^{26}$ +56·9° in $CHCl_3$ (acetate, m.p. 165—168°, $[\alpha]_D^{27}$ +60·5° in $CHCl_3$; benzoate, m.p. 210—212°, $[\alpha]_D^{26}$ +73·84° in $CHCl_3$).—See A., 1944, III, 383.

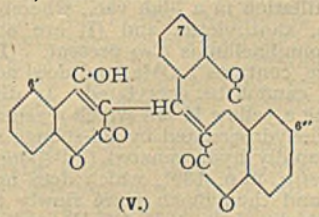
VI.—HETEROCYCLIC.

Synthesis of δ-3 : 4-dicarboxy-2-furyl-*n*-valeric acid and its derivatives. K. Hofmann (*J. Amer. Chem. Soc.*, 1944, **66**, 51—53).—β-2-*Furylacrylidenemalonic acid* [prep. from β-2-furylacraldehyde, $CH_2(CO_2H)_2$, and a little piperidine in C_5H_5N], decomp. 190—195°, gives, by hydrogenation (Pd–C; MeOH; 0·1 atm.) and subsequent heating in C_5H_5N at 130—140°, δ-2-*furyl*-n-*valeric acid*, m.p. 42—43° (*anilide*, m.p. 75—76°), which with (⁝C·CO_2Et)$_2$ at 100° gives an adduct, hydrogenated (Pd-black) in EtOAc to δ-1 : 4-epoxy-2 : 3-dicarbethoxy-Δ^2-*cyclo*hexenyl-*n*-valeric acid. At 190—200°/16 mm. this gives C_2H_4 and δ-3 : 4-dicarbethoxy-2-furyl-*n*-valeric acid, hydrolysed by 5N-KOH at the b.p. to δ-3 : 4-*dicarboxy*-2-*furyl*-n-*valeric acid*, m.p. 188—190° (Et_3 ester, b.p. 165—166°/0·02 mm.; absorption spectrum resembles that of furan-3 : 4-dicarboxylic acid), and converted by $SOCl_2$ into the acid chloride, b.p. 177—178°/0·02 mm. Thence are obtained δ-3 : 4-dicarbethoxy-, b.p. 210—211°/0·02 mm., and δ-3 : 4-*dicarboxy*-2-*furyl*-n-*valeropiperidide*, m.p. 132—133°. M.p. are corr. R. S. C.

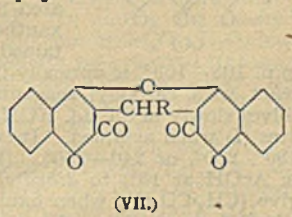
Synthesis of two stereoisomeric 3 : 4-diaminotetrahydro-2-furyl-*n*-valeric acids. K. Hofmann (*J. Amer. Chem. Soc.*, 1944, **66**, 157).—δ-2-Furyl-*n*-amyl alcohol (α-*naphthylurethane*, m.p. 58—59°) by condensation with (⁝C·CO_2Et)$_2$ and then high-pressure hydrogenation gives δ-3 : 4-dicarbethoxytetrahydro-2-furyl-*n*-amyl alcohol, which yields *dihydrazides*, m.p. 208—211° and 177—180°, and thence successively (Curtius) ε-3 : 4-*di*(*carbethoxyamino*)*tetrahydro*-2-*furyl*-n-*amyl alcohols*, m.p. 110—113° and 128—130°, (CrO_3–AcOH) the derived n-*valeric acids*, m.p. 118—124° and 157—159°, and [conc. $Ba(OH)_2$] δ-3 : 4-diaminotetrahydro-2-furyl-*n*-valeric acids (Bz_2 derivatives of the *Me* esters, m.p. 183—186° and 171—172°), respectively. R. S. C.

4-Hydroxycoumarins. I. Synthesis of 4-hydroxycoumarins. M. A. Stahmann, I. Wolff, and K. P. Link. **II. Condensation of aldehydes with 4-hydroxycoumarins.** W. R. Sullivan, C. F. Huebner, M. A. Stahmann, and K. P. Link. **III. Dehydration of the aldehyde condensation products.** C. F. Huebner, W. R. Sullivan, M. A. Stahmann, and K. P. Link (*J. Amer. Chem. Soc.*, 1943, **65**, 2285—2287, 2288—2291, 2292—2296).—I. *o*-OAc·C_6H_4·CO_2Me [prep. from *o*-OH·C_6H_4·CO_2Me (I) by Ac_2O and a little H_2SO_4 at 40°; 95% yield], m.p. 47—49°, and Na give ≯13% of 4-hydroxycoumarin (II) by the method of Pauly *et al.* (A., 1915, i, 146), but 22% is obtained in liquid paraffin at 240—250°; other alkaline condensing agents offer no advantage; by-products include *o*-OH·C_6H_4·CO_2H, PhOH, PhOMe, MeOAc, AcOH, and acidic substances separating at pH 5·5—6 (and thus removable). Pure (II) has m.p. 214—216° (lit. 204—206°). *Me* O-*propionylsalicylate*, b.p. 141—142°/9 mm., is obtained as above. RCOCl and (I) at the b.p. give *Me* O-n- (81%), b.p. 155—156°/12 mm., and O-iso-*butyryl*- (68%), b.p. 140—143°/6 mm., O-n- (65%), b.p. 158—159°/8 mm., and O-iso-*valeryl*- (71%), b.p. 151—152°/8 mm., O-n-*hexoyl*- (56%), b.p. 173—174°/9 mm., O-n-*heptoyl*- (73%), b.p. 181—182°/9 mm., O-*stearyl*- (47%), m.p. 41—43°, b.p. 226—230°/0·05 mm., O-β-*phenylpropionyl*- (74%), b.p. 197—201°/5 mm., and *O*-phenylacetyl- (63%), m.p. 59—60° (lit. 50°), -*salicylate*. With Na in liquid paraffin at 240—250° these esters give 4-hydroxy-3-methyl- (28%), m.p. 227—228° (lit. 230°), -3-*ethyl*- (28%), m.p. 155—156°, -3-n- (32%), m.p. 134—135°, and -3-iso-*propyl*- (25%), m.p. 172—174°, -3-n-*butyl*- (26%), m.p. 158—159°, -3-n-*amyl*- (30%), m.p. 137—139°, -3-*hexadecyl*- (21%), m.p. 96—97°, -3-phenyl- (25%), m.p. 234—235° (lit. 236°), and -3-benzylcoumarin (22%), m.p. 202—205°. The 3-alkylcoumarins have slight anticoagulant activity, increasing with the size of the alkyl and being greater for 3-aryl derivatives.

II. *o*-OH·C_6H_4·CHO (III) (1 mol.) and (II) (1 mol.) in EtOH at the b.p. (10 min.) and then 25° (1 hr.) give 2 : 5-*diketo*-3-*salicylidenechroman* (IV) (20%), yellow, m.p. 175°, and other products. 1 mol. each of (IV) and (III) in boiling EtOH (5 hr.) give colourless 4-4′-*hydroxycoumarinylcoumarino*-4′ : 3′-2 : 3-1 : 4-*benzpyran* (V) (76·3%), m.p. 245° (decomp.), also obtained (44%) from (III) (0·031) and (II) (0·019 mol.) in boiling EtOH (1 hr.) or (73·2%) by boiling (IV) in EtOH for 13·5 hr. The structure of (V) is proved by electrometric titration (one deflexion; at pH 5·7), by its anticoagulant activity, and conversion by NH_2Ph at 180° into the anil of (II). Similar reactions of (II) with 2 : 4 : 1-$(OH)_2C_6H_3$·CHO lead to the 7-*OH*-derivative, m.p. 251° (decomp.) [*acetate*, m.p. 236° (decomp.); *Me ether*, m.p. 301—304° (decomp.)], of (V) and 2 : 4-*diketo*-3-2′ : 4′-*dihydroxybenzylidenechroman*, decomp. 224°. 4-Hydroxy-6-methylcoumarin and (IV) in hot EtOH (5 hr.) give the 6′- and 6″-*Me* derivative (61·7%), m.p. 277—278° (decomp.), of (V). Simple bis-condensation of RCHO (0·5—0·7) and (II) (1 mol.) in boiling EtOH leads to 3 : 3′-ethylidene- (67%), m.p. 176—178° (lit. 165°), 3 : 3′-*propylidene*- (69%), m.p. 144—145° (*Me*$_2$ *ether*, m.p. 129°), 3 : 3′-n- (86%), m.p. 123—124° (*Me*$_2$ *ether*, m.p. 118—120°), and 3 : 3′-iso-*butylidene*- (78%), m.p. 199—200° (*Me*$_2$ *ether*, m.p. 214—215°), 3 : 3′-n- (75%), m.p. 113° (*Me*$_2$ *ether*, m.p. 129—130°), and 3 : 3′-iso-*pentylidene*-, m.p. 142—143° (*Me*$_2$ *ether*, m.p. 148°), 3 : 3′-n-*hexylidene*- (prep. in presence of 0·25 mol. of $AlCl_3$) (18%), m.p. 104—105° (*Me*$_2$ *ether*, m.p. 113—115°), 3 : 3′-*benzylidene*- (91%), m.p. 228—229° (*Me*$_2$ *ether*, m.p. 181—183°), 3 : 3′-β-*phenylethylidene*- (40%), m.p. 175—177°, 3 : 3′-γ-*phenylpropylidene*- (85%), m.p. 197—198° (*Me*$_2$ *ether*, m.p. 170—173°), 3 : 3′-p-*anisylidene*- (80%), m.p. 242° (decomp.) (*Me*$_2$ *ether*, m.p. 170—171°), 3 : 3′-4″-*hydroxy*-3″-*methoxybenzylidene*- (93%), m.p. 213—215°, 3 : 3′-3″ : 4″-*methylenedioxybenzylidene*- (67%), m.p. 256° (decomp.), 3 : 3′-p-*dimethylaminobenzylidene*- (76%), m.p. 210° (decomp.), and 3 : 3′-*carboxymethylene*- (prep. from CHO·CO_2H in boiling H_2O; 76%), m.p. 244—245° (*Me*$_2$ *ether Me* ester, m.p. 160—161°), -*bis*-4-*hydroxycoumarin*. $[CH_2]_4(CHO)_2$, (II), and a little $H_2C_2O_4$ in hot EtOH give 3 : 3′ : 3″ : 3‴-*hexamethylenetetrakis*-4-*hydroxycoumarin* (38%), m.p. 219—220° (*Me*$_4$ *ether*, m.p. 230—232°). The ethers are obtained by CH_2N_2.



(V.)



(VII.)

III. 3 : 3′-Methylenebis-4-hydroxycoumarin (VI) is not dehydrated by Ac_2O–C_5H_5N (cf. A., 1941, II, 202) but with $KHSO_4$ at 270°, red P–I–AcOH–H_2O at 155—165°, or $(OPh)_2POCl$–C_5H_5N at room temp. gives 4 : 4′-*epoxy*-3 : 3′-*methylenebiscoumarin* [3 : 2-5 : 6-*di*-(3′ : 4′-*coumarino*)-4-*pyran*] [(VII), R = H], m.p. 321—323° (decomp.). (VII) are obtained from 3 : 3′-alkylidene- and 3 : 3′-arylidene-analogues of (VI) by Ac_2O–C_5H_5N at room temp., there being thus obtained derivatives of (VII) in which R = *Me*, m.p. 322—323° (decomp.), *Et*, m.p. 292—294° (decomp.), *Pr*$^{\alpha}$, m.p. 246° (decomp.), *Pr*$^{\beta}$, m.p. 303°, *Bu*$^{\alpha}$, m.p. 231°, *Bu*$^{\beta}$, m.p. 290°, n-*amyl*, m.p. 182°, *Ph*, m.p. 393—395°, *CH*$_2$*Ph*, m.p. 385° (decomp.), *Ph*·[*CH*$_2$]$_3$, m.p. 243—245°, p-*anisyl*-, m.p. 345° (decomp.), 3 : 4 : 1-

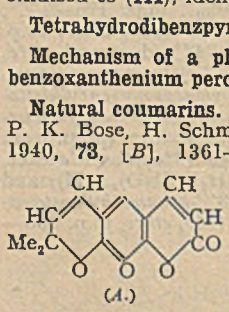
$OMe{\cdot}C_6H_3(OAc)$· (from 3 : 3′-*vanillylidenebis-4-hydroxycoumarin* after acetylation thereof), m.p. 288—289°, and 3 : 4 : 1-$CH_2O_2{:}C_6H_3$, m.p. 355—356°. Dehydration is the easier the larger is R. Mono-*O*-Me, -Bz, and PO_3Me_2 derivatives of (**VI**) give (**VII**) by loss of MeOH, BzOH, and Me_2HPO_4, respectively. Diacyl derivatives of (**VI**) and its analogues resist dehydration so that Ac_2O–C_5H_5N probably effects it by way of the monoacetate. PCl_5 and (**VI**) in C_6H_6 give a mixture, converted by hot MeOH into the 4-PO_3Me_2 derivative (**VIII**), m.p. 186—187°, of (**VI**); this is hydrolysed to (**VI**) by hot 3% HCl–MeOH but is converted in 94—97% yield into (**VII**), R = H, by hot NaOMe–MeOH or aq. KOH at 25° or, less well, by heating at 200°. 0·5N-NaOMe converts (**VII**), R = H, into the 4-*Me ether* (**IX**), m.p. 171—172°, of (**VI**); with CH_2N_2 this gives the 4 : 4′-Me_2 ether but at 180° regenerates (**VII**), R = H. The Na_1 salt (prep. by 1 equiv. of hot, aq. 0·05N-NaOH) of (**VI**) gives the Ag_1 salt, which with a deficiency of BzCl and $CaSO_4$ in C_6H_6 at room temp. gives the 4-*Bz* derivative, m.p. 225—229°; at > the m.p. this gives BzOH and (**VII**), R = H, with 1 mol. of NaOMe–MeOH at 65° gives a mixture of (i) (**VII**), R = H, and NaOBz with (ii) MeOBz and the Na salt of (**VI**). CH_2N_2–Et_2O converts (**VIII**) into the 4-*Me ether* 4′-PO_3Me_2 derivative, m.p. 140—141°, which is also obtained from (**IX**) by $POCl_3$–C_5H_5N at 0° and then MeOH. The epoxy-ring of (**VII**) is stable to aq. alkali or acid or boiling NH_2Ph, but is opened by NaOMe (see above); fusion with KOH gives a small amount of *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$. (**VII**) give no colour with $FeCl_3$, give a yellow to orange solution in conc. H_2SO_4, and have no anticoagulant action. Prep. of (**VII**), R = Ph, by dehydration by boiling 58% HBr–AcOH is described. The 4-Et_1 *ether*, m.p. 163—166°, of (**VI**) and 3 : 3′-*ethylidenebis-4-hydroxycoumarin* 4-Me_1 *ether*, m.p. 154—155°, are also prepared. R. S. C.

Egonol. XIII. 4-Bromo- and 3-nitro-acetylegonol and a new degradation of the 3-nitrofuran ring. S. Kawai, T. Nakamura, Y. Kitazawa, and K. Komatsu (*Ber.*, 1940, **73**, [*B*], 1328—1337).—3-Nitroacetylegonol (**I**) is converted by boiling 2% KOH–EtOH into KNO_2, piperonylic acid, *α-keto-β-ethoxy-α-3 : 4-methylenedioxyphenyl-β-2-hydroxy-3-methoxy-5-γ-hydroxy-n-propylphenylethane*, m.p. 147° (non-cryst. oxime), and an oily material not identical with styraxinolaldehyde and from which the *di-p-nitrobenzoate* of 2-methoxy-6-ethoxymethyl-4-γ-hydroxy-*n*-propylphenol, m.p. 130—130·5°, is derived. (**I**) and boiling 1·7% KOH–MeOH afford only 3-nitroegonol, m.p. 151°. 4-*Bromo-3-nitroacetylegonol* (**II**), m.p. 139°, is obtained from (**I**) and Br in AcOH at room temp. or by addition of HNO_3 (*d* 1·4) to 4-bromoacetylegonol in well-cooled AcO. (**II**) is transformed by boiling NaOEt–EtOH into 4-*bromo-3-nitro-2-hydroxy-2 : 3-dihydroegonol*, m.p. 166·5°, converted by boiling 2N. aq. KOH into 5-*bromo-2-methoxy-6-hydroxymethyl-4-γ-hydroxy-n-propylphenol*, m.p. 129·5° (*tri-p-nitrobenzoate*, m.p. 189·5°), which is methylated and oxidised ($KMnO_4$ in $COMe_2$) to 2-bromo-4 : 5-dimethoxybenzene-1 : 3-dicarboxylic acid (**III**), identified as the *diphenacyl* ester (**IV**), m.p. 153·5°. 6-Bromovanillin is transformed by $CH_2{:}CH{\cdot}CH_2Br$ and dry K_2CO_3 in boiling anhyd. $COMe_2$ into the *allyl ether*, m.p. 89°, isomerised at 230—250° to 6-*bromo-5-allylvanillin*, m.p. 134°. This is transformed into the *Me ether*, m.p. 63—64°, which is oxidised to (**III**), identified as (**IV**). H. W.

Tetrahydrodibenzpyran.—See B., 1944, III, 74.

Mechanism of a photo-disproportionation reaction [13-phenyldibenzoxanthenium perchlorate].—See A., 1944, I, 110.

Natural coumarins. LIV. Constitution of luvangetin. E. Späth, P. K. Bose, H. Schmid, E. Dobrovolny, and A. Mookerjee (*Ber.*, 1940, **73**, [*B*], 1361—1368).—Luvangetin (**I**) is *A*. The finely-divided ripe fruits of *Luvanga scandens*, Ham., are extracted with Et_2O, the extract is subjected to the lactone separation, and the total non-phenolic coumarins are separated by distillation in a high vac., whereby xanthotoxin, xanthyletin, and (**I**) are obtained; *iso*pimpinellin is also present. (**I**), m.p. 108—109°, is optically inactive, contains 1 OMe, and does not react with carbonyl reagents. It cannot be acetylated. It dissolves slowly in dil. aq. KOH, giving a yellow K salt which regenerates (**I**) when acidified. It is not dehydrogenated by Pd-sponge at 180°, 200°, or 240—250°. (**I**) is rapidly hydrogenated (Pd-sponge in AcOH at 16°) to *dihydroluvangetin*, m.p. 130°, which does not give $(CH_2{\cdot}CO_2H)_2$ when oxidised, and then much more slowly to *tetrahydroluvangetin*, m.p. 99°, which gives $(CH_2{\cdot}CO_2H)_2$ when treated with HNO_3 (*d* 1·4). (**I**) is converted by successive treatments with red P and 48% HBr at 150°, CH_2N_2 in MeOH–Et_2O, NaOH and Me_2SO_4, and 3% aq. NaOH into 2 : 3 : 4 : 1-$(OMe)_3C_6H_2{\cdot}CO_2H$. Ozonisation of (**I**) and decomp. of the ozonide by boiling H_2O leads to 7-*hydroxy-8-methoxycoumarin-6-aldehyde*, m.p. 197·5—198·5° (vac.), also obtained by ozonisation of xanthotoxin. $OH{\cdot}CMe_2{\cdot}CO_2H$ is obtained by oxidation of (**I**) by $KMnO_4$. H. W.


(A.)

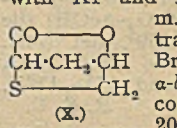
Tetramethylpopulnetin, m.p. 164—166°.—See A., 1944, III, 384.

Thiophan compounds. II. Thiophan-3-one. P. Karrer and H. Schmid. **Thiophan compounds. III.** H. Schmid. **Thiophan compounds. IV.** P. Karrer and F. Kehrer (*Helv. Chim. Acta*, 1944, **27**, 116—123, 124—127, 127—142, 142—151).—II. I·$[CH_2]_2$·COCl (**I**), b.p. 71—75°/11 mm., obtained from I·$[CH_2]_2{\cdot}CO_2H$ and $SOCl_2$ in 90% yield, is converted by CH_2N_2 in Et_2O followed by HCl into CH_2Cl *β-iodoethyl ketone*, m.p. 54—55°, which can be kept only when pure. Gradual addition of Na_2S to a solution of it in much EtOH leads to *thiophan-3-one* (**II**), b.p. 84—85°/24 mm., separated as the *semicarbazone*, m.p. 191—192° (decomp.). Smaller yields are obtained if (**I**) is replaced by Cl·$[CH_2]_2$·COCl probably because of the too great differences in the reactivities of the Cl atoms. Cl·$[CH_2]_2{\cdot}CO_2Na$, SH·$CH_2{\cdot}CO_2H$, and KOH in boiling H_2O afford $CO_2H{\cdot}CH_2{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 94° (yield nearly quant.), converted by HCl–EtOH into the Et_2 ester, b.p. 148—150°/10 mm., which is ring-closed by NaOEt or $NaNH_2$ to Et 3-ketothiophancarboxylate (**III**), b.p. 123—127°/11 mm. This gives a red-violet colour with $FeCl_3$ and is hydrolysed and decarboxylated by boiling 10% H_2SO_4 to (**II**). Methylation and subsequent decarboxylation of (**III**) gives 4-methylthiophan-3-one (**IV**), isolated as the *semicarbazone*, decomp. 192·5—193·5°.

II. SH·$[CH_2]_2{\cdot}CO_2H$ is converted by boiling abs. EtOH–H_2SO_4 under CO_2 into *Et β-thiolpropionate*, b.p. 77·5°/20 mm., which is transformed by CHMeBr·CO_2Et and NaOEt in abs. EtOH into Et_2 *sulphido-α-propionate-β-propionate*, b.p. 149—153°/10·5 mm. This is cyclised by $NaNH_2$ in abs. EtOH at 40—50° to *Et 3-keto-2-methylthiophan-4-carboxylate*, b.p. 125—128° (bath)/9 mm., which gives a marked red-violet colour with $FeCl_3$. This is hydrolysed and decarboxylated by boiling 10% H_2SO_4 to 2-*methylthiophan-3-one*, b.p. 90—100° (bath)/11 mm. [*semicarbazone*, m.p. 183—184° (decomp.)], thus indirectly establishing the structure of (**IV**). The isolation of two isomeric *phenylhydrazones*, m.p. 141·5—142·5° and 167° respectively, proves that (**III**) is a mixture of Et 3-ketothiophan-2- and -4-carboxylate.

III. Br·$[CH_2]_4$·Br, b.p. 78—81°/11 mm., obtained in 58% yield from $[CH_2]_4(CO_2Ag)_2$ and Br in CCl_4, is converted by NaOMe in MeOH–C_6H_6 into *Me δ-bromo-n-butyl ether*, b.p. 70—82°/34—35 mm., which is transformed with aid of $CHNa(CO_2Et)_2$ into Et_2 *δ-methoxybutylmalonate*, b.p. 146°/8·5 mm., hydrolysed by alkali to the non-cryst. *acid*. This is converted by Br in Et_2O–CCl_4 into *α-bromo-δ-methoxybutylmalonic acid*, m.p. 122—123° (decomp.), which passes at 120—130°/vac. into *α-bromo-ε-methoxyhexoic acid*, b.p. 124—128° (bath)/0·08 mm. The *Et* ester, b.p. 128—132°/10 mm. (corresponding *Me* ester, b.p. 120—124°/10 mm.), is condensed with SH·$[CH_2]_2{\cdot}CO_2Et$ by NaOEt–EtOH to Et_2 *sulphido-β-propionate α-ε-methoxyhexoate*, b.p. 145—148°/0·02 mm., cyclised by NaOMe in PhMe at 45—50° to *Et 3-keto-2-δ-methoxy-n-butylthiophan-4-carboxylate* (**V**), b.p. 115° (bath)/0·01 mm. [*oxime* (**VI**), b.p. 145—155° (bath)/0·02 mm.; non-cryst. *phenylhydrazone*], which gives a marked red-violet colour with $FeCl_3$ in EtOH–H_2O. (**VI**) is reduced by Al–Hg in moist Et_2O to *Et 3-amino-2-δ-methoxy-n-butylthiophan-4-carboxylate*. (**V**) is hydrolysed and decarboxylated by boiling H_2O–AcOH–H_2SO_4 under N_2 to 2-*δ-methoxy-n-butylthiophan-3-one* (**VII**), b.p. 102—103°/0·05 mm. This is oxidised by Br in aq. MeOH containing $CaCO_3$ to 4-hydroxy-2-δ-methoxy-*n*-butylthiophan-3-one, which strongly reduces Ag_2O–NH_3 but could not be purified; it is converted by NH_2OH,HCl and KOAc in H_2O at 40° into 2-*δ-methoxy-n-butylthiophan-3 : 4-dionedioxime* (**VIII**), m.p. 189° [corresponding *phenylosazone* (**IX**), m.p. 141° (decomp.)]. (**VII**) could not be converted into 3 : 4-diamino-2-δ-methoxy-*n*-butylthiophan. Reduction of (**VII**) by Na–Hg in EtOH–AcOH at ~50° leads to 4(3)-*amino-3(4)-hydroxy-2-δ-methoxy-n-butylthiophan*, m.p. 107—108°, which is very hygroscopic and avidly absorbs atm. CO_2; under completely anhyd. conditions the product is non-homogeneous. Na in boiling EtOH reduces (**VIII**) to an oil with 8·6% N. H_2 at 70°/24 atm. in abs. EtOH containing Raney Ni does not attack (**VIII**). With Al–Hg and H_2O in EtOH–Et_2O (**VIII**) appears to give 3(4)-*amino-2-δ-methoxy-n-butylthiophan*, m.p. 157°, softens at 151°. Attempted reduction of (**IX**) by Na–Hg in EtOH–AcOH gives ill-defined results. Me_2 *sulphido-β-α-methoxypropionate-α-ε-methoxyhexoate*, b.p. 140—145° (bath)/0·005 mm., is cylised by NaOEt in PhMe at 18° and then at 40° to a non-homogeneous product, hydrolysed and decarboxylated to (**VII**). (**II**) is converted by $C_5H_{11}{\cdot}O{\cdot}NO$ and conc. HCl into 2 : 4-*dioximinothiophan-3-one*, decomp. 210°, becoming increasingly discoloured at >170°. (**III**) couples with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ in aq. EtOH to a mixture, m.p. 145—150°, of Et 2-*p*-nitrobenzeneazo-3-ketothiophan-4-carboxylate and Et 4-*p*-nitrobenzeneazo-3-ketothiophan-2-carboxylate with some *Et 4-p-nitrobenzeneazo-3-ketothiophan-4-carboxylate*, m.p. 168—169°. Reduction of these dyes gives *p*-$C_6H_4(NH_2)_2$ as sole recognisable product.

IV. $CO{<}CHBr{\cdot}CH_2{>}O{>}CH{\cdot}CH_2Cl$ is converted by successive treatment with KI and Na_2S into *4-hydroxythiophan-2-carboxylactone* (**X**), m.p. 60·5°, in very poor yield. $[CH_2]_4(CO_2H)_2$ is transformed by successive treatments with $SOCl_2$, Br at 60° with irradiation, and EtOH into Et_2 *α-bromoglutarate*, b.p. 136—144°/11 mm., which is condensed with *Et β-bromopropionate*, b.p. 77—78°/20 mm., to Et_3 *sulphido-β-propionate-α-glutarate*, b.p. 150—153°/0·02 mm., which is cyclised by NaOEt in PhMe at room


(X.)

temp. and then at 55—60° to Et_2 3-*ketothiophan*-4-*carboxylate*-2-β-*propionate* (**XI**), b.p. 130—133°/0·04 mm., hydrolysed and decarboxylated by boiling 10% H_2SO_4 to 3-*ketothiophan*-2-β-*propionic acid* (**XII**), b.p. 132—135° (bath)/0·03 mm., m.p. 51° (*Me* ester). Attempts to convert (**XII**) into its :N·OH derivative were unsuccessful. (**XI**) couples with p-NO_2·C_6H_4·N_2Cl to (?) Et_2 4-p-*nitrobenzeneazo*-3-*ketothiophan*-4-*carboxylate*-2-β-*propionate*, which could not be reduced to the NH_2-ketone. Cautious bromination of (**XII**) in presence of $CaCO_3$ gives the unstable 4-Br-compound and thence 4-*hydroxy*-3-*ketothiophan*-2-β-*propionic acid*, m.p. 129—130° (slight decomp.). This is converted by NH_2OH,HCl and KOAc at 100° into 3 : 4-*dioximinothiophan*-2-β-*propionic acid*, decomp. 185—189° (corresponding *phenylosazone*, decomp. 112—115°), which could not be satisfactorily reduced to the diamine. (**XI**) is transformed by Br in light petroleum followed by boiling 10% H_2SO_4 into 3 : 4-*dihydroxythiophen*-2-β-*propionic acid*, decomp. 194—197°, which gives a blue-green colour with $FeCl_3$. H. W.

Synthesis of 3-alkylpiperidones. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 2458—2459).—CH_2:CH·CN and $CHNa(CO_2Et)_2$ in EtOH at 40° and then 65° give *Et* γ-*cyano*-α-*carbethoxy*-n-*butyrate* (40—45%), b.p. 175—180°/25 mm., which is hydrogenated and cyclised by H_2–Raney Ni (no solvent) at 100°/2000 lb. to yield *Et* 2-*piperidone*-3-*carboxylate* (57%), m.p. 78—79°, b.p. 205—215°/15 mm. With NaOEt and then EtI in boiling EtOH, this gives *Et* 3-*ethyl*-2-*piperidone*-3-*carboxylate* (66%), m.p. 46—49°, b.p. 190—198°/12 mm., hydrolysed by aq. KOH at 105° to the syrupy acid, which, when distilled, yields 3-*ethyl*-2-*piperidone*, m.p. 66—68°, b.p. 149°/15 mm. (reduced by Na–BuOH to 3-ethylpiperidine). Adding CH_2:CH·CO_2Me (**I**) to CN·CHNa·CO_2Et (**II**) in EtOH and then heating yields Et_2 α-*cyanoglutarate*, b.p. 180°/25 mm., which with H_2–Raney Ni in EtOH at 140°/2000 lb. gives *Et* 2-*piperidone*-5-*carboxylate*, m.p. 62—64°, b.p. 163°/2 mm. (partial decomp. at 20 mm.). Adding CH_2PhCl to the Na derivative from (**I**) and (**II**) in EtOH and then boiling gives Et_2 α-*cyano*-α-*benzylglutarate*, b.p. 187—195°/2 mm., converted by H_2–Raney Ni in EtOH at 165°/2000 lb. into *Et* 5-*benzyl*-2-*piperidone*-5-*carboxylate*, +H_2O, m.p. 64—68°, which is hydrolysed by 2% NaOH to the corresponding *acid*, m.p. 221—222°. R. S. C.

Synthesis of 4-phenylpiperidines. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 2459—2460).—CO_2Et·CH_2·CHPh·CH(CN)·CO_2Et (from CHPh:CH·CO_2Et and CN·CHNa·CO_2Et), b.p. 172—175°/2 mm., with H_2–Raney Ni at 140°/2000 lb. gives *Et* 4-*phenyl*-2-*piperidone*-5-*carboxylate* (67%), m.p. 102—103° (crude, 91—94°, ? stereoisomerides) (derived *acid*, m.p. 214—215°), which with Na–BuOH gives 4-phenylpiperidine-3-carboxylic acid [*hydrochloride* (**I**), yellow at 150°, sinters 250°, m.p. 257—259° (gas)]. With 40% CH_2O at 100°, (**I**) gives 4-*phenyl*-1-*methylpiperidine*-3-*carboxylic acid hydrochloride*, m.p. 219—222° (*Et* ester *hydrochloride*, m.p. 171—173°). *Et* γ-*cyano*-α-*carbethoxy*-β-*phenyl*-n-*butyrate* [from CHPh:CH·CN, $CH_2(CO_2Et)_2$, and NaOEt in boiling EtOH; 83% yield], m.p. 43—45°, b.p. 190—195°/0·5 mm., with H_2–Raney Ni at 155°/2000 lb. gives Et 4-phenyl-2-piperidone-3-carboxylate, a syrup, and 4-*phenyl*-2-*piperidone* (**II**), m.p. 137—139°. Na–BuOH reduces (**II**) to 4-phenylpiperidine, m.p. 57—60° (lit., 57—58°), b.p. 137—147°/21 mm. (and a base, m.p. 137°, b.p. 160—220°/18 mm.), the hydrochloride, sinters 110°, m.p. 164—165° (slow heating), 150° (decomp.; immediate), of which with an excess of aq. CH_2O at 100° gives 4-phenyl-1-methylpiperidine, b.p. 138—140°/17 mm. (*hydrochloride*, m.p. 185—187°), and (?) methylenebis-4-phenylpiperidine, m.p. 101—103°. R. S. C.

Two syntheses of β-1-benzoyl-4-piperidylpropionic acid. C. F. Koelsch (*J. Amer. Chem. Soc.*, 1943, **65**, 2460—2465).—Epichlorohydrin with H_2SO_4 in boiling MeOH gives OMe·CH_2·CH(OH)·CH_2Cl (**I**) (75—85%), b.p. 75—78°/12 mm., and CH_2Cl·CH(OH)·CH_2·O·SO_3H (deliquescent *Na* salt). With aq. NaCN at 44—46°, rising later to 50°, (**I**) gives β-*hydroxy*-γ-*methoxy*-n-*butyronitrile* (**II**) (77—92%), b.p. 133°/18 mm., which is converted into γ-*methoxycrotononitrile* (**III**), b.p. 175—185°, by distillation from K_2CO_3 (70% yield) or by acetylation (boiling Ac_2O) into β-*acetoxy*-γ-*methoxy*-n-*butyronitrile* (96%), b.p. 128—130°/21 mm. (hydrolysed by boiling 0·1N-NaOH in 1 min.), which yields (**III**) (83%) when distilled from a little KOAc. $CH_2(CO_2Et)_2$ or CN·CH_2·CO_2Et does not condense with (**II**), but $CHNa(CO_2Et)_2$ and (**III**) in hot EtOH give *Et* γ-*cyano*-α-*carbethoxy*-β-*methoxymethyl*-n-*butyric acid* (77%), b.p. 180—185°/20 mm., which with H_2–Raney Ni in 95% EtOH at 140—155°/2500 lb. gives *Et* 4-*methoxy*-2-*piperidone*-3-*carboxylate* (60%), b.p. 220—225°/30 mm., whence hydrolysis (aq. KOH) and distillation yields 4-*methoxymethyl*-2-*piperidone* (**IV**) (83%), m.p. 59—62°, b.p. 179—181°/21 mm. Na (4 atoms utilised)–BuOH reduces (**IV**) to 4-*methoxymethylpiperidine* (60—68%), hygroscopic, m.p. ~0°, b.p. 80—81°/27 mm. [*picrate*, m.p. 146—148°; *hydrochloride*, m.p. 150°; *hydrobromide* (**V**), m.p. 143°; p-NO_2·C_6H_4·CO derivative, m.p. 84—86°; *NO*-derivative, b.p. 158—160°, with Zn–H_2SO_4 at 55—60° gives the 1-NH_2-derivative, b.p. 100—115°/25 mm. (*hydrobromide*, m.p. 102—104°)]. (**V**) is converted by boiling 48% HBr in 10 min. into 4-*hydroxymethyl*-, m.p. 150—151°, and in 7 hr. into impure 4-bromomethyl-piperidine hydrobromide (**VI**), hygroscopic, identified by conversion by 5% NaOH into 1-azadi*cyclo*[1, 2, 2]heptane. 1-*Benzoyl*-4-*bromomethylpiperidide* (**VII**) [prep. from, best, pure (**VI**) by BzCl–aq. Na_2CO_3 at 0°; 73%], m.p. 88—90°, does not condense with the *Na* derivative of Et β-keto-β-4-quinolylpropionate [sulphate, m.p. 150° (decomp.); *picrate*, m.p. 160—163°] in EtOH and in Et_2CO_3 gives tars, but with the *Ag* derivative at 100° gives 1-*benzoyl*-4-*piperidylmethyl cinchonate*, m.p. 132—133° (*picrate*, sinters 165°, m.p. 170—172°), also obtained from (**VII**) and Ag cinchonate at 100°. Et cinchonate picrate, m.p. 183—185°, is described. $CHNa(CO_2Et)_2$ and (**VII**) (28 g.) in hot EtOH give a syrupy ester, which, when hydrolysed by NaOH–H_2O–EtOH and then heated at 185°, gives β-1-*benzoyl*-4-*piperidylpropionic acid* (**VIII**) (5·2 g.), m.p. 145—147°, and its Et ester (7·7 g.), b.p. 240—245°/6 mm. Pyridine-4-carboxylic acid (prep. from 4-methylpyridine by boiling aq. $KMnO_4$ in 45—62·4% yield) and H_2SO_4–EtOH give the Et ester (67%), which with NaOEt and EtOAc in boiling EtOH–Et_2O gives Et β-keto-β-4-pyridylpropionate (53·5%). With H_2–Raney Ni in EtOH at 100°/2200 lb. this gives Et β-4-pyridylhydracrylate, an oil (*hydrochloride*, sinters 153°, m.p. 155—157°), hydrolysed by hot HCl to β-4-*pyridylhydracrylic acid*, sinters 193°, m.p. 201—202° [purified by way of the *Cu* salt, m.p. 207—208° (decomp.); *hydrochloride*, sinters 170°, m.p. 173—175°]. 1 : 1 (vol.) H_2SO_4–H_2O at the b.p. then gives β-4-pyridylacrylic acid, brown at 190°, m.p. 280—285° (decomp.) [lit., 296° (corr.)] {*Cu* salt, brown at 235°, m.p. 255° (gas) [lit., 296° (corr.)]}, which with Na–EtOH and then BzCl–NaOH gives (**VIII**). R. S. C.

2-Chloroacetylpyrrole. F. F. Blicke, J. A. Faust, J. E. Gearien, and R. J. Warzynski (*J. Amer. Chem. Soc.*, 1943, **65**, 2465—2466).—2-Chloroacetylpyrrole (**I**), m.p. 118—119° (lit., 115°), is obtained from the product of interaction of pyrrole and MgEtBr and CH_2Cl·CN in Et_2O at 0° and then the b.p. (16% yield) or from pyrrole, CH_2Cl·CN, and HCl in Et_2O (20% yield). Use of MgEtI gives only 2-acetylpyrrole. NaI–$COMe_2$ converts (**I**) into 2-iodoacetylpyrrole (95%), m.p. 130—131° (lit., 81°), which with AgOAc in boiling C_6H_6 gives 2-*acetoxyacetylpyrrole* (90%), m.p. 70—71°. R. S. C.

Pyridinesulphonamide.—See B., 1944, III, 73.

Vitamin-B_6.—See B., 1944, III, 74.

Boron fluoride as a condensing agent in the Fischer indole synthesis. H. R. Snyder and C. W. Smith (*J. Amer. Chem. Soc.*, 1943, **65**, 2452—2454).—BF_3 or BF_3,Et_2O is usually approx. as effective (16 examples) as other reagents in converting hydrazones into indoles, and the products are easily isolated. In successful cases, a coloured complex is first formed which is then decomposed by heat; a solvent (AcOH) may be used. The colour indicates the following reaction mechanism: CRMe:N·NHAr⟶BF_3 (**I**) ⇌ CHMeR·N:NAr⟶BF_3; (**I**) → CH_2:CR·NH·NHAr→BF_3 → *o*-NH_2·CR:CH·C_6H_4·NH_2→BF_3 etc. → indole derivative. This is in line with recovery of phenylhydrazones in other forms, *e.g.*, α-keto-γ-butyrolactonephenylhydrazone, m.p. 100·5°, and *Et* α-*keto*-γ-*cyanobutyratephenylhydrazone*, m.p. 84·5°. 3-*iso*Propylindole, b.p. 138—142°/6 mm., gives a picrate, m.p. 117·5° (lit., 98—99°). Failures of the BF_3 synthesis include CHMe:N·NHPh and CMe_2:N·NHPh. R. S. C.

Improved synthesis of quinaldines and 3-alkylquinolines. W. P. Utermohlen, jun. (*J. Org. Chem.*, 1943, **8**, 544—549).—A suitable oxidising agent (*O*) is obtained by running $PhNO_2$ into 20% oleum at 20—30° and then heating the mixture at 60—70° until it is completely sol. in H_2O. The following methods are used: (*A*) adding the base to a mixture of *O* and H_2O, raising the temp. to 125°, adding the aldehyde diacetate gradually, and then slowly raising the temp. to 175° while allowing H_2O and AcOH to distil; (*B*) adding the aldehyde dropwise to a mixture obtained as under (*A*) and heated at 105—110° and finally to 135° with distillation of H_2O; (*C*) Doebner–von Miller method; (*D*) adding the aldehyde dipropionate slowly to a hot, stirred mixture of As_2O_5, H_2O, base, and conc. H_2SO_4. The following -quinolines are prepared (the name of the non-basic reactant, method of prep., and % yield being placed in brackets: 2-methyl- [CHMe:CH·CHO (**I**), *B*, 43; CHMe:CH·CH(OAc)$_2$ (**II**), *A*, 49·5]; 2 : 7-dimethyl- [(**II**), *A*, 47; (**I**), *B*, 62·5]; 7-chloro-2-methyl- [(**I**), *B*, 60]; 6-chloro-2-methyl- [(**II**), *A*, 55]; 2 : 6-dimethyl- [CHMe:CH·CH(O·COEt)$_2$, *A*, 49]; 6-nitro-2-methyl- [(**II**), *D*, 30]; 3-methyl-, b.p. 252—253° (picrate, m.p. 187·5°; *ethiodide*, m.p. 226·5°) [CH_2:CMe·CH(OAc)$_2$ (**III**), *A*, 49; CH_2:CMe·CH(O·COEt)$_2$ (**IV**), *A*, 46; CH_2:CMe·CHO (**V**), *B*, 30]; 3-ethyl-, b.p. 265—266° (picrate, m.p. 199°; *ethiodide*, m.p. 215°) [CH_2:CEt·CH(OAc)$_2$ (**VI**), *A*, 54; CH_2:CEt·CHO (**VII**), *B*, 42; (**VII**), *C*, 2·5]; 3 : 6-dimethyl-, b.p. 270—271·5°, m.p. 56·5° (picrate, m.p. 251°; *ethiodide*, m.p. 181°) [(**III**), *A*, 54]; 3 : 7-dimethyl-, b.p. 270—271·5°, m.p. 78·5° (picrate, m.p. 240·5°; *ethiodide*, m.p. 250°) [(**III**), *A*, 65; (**V**), *B*, 25]; 3 : 8-dimethyl-, b.p. 260—262° (picrate, m.p. 208·5°; *ethiodide*, m.p. 192°) [(**III**), *A*, 45]; 6-*nitro*-3-*methyl*-, m.p. 151 (picrate, m.p. 200°) [(**IV**), *D*, 35]; 7-chloro-3-methyl-, b.p. 142—144°/10 mm., m.p. 84·5° (corr.) (picrate m.p. 187·5°; *ethiodide*, m.p. 270°) [(**III**), *A*, 52]; 6-methyl-3-ethyl- b.p. 284—285·5° (picrate, m.p. 247°; *ethiodide*, m.p. 204°) [(**VI**), *A*,

32]; 7-methyl-3-ethyl-, b.p. 282—283° (picrate, m.p. 224·5°; *ethiodide*, m.p. 180°) [(VI), *A*, 34; (VII), *B*, 35]. M.p. are corr. H. W.

5- and 7-Trifluoromethylquinolines. H. Gilman and D. Blume (*J. Amer. Chem. Soc.*, 1943, **65**, 2467—2468).—*m*-$CF_3 \cdot C_6H_4 \cdot NH_2$ (0·4), glycerol (1·3), As_2O_5 (0·4), and H_2SO_4 (1·1 mol.) give, after boiling, a mixture, fractionation of which yields pure 7- (I) (31·8%), m.p. 66—68°, b.p. 219—221°/731 mm., and 5-*trifluoromethylquinoline* (5·7%), b.p. 214—215°/732 mm. (oxalate), the structure of which is proved by hydrolysis by boiling 80% H_2SO_4 to quinoline-7- and -5-carboxylic acid, m.p. 341—343° (lit., 338—340°), respectively. $Li \cdot C_6H_4Me$-*p* adds normally to (I) in Et_2O, yielding a product which with $PhNO_2$ in Et_2O gives 2-p-*tolyl*-7-*trifluoromethylquinoline* (61%), m.p. 131—133°. R. S. C.

αβ-Diamino-ketones. I. Reactions of heterocyclic *sec.*-amines with α-bromo-β-amino-ketones. N. H. Cromwell, C. E. Harris, and D. J. Cram (*J. Amer. Chem. Soc.*, 1944, **66**, 134—137).—The following reactions conform to the mechanism previously postulated (A., 1943, II, 243). α-Bromo-β-morpholino-β-phenylethyl Me ketone (I) with tetrahydroquinoline (II) [a weaker base than morpholine (III)] in EtOH (51% yield) or Et_2O (20·4% yield) at room temp. gives α-*morpholino*-β-*tetrahydroquinolino*-β-*phenylethyl Me ketone*, m.p. 173°, hydrolysed by acid to PhCHO, (II), and morpholinoacetone (*oxime*, m.p. 104—106°). With piperidine (IV), which is weaker than (III), in EtOH, (I) gives an inseparable mixture of amines but the mixed product produced in Et_2O yields 10% of β-*piperidino*-α-*morpholino*-β-*phenylethyl Me ketone*, m.p. 123°. α-Bromo-β-piperidino-β-phenylethyl Me ketone with (III) in EtOH (32%) or Et_2O (90·2% yield) gives α-*piperidino*-β-*morpholino*-β-*phenylethyl Me ketone*, *forms*, m.p. 117° and 101° (hydrolysed to α-piperidinoacetone). CHPh:CBr·COPh and tetrahydro*iso*quinoline (V) in Et_2O–light petroleum at −10° give α-*bromo*-β-*tetrahydroisoquinolino*-β-*phenylpropiophenone* (VI) (85%), m.p. 117°, which with NaOEt gives (?) α-tetrahydro*iso*quinolino-β-phenylacrylophenone, an oil, but in EtOH at room temp. slowly (cf. *loc. cit.*) yields αβ-*ditetrahydroisoquinolino*-β-*phenylpropiophenone*, m.p. 184—186°, also obtained (m.p. 187°; 57% yield) from CHPhBr·CHBr·COPh by (V) in EtOH at 0° and then room temp. With (III), which is weaker than (V), (VI) in EtOH at room temp. gives β-*morpholino*-α-*tetrahydroisoquinolino*- (30%), m.p. 177° (hydrolysed to ω-tetrahydro*iso*quinolinoacetophenone), and with (II) (a weaker base) gives α-*tetrahydroisoquinolino*-β-*tetrahydroquinolino*-β-*phenylpropiophenone* (47%), m.p. 164°. α-Bromo-β-morpholino-β-phenylpropiophenone with (V) gives a mixed product, whence 13% of impure α-morpholino-β-tetrahydro*iso*quinolino-β-phenylpropiophenone, m.p. 163°, is obtained. α-Bromo-β-piperidino-β-phenylpropiophenone with (V), which is weaker than (IV), gives α-*piperidino*-β-*tetrahydroisoquinolino*- (37%), m.p. 165° (identified by hydrolysis), and with *cyclo*hexylamine, which is weaker than (IV), gives α-*piperidino*-β-cyclo*hexylamino*-β-*phenylpropiophenone* (20%), m.p. 155°. M.p. are corr. R. S. C.

Purification of 2-nitro-5-amino-7-ethoxyacridine. A. Albert and W. Gledhill (*J.S.C.I.*, 1944, **63**, 96).—2-Nitro-7-ethoxyacridine, occurring as impurity in the prep. of the 2-nitro-5-amino-compound (I) (cf. A., 1942, II, 425), may be removed most suitably as its EtOH-sol. Na salt. A more conc. aq. solution of (I) may be obtained by dissolving in boiling H_2O containing lactic acid. F. R. S.

Transamination reaction. Effect of various nuclear substituted α-amino-α-phenylacetic acids on the course of the reaction.—See A., 1944, II, 161.

Pyrimidines. CLXXXI. Reactions characterising the oxide of 5-chloro-6-hydroxy-6-methyl-1 : 5-dic*yclo*uracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1944, **66**, 146—148; cf. A., 1943, II, 340).—The compound (I), $(NH<^{CO \cdot CCl}_{CO \cdot N}>CMe)_2O$, with H_2O_2 in conc. HCl at room temp. gives 5 : 5-*dichloro*-6-*hydroxyhydro*-*orotic acid* (II), $NH<^{CO \cdot CCl_2}_{CO \cdot NH}>C(OH) \cdot CO_2H$, m.p. 182—183° (gas), reduced by red P–HI to 5-chloro-orotic acid (III). With conc. HNO_3 at room temp. (I) gives (III), and with Br–H_2O at room temp. gives 5-*chloro*-5-*bromo*-6-*hydroxyhydro*-*orotic acid*, m.p. 192—193°. $Ba(OH)_2$ converts (II) or (IV) into dialuric acid, the colour test for which is thus not sp. R. S. C.

Acid hydrolysis of a 5 : 5-dichlorohydroxy-6-arylhydrouracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1944, **66**, 148—150).—6-Phenyluracil and H_2O_2–conc. HCl give 5 : 5-*dichloro*-6-*hydroxy*-6-*phenylhydrouracil*, m.p. 209—210° (decomp.), which with red P–HI at 100° gives 5-*chloro*-6-*phenyluracil* (I), m.p. 260—261°, and in hot conc. HCl gives NH_4Cl and BzOH (100%) with a trace of (I). R. S. C.

Biological effects of benziminazole and their reversed by purines. D. W. Woolley (*J. Biol. Chem.*, 1944, **152**, 225—232).—See A., 1944, III, 435).—5-*Aminobenziminazole*, m.p. 105—106° (uncorr.), was prepared by condensing 1 : 2 : 4-$C_6H_3(NH_2)_3$ with HCO_2H. It differed (mixed m.p. depression) from the *compound*, m.p. 104—105°, obtained by reducing Bamberger and Berlé's nitrobenziminazole (A., 1893, i, 435); these are therefore the 4-NH_2- and 4-NO_2-compounds.

Isatoic anhydride. I. Reactions with primary and secondary amines and with some amides. R. H. Clark and E. C. Wagner (*J. Org. Chem.*, 1944, **9**, 55—67).—Isatoic anhydride (I) is conveniently obtained by passing $COCl_2$ into a solution of *o*-$NH_2 \cdot C_6H_4 \cdot CO_2H$ in dil. HCl at 50°. Strongly basic primary amines react readily with (I) at room temp. to 130° in most cases and some even in H_2O. Aromatic primary amines with *o*-substituents or with negative substituents in *o*- and *p*-substituents react less readily and yield largely or almost entirely "abnormal" products. The amount of CO_2 evolved in the "abnormal" reaction indicates the nearly quant. participation of (I). The normal change is (I) + NH_2R → *o*-$NH_2 \cdot C_6H_4 \cdot CO \cdot NHR$ (II) + CO_2; the "abnormal" reaction follows thus: (I) + (II) → $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NHR$ → $NH_2 \cdot C_6H_4 \cdot CO \cdot [NH \cdot C_6H_4 \cdot CO]_x \cdot NHR$. In support of this mechanism it is found that no isolable normal product is obtained from equiv. amounts of (I) and *o*-$C_6H_4Br \cdot NH_2$ whereas some *anthranil*-o-*bromophenylamide*, m.p. 115·5—116·0°, is obtained if a large excess of base is used. The interaction of equiv. amounts of (I) and NH_2Ph is normal but when 2 equivs. of (I) are used the product is amorphous. When pure *o*-$NH_2 \cdot C_6H_4 \cdot CO \cdot NHPh$ (III) a (normal product) is heated with an equiv. amount of (I), the theoretical amount of CO_2 is evolved and the abnormal product results. Hydrolysis of the "abnormal" product from (I) and (III) by conc. HCl under pressure gives *o*-$NH_2 \cdot C_6H_4 \cdot CO_2H$ and NH_3, the amount of the latter indicating $x = 2$. The following *anthranil-amides* are obtained: -ethyl-, m.p. 102—103° (uncorr.); -n-*propyl*-, m.p. 98·5—100°; -n-*butyl*-, m.p. 83—84°; -n-*amyl*-, m.p. 80·0—81·0°; -iso*amyl*-, m.p. 69—70°; -cyclo*hexyl*-, m.p. 155·5—156·5°; -*benzyl*-, m.p. 123·0—123·5°; -phenyl-, m.p. 125·5—126·5°; -*p*-tolyl-, m.p. 150—151·0°; -*p*-anisyl-, m.p. 125·0—126·0°; -m-*bromophenyl*-, m.p. 147·5—149°; -*p*-bromophenyl-, m.p. 148·0—149·0°; -m-*chlorophenyl*-, m.p. 130·0—131·5°; -p-*chlorophenyl*-, m.p. 140—141·5°; -2 : 4-dimethylphenyl-, m.p. 137—138° (uncorr.); -*o*-carboxyphenyl-, m.p. 205·5—206·5°; -2-*pyridyl*-, m.p. 132·0—133·0°; -4-*methyl*-2-*thiazolyl*-, m.p. 117·5—118·5°; -6-*methyl*-2-*benzthiazolyl*-, m.p. 186·0—187·0°; -*phenylimino*-, m.p. 172·0—173·0° (uncorr.); -*hydroxy*-, m.p. 78° (uncorr.); -*o*-carbethoxyphenyl-, m.p. 93·5—94·5°; -o-*carbomethoxyphenyl*-, m.p. 114·5—115·5°. M.p. are corr. unless otherwise indicated. Reaction is largely abnormal with *m*-2- and *m*-5-xylidine, *o*-$NH_2 \cdot C_6H_4 \cdot CO \cdot NH_2$, *o*- and *p*-$NO_2 \cdot C_6H_4 \cdot NH_2$. $(CH_2 \cdot NH_2)_2$ and $CH_2(CH_2 \cdot NH_2)_2$ give the corresponding 5-*dianthranoyldiamines*, m.p. 242·0—243·0° (uncorr.) and 183·0—184·0° respectively. When equiv. amounts of (I) and *sec.* amines are heated CO_2 is evolved but "normal" products are obtained usually in small yield if at all, the reaction products being generally resinous, gummy mixtures from which well-defined compounds cannot be isolated. If the base is kept in marked excess and conditions for rapid action are chosen moderate yields of normal products are sometimes secured. The following *anthranil-amides* are thus obtained: -*diethyl*-, b.p. 147—148°/1 mm., 158—160°/4 mm., m.p. 70—70·5° (uncorr.); -*di*-n-*propyl*-, b.p. 174—177°/4 mm. (*picrate*, m.p. 104—104·5°); -*piperidyl*-, b.p. 160—163°/1—2 mm., m.p. 73·0—74·0°; -phenylmethyl-, m.p. 127—127·5°; -*phenylethyl*-, m.p. 102·5—103°; -*phenyl*-n-*propyl*-, m.p. 75·5—76·5°. (I) and NH_2Ac at 180° slowly yield amorphous products, apparently mixtures. Benzoylenecarbamide with considerable amorphous material results from (I) and $CO(NH_2)_2$ or $NH_2 \cdot CO_2Et$. 3 : 4-Dihydroquinazol-4-one, m.p. 136—136·5°, and its *p*-tolyl, m.p. 144—145°, and *p*-anisyl, m.p. 194—195°, derivatives are obtained from the requisite base, (I), and boiling $CH(OEt)_3$. Attempts to extend the synthesis by use of $CMe(OEt)_3$ were unsuccessful. H. W.

Transformation of verdohæmochromogens into monoazahæmins. R. Lemberg (*Austral. J. Exp. Biol.*, 1943, **21**, 239—247; cf. A., 1935, 884).—A modification of the method of preparing pyridine verdohæmochromogen and verdomesohæmochromogen is described. At room temp. in presence or absence of O_2, NH_3 (but not NH_2Me) converts these compounds into monoaza-hæmin and -mesohæmin respectively. N_2H_4,H_2O in AcOH (but not conc. H_2SO_4) removes Fe from monoazahæmins, the monoazaporphyrins thus obtained being identical with Fischer's monoimidoporphyrins. The spectroscopic properties of some monoazahæmatin compounds are described and an explanation is suggested of the stability of the Fe linkage in azahæmins and its instability in verdohæmatins. W. McC.

Tetrahydrofuryl-amino-alcohols. A. Burger and G. H. Harnest (*J. Amer. Chem. Soc.*, 1943, **65**, 2382—2383).—2-Furoyl chloride and CH_2N_2–Et_2O at 0° and then room temp. give a solution of crude diazoketone, which with conc. aq. HCl gives 2-chloroacetylfuran (88%), m.p. <0°. With piperidine (2·5 mols.) in Et_2O at 0° and then room temp., this gives 2-*piperidinoacetylfuran* (73%), b.p. 139—140°/4 mm., which in presence of Ni or Pt absorbs >3 mols. of H_2, but, as *hydrochloride*, m.p. 264—266° (decomp.), is reduced by boiling 3N-$Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ to 2-α-*hydroxy*-β-*piperidinoethylfuran* (38%), b.p. 127—128°/5 mm. (*hydrochloride*, m.p. 172—174°).

H_2–Raney Ni in EtOH at 1 atm. then yields 2-*α-hydroxy-β-piperidinoethyltetrahydrofuran* (64%), b.p. 125—126°/4 mm. (*hydrochloride*, m.p. 170—173°; *acetate hydrochloride*, m.p. 191—194°). The following are similarly prepared: 2-morpholino- (49%) (*hydrochloride*, m.p. 221—229°), and 2-4′-*methylpiperidino-acetylfuran* (51%), b.p. 133—139°/4 mm. (*hydrochloride*, m.p. 253—265°); 2-*α-hydroxy-β-morpholino-* (70%), m.p. 67—68°, b.p. 146—150°/1 mm. (*hydrochloride*, m.p. 185—186° (decomp.); *acetate hydrochloride*, m.p. 166—167° (decomp.)], and -*β*-4-*methylpiperidino-ethylfuran* (74%), m.p. 70—72°, b.p. 126—128°/4 mm. [*acetate hydrochloride*, m.p. 179—181° (decomp.)]; 2-*α-hydroxy-β-morpholino-* (41%), b.p. 138—140°/12 mm. (hygroscopic *hydrochloride*, m.p. 170—176°), and -*β*-4-*methylpiperidino-ethyltetrahydrofuran* (33%), b.p. 131—132°/4 mm. 3-Acetyl-2 : 5-dimethylfuran, paraformaldehyde, and $NHMe_2$,HCl give 3-*β-dimethylaminopropionyl*-2 : 5-*dimethylfuran hydrochloride*, m.p. 175—177°. R. S. C.

Substituted aminobenzfuranoquinolines. R. Adams, J. H. Clark, N. Kornblum, and H. Wolff (*J. Amer. Chem. Soc.*, 1944, **66**, 22—26).—Separation of benzfurano-2′ : 1′-6 : 7- (I) from -1′ : 2′-5 : 6-quinoline (II) is improved (cf. Mosettig *et al.*, A., 1935, 871). With HNO_3 (*d* 1·50) in 30 sec., (I) gives a NO_2- (84%), m.p. 267—268°, and thence (H_2–Raney Ni; EtOH; 2—3 atm.) an NH_2-derivative, m.p. 236·5—247°, which with Cl·$[CH_2]_3$·NH_2,HCl or 4-*γ*-chloro-*n*-propylmorpholine hydrochloride in Bu^aOH at 140—150° gives the *γ-diethylamino*-n-*propylamino*-, an oil, and *γ-morpholino*-n-*propylamino*-derivative, m.p. 120°, respectively. With HNO_3 (*d* 1·50), (II) gives NO_2-derivatives, m.p. 297—298° and 282°, reduced to NH_2-derivatives, m.p. 200° and 233°, which yield (diazo-reactions) *Br*-derivatives, m.p. 180—182° and 204°, respectively. 2-Acetamidodibenzfuran (modified prep.), m.p. 183° (lit. 178°), and HNO_3 (*d* 1·5) in AcOH give the 3-NO_2-derivative (73%), m.p. 205° (lit. 196°) (and a substance, m.p. 261—262°), hydrolysed to 3-nitro-2-aminodibenzfuran (III), m.p. 232—233° (lit. 222°), which with glycerol, H_3AsO_4, and H_2SO_4 at 130—140° gives 8-*nitrobenzfurano*-1′ : 2′-5 : 6-*quinoline* (24%), m.p. 206—207° (cf. Kirkpatrick *et al.*, A., 1935, 985); H_2–Raney Ni + a trace of PtO_2 in EtOH at 50°/3 atm. then yields the 8-NH_2-, m.p. 197—198°, and thence, as above, the 8-*γ-morpholino*-n-*propylamino*-derivative, b.p. 238—240°/0·03 mm. 2-*Benzenesulphonamidodibenzfuran*, m.p. 162—163°, with HNO_3 (*d* 1·5) in AcOH at 18° gives the 3-NO_2-derivative (IV), m.p. 226—227°, hydrolysed by 25% HCl to (III), which with $PhSO_2Cl$ in hot C_5H_5N gives (IV) and the 3-*nitro*-2-*dibenzenesulphonamido*-derivative, m.p. 263—265°. H_2–PtO_2 reduces (IV) in EtOH at 2—3 atm. to 3-*amino*-2-*benzenesulphonamidodibenzfuran*, m.p. 227—288°, which with glycerol, $PhNO_2$, and H_2SO_4 at 145—150° gives 5-*benzenesulphonamido*- (45%), m.p. 197—198°, and thence [3 : 1 (vol.) H_2SO_4–H_2O at 145°] 5-*amino*- (V), m.p. 139—140°, and impure 8-*diethylamino-α-methyl*-n-*butylamino-benzfurano*-2′ : 1′-5 : 6-*quinoline*, an oil. Deamination ($NaNO_2$–HCl; HPO_3) of (V) gives *benzfurano*-2′ : 1′-5 : 6-*quinoline*, m.p. 82—83·5° (cf. *loc. cit.*). M.p. are corr. R. S. C.

5-(*p*-Aminobenzenesulphonamido)thiazole. M. H. M. Arnold and C. W. Scaife (*J.C.S.*, 1944, 103—104).—Chrysean, prepared from H_2S, NaCN, with a little aq. NH_3, is 5-aminothiazole-2-thioamide (I), m.p. 204° (decomp.), obtained in 15—20% yield. (I) with $Pb(OAc)_2$ gives 5-aminothiazole-2-nitrile, which, with $CaCO_3$ followed by cautious evaporation, leads to the 2-*amide*, decomp. 156°, with dil. HCl affords the 2-*carboxylic acid*, decomp. 185°, and with PhCHO yields 5-*benzylideneaminothiazole*-2-*nitrile*, m.p. 141°. *p*-NO_2·C_6H_4·SO_2Cl and (I) in C_5H_5N form 5-(p-*nitrobenzenesulphonamido*)*thiazole*-2-*thioamide*, m.p. 185° (decomp.), whilst the -2-*nitrile*, m.p. 148°, and 5-(p-*acetamidobenzenesulphonamido*)*thiazole*-2-*thioamide* (II), m.p. 237°, and -2-*amide*, m.p. 253—255° (decomp.), are similarly prepared. Hydrolysis (NaOH–$PbCO_3$) of (II) gives 5-(p-*aminobenzenesulphonamido*)*thiazole*, m.p. 185° (decomp.), which is not pharmaceutically promising. F. R. S.

Reactions of nitriles as acid anammonides. E. L. Hölljes and E. C. Wagner (*J. Org. Chem.*, 1944, **9**, 31—49).—Closure of the glyoxaline, oxazole, and pyrimidine rings is effected by interaction of 1 : 2- or 1 : 3-$(NH_2)_2$-compounds or of *o*-NH_2·C_6H_4·OH and nitriles, the processes being essentially identical with conventional ring-closures of the Ladenburg type as effected (at lower temp.) by carboxylic acids and their anhydrides. The cases studied comprise the formation of 2-alkyl- or 2-aryl-glyoxalines from *o*-$C_6H_4(NH_2)_2$, of 2-alkyl- or 2-aryl-benzoxazoles from *o*-NH_2·C_6H_4·OH, of 2-substituted pyrimidines from 1 : 8-$C_{10}H_6(NH_2)_2$, and of 2-substituted dihydroquinazolones from *o*-NH_2·C_6H_4·CO·NH_2. In these reactions the nitrile C is incorporated into the ring; the nitrile N is finally present as NH_4 salt or NH_3. These reactions require the presence of acid and appear to be catalysed by H. Reaction occurs slowly in absence of added acid if one of the reactants is acidic in character (*e.g.*, *o*-NH_2·C_6H_4·OH) but is markedly promoted by the presence of a strong acid which may be introduced as a salt of the NH_2-compound used. Closure of the glyoxaline and oxazole ring when HCl is used as catalyst appears to depend on the preliminary formation of the iminochloride by additive union of nitrile and acids. This reacts with an NH_2-group to yield the substituted amidine (an ammono-acyl compound), which undergoes ring-closure as do the analogous aquo-acyl compounds of the O system. The first step is relatively slow and requires the use of high temp. and extended reaction periods. The subsequent steps, each realised separately, proceed rapidly and almost quantitatively. The acid is rendered available for another cycle by the thermal dissociation of NH_4Cl, which is the by-product. 2-n-*Butyl*-, b.p. 68—70°/20 mm., and 2-n-*amyl-benzoxazole*, b.p. 114—114·5°/2 mm., appear new. H. W.

Photochemical reactions of leuco-dyes in rigid solvents. Quantum efficiency of photo-oxidation.—See A., 1944, I, 109.

Dehydrothio-*p*-toluidine. H. E. Fierz-David [with W. Brunner] (*Helv. Chim. Acta*, 1944, **27**, 1—8).—The crude primuline melt obtained from *p*-toluidine and S is separable into at least 4 components by successive use of EtOH, PhCl, and *o*-$C_6H_4Cl_2$. Distillation of it in a high vac. and without previous purification gives ~50% of pure dehydrothio-*p*-toluidine (I). The alcoholic extract contains also didehydrothio-*p*-toluidine, which can be sublimed unchanged at 220°/0·001 mm., but decomposes at a higher pressure and hence during the distillation of (I). Quant. measurements confirm the view that naphthamine-yellow *NN* (II) obtained by oxidising dehydrothio-*p*-toluidinesulphonic acid (III) with OCl′, $K_3Fe(CN)_6$, and other oxidising agents is (SO_3H·C_6H_2Me<N/S>C·C_6H_4·N)$_2$; it is most simply prepared by oxidising (III) to the azoxy-compound, which is then reduced to the azo-substance by Na_2S, Na_2SO_3, or glucose but not $Na_2S_2O_4$. Similarly (I) is quantitatively oxidised by Cl_2 in NaOH–EtOH to the unstable azoxy-compound, directly reduced to the *azo*-derivative, (C_6H_3Me<N/S>C·C_6H_4·N:)$_2$ (III), m.p. 322·5° (corr.), reduced by $ZnCl_2$ and HCl in EtOH to (I). Sulphonation of (III) gives an *isomeride* of (II) superior in shade and fastness to light; it probably contains SO_3H vicinal to N of the thiazole ring. pp′-2-*Benzthiazolylazobenzene*, m.p. 304° (corr.), is obtained by oxidation of 4-*p*′-aminophenylbenzthiazole with NaOCl and subsequent reduction with NaOCl or Na_2S, from azobenzene-1 : 4′-dicarboxylic acid and *o*-NH_2·C_6H_4·SH, and by condensation of *p*-NO_2·C_6H_4·COCl with *o*-NH_2·C_6H_4·SH and reduction of the nitrothiazole with Zn dust and NaOH. H. W.

4-Methylthiazolo(2, 3-*b*)tetrahydropyrimidine hydrobromide. F. C. Whitmore and A. W. Rytina (*J. Amer. Chem. Soc.*, 1943, **65**, 2472—2473).—2-Amino-4-methylthiazole and Br·$[CH_2]_3$·Br in boiling EtOH give 4′-*methyl*-3 : 4 : 5 : 6-*tetrahydrothiazolo*-2′ : 3′-2 : 3-*pyrimidine hydrobromide*, m.p. 235·5—237°. R. S. C.

VII.—ALKALOIDS.

Cupreine derivatives.—See B., 1944, III, 74.

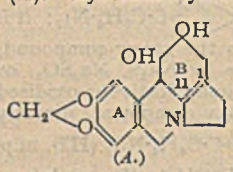
Thiocarbimides of the hydroquinine series and radical exchange with thiocarbimides and thiocarbamides. F. Zetzsche and A. Fredrich (*Ber.*, 1940, **73**, [*B*], 1420—1424).—Radical exchanges between amines or thiocarbamides and thiocarbimides are recorded. 5-*Thiocarbimidohydroquinine*, m.p. 198—200° (decomp.), is obtained from 5-aminohydroquinine and CS_2 or PhNCS in boiling C_6H_6. A similar reaction is observed with *p*-NMe_2·C_6H_4·NCS but not with CH_2:CH·CH_2·NCS or Bu^sNCS. 5-*Thiocarbimido-optoquin*, m.p. 196—198° (decomp.), $[\alpha]_D$ +156·3° in $CHCl_3$ (*picrate*, decomp. 150—152°), is obtained similarly. CO(NH·C_6H_4·NMe_2-*p*)$_2$ or freshly prepared *p*-NH_2·C_6H_4·NMe_2 and PhNCS at 160° afford *p*-NMe_2·C_6H_4·NCS, m.p. 65—67°. Benzidine (I) and boiling PhNCS yield di-4 : 4′-thiocarbimidodiphenyl, m.p. 204°, and a substance, m.p. 313—315°, which is the main product of the action of (I) with PhNCS in boiling $COMe_2$ or C_6H_6 or with CS(NHPh)$_2$ in boiling EtOH. (I) and boiling CS_2 give a material of m.p. 280—285°. H. W.

Cinchona alkaloids in pneumonia. XII. Derivatives of 6′-amino-*apo*cinchonidine. A. G. Renfrew, W. W. Carlson, and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1943, **65**, 2309—2310; cf. A., 1943, II, 344).—*apo*Cupreine (I) (0·2 mol.) with $NaHSO_3$ (1 mol.) and NH_2·$[CH_2]_2$·OH (1·7) or NH_2·$[CH_2]_2$·NEt_2 (1·1 mols.) in H_2O at 160° give 6′-*β-hydroxy*- (30%), $[\alpha]_D$ −291° in EtOH [*dihydrochloride* (II)], and 6′-*β-diethylamino-ethylamino*apo*cupreine* (37%), $[\alpha]_D$ −231° in EtOH {*H camphorate*, $[\alpha]_D$ −113° in H_2O; *H* d-*tartrate* (III), $[\alpha]_D$ −150° in H_2O}. Bacteriostatic concns. against *Pneumococcus* II and intraperitoneal toxicities, respectively, are (I) 1 in 3 × 10^5, 6—8 mg., (II) 1 in 5 × 10^4, 6—7 mg., and (III) — (confluent growth at 1 in 5 × 10^4), 2 mg. per 20-g. mouse. R. S. C.

***Strychnos* alkaloids. CXIII. *N*-Acetyl derivatives of *sec.-ψ*-strychnine and their oxidation.** H. Leuchs (*Ber.*, 1940, **73**, [*B*], 1392—1397).—Prolonged treatment of *ψ*-strychnine containing strychnine (I) with Ac_2O and C_5H_5N at 100° gives (I) and N-*acetyl*-sec.-*ψ-strychnine* (II), $C_{23}H_{24}O_4N_2$,$CHCl_3$, which does not react with NH_2·CO·NH·NH_2 and is hydrogenated (PtO_2 in AcOH) to acetyl-

dihydro-*sec.*-*ψ*-strychnine, m.p. 269° (vac.). (II) is oxidised by $KMnO_4$ in $COMe_2$ at 20° to the *keto-acid*, $C_{23}H_{24}O_7N_2$ (III), m.p. 225—230° (decomp.) after softening and darkening, $[\alpha]_D^{20}$ +321°/*d* in AcOH [*Me* ester, m.p. 230°, softens at 225°; *amide* (IV), m.p. 230—240° (decomp.), softens at 210°; *semicarbazone*, m.p. 205° (decomp.), occasionally up to 220°, becomes brown at 190°]. (III) scarcely absorbs H_2 (PtO_2 in AcOH) and does not give cryst. products with Na–Hg and H_2O. (III) is transformed by 0·5N-NaOH at 100° into a *substance*, $C_{21}H_{20}O_4N_2$ [also +1 MeOH, m.p. 280° (decomp.), softens at 260°], also obtained from (IV) and 13N-NH_3 at 100°. *ψ*-Brucine when similarly treated affords N-*acetyl*-sec.-*ψ*-*brucine*, which could not be obtained cryst. It is oxidised to a *keto-acid* (V), $C_{25}H_{28}O_9N_2$, m.p. 235—238°, softens and becomes discoloured at 225° from MeOH or m.p. 195—200° (decomp.) from H_2O, $[\alpha]_D^{20}$ +280°/*d* in AcOH [non-cryst. *Me* ester; *amide*, m.p. 170—188° to a resin which becomes brown at 195° and foams at 205°; *semicarbazone*, anhyd. m.p. ~215° (decomp.), darkens at 195°]. (V) is reduced (Na–Hg in H_2O) to the *acid*, $C_{25}H_{30}O_8N_2$, m.p. 235—237° (slight decomp.), softens at 225°, and is converted by 0·5N-NaOH at 100° into the *compound*, $C_{23}H_{24}O_6N_2$, m.p. 229—231° (vac.), softens at 225°. H. W.

Lycoris **alkaloids. XVII. Constitution of lycorine.** H. Kondo and H. Katsura (*Ber.*, 1940, **73**, [*B*], 1424—1430).—Lycorine (I) is (*A*). Lycorinanhydrohydromethine (II), m.p. 71—71·5°, obtained by the Emde degradation of the α(*β*)-methochloride of (I), yields CH_2O but not MeCHO when ozonised in $CHCl_3$. Catalytic hydrogenation (PtO_2 in AcOH) of (II) yields the H_6-derivative, m.p. 70—72° (*picrate*, m.p. 218—221°). Oxidation ($KMnO_4$ at 30°) of (II) leads to hydrastic acid. An unusual addition of H to nucleus B therefore occurs during the Emde degradation. (II) is converted into the *methiodide*, m.p. 235°, and thence into the methochloride, which is reduced (Na–Hg–H_2O) to the *compound*, $C_{18}H_{21}O_2N$, b.p. 165° (bath)/0·01 mm. (*picrate*, m.p. 147—148°), which gives a *methiodide*, m.p. 186—187°, and thence a methochloride, reduced to *de*-N-*anhydrohydrolycorine*, b.p. 160—170° (bath)/0·03 mm. Reduction (Na–Hg) of the lycorinanhydromethine obtained by the Hofmann degradation gives a product not identical with (II). Reduction (Na–Hg) of lycorinanhydromethine methochloride (corresponding *methiodide*, decomp. 226°) leads to (II). Spectrographic curves of (I), dihydrolycorine, and the two Ac derivatives are closely similar, showing that the double linking in the B nucleus of (I) is not conjugated with that of the nucleus and lies between $C_{(11)}$ and $C_{(1)}$. The curve of (II) is completely different, showing that in it the double linking $C_{(11)}$–$C_{(1)}$ has been hydrogenated and that the remaining double linking is conjugated with that of nucleus A. H. W.



Delphinium **alkaloids. II. Ajacine.** J. A. Goodson (*J.C.S.*, 1944, 108—109).—Ajacine, $C_{34}H_{46}O_9N_2,2H_2O$, m.p. 154°, $[\alpha]_D^{22}$ +49·5° in EtOH, is acetylanthranoyl-lycoctonine; since on hydrolysis with NaOH–EtOH it gives *o*-NHAc·C_6H_4·CO_2H and lycoctonine, and with 10% HCl affords AcOH and anthranoyl-lycoctonine. F. R. S.

VIII.—ORGANO-METALLIC COMPOUNDS.

Aliphatic arsonic acids. VI. Attempted preparation of diarsonosuccinic acid and its salts. A. R. Marquez (*Rev. Fac. Cienc. Quim., La Plata*, 1942, **17**, 109—116).—$(CHBr·CO_2Et)_2$ with As_2O_3 in NaOH yields a solution, which with $BaCl_2$ gives *Ba*$_2$ *αα'-diarsonosuccinate* (*Ca*$_2$ and *Na*$_4$ *salts*). F. R. G.

Relations between chemical activity and absorption in the ultraviolet of organic molecules. V. Interaction of atoxyl with the halogen derivatives of substituted amides of malonic acid. K. G. Naik, R. K. Trivedi, and C. M. Mehta (*J. Indian Chem. Soc.*, 1943, **20**, 372—373).—$CHBr(CO·NHAr)_2$ but not $CCl_2(CO·NHAr)_2$ react with atoxyl in boiling aq. EtOH to give p-*arsonoanilinomalondi*-p-*bromoanilide*, m.p. 251—253° (decomp.), -p-*toluidide*, m.p. 233° (decomp.), and -*benzylamide*, m.p. 266° (decomp.). H. M. C.

Mercurials from aliphatic glycols. A. J. Shukis and R. C. Tallman (*J. Amer. Chem. Soc.*, 1943, **65**, 2365—2366).—R·(O·$[CH_2]_2)_n$·OH (R = H or alkyl) with C_2H_4 and $Hg(OAc)_2$ at 70—90° and then aq. NaCl gives OEt·$[CH_2]_2$·HgCl, m.p. 92°, *compounds*, Et·(O·$[CH_2]_2)_x$·O·$[CH_2]_2$·HgCl in which x = 1, m.p. 34—35° (lit., an oil), 2, m.p. 50° (lit., an oil), 3, m.p. 53—54°, and 4, an oil, *Hg β-β'-β''-hydroxyethoxyethoxyethyl chloride*, m.p. 70—72°, and *Hg β-β'-hydroxyethoxyethyl chloride*, m.p. 88—89°. OH·$[CH_2]_2$·Cl gives similarly *Hg β-β'-chloroethoxyethyl chloride*, m.p. 54°. The appropriate glycols yield *compounds*, OH·$[CH_2]_n$·O·$[CH_2]_2$·HgCl, in which n = 3, m.p. 114—116°, 4, m.p. 92—93°, and 6, m.p. 98—99°. OH·CH_2·CHMe·OH gives a *compound*, m.p. 80—81°. OH·CH(CH_2·OH)$_2$ gives a *compound*, m.p. 88—91°. Distribution coeffs. (solubility in C_6H_6/solubility in H_2O) and bacteriostatic activity against *Staph. aureus* are recorded for the products; close parallelism exists. R. S. C.

Mercuri derivatives.—See B., 1944, III, 75.

IX.—PROTEINS.

Conversion of globular into oriented fibrous proteins. I. By heat and mechanical working. F. R. Senti, C. R. Eddy, and G. C. Nutting (*J. Amer. Chem. Soc.*, 1943, **65**, 2473).—Heating casein, *β*-lactoglobulin (I), hæmoglobin, ovalbumin (II), edestin, zein, or proteins from peanuts or soya beans in H_2O and then stretching or extruding them in hot or cold H_2O or H_2O vapour gives products having *β*-keratin structure (*X*-ray). *X*-Ray spacings are quoted for (I) and (II). The tensile strength of protein fibres, thus treated, is greatly increased. R. S. C.

***o*-Benzoic sulphinide ferridehæmoglobin. Reaction of hæmoglobin with nitrite. Verdohæmochromogens.**—See A., 1944, III, 323.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

American musk. II. Scent glands of the beaver. P. G. Stevens (*J. Amer. Chem. Soc.*, 1943, **65**, 2471; cf. A., 1942, II, 178).—The neutral products (6·3 g.) obtained by boiling 10% KOH–EtOH from the Et_2O-extract of dried beaver-glands (113 g.) yield an oily, unsaturated *substance*, $C_{11}H_{18}O_2$, b.p. 147—155°/1 mm., having a spicy odour. The neutral products from another sample of glands yielded a mixture containing a similar liquid and a small amount of cholesterol. The acidic products include BzOH, *p*-anisic, and amorphous castoric acids. Large-ring ketones and fatty acids are absent. R. S. C.

Lignin and related compounds. LXXV. Alkaline nitrobenzene oxidation of plant materials and application to taxonomic classification. R. H. J. Creighton, R. D. Gibbs, and H. Hibbert. **LXXVI. Alkaline nitrobenzene oxidation of maize stalks. Isolation of *p*-hydroxybenzaldehyde.** R. H. J. Creighton and H. Hibbert. **LXXVII. Re-investigation of the ethanolysis products of maple wood.** M. Kulka, H. E. Fisher, S. B. Baker, and H. Hibbert. **LXXVIII. Chromic acid oxidation of lignin-type substances, wood ethanolysis products, and wood.** W. S. MacGregor, T. H. Evans, and H. Hibbert (*J. Amer. Chem. Soc.*, 1944, **66**, 32—37, 37—38, 39—41, 41—44; cf. A., 1944, II, 162).—LXXV. Alkaline $PhNO_2$-oxidation of 47 woods, almost all gymnosperms, yields only vanillin (I) (15—24% calc. on Klason lignin) and of angiosperms yields generally a 1 : 3 mixture (35—51%) of (I) and syringaldehyde (II). Certain primitive angiosperms yield a 1 : 1 mixture of (I) and (II). Gnetales genera yield (I) and (II) and may thus be angiosperms. Very few Coniferales yield both (I) and (II). Behaviour on oxidation parallels that in the Maule reaction and may be used for taxonomic classification.

LXXVI. Maize-stalk meal with $PhNO_2$–aq. NaOH at 160° yields 4·5, 2·6, and 1·4% of pure (I), (II), and *p*-OH·C_6H_4·CHO (III), respectively. OMe-contents of *m*-nitrobenzoylhydrazides indicate the possibility of existence of (III) also in maize cobs, bamboo and rye straw; presence of (III) may distinguish mono- from di-cotyledons.

LXXVII. The alkali-sol. part of the H_2O-sol. ethanolysis of maple wood lignin yields, by improved methods (cf. A., 1939, II, 172), 3·1% of 4 : 3 : 1-OH·C_6H_3(OMe)·CO·CHMe·OEt and 3·2% of 4 : 3 : 5 : 1-OH·C_6H_2(OMe)$_2$·CO·CHMe·OEt, m.p. 73—74° (lit. an oil), and a mixture yielding a 1 : 3 mixture of the respective derived Me ethers. Pure compounds isolated by ethanolysis of maple wood amount to 9·8% of the Klason lignin, but the actual contents are considered to be much higher.

LXXXVIII. CrO_3-oxidation of compounds containing Ar–C_3 gives 0·9—0·95 mol. of AcOH (reduced somewhat if the Ar is very stable) if the C_3 includes a terminal Me, but only traces of AcOH if no terminal Me is present. Spruce or maple wood gives ≯ traces of AcOH. Extracted amorphous maple EtOH-lignin gives very little AcOH, but that from spruce gives 1 AcOH per 4—5 Ar–C_3 units; more AcOH is obtained if the spruce lignin is subjected again to HCl–EtOH. Support is thus given to the view that native lignin contains no terminal Me and that its presence in products from wood is due to rearrangement of products of hydroxyconiferyl alcohol type. R. S. C.

Lignin. XLII. Vanillincarboxylic acid and related acids.—See A., 1944, II, 161.

Pigments of cottonseed.—See A., 1944, III, 444.

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JUNE, 1944.

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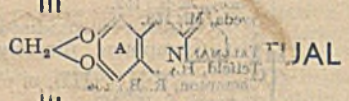

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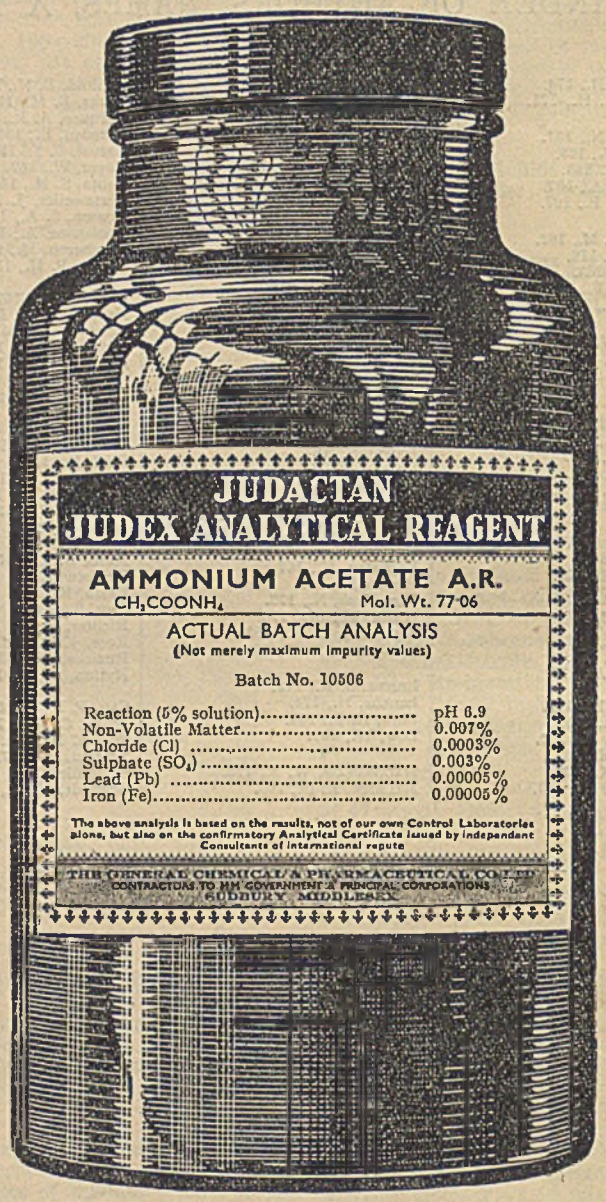

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