BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

OCTOBER, 1942.

I.—ALIPHATIC.

Classical methods in the analysis of the fine structure of carbon compounds. A. Lüttringhaus (*Naturwiss.*, 1942, **30**, 40—45). H. W.

Preparation and reactions of free methyl at low temperatures. G. Semerano and L. Riccoboni (*Z. physikal. Chem.*, 1941, **189, A**, 203—218).—At −40° AgMe decomposes yielding free Me which is rapidly converted into C_2H_6. The properties of Me are discussed. C. R. H.

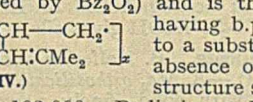
Allylic rearrangements. XII. Action of dioxan on magnesium butenyl bromide. W. G. Young and H. H. Pokras (*J. Org. Chem.*, 1942, **7**, 233—240).—Addition of dioxan to Mg butenyl bromide (**I**) in Et_2O produces a solution of Mg dibutenyl (**II**) and a ppt. containing a (**I**)–dioxan complex (**III**). Hydrolysis of (**II**) gives 44·5% of CH_2:CHEt (**IV**), 32·2% of *cis*-CHMe:CHMe (**V**), and 23·2% of *trans*-CHMe:CHMe (**VI**) and hydrolysis of (**III**) yields 55% of (**IV**), 28% of (**V**), and 17% of (**VI**). An allylic rearrangement is considered to occur during the formation of (**II**). H. W.

Catalytic dimerisation of *iso*butene by activated copper sulphide. A. Wassermann and W. T. Weller (*Nature*, 1942, **149**, 669).—The main product is a mixture of the two ββδ-trimethylpentenes. A. A. E.

[Preparation of] conjugated diolefines by displacement of ethylenic linkings. A. L. Henne and A. Turk (*J. Amer. Chem. Soc.*, 1942, **64**, 826—828).—When passed over activated Al_2O_3 at 365°, $(CH_2{\cdot}CH{:}CH_2)_2$ gives $(CH{:}CHMe)_2$ (39%), b.p. 82·0°, and $CH_2{:}CH{\cdot}CH{:}CHEt$ (3%), b.p. 72·9°; $(CH_2{:}CMe{\cdot}CH_2)_2$ gives $(CH{:}CMe_2)_2$ (81%), f.p. 13·94°, b.p. 134·5°; $CH_2{:}CMe{\cdot}[CH_2]_2{\cdot}CH{:}CH_2$ gives $CMe_2{:}CH{\cdot}CH{:}CHMe$ (58%), m.p. −74·6°, b.p. 111·5°; $CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2$ gives (?) $CH_2{:}CH{\cdot}CH{:}CMeEt$ (14%), b.p. 111°; $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CH{:}CHMe$ gives $CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2$ (8%) and, by rearrangement, $CHMe{:}CH{\cdot}CH{:}CHEt$ (6%), b.p. 109·6°; $CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CHMe$ gives $CHMe{:}CH{\cdot}CH{:}CMeEt$ (4%), b.p. 135·2°; $(CH_2{\cdot}CH{:}CHMe)_2$ gives $(CH{:}CHEt)_2$ (0·5%). Rearrangement to conjugated dienes is easiest when the ethylenic linking moves towards the centre of the chain and is further facilitated by presence of Me on one of the C of this linking. $(CH{:}CHR)_2$ give cryst., but $(CH{:}CR_2)_2$ or $CHR{:}CH{\cdot}CH{:}CR_2$ give polymeric, adducts with $(:CH{\cdot}CO)_2O$. 3-*Ethyl*-, m.p. 52°, 3 : 4 : 6-*trimethyl*-, m.p. 76°, and 3-*methyl*-6-*ethyl*-, m.p. 70·5°, -1 : 2 : 3 : 6-*tetrahydrophthalic anhydride* are described. R. S. C.

Macromolecular compounds. CCXCII. Poly*iso*butylene. H. Staudinger, G. Berger, and K. Fischer (*J. pr. Chem.*, 1942, [ii], **160**, 95—119).—Properties of poly*iso*butylene of varying degrees of polymerisation are recorded, and the relationship between η and polymerisation is examined. A. T. P.

Isolation of δ-methyl-$\Delta^{\alpha\gamma}$-pentadiene. G. B. Bachman and C. G. Goebel (*J. Amer. Chem. Soc.*, 1942, **64**, 787—790).—$CMe_2{:}CH{\cdot}CH{:}CH_2$ (**I**) and $CH_2{:}CMe{\cdot}CH{:}CHMe$ (**II**), obtained by dehydration of $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, are separated by heating with $(:CH{\cdot}CO)_2O$ (**III**) alone or in PhMe or dioxan. (**II**) yields 3 : 5-dimethyl-Δ^4-tetrahydrophthalic anhydride. (**I**) is unchanged or forms a linear co-polymeride (**IV**) (reaction inhibited by quinol and accelerated by Bz_2O_2) and is thus obtained in 23% yield, having b.p. 76·3°. Oxidation of (**IV**) to a substance having the same η, *i.e.*, absence of ring-fission, indicates the structure shown, the mol. wt. varying from 8700 to 103,000. Preliminary data are recorded for hetero-polymerisation of (**I**), (**III**), and other unsaturated compounds. R. S. C.



(IV.)

Prolycopene. A. L. LeRosen and L. Zechmeister (*J. Amer. Chem. Soc.*, 1942, **64**, 1075—1079).—The pigments of ripe fruits of *Lycopersicum esculentum* (tangerine tomato) are separated by adsorption on $Ca(OH)_2$ into *prolycopene* (**I**), $C_{40}H_{56}$, m.p. 111° (corr.; block) (main constituent; 18·7 mg. per kg. of fruit) (cf. A., 1942, II, 126), lycopene (**II**), and neolycopene-*A*. The absorption (max. at 470 and 443·5 mμ. in light petroleum; given also for 10 other solvents) indicates that 5—7 of the ethylenic linkings of (**I**) are *cis* and the remainder *trans*. (**I**) absorbs O_2 very readily in air but is stable in solution, *e.g.*, in boiling light petroleum. When melted in CO_2 it gives ~12 layers on chromatography, due mainly to stereoisomerides of (**II**) and including pigments having absorption max. at 464 and 438 mμ. With I in light petroleum it gives very rapidly a complex mixture including much (**II**). R. S. C.

New method of β-chloroethylation. L. Bert (*Compt. rend.*, 1941, **213**, 1015—1016).—$Cl{\cdot}[CH_2]_2$ derivatives are prepared from *Cl·[CH$_2$]$_2$ benzenesulphonate* (from $PhSO_2Cl$ and $Cl{\cdot}[CH_2]_2{\cdot}OH$), b.p. 192°/15 mm., and RMgX in Et_2O. A. Lɪ.

Dielectric behaviour, supercooling, and vitrification of chlorobutanes and chloropentanes.—See A., 1942, I, 289.

Synthesis of aliphatic difluorides. (Miss) M. W. Renoll (*J. Amer. Chem. Soc.*, 1942, **64**, 1115—1116).—$CH_2{:}CRCl$ or $CHR{:}CRCl$, when mixed with HF at −78° and warmed slowly to 35—46° with occasional release of HCl (4—11 atm.), gives 59—70% of $CRR'F_2$ with a little $CRR'ClF$ and ≯25% of $CRR'Cl_2$. $CHR{:}CRCl$ is the main product when $COR{:}CH_2R$ reacts with PCl_5 at 20—30°. Thus, in HF $CH_2{:}CPr^{\alpha}Cl$ gives $CMePr^{\alpha}F_2$ (64·1%), f.p. −98·1°, b.p. 60·1°, and $CMeEtCl_2$ (13·9%). $CH_2{:}CEtCl$ or $CHMe{:}CMeCl$ gives 67% of $CMeEtF_2$, f.p. −114·0°, b.p. 31·0°. $CHMe{:}CEtCl$ gives *γγ-difluoro-n-pentane* (59·7%), f.p. −94·0°, b.p. 60·8°. $CH_2{:}CBu^{\beta}Cl$ gives *ββ-difluoro*isohexane (70·5%), f.p. −112·7°, b.p. 78·2°. $n\text{-}C_5H_{11}{\cdot}CH{:}CMeCl$ gives *ββ-difluoro-n-octane* (58·9%), f.p. −50·0°, b.p. 136·3—136·6°/760 mm. (slight decomp.), 66·2—66·6°/60 mm. R. S. C.

Preparation and directed chlorination of aaa-trifluoropropane. A. L. Henne and A. M. Whaley (*J. Amer. Chem. Soc.*, 1942, **64**, 1157—1159).—$CHMeCl{\cdot}CHCl_2$ [prep. from $CHMeCl{\cdot}CH_2Cl$ by Cl_2 and Fe filings at the b.p. (dark)], b.p. 130—133°, with 20% aq. KOH gives $CHMe{:}CCl_2$ (90%), b.p. 75—77°, which with HF at 75° and later 95° (intermittent removal of HCl; 20 atm.) and then with SbF_3–Cl_2 at 13 atm. (free flame) gives *aaa-trifluoropropane* (**I**) (36%), f.p. −148·8°, b.p. −13°, and *a-chloro-aa-difluoropropane* (**II**) (36%), b.p. 25·8° [as above yields (**I**)]. With HCl–$AlCl_3$ (2—3%), $CHMe{:}CCl_2$ gives $CEtCl_3$ (45%), which with SbF_3 loses much HCl, giving 5—10% of (**I**) and 10% of (**II**) + $CEtCl_2F$, b.p. 66·6°. No exchange of halogen occurs with $CH_2{:}CH{\cdot}CCl_3$ and SbF_3. With Cl_2–H_2O in llght, (**I**) gives, successively, γ-chloro- (**III**), f.p. −106·2°, b.p. 45·1°, *γγ-dichloro-* (**IV**), f.p. −93·2°, b.p. 72·4°, *γγγ-trichloro-* (**V**), f.p. −41·7°, b.p. 95·1°, and *ββγγγ-pentachloro-* (**VI**), f.p. −109·0°, b.p. 153·1°, *-aaa-trifluoropropane*. Under similar conditions $CEtCl_3$ gives $CHMeCl{\cdot}CCl_3$ (15—20%), $Cl{\cdot}[CH_2]_2{\cdot}CCl_3$ (5—10%), $CMeCl_2{\cdot}CCl_3$ (30%), $CH_2Cl{\cdot}CHCl{\cdot}CCl_3$ (10—15%), and $CHCl_2{\cdot}CH_2{\cdot}CCl_3$ (5%). $CHMeCl{\cdot}CCl_3$ with HF and HgO at 100° give *β-chloro-aaa-trifluoropropane* (80%), b.p. 30°, and thence *ββ-*, f.p. 13·8°, b.p. 48·8°, + *βγ-dichloro-aaa-trifluoropropane*, b.p. 76·7°, and (**VI**). With alcoholic alkali, (**IV**) gives $CHCl{:}CH{\cdot}CF_3$, which with Cl_2 gives $CHCl_2{\cdot}CHCl{\cdot}CF_3$, b.p. 106·8°. (**III**) does not react with Mg or MgEtBr and with KOH loses HCl. (**IV**) and alcoholic alkali give $CHCl{:}CH{\cdot}CF_3$ (100%). (**V**) loses HCl to alkali, and with HgF_3 gives $CH_2(CF_3)_2$. With $SbCl_2F_3$, (**VI**) gives *ββγγ-tetrachloro-aaaγ-tetrafluoro-*, f.p. 41·74° b.p. 112·4°, and *ββγ-trichloro-aaaγγγ-pentafluoro-propane*, f.p. −4·3°, b.p. 72·0°. $CHMe{:}CClF$, b.p. 24·8°, *aaβ-tri-*, f.p. −114·7°, b.p. 88·3°, *aβ-*, f.p. −109·2°, b.p. 53·7°, and *aa-di-chloro-γγγ-trifluoropropylene*, f.p. −87·2°, b.p. 55·1°, are also described. R. S. C.

Manufacture of organic nitro-compounds.—See B., 1942, II, 249.

Number of stereoisomeric alcohols. E. S. Allen and H. Diehl (*Iowa State Coll. J. Sci.*, 1942, **16**, 161—167).—A method is given for computing the no. of stereoisomeric monosubstituted saturated hydrocarbons having a given no. of C atoms, by considering the groups attached to the substituted C atom. A. Lɪ.

Action of hydrogen fluoride, sulphuric acid, and phosphoric acid on optically active butan-β-ol. R. L. Burwell, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1025—1031).—Optically active butan-β-ol (**I**) is racemised {first order with respect to (**I**) and decreases with $[H_2O]$} by H_2SO_4 under less drastic conditions than those which promote alkylation, polymerisation, or butylene evolution. The activation energy is ~22,000 g.-cal. and, on the carbonium ion hypothesis, the racemisation has been correlated with other reactions between H_2SO_4 and (**I**). Similar reactions occur with HF but much larger ratios of acid to alcohol are required. Only slight racemisation occurs with H_3PO_4

Order of addition of hydrogen halides to halogenated α-oxides. A. A. Petrov (*J. Gen. Chem. Russ.*, 1941, **11**, 713—721).—α- and α′-Methylepichlorohydrins and the corresponding bromohydrins undergo ring fission with H halides, giving rise to alcohols $CHMeHal{\cdot}CH(OH){\cdot}CH_2Hal$. Crotyl bromide, b.p. 104·5—106·5°, is hydrolysed to a mixture of $OH{\cdot}CHMe{\cdot}CH{:}CH_2$, b.p. 95—97°, and $CHMe{:}CH{\cdot}CH_2{\cdot}OH$, b.p. 121—122°, separated by fractionation. Addition of Br in $CHCl_3$ affords, respectively, *γδ-dibromobutan-β-ol*, b.p. 94·5°/10 mm. (*acetate*, b.p. 108—108·5°/10 mm.), and *βγ-dibromobutan-α-ol*, b.p. 99·5°/10 mm. (*acetate*, b.p. 109·5°/10 mm.). With aq. KOH these yield *α-methyl-α′-bromomethylethylene oxide* (**I**) (70%), b.p. 144—145·5°, 54·5—55°/25 mm., and *α-bromoethylethylene oxide* (50%), evidently a mixture of two stereoisomerides, the main fraction (**II**), b.p. 142—148°, and (**III**), b.p. 152—154°; these are accompanied by (?) divinyl oxide, b.p. 62—68°. (**II**) with fuming HCl yields *α-chloro-γ-bromobutan-β-ol* (**IV**), b.p. 76—76·5°/10 mm. (*acetate*, b.p. 92·5—93°/10 mm.), oxidised to α-chloro-γ-bromobutanone, b.p. 67—68°/10 mm. (**II**) with HBr gives *αγ-dibromobutan-β-ol* (**V**), b.p. 90·5—91°/10 mm. (*acetate*, b.p. 105—106°/10 mm.); (**III**) gives an isomeride, b.p. 90·5—91°/10 mm.; both are oxidised to the same *αγ-dibromobutanone*, b.p. 76·5—77°/10 mm.; with KOH both give the same oxide (**I**). (**I**) with HCl affords *γ-chloro-α-bromobutan-β-ol* (**VI**), b.p. 76·5—77°/10 mm. (*acetate*, b.p. 94·5—95·5°/10 mm.), oxidised to *γ-chloro-α-bromobutanone*, b.p. 64·5—65°/10 mm. (**I**) with HBr gives (**V**). (**IV**) with KOH gives *α-methyl-α′-chloromethylethylene oxide* (**VII**), b.p. 124—125·5°; (**VI**) similarly gives *α-chloroethylethylene oxide* (**VIII**), b.p. 118—124°, and a smaller amount of an *isomeride*, b.p. 133—135°. (**VIII**) with HCl gives *αγ-dichlorobutan-β-ol* (**IX**), b.p. 63—64°/10 mm. (*acetate*, b.p. 82·5—83·5°/10 mm.); the higher-boiling isomeride of (**VIII**) gives a product, b.p. 63—64°/10 mm.; both are oxidised to αγ-dichlorobutan-β-one, b.p. 55—55·5°/10 mm. (**VIII**) with HBr gives (**VI**). (**VII**) with HCl gives (**IX**) and with HBr, (**IV**). All the halogenated ketones are reduced with Zn andAcOH to COMeEt.

G. A. R. K.

Migratory ability of acetylenic radicals in transposition reactions. Study of the heptinene radical in the dehalogenation by magnesium of the chlorohydrin $C_5H_{11}{\cdot}C{:}C{\cdot}CR(OH){\cdot}CH_2Cl$. M. Tiffeneau and Y. Deux (*Compt. rend.*, 1941, **213**, 753—758).—Mg heptinyl bromide (**I**) (obtained from MgEtBr and heptinene) with $COMe{\cdot}CH_2Cl$ affords *α-chloro-β-methyl-Δ$^{\gamma}$-noninen-β-ol*, giving at 110° Δ$^{\delta}$-decinen-β-one (**II**), b.p. 94—95°/20 mm. (semicarbazone, m.p. 128°), not identical with Δ$^{\delta}$-decinen-γ-one (semicarbazone, m.p. 108—109°), from EtCOCl and Na compound of heptinene. Hydrogenation of (**II**) (Raney Ni) yields decan-β-one (semicarbazone, m.p. 120°) identical with that afforded by decan-β-ol (from Mg octyl bromide and MeCHO) and CrO_3. (**I**) and α-chlorobutan-β-one afford *α-chloro-β-ethyl-Δ$^{\gamma}$-noninen-β-ol*, giving at 110° Δ$^{\varepsilon}$-undecinen-δ-one, b.p. 100—101°/20 mm. (semicarbazone, m.p. 143—144°), identical with that from Pr$^{\alpha}$COCl and the Na derivative of heptinene. (**I**) and $COPh{\cdot}CH_2Cl$ yield *α-chloro-β-phenyl-Δ$^{\gamma}$-noninen-β-ol*, which at 110° gives α-phenyl-Δ$^{\gamma}$-noninen-β-one, b.p. 170°/18 mm. (semicarbazone, m.p. 84—85°), identical with that from $CH_2Ph{\cdot}COCl$ and the Na derivative of heptinene. Migratory ability is Ph, Et > heptinenyl > Me. The heptinenyl radical is of the "aliphatic" type, but $CH{:}C$ (work in progress) may be of the "aromatic" type (cf. vinyl) and C_5H_{11}-substitution may have a weakening effect. Me migrates in βδεη-tetramethyl-Δ$^{\beta\zeta}$-octadiene-δε-diol to yield ββδη-tetramethyl-Δ$^{\delta\zeta}$-octadien-ε-one. Thus, substitution in vinyl to give *iso*butenyl has made its migratory power weaker than Me.

C. S.

Utilisation of aliphatic nitro-compounds. III. Nitro-alcohols prepared from aldehydes containing no other functional groups. C. A. Sprang with E. F. Degering (*J. Amer. Chem. Soc.*, 1942, **64**, 1063—1064; cf. A., 1940, II, 3).—$CH_2R{\cdot}NO_2$ and R′CHO are condensed by alkali to give $NO_2{\cdot}CHR{\cdot}CHR'{\cdot}OH$, the best conditions depending on the nature of R and R′. Thus are obtained *α-nitro*-n-*nonan-β-ol*, b.p. 120—121°/1 mm., *-n*-octan-β-ol, b.p. 120°/2 mm., and *-n-hendecan-β-ol*, b.p. 140°/2 mm., *β-nitro*-n-*nonan-γ-ol*, b.p. 110°/1·5 mm., -n-*decan-γ-ol*, b.p. 125°/2 mm., -n-*hendecan-γ-ol*, b.p. 128°/1·8 mm., -n-*tridecan-γ-ol*, b.p. 153—155°/2 mm., *-β-methyl*-n-*nonan-γ-ol*, b.p. 109°/1 mm., *-β-methyl*-n-*decan-γ-ol*, b.p. 124—125°/1·2 mm., and *-β-methyl*-n-*hendecan-γ-ol*, b.p. 125°/3 mm., *γ-nitro*-n-*hendecan-δ-ol*, b.p. 128°/2 mm., -n-*dodecan-δ-ol*, b.p. 138—140°/2·2 mm., -n-*tetradecan-δ-ol*, b.p. 150—155°/1·5 mm., *-γ-methyl*-n-*hexan-β-ol*, b.p. 97°/5 mm., *-γ-methyl*-n-*nonan-δ-ol*, b.p. 99—101°/1·5 mm., *-γ-methyl*-n-*octan-δ-ol*, b.p. 90—94°/2·5 mm., *-γ-methyl*-n-*decan-δ-ol*, b.p. 128°/1·3 mm., and *-γ-methyl*-n-*hendecan-δ-ol*, b.p. 111°/1·5 mm., and *δ-nitro*-n-*hendecan-ε-ol*, b.p. 135°/2 mm., and -n-*dodecan-ε-ol*, b.p. 130°/1·2 mm. *n* and *d* are given.

R. S. C.

Synthesis of *dl*-octane-αβ-diol and its homologues. C. Niemann and C. D. Wagner (*J. Org. Chem.*, 1942, **7**, 227—232).—Addition of $OEt{\cdot}CHBr{\cdot}CH_2Br$ to *n*-$C_{14}H_{29}{\cdot}MgBr$ in Et_2O affords *n*-octacosane, m.p. 61·5°, and Et β-bromo-α-tetradecyl ether, b.p. 145—165°/2 mm., m.p. 23·5°, transformed by Zn dust in boiling Bu$^{\alpha}$OH into Δ$^{\alpha}$-hexadecene (**I**), b.p. 122·0—122·5°/3 mm., m.p. 4°, and tetradecanol. (**I**) is converted by AgOBz and I in boiling C_6H_6 followed by [illegible] into hexadecane-αβ-diol, m.p. 73·1—73·6° (*:CMe$_2$ ether*, m.p. 22·9°; *diacetate*, m.p. 30°; *di*-N-*phenylcarbamate*, m.p. 95°). Similarly, *n*-$C_{16}H_{33}Br$ gives Et β-bromo-α-hexadecyl ether, m.p. 28·5—29·5° (with dotriacontane, m.p. 69·0°), and thence Δ$^{\alpha}$-octodecene, b.p. 144—146°/3 mm., m.p. 17·5, and *octadecane-αβ-diol*, m.p. 79·0—79·5° (*:CMe$_2$ ether*, m.p. 31·3°; *diacetate*, m.p. 40°; *di*-N-*phenylcarbamate*, m.p. 99·5°). Analogously, *n*-$C_{18}H_{37}Br$ gives successively Et β-bromo-α-octadecyl ether, which could not be distilled without decomp., Δ$^{\alpha}$-eicosene, b.p. 151°/1·5 mm., m.p. 28·5°, and *eicosane-αβ-diol*, m.p. 84·3—84·8° (*:CMe$_2$ ether*, m.p. 36·7°; *diacetate*, m.p. 47°; *di*-N-*phenylcarbamate*, m.p. 103·5°).

H. W.

Structure of αγδζ-dimethylenedulcitol. R. M. Hann, W. T. Haskins, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 986—987).—The structure of αγδζ-dimethylenedulcitol (prep. from dulcitol by warm 37% CH_2O–conc. HCl; cf. Weber *et al.*, A., 1898, i, 60), new m.p. 249—250° (dibenzoate, new m.p. 233—234°), is proved by (i) conversion of the βε-diacetate, new m.p. 264—265°, by boiling CH_2PhCl–KOH–PhMe into *αγδζ-dimethylenedulcitol βε-(CH$_2$Ph)$_2$ ether*, m.p. 164°, which is hydrolysed to dulcitol βε-$(CH_2Ph)_2$ ether, m.p. 168—169°, by HCl–aq. EtOH at 100° and regenerated therefrom by 37% CH_2O–conc. HCl–dioxan at 100°, and (ii) the stability of the *βζ-di*-p-*toluenesulphonate*, darkens at 220°, towards boiling NaI–Ac_2O. M.p. are corr.

R. S. C.

Structure of βγδε-di*iso*propylidene-*L*-fucitol. A. T. Ness, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 982—985).—*L*-Fucitol and HCl–$COMe_2$ at 20° give the βγδε-(*CMe$_2$*:)$_2$ derivative (**I**), m.p. 59—60°, [α] +11·7° in EtOH (*α-acetate*, m.p. 46—47°, [α] +26·1° in $CHCl_3$). The *α-benzoate*, m.p. 56·5—58°, [α] +18·7° in $CHCl_3$, of (**I**) in boiling 80% AcOH gives L-*fucitol α-benzoate* (**II**), m.p. 177—178°, [α] +4·30° in C_5H_5N, and slowly consumes 3 HIO_4 in aq. dioxan (no CH_2O formed) by hydrolysis to (**II**) and oxidations thereof. In AcOH, (**II**) rapidly consumes 3 equivs. of $Pb(OAc)_4$ and then, by oxidation of HCO_2H, slowly 2 further equivs.; CH_2O is not produced. With BzCl– or Ac_2O–C_5H_5N at room temp., (**II**) gives L-*fucitol pentabenzoate*, m.p. 149—150°, [α] −5·96° in $CHCl_3$, or *α-benzoate βγδε-tetra-acetate*, m.p. 116—117°, [α] +18·6° in $CHCl_3$, respectively. With *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N at 0°, later 23—24° and 40°, (**II**) gives L-*fucitol α-benzoate tri-* (22%), m.p. 155—157°, [α] +13·8° in $CHCl_3$, and *βγδε-tetra*-p-*toluenesulphonate*, m.p. 143—145°, [α] +18·0° in $CHCl_3$. (**I**) yields similarly *βγδε-*diiso*propylidene*-L-*fucitol α*-p-*toluenesulphonate*, m.p. 78—79°, [α] +19·7° in $CHCl_3$, and thence (NaI–$COMe_2$; 100°) *α-iodide*, m.p. 35—36°, [α] +28·9° in $CHCl_3$, which with H_2–Raney Ni in MeOH–H_2O–NaOH gives *αζ-bisdeoxy-βγδε-*diiso*propylidene-dulcitol* (**III**) (94%), m.p. 63—64°, α 0° in $CHCl_3$ (crystallo-optical data given), hydrolysed by boiling 80% AcOH to *αζ-bisdeoxy-dulcitol* (38%), m.p. 183—184°, α 0° in EtOH (consumes 3 $NaIO_4$, giving 2 HCO_2H). *βγδε-*Diiso*propylidenedulcitol αζ-*iodide is similarly reduced to (**III**). M.p. are corr. [α] are $[\alpha]_D^{20}$.

R. S. C.

Keten acetals. IX. Keten dialkyl acetals. S. M. McElvain and P. M. Walters (*J. Amer. Chem. Soc.*, 1942, **64**, 1059—1060; cf. A., 1942, II, 227).—Pr$^{\alpha}_2$, b.p. 94—95°/19 mm., Bu$^{\beta}_2$, b.p. 109—110°/19 mm., and di*iso*amyl *bromoacetal*, b.p. 137—139°/20 mm., are obtained from $CH_2{:}CH{\cdot}OAc$ and Br in ROH (50—60% yield) or $CHMe(OR)_2$ and Br, and with KOBu$^{\gamma}$–Bu$^{\gamma}$OH give *keten Pr$^{\alpha}_2$* (52%), b.p. 58—59°/16 mm., 153—154°/760 mm., Bu$^{\beta}_2$ (47%), b.p. 76—77°/17 mm., 180—181°/760 mm., and di*iso*amyl *acetal* (51%), b.p. 105—106°/17 mm., 210—211°/760 mm., respectively.

R. S. C.

Esters of thiodiglycol. W. R. Clayton and E. E. Reid (*J. Amer. Chem. Soc.*, 1942, **64**, 908—909).—Thiodiglycol (purification described) has m.p. −10°, b.p. 147·5°/6 mm., is stable at 180°, is decomposed by 0·1—1N-NaOH, $Pb(OAc)_2$, or $Cu(NO_3)_2$ at 100°, but is unaffected by solid NaOH at 140°, $Ba(OH)_2$, CaO, or Al_2O_3 at 180°. With $(RCO)_2O$ or RCO_2H at 150—160° it gives the diformate, m.p. −15·5°, b.p. 134·5°/8 mm., diacetate, b.p. 139·5°/8 mm., *dipropionate*, m.p. −23°, b.p. 158°/8 mm., *dibutyrate*, m.p. −28°, b.p. 172°/8 mm. [also obtained from $S[(CH_2)_2{\cdot}Cl]_2$ (**I**) and Pr$^{\alpha}CO_2K$], di*isovalerate*, b.p. 181—182°/8 mm. [also obtained from (**I**)], and *di*-n-*hexoate*, m.p. 7°, b.p. 207°/7 mm. With $NPhMe_2$–$ZnCl_2$ at 120—160° it gives an oil, b.p. 204—210°/8 mm. $(Cl{\cdot}[CH_2]_2)_2SO$ does not react with KOAc in boiling AcOH or EtOH, but the sulphone and KOAc– or Bu$^{\beta}CO_2K$–AcOH gives oils.

R. S. C.

Potassium trimethyl orthosilicate. B. Helferich and K. Krenkler (*Ber.*, 1942, **75**, [*B*], 530—531).—*K Me$_3$ orthosilicate* is obtained by boiling $Si(OMe)_4$ (0·2 mol.) with solid, finely powdered anhyd. KOH (0·1 mol.) for 1 hr. and treating the supernatant liquid with $Si(OMe)_4$ (0·1 mol.); the cryst. product is washed with dry C_6H_6.

H. W.

Products of the conjoint action of sulphur dioxide and chlorine on aliphatic hydrocarbons in ultra-violet light. III. Sulphochlorination of *iso*butane and formation of isomerides during the sulphochlorination and chlorination of gaseous hydrocarbons. F. Asinger and F. Ebeneder (*Ber.*, 1942, **75**, [*B*], 344—349).—Sulphochlorination of $CHMe_3$ gives iso*butane-α-sulphonyl chloride* (**I**), b.p. 87°/15 mm. (corresponding cyclo*hexylamide*, m.p. 45°), in ~75% yield. Other products are a mixture of chloroisobutanesulphonyl chlorides and a little *β-methylpropane-αγ-disulphonic anhydride*, m.p. 188°

(corresponding *dianilide*, m.p. 118°; H of CH does not appear to be replaced). (**I**) is also obtained from Cl_2 and the corresponding thiocyanate. *β-Methylpropane-β-sulphonyl chloride*, b.p. 80°/15 mm. cannot be obtained by the thiocyanate or thiocarbamide method but is derived from $Bu^{\gamma}SO_3H$ and PCl_5. The same relationships appear to exist in the chlorosulphonation of C_3H_8 and n-C_4H_{10} in CCl_4 at ~20—30° as in the direct chlorination of these hydrocarbons under similar conditions or in the gas phase at 300° if an excess of hydrocarbon is present. This is true also for n- and iso-C_4H_{10} and n- and iso-C_5H_{12} except that *tert.* H is replaced by Cl but not by SO_2Cl. With a deficiency of hydrocarbon sulphochlorination is the simpler process since *gem*- and *αβ*-disubstitution are not observed. H. W.

Di[alkylsulphon]imides. B. Helferich and H. Flechsig (*Ber.*, 1942, **75**, [*B*], 532—536).—Gradual simultaneous addition of $MeSO_2Cl$ and 5N-NaOH to $MeSO_2{\cdot}NH_2$ in H_2O at ≯8° gives *dimethanesulphonimide* (anhyd.), b.p. 170°/0·5 mm. (also $+2H_2O$), which behaves as a strong acid, giving anhyd. *K*, *NH*$_4$, *Sr*, *Pb*, *Ti*^{I}, and C_5H_5N salts, Li ($+H_2O$), Na ($+H_2O$), Ba ($+2H_2O$), Cu ($+4H_2O$), Ni ($+4H_2O$), Co ($+4H_2O$), Mn ($+4H_2O$), and Cd ($+4H_2O$) salts. Simultaneous addition of $EtSO_2Cl$ (2 mols.) and 5N-NaOH (4 mols.) to NH_4Cl (1 mol.) in H_2O so that the solution is slightly alkaline gives *diethanesulphonimide*, m.p. 78·5—79° (*Na* salt, m.p. 157—158°), which can be accurately titrated with NaOH in presence of Me-orange. *Di*-n-*butanesulphonimide*, m.p. 84—85° (*Na* salt), is described. *Di*-n-*hexane*-, m.p. 88—89°, and *di*-n-*butane*-, m.p. 98°, -*sulphonimide* give *Na* salts which foam strongly in H_2O. $MeSO_2{\cdot}NH_2$, $EtSO_2Cl$, and 5N-NaOH yield *methanesulphonethanesulphonimide*, m.p. 103—104° [*Na* salt ($+1H_2O$), m.p. 163°]. cyclo*Hexanesulphonmethylsulphonimide*, m.p. 94—95°, is obtained analogously using $MeSO_2Cl$. H. W.

Acids and bases in organic chemistry. D. Davidson (*J. Chem. Educ.*, 1942, **19**, 154—160). L. S. T.

Ether-like compounds. XXVI. Rate of reaction and intramolecular forces. M. H. Palomaa [with T. Kaski, R. Korte, and T. A. Siitonen] (*Ber.*, 1942, **75**, [*B*], 336—339).—Measurements of the rates of esterification of $CH_2Cl{\cdot}CO_2H$ and $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$ (in comparison with $OMe{\cdot}[CH_2]_2{\cdot}CO_2H$) and of the hydrolysis of $CH_2Cl{\cdot}CO_2Me$, $Cl{\cdot}[CH_2]_2{\cdot}CO_2Me$, $Cl{\cdot}[CH_2]_3{\cdot}CO_2Me$, $Cl{\cdot}[CH_2]_3{\cdot}CO_2Et$, and $Br{\cdot}[CH_2]_3{\cdot}CO_2Et$ show that Cl causes a more pronounced min. than ethereal O in the rate of catalytic esterification and hydrolysis. This effect, as with O, is most pronounced in the β-position. Cl with at. refraction 5·957 causes a less pronounced min. than Br with at. refraction 8·748. H. W.

Polymerisation of methyl methacrylate under the influence of benzoyl peroxide.—See A., 1942, I, 332.

Cerebrosides. XVII. Occurrence of a hexacosenoic acid amongst the fatty acids of cerebroside of brain. E. Klenk and E. Schumann (*Z. physiol. Chem.*, 1942, **272**, 177—188).—Cerebronic acid consists almost entirely of α-hydroxytetracosanoic acid but lignoceric acid is a mixture, probably of C_{22}, C_{24}, and C_{26} acids. The isolation by esterification, fractionation, and, in some cases, hydrogenation of a hexacosenoic acid, m.p. 45·0—45·5°, nervonic, and other (impure) acids (C_{16} to more than C_{26}) from the unsaturated acids of cerebrosides is described. W. McC.

Autoxidation of oxygen-active acids. II. Viscosimetric analysis of the addition of oxygen to the methyl esters. W. Treibs (*Ber.*, 1942, **75**, [*B*], 331—335; cf. A., 1942, II, 277).—Determinations of η of Me linolenate (**I**), linoleate (**II**), oleate, ricinoleate, *iso*elæostearate, α-elæostearate (**III**), glyceryl dilinolenate, linoleate, and trielæostearate show a diminution with increasing no of isolated and increase with increasing no. of conjugated double linkings. The course of autoxidation of the esters is viscosimetrically analysed by observing the rate of rise of the ester in a narrow strip of filter-paper. (**III**) is shown to be immediately converted by O_2 into a polymeric monoperoxide whereas (**I**) and (**II**) give monomeric monoperoxides; polymerisation and loss of H_2O accompany further addition of O. H. W.

Derivatives of octadecenoic acids. I. *p*-Phenylphenacyl esters. II. *S*-Benzylthiuronium salts. J. P. Kass, J. Nichols, and G. O. Burr (*J. Amer. Chem. Soc.*, 1942, **64**, 1061—1062).—*p*-Phenylphenacyl oleate (**I**), m.p. 61—62° (lit. 60·5°), elaidate (**II**), m.p. 72—73° (lit. 73·5°), linoleate, m.p. 37—37·5° (clear at 46·5—47°), linolelaidate, m.p. 73—75°, linolenate, m.p. 37·5—38° (clear at 38—39°), β-elæostearate, m.p. 89—90°, and *θικλ*-tetrabromostearate, m.p. 107—108°, and the corresponding *S*-benzylthiuronium salts, m.p. 125—125·5°, 123·5—125°, 122—123°, 122—124°, 115—130°, and 129—130°, respectively, are prepared. Of the unsaturated compounds only (**I**) and (**II**) have the correct I val. The salts are very unstable. R. S. C.

Branched-chain fatty acids. I. Synthesis of ρ-methyloctadecoic acid. J. Cason (*J. Amer. Chem. Soc.*, 1942, **64**, 1106—1110).—$CH_2Bu^{\beta}Br$ with Mg and then $CdCl_2$ in Et_2O gives $Cd(CH_2Bu^{\beta})_2$ (**I**), which with $CO_2Me{\cdot}[CH_2]_2{\cdot}COCl$ [prep. from $(CH_2{\cdot}CO)_2O$ (**II**) by way of the Me H ester, m.p. 53—57°, b.p. 110—111°/2 mm., modified], b.p. 85—87°, gives, after boiling, *Me γ-keto-ζ-methyl*-n-*octoate*, b.p. 122—125°/13 mm. (*semicarbazone*, sinters at 70°, m.p. 78—84°), hydrolysed by N-NaOH at 60±5° to the *acid*, m.p. 48—50°, b.p. 134°/2 mm. [*semicarbazone*, m.p. varies, 138—140° (decomp.)], which is obtained in poor yield from (**I**) and (**II**). Clemmensen reduction then gives $Bu^{\beta}{\cdot}[CH_2]_4{\cdot}CO_2H$, b.p. 103—105°/2 mm., the Et ester, b.p. 102°/12 mm., of which with Na–EtOH gives $Bu^{\beta}{\cdot}[CH_2]_5{\cdot}OH$ (**III**) (57%), b.p. 100°/13 mm., also obtained from $CH_2Bu^{\beta}{\cdot}MgBr$ by $(CH_2)_2O$ by way of $Bu^{\beta}{\cdot}[CH_2]_3{\cdot}OH$, b.p. 98—101°/45 mm., and *ζ-methyl*-n-*hexyl bromide*, b.p. 83°/45 mm. With 48% HBr, (**III**) gives *θ-methyl*-n-*octyl bromide*, b.p. 92—93°/12 mm., and thence $Cd([CH_2]_5{\cdot}Bu^{\beta})_2$, which with $CO_2Et{\cdot}[CH_2]_8{\cdot}COCl$ (modified prep.), b.p. 171—172°/12 mm., gives *Et ι-keto-ρ-methyl*-n-*octadecoate* (46%; 20% obtained by the MgBr derivative), b.p. 197°/1—2 mm. Hydrolysis then gives the *CO-acid*, m.p. 73·5—74·5° (*semicarbazone*, m.p. 97·5—97·7°), reduced (Clemmensen) to *ρ-methyloctadecoic acid*, m.p. 67·0—67·6° (*Pb* salt; *amide*, m.p. 100·2—101·3°; *tribromoanilide*, m.p. 112·0—112·5°), purified by way of the *Me* ester, m.p. 26—28°, b.p. 171—172°/1—2 mm. M.p. are corr. R. S. C.

Cardiolipin, $[\alpha]_D$ +7·0° in EtOH, from ox heart.—See A., 1942, III, 577.

Action of ethyl orthoformate on diacetyl and acetylacetone. L. N. Parfentiev and A. M. Mirzaev (*J. Gen. Chem. Russ.*, 1941, **11**, 707—712).—$CH(OEt)_3$ condenses with Ac_2 in presence of H_2SO_4 to *diacetyl tetra-acetal*, b.p. 51—52°/21 mm. $CH(OEt)_3$ and CH_2Ac_2 give a mixture containing *diethoxydimethylallene*, b.p. 128—129° (*tetrabromide*, an oil), formed by loss of EtOH from the tetra-acetal first produced, also a *solid*, m.p. 39°, b.p. 140—141°/20 mm., regarded as $CH(CHAc_2)_3$. G. A. R. K.

Synthesis of α-bromo-β-methoxy-*n*-butyric acid. H. E. Carter and L. F. Ney (*J. Amer. Chem. Soc.*, 1942, **64**, 1223—1224).—$CHMeBr{\cdot}CHBr{\cdot}CO_2Et$ (1 mol.) and NaOMe (1·25 mol.) (1 mol. gives mainly $CHMe{:}CBr{\cdot}CO_2Et$) in MeOH at −5° to 25° give $OMe{\cdot}CHMe{\cdot}CHBr{\cdot}CO_2Et$ (80—90%), b.p. 90—100°/18 mm., converted by aq. NaOH at 15—20° into the acid and thence *allo*-threonine (best method of prep.). R. S. C.

Preparation and reactions of acetopyruvic (αγ-diketo-*n*-valeric) acid. A. L. Lehninger and E. J. Witzemann (*J. Amer. Chem. Soc.*, 1942, **64**, 874—878).—When $Et_2C_2O_4$ is condensed with $COMe_2$ and NaOEt, and the resultant $CHAc{:}C(ONa){\cdot}CO_2Et$ is treated in H_2O with 1·00 mol. of N-NaOH, 70% of $CH_2Ac{\cdot}CO{\cdot}CO_2H$, m.p. 98° (corr.) (*Cu* salt), is obtained. With 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$,HCl in hot EtOH it gives 1-2′ : 4′-*dinitrophenyl-5-methylpyrazole-3-carboxylic acid*, m.p. 239—241° (corr.). In excess (≮2 mols.) of aq. NaOH it is hydrolysed to $H_2C_2O_4$ and $COMe_2$, the (unimol.) rate depending on the [NaOH]. It is stable in aq. acid at ≯38° and in H_2O or in vac. at 0°. It is dibasic (potentiometric titration), having k_1 2·6 × 10^{-3} and k_2 3·2 × 10^{-9}. With $KMnO_4$ (0·4 mol.) in H_2SO_4 it gives $COMe_2$, $H_2C_2O_4$, CO_2, and (?) $CH_2Ac{\cdot}OH$ and $AcCO_2H$, by way of, mainly, $CH_2Ac{\cdot}CO_2H$. In very dil. alkali it gives CO_2 and AcOH, but in more conc. alkali gives also $H_2C_2O_4$ by way of $Me{\cdot}[CO]_3{\cdot}CO_2H$. Its stability is too great to permit it to function as a biological intermediate. R. S. C.

Action of monoethanolamine on ethyl bromomalonate. C. B. Kremer, M. Meltsner, and H. Hindin (*J. Amer. Chem. Soc.*, 1942, **64**, 1010).—$CHBr(CO_2Et)_2$ and $NH_2{\cdot}[CH_2]_2{\cdot}OH$ at the b.p. give $CH_2(CO_2Et)_2$. R. S. C.

Preparation of dicarboxylic acids related to civetone. I. Preparation of *cis*- and *trans*-Δ$^{\iota}$-octadecene-αα-dicarboxylic acid. L. Ruzicka, P. A. Plattner, and W. Widmer (*Helv. Chim. Acta*, 1942, **25**, 604—620).—Condensation of Me undecenoate by Na in xylene gives ~50% of Δ$^{\alpha\chi}$-*docosadien-λ-ol-μ-one* (**I**), m.p. 45—47° (softens at 41·5°), which does not give a yellow colour with $C(NO_2)_4$, and ~2% of the corresponding *diketone* (**II**), m.p. 52—53° [*phenylosazone*, m.p. 69—70° (softens at 65°), obtained from (**I**) or (**II**); *disemicarbazone*, m.p. 236—238° (decomp.)]. (**II**) is oxidised by H_2O_2 and alkali to undecenoic acid. Catalytic reduction (Raney Ni) of (**I**) or (**II**) affords β-, m.p. 128—129°, and α-, m.p. 82·5—83·5°, -*docosane-λμ-diol*. Na and EtOH reduce (**I**) to β- (**III**), m.p. 114·5—115·5°, and α- (**IV**), m.p. 62—63° (softens at 60°), -Δ$^{\alpha\chi}$-*docosadiene-λμ-diol* with some Δ$^{\alpha\chi}$-*docosadien-λ-ol*, m.p. 54—56°. Better results are obtained by the reduction of (**I**) or (**II**) by $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$. (**III**) gives a :CMe_2 derivative, b.p. 151—153°/0·03 mm., and a *diacetate* (**V**), b.p. 210° (bath)/0·02 mm. The :CMe_2 derivative, b.p. 156—157°/0·07 mm., and *diacetate* (**VI**) of (**IV**) are described. Ozonisation of (**V**) in CCl_4 and oxidation of the product with $KMnO_4$ leads to *β-ικ-dihydroxyoctadecane-αα-dicarboxylic acid* (**VII**), m.p. 142·5—144° (Me_2 ester, m.p. 94—95°), whilst similar treatment of (**VI**) leads to the corresponding *α-acid* (**VIII**), m.p. 119—123° after softening at 110° (Me_2 ester, m.p. 69—71·5°). (**VII**) and 33% HBr–AcOH at 100° give the (impure) *β-ικ-dibromo-octadecane-αα-dicarboxylic acid*, m.p. 78—82° [Me_2 ester (**IX**), m.p. 35—36°]; the corresponding *α-Br*$_2$-acid, m.p. 98—100° (softens at 81°), and its Me_2 ester (**X**), m.p. 57·5—58·5° (softens at 55°), are described. (**IX**) is converted by NaI and Zn dust in boiling $COMe_2$ followed by CH_2N_2 into Me_2 *β-*Δ$^{\iota}$-*octadecene-αα-dicarboxylate*, m.p. 30·5—31·5° [*acid* (**XI**), m.p. 80—81°], hydrogenated (Raney Ni in EtOH) and

then hydrolysed to octadecane-$\alpha\sigma$-dicarboxylic acid, m.p. 124—125° (Me_2 ester, m.p. 65—65·5°). Similarly (**X**) affords *Me_2 α-Δ$^{\iota}$-octadecene-ασ-dicarboxylate*, m.p. 42·5—44·5° (*acid*, m.p. 112·5—113·5°). Ozonisation of (**XI**) gives sebacic acid. M.p. are corr. H. W.

Tracer studies with radioactive carbon and hydrogen. Synthesis and oxidation of fumaric acid. M. B. Allen and S. Ruben (*J. Amer. Chem. Soc.*, 1942, **64**, 948—950).—^{11}C is converted by way of $^{11}CO_2$, $K^{11}CN$, and $(CH_2{\cdot}^{11}CN)_2$ into fumaric acid (**I**), $(CH{\cdot}^{11}CO_2H)_2$. When this is oxidised by $KMnO_4$–H_2SO_4 (to give $3CO_2 + 1HCO_2H$), the HCO_2H produced is not radioactive and thus originates in the CH of (**I**). When non-radioactive (**I**) is oxidised in a solution containing ^3H_2O (no exchange of H occurs), the HCO_2H is not radioactive. The C–H linking of the CH of (**I**) thus remains intact. The mechanism of oxidation is thus: (**I**) $\rightarrow CO_2H{\cdot}C(OH){:}CH{\cdot}CO_2H \rightarrow CO_2 + OH{\cdot}CH(CO_2H)_2 \rightarrow CO_2 + CHO{\cdot}CO_2H \rightarrow HCO_2H + CO_2$. R. S. C.

Modern methods of preparative organic chemistry. XVI. Diene syntheses. K. Alder (*Angew. Chem.*, 1942, **55**, 53—58).—A lecture.

Components of Fehling's solution.—See A., 1942, I, 334.

Carbonyl compounds as oxidising agents. H. Adkins (*J. Chem. Educ.*, 1942, **19**, 218—221). L. S. T.

Formaldehyde condensation as organic autocatalysis. W. Langenbeck [with W. Sander and F. Kühn] (*Naturwiss.*, 1942, **30**, 30—34).—The autocatalytic character of the condensation of CH_2O is established kinetically in presence of $CO(CH_2{\cdot}OH)_2$ (**I**), $OH{\cdot}CH_2{\cdot}CHO$ (**II**), fructose, $CHPhBz{\cdot}OH$–CH_2O compound (**III**), glucose, $CHPhBz{\cdot}OH$ (**IV**), anisoin, and acetoin. The individual catalysts differ only in their period of incidence and the max. acceleration is the same for each. The most active catalysts are (**I**) and (**II**) and these are doubtless the actual autocatalysts since there is no induction period. (**III**) is more active than (**IV**). (**III**) is $OH{\cdot}CH_2{\cdot}CPhBz{\cdot}OH$ since it is oxidised by $Pb(OAc)_4$ to Bz_2 and CH_2O and its oxime is transformed by Ac_2O into PhCN and $CH_2Bz{\cdot}OAc$. The mechanism of the action is discussed. H. W.

Formation and decomposition of hexamethylenetetramine. E. Baur and W. Rüetschi (*Helv. Chim. Acta*, 1941, **24**, 754—767).—The reaction between CH_2O and NH_3 in presence of an excess of either reactant and at temp. between 0° and 50° is shown by acidimetric titration in presence of phenol-red to be probably of the third order and to proceed mainly through $(CH_2{\cdot}NH)_3$. The synthesis of $(CH_2)_6N_4$ from $(NH_4)_2SO_4$ and CH_2O in presence of an OAc′–AcOH buffer has been followed at temp. between 0° and 60° by argentometric determination of CH_2O and measurement of p_H by the quinhydrone electrode and the decomp. of $(CH_2)_6N_4$ has been investigated similarly. At higher temp. $(CH_2)_6N_4$ fulfils the conditions of Guldberg's theorem of the independence of equilibrium on the direction, whereas at lower temp., abnormalities are observed in the sense of Baur's theorem. H. W.

Novel type of Cannizzaro reaction. E. M. Fry, E. J. Wilson, jun., and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 872—873).—In N-NaOH at 100°, *L′*-methoxy-*L*-methyldiglycollic dialdehyde (obtained from α-methyl-*L*-rhamnopyranoside) consumes 1 mol. of NaOH and undergoes intramol. disproportionation, giving $CO_2H{\cdot}CH(OMe){\cdot}O{\cdot}CHMe{\cdot}CH_2{\cdot}OH$ (60%) and $OH{\cdot}CH_2{\cdot}CH(OMe){\cdot}CHMe{\cdot}CO_2H$ (40%). These products could not be isolated as such but are identified by hydrolysis by aq. HCl at 100° to $CHO{\cdot}CO_2H$ (semicarbazone), $CH_2(CH_2{\cdot}OH)_2$ (diphenylurethane), $CHO{\cdot}CH_2{\cdot}OH$ (phenylosazone), and *L*-lactic acid (Zn salt). R. S. C.

Manufacture of unsaturated ketones.—See B., 1942, II, 251.

Condensation of ketones with alcohols in the presence of mixed catalysts. V. N. Ipatiev and V. Haensel (*J. Org. Chem.*, 1942, **7**, 189—198).—Ketones with reactive ·COMe and alcohols with the terminal group $\cdot CH_2{\cdot}OH$ or $\cdot CHMe{\cdot}OH$ give large yields of higher ketones at >200°/1—50 atm. These ketones contain the no. of C atoms equiv. to the sum of the C atoms of the original ketone and alcohol. Only catalysts having both dehydrogenating and dehydrating properties can effect the condensation. The extent of the reaction and purity of the product depend largely on the initial alcohol : ketone ratio. There is no conclusive proof of the mechanism of the change. An intermediate H disproportionation reaction is involved and a mol. of H_2O is eliminated from ketone + alcohol. Primary alcohols (**I**) and ketones afford higher ketones by a similar mechanism. (**I**) alone in the presence of the same catalyst produce esters which are formed through a Cannizzaro reaction. The following changes are described. $Pr^{\beta}OH + COMe_2$ to $COMeBu^{\beta}$ and $COBu^{\beta}_2$; $Pr^{\beta}OH + COMeEt$ to $COPr^{\alpha}{\cdot}CH_2{\cdot}CHMeEt$, $COMe{\cdot}CH_2{\cdot}CHMeEt$, and $COEtBu^{\beta}$; $COMe_2 + CHPr^{\beta}{\cdot}OH$ to $COPr^{\beta}_2$ with a little $COMeBu^{\beta}$; $Pr^{\beta}OH$ + *cyclo*hexanone to (?) *cyclo*hexylacetone; $Bu^{\alpha}OH + COMe_2$ to $COMe{\cdot}C_6H_{11} + PrCO_2Bu^{\alpha}$; $COMe_2 + Pr^{\alpha}OH$ to $COMeBu + EtCO_2Pr^{\alpha}$; $EtOH + COMe_2$ to $COMePr^{\alpha}$ and $COPr^{\alpha}_2$; $Bu^{\beta}OH$ to $Pr^{\beta}CO_2Bu^{\beta}$ with a little $Pr^{\beta}CHO$; $Pr^{\alpha}OH$ to $COEt_2$, EtCHO $CHEt_2{\cdot}OH$, and $EtCO_2Pr^{\alpha}$. H. W.

Dipole moments and structures of diketen, and of acid anhydrides and related oxygen and sulphur compounds.—See A., 1942, I, 289.

Behaviour of γ-diketones. I. H. Hunsdiecker (*Ber.*, 1942, **75**, [*B*], 447—454).—Various methods of prep. are discussed and illustrated. 5-Methylfurfuraldehyde, COMePr, and dil. NaOH at room temp. slowly afford 5-methylfurfurylidenemethyl Pr ketone, b.p. 138·5°/5 mm., reduced by Na–Hg and EtOH at 10—15° but not catalytically (PtO_2 or Pd–$BaCO_3$) to 5-methyl-2-γ-ketohexylfuran, b.p. 89—90°/1·5 mm., which is converted according to Wolff–Kishner but not Clemmensen into 5-methyl-2-*n*-hexylfuran, b.p. 96°/20 mm. This is transformed by aq. AcOH–H_2SO_4 at 120° into *undecane-βε-dione*, m.p. 33°. Furfurylideneacetone in converted by boiling HCl–EtOH into *γζ-diketo-octoic acid* (**I**), m.p. 77—78°, with large amounts of resin which is reduced if the ketone is added slowly to the gently boiling acid. Similarly furylidenemethyl Et ketone gives γζ-diketononoic acid (**II**). The following are obtained by electrolysis between Pt electrodes of solutions of diketo-acids and fatty acids which have been neutralised to a small extent by NaOMe: (**I**) with $EtCO_2H$ gives *nonane-βε-dione*, b.p. 113°/15 mm., with $Pr^{\alpha}CO_2H$ *decane-βε-dione*, b.p. 132°/17 mm., with $Bu^{\alpha}CO_2H$ *undecane-βε-dione*, b.p. 141°/14 mm., m.p. 33°, with $Bu^{\beta}CO_2H$ *ι-methyldecane-βε-dione*, b.p. 130°/13 mm., with $n\text{-}C_5H_{11}{\cdot}CO_2H$ *dodecane-βε-dione*, b.p. 148°/12 mm., m.p. 40·5°, with $n\text{-}C_7H_{15}{\cdot}CO_2H$ *tetradecane-βε-dione*, b.p. 158°/14 mm., m.p. 51°, with lauric acid *octadecane-βε-dione*, b.p. 170°/1 mm., m.p. 71°, with $OMe{\cdot}[CH_2]_4{\cdot}CO_2H$ *λ-methoxyundecane-βε-dione*, b.p. 167°/13 mm., m.p. 23°, with $CO_2H{\cdot}[CH_2]_2{\cdot}CO_2Me$, *Me εθ-diketodecoate*, b.p. 195°/18 mm., with $CO_2H{\cdot}[CH_2]_4{\cdot}CO_2Me$, *Me ηκ-diketododecoate*, b.p. 164°/1 mm., m.p. 32°, with γ-*iso*amyloxybutyric acid, ι-iso*amyloxydecane-βε-dione*, b.p. 139°/2 mm., whilst (**II**) and $Bu^{\alpha}CO_2H$ yield *dodecane-γζ-dione*, b.p. 150°/16 mm., m.p. 41°. *Tetradecane-βεκν-tetraone*, m.p. 105°, and *hexadecane-γζλχ-tetraone*, m.p. 116°, are derived from (**I**) and (**II**) respectively. Interaction of $CHNaAc{\cdot}CO_2Et$ (10% excess) with the requisite acid chloride gives a 75—85% yield of the acylacetoacetate, converted by NaOMe in MeOH at room temp. into the acylacetic ester (**III**); thus are obtained *Me* iso*valeryl-*, b.p. 64°/2 mm., *Me hexoyl-*, b.p. 109°/11 mm., *Me heptoyl-*, b.p. 115°/7 mm., and *Me phenylacetyl-*, b.p. 125°/3 mm., *-acetate*. The Na derivatives of (**I**) are condensed with $COMe{\cdot}CH_2Br$ ($COPh{\cdot}CH_2Br$, $CHMeBr{\cdot}COMe$, etc.), giving thus *Me-α-hexoyl-*, b.p. 143°/2·5 mm., *Me α-heptenoyl-*, b.p. 123°/0·5 mm., and *Me β-methyl-α-*iso*valeryllævulate*, b.p. 142°/12 mm. H. W.

Manufacture of keto-alcohols.—See B., 1942, II, 251.

Keto-ethers. IX. Propoxymethyl alkyl (or phenyl) ketones. H. R. Henze, (Miss) V. B. Duff, W. H. Matthews, jun., J. W. Melton, and E. O. Forman (*J. Amer. Chem. Soc.*, 1942, **64**, 1222—1223; cf. A., 1941, II, 351).—*CH_2Cl Pr^{α}* [prep. from $Pr^{\alpha}OH$ by $(CH_2O)_3$– or 60% aq. CH_2O–HCl gas; 60% yield], b.p. 26—28°/32 mm., 110°/755 mm., and *Pr^{β} ketone* (prep. from $Pr^{\beta}OH$ by 36% aq. CH_2O–HCl; 49% yield), b.p. 36°/45 mm., 101°/750 mm., with anhyd. CuCN in boiling Et_2O gives n- (55%), b.p. 56°/40 mm., 152°/751 mm., and iso-*propoxyacetonitrile*, b.p. 74°/53 mm., 145—146°/748 mm., respectively, converted by MgRHal–Et_2O and then cold HCl into $OPr{\cdot}CH_2{\cdot}COR$. n- and iso-*Propoxymethyl alkyl* (or aryl) *ketone*, successively, are described in which R = Me, b.p. 49°/6 mm. (150°/763 mm.), 35°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 144°), *Et*, b.p. 56°/4 mm., 47°/11 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 103°), *Pr^{α}*, b.p. 64°/4 mm., 56°/8 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 98°), *Pr^{β}*, b.p. 79°/60 mm., 42°/6 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 89°), *Bu^{α}*, b.p. 81°/12 mm., 63°/7 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 78°), *Bu^{β}* b.p. —, 56°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 95°), *CHMeEt*, b.p. —, 50°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 61°), n-, b.p. 120°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 73°), 83°/8 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 77°), and iso-*amyl*, b.p. 111°/26 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 79°), 83°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 82°). *Ph* n-, b.p. 118°/6 mm., and iso-*propoxymethyl ketone*, b.p. 112°/6 mm., are also prepared. Temp. are corr. R. S. C.

Production of unsaturated amines.—See B., 1942, II, 251.

Alkylammonium borates.—See A., 1942, I, 335.

Ethanol- and chloroethyl-ammonium metallic chlorides.—See A., 1942, I, 337.

Cobaltous and chromic ethanolamine complexes.—See A., 1942, I, 337.

Derivatives of alcohol amines [hydroxyalkylamines].—See B., 1942, II, 252.

Copper, nickel, and uranyl compounds of ethylenediaminetetraacetic acid.—See A., 1942, I, 334.

Esters of choline and its homologues. II. S. I. Lurie, Z. I. Fedorova, and E. D. Volkova (*J. Gen. Chem. Russ.*, 1941, **11**, 739—744; cf. A., 1940, II, 156).—Halides of esters of choline and ethylcholine with substituted benzoic acids are cryst. and readily purified, but those of homocholine crystallise with difficulty and are hygroscopic. Alkylamine esters of $m\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2H$ are obtained in yields >82%, but those of *p*-nitro- and *p*-chloro-benzoic acid in

55—58% yield; this is explained on an electronic basis. Bromocholine bromide (I) and *p*-NHAc·C_6H_4·CO_2Ag (II) give *choline p-acetamidobenzoate bromide*, m.p. 257—258°. Chlorohomocholine bromide and (II) give *homocholine p-acetamidobenzoate chloride* and the *chloride* of *ethylhomocholine p-acetamidobenzoate*, hygroscopic crystals, is formed from (II) and chloroethylaminopropyl iodide; with EtBr this gives *ethylhomocholine p-acetamidobenzoate bromide* (IV), m.p. 211—212°, also obtained by the action of EtBr on the reaction product of γ-diethylaminopropyl chloride and *p*-NHAc·C_6H_4·CO_2H. (I) and *p*-NHBu·C_6H_4·CO_2Ag give *choline* p-n-*butylaminobenzoate bromide*, m.p. 163—164·5°. *Ethylhomocholine* p-*hydroxybenzoate iodide*, hygroscopic crystals, is obtained by the action of EtI on the product, m.p. 100—102°, formed by heating γ-diethylaminopropyl *p*-hydroxybenzoate. By a similar method *ethylhomocholine*-m-, pale cream crystals, m.p. 179°, and -p-*nitrobenzoate bromide*, pale cream crystals, m.p. 204—206°, have been obtained. (I) and *p*-C_6H_4Cl·CO_2Ag give *choline* p-*chlorobenzoate bromide*, m.p. 194—196°. γ-*Diethylaminopropyl* p-*chlorobenzoate* has m.p. 234—235°. (IV) causes intestinal peristalsis comparable with that due to eserine.

G. A. R. K.

Syntheses of aminopropanols. II. O. Hromatka (*Ber.*, 1942, **75**, [*B*], 379—383; cf. A., 1942, II, 278).—The prep. of γ-aminopropanols from CH_2:CH·CH_2·OH (I) and amines under the influence of alkali is a general reaction. Protracted heating of a suspension of sarcosine in (I) containing CH_2:CH·CH_2·ONa at 108° and esterification (MeOH–HCl) of the product gives *Me methyl-γ-hydroxypropylaminoacetate*, b.p. 133—138°/18 mm. (*benzoate hydrochloride*, m.p. 151—153°). Similarly Ph·$[CH_2]_2$·NH_2 affords *β-phenylethyl-γ-hydroxypropylamine*, b.p. 127—135°/0·7 mm. (*picrate*, m.p. 138°), and *β-phenylethyldi-γ'-hydroxypropylamine*, b.p. 187—190°/0·8 mm. NH_2Ph gives γ-hydroxypropylaniline, b.p. 140°/0·4 mm. (*picrate*, m.p. 113—114°). $NHEt_2$ and CH_2:CH·CHEt·ONa (II) in PhMe give NEt_2·$[CH_2]_2$·CHEt·OH [*styphnate*, m.p. 103° (vac.)], also obtained from OH·CHEt·$[CH_2]$·Cl (III) and $NHEt_2$. Similarly (II) and piperidine afford *α-piperidinopentan-γ-ol*, b.p. 115°/12 mm. [*styphnate*, m.p. 98—99°; p-*nitrobenzoate hydrochloride*, m.p. 174° (vac.)], obtained also from (III). γ-Piperidino-γη-dimethyl-Δ^5-octen-α-ol (*picrate*, m.p. 116°) is derived from geraniol.

H. W.

Optically active phenylurethane anæsthetics. M. S. Raasch and W. R. Brode (*J. Amer. Chem. Soc.*, 1942, **64**, 1112—1114).—*dl-α*-Piperidinopropane-*βγ*-diol (I) is resolved by *l*-menthoxyacetic acid in $COMe_2$ into the *l*- (*l*-menthoxyacetate, m.p. 106°, $[\alpha]_D^{24}$ −67° in EtOH) and d-*diols*, b.p. 137°/12 mm., $[\alpha]_D^{20}$ ±13·1° in EtOH, which afford the *l*-' (II), m.p. 96—98°, $[\alpha]_D^{24}$ −14·3° in H_2O, and d-*diphenylurethane hydrochloride* (III), +COMeEt, m.p. 98—99°, $[\alpha]_D^{24}$ +14·5°, and l- and d-*phenylurethane hydrochloride*, m.p. 187—188°, $[\alpha]_D^{21}$ −15·6°, $[\alpha]_D^{30}$ +15·7° in MeOH. By means of camphoric acid *dl*- gives *d*-, b.p. 156·5—157°, $[\alpha]_D^{26}$ +46·7° (d-*camphorsulphonate*, m.p. 126—127°, $[\alpha]_D^{24}$ +41·8° in EtOH), and l-*α-diethylaminopropan-β-ol*, b.p. 157°, $[\alpha]_D^{24}$ −46·2° in EtOH (l-*camphorsulphonate*, m.p. 125—126°, $[\alpha]_D^{24}$ −41·5° in EtOH), and thence the d- (IV) and l-*phenylurethane hydrochloride* (V), m.p. 165°, $[\alpha]_D^{24}$ +10·3° in EtOH. (II), (III), and the *dl*-isomeride, freed from COMeEt, have equal anæsthetic activity (rabbit's cornea), but +COMeEt the *l*-form is the most effective; intravenous toxicities are *l*- 25, *d*- = *dl*- 18 mg. per kg. body wt. The monophenylurethane of (I) is a weak anæsthetic, as also are (IV), (V), and the *dl*-isomeride, which have equal effect.

R. S. C.

Esters of *C*-dialkylglycines [α-amino*iso*butyric acids].—See B., 1942, II, 252.

Adsorption behaviour of fission products of proteins. II. Chromatography of aminodicarboxylic acids on alumina. F. Turba and M. Richter (*Ber.*, 1942, **75**, [*B*], 340—344).—Untreated Al_2O_3 is not active enough; its activity is greatly improved by pre-treatment with N-HCl but for full development requires the use of a 0·05N-AcOH–OAc' buffer with p_H 3·3. Under these conditions aspartic (I) and glutamic acid (II) are quantitatively adsorbed and can be completely recovered by elution with dil. alkali. They can thus be quantitatively separated from glycine, alanine, leucine, serine, arginine, histidine, tryptophan, proline, cystine, and methionine. They can also be separated from one another since (II) is quantitatively washed into the filtrate by N-AcOH–OAc' buffer whilst (I) is retained by the Al_2O_3, from which it is removed by dil. alkali.

H. W.

[Preparation of] aliphatic vinyl tertiary amides.—See B., 1942, II, 252.

Preparation of γ-alkylamides of glutamic acid. N Lichtenstein [with S. Gertner] (*J. Amer. Chem. Soc.*, 1942, **64**, 1021—1022).—Pyrrolidonecarboxylic acid with 17% aq. NH_2Me or 33% aq. $NHEt_2$ at 37° gives *glutam-γ-methyl-*, m.p. 192°, $[\alpha]_D^{26}$ +6·45°, and *-ethylamide*, m.p. 200°, $[\alpha]_D^{24}$ +6·25°, respectively, the structure of which is proved by non-formation of NH_2R by $Ba(OH)_2$ at 35—40° but liberation thereof by $Ca(OH)_2$ at 35—40° after hydrolysis by 20% HCl. The products give high Van Slyke vals., probably owing to formation of the γ-OH-acid and thence of the lactone.

R. S. C.

Preparation of monosubstituted ureas.—See B., 1942, II, 252.

Synthesis of a cyanogenetic substance by oxidation of formaldehyde and ammonia. R. Fosse, R. de Larambergue, and J. Gaiddon (*Compt. rend.*, 1941, **213**, 329—331).—Oxidation of a mixture of CH_2O and NH_3 with $KMnO_4$ and $(NH_4)_2SO_4$ does not give free HCN in appreciable amount but yields an intermediate which gives HCN when the solution is distilled and a ppt. of AgCN when heated with $AgNO_3$–HNO_3. Successive additions of $AgNO_3$ and HCl to the solution give free HCN, which is not liberated by HCl alone.

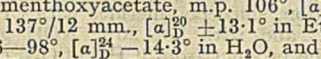
C. S.

II.—SUGARS AND GLUCOSIDES.

2 : 3-Dimethylrhamnose. O. T. Schmidt, E. Plankenhorn, and F. Kübler (*Ber.*, 1942, **75**, [*B*], 579—582).—*iso*Propylidenerhamnose, powdered KOH, and CH_2PhCl at 100° give 1 : 5-*dibenzyl*-2 : 3-iso-*propylidenerhamnofuranose* (I), m.p. 104°, $[\alpha]_D^{20}$ +30·3° in $COMe_2$, with smaller amounts of an *isomeride*, m.p. 84°, $[\alpha]_D^{20}$ −15·44° in $COMe_2$. (I) is hydrolysed by 0·05N-HCl at 100° to 1 : 5-*dibenzylrhamnofuranoside*, m.p. 77·5°, $[\alpha]_D^{20}$ +48·2° in $COMe_2$, converted by Me_2SO_4–KOH at 50° into 1 : 5-*dibenzyl*-2 : 3-*dimethylrhamnofuranoside* (II), m.p. 119°, $[\alpha]_D^{20}$ +71·7° in $COMe_2$, which is transformed by H_2–PdO in MeOH into 2 : 3-*dimethylrhamnose* (III), b.p. 125—130°/0·01 mm., $[\alpha]_D^{23}$ +47·6° in H_2O; this with $NHPh·NH_2$ in AcOH under N_2 gives 3-*methylrhamnosephenylosazone*, m.p. 128—130° [or, hydrated, m.p. 118° (decomp.)], $[\alpha]_D^{20}$ +57° in C_5H_5N–EtOH (2 : 3) after 17 hr. (II) and boiling MeOH containing 1% of conc. HCl yield 5-*benzyl*-2 : 3-*dimethylmethylrhamnofuranoside*, m.p. 93°, $[\alpha]_D^{20}$ −72° in $COMe_2$, hydrogenated to 2 : 3-*dimethylmethylrhamnoside*, b.p. 100°/0·1 mm. (III) and azobenzoyl chloride in abs. C_5H_5N at 40° afford two cryst. *diesters*, $C_{34}H_{32}O_7N_2$, m.p. 241°, $[\alpha]_{6252}^{20}$ +33·7° in $CHCl_3$, and m.p. 165°, $[\alpha]_{6252}^{20}$ −3·5° in $CHCl_3$.

H. W.

Thiosugar of yeast. G. Wendt (*Z. physiol. Chem.*, 1942, **272**, 152—156; cf. A., 1926, 52, 96).—The methylthiolpentose (triacetate, m.p. 66—67°), obtained from the adenylmethylthiolpentose of yeast by acid hydrolysis, consumes 4 I when treated with HOI, yielding SMe·CH_2·$[CH(OH)]_3$·CO_2H, also obtained by oxidation with dil. HNO_3. The product of reduction with Hg–Na, SMe·CH_2·$[CH(OH)]_3$·CH_2·OH, m.p. 118°, contains no SH and is converted with consumption of 2 I into the corresponding sulphoxide, SOMe·CH_2·$[CH(OH)]_3$·CH_2·OH. With $Pb(OAc)_4$ the reduction product yields ~1 mol. of CH_2O whereas the pentose itself yields no CH_2O thus. The results indicate that the pentose probably is



Its configuration probably corresponds with that of *d*-ribose.

W. McC.

Synthesis of glucose and gentiobiose derivatives. D. D. Reynolds and W. O. Kenyon (*J. Amer. Chem. Soc.*, 1942, **64**, 1110—1112).—Addition of $COCl_2$–PhMe to *β-d*-glucose 1 : 2 : 3 : 4-tetra-acetate (I) and $CaSO_4$ in C_5H_5N gives *di*-1 : 2 : 3 : 4-*tetra-acetyl*- (82%), m.p. 198—199°, $[\alpha]_{5461}^{26·5}$ +12·15° in $CHCl_3$, converted by HBr–AcOH at room temp. into *di*-1-*bromo*-2 : 3 : 4-*triacetyl-β-d-glucosyl carbonate*, m.p. 147—148°, $[\alpha]_{5461}^{26·5}$ +258° in $CHCl_3$. With Ag_2O–$CaSO_4$–MeOH this gives *di*-2 : 3 : 4-*triacetyl-β-d-methylglucosidyl carbonate*, m.p. 191—192°, $[\alpha]_{5461}^{26}$ −75·0°, and with (I)–Ag_2O–$CaSO_4$–$CHCl_3$ gives *di*-1 : 2 : 3 : 4 : 2' : 3' : 4'-*hepta-acetyl-β-gentiobiosyl carbonate* (40%), m.p. 237—238°, $[\alpha]_{5461}^{26}$ −28·8° in $CHCl_3$, hydrolysed by NaOMe–MeOH–$CHCl_3$ at room temp. to gentiobiose (76%).

R. S. C.

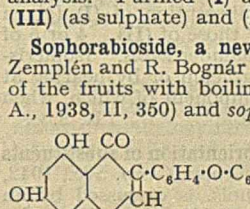
Synthesis of primverin, the principal glucoside of the primrose (*Primula officinalis*). F. Mauthner (*J. pr. Chem.*, 1941, [ii], **159**, 36—38).—*β*-Resorcylic acid and Me_2SO_4–aq. NaOH first at room temp. and then at the b.p. afford (after hydrolysis) the 4-Me ether, m.p. 158—159°, the Me ester, m.p. 48—49°, of which with α-acetobromoprimverose (Zemplén *et al.*, A., 1939, II, 99) and quinoline–Ag_2O yields primverin hexa-acetate, m.p. 210—211°, converted by NH_3–MeOH at 0° into primverin, m.p. 203—204°.

A. T. P.

Ganglioside; a new group of sugar-containing cerebral lipins. E. Klenk (*Z. physiol. Chem.*, 1942, **273**, 76—86; cf. *ibid.*, 1941, **270**, 185).—Ganglioside (I), decomp. ~205°, from the protagon fraction of brain, is a sugar-containing lipin, probably derived as follows: $C_{18}H_{36}O_2$ (stearic acid) (II) + $C_{18}H_{37}O_2N$ (sphingosin or related compound) (III) + $C_{10}H_{19}O_9N$ (neuramic acid) + $3C_6H_{12}O_6$ (galactose) (IV) = $C_{84}H_{118}O_{26}N_2$ (I) + $5H_2O$. Purification of (I) from cerebrosides and phosphatides is effected through decomp. of the Pb salt, followed by solvent extraction and chromatographic analysis. Purified (I) and boiling 10% H_2SO_4–MeOH give (II) + (III) (as sulphate) and (I)–10% HCl afford (IV).

A. T. P.

Sophorabioside, a new glucoside from *Sophora japonica*, L. G. Zemplén and R. Bognár (*Ber.*, 1942, **75**, [*B*], 482—489).—Extraction of the fruits with boiling EtOH yields sophoricoside (I) (Charaux, A., 1938, II, 350) and *sophorabioside* (II) but no sophoraflavonoloside (Rabaté *et al.*, A., 1938, II, 350). (I) is (*A*). (II) (anhyd.), softens at 240°, m.p. 248° (incipient decomp.), $[\alpha]_D^{19}$ −72·5° in C_5H_5N, (+3H_2O), m.p. 245—248° after softening at 150°, melting at 156—160° (decomp.), resolidifying at



(*A*.)

190—200°, and re-melting at 245—248°, $[\alpha]_D^{19}$ −66·3° in C_5H_5N, is hydrolysed by acids to genistein [triacetate, m.p. 205—206° (corr.)], *d*-glucose, and *l*-rhamnose. Ozonisation of (**II**) gives an amorphous biose (amorphous *acetate*, $[\alpha]_D^{20}$ −20·0° in $CHCl_3$). Oxidation of (**II**) by OI′ leaves the *l*-rhamnose component unchanged. Sophorabiose is therefore a rhamnosidoglucose different from rutinose and closely analogous to neohesperidose. (**II**) gives an *octa-acetate*, m.p. 254—255°, softens at 240°, $[\alpha]_D^{15}$ −52·7° in C_5H_5N. Methylation (Me_2SO_4 and warm NaOH) of (**II**) gives an amorphous product containing sugar which is hydrolysed by acids to 2 : 4 : 6-*trimethoxyphenyl* p-*hydroxybenzyl ketone*, m.p. 165·5—170·5° (corr.), identical with the compound obtained from (**I**) and by the Hoesch synthesis from 2 : 4 : 6-$C_6H_3(OMe)_3$ and *p*-OH·C_6H_4·CH_2·CN. With Me_2SO_4 and cold alkali (**II**) gives an amorphous product, hydrolysed to *genistein* 5 : 7-Me_2 *ether* (**III**), m.p. 266—266·5° [*acetate*, m.p. 187° (corr.), softens at 185°]. CH_2N_2 and (**II**) afford *sophorabioside* 5 : 7-Me_2 *ether* (anhyd.), softens at 162°, m.p. 166—168°, (+$4H_2O$), softens at 130°, m.p. ~140° (slight decomp.), $[\alpha]_D^{20}$ −61·1° in C_5H_5N (hexa-acetate, m.p. 208·5—209° (corr.), $[\alpha]_D^{20}$ −55·6° in C_5H_5N), hydrolysed to (**III**), which is oxidised by H_2O_2 to *p*-OH·C_6H_4·CO_2H but no *p*-OMe·C_6H_4·CO_2H, (**II**) is therefore (*A*) but with the side-chain ·C_6H_4·O·$C_6H_{10}O_4$·O·$C_6H_{11}O_4$. H. W.

Neolinarin, a new glucoside from *Linaria vulgaris*, L. G. Zemplén, R. Bognár, and L. Mester (*Ber.*, 1942, **75**, [*B*], 489—495).—Extraction of the foliage and blossoms of the plant with EtOH and purification of the ppt. with C_6H_6 followed by crystallisation from 80% EtOH yields a gelatinous ppt. of pectolinarin (**I**); the mother-liquors yield *neolinarin* (**II**) (+$2H_2O$), m.p. 232—233°, $[\alpha]_D^{18}$ −88·3° in C_5H_5N, −118·5° in AcOH, hydrolysed by acid to pectolinarigenin (**III**) [6-methoxyacacetin], *d*-glucose, and *l*-rhamnose. Ozonisation of (**II**) in AcOH leads to rutinose hepta-acetate, m.p. 169—169·5°, $[\alpha]_D^{20}$ −27·7° in $CHCl_3$. HBr in AcOH converts completely acetylated (**II**) into *monoacetylpectolinarigeninglucoside triacetate* (**IV**), m.p. 198—199° (corr.), $[\alpha]_D^{22}$ −39·6° in C_5H_5N. (**III**) and acetobromoglucose give a *pectolinarigeninglucoside tetra-acetate*, m.p. 197·2° (corr.), darkening at 194°, $[\alpha]_D^{17.5}$ −26·2° in $CHCl_3$, converted by Ac_2O and C_5H_5N into *pectolinarigeninglucoside penta-acetate*, m.p. 196° (corr.), softens at 193°, $[\alpha]_D^{25}$ −14·5° in $CHCl_3$, $[\alpha]_D^{23}$ −54·6° in C_6H_6 [also obtained from (**IV**)], and hydrolysed to *pectolinarigeninglucoside*, m.p. 257—258° (decomp.), $[\alpha]_D^{24}$ −70·0° in C_5H_5N. Very probably (**II**) is a cryst. form of (**I**). (**II**) is transformed into (**I**) by alkali but the reverse change has not been effected. H. W.

Anhydro-derivative of *D*-mannosan<1, 5>β<1, 6> (presumably 3 : 4-anhydro-*D*-talosan<1, 5>β<1, 6>). R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 925—928).—2 : 3-*iso*-Propylidene-*D*-mannosan 4-*p*-toluenesulphonate in boiling 20% AcOH gives D-*mannosan*<1, 5>β<1, 6> 4-p-*toluenesulphonate*, m.p. 168°, $[\alpha]_D^{20}$ −80·3° in abs. EtOH (2 : 3-*diacetate*, m.p. 115—116°, $[\alpha]_D^{20}$ −103·4° in $CHCl_3$), which with NaOMe–MeOH at 35° and later room temp. or aq. NaOH at 100° gives 3 : 4-*anhydro*-D-*talosan*<1, 5>β<1, 6>, m.p. 73—74°, $[\alpha]_D^{20}$ −49·5° in H_2O (structure by analogy; 2-p-*toluenesulphonate*, m.p. 147—148°, $[\alpha]_D^{20}$ −19·0° in $CHCl_3$). When this is treated with, successively, Ac_2O–H_2SO_4 at <0° (later 10° and 20°), NaOMe–MeOH–$CHCl_3$, and H_2–Raney Ni in H_2O at 100°/167 atm., it yields *D*-mannitol and *D*-iditol [hexa-acetate (**I**), m.p. 121—122°, $[\alpha]_D^{20}$ −25·5° in $CHCl_3$]. Crystallographic properties of (**I**), its *L*- and dl-, m.p. 165—166°, *-isomerides*, and of *D*-mannitol hexa-acetate are described for identification. M.p. are corr. R. S. C.

***X*-Ray diffraction patterns of starches.**—See A., 1942, I, 291.

Starch. XVIII. Fractionation of native starch by dilute alcohol. K. H. Meyer and M. Fuld (*Helv. Chim. Acta*, 1941, **24**, 1408—1409).—The "cryst. amylose" obtained by Wiegel (A., 1942, II, 191) is a mixture of amylose and amylopectin. H. W.

III.—HOMOCYCLIC.

Pro-γ-carotene. L. Zechmeister and W. A. Schroeder (*J. Amer. Chem. Soc.*, 1942, **64**, 1173—1177).—Chromatography of the pigments from the ripe fruit of *Butia capitata* yields *pro-γ-carotene* (**I**) (0·3 mg. per kg.), m.p. 118—119° (corr.; block; after sintering) (photomicrograph), rubixanthin, neolycopene, a prolycopene, γ-carotene (**II**) (2 zones), neo-γ-carotene, β-carotene and an isomeride thereof, and 2 unknown pigments. The absorption of (**I**) (given for 12 solvents) shows max. at 4—6 mμ. < those of (**II**). 4 or 5 of the ethylenic linkings in (**I**) are *cis*, the remainder *trans*. Isomerisation of (**I**) by I or conc. HCl in light petroleum or by heating at 130—135° gives complex mixtures, each component of which, when similarly isomerised, gives a similar mixture. R. S. C.

Quantum-mechanical investigation of the orientation of substituents in aromatic molecules. G. W. Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900—908).—Orientation in aromatic mols. is discussed by an essentially mol. orbital method involving consideration of energies of those structures contributing to the activated complex in which a covalent bond is formed between the aromatic ring and the reagent. Substitutions by electrophilic, nucleophilic, and radical reagents can be treated and qual. agreement is obtained. W. R. A.

Alkylation of benzene in presence of acid catalysts. R. L. Burwell, jun., and S. Archer (*J. Amer. Chem. Soc.*, 1942, **64**, 1032—1034).—CHMeEt·OH, α_D^{20} −4·14°, and C_6H_6 in presence of 100% H_3PO_4 at 70°, H_2SO_4 at 53°, or BF_3 at 20° give CHPhMeEt, α_D^{22} +0·055, 0·03°, and 0·065°, respectively. Condensation in presence of H_3PO_4 is as fast as dehydration. Racemisation does not precede reaction since α of CHMeEt·OH is not affected by H_3PO_4. $CHMeEt^+$ is probably an intermediate. BF_3 catalyses condensation of C_6H_6 with *cyclo*hexyl fluoride, but not with the bromide. R. S. C.

Thermal fission of *p*-cymene. H. Breneck and H. F. Müller (*Ber.*, 1942, **75**, [*B*], 554—560).—The chief products of the thermal fission of *p*-$C_6H_4MePr^\beta$ (**I**) are *p*-C_6H_4Me·$CH{:}CH_2$ (**II**), unchanged (**I**), PhMe, and products of higher b.p. Under the most favourable conditions (650°; C catalyst and complete absence of metals; use of diminished pressure gives no advantage) the yield of (**II**) is 54% of the crude (**I**) obtained from sulphite-cellulose manufacture, or 62·5% of the pure (**I**) contained therein. Other C_6H_6 derivatives with Pr^β side-chain behave similarly. $PhPr^\beta$ and *iso*thymol give similar yields of styrene derivatives. C has no advantage over other catalysts in the thermal fission of PhEt or C_6H_4MeEt; it appears to have a sp. effect on the elimination of CH_4 from the Pr^β side-chain. H. W.

Influence of hydrogen acceptors on the polymerisation of vinyl derivatives. J. W. Breitenbach and H. L. Breitenbach (*Ber.*, 1942, **75**, [*B*], 505—509).—Diminution of the rate of polymerisation and of the mean chain length of the polymeride is observed as the influence of Bz_2O_2 and chloranil on $CHPh{:}CH_2$. The quinone effect is also observed with Me acrylate, methacrylate, and vinyl-acetate. H. W.

Addition polymerisation catalysed by substituted acyl peroxides. C. C. Price, R. W. Kell, and E. Krebs (*J. Amer. Chem. Soc.*, 1942, **64**, 1103—1106).—That catalysis of the polymerisation of $CHPh{:}CH_2$ and $CH_2{:}CH{\cdot}CO_2Me$ by $(RCO_2)_2$ is due to decomp. to $RCO_2{\cdot}$ + R· + CO_2 is proved by inclusion of Br, OMe, and Cl in the polymerides (prep., usually, in dioxan) when R = *p*-C_6H_4Br, OMe·C_6H_4, and CH_2Cl, respectively. This accords with the data of Schulz *et al.* (A., 1938, II, 437). *p*-C_6H_4Br·, but not *p*-$C_6H_4Br{\cdot}CO_2{\cdot}$, intervenes in the reaction, since polymerides with $CHPh{:}CH_2$ contain only C, H, and Br, and with hot 20% KOH give no *p*-$C_6H_4Br{\cdot}CO_2H$. However, the product from $(CH_2Cl{\cdot}CO_2)_2$ contains O. Prep. of the peroxides (differing for various R) is detailed (cf. Vanino *et al.*, A., 1900, i, 371). R. S. C.

Polymerisation action of dimethyl sulphate. II. Dimerisation of αα-diphenylethylene and the polymerising action of analogues of dimethyl sulphate. V. N. Belov and B. M. Lebedev (*J. Gen. Chem. Russ.*, 1941, **11**, 745—749).—In addition to Me_2SO_4 (A., 1941, II, 284), Et_2SO_4 and *p*-$C_6H_4Me{\cdot}SO_3Me$ (in order of their activity) cause polymerisation of $CPh_2{:}CH_2$, but not $EtNO_3$, $(C_6H_4Me)_3PO_4$, or EtOAc. After short treatment a third dimeride (**I**) of $CPh_2{:}CH_2$, m.p. 200—201°, is isolated (cf. Hughes and Ingold, A., 1933, 262) (yield <4%). Longer treatment causes no increase of (**I**), but formation of *ααγγ*-tetraphenyl-Δ^α-butene (**II**), m.p. 113°, further polymerised to 1 : 1 : 3-triphenyl-3-methylhydrindene, m.p. 143°. (**I**) cannot be further polymerised by heating with Me_2SO_4, does not absorb Br, and is oxidised by CrO_3 to $COPh_2$; it is assumed to be 1 : 1 : 3 : 3-tetraphenyl*cyclo*butane. The polymerising action of Me_2SO_4 is due to its decomp. products, probably $MeHSO_4$. G. A. R. K.

Preparation of *ααβ*-triphenylethane. P. Bert (*Compt. rend.*, 1941, **213**, 792—793).—C_6H_6 (10 mols.), $CH_2Cl{\cdot}CHCl_2$ (**I**) (1 mol.), and $AlCl_3$ (10 g.) at 100° yield 80% of $CHPh_2{\cdot}CH_2Ph$ (**II**), b.p. 211°/14 mm., accompanied by CH_2Ph_2 and $(CHPh{:})_2$ due to formation of CH_2Cl_2 and $(CHCl{:})_2$ from (**I**). C_6H_6 and $(CHCl{:})_2$ also afford (**II**). C. S.

Substituted diphenylbutadienes. I. Addition of bromine to α-phenyl-δ-*p*-bromophenyl-$\Delta^{\alpha\gamma}$-butadiene. K. A. Huggins and O. E. Yokley (*J. Amer. Chem. Soc.*, 1942, **64**, 1160—1161).—*p*-$C_6H_4Br{\cdot}CH_2{\cdot}CO_2H$, $CHPh{:}CH{\cdot}CO_2H$, Ac_2O, and PbO give *α-phenyl-δ-p-bromophenyl-$\Delta^{\alpha\gamma}$-butadiene* (**I**) (18·4%), m.p. 163° [$(CH{\cdot}CO)_2O$ *adduct*, m.p. 226°]. With Br in $CHCl_3$ at 0° (**I**) gives *αβγδ-tetrabromo-α-phenyl-δ-p-bromophenyl-n-butane*, m.p. 230°, or with 1 mol. at 0° or <0° in accordance with Ingold's theory (A., 1931, 1267), only *γδ-dibromo-δ-phenyl-α-p-bromophenyl-Δ^α-n-butene*, m.p. 129—130°, oxidised by O_3 in $CHCl_3$ or $KMnO_4$–$MgSO_4$–$COMe_2$ to $CHPhBr{\cdot}CHBr{\cdot}CO_2H$ (64·8%) and *p*-$C_6H_4Br{\cdot}CHO$ (62·26%). R. S. C.

Attempted synthetic preparation of the antirachitic vitamins. X. New path to the synthesis of the unsaturated system. K. Dimroth and E. Stockstrom (*Ber.*, 1942, **75**, [*B*], 582—586).—2-Dimethylaminomethyl*cyclo*hexyl chloride is converted by successive treatment with Mg and 1-decahydronaphthylideneacetaldehyde into α-2-dimethylaminomethyl*cyclo*hexyl-β-1′-decahydronaphthylidene-ethyl alcohol, which is degraded (Hofmann) to 2-methylenedeca-

hydronaphthylidene-ethylidene*cyclo*hexane [adduct with $(CH\cdot CO)_2O$, m.p. 180—181°]. H. W.

Diterpenes. XLIX. Synthesis of 1-methyl-7-ethylphenanthrene and of 1-methyl-7-*sec.*-butylphenanthrene. β-Ethylretene. L. Ruzicka and S. Kaufmann [with M. Hinder, J. Pataki, G. Sagen, T. Grauer, W. Janett, R. Tanner, H. Simon, L. Werner, and T. Suter] (*Helv. Chim. Acta*, 1941, **24**, 939—945).—2-$C_{10}H_7Et$, $(CH_2\cdot CO)_2O$, and $AlCl_3$ give *γ-keto-γ-6-ethyl-2-naphthylbutyric acid*, m.p. 170—171°, the *Me* ester, m.p. 69·5°, of which is transformed by MgMeI followed by hydrolysis into *γ-6-ethyl-2-naphthyl-Δβ-pentenoic acid*, m.p. 135—137°, reduced to the *-valeric acid*, m.p. 120°. This is converted by P_4O_{10} in dry C_6H_6 into *4-keto-1-methyl-7-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene* [additive *compound*, m.p. 99—100°, with $C_6H_3(NO_2)_3$], transformed (Wolff–Kishner) and dehydrogenated (Pd–C at 300°) to *1-methyl-7-ethylphenanthrene*, m.p. 87·5° [additive *compound*, m.p. 134°, with $C_6H_3(NO_2)_3$]. 2-$C_{10}H_7Ac$ and MgEtI afford 2-sec.-*butenylnaphthalene*, b.p. 153—154°/13 mm., hydrogenated (Raney Ni) to 2-sec.-*butylnaphthalene*, b.p. 138—139°/14·5 mm. This gives successively *γ-keto-γ-6-sec.-butylnaphthylbutyric acid*, m.p. 130—130·5°, its *Me* ester, m.p. 58·5—59°, *γ-6-sec.-butyl-2-naphthyl-Δβ-pentenoic acid*, m.p. 113°, *γ-6-sec.-butyl-2-naphthylvaleric acid*, m.p. 91·5°, *4-keto-1-methyl-7-sec.-butyl-1 : 2 : 3 : 4-tetrahydrophenanthrene* [additive *compound*, m.p. 76·5—77·5°, with $C_6H_3(NO_2)_3$], *1-methyl-7-sec.-butyl-1 : 2 : 3 : 4-tetrahydrophenanthrene*, a liquid [additive *compound*, m.p. 57—60°, with $C_6H_3(NO_2)_3$], and *1-methyl-7-sec.-butylphenanthrene*, m.p. 62·5—63° [additive *compound*, m.p. 132—133°, with $C_6H_3(NO_2)_3$]. β-Ethyldihydroretene is dehydrogenated by Pd–C at 320° to β-ethylretene, m.p. 91—93° [additive *compound*, m.p. 153—154° with $C_6H_3(NO_2)_3$; corresponding *quinoxaline* derivative, m.p. 133—134°]. M.p. are corr. H. W.

Optically active vasopressor amines. W. R. Brode and M. S. Raasch (*J. Amer. Chem. Soc.*, 1942, **64**, 1449—1450).—$CHPhMe\cdot CH_2\cdot NH_2$ with *l*-malic acid in EtOH and from the mother-liquors by the *d*-acid gives the *d*-base *l*-malate and *l*-base *d*-malate, m.p. 182—184°, $[\alpha]_D^{22-26}$ ±21·9° in H_2O; resolution by *d*-tartaric acid is slow, giving the d-*base* (10—15%), b.p. 102°/2 mm., $[\alpha]_D^{29}$ +35·4° in EtOH; resolution by camphorsulphonic (**I**) or menthoxyacetic acid is very slow. CHPhMe·CH_2·NHMe with *d*-(**I**) in EtOAc and from the mother-liquors by *d*-mandelic acid in EtOH–Et_2O gives the d-, b.p. 103°/21 mm., $[\alpha]_D^{23}$ +32·2° in EtOH (*d*-camphorsulphonate, m.p. 118—119°, $[\alpha]_D^{25}$ +28·8° in H_2O), and *l-amine*, b.p. 101—102°/19 mm., $[\alpha]_D^{22}$ −31·7° in EtOH (*d*-mandelate, m.p. 86—87°, $[\alpha]_D^{22}$ +39·8°), respectively. R. S. C.

Action of potassium hypobromite on β-phenyl-αα-dimethylpropionamide. C. Mentzer (*Compt. rend.*, 1941, **213**, 581—584).—$CH_2Ph\cdot CMe_2\cdot CO\cdot NH_2$ and cold aq. KOBr give *β-phenyl-αα-dimethylethylcarbimide* (**I**), b.p. 112—115°/20 mm., 225°/760 mm.; at 60° *s-di-(β-phenyl-αα-dimethylethyl)carbamide*, m.p. 184—185° [with $Ca(OH)_2$ at 230° affords *β-phenyl-αα-dimethylethylamine* (**II**), b.p. 203—205°/760 mm.], results. PhNCO and (**II**) or NH_2Ph and (**I**) give *N-phenyl-N'-β-phenyl-αα-dimethylethylcarbamide*, m.p. 150—151°. W. C. J. R.

Colour reactions of sympathomimetic amines with diazonium compounds. K. H. Beyer (*J. Amer. Chem. Soc.*, 1942, **64**, 1318—1322).—Sympathomimetic aralkylamines are coupled with *p*-$NO_2\cdot C_6H_4\cdot N_2Cl$ (**I**) (M/1600) at 21°, treated after 1 hr. slowly with 1·1% Na_2CO_3 and 10 min. later with 10% NaOH, and extracted with $Bu^{\alpha}OH$; the colour in the $Bu^{\alpha}OH$ is then measured. (*A*) Primary amines having no phenolic OH (12 examples) give a red colour, the reactions being: NH_2R + (**I**) → $NHR\cdot HCl\cdot N:N\cdot C_6H_4\cdot NO_2$ → $NHR\cdot N:N\cdot C_6H_4\cdot NO_2$ ⟷ (Na_2CO_3) $NR:N\cdot NH\cdot C_6H_4\cdot NO_2$ ⟷ $NR:N\cdot N:C_6H_4:NO\cdot OH$ (pale yellow) ⟷ (NaOH) $NR:N\cdot N:C_6H_4:NO\cdot ONa$-*p* (red). Evidence for these reactions is: (i) immediate addition of NaOH (to give p_H ~11) prevents colour formation; (ii) migration of H and development of colour is prevented by use of *sec.* or *tert.* amines; (iii) the NO_2 is essential since *p*-$SO_3H\cdot C_6H_4\cdot N_2Cl$ or *p*-$C_6H_4Me\cdot N_2Cl$ (**II**) gives no colour; (iv) quinonoid structure is essential since (**II**), *m*-$NO_2\cdot C_6H_4\cdot N_2Cl$ (**III**), and 4 : 2 : 1-$NO_2\cdot C_6H_3Cl\cdot N_2Cl$ (**IV**) give no colour; and (v) the final step is reversible by HCl–NaOH. Absorption spectra (detailed) have absorption max. at 525±5 mμ., but the mol. extinction coeff. varies from ~200 to ~1250. (*B*) Amines having one phenolic OH (9 examples) give red colours, the reactions being: → 1 : 4 : 2-$OH\cdot C_6H_3X\cdot N:N\cdot C_6H_4\cdot NO_2$ (X = side-chain carrying the N) → (Na_2CO_3) 1 : 4 : 2-$O:C_6H_3X:N\cdot NH\cdot C_6H_4\cdot NO_2$ → 1 : 4 : 2-$O:C_6H_3X:N\cdot N:C_6H_4:NO\cdot OH$-*p* ⇌ 1:4:2-$O:C_6H_3X:N\cdot N:C_6H_4:NO\cdot ONa$-*p* (red). Evidence is: (i) reaction is not at the N since *sec.* amines give the colour [cf. class (*A*)]; (ii) the *o*-quinonoid structure may be the reason why ε is > in class (*A*) but is not the sole cause of colour since (**IV**) gives only a very faint colour; (iii) the *p*-NO_2 is involved since (**III**) gives an orange, and (**II**) a yellow, colour. OH (or α-CO) in the side-chain inhibits the reactivity of the phenolic OH but decreases the intensity of sp. absorption bands (also lower for *sec.* amines). (*C*) Pyrocatechol derivatives (4 examples) give green colours, reactions being probably as above but leading to 1 : 5 : 2 : 4-$O:C_6H_2X(OH):N\cdot N:C_6H_4:NO\cdot ONa$-*p* (absorption max. at 640±5 mμ.). If the side-chain is omitted, the colour is yellow and divided between the alkaline and BuOH layers; Me as side-chain deepens the colour and increases its solubility in BuOH. Other details are also discussed. R. S. C.

Regularities in the hydrogenative fission of *N*-benzyl compounds. L. Birkofer (*Ber.*, 1942, **72**, [*B*], 429—441).—$CH_2Ph\cdot NH_2$, $NH(CH_2Ph)_2$, and NHAlk·CH_2Ph are unaffected by H_2 in presence of PdO. $N(CH_2Ph)_3$ in AcOH and $N(CH_2Ph)_3$,HCl in H_2O give $NH(CH_2Ph)_2$. Benzylmethyl-laurylamine and -cetylamine are converted into methyl-laurylamine and -cetylamine, respectively. Dibenzyldodecylamine is hydrogenated (PtO_2 in AcOH) to hexahydrobenzyldodecylamine (*hydrochloride*, m.p. 218°). $NH_2\cdot N(CH_2Ph)_2$ yields (H_2, PdO, EtOH) $NH_2\cdot NH\cdot CH_2Ph$, whilst $[N\cdot N(CH_2Ph)_2]_2$ gives $NH(CH_2Ph)_2$. $N(CH_2Ph)_3Me\cdot OH$ readily affords $CH_2Ph\cdot NHMe$ (*flavianate*, m.p. 190°; *picrolonate*, m.p. 210°) whereas $N(CH_2Ph)_3MeI$ is not reduced. $NPh(CH_2Ph)Me_2Cl$ yields *cyclo*hexyldimethylamine. 2-Benzyldihydro*iso*indole gives dihydro*iso*indole. 1 : 4-Dibenzylpiperazine loses 2 mols. of PhMe and 5-amino-1-benzyl-1 : 2 : 3 : 4-tetrazole is hydrogenated to aminotetrazole. 2 : 4 : 6-*Tri-imino*-1 : 3 : 5-*tribenzyl*-1 : 3 : 5-*triazine* (**I**), m.p. 129—130° (obtained by addition of Br in EtOAc to $CH_2Ph\cdot NH_2$ and KCN in aq. EtOAc and treatment of the product with NaOH), gives melamine. Elimination of CH_2Ph from 2-imino-1-benzyl-1 : 2-dihydropyridine is slow and incomplete and accompanied by nuclear hydrogenation, the products being 2-amino-3 : 4 : 5 : 6-tetrahydropyridine and 2-imino-1-benzylpiperidine (*picrate*, m.p. 106°). 2-Benzylaminopyridine does not lose CH_2Ph but is hydrogenated to 2-*benzylamino*-3 : 4 : 5 : 6-*tetrahydropyridine*, m.p. 40—41° (*picrate*, m.p. 131°; *picrolonate*, m.p. 199°). Aromatic rings, CO_2H, and CN activate so that CH_2Ph is removed from *sec.* N. $NHPh\cdot CH_2Ph$ gives quantitatively (PdO) NH_2Ph and PhMe or (PtO_2) mainly *cyclo*hexylhexahydrobenzylamine with minor quantities of *cyclo*hexylamine and hexahydrotoluene. $NPh(CH_2Ph)_2$ yields NH_2Ph and PhMe whilst 2-*dibenzylaminonaphthalene*, m.p. 119°, affords β-$C_{10}H_7\cdot NH_2$ and PhMe. *Dibenzylglycine*, m.p. 200°, and its *Me* ester, m.p. 41°, afford glycine and $NH_2\cdot CH_2\cdot CO_2Me$, respectively. $CN\cdot N(CH_2Ph)_2$ yields $CN\cdot NH_2$ or (**I**) owing to polymerisation of $CN\cdot NH\cdot CH_2Ph$ if hydrogenation is interrupted before it is complete. $(CO\cdot NH\cdot CH_2Ph)_2$ and *NN-dibenzylurethane*, b.p. 169°/2 mm., are stable towards H_2. H. W.

Catalytic activity of an intermetallic compound of cadmium and copper in the vapour-phase reduction of nitrobenzene.—See A., 1942, I, 333.

Nitroamines. IX. Formation of nitroamines and their conversion into nitroanilines. E. Macciotta (*Gazzetta*, 1941, **71**, 81—94).—*o*- and *p*-$NO_2\cdot C_6H_4\cdot NH_2$ in AcOH with HNO_3 (*d* 1·52) and Ac_2O give *o*- (**I**) and *p*-$NO_2\cdot C_6H_4\cdot NH\cdot NO_2$ (**II**), respectively. In conc. H_2SO_4, (**I**) gives 2 : 4 : 1- (**III**) and 2 : 6 : 1-$(NO_2)_2C_6H_3\cdot NH_2$; (**II**) gives (**III**). Similarly 2 : 3 : 1-$(NO_2)_2C_6H_3\cdot NH\cdot NO_2$ gives 2 : 3 : 6- (**IV**), m.p. 234° (? 134°) (80%), and 2 : 3 : 4-*trinitroaniline* (**V**), m.p. 210° (20%). With 20% NaOH and MeOH, (**IV**) gives the *Me ether*, m.p. 177—178°, of 2 : 4-dinitro-3-aminophenol, m.p. 202°, obtained from (**IV**) and $Ba(OH)_2$–MeOH. In conc. H_2SO_4, the Ag salt of 2 : 5 : 1-$(NO_2)_2C_6H_3\cdot NH\cdot NO_2$ gives (**IV**) (70%) and 2 : 4 : 5-*trinitroaniline* (**VI**), m.p. 202° (30%), which with $Ba(OH)_2$–MeOH gives 4 : 6-dinitro-3-aminophenol, m.p. 225°. Similarly the Hg salt of 3 : 4 : 1-$(NO_2)_2C_6H_3\cdot NH\cdot NO_2$ gives (**VI**) (70%) and (**V**) (30%). The results are discussed in relation to the Koerner structure for C_6H_6, and to electronic theories of substitution. E. W. W.

Amino-alcohols. X. Intermediates of pentryl analogues. Chloronitroanilinoalkanols. C. B. Kremer and M. Meltsner (*J. Amer. Chem. Soc.*, 1942, **64**, 1285—1286; cf. A., 1940, II, 276).—The appropriate $C_6H_3Cl_2\cdot NO_2$ and amine in boiling $Bu^{\alpha}OH$ give β-4-*chloro*-2-*nitroanilino-ethyl*, m.p. 107·5°, -iso*propyl*, m.p. 116·5°, -tert.-, m.p. 121·5°, and -iso-*butyl*, m.p. 122°, *γ-4-chloro-2-nitroanilino*-n-*propyl*, m.p. 60°, *β-2-chloro-4-nitroanilino-ethyl*, m.p. 120°, -iso*propyl*, m.p. 144°, and -tert.-*butyl*, m.p. 71·5°, *γ-2-chloro-4-nitroanilino*-n-*propyl*, m.p. 73°, *β-5-chloro-2-nitroanilino-ethyl*, m.p. 116°, -iso*propyl*, m.p. 109°, and -tert.-*butyl*, m.p. 127°, *γ-5-chloro-2-nitroanilino*-n-*propyl*, m.p. 78·5°, *β-3-chloro-2-nitroanilino-ethyl*, m.p. 78·5°, -iso*propyl*, m.p. 83·5°, and -tert.-*butyl*, m.p. 98·5°, and β-6-*chloro*-2-*nitroanilinoethyl*, b.p. 155—157°/2 mm., *alcohol*. Thence $Na_2S_2O_4$ in weak aq. alkali yields *β-4-chloro-2-aminoanilino-ethyl*, m.p. 122·5°, -iso*propyl*, m.p. 130°, -tert.-, m.p. 121°, and -iso-*butyl*, *β-5-chloro-2-aminoanilino-ethyl*, m.p. 104·5°, and -iso*propyl*, m.p. 101·5°, *γ-5-chloro-2-aminoanilino*-n-*propyl*, m.p. 73·5°, *β*-3-, m.p. 74°, and *β-6-chloro-2-aminoanilinoethyl*, b.p. 135—137°/2 mm., *alcohol*. R. S. C.

Restricted rotation in arylamines. III. Preparation and resolution of 1-*N*-methyl-β-carboxypropionamido-2-methylnaphthalene and -4-chloro-2-methylnaphthalene. R. Adams and A. A. Albert (*J. Amer. Chem. Soc.*, 1942, **64**, 1475—1478; cf. A., 1942, II, 138).—The *peri*-CH of a $C_{10}H_8$ ring offers less interference than does Me in a C_6H_6 ring. 2 : 1-$C_{10}H_6Me\cdot NH_2$ (**I**) (prep. from the NO_2-compound by H_2–Raney Ni in EtOH at room temp./1—3 atm.) with Me_2SO_4–H_2O and then OH·CHPh·SO_3Na gives *1-methylamino-2-methylnaphthalene* (81%), b.p. 106—108°/2 mm., the *β-carboxypropionyl* derivative

[prep. by $(CH_2{\cdot}CO)_2O$ and a drop of H_2SO_4 in C_6H_6], m.p. 109°, of which is resolved by quinine in EtOAc to l-, m.p. 108° (*quinine* salt, +0·5EtOAc, m.p. 129·5°, $[\alpha]_D^{27}$ −128°), and d-*forms*, m.p. 107—108° (quinine salt, m.p. 99—100°, $[\alpha]_D^{27}$ −57°), $[\alpha]_D^{27}$ −75°, +74°, which in boiling $Bu^{\alpha}OH$ have a half-life period 5·7 hr. 2 : 4 : 1-$C_{10}H_5MeCl{\cdot}NH_2$ gives similarly 4-*chloro*-1-*methylamino*-2-*methylnaphthalene*, m.p. 30°, b.p. 136—137°/0·5 mm., and its dl-, m.p. 167·5—168·5°, d-, m.p. 115·5—116°, $[\alpha]_D^{30}$ +56° (*quinine* salt, +0·5EtOAc, m.p. 117—119°, $[\alpha]_D^{30}$ −56°), and impure l-*β-carboxypropionyl* derivative, softens at 116°, m.p. up to 163—167°, $[\alpha]_D^{30}$ −36°; the half-life period in boiling $Bu^{\alpha}OH$ is 4·1 hr. (**I**) gives similarly 1-*ethylamino*-2-*methylnaphthalene*, m.p. 108—109°/0·3 mm., but the *β-carboxypropionyl* derivative, m.p. 123°, thereof could not be resolved. M.p. are corr. [α] are in EtOH. R. S. C.

Sulphonating action of dialkyl sulphates. I. Interaction of dimethyl sulphate with diphenylmethyl- and triphenyl-amine. V. N. Belov (*J. Gen. Chem. Russ.*, 1941, **11**, 750—756).—NPh_2Me heated with Me_2SO_4 yields, in addition to the quaternary salt, Me_2O and sulphonation products of NPh_2Me. NPh_3 and Me_2SO_4 at 150° form no quaternary salt, but give Me_2O, MeOH, and sulphonation products of NPh_3. The formation of sulphonation products is attributed to $MeHSO_4$ formed by hydrolysis of Me_2SO_4 by traces of moisture. A similar process may account for the isolation of Me_2O during the methylation of certain brucidine derivatives (A., 1935, 1389). G. A. R. K.

Chemotherapeutic pyroplasmocidal compounds. I. Dialkylaminophenylcarbamides. M. P. Gertschuk (*J. Gen. Chem. Russ.*, 1941, **11**, 731—738).—(p-$NAlk_2{\cdot}C_6H_4{\cdot}NH)_2CO$ have been prepared in the hope of improving on the chemotherapeutic properties of akaprin (pyroplasmin) (**I**); one of them, the hydrochloride of (**III**) (below), is effective in cattle infected with *Babasiella bovis* and its M.T.D. is 10—20 times that of (**I**). p-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$ (**II**) and $CO(NH_2)_2$ at 148° afford (p-$NMe_2{\cdot}C_6H_4{\cdot}NH)_2CO$ (**III**), m.p. 253—255° (*dihydrochloride*, m.p. 242°; *dimethosulphate*, m.p. 215°). (**II**) and p-$NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO_2Et$ give a base, m.p. 253°. p-$NH_2{\cdot}C_6H_4{\cdot}NEt_2$ and $CO(NH_2)_2$ give (p-$NEt_2{\cdot}C_6H_4{\cdot}NH)_2CO$, m.p. 218—220° (cf. Zetzsche and Nerger, *Ber.*, 1940, **73**, [*B*], 476) (*dihydrochloride*, m.p. 240—241°). The p-NO-derivative of $NPhPr_2$ (improved prep.) is reduced by Zn and HCl to p-$NH_2{\cdot}C_6H_4{\cdot}NPr_2$, which with $CO(NH_2)_2$ in PhOH gives NN′-*di*-p-*dipropylaminophenylcarbamide*, m.p. 186° (*dihydrochloride*, m.p. 224—225°; *dimethosulphate*, m.p. 233°). (**III**) affords a $(NO_2)_2$-compound, m.p. 188—189°. The *methosulphate* of p-$NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NHPh$ has m.p. 177—178°. G. A. R. K.

Long-chain sulphonamides and their therapeutic properties. H. Arnold, E. Helmert, T. Möbus, R. Prigge, H. Rauen, and T. Wagner-Jauregg (*Ber.*, 1942, **75**, [*B*], 369—378).—*Na hydnocarpylsulphonate*, decomp. 150—155°, shrinks at 135°, *hydnocarpylsulphonamide* (**I**), m.p. 90—92°, N^4-*undecenoyl*- (**II**), m.p. 196—198°, N^4-*chaulmoogroyl*- (**III**), m.p. 185—187° after softening, N^4-*dodecoyl*- (**IV**), m.p. 207—208°, N^1-dodecoyl- (**V**), m.p. 113—114° (lit. 120—122°), N^4-acetyl-N^1-oleyl-, m.p. 126—127° (lit. 131—135°), N^1-oleyl- (**VI**), m.p. 120°, N^4-*acetyl*-N^{1}N^4-*dioleyl*-, m.p. 92°, and N^1-*hydnocarpyl*- (**VII**), m.p. 116°, -*sulphanilamide*, and *Na* N^1-*oleylsulphanilamidoformaldehyde H sulphite* are described. Towards pneumococcus infection (**III**) and N^4-undecoylsulphanilamide (**VIII**) are inactive, (**II**) is possibly somewhat active, (**IV**) as potent as the unsubstituted material, whereas (**V**) is less active. 2-Aminobenzthiazole-6-sulphonamide and its 6-Ac derivative have little therapeutic action towards pneumococcus infection whereas 2-dodecoamido- and 2-chaulmoogroylamido-benzthiazole-6-sulphonamide are noticeably active, possibly owing to better tolerance. Sulphapyridine and (**V**) are ineffective against tuberculosis in guinea-pigs, and (**IV**), (**V**), and (**VIII**) and lauroylsulphapyridine are without action towards leprosy in rats, as are also (**VI**) and (**VII**), whereas (**I**) is slightly active. H. W.

Sulphonamides. J. C. Somaglino (*Rev. Fac. Cienc. Quím., La Plata*, 1941, **16**, 227—234).—4′-Nitro- was reduced (Sn, HCl) to 4′-*amino-diphenyl*-4-*sulphonamide*, m.p. 262—263° (decomp.). p-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2Cl$-$p$ with NH_2Ph yields 4′-*nitro*-, m.p. 182—183°, reduced (Sn, HCl) to 4′-*amino-diphenyl*-4-*sulphonanilide*, m.p. 182—183°. p-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$, p-$C_6H_4Ph{\cdot}NH_2$, and C_5H_5N in $COMe_2$ give the *Ac* derivative, m.p. 169°, of 4-*sulphanilamidodiphenyl*, m.p. 247°. The *Ac* derivative, m.p. 245°, of 2-*sulphanilamidofluorene*, m.p. 239°, was prepared similarly. F. R. G.

NN′-Diacetylsulphanilyl- and NN′-disulphanilyl-*l*-cystine. F. Irreverre and M. X. Sullivan (*J. Amer. Chem. Soc.*, 1942, **64**, 1488—1489).—*l*-Cystine and p-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in aq. NaOH give NN′-*di*-N^4-*acetylsulphanilyl*-, m.p. 204—206° (decomp.), and thence (hot 10% HCl) NN′-*disulphanilyl*-l-*cystine*, m.p. 193—194° (decomp.). R. S. C.

Sulphonamide [derivatives]. III. *N*-Substituted derivatives. N. Giovambattista (*Rev. Fac. Cienc. Quím., La Plata*, 1941, **16**, 217—226; cf. Novelli *et al.*, A., 1941, II, 165).—$CH_2(C_6H_4{\cdot}NH_2$-$p)_2$, p-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$, and C_5H_5N in $COMe_2$ yield the Ac_2 derivative (+$2H_2O$), m.p. 243·5—245°, of 4 : 4′-*disulphanilamidodiphenylmethane*, m.p. 219·5—220·5°. 4 : 4′-*Disulphanilamidodiphenylsulphone* (+1·5C_6H_6), translucent at 136°, melting commences at 141—142°, is prepared by hydrolysis (aq. NaOH) of its Ac_2 derivative, new m.p. 292—293°. Similarly prepared were 4-*nitro*-4′-*sulphanilamidodiphenylsulphone*, m.p. 191—192° (*Ac* derivative, m.p. 279—280°), and *sulphoxide*, m.p. 238—239° (decomp.) [*Ac* derivative, m.p. 263—264·5° (decomp.)]. F. R. G.

***p*-Acylamidobenzenesulphonhydroxylamides.**—See B., 1942, III, 203.

Polysulphanilamido-compounds.—See B., 1942, III, 203.

Reactions of diazonium salts of arylazo-β-naphthylamines. H. H. Hodgson and C. K. Foster (*J.C.S.*, 1942, 435—437).—Solid 1 : 2-$NAr{\cdot}N{\cdot}C_{10}H_6{\cdot}N_2X$ (**I**) are obtained (exceptions noted) from the amine (*A*) by addition of solid $NaNO_2$ to (*A*) in AcOH–HCl (*d* 1·16; limited amount) or by use of $AcOH–NO{\cdot}SO_4H$ (alternative procedures). (**I**) readily afford the corresponding naphthols with a very small amount of H_2O (*e.g.*, during prep.; action of EtOH), with AcOH–Br give diazo-perbromides (when heated yield N_2 and Br-derivatives), do not couple with phenols, and do not afford hydrazines with $SnCl_2$–HCl. 2-*Bromo*-1-2′ : 5′-*dichloro*-, m.p. 138°, and -1-m-*chloro-benzeneazonaphthalene*, m.p. 123°, are described. The compound, m.p. 204°, obtained by Zincke *et al.* (A., 1888, 159) by reduction of (**I**) (Ar = Ph, X = HSO_4) is formulated as $C_{10}H_6\langle{}^{N(NHPh)}_{NH}\rangle NH$; an analogous *compound*, $C_{16}H_{13}N_4Cl$, m.p. 196°, decomp. 197°, is formed from (**I**) (Ar = o-C_6H_4Cl, X = HSO_4) and $SnCl_2$–HCl. C. S.

Reactions between *s*-diphenyltriazen and mercuric salts. C. M. Knowles and G. W. Watt (*J. Amer. Chem. Soc.*, 1942, **64**, 935—937).—Contrary to Mandal (*Sci. & Cult.*, 1940, **6**, 59), NHPh·N:NPh (**I**) with $HgCl_2$ or $HgBr_2$ in EtOH gives *compounds*, 2(**I**),$HgCl_2$, m.p. 161—165° (decomp.), and 2(**I**),$HgBr_2$, m.p. 132—134° (decomp.), respectively, with $Hg(OAc)_2$–EtOH gives the yellow salt (**II**) $Hg(NPh{\cdot}N{\cdot}NPh)_2$, m.p. 232° (decomp.; rapid heating) or 227° (decomp.; slow heating), and with $Hg(NO_3)_2$ gives, according to the conditions, (**II**), a red, m.p. 212° (decomp.) or (+$2C_5H_5N$) 216° (decomp.), or orange *isomeride*, m.p. 187° (decomp.), or substances of lower N content. M.p. are corr. R. S. C.

Nuclear methylation of phenols.—See B., 1942, II, 313.

Soluble derivatives of chlorocresol. W. H. Linnell (*Quart. J. Pharm.*, 1942, **15**, 111—118).—6-Chloro-4-amino-*m*-cresol (**I**) (prep. described) with PhCHO yields the :*CHPh* derivative, m.p. 128—129°, which does not form a stable compound with H_2SO_3 or $NaHSO_3$. The *cinnamylidene* derivative, m.p. 124·5—126°, of (**I**) combines with H_2SO_3; the product is isolated first as *Ba* and then Na_2 6-*chloro*-4-(α*γ*-*disulpho*-*γ*-*phenylpropylamino*)-m-*cresol*. It is not bactericidal. J. N. A.

Production of cresols and higher phenols by fusion.—See B., 1942, II, 313.

Coupling of *m*-halogenophenols with diazotised aniline and existence of chromoisomerism among 3-halogeno-4-benzeneazophenols. H. H. Hodgson and G. Turner (*J.C.S.*, 1942, 433—435; cf. A., 1942, II, 9).—PhN_2Cl and m-$C_6H_4Cl{\cdot}OH$ couple in aq. Na_2CO_3 (not NaOAc) to 3-chloro-4-benzeneazophenol, forms, m.p. 95°, 104°, and 114°, and in aq. NaOH (even with equimol. quantities) to 3-chloro-2 : 4-bisbenzeneazophenol (**I**), m.p. 181° (no trisazo-derivative formed). m-$C_6H_4Br{\cdot}OH$ affords similarly and respectively 3-*bromo*-4-*benzeneazophenol*, forms, m.p. 128° and 161—163°, and 3-*bromo*-2 : 4-*bisbenzeneazophenol* (**II**), m.p. 175°, whilst m-$C_6H_4I{\cdot}OH$ gives 3-*iodo*-4-*benzeneazophenol*, forms, m.p. 138° and 145°, and 3-*iodo*-2 : 4-*bisbenzeneazophenol* (**III**), m.p. 187°. The above forms are chromoisomerides; they are reduced to 4 : 3 : 1-$NH_2{\cdot}C_6H_3Hal{\cdot}OH$ and thence oxidised to 2-halogenobenzoquinones. (**II**) and (**III**), but not (**I**), with boiling aq. KOH give 2 : 4-bisbenzeneazoresorcinol. (**I**) with $Na_2S_2O_4$ yields 3-*chloro*-2 : 4-*diaminophenol*, m.p. 200° (*Bz*$_2$ derivative m.p. 192°), converted ($NO{\cdot}SO_4H$ in AcOH, then CuCl) into 2 : 3 : 4 : 1-$C_6H_2Cl_3{\cdot}OH$. 4 : 6 : 3 : 1-$(NO_2)_2C_6H_2Cl{\cdot}OH$ is reduced (Zn–HCl) to 4 : 6 : 3 : 1-$(NH_2)_2C_6H_2Cl{\cdot}OH$ (*Bz*$_2$ derivative, m.p. 215°). C. S.

Vicinal substituted resorcinols. II. Alkylresorcinols. Synthesis of *γ*-*n*-hexyl-, *γ*-*n*-heptyl-, and *γ*-*n*-octyl-resorcinol. A. Russell and H. C. Gulledge (*J. Amer. Chem. Soc.*, 1942, **64**, 1313—1315; cf. A., 1940, II, 304).—2 : 6 : 1-$(OMe)_2C_6H_3{\cdot}CN$ (**I**) and MgRCl in Et_2O and later boiling PhMe (N_2) give 2-n-*hexoyl*- (70%), b.p. 142°/2 mm., -*heptoyl*- (83·2%), b.p. 160—164°/2 mm., and -*octoyl*-*resorcinol Me*$_2$ *ether* (57%), b.p. 163—165°/1·5 mm., converted by $AlCl_3$ in PhMe at ≯120° (bath) into 2-n-*hexoyl*- (64·8%), m.p. 74°, -*heptoyl*- (71%), m.p. 75°, and -*octoyl*-*resorcinol* (61·5%), m.p. 78°, which are reduced by Zn–Hg–HCl–AcOH–H_2O to 2-n-*hexyl*- (42·9%), m.p. 67°, -*heptyl*- (49%), m.p. 51—52°, and -*octyl*-*resorcinol* (63%), m.p. 55—56° (no $FeCl_3$ colours). n-$C_{12}H_{25}{\cdot}MgBr$ and (**I**) give only n-$C_{24}H_{50}$ (21%). R. S. C.

Reduction of dipole moment by steric hindrance in di-*tert*.-butylquinol and its dimethyl ether.—See A., 1942, I, 289.

Halogenation of phenolic ethers and anilides. Arrhenius activation energies.—See A., 1942, I, 332.

Synthesis of eugenol. L. J. Briusova and M. L. Joffe (*J. Gen. Chem. Russ.*, 1941, **11**, 722—728).—Guaiacol allyl ether (**I**) with BF_3 in kerosene solution, or with BF_3,2AcOH without a solvent, affords 20—22% of eugenol, 10—15% of guaiacol, and 30% of unchanged (**I**). Possible by-products are allyleugenol, its allyl ether, and allylguaiacol allyl ether. G. A. R. K.

Fission of phenolic ethers by pyridine hydrochloride. II. V. Prey (*Ber.*, 1942, **75**, [*B*], 350—356).—PhOMe and C_5H_5N,HCl (**I**) are heated at 220° and periodical determinations are made of (**I**) acidimetrically, total Cl argentometrically, and PhOMe gravimetrically. After 2 hr. no PhOMe remains and there is no further consumption of (**I**). Total Cl is little changed, indicating that liberated MeCl is completely retained and suggesting the existence of an additive compound of (**I**) and PhOMe. C_5H_5NMeCl and dry HCl at 220° give almost quantitatively MeCl and C_5H_5N,2HCl (**II**), later $(C_5H_5N)_2$,3HCl (**III**). Complete fission of ethers, except PhOMe, is caused by dry HCl + 20% of (**I**) at 200°. Apparently PhOMe is affected only by (**I**) whereas guaiacol (**IV**) etc. is acted on by added HCl and thus by (**II**) or (**III**). Veratrole, nerolin, and (**IV**) are completely hydrolysed by HCl and 10% of C_5H_5N at 210° and reaction can be effected slowly with (**IV**) in presence of 1% of C_5H_5N. H. W.

Sulphonating action of dialkyl sulphates. II. Interaction of dimethyl sulphate with ethers. V. N. Belov and E. I. Schepelenkova (*J. Gen. Chem. Russ.*, 1941, **11**, 757—762).—Me_2SO_4 heated with phenolic ethers gives sulphonic acids and Me_2O. Thus, PhOMe affords *p*-OMe·C_6H_4·SO_3H (40%) and its Me ester (27%) (cf. A., 1923, i, 462); Ph_2O gives *p*-OPh·C_6H_4·SO_3H (69%) and its Me ester (22%); β-$C_{10}H_7$·OMe affords 2 : 6-OMe·$C_{10}H_6$·SO_3H and its Me ester (total yield of sulphonation products 76%). CH_2Ph·OMe and aliphatic ethers such as di*iso*amyl ether are not sulphonated and undergo decomp. with formation of Me_2O and SO_3. G. A. R. K.

Phenol- and amino-plastics. I. Phenol-alcohols and their reaction with amines [and carbamide]. H. von Euler and H. Nyström (*J. pr. Chem.*, 1941, [ii], **159**, 121—129).—1 : 4 : 6 : 2-OH·$C_6H_2Me_2$·CH_2·OH (**I**) and $CO(NH_2)_2$ (**II**) in boiling aq. acid (p_H~2) afford 2-*hydroxy*-3 : 5-*dimethylbenzylcarbamide*, m.p. 192·5°. 1 : 4 : 2 : 6-OH·$C_6H_2Me(CH_2·OH)_2$ (**III**) and (**II**) yield 3 : 5-*di*(*carbamidomethyl*)-*p-cresol*, m.p. 210·5°, whilst 1 : 2 : 6 : 4-OH·$C_6H_2Me_2$·CH_2·OH and (**II**) afford s-*di*-(4-*hydroxy*-3 : 5-*dimethylbenzyl*)*carbamide*, m.p. 213°. (**I**) and NH_2·CO·NHMe afford N-2-*hydroxy*-3 : 5-*dimethylbenzyl*-N- (or N'-)*methylcarbamide*, m.p. 149·5°. (**I**) (2 mols.) with $(CH_2·NH_2)_2$ (**IV**) (1 mol.) in alkaline solution gives NN'-*di*-(2-*hydroxy*-3 : 5-*dimethylbenzyl*)*ethylenediamine*, m.p. 100°, but (**III**) and (**IV**) afford similarly 2 : 2'-*dihydroxy*-5 : 5'-*dimethyl*-3 : 3'-*di*(*hydroxymethyl*)*diphenylmethane*. (**I**) with boiling N_2H_4,H_2O (5 mols.) yields 2-hydroxy-3 : 5-dimethylbenzylhydrazine (an oil) (ON-*Ac*$_2$ derivative, m.p. 162°) and with NHPh·NH_2 yields α-*phenyl*-β-2-*hydroxy*-3 : 5-*dimethylbenzylhydrazine*, m.p. 104°. (**I**) and NH_2Ar,HCl give 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·NHAr [Ar = Ph, m.p. 85° (NO-derivative, m.p. 118·5°); Ar = *p*-C_6H_4Me, m.p. 99°]. Resins are formed from (**I**) or (**III**) and *p*-NH_2·C_6H_4·OH. C. S.

Hydrogenation of diaryl disulphides.—See B., 1942, II, 313.

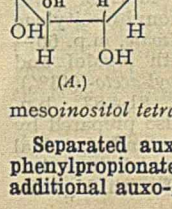
Catalytic hydrogenation of organic compounds. II. Benzaldehyde. III. Aromatic carbonyl compounds. K. Akashi (*Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 556—562, 563—568).—With Ni–Cu–Al_2O_3–kieselguhr catalysts supported on Cu wire, vapour-phase hydrogenation of PhCHO, *p*-C_6H_4Me·CHO, *o*-OMe·C_6H_4·CHO, piperonal, CHPh:CH·CHO, and COPhMe affords (mainly) the corresponding alcohol; $COPh_2$ yields CH_2Ph_2. F. O. H.

Reactions of propargyl derivatives. K. Zeile and H. Meyer (*Ber.*, 1942, **75**, [*B*], 356—362).—CH:C·CH_2Br, Zn, and *cyclo*hexanone (**I**) give γ-1-*hydroxy*cyclo*hexyl*-Δ^{α}-*propinene*, b.p. 80—83°/10 mm., m.p. 56·5° [hydrogenated (Pd-black in EtOH) to 1-propyl*cyclo*hexanol], 2-*cyclo*hexylidene*cyclo*hexanone, b.p. 95—96°/0·17 mm. (semicarbazone, m.p. 192—194°), and αγ-*di*-1-*hydroxy*cyclo*hexyl*-Δ^{α}-*propinene*, m.p. 113° [*di*-3 : 5-*dinitrobenzoate*, m.p. 159·5°; *diacetate* (**II**), b.p. 155—157°/0·6 mm.], which is hydrogenated (Pd-black in EtOH) to αγ-*di*-1-*hydroxy*cyclo*hexylpropane*, m.p. 120°, and (Pd-black in AcOH) to α-*cyclo*hexyl-γ-1-hydroxy*cyclo*hexylpropane, an oil (3 : 5-*dinitrobenzoate*, m.p. 88°). Addition of 1 H_2 (Pd-black, MeOH) to (**II**) and treatment of the product with $(CH·CO)_2O$ gives an *adduct*, $C_{21}H_{28}O_5$, m.p. 141·5°. Successive addition of CH:C·CH_2·OH (**III**) and (**I**) in C_6H_6 to MgEtBr in Et_2O yields γ-1-*hydroxy*cyclo*hexyl*-Δ^{β}-*propinen*-α-ol, b.p. 130—134° 0·5 mm., m.p. 51° (*formate*, b.p. 149—150°/12 mm.; *monobenzoate*, b.p. 166—167°/4 mm., m.p. 47°; *diacetate*, b.p. 151—155°/11·5 mm.). (**III**) and $MeSO_2Cl$ in 30% NaOH give the *methanesulphonate*, b.p. 109—110°/13 mm.; *p*-$C_6H_4Me·SO_2Cl$ and well-cooled 20% NaOH afford the p-*toluenesulphonate*, b.p. 117—120°/0·3 mm. *CP*h_3 *propargyl ether*, m.p. 111°, is converted by MgEtBr into *CP*h_3 δδδ-*triphenyl*-Δ^{β}-*butinenyl ether*, m.p. 191°, hydrogenated (Pd-black in C_6H_6) to *CP*h_3 δδδ-*triphenyl*-n-*butyl ether*, m.p. 181—182°. H. W.

Preparation of quinitol semiesters and of 4-hydroxy*cyclo*hexanone. K. Dimroth, E. Schmeil, and W. Daake *Ber.*, 1942, **75** [*B*], 317—321).—The mixture of quinitol (**I**) with its mono- and di-acetate is treated with BzCl in C_5H_5N and the product is hydrolysed with H_2SO_4–EtOH, whereby only Ac is removed, leaving a residue containing (**I**), *cis*- (**II**) and *trans*- (**III**) -mono-, and the isomeric di- (**IV**) -benzoates. (**IV**) are mainly pptd. when the alcoholic solution of the mixture is cooled and (**I**) remains in the aq. liquors when the filtrates are diluted and extracted with Et_2O. The residue readily deposits (**III**), m.p. 86°, whereas (**II**) is isolated with greater difficulty. Oxidation (CrO_3 in AcOH) of (**II**) or (**III**) gives 4-*keto*cyclo*hexyl benzoate*, b.p. 142°/0·02 mm., m.p. 63—64° (2 : 4-*dinitrophenylhydrazone*, m.p. 161°). The prep. of 4-keto*cyclo*hexyl acetate by oxidising (**I**) in Ac_2O with CrO_3 (Sabetay *et al.*, A., 1930, 1179) is unsatisfactory. H. W.

Phenol–formaldehyde resins. III. Quinonemethides as intermediates in the hardening process. K. Hultzsch (*J. pr. Chem.*, 1941, [ii], **159**, 155—179).—Four phenol-alcohols have been found to behave like 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (*o*-hydroxymesityl alcohol) on heating. *p*-Cresol, *cyclo*hexanol, and 72% H_2SO_4 at 60° afford 3-*cyclo*hexyl-*p*-cresol, b.p. 160—170°, converted into 2-*hydroxy*-3-cyclo*hexyl*-5-*methylbenzyl alcohol* (**I**), m.p. 66·5°. 2 : 5 : 3 : 1-OH·$C_6H_2MeBu^{\gamma}$·CH_2·OH (**II**), an oil, is also prepared. 2-Hydroxy-5-*cyclo*hexyl-3-methylbenzyl alcohol (**III**) at 175°/2 hr. yields *di*-(2-*hydroxy*-5-cyclo*hexyl*-3-*methylbenzyl*) *ether*, m.p. 145°, which at 190—200°/30 mm. gives trimeric 5-cyclo*hexyl*-3-*methyl*-o-*quinonemethide* (**IV**), amorphous, m.p. 140°. At 240°, (**III**) gives 2-hydroxy-5-*cyclo*hexyl-3-methylbenzaldehyde, b.p. 150—160°/1·5 mm. (*semicarbazone*, m.p. 196°), a *compound*, $C_{36}H_{40}O_2$, m.p. 157° (*diacetate*, m.p. 168°) [also obtained from CH_2O and 5-*cyclo*hexyl-*o*-cresol in EtOH–conc. HCl together with *di*-(2-*hydroxy*-5-cyclo*hexyl*-3-*methylphenyl*)*methane* (**V**), m.p. 106—108° (*diacetate*, m.p. 125°)], and a residue, m.p. ~114°. (**V**) is obtained from (**III**) and boiling dil. aq. NaOH. (**III**) with AcOH–HCl affords 2-hydroxy-5-*cyclo*hexyl-3-methylbenzyl chloride, which with aq. Na_2CO_3–Et_2O gives (**IV**) (m.p. 120—130°). 2 : 3 : 5 : 1-OH·$C_6H_2MeBu^{\gamma}$·CH_2·OH (**VI**) at 160° affords CH_2O and *di*-(2-*hydroxy*-3-*methyl*-5-tert.-*butylbenzyl*) *ether*, m.p. 131·5° (*diacetate*, m.p. 143°); the residue with NaOH yields dimeric 3-*methyl*-5-tert.-*butyl*-o-*quinonemethide* (**VII**), m.p. 50°. At 240°, (**VI**) gives 2 : 3 : 5 : 1-OH·$C_6H_2MeBu^{\gamma}$·CHO, b.p. 115°/2 mm. (*semicarbazone*, m.p. 168—181°), αβ-*di*-(2-*hydroxy*-3-*methyl*-5-tert.-*butylphenyl*)*ethane*, b.p. 225—230°/2 mm., m.p. 72° (*diacetate*, m.p. 113·5°), and a residue, m.p. ~100°. 2 : 4 : 1-$C_6H_3MeBu^{\gamma}$·OH and CH_2O afford *di*-(2-*hydroxy*-3-*methyl*-5-tert.-*butylphenyl*)*methane*, m.p. 140° (*diacetate*, m.p. 70—71°). (**VI**) and AcOH–HCl afford 2-*hydroxy*-3-*methyl*-5-tert.-*butylbenzyl chloride*, converted (Na_2CO_3–Et_2O) into (**VII**) (m.p. 57°). (**I**) at 200° yields *di*-(2-*hydroxy*-3-cyclo*hexyl*-5-*methylbenzyl*) *ether* (**VIII**), m.p. 172·5°, and polymeric 3-cyclo*hexyl*-5-*methyl*-o-*quinonemethide* (**IX**), m.p. 175°. At 240°, (**I**) gives 2-*hydroxy*-3-cyclo*hexyl*-5-*methylbenzaldehyde*, b.p. 160—170°/2 mm., m.p. 128·5°, a xanthen *derivative*, $C_{27}H_{34}O$, m.p. 215°, αβ-*di*-(2-*hydroxy*-3-cyclo*hexyl*-5-*methylphenyl*)*ethane*, m.p. 137° (*diacetate*, m.p. 137°), and a residue, m.p. ~120°. *Di*-(2-*hydroxy*-3-cyclo*hexyl*-5-*methylphenyl*)*methane* (*diacetate*, m.p. 158°) has m.p. 134°. (**I**) and AcOH–HCl give the *chloride*, b.p. 175°/1·5 mm., m.p. 55—56° [another experiment gave (**VIII**)], converted (Na_2CO_3–Et_2O) into (**IX**). At 155°, (**II**) affords *di*-(2-*hydroxy*-5-*methyl*-3-tert.-*butylbenzyl*) *ether*, m.p. 93°, and ? *di*-(2-*hydroxy*-5-*methyl*-3-tert.-*butylphenyl*)*methane* (**X**), m.p. 131° [alkali-insol.; also obtained from 4 : 2 : 1-$C_6H_3MeBu^{\gamma}$·OH (**XI**), m.p. 53·5° (lit. 44°), and CH_2O in EtOH–conc. HCl; *mono*- or *di*-*acetate*, m.p. 110—112°; *mono*- or *di*-*benzoate*, m.p. 148°]. At 235°, (**II**) gives (**X**), (**XI**), resinous material, and a residue, m.p. 100°. C. S.

Acetonisation and configuration of *meso*inositol. G. Dangschat (*Naturwiss.*, 1942, **30**, 146—147).—*meso*Inositol (**I**) with a large excess of $COMe_2$ containing 10% of $ZnCl_2$ and 10% of AcOH followed by acetylation with Ac_2O–C_5H_5N gives iso*propylidene*meso*inositol tetra-acetate*, m.p. 123—124°, hydrolysed by NH_3–MeOH to iso*propylidene*meso*inositol*, decomp. 182—183°, by dil. HCl to meso*inositol tetra-acetate* (**II**), m.p. 132—133°, and by successive hydrolyses with acid and alkali to (**I**). (**II**) is indifferent to HIO_4 in AcOH but is oxidised by $Pb(OAc)_4$ in warm C_6H_6 to a non-cryst. dialdehyde (*bisphenylhydrazone*, decomp. 154°; *bis*-p-*nitrophenylhydrazone*, decomp. 183°; *bisdinitrophenylhydrazone*, decomp. 232°), converted by Ac_2O followed by diazoethane into *Et*$_2$ r-*tetra-acetylidosaccharate* (**III**), m.p. 98°; r-*idosaccharic acid* (**IV**) (*diamide*, decomp. 185—186°, and its *tetra-acetate*, m.p. 199°; *bisphenylhydrazide*, decomp. 214°) is non-cryst. The K salt appears to be transformed by AcOH into the K salt of a lactonic acid. *l*- and *d*-Xylose are converted by addition of HCN and oxidation into the active idosaccharic acids which when acetylated, esterified (diazoethane), and mixed in equal proportions give (**III**), thus confirming the constitution of (**IV**). (**I**) is therefore (*A*). *Methylene*-meso*inositol tetra-acetate* has m.p. 112°. H. W.


(*A*.)

Separated auxo-enoid systems. XVI. Colour of β-2 : 4-dinitrophenylpropionates and *p*-nitrocinnamates of phenols containing an additional auxo-group, and conclusions from previous investigations.

V. A. Izmailski and A. V. Belotzvetov (*J. Gen. Chem. Russ.*, 1941, **11**, 691—706; cf. A., 1942, II, 258).—β-2 : 4-Dinitrophenylpropionates of phenols containing an additional auxo-group (OH, OMe, NHAc) in the *p*-position are colourless except that of the *p*-NMe_2·C_6H_4 ester (**I**), which is orange-yellow. The corresponding *p*-nitrocinnamates are much darker and approximate to the 3 : 5-dinitrobenzoates in depth of colour. The colour of (**I**) shows that the coloration of the *p*-nitrobenzoates and the corresponding arylamides cannot be attributed to mesomerism in the groups –CO·O– and –CO·NH–, but to (probably intermol.) complex formation between the auxoenoid and the nitro-enoid systems. The order of intensity of colour is explained by the structural conditions affecting these systems. Acyl groups form the series β-*p*-nitrophenylpropionyl (and *p*-nitrophenylacetyl) < β-2 : 4-dinitrophenylpropionyl < *p*-NO_2·C_6H_4·CO < *p*-nitrocinnamoyl and 3 : 5-$(NO_2)_2C_6H_3$·CO in order of their chromophoric effect. Structural conditions are discussed in the light of mesomerism and the principle of counter-polarising effects. The weakening of the auxochromic power of N and O atoms on acylation is attributed to the scattering of the electromeric effect.

The following have been prepared: p-*nitrocinnamoyl chloride*, m.p. 150·5—152·5°; β-2 : 4-dinitrophenylpropionyl chloride, m.p. 127—128·5°; *p*-nitrocinnamates: Ph, m.p. 152·2—152·7°, p-*anisyl*, m.p. 157·1—157·5°, p-*dimethylaminophenyl*, m.p. 198·8—199·5°, p-*acetamidophenyl*, m.p. 235—235·5° (also a colourless form converted into the yellow at ~100°), *quinol mono-*, m.p. 217—218·2°, and *di-*, m.p. 322—323°; β-2 : 4-*dinitrophenylpropionates*: *Ph*, m.p. 84—84·4°, p-*anisyl*, m.p. 105·3—105·8°, p-*dimethylaminophenyl*, m.p. 120·3—120·7°, *quinol mono-*, m.p. 142·7—144°, and *di-*, m.p. 179—181°. G. A. R. K.

Iodinated organic compounds as contrast media for radiographic diagnoses. I. Iodinated aracyl esters. W. H. Strain, J. T. Plati, and S. L. Warren (*J. Amer. Chem. Soc.*, 1942, **64**, 1436—1440).—RCO_2Na and CH_2Cl·CO_2R' at 160—170° give *Et* o-*iodobenzoyloxy*- (63%), b.p. 169°/0·02 mm., β-p-*iodophenylpropionoxy*- (51%), m.p. 41—42°, and *undecenoyloxy*- (61%), b.p. 145°/0·2 mm., and *ethylene glycol di*-o-*iodobenzoyloxy*- (69%), m.p. 80—81°, -*acetate* but κ-I·$C_{10}H_{20}$·CO_2Na gives tars. $(CH_2Cl·CO_2·CH_2)_2$ is obtained (35%) from $(CH_2·OH)_2$, $CH_2Cl·CO_2H$, and $ZnCl_2$ at 100°. *p*-$C_6H_4I·CH_2Br$, $CH_2(CO_2Et)_2$, and NaOEt–EtOH give *Et* p-*iodobenzylmalonate* (54%), b.p. 180—183°/3 mm., and thence (alkali; 80% EtOH) the derived acid, m.p. 164—165° (decomp.), and (at 160—170°) *p*-$C_6H_4I·[CH_2]_2·CO_2H$. *o*-$C_6H_4I·OH$ (**I**) and $Br·[CH_2]_3$·Br in boiling aq. NaOH give *o*-$C_6H_4I·O·[CH_2]_3$·Br (58%), b.p. 154—156°/0·2 mm., and thence (NaCN) the nitrile (55%), b.p. 160°/0·2 mm., and (H_2SO_4–EtOH) *Et* γ-o-*iodophenoxy*-n-*butyrate* (~100%), b.p. 158°/0·1—0·2 mm. $(CH_2Br)_2$ (2 mols.) and (**I**) (1 mol.) with NaOEt (1 mol.) in boiling EtOH give β-o-*iodophenoxyethyl bromide* (34%), m.p. 50—51°, and αβ-*di*-o-*iodophenoxyethane* (10%), m.p. 120—121°. κ-Br·$C_{10}H_{20}$·CO_2Et and *o*-$C_6H_4I·ONa$ at ~110° give *Et* κ-o-*iodophenoxyundecoate* (48%), b.p. 235—240°/2 mm., and thence the *acid*, m.p. 49—50·5°. $C_{10}H_{19}·CO_2Et$, PhI, and $AlCl_3$ at 0—8° give mixed *Et iodophenylundecoates* (**II**) (40%), b.p. 205—213°/1·5 mm. (and di-condensation products), giving by hydrolysis and subsequent oxidation 12% of *p*-$C_6H_4I·CO_2H$; PhBr gives similarly mixed *Et bromophenylundecoates* (45%), b.p. 186—189°/1·5 mm. PhI, Et oleate, and $AlCl_3$ give *Et iodophenylstearate* (22%; ? pure), b.p. 242—258°/2 mm. $(CH_2·CO)_2O$, PhI, and $AlCl_3$ give exothermally a mixture including γ-*keto*-γ-p-*iodophenyl*-n-*butyric acid* (13%), m.p. 177—178° [*Et* (**III**), m.p. 64—65°, and *Me* ester, m.p. 67·5—68·5°], *p*- and *o*-$C_6H_4I_2$. Clemmensen reduction of (**III**) gives a poor yield of γ-p-*iodophenyl*-n-*butyric acid*, m.p. 89—89·5° [*Et* ester, b.p. 183°/10 mm.; oxidised to *p*-$C_6H_4I·CO_2H$ (63%)]. $CO_2Et·[CH_2]_4·COCl$, PhI, and $AlCl_3$ give similarly ε-*keto*-ε-p-*iodophenyl*-, m.p. 154—156° (*Et* ester, m.p. 66—67°), and ε-p-*iodophenyl*-n-*hexoic acid*, m.p. 66—67° (*Et* ester, b.p. 205—210°/10 mm.). Of the products, (**II**) is the best liquid contrast medium for radiographic purposes. R. S. C.

Stability of di-iodotyrosine solutions. K. Kraft and F. Dengel (*Z. physiol. Chem.*, 1942, **272**, 147—151).—Concns. of di-iodotyrosine >0·5% cannot be obtained by dissolution in org. and inorg. acids. Decomp. and conversion into thyroxine by alkali is almost entirely prevented by employing <2·1N. aq. NaOH. W. McC.

Reaction of the Grignard reagent with esters of highly hindered acids. R. C. Fuson, E. M. Bottorff, and S. B. Speck (*J. Amer. Chem. Soc.*, 1942, **64**, 1450—1453).—Alkyl (Me, CH_2Ph) mesitoates with MgRHal (R = $Bu^α$ or Ph) in Bu_2O give mesitoic acid (**I**) (25—65%) and alkyl halide (20—70%); with MgI 80—97% of (**I**) results. p-*Tolyl mesitoate* (**II**), m.p. 73°, with MgMeI or MeEtBr gives *p*-cresol (**III**) (76, 54%) and acetyl- (45%) or propionyl-mesitylene (61%), respectively. p-*Tolyl* 2 : 4 : 6-*tri*isopropylbenzoate, m.p. 66—68°, b.p. 181—184°/3 mm., behaves similarly with MgMeI and MgEtBr, yielding (**III**) (78%) and 2 : 4 : 6-*tri*isopropyl-*aceto*- (46%), m.p. 87·5—88°, and -*propio*-*phenone* (43%), m.p. 81—83°, b.p. 123—126°/3 mm., respectively; both ketones are also prepared by Friedel–Crafts reaction in CS_2 at 10°. Aryl mesitoates and MgArHal in Bu_2O give similarly first the phenol (40—95%) and ketone, but o-arylation of the ketone then occurs. Thus (**II**) with MgArBr gives 2-*mesitoyl*-5 : 4′-*dimethyldiphenyl* (13%), m.p. 101°, and *mesityl* 2-1′-*naphthyl*-1-*naphthyl* (a trace), m.p. 180°, 2′-*methoxy*-2-*diphenylyl* (13%), m.p. 94°, and 3′-*methoxy*-(? 5 : 3′-*dimethoxy*-)2-*diphenylyl* (6%), m.p. 144°, *ketone*. With 2 : 4 : 6 : 1-$C_6H_2Me_3$·MgBr, (**II**) gives (**III**) (85%), dimesityl ketone (3%) and diketone (**IV**) (a trace). With CH_2Ph·MgCl, (**II**) gives (**III**) (55%) and a small amount of (**IV**). Bu, b.p. 119—121°/3 mm., and *CH_2Ph mesitoate*, m.p. 38—39°, b.p. 164—169°/2·5 mm., are described. M.p. are corr. R. S. C.

Inter-relation of first- and second-order asymmetric transformations. (Miss) M. M. Jamison and E. E. Turner (*J.C.S.*, 1942, 437—440; cf. A., 1940, II, 173).—Corbellini and Angeletti's work (A., 1933, 64) has been repeated on 2′-(α-hydroxy*iso*propyl)diphenyl-2-carboxylic acid (**I**) (improved prep.). Discrepancies in the mutarotation results for the brucine *l*-acid salt (**II**) in $CHCl_3$ are attributed to the formation of the optically inactive lactone, m.p. 124—125°, of (**I**). The brucine salt of (**I**) undergoes first-order asymmetric transformation in $CHCl_3$ [brucine *d*-acid salt optically more stable; hence (**II**) separates first]; the experiments recorded constitute the first example of the application of the van't Hoff–Dimroth rule to asymmetric transformation in which both first- and second-order changes can be realised. Mutarotation is also observed in dextrodirection with quinidine and *dl*-(**I**) in mol. proportions in $CHCl_3$, and lævo- with quinine or cinchonidine. C. S.

Conjugated diolefines.—See A., 1942, II, 293.

Isomerism of disalicylides. II. Re-examination of the data concerning the composition and mol. wt. of β-disalicylide. L. Anschütz and A. Mayer (*J. pr. Chem.*, 1942, [ii], **159**, 343—344).—Elementary analyses and determinations of the mol. wt. of β-disalicylide in camphor, dioxan, PhOH, and $CHCl_3$ confirm the formula, $C_{14}H_8O_4$. The two disalicylides are therefore isomerides. H. W.

Preparation of acetylsalicylyl and salicylyl disulphides. B. Riegel and H. Wittcoff (*J. Amer. Chem. Soc.*, 1942, **64**, 1486—1487).—*o*-OAc·C_6H_4·COCl (prep. by $SOCl_2$–C_5H_5N), b.p. 115°/5 mm., m.p. 52° (turbid), 60° (clear), with anhyd. NaSH–EtOH (prep. described) and then I–EtOH gives *disalicylyl disulphide* (**I**), m.p. 142° (Pyrex), which with Ac_2O and a little H_2SO_4 at room temp. gives the *diacetate* (**II**), m.p. 101·2°. M.p. are corr. (**I**) and (**II**) are non-toxic but do not appear to have much antipruritic activity. R. S. C.

Naphtol AS series. V. Synthetic experiments. II. R. V. Bhat and K. Venkataraman (*J. Soc. Dyers and Col.*, 1942, **58**, 155—161; cf. B., 1940, 428).—2 : 3-OH·$C_{10}H_6$·COCl (**I**) and *p*-$C_6H_4Me·SO_2·NMe·C_6H_4·NH_2$-*m* or -*p* in solvent naphtha or $C_2H_2Cl_4$ respectively, at 150—160°, afford *toluene*-p-*sulphon*-N-*methyl*-m′-, m.p. 212—213°, or -p′-2″-*hydroxy*-3″-*naphthoylaminoanilide*, m.p. 230°, respectively. Similarly prepared from (**I**) and the appropriate base are: *toluene*-p-*sulphon*-p′-2″-*hydroxy*-3″-*naphthoylaminoanilide*, m.p. 261—262°; 2-2′-*hydroxy*-3′-*naphthoylaminothiazole*, m.p. 299—300° (decomp.); 1 : 2-*di*-2′-*hydroxy*-3′-*naphthoylaminonaphthalene*, m.p. 296—297°; 8-(2′-*hydroxy*-3′-*naphthoylamino*)-1-*naphthylamine*, m.p. 264—265°; m-, m.p. 273—274°, and p-2′-*hydroxy*-3′-*naphthoylaminobenzanilide*, m.p. 290—291° (also obtained from p-2′-*hydroxy*-3′-*naphthoylaminobenzoic acid*, m.p. 315—316°, and NH_2Ph–C_5H_5N–PCl_3); 4-2′-*hydroxy*-3′-*naphthoylamino*-*acetophenone*, m.p. 263—264°, or -*benzophenone*, m.p. 255°. *Mono*-2-*hydroxy*-3-*naphthoyl*-m-*phenylenediamine*, m.p. 198—199°, and BzCl–dioxan give N′-*benzoyl*-N-2-*hydroxy*-3-*naphthoyl*-m-*phenylenediamine*, m.p. 281—282°, also prepared from (**I**) and *m*-$NH_2·C_6H_4·NHBz$. Substantivity and fastness tests are carried out on the compounds. A. T. P.

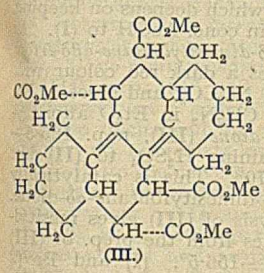
Molecular rearrangements involving optically active radicals. XI. Rearrangements in the truxillic acids and their bearing on theories of molecular rearrangements and optical rotatory power. H. I. Bernstein and E. S. Wallis (*J. Org. Chem.*, 1942, **7**, 261—273).—(+)-γ-Truxillamidic acid is converted by NaOCl at 38—40° followed by CO_2 into (−)-γ-truxillamic acid (**I**), m.p. 211—214° (decomp.) in bath at 200° {*hydrochloride*, m.p. 268° (decomp.), $[α]^{20}_{6563}$ −16·6°, $[α]^{20}_{5893}$ −22·7°, $[α]^{20}_{5463}$ −28·8° in MeOH; *Me* ester *hydrochloride*, m.p. 269° (decomp.) in bath at 250°, $[α]^{20}_{6563}$ −24·7°, $[α]^{20}_{5893}$ −29·6°, $[α]^{20}_{5463}$ −36·8° in MeOH}. (**I**) and NOBr in Et_2O at <−5° give the (+)-lactone, m.p. 138°, $[α]^{20}_{6563}$ +11·2°, $[α]^{20}_{6593}$ +15·5°, $[α]^{20}_{5463}$ +19·6° in MeOH, whilst the (+)-acid yields the (−)-*lactone* (**II**), m.p. 139°, $[α]^{20}_{6563}$ −10·2°, $[α]^{20}_{5893}$ −14·4°, $[α]^{20}_{5463}$ −19·5° in MeOH, $[α]^{20}_{6563}$ +30·6°, $[α]^{20}_{5893}$ +35·2°, $[α]^{20}_{5463}$ +41·8° in C_6H_6. (**II**) and KOH–EtOH afford (−)-3ᶜ-*phenyl*-2ᶜ-α-*hydroxybenzylcyclopropane*-1ᶜ-*carboxylic acid* (**III**), m.p. 150° (decomp.) if placed in bath at 141°, $[α]^{20}_{6563}$ −78·4°, $[α]^{20}_{5893}$ −101·4°, $[α]^{20}_{5463}$ −121·4° in MeOH, whilst the (+)-OH-acid (**IV**) has m.p. 146°, $[α]^{20}_{6563}$ +75·4°, $[α]^{20}_{5893}$ +96·6°, $[α]^{20}_{5463}$ +116·6° in MeOH. (**III**) and CH_2N_2 give (**II**) or, under somewhat different conditions, the *Me* ester of (**III**), m.p. 145° (decomp.), $[α]^{20}_{6563}$ −89·4°, $[α]^{20}_{5983}$ −118·5°, $[α]^{20}_{5463}$ −141·7° in MeOH. (**IV**) yields the corresponding *Me* ester, m.p. 146°, $[α]^{20}_{6563}$ +95°, $[α]^{20}_{5893}$ +127°, $[α]^{20}_{5463}$ +140° in MeOH, and an equimol. mixture of ester and lactone. Oxidation (CrO_3 in AcOH) of the (−)-Me ester gives *Me* (+)-2ᶜ-*benzoyl*-3ᶜ-*phenylcyclopropane*-1ᶜ-*carboxylate*, m.p. 109°, $[α]^{20}_{6563}$ +5·4°, $[α]^{20}_{5893}$ +6·0°, $[α]^{20}_{5463}$ +7·21° in MeOH, transformed by NH_2OH,HCl in

boiling EtOH into the corresponding (+)-*dihydro-orthoxazine*, N<O·CO·CH / CPh—CH>CHPh, m.p. 180°, $[\alpha]^{20}_{6563}$ +177°, $[\alpha]^{20}_{5893}$ +226°, $[\alpha]^{20}_{5463}$ +271° in MeOH. (**II**) and boiling 50% KOH–EtOH afford (+)-3^c-*phenyl*-2^c-*α-hydroxybenzyl*cyclo*propane*-1^t-*carboxylic acid*, m.p. 160° (decomp.), $[\alpha]^{20}_{6563}$ +43·2°, $[\alpha]^{20}_{5893}$ +56·4°, $[\alpha]^{20}_{5463}$ +68·3° in MeOH (Me ester, $[\alpha]^{20}_{6563}$ +47·3°, $[\alpha]^{20}_{5893}$ +60·6°, $[\alpha]^{20}_{5463}$ +73·2° in MeOH); the (−)-acid has m.p. 161—162° (decomp.), $[\alpha]^{20}_{6563}$ −43·3°, $[\alpha]^{20}_{5893}$ −56·0°, $[\alpha]^{20}_{5463}$ −67·8° in MeOH {Me ester (**V**), $[\alpha]^{20}_{6563}$ −47·4°, $[\alpha]^{20}_{5893}$ −61·4°, $[\alpha]^{20}_{5463}$ −74·9° in MeOH}. *Me* 2-*benzoyl*-3-*phenyl*cyclo*propane*-1-*carboxylate*, m.p. 85°, $[\alpha]^{20}_{6563}$ −121·2°, $[\alpha]^{20}_{5893}$ −158·6°, $[\alpha]^{20}_{5463}$ −192·5° in MeOH, is prepared from (**V**). The instances of Walden inversion recorded above are considered in terms of the electronic theory of mol. rearrangement. The direction of the shift in optical rotatory power in the formation of dicyclic lactones, imides, and lactams from the corresponding monocyclic acids is shown to be random; this behaviour is discussed in the light of newer theories of optical rotatory power. H. W.

Synthesis of 4 : 4′-dicyanostilbene. S. C. Fu and P. P. T. Sah (*J. Amer. Chem. Soc.*, 1942, **64**, 1482).—Pyrolysis of 4 : 4′-*dicyanobenzaldazine* (prep. from *p*-CN·C$_6$H$_4$·CHO by N_2H_4,H_2O in boiling abs. EtOH), m.p. 118—120°, gives 25% of (*p*-CN·C$_6$H$_4$·CH:)$_2$. R. S. C.

Synthesis of 4 : 4′-diamidinostilbene hydrochloride. P. P. T. Sah (*J. Amer. Chem. Soc.*, 1942, **64**, 1487—1488).—*p*-C$_6$H$_4$I·CHO (prep. by $SnCl_2$–HCl–Et_2O etc. from *p*-C$_6$H$_4$I·CN), m.p. 77—78° (semicarbazone, m.p. 225°; oxime, m.p. 111—112°) (cf. lit.), with N_2H_4,H_2O gives the azine, m.p. 230—232° (decomp.), which, when sublimed, gives (*p*-C$_6$H$_4$I·CH:)$_2$, m.p. 259—260° (lit. 257—259°), also obtained (diazo-reaction) from (*p*-NH$_2$·C$_6$H$_4$·CH:)$_2$. The Grignard reagent thereof with CH(OEt)$_3$ in Et_2O gives an impure, syrupy *ester*, converted by dry NH_3–EtOH at 30° into 4 : 4′-diamidinostilbene, m.p. indefinite (*dihydrochloride*, m.p. >300°). R. S. C.

Synthesis of condensed ring compounds. VIII. Di-inene double addition reactions. L. W. Butz and L. M. Joshel (*J. Amer. Chem. Soc.*, 1942, **64**, 1311—1313).—Di*cyclo*hexenylacetylene (**I**) (1 mol.) with Me_2 (**II**) (N_2) or Et_2 fumarate (CO_2) (>2 mols.) at, best, 175° gives Me_4 (**III**) (15%), m.p. 111·6—112·6°, and Et_4 $\Delta^{8(14):9}$-*chrysitadiene*-cis-6 : 7-cis-11 : 12-*tetracarboxylate* (7%), m.p. 90—91°.



(III.)

The adduct (A., 1942, II, 142) from (**I**) and (CH·CO)$_2$O is converted by N-KOH into $\Delta^{8(14):9}$-*chrysitadiene*-cis-6 : 7-cis-11 : 12-*tetracarboxylic acid* (97%), m.p. 256·5—258° (decomp.), which with CH_2N_2 gives the Me_4 ester [cf. (**III**)], m.p. 121—122·5°, hydrogenated (PtO_2, AcOH) to Me_4 Δ^8-*chrysitene*-cis-6 : 7-cis-11 : 12-*tetracarboxylate* (85%), m.p. 158—159°. (**III**) resists hydrogenation. *cyclo*Pentenyl-4-methoxy*cyclo*hexenylacetylene and (**II**) at 175° (N_2) give Me_4 3-*methoxy*-$\Delta^{8(14):9}$-*steradiene*-trans-6 : 7-trans-11 : 12-*tetracarboxylate* (45%), b.p. ~150° (bath)/0·001 mm. M.p. are corr. R. S. C.

Condensation of aldehydes with amides. X. Condensation of *m*- and *p*-nitrobenzaldehyde and 2 : 4-dinitrobenzaldehyde. P. I. Ittyerah and K. C. Pandya (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 258—263).—The aldehydes and amides (1 : 2) are heated at 130—140°, rapidity of reaction and yield diminishing in the sequence, *p* > *m* > *o*. 2 : 4 : 1-(NO$_2$)$_2$C$_6$H$_3$·CHO could not be condensed with NH_2Ac or NH_2Bz. The products do not give a colour with cold conc. H_2SO_4 and are hydrolysed by the hot, dil. acid. Attempted nitration causes decomp. The following are described: m-*nitrobenzylidenediformamide*, m.p. 168°, -diacetamide, m.p. 255—256° (lit. 236—237°), -*dipropionamide*, m.p. 220—221°, -*di*-n-*butyramide*, m.p. 194°, -*di*-n-*heptoamide*, m.p. 149°, -dibenzamide, m.p. 228—230° (lit. 224°), and -*bisphenylacetamide*, m.p. 214—216°; p-*nitrobenzylidene-diformamide*, m.p. 194° or (apparently polymerised) m.p. 210—220°, -*diacetamide*, m.p. 272°, -*dipropionamide*, m.p. 252°, -*di*-n-*butyramide*, m.p. 224°, -*di*-n-*heptoamide*, m.p. 170°, -*dibenzamide*, m.p. 258—259°, and -*bisphenylacetamide*, m.p. 248°. H. W.

Internally complex salts of α-amino-acid esters. P. Pfeiffer, W. Offermann, and H. Werner (*J. pr. Chem.*, 1942, [ii], **159**, 313—333).—The Cu derivative (**I**) of *o*-OH·C$_6$H$_4$·CHO with NH$_2$·CH$_2$·CO$_2$Et,HCl and anhyd. NaOAc in boiling EtOH affords *Cu Et salicylideneaminoacetate* (**II**), m.p. 200° (decomp.). *l*-Menthol and CH$_2$Cl·COCl in $CHCl_3$ afford l-*menthyl chloroacetate*, m.p. 38°, transformed by NH_3 in dioxan into l-*menthyl aminoacetate hydrochloride*, m.p. ~175°, which has normal rotation dispersion in H_2O; with (**I**) it gives a *Cu* complex, $C_{38}H_{52}O_6N_2Cu$, which shows a marked Cotton effect. Similarly the Ni complex (**III**) of *o*-OH·C$_6$H$_4$·CHO and NH$_2$·CH$_2$·CO$_2$Et affords the *complex*, $C_{22}H_{24}O_6N_2Ni$, m.p. 230° (decomp.), and the l-*menthyl* complex, $C_{38}H_{52}O_6N_2Ni$. Alanine and *l*-phenylalanine Et esters yield the analogous *complexes*, $C_{24}H_{28}O_6N_2Cu$ and optically inactive $C_{36}H_{38}O_6N_2Cu$. *o*-OH·C$_6$H$_4$·CHO, Cu(OAc)$_2$, NaOAc, and *l*-ornithine dihydrochloride in EtOH give the *compound*, $C_{38}H_{34}O_8N_4Cu_3$ (also +3C$_5$H$_5$N). Similarly *l*-lysine dihydrochloride gives the *complex*, $C_{20}H_{20}O_4N_2Cu$ (+1 or 2C$_5$H$_5$N), and its Et ester affords the *salt*, $C_{22}H_{24}O_4N_4Cu$. (**I**) and (**III**) with *l*-leucine Et ester in presence of air give the salicylaldehydeimine *compounds*, $C_{14}H_{12}O_2N_2Cu$ and $C_{14}H_{12}O_2N_2Ni$ (**IV**). Attempts to isolate a normal condensation product from (**III**) and *l*-phenylalanine ester were unsuccessful; (**IV**) is isolable. The Cu compound of 2 : 1-OH·C$_{10}$H$_6$·CHO with NH$_2$·CH$_2$·CO$_2$Et,HCl and anhyd. NaOAc in boiling EtOH give the *complex*, $C_{30}H_{28}O_6N_2Cu$ (**V**), decomp., ~186°. (**II**) and the corresponding Ni compound readily undergo ester-interchange. Thus in boiling MeOH they give the *Me* esters, $C_{20}H_{20}O_6N_2Cu$, m.p. 213° (decomp.), and $C_{20}H_{20}O_6N_2Ni$, m.p. 236° (decomp.). The reaction is reversible. The *Pr*^{α} esters, m.p. 182° (decomp.) and 208° (decomp.), respectively are obtained from the Et esters but the reverse change does not appear to take place. The *Bu*^{α} esters, m.p. 166° (decomp.) and 203° (decomp.), respectively, are obtained from the Et esters and also directly from NH$_2$·CH$_2$·CO$_2$Bu,HCl. The iso*amyl* ester, $C_{28}H_{36}O_6N_2Ni$, has m.p. 194—195° (decomp.). Re-esterification with CH$_2$Ph·OH appears more difficult. (**V**) gives the *Bu* ester, $C_{34}H_{36}O_6N_2Cu$, softens ~177°. H. W.

Vanillin from lignin materials. [Its determination.] I. A. Pearl (*J. Amer. Chem. Soc.*, 1942, **64**, 1429—1431).—The solids from sulphite waste liquor or BuOH-lignin with aq. $CuSO_4$–NaOH or –CaO at 160° or, less well, the b.p. give 9·7—21·9% of vanillin (**I**). "Meadol" gives also syringaldehyde [~3 parts for each part of (**I**)]. (**I**) is best determined as 2 : 4-dinitrophenylhydrazone, the acidity not being crit. R. S. C.

Phenol–formaldehyde resins. IX. Formation of aldehyde groups during the hardening of phenoldialcohols. K. Hultzsch and G. Schiemann (*Ber.*, 1942, **75**, [*B*], 363—368).—1 : 4 : 2 : 6-OH·C$_6$H$_2$Bu^γ(CH$_2$·OH)$_2$ when heated in CO$_2$ at 230° evolves CH_2O and H_2O giving a residue which at 120—160°/2 mm. gives a distillate containing 2-*hydroxy*-5-tert.-*butylisophthalaldehyde*, m.p. 105·5° (*dioxime*, m.p. 184—185·5°), 2-*hydroxy*-3-*methyl*-5-tert.-*butylbenzaldehyde* (**I**), m.p. 44—45°, and 2 : 6 : 4 : 1-C$_6$H$_2$Me$_2$Bu^γ·OH, m.p. 80°. The residue from the distillation contains ·CHO. Similarly 2 : 6-di(hydroxymethyl)-4-*aaγγ*-tetramethyl-*n*-butylphenol at 230° yields H_2O and CH_2O and the residue on distillation affords 2-hydroxy-5-*aaγγ*-tetramethyl-*n*-butyl*iso*phthalaldehyde (*dioxime*, m.p. 168°), and 2-hydroxy-3-methyl-5-*aaγγ*-tetramethyl-*n*-butylbenzaldehyde (*oxime*, m.p. 123—126°); the non-volatile residue contains ·CHO. (**I**) is obtained from 2 : 3 : 5 : 1-OH·C$_6$H$_2$MeBu^γ·CH$_2$·OH and *m*-NO$_2$·C$_6$H$_4$·SO$_3$Na in boiling 10% NaOH. ·CHO is not present in the resin from *o*-hydroxymesityl alcohol but is abundantly formed when 1 : 4 : 2 : 6-OH·C$_6$H$_2$Me(CH$_2$·OH)$_2$ is hardened between 155° and 230°. H. W.

Phenoxyacetones. D. S. Tarbell (*J. Org. Chem.*, 1942, **7**, 251—260).—*p*-C$_6$H$_4$Me·O·CH$_2$·COMe (**I**), b.p. 107—109°/5 mm. (*semicarbazone*, m.p. 179—180°), prepared from *p*-C$_6$H$_4$Me·ONa and CH$_2$Br·COMe in C$_6$H$_6$ or by ozonisation of *p*-C$_6$H$_4$Me·O·CH$_2$·CMe:CH$_2$, is largely unchanged at 250—260° if pure, yielding only a small proportion of *p*-cresol. 2 : 4 : 1-CH$_2$:CMe·CH$_2$·C$_6$H$_3$Me·OH is ozonised to 2 : 4 : 1-COMe·CH$_2$·C$_6$H$_3$Me·OH [*semicarbazone*, m.p. 187—188° (decomp.)]. 2 : 6-Dimethylphenoxyacetone (**II**), b.p. 110—113°/4 mm. (*semicarbazone*, m.p. 163—165°), gives *m*-2-xylenol when kept and is partly decomposed when heated at 200—205° for 1 hr. 2 : 4-Dimethyl- (**III**), b.p. 120°/6 mm. (*semicarbazone*, m.p. 143—144·5°), p-*bromo*- (**IV**), m.p. 42·5—44° (*semicarbazone*, m.p. 196—205° depending on the rate of heating), *o*-nitro- (**V**), *m*-nitro- (**VI**), m.p. 79—81° (lit. 83—84°), *p*-nitro- (**VII**), 6-*nitro*-2 : 4-*dimethyl*- (**VIII**), m.p. 68—69°, and 4-*nitro*-2 : 6-*dimethyl*- (**IX**), m.p. 111·5—113° [semicarbazone, m.p. 197—199° (decomp.)], -*phenoxyacetone* are described. (**I**) and (**II**) do not rearrange when heated. The phenoxyacetones can be partly extracted from C$_6$H$_6$ or light petroleum by Claisen's alkali; (**VII**) and (**IX**) are thus cleaved, giving the corresponding nitrophenols, whereas (**V**) and (**VIII**) undergo complete decomp. (**VI**) is extracted from C$_6$H$_6$ without cleavage and its acidity is attributed to the increase of the electron-attracting effect of the OPh group by NO$_2$ making H attached to C next to the ether O more acidic. (**VII**) and (**IX**) are cleaved by NaOMe in MeOH at room temp. at about the same rate whilst (**V**) is decomposed very much more rapidly and (**IV**) is scarcely affected. M.p. are corr. H. W.

Mechanism of the haloform reaction. Preparation of mixed haloforms. J. G. Aston, J. D. Newkirk, J. Dorsky, and D. M. Jenkins (*J. Amer. Chem. Soc.*, 1942, **64**, 1413—1416).—Prep. of COPh·CCl$_3$ (**I**) from COPh·CHCl$_2$ by Cl$_2$–AcOH and of *aaa-tribromoacetophenone* (**II**), m.p. 65—66°, from COPhMe by Br–AcOH requires addition of NaOAc. In 5N-NaOH at 0°, (**II**) is stable and (**I**) is only slowly decomposed; decomp. of (**II**) in N-NaOH at 80° is slow; however, decomp. of (**II**) by NaOH (1 mol.) in 1 : 2 H_2O–dioxan is rapid. Differences are due to relative solubilities. Similarly, some (**I**) is obtained when COPh·CHCl$_2$ is treated with NaOCl–NaOH, particularly if little NaOH is used, and (**I**) is the sole product at 0°. COPh·CH$_2$Cl and Br–AcOH–NaOAc give COPh·CCl$_2$Br (30%) and (**II**) (formed by interaction with NaBr), the amounts formed being determined by cleavage by NaOAc–MeOH to CHCl$_2$Br and CHBr$_3$. COPh·CHCl$_2$ and NaBr in AcOH give COPh·CHClBr. R. S.

p-Dimethylaminobenzylidene derivatives of 3 : 5-dinitro-2 : 6-dimethyl-4-*tert.*-butylacetophenone (musk ketone) and 2 : 6-dimethyl-4-*tert.*-butylacetophenone. A. Müller (*J. pr. Chem.*, 1941, [ii], **159**, 139—145).—3 : 5 : 2 : 6 : 4 : 1-$(NO_2)_2C_6Me_2Bu^{\gamma}$·COMe (**I**) and *p*-$NMe_2$·$C_6H_4$·CHO (**II**) in 4% EtOH–NaOEt afford 3 : 5-*dinitro*-2 : 6-*dimethyl*-4-tert.-*butylphenyl* p-*dimethylaminostyryl ketone* (**III**), reddish-yellow, m.p. 204·5—205·5° (corr.); 1 mg. of (**I**) is detectable. (**III**) (solid; in EtOH or AcOH) shows green fluorescence in filtered ultra-violet light. 2 : 6 : 4 : 1-$C_6H_2Me_2Bu^{\gamma}$·COMe and (**II**) similarly give 2 : 6-*dimethyl*-4-tert.-*butylphenyl* p-*dimethylaminostyryl ketone* (**IV**), yellow-green, m.p. 126·5° (corr.) (red-orange salts), which (as above) shows yellow-green fluorescence. (**I**) does not react with the *EM* reagent (cf. A., 1939, II, 329) in acid solution. Colourless salts of (**III**) are due to the addition of a proton to N and not CO. Coloured salts of (**IV**) result from a mesomeric system.
$CO(C_6H_4$·NMe_2-$p)_2$ and *p*-NO·C_6H_4·NMe_2 do not condense with β-ionone or (**I**) and are unsuitable as substitutes for (**II**) in the *EM* reagent. C. S.

1-Methylphenanthrene series. III. Synthesis of 3-acetyl-1-methylphenanthrene. T. Hasselstrom and D. Todd (*J. Amer. Chem. Soc.*, 1942, **64**, 1225—1226; cf. A., 1942, II, 9).—Addition of $AlCl_3$ to 1-methylphenanthrene and AcCl in $PhNO_2$ at 0° gives 3-*acetyl*-1-*methylphenanthrene*, m.p. 111·5—112·5° [*picrate*, m.p. 137—137·5°; structure proved by oxidation by HNO_3–H_2O at 190° to 1 : 2 : 3 : 5-$C_6H_2(CO_2H)_4$], the *oxime* (**I**), m.p. 180·5—181°, of which with PCl_5–Et_2O at 15—20° gives 3-*acetamido*-1-*methylphenanthrene*, m.p. 188·5—189·5° (with boiling Ac_2O–NaOAc yields the Ac_2 compound, m.p. 162—162·5°). With dry HCl–AcOH–Ac_2O and then HCl–AcOH–H_2O, (**I**) gives 3-*amino*-1-*methylphenanthrene*, m.p. 126—127° (uncorr.), and thence 1-*methyl*-3-*phenanthrol*, m.p. 160—161°. M.p. are corr. R. S. C.

Oxidation of benzophenoxime. W. M. Lauer and W. S. Dyer (*J. Amer. Chem. Soc.*, 1942, **64**, 1453—1456).—CPh_2:N·OH and $K_3Fe(CN)_6$ in KOH–EtOH–H_2O at 35° give $COPh_2$, diphenylketazine oxide, CPh_2:N·N(→O):CPh_2 (**I**), m.p. 156—159°, yellow, and (?) the *benzophenoxime* ester of *aci*-nitrodiphenylmethane, CPh_2:N·O·N(→O):CPh_2 (**II**), m.p. 193° (decomp.) (cf. Hunter *et al.*, A., 1934, 191; von Auwers *et al.*, A., 1933, 505; 1935, 980); at −3° to −8° no (**I**) results. The structure of (**I**) follows from pyrolysis at 160—180° to $(CPh_2$:N·$)_2$ and $COPh_2$, hydrolysis by boiling conc. HCl to $COPh_2$, and hydrogenation (PtO_2, EtOH) to $(CPh_2$:N·$)_2$ (100%). In boiling $CHCl_3$, (**II**) gives the *substance*, $(CPh_2$:N$)_2O$ (**III**), m.p. 167°, and CPh_2:N·OH, in boiling C_6H_6 gives (**III**), CPh_2:N·OH, and $COPh_2$, and in AcOH gives N_2 and equiv. amounts of CPh_2:N·OH and $COPh_2$. At 194°, (**II**) gives N_2 (64·7%), (**III**), $(CPh_2$:N·$)_2$, and $COPh_2$. With Bu^n_2O–MgPhBr, (**II**) gives N_2 (68%), (**III**), CPh_3·OH, and a little PhOH; with MgMeI, CPh_2Me·OH is obtained. (**II**) is stable to NaOMe, NaOEt, and Na–Hg–EtOH–C_6H_6. AcOH containing a little Ac_2O hydrolyses (**III**) to CPh_2:N·OH (90%). R. S. C.

Grignard reactions involving the benzene nucleus. R. C. Fuson, M. D. Armstrong, and S. B. Speck (*J. Org. Chem.*, 1942, **7**, 297—302).—Benzoylmesitylene (**I**) condenses with MgPhBr in the 1 : 4 manner to the conjugated system formed by CO and a double linking of the Ph group. (**I**) and MgPhBr in dry Et_2O give mainly *o-phenylbenzoylmesitylene* (**II**), m.p. 89—90°, accompanied by Ph_2, unchanged material, a white *compound* (**III**), $C_{22}H_{22}O_2$, m.p. 245—246° [*acetate*, m.p. 101° (corr.)], and tar. (**II**) is degraded by syrupy H_3PO_4 to *o*-C_6H_4Ph·CO_2H. (**II**) is obtained synthetically from 2 : 4 : 6 : 1-$C_6H_2Me_3$·COCl and *o*-C_6H_4Ph·MgI. Oxidation of the enol intermediate obtained from (**I**) and MgPhBr gives some (**III**). 1-Naphthoylmesitylene and MgPhBr give a tar from which 2 : 1-$C_{10}H_6Ph$·OH, m.p. 210—211°, mesitoic acid, and apparently a dinaphthone, m.p. >220°, are isolated. *p*-C_6H_4Br·COCl, *s*-$C_6H_3Me_3$, and $AlCl_3$ in Cl_2 yield p-*bromobenzoylmesitylene* (**IV**), m.p. 72—73° (corr.), converted by MgPhBr into a *compound* (**IV**), $C_{22}H_{21}OBr$, m.p. 121° (corr.), and a yellow *isomeride*, m.p. 131° (corr.). (**IV**) does not give a ppt. with $AgNO_3$ in EtOH. It could not be acetylated, reduced, or dehydrogenated. It does not condense with $(CH_2{\cdot}CO)_2O$ and does not contain active H. When brominated in AcOH it gives the *substance*, $C_{22}H_{19}OBr_5$, m.p. 175° (corr.). 1-$C_{10}H_7$·MgBr and (**IV**) give isomeric *compounds*, $C_{26}H_{23}OBr$, m.p. 195° (corr.) and 143° (corr.). 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·C_6H_4Me-*p* and *p*-C_6H_4Me·MgBr give, *inter alia*, 2-*mesitoyl*-5 : 4′-*dimethyldiphenyl*, m.p. 101° (corr.). H. W.

Difficultly reactive carbonyl groups. W. Dilthey and W. Schneider-Windmüller (*J. pr. Chem.*, 1942, [ii], **159**, 273—291).—The reactivity of CO in compounds C_6H_4R·CO·CHPh·CHPh·CO·C_6H_4R' and allied types is studied by oximation, reduction to cyclic substances, and salt formation and the observed steric hindrance is explained by the theory of induced polarities. αε-*Diketo*-αβγ-*triphenyl*-ε-p-*bromophenylpentane*, m.p. 235—237°, loses Br when reduced by Zn dust and AcOH, yields a *salt*, $C_{29}H_{20}OCl_4BrFe$, m.p. 235° (with anhyd. $FeCl_3$ in Ac_2O), and a *mono-oxime*, m.p. 237°.
p-CHPh:N·C_6H_4·CO·CH:CHPh, m.p. 154° (lit. 143—144°), and CH_2PhBz in C_5H_5N containing NaOMe afford αε-*diketo*-αβγ-*triphenyl*-ε-p-*benzylideneaminophenylpentane*, m.p. 218—219°, which is hydrolysed (HCl–MeOH) to the NH_2-*diketone*, m.p. 237° (*Bz* derivative, m.p. 248°); these compounds give resins when treated with Zn and AcOH. *p*-OH·C_6H_4·CO·CH_2Ph (**I**), m.p. 146—147° [lit. 142° (corr.)], does not give a red colour with alkali and is not smoothly reduced; its acetate, m.p. 85—86°, is reduced to βγ-*dihydroxy*-αδ-*diphenyl*-βγ-*di*-p-*acetoxyphenylbutane*, m.p. 206—207°, with an unidentified by-product, m.p. 148°. (**I**), CH_2O, and KOH in aq. MeOH yield αε-diketo-βδ-diphenyl-αε-di-*p*-hydroxyphenylpentane, m.p. 161—163°; the *diacetate*, m.p. 176—177°, is reduced to the corresponding *pinacol*, $C_{33}H_{30}O_2$, m.p. 204—205°. αε-*Diketo*-βγε-*triphenyl*-α-p-*hydroxyphenylpentane*, m.p. 203—204°, and its *acetate*, m.p. 191°, could not be reduced satisfactorily. αε-*Diketo*-βγε-*triphenyl*-α-p-*anisylpentane*, m.p. 188—189°, resists attempted reduction and is converted by a large excess of NH_2OH into a *mono-oxime*, m.p. 232°. αε-*Diketo*-βγ-*diphenyl*-αε-*di*-p-*anisylpentane*, m.p. 203—204°, is very resistant to oximation and reduction whereas αε-*diketo*-βε-*diphenyl*-αγ-*di*-p-*anisylpentane*, m.p. 163—164°, affords a *mono-oxime*, m.p. 190°, but is not reduced by Zn dust–AcOH or by Al–Hg in EtOH. αε-*Diketo*-βγε-*triphenyl*-α-p-*tolylpentane*, m.p. 190°, gives a *mono-oxime*, m.p. 222—223°, but is not reduced whilst αε-*diketo*-βγ-*diphenyl*-α-p-*tolyl*-ε-p-*anisylpentane*, m.p. 193—194°, does not react with NH_2OH or Zn–AcOH. (**I**), PhCHO, and piperidine at room temp. give the unstable piperidinobenzylidene-*p*-hydroxydeoxybenzoin, m.p. 155—157°, which passes in boiling AcOH into *benzylidene*-p-*hydroxydeoxybenzoin*, m.p. 191—192° (*acetate*, m.p. 122—123°), reduced by Zn dust and AcOH to *benzyl*-p-*hydroxydeoxybenzoin*, m.p. 196—198°. *Benzylidene*-, m.p. 90—91°, and *benzyl*- (**II**), m.p. 101—102°, -p-*methoxydeoxybenzoin* are obtained analogously. (**II**) is also obtained from *p*-OMe·C_6H_4·CO·CH_2Ph, CH_2PhCl, and powdered KOH. *Anisylidene*-p-*hydroxydeoxybenzoin* has m.p. 171—172° (possibly a second *form*, m.p. 183—184°), αε-Diketo-γ-phenyl-αε-di-*p*-tolylpentane, m.p. 115°, affords a *dioxime*, m.p. 186°, and is reduced by Zn dust–AcOH to 5-*phenyl*-2 : 3-*di*-p-*tolyl*-$\Delta^{2:4}$-cyclo*pentadiene*, m.p. 100—101° H. W.

Bromo-derivatives of αδ-dimesitylbutane-αβδ-trione enol. R. E. Lutz and D. H. Terry (*J. Org. Chem.*, 1942, **7**, 274—279).—Dimesitylbutanetrione enol (**I**) is converted by Br (1 equiv.) in CCl_4 at 0° followed by treatment of the product with conc. AcOH at 60° into γ-*bromo*-αδ-*dimesitylbutane*-αβδ-*trione*, m.p. 105·5—106°, which gives a pale red colour with $FeCl_3$–EtOH which deepens on keeping. It is reduced by SO_2 in EtOH or by KI in conc. AcOH to (**I**). Br in $CHCl_3$ and (**I**) at 15° afford γ-*bromo*-αδ-*dimesitylbutane*-αβδ-*trione enol* (**II**), m.p. 106·5—107·5°, which gives a dark red colour with $FeCl_3$ in EtOH, is sol. in aq. NaOH or Na_2CO_3, and gives a Na, m.p. 206—209°, and Ag salt. (**II**) and CH_2N_2 in Et_2O afford γ-*bromo*-β-*methoxy*-αδ-*dimesityl*-Δβ-*butene*-αδ-*dione* (**III**), m.p. 125·5—126°, hydrolysed by conc. AcOH containing H_2SO_4 to (**II**) but stable towards KI in conc. AcOH at 70°. This is catalytically reduced (PtO_2 in EtOH) to β-methoxy-αδ-dimesitylbutane-αδ-dione. (**III**) is unaffected by sunlight. Ozonolysis of (**III**) gives mesitylglyoxylic and mesitoic acid. The residues from the prep. of (**III**) afford an isomeric *Me ether*, m.p. 156—156·5°. (**I**) and Br (2 equivs.) in EtOH at −10° yield γγ-*dibromo*-αδ-*dimesitylbutane*-αβδ-*trione*, m.p. 152—152·5°, whilst (**I**) and $PhICl_2$ in $CHCl_3$ at room temp. give a *compound*, $C_{22}H_{21}O_3Cl_3$, m.p. 142—142·5°. H. W.

Acylation of αδ-dimesitylbutane-αβδ-trione enol. R. E. Lutz and D. H. Terry (*J. Amer. Chem. Soc.*, 1942, **64**, 1375—1377).—Acylation of αδ-dimesitylbutane-αβδ-trione enol (**I**) gives *O*-acyl derivatives (cf. the Ph_2-trione, A., 1936, 1524; 1939, II, 375). The Na enolate with BzCl in boiling Pr^{β}_2O or 10% NaOH at room temp. gives 60 or 24%, respectively, of β-*O*-benzoate (**II**), m.p. 141—141·5°, hydrolysed by boiling HCl–AcOH–H_2O to (**I**) and hydrogenated (PtO_2; EtOH) to OH·CR:C(OBz)·CH:CR·OH (here and below R = mesityl) (not isolated), which when kept gives β-*benzoyloxy*-αδ-*dimesitylbutane*-αδ-*dione* (**III**), m.p. 153·5—154°, or with piperidine (2 drops) gives $(CH{\cdot}COR)_2$ (**IV**) (65%) + BzOH, or with I regenerates (**II**). With O_3 in $CHCl_3$ at 0°, (**II**) gives RCO·CO_2H (43%), RCO_2H (31%), and BzOH (56%). HCl–AcOH–H_2O hydrolyses (**III**) to RCO·CH(OH)·CH_2·COR (**V**) and (**I**). BzCl and $[CO{\cdot}CH(OH)\cdot]_2$ (**VI**) give βγ-*dibenzoyloxy*-αδ-*dimesitylbutane*-αδ-*dione*, m.p. 162° [and some (**II**)], which with boiling BzCl gives a substance, m.p. 180—182°, and is hydrolysed to (**II**). 5% NaOH–MeOH at 60—70° converts (**VI**) into (**I**) (65%). BzCl and (**V**) give only (**IV**). The Na enolate of (**I**) with boiling AcCl–Pr^{β}_2O or the Ag enolate with AcCl–abs. EtOH at 0°—room temp. gives 72 or 35%, respectively, of the β-*O*-acetate (**VII**), m.p. 144°, hydrolysed to (**I**); similarly, (**VI**) and Ac_2O–H_2SO_4 at 0° and later 70° give the βγ-diacetate, m.p. 181°, stable to BzCl and hydrolysed by NaOMe at room temp. to (**I**) or by acid to (**VII**). R. S. C.

Reduction of *cis*- and *trans*-β-enol methyl ethers of αδ-dimesitylbutane-αβδ-trione. R. E. Lutz and D. H. Terry (*J. Org. Chem.*, 1942, **7**, 280—285).—Reduction ($Na_2S_2O_4$) of *cis*- (**I**) and *trans*- (**II**) -β-methoxy-αδ-dimesityl-Δβ-butene-αδ-dione proceeds similarly in each case giving β-methoxy-αδ-dimesitylbutane-αδ-dione (**III**) and, mainly, the fission products, mesitoic acid and acetylmesitylene. (**I**) gives a small amount of mesitylglyoxal hydrate (**III**) whilst (**II**) gives a small amount of an unidentified compound. Dimesityl-

butanedione (V) is not formed. Dimesitylbutanetrione enol is reduced ($Na_2S_2O_4$) to a small quantity of αδ-dimesitylbutane-αδ-dion-β-ol, a large amount of δ-hydroxy-αδ-dimesitylbutane-αγ-dione enol, and a trace of (IV); cleavage is relatively small. Catalytic reduction of (II) affords 65% of (III) and 25% of (V) whereas (V) is obtained almost quantitatively from (I). The mechanism of the reactions is described. H. W.

Phenol–formaldehyde resins. IV. Influence of substituents on the polymerisation of *o*-quinonemethides. K. Hultzsch (*J. pr. Chem.*, 1941, [ii], **159**, 180—188).—Polymeric quinonemethides are obtained by shaking 1 : 4 : 2 : 6-$OH{\cdot}C_6H_2R(CH_2Cl)_2$ (I) [from $OH{\cdot}C_6H_2R(CH_2{\cdot}OH)_2$ and AcOH–HCl] with aq. Na_2CO_3 in Et_2O. *4-tert.*-Butyl-2 : 6-di(chloromethyl)phenol, m.p. 68°, thus affords trimeric 5-tert.-*butyl*-3-*chloromethyl*-2-*quinonemethide*, m.p. 175°; (I) (R = Me) yields trimeric 5-*methyl*-3-*chloromethyl*-2-*quinonemethide*, m.p. 163°; 4-*αayy-tetramethylbutyl*-2 : 6-*di*(*chloromethyl*)*phenol*, m.p. 87°, gives polymeric 5-*αayy-tetramethylbutyl*-3-*chloromethyl*-2-*quinonemethide*, amorphous (*M* 1065, 1515; Cl 10·47, 9·04%). C. S.

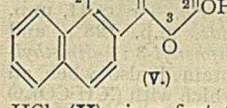
Tetrahydroresorcinol [3-hydroxy*cyclo*hexanone]. K. Dimroth and K. Resin (*Ber.*, 1942, **75**, [*B*], 322—326).—*m*-$C_6H_4(OH)_2$ is hydrogenated (Ni in EtOH) at 150—160° (max.) to *cyclo*hexane-1 : 3-diol (I), partly esterified (BzCl in $CHCl_3$) to the benzoate (II), which is treated with 3 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}COCl$ in C_5H_5N and then separated by crystallisation followed by chromatography into cis-, m.p. 169°, and trans-, m.p. 123—124°, -*cyclohexane*-1 : 3-*diol benzoate* 3 : 5-*dinitrobenzoate*. (II) is oxidised by CrO_3 in cold AcOH to 3-*keto*-cyclo*hexyl benzoate*, m.p. 61—62° (2 : 4-*dinitrophenylhydrazone*, m.p. 146—148°), which readily loses BzOH when heated, with formation of Δ²-*cyclo*hexenone (2 : 4-*dinitrophenylhydrazone*, m.p. 167·5—169°). Partial acetylation of (I) by AcCl in boiling $CHCl_3$ gives the *monoacetate*, b.p. 131—132·5°/13 mm. (62%), oxidised to 3-*keto*cyclo*hexyl acetate*, b.p. 116—118°/11·5 mm., readily hydrolysed by 3% NaOH at room temp. to tetrahydroresorcinol, b.p. 95°/1 mm. H. W.

Attempted synthesis of the antirachitic vitamin. VII. Preliminary experiments on the introduction of the hydroxyl group into ring A. K. Dimroth and E. Stockstrom (*Ber.*, 1942, **75**, [*B*], 326—331).—*cyclo*Hexanone, NH_2Me_2Cl, and 33·3% CH_2O condense in amyl alcohol, decahydronaphthalene, or, best, $CH_2Ph{\cdot}OH$ to 2-dimethylaminomethyl*cyclo*hexanone and a *compound*, $C_{10}H_{22}O_3NCl$, m.p. 98° (corresponding *picrate*, $C_{16}H_{22}O_9N_4$, m.p. 147—148°). Similarly 3-keto*cyclo*hexyl acetate gives α- (I), m.p. 154°, and β- (II), m.p. 92°, -3-*keto*-2-*dimethylaminomethyl*cyclo*hexyl acetate hydrochloride* and α- (III), m.p. 191°, and β- (IV), m.p. 165°, -3-*keto*-4-*dimethylaminomethyl*cyclo*hexyl acetate hydrochloride*. The free bases cannot be distilled unchanged but are obtained as oils by the action of 30% KOH and immediate extraction with Et_2O. (III) is thus transformed into the corresponding *picrate*, m.p. 133—134°. The β-compounds are isomerised by HCl in Ac_2O at 100° to the corresponding α-derivatives. (III) and (IV) are converted by the successive action of 30% KOH at room temp. and MgMeI in Et_2O followed by an excess of MeI and heating of the product with Pt at 100—110° into *o*-4-xylenol (3 : 5-*dinitrobenzoate*, m.p. 182°); (I) and (II) are converted similarly into *o*-3-xylenol. H. W.

2-*cyclo*Hexylidene*cyclo*hexanone, an isomeride of 2-Δ¹-*cyclo*hexenyl*cyclo*hexanone. J. Reese (*Ber.*, 1942, **75**, [*B*], 384—394).—Wallach's liquid ketone is shown to be 2-Δ¹-*cyclo*hexenyl*cyclo*hexanone (I) and an isomeride, 2-cyclo*hexylidene*cyclo*hexanone* (II) is described. 2-1′-Chloro*cyclo*hexyl*cyclo*hexanone in Et_2O is converted by NaOMe in well-cooled MeOH into (II), b.p. 105°/2 mm., m.p. 57°, which gives a *semicarbazone*, softens at 178°, m.p. 180°, re-solidifies at 183°, and melts at 186—188° (decomp.), with an unidentified, non-cryst. material. Optical data support the constitutions assigned to (I) and (II). Titration of (II) with BzO_2H gives the *oxidoketone* (III), $C_{12}H_{18}O_2$, m.p. 98°. (II) is hydrogenated (PtO_2 in EtOAc) to 2-*cyclo*hexyl*cyclo*hexanone. Gentle oxidation ($KMnO_4$) of (II) gives adipic acid (IV) in good yield with a small amount of *cyclo*hexanone (V); under like treatment (I) yields resinous acids, a little (IV), but no (V). (II) and alkaline H_2O_2 afford (III), which does not give a semicarbazone; it is hydrogenated to the *oxido-alcohol*, m.p. ~94°, re-oxidised to (III). Distillation of (III) is accompanied by isomerisation to a *spiro*diketone, $C_{12}H_{18}O_2$ (*semicarbazone*, m.p. 224°). By H_2O_2 with sufficient alkali (I) is converted into ε-*hydroxy*-ε-Δ¹-cyclo*hexenylhexoic acid* (VI), m.p. 70°, with a small proportion of (III). (VI) is reduced (H_2–PtO_2–EtOAc) to ε-*hydroxy*-, m.p. 41°, oxidised (CrO_3 in AcOH at room temp.) to ε-keto-ε-*cyclo*hexylhexoic acid, m.p. 57—58° (semicarbazone, new m.p. 176—177°). Distillation of (VI) under 2 mm. gives ε-Δ¹-cyclo*hexenyl*-Δ⁵-*hexenoic acid*, b.p. 173—180°/2 mm., hydrogenated (PtO_2 in EtOAc) to ε-*cyclo*hexylhexoic acid. (II) is stable at 100° but is partly isomerised to (I) at 150°. 2-1′-Chloro-3′-methyl*cyclo*hexyl-3-methyl*cyclo*hexanone is transformed by NaOMe in MeOH at 0° into 2-3′-*methyl*cyclo*hexylidene*-3-*methyl*cyclo*hexanone*, m.p. 71° (*semicarbazone*, m.p. 171°). H. W.

Syntheses with β-chloroethyl-ketones. J. Décombe (*Compt. rend.*, 1941, **213**, 579—581).—*cyclo*Hexanone, CH_2O, and K_2CO_3 yield +30% of 2-hydroxymethyl-, b.p. 164—165°/12 mm. (*phenylhydrazone*, m.p. 132°), and then (cold HCl–Et_2O) 2-chloromethyl-*cyclo*hexanone, which with $CHNaAc{\cdot}CO_2Et$ gives *Et* α-*acetyl*-β-2-*keto*-cyclo*hexyl propionate*, m.p. 145—146°, hydrolysed (cold KOH) to the 3-CO_2H-derivative (loses CO_2 at 100°) of 2-keto-Δ¹·⁹-octahydronaphthalene, b.p. 137°/14 mm. (Mannich *et al.*, A., 1937, II, 153). $Cl{\cdot}[CH_2]_2{\cdot}COMe$ (I) and sodio-2-methyl*cyclo*hexanone afford a product hydrolysed (KOH–EtOH) to 10% of 2-*keto*-10-*methyl*-Δ¹·⁹-*octahydronaphthalene*, b.p. 142—148°/14 mm. (*semicarbazone*, m.p. 220—225°). (I) and sodio-2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (or better its Et carbonate) afford 2-ketohexahydrophenanthrene, m.p. 80° (*loc. cit.*). W. C. J. R.

Synthesis of 2′-ketodihydro-1 : 2-*cyclo*pentenophenanthrene and derivatives of phenanthro[1, 2-*b*]furan. A. L. Wilds (*J. Amer. Chem. Soc.*, 1942, **64**, 1421—1429).—2-Bromo-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (I) (prep. starting from α-$C_{10}H_7{\cdot}[CH_2]_2{\cdot}OH$ improved), m.p. 87—88° (lit. 84—85°), and $CHAcNa{\cdot}CO_2Et$ in C_6H_6–EtOH give *Et* 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*phenanthrylacetoacetate* (II) (77%), m.p. partly 108—112°, partly 130—135° (with, in one experiment, a *substance*, m.p. 138—141°), which with 5% KOH at 80° and later 115° (N_2) gives 16-*keto*-11 : 12 : 13 : 17-*tetrahydro*-Δ¹⁴·¹⁵-cyclo*pentenophenanthrene* (III) (numbering as for cholane) (84%), m.p. 185—185·5° [*oxime*, m.p. 247—250° (decomp.) [and 13% of 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*phenanthrylacetic acid* (IV), m.p. 187·5—188·5° (*Me* ester, m.p. 106—106·5°)]. Zn–Hg–HCl–AcOH–PhMe reduces (III) to an oil, which with Pd–C–N_2 at 300—320° gives 1 : 2-*cyclo*pentenophenanthrene. H_2–Pd–C in dioxan reduces (III) to 16-*keto*-11 : 12 : 13 : 14-*tetrahydro*cyclo*pentanophenanthrene* (91%), *forms*, m.p. 115—116° and 146—147·5° (mixed *oximes*, sinter at 155°, m.p. 163—168°). NaOMe–MeOH converts (II) into 2-*hydroxy*-1-*acetyl*-10 : 11-*dihydrophenanthro*[1, 2-*b*]*furan* (V) (84%), m.p. 220—223° (decomp.), stable to alkali [also obtained by NaOEt–EtOH without isolation of (II)], or, in one experiment, 2-*methyl*-10 : 11-*dihydrophenanthro*[1, 2-*b*]-*furan*-1-*carboxylic acid* (VI) (30%), m.p. 328—331° (block) [*Me* ester, m.p. 121·5—122·5°, and *Et* ester (VII), *forms*, m.p. 88·5—90° and 78—80°, also obtained from (V) by HCl–EtOH]. With boiling AcOH–conc. HCl, (II) gives first (V) and then 1-*keto*-2-*acetonyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (80%), m.p. 97—98°. Pd–C–N_2 at 200—210° dehydrogenates (VII) to *Et* 2-*methylphenanthro*[1, 2-*b*]*furan*-1-*carboxylate* (92%), m.p. (bath preheated at 110°) 116·5—124° or (bath preheated at 120°) 123·5—124° after melting and resolidification (corresponding *Me* ester, m.p. 142·5—144°, similarly prepared), and thence (KOH–MeOH–H_2O) the *acid* (VIII), m.p. 323—325° (block). Cu chromite in boiling quinoline decarboxylates (VI) to 2-*methyl*-10 : 11-*dihydrophenanthro*[1, 2-*b*]*furan* (69%), m.p. 72—74°, and (VIII) to 2-*methylphenanthro*[1, 2-*b*]*furan* (67%), m.p. 112—112·5°. $CHNa(CO_2Et)_2$ and (I) in C_6H_6–EtOH followed by EtOH–NaOEt give *Et* 2-*hydroxy*-10 : 11-*dihydrophenanthro*[1, 2-*b*]*furan*-1-*carboxylate* (IX) (60%), m.p. 126—127·5° [and a little of a *substance*, $C_{22}H_{20}O_5$, m.p. 220—222° (decomp.)]; hydrolysis and decarboxylation in boiling H_2O (or at 180°) of the malonate yields (IV) (73—84%), reduced (Clemmensen–Martin) to 1 : 2 : 3 : 4-*tetrahydro*-2-*phenanthrylacetic acid* (84—89%), m.p. 167—168°. The derived *Me* ester, m.p. 67—68°, is dehydrogenated (Pd–C; 240—250°) to Me 2-phenanthrylacetate (X), m.p. 78·5—79° (lit. 78—78·5°) [derived acid, m.p. 194·5—195·5° (lit. 183·5—184·5°, ? another form). When distilled (0·5 mm.) (79%) or boiled in AcOH (74%), (V) gives 2-*phenanthrylacetone* (XI), m.p. 91—91·5° (*oxime*, m.p. 197—198°) [(IX) gives mixtures by these methods], reduced (Clemmensen–Martin) to 2-*n*-propylphenanthrene [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 102·5—103·5°]. MgMeI with (X) or (XI) gives 2-*phenanthryl*-tert.-*butyl alcohol*, m.p. 119·5—120°. $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ and (XI) give β-2-*phenanthrylisopropyl alcohol*, m.p. 107—107·5°. R. S. C.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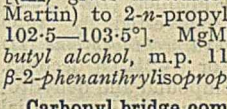
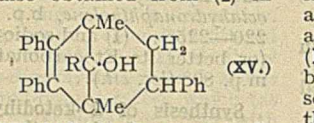

(II.)

Carbonyl bridge compounds. C. F. H. Allen and J. Van Allan (*J. Amer. Chem. Soc.*, 1942, **64**, 1260—1267).—Loss of the *endo*-CO from within six-membered rings by heat alone (200°) or in solution occurs only by the fission, C:C·C·CO → C:C·C + CO, and only when it is necessary for formation of an aromatic ring; in other respects the CO behaves normally. The bimol. product from 4-hydroxy-3 : 4-diphenyl-2 : 5-dimethyl-Δ²-*cyclo*pentenone [αβ-dimethylanhydroacetonebenzil] (I) (Gray, *J.C.S.*, 1909, **95**, 2134) is 4 : 7-endo*keto*-3 : 5 : 6 : 9-*tetraphenyl*-2 : 4 : 7 : 8-*tetramethyl*-4 : 7 : 8 : 9-*tetrahydroinden*-1-*one* (II) (cf. the unmethylated homologue, A., 1933, 1164). (II) reacts largely as the monomeric 3 : 4-diphenyl-2 : 5-dimethyl*cyclo*pentadienone (III). Solid (II) is colourless, but the solution is red in hot solvents, 20% dissociation being indicated in boiling C_6H_6; no coloured substance could, however, be isolated. (II) gives the 2 : 4-*dinitrophenylhydrazone*, m.p. 242° [also obtained from (I)], of (III) and is reduced (Clemmensen–Martin) to 3 : 4-diphenyl-2 : 5-dimethyl*cyclo*pentanone. Reacting as (III), (II) adds as diene in the Diels–Alder reaction: thus with $CHPh{:}CH_2$ it gives 3 : 6-endo*keto*-1 : 2 : 4-*triphenyl*-3 : 6-*dimethyl*-Δ¹-cyclo*hexene* (IV) (90%), m.p. 131°; with $CHPh{:}CH{\cdot}NO_2$ it gives

5-*nitro*-3 : 6-endo*keto*-1 : 2 : 4-*triphenyl*-3 : 6-*dimethyl*-Δ^1-cyclo*hexene* (**V**) (91%), m.p. 176° (5-*Br*-derivative, m.p. 148°, formed by Br–NaOEt–EtOH–C_6H_6); with $(CH{\cdot}CO)_2O$ it gives 3 : 6-endo*keto*-4 : 5-*diphenyl*-3 : 6-*dimethyl*-Δ^4-*tetrahydrophthalic anhydride* (**VI**) (99%), m.p. 191°, or with an excess the *substance* (**VII**) (95%), m.p. 320° [also obtained from (**VI**)], which are also obtained from (**I**) in

(VII.)

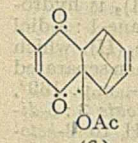


(XV.)

presence of a drop of H_2SO_4; with $COPh{\cdot}CH{:}CH_2$ it gives 3 : 6-endo*keto*-4-*benzoyl*-1 : 2-*diphenyl*-3 : 6-*dimethyl*-Δ^1-cyclo*hexene* (**VIII**) (77%), m.p. 147°; with C_2H_2 it gives, with loss of CO, 2 : 3-*diphenyl*-p-*xylene* (**IX**) (51%), m.p. 109°; with $CPh{:}CH$ it gives similarly *triphenyl*-p-*xylene* (**X**) (90%), m.p. 157°; with Me_2 maleate or fumarate it gives *Me*$_2$ 3 : 6-endo*keto*-4 : 5-*diphenyl*-3 : 6-*dimethyl*-Δ^4-*tetrahydro*-trans- (**XI**) (83%), m.p. 144°, and -cis-*phthalate* (**XII**) (73%), m.p. 128°, respectively; with Et_2 maleate it gives, with loss of CO, *Et*$_2$ 4 : 5-*diphenyl*-3 : 6-*dimethyl*-1 : 2-*dihydrophthalate* (64%), b.p. 210—213°/3 mm.; with $(C{\cdot}CO_2R)_2$ it gives, with loss of CO, *Me*$_2$ (**XIII**) (90%), m.p. 212°, and *Et*$_2$ 4 : 5-*diphenyl*-3 : 6-*dimethylphthalate* (81%), m.p. 132°; with $CH_2{:}CH{\cdot}CO_2Me$ it gives *Me* 2 : 5-endo*keto*-3 : 4-*diphenyl*-2 : 5-*dimethyl*-Δ^3-*tetrahydrobenzoate* (**XIV**) (92%), m.p. 115°; with $CHEt{:}CH{\cdot}CO_2H$ it gives 2 : 5-endo*keto*-3 : 4-*diphenyl*-2 : 5-*dimethyl*-6-*ethyl*-Δ^3-*tetrahydrobenzoic acid* (75%), m.p. 188°. With Br in CCl_4 or $CHCl_3$, (**I**) or (**II**) gives HBr and a *substance*, $C_{38}H_{32}O_2Br_6$, m.p. 136° (decomp.). At 200° (**IV**) gives CO and 2 : 3 : 5-triphenyl-5 : 6-dihydro-*p*-xylene, readily dehydrogenated by Br–$CHCl_3$ to (**X**), which is obtained directly (loss of CO and HNO_2) from (**V**). The CO of (**IV**) is not sterically hindered : it gives readily a 2 : 4-*dinitrophenylhydrazone*, m.p. 200°; with MgMeI it shows 1 active H and no addition; with MgRX (" forced ") it gives *carbinols* (**XV**) (89—93%), R = *Me*, m.p. 119°, *Ph*, +*x*AcOH, m.p. 107° (decomp.) (with AcCl gives the *chloride*, m.p. 128°), and α-$C_{10}H_7$, m.p. 98°. At 200° (**VI**) gives 4 : 5-*diphenyl*-3 : 6-*dimethyl*-1 : 2-*dihydrophthalic anhydride*, m.p. 158° [obtained also when an attempt is made to prepare (**VII**) in $C_6H_3Cl_3$], which with $(CH{\cdot}CO)_2O$ gives (**VII**) and is dehydrogenated (Br, KOH–EtOH) to 4 : 5-*diphenyl*-3 : 6-*dimethylphthalic anhydride* (**XVI**), m.p. 281°, converted into (**IX**) by distillation with soda-lime. At 200° (**VIII**) loses CO and 2 H, giving 3 : 4-*diphenyl*-2 : 5-*dimethylbenzophenone*, m.p. 160°; with $NaNH_2$ this gives (**IX**) and with MgMeI (" forced ") gives 2 : 3-*diphenyl*-6-*a*-*phenylvinyl*-p-*xylene* (90%), m.p. 151°, whence it is regenerated by oxidation. (**IX**) is also formed by heating (**VII**) with $Ba(OH)_2$, one mol. of $(CH{\cdot}CO)_2O$ being eliminated. At 200° (**XI**) and (**XII**) give *Me*$_2$ trans- (**XVII**) (86%), m.p. 131°, and cis-4 : 5-*diphenyl*-3 : 6-*dimethyl*-1 : 2-*dihydrophthalate* (**XVIII**) (99%), b.p. 197—200°/2 mm., both dehydrogenated by $KMnO_4$ in boiling $COMe_2$ to (**XIII**) and converted by 100% H_2SO_4 into (**XVI**), which is also obtained from (**XIII**) by KOH–EtOH and from (**XVIII**) by Br, followed by KOH–EtOH. With Br, (**XVII**) gives *Me*$_2$ 1 : 2 : 3 : 6-*tetrabromo*-4 : 5-*diphenyl*-3 : 6-*dimethyl*-Δ^4-*tetrahydrophthalate*, m.p. 181, converted into (**XVI**) by KOH–EtOH. Heating (**XIV**) and subsequently oxidising ($KMnO_4$) gives *Me* 3 : 4-*diphenyl*-2 : 5-*dimethylbenzoate*, m.p. 116°, which is also obtained as a by-product during one prep. of (**XI**). With MgRBr (" forced "), (**II**) gives 4 : 7-endo*keto*-1 : 3 : 5 : 6 : 9-*pentaphenyl*-2 : 4 : 7 : 8-*tetramethyl*-, m.p. 223°, and 4 : 7-endo*keto*-3 : 5 : 6 : 9-*tetraphenyl*-1 : 2 : 4 : 7 : 8-*pentamethyl*-, m.p. 205°, -4 : 7 : 8 : 9-*tetrahydroinden*-1-*ol*. R. S. C.

Dehydroechinochrome. R. Kuhn and K. Wallenfels (*Ber.*, 1942, **75**, [*B*], 407—413).—Echinochrome (**I**) is converted by Ag_2O in dry Et_2O or by aq. HOCl at 0—5° into *dehydroechinochrome* (**II**) (+H_2O), softens at 70°, decomp. 90—100°, or (+2H_2O) decomp. 160—165°. Conversion of (**I**) into its leuco-compound and dehydrogenation of it to (**II**) are reversible processes occurring in potential ranges corresponding with those of known dehydrogenase systems. (**II**) is reduced to (**I**) by fermenting yeast. Absorption spectrum, solubility, formation of hydrates, and behaviour towards reducing agents indicate that (**II**) is not a substituted naphtha-1 : 4 : 5 : 8-diquinone but a derivative of 1 : 2 : 3 : 4-tetraketotetrahydronaphthalene. 2 : 3-Dihydroxynaphthazarin is oxidised by Ag_2O to 5 : 8-*dihydroxy*-1 : 2 : 3 : 4-*tetraketotetrahydronaphthalene* (**III**) (+H_2O), m.p. ~175° (decomp.), which resembles (**II**) in absorption spectrum, ability to form hydrates, sp. behaviour towards H_2S, and in solubility. (**II**) and (**III**) differ in absorption spectrum from 2-methylnaphtha-1 : 4-5 : 8-diquinone. Also, the undoubted 1 : 2 : 3 : 4-tetraketotetrahydronaphthalene resembles (**II**) and (**III**) in very many of its properties and shows marked differences from the isomeric naphtha-1 : 4-5 : 8-diquinone. (**II**) is undoubtedly 5 : 6 : 8-*trihydroxy*-1 : 2 : 3 : 4-*tetraketo*-7-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. H. W.

Synthesis of condensed ring compounds. IX. Reaction of 4-acetoxy-*p*-tolu-2 : 5-quinone with conjugated dienes and the rules of Alder. E. W. J. Butz and L. W. Butz (*J. Org. Chem.*, 1942, **7**, 199—226).—The dienes react with the OAc·C:C linking of the quinone to an equal or greater extent than with the CMe:C linking. Hexatriene and 2 : 1 : 4 : 5-O:C_6HMe(OAc):O (**I**) in EtOH and CO_2 at 70° or 95° give the following compounds : (*A*) 1 : 4-*diketo*-9-*acetoxy*-3-*methyl*-5(or 8)-*vinyl*-5 : 8 : 9 : 10-*tetrahydronaphthalene* (**II**), m.p. 109—110°, in 45% yield; (*B*) a colourless *compound* (**III**), $C_{13}H_{14}O_3$, m.p. 206—210° after decomp. at 195°, and (*C*) a small amount of a *substance* (**IV**), $C_{15}H_{16}O_4$, m.p. (indef.) 135—140°, isolated on a single occasion. (**II**) does not give a colour with $FeCl_3$ and could not be hydrolysed to a product giving such a colour; at 200—215°/80 mm. it gives AcOH and unidentified tarry matter. (**III**) dissolves in cold dil. aq. NaOH and can be repptd. unchanged by HCl from the solution. It gives a purple-black to brown-black solution with $FeCl_3$. The relatively high temp. of decomp. indicates the possibility that (**III**) is a dienol. (**IV**) gives a green solution with $FeCl_3$. It is decomposed by hot H_2O with formation of (**III**). The identity of the compound, $C_{15}H_{16}O_4$ (A., 1938, II, 104), is in doubt. At 65°, (**I**) and *cyclo*hexadiene yield (*D*) a *substance* (**V**), $C_{15}H_{16}O_4$, m.p. 123—124°, obtained in 55% yield, (*E*) a *compound*, (**VI**), $C_{13}H_{14}O_3$, m.p. 152—153°, and (*F*) 6% of a *substance* (**VII**) $C_{15}H_{16}O_4$, m.p. 84—87°. (**V**) is not an enol acetate since it does not give a colour with $FeCl_3$ either before or after attempted hydrolysis. When heated at 210—215° (bath)/100—110 mm. it gives AcOH and 1 : 2 : 4-O:$C_{10}H_5$Me:O (**VIII**) and hence is (*G*). (**VI**) is sol. in dil. aq. NaOH, gives a brown colour with $FeCl_3$, and has evidently been formed by hydrolysis of an enol acetate. (**VII**) cannot be an enol acetate since it does not hydrolyse to an enol but decomposes on heating into AcOH and (**VIII**). Hence (**VII**) and (**V**) are isomeric, the relationship being probably of the *endo–exo* type.



(*G.*)

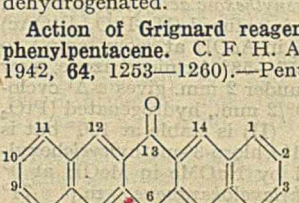
[With A. M. Gaddis.] (**I**) and $(CH_2{:}CMe{\cdot})_2$ in EtOH at 95° afford 1 : 4-*diketo*-9-*acetoxy*-3 : 6 : 7-*trimethyl*-5 : 8 : 9 : 10-*tetrahydronaphthalene*, m.p. 116—117°, in 42% yield. It is not converted into an enol when heated with dil. AcOH. At 210—215°/80—85 mm. it gives AcOH and a cryst. residue from which a quinol (?), m.p. 170—175°, could be isolated and which is oxidised by $FeCl_3$ to 2 : 6 : 7-trimethyl-1 : 4-naphthaquinone in good yield. M.p. are corr.

It is shown that the rules of Alder and Stein can be applied when the max. density of double linkings is determinable by inspection of conventional formulæ drawn to scale and suitably juxtaposed, when the max. density cannot be thus ascertained but can be deduced from measurements of such drawings supported by simple calculations, and in the presence of double linkings in mobile groups; in the last case the position of nearest approach of the mobile double linking to the other double linkings must be determined and the measurements and calculations made as above. H. W.

Successive diene addition and dehydrogenation in nitrobenzene solution without isolation of the hydroaromatic intermediate. E. Bergmann, L. Haskelberg, and F. Bergmann (*J. Org. Chem.*, 1942, **7**, 303—306).—In hot $PhNO_2$ $CHPh{:}CH{\cdot}CH{:}CH_2$ with *p*-O:C_6H_4:O (**I**) and 1 : 4-O:$C_{10}H_6$:O (**II**) give respectively 1 : 5-diphenyl-, m.p. 355°, and 1-phenyl-, m.p. 177°, -anthraquinone. Analogously $(CHPh{:}CH{\cdot})_2$ with (**I**) and (**II**) affords 1 : 4 : 5 : 8-tetraphenyl-, m.p. 355°, and 1 : 4-diphenyl-anthraquinone. 3 : 4-*Diphenyl*-6-*methylphthalic anhydride*, m.p. 161°, is obtained from $\alpha\beta$-diphenyl-$\Delta^{\alpha\gamma}$-pentadiene and $(CH{\cdot}CO)_2O$ (**III**) in boiling $PhNO_2$. $\alpha\beta\delta$-Triphenyl-$\Delta^{\alpha\gamma}$-butadiene and (**III**) in $PhNO_2$ at 100° give 3 : 4 : 6-*triphenylphthalic acid* (+H_2O), m.p. 172°. 9-Δ^1-*cyclo*Pentenylphenanthrene and (**III**) in boiling $PhNO_2$ yield 1 : 2-*cyclo*pentenotriphenylene-3 : 4-dicarboxylic anhydride, m.p. 284°. 9-*Methyl*-, m.p. 164°, or 9-*phenyl*-, m.p. 221°, 1—11 : 14-*dodecahydrophenanthrene*-10-*carboxylic acid* are derived, however, from di*cyclo*hexenyl (**IV**) and $CHMe{:}CH{\cdot}CO_2H$ or $CHPh{:}CH{\cdot}CO_2H$, respectively, in boiling $PhNO_2$, whilst (**III**) and (**IV**) analogously give 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene-9 : 10-dicarboxylic anhydride, m.p. 305°. H. W.

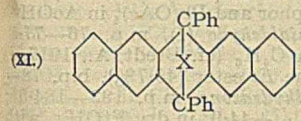
Dehydrogenation of echinochrome and other 2 : 3-dihydroxynaphthaquinones by peroxidase and hydrogen peroxide. K. Wallenfels and A. Gauhe (*Ber.*, 1942, **75**, [*B*], 413—424).—Echinochrome (**I**) is not dehydrogenated by H_2O_2 alone but the change occurs rapidly in the presence of peroxidase, best at p_H 4·7; (**I**) is regenerated by passing H_2S into the solution. The change is of the first order and is restricted by increase of $[H_2O_2]$. Examination of many naphthaquinones shows that dehydrogenation does not depend on a corresponding redox potential but on a sp. arrangement of OH groups. Only those compounds with OH at $C_{(2)}$ and $C_{(3)}$ are dehydrogenated. H. W.

Action of Grignard reagents on pentacenequinones. 6 : 13-Diphenylpentacene. C. F. H. Allen and A. Bell (*J. Amer. Chem. Soc.*, 1942, **64**, 1253—1260).—Pentacene-6 : 13-quinone (in conc. H_2SO_4 blue with red fluorescence) has the bond-structure (**I**), since with MgPhBr it behaves as an $\alpha\beta$-unsaturated diketone having a crossed conjugated system : in Et_2O–Bu_2O, later Bu_2O at 100°, it gives, by 1 : 2-addition, trans-6 : 13-*diphenyl*-6 : 13-*dihydropentacene*-6 : 13-*diol* (**II**) (70%), m.p. 315°, and, by 1 : 4-addition, 5 : 14-diphenyl-5 : 5*a* : 13*a* : 14-tetrahydro- (15%), oxidised by air in KOH–EtOH to 5 : 14-*diphenyl*-

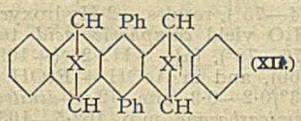


(I.)

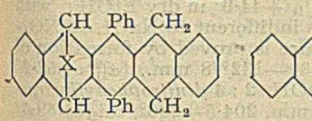
pentacene-6 : 13-*quinone* (**III**), m.p. 309° (blue in H_2SO_4; unaffected by $Na_2S_2O_4$). The structure of (**III**) is proved by cleavage by KOH at 310° (later 290°) to 1 : 4-$C_{10}H_6Ph_2$, 1 : 4 : 2-$C_{10}H_5Ph_2{\cdot}CO_2H$, and β-$C_{10}H_7{\cdot}CO_2H$. With MgPhBr–Et_2O at room temp., (**III**) gives, by 1 : 4-addition, 5 : 7 : 12 : 14-*tetraphenyl*-5 : 5a : 13a : 14-*tetrahydro*- (60%), forms, m.p. 272° and 266°, converted at 300° by loss of H_2 into 5 : 7 : 12 : 14-*tetraphenylpentacene*-6 : 13-*quinone*, m.p. 397° (with $NaNH_2$ in cymene gives 75% of 1 : 4-$C_{10}H_6Ph_2$) 1 : 2-Addition to (**III**) occurs with LiPh in Et_2O, yielding 5 : 6 : 13 : 14-*tetraphenyl*-6 : 13-*dihydropentacene*-6 : 13-*diol*, m.p. 392° (stable to KI–AcOH). KI reduces (**II**) to 6 : 13-*diphenylpentacene* (**IV**), violet-blue, m.p. 318—320°, which in C_6H_6 (magenta; orange-red fluorescence in ultra-violet light) is stable in the dark but in CS_2 and light gives the 6 : 13-*peroxide*, +0·25CS_2 and solvent-free, m.p. 221—222° (purple at ~208°), reduced by H_2–Raney Ni in dioxan at 100° to the *cis*-*isomeride* (**V**), m.p. 269—270°, of (**II**). KI–AcOH reduces (**V**) to (**IV**). In H_2SO_4–MeOH at 0°, (**II**) gives the *Me*$_2$ *ether*, m.p. 258°, stable to Na. Boiling AcBr or HBr–AcOH converts (**II**) or (**V**) into 6 : 13-*dibromo*-6 : 13-*diphenyl*-6 : 13-*dihydropentacene*, m.p. (preheated at 200°) 250—252° (decomp.) or (not preheated) >320° after darkening and sintering at 220°, which in boiling $COMe_2$, C_6H_6, or AcOH gives (**IV**) and Br ($CH_2Br{\cdot}COMe$ in $COMe_2$). CrO_3 oxidises (**IV**) in boiling AcOH to 6 : 13-*diphenylpentacene*-5 : 7 : 12 : 14-*diquinone* (**VI**), m.p. 423°, converted by KOH at 290—300° into *p*-$C_6H_4Ph_2$, *o*-$C_6H_4(CO_2H)_2$ (73%), and BzOH (16%), and by MgPhBr–Et_2O–C_6H_6 into 5 : 6 : 7 : 12 : 13 : 14-*hexaphenyl*-5 : 7 : 12 : 14-*tetrahydropentacene*-5 : 7 : 12 : 14-*tetraol*, m.p. 304°, stable to KI–AcOH. With Br in CCl_4, (**IV**) gives 5 : 14-*dibromo*-6 : 13-*diphenyl*-5 : 14-*dihydro*-, m.p. 235° (decomp.), and then 5 : 7 : 12 : 14-*tetrabromo*-6 : 13-*diphenyl*-5 : 7 : 12 : 14-*tetrahydro*-*pentacene*, m.p. 205° (decomp.), fluorescent, stable in boiling solvents, reduced to (**IV**) by Zn dust in hot C_6H_6, and at > the m.p. giving HBr and an amorphous Br-containing product, m.p. >500°. (**IV**) is not reduced by Na–Hg and does not add Na, but with H_2–Raney Ni in dioxan at 95—100° gives a 7 : 12-H_2- (**VII**), white, m.p. 247—248° (yellow *dioxide*, m.p. 247—248°), and then the 5 : 7 : 12 : 14-H_4- (**VIII**), m.p. 329—331° (not further hydrogenated), and (? 1 : 2 : 3 : 4 : 5 : 14-)H_6- (**IX**), m.p. 252° (stable to H_2), or, in one experiment, the 1 : 4-H_2- derivative (**X**), m.p. 295°; CrO_3 oxidises (**VII**) or (**VIII**) to (**VI**), but (**IX**) or (**X**) gives an amorphous *substance*, $C_{34}H_{25}O_7$, m.p. 167°. With $(CH{\cdot}CO)_2O$ in boiling xylene, (**IV**) gives *adducts* (**XI**), m.p. 335—337°, and (**XII**), m.p. 255° (decomp.) [not formed from (**XI**)];



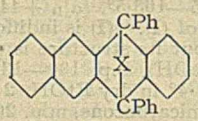
(**XI.**)



(**XII.**)



(**XIII.**)



(**XIV.**)

X = —CH·CO>O —CH·CO

(**VII**) gives the *adduct* (**XIII**), m.p. 190° (decomp.); (**VIII**) does not react; naphthacene and 5 : 12-diphenylnaphthacene give adducts, m.p. 293—294° (lit. 273—282°) and 331° (**XIV**), respectively. Pentacene-5 : 7 : 12 : 14-diquinone and MgPhBr in Et_2O, later Bu_2O, give 5 : 7 : 12 : 14-*tetraphenyl*-5 : 7 : 12 : 14-*tetrahydropentacene*-5 : 7 : 12 : 14-*tetraol* (76%), m.p. 270°, reduced by KI–AcOH to 5 : 7 : 12 : 14-*tetraphenylpentacene* (**XV**), purple, m.p. 306—308° (*peroxide*, m.p. 250°). Absorption spectra of (**IV**) and (**XV**) are given. R. S. C.

Ixone, a tetrabenzopyrenequinone. C. Dufraisse and M. Loury (*Compt. rend.*, 1941, **213**, 689—692).—Cyclisation (H_2SO_4) of 6 : 12-diphenylnaphthacene-5 : 11-dicarboxylic acid yields 1 : 2 : 4 : 5 : 6 : 7 : 9 : 10-*tetrabenzopyrene*-3 : 8-*quinone* [*ixone*] (**I**), dimorphous, m.p. 393—394°, reduced by $Na_2S_2O_4$ to the quinol (*diacetate*, m.p. 256—257°). (**I**) dyes (vat) cotton and rayon bright green. W. C. J. R.

IV.—STEROLS AND STEROID SAPOGENINS.

Provitamin-*D*.—See B., 1942, III, 203.

Light absorption of geometrical isomerides and structure of vitamin-*D*.—See A., 1942, II, 280.

Photo-oxidation of cholesterol. A. Windaus, K. Bursian, and U. Riemann (*Z. physiol. Chem.*, 1941, **271**, 177—182).—Cholesterol, in a thin layer on a glass plate, was irradiated by ultra-violet light. Fractionation of the product by org. solvents and chromatograms afforded a hydroxycholesterol, m.p. 177° (*dibenzoate*, m.p. 133°; *bisdinitrobenzoate*, m.p. 176°), α-7-hydroxycholesterol, and Δ^4-*cholestene*-3 : 6-*diol*, m.p. >247° (diacetate, m.p. 133°; dibenzoate, m.p. 180—181°). F. O. H.

Sterol fraction of Australian marine mollusca.—See A., 1942, III, 695.

Thiosteroids.—See B., 1942, III, 204.

3-Halogenobisnor*allo*cholanic acid compounds.—See B., 1942, III, 203.

Sterols. CXLII. 17-Methylpregnan-3(β)-ol-20-one and related compounds. R. E. Marker and R. B. Wagner (*J. Amer. Chem. Soc.*, 1942, **64**, 1273—1275).—Me 3(β)-acetoxy-17-methylætiocholanate (A., 1942, II, 230) and MgMeI in Et_2O, later boiling C_6H_6, give, by dehydration of the intermediate carbinol, 17-*methyl*-20-*methylene*-*pregnan*-3(β)-*ol*, m.p. 167—168° [*acetate* (**I**), m.p. 136—138°, stable to $POCl_3$–C_5H_5N at 135°], reduced by H_2–PtO_2 in AcOH at 3 atm. to 17 : 20-*dimethylpregnan*-3(β)-*ol*, m.p. 176—177°, and converted by O_3 in $CHCl_3$ into 17-*methylpregnan*-3(β)-*ol*-20-*one* (**II**), *forms*, m.p. 169—171° and 184—187°, also obtained from (**I**) by CrO_3–AcOH and subsequently 5% KOH–MeOH. CrO_3–AcOH oxidises (**II**) to 17-*methylpregnane*-3 : 20-*dione*, m.p. 131—134°. 3(β)-Acetoxy-17-methylætiocholanic acid by treatment with, successively, $SOCl_2$ at 0—5°, CH_2N_2–Et_2O, and gaseous HCl–Et_2O gives 17-*methylpregnane*-3(β) : 21-*diol*-20-*one*, m.p. 140—142°, but the chloride acetate with $ZnMe_2$ in tetrahydronaphthalene–N_2 at room temp. and later 100° and then 5% KOH–MeOH gives (**II**). R. S. C.

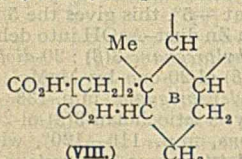
Sterols. CXLIII. Conversion of Δ⁵-pregnen-3(β)-ol-20-one into dehydro*iso*androsterone. R. E. Marker, H. M. Crooks, jun., E. M. Jones, and A. C. Shabica (*J. Amer. Chem. Soc.*, 1942, **64**, 1276—1280).—3(β)-Acetoxy-Δ⁵-pregnen-20-one (**I**). and MgMeI in Et_2O (later boiling C_6H_6) give 20-*methyl*-Δ⁵-*pregnene*-3 : 20-*diol*, m.p. 194—195°, converted by boiling AcOH and later Ac_2O into 3(β)-*acetoxy*-20-*methyl*-$\Delta^{5:17}$-*pregnadiene*, m.p. 139—141° [corresponding 3(β)-*OH*-compound, m.p. 72°; some migration of the ethylenic linking into the ring is indicated by isolation of acid after ozonolysis of (**II**) (below)]. With Br (1 mol.) in $CHCl_3$ at −5°, this gives the 5 : 6-dibromide (**II**), converted by O_3 and then Zn dust–AcOH into dehydro-*iso*androsterone acetate (**III**). 20-*Methylpregnane*-3(β) : 20-*diol*, m.p. 170—172°, obtained from pregnan-3(β)-ol-20-one by MgMeI, gives by dehydration ? 3(β)-*acetoxy*-20-*methylenepregnane*, m.p. 133—135°, and thence by ozonolysis and hydrolysis ætiochalan-3(β)-ol-20-one. (**I**) or 3(β)-*propionoxy*-Δ⁵-*pregnen*-20-*one*, m.p. 119—120°, with Br (3 mols.) in AcOH gives 5 : 6 : 17 : 21-*tetrabromo*-3(β)-*acetoxy*- (**IV**), m.p. 172° (decomp.), or in $EtCO_2H$ gives -3(β)-*propionoxy*-*pregnan*-20-*one*, m.p. 175° (decomp.) (also obtained from the OH-compound in AcOH or PrOH, respectively). With Fe–AcOH at 100°, (**IV**) regenerates (**I**), and with NaI in boiling EtOH and then KOH–MeOH gives 3(β)-*hydroxy*-$\Delta^{5:17}$-*pregnadiene*-21-*carboxylic acid* (**V**), m.p. 252—253° (digitonide), which is hydrogenated (PtO_2; AcOH; 3 atm.) to allo*pregnan*-3(β)-*ol*-21-*carboxylic acid*, m.p. 228—230° [acetate, m.p. 191—193°, affords as above (Br, O_3, Zn–AcOH) (**III**)]. Reichstein's supposed (**V**) (A., 1939, II, 318; m.p. 217—218°) may have been the $\Delta^{5:16}$-isomeride. R. S. C.

Sterols. CXLIV. 16-Alkyl-pregnenolones and -progesterones. R. E. Marker and H. M. Crooks, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1280—1281).—$\Delta^{5:16}$-Pregnadien-3(β)-ol-20-one or its acetate with an excess of MgRHal in Et_2O, later boiling PhMe, gives (cf. Whitmore *et al.*, A., 1941, II, 170) 16-*methyl*- (**I**) (~30%), +x$COMe_2$, m.p. 191—192° [*semicarbazone*, m.p. 245° (decomp.); *acetate*, m.p. 177·5—178·5°], 16-iso*propyl*- (**II**), m.p. 157—158° (*acetate*, m.p. 131—132°; no semicarbazone), and 16-tert.-*butyl*-Δ⁵-*pregnen*-3(β)-*ol*-20-*one* (**III**), m.p. 189—192° (*acetate*, m.p. 156—158°; no semicarbazone), oxidised by $Al(OBu^{\gamma})_3$–$COMe_2$–PhMe to 16-*methyl*-, m.p. 133—135°, 16-iso*propyl*-, m.p. 106·5—108°, and 16-tert.-*butyl*-*progesterone*, m.p. 154—155°, respectively. (**I**) is accompanied by (?) $\Delta^{5:16}$-bisnorcholadiene-3(β) : 20-diol (~35%) (*acetate*, m.p. 173—175°). With Na–EtOH, (**II**) gives a difficultly crystallisable substance, m.p. 130—134°, and (**III**) gives a *compound*, $C_{25}H_{42}O_2$, m.p. 178—180°. R. S. C.

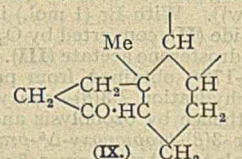
Sterols. CXLV. 21-Benzylidene-Δ⁵-pregnen-3(β)-ol-20-one and allied compounds. R. E. Marker, E. L. Wittle, E. M. Jones, and H. M. Crooks, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1282—1283).—3(β)-Acetoxy-21-benzylidenepregnan-20-one (A., 1939 II, 371) with CrO_3–AcOH at 60—90° and later KOH–EtOH gives 3(β)-*hydroxy*-*ætiocholanic acid* (70%), m.p. 229—230° (*Me* ester, m.p. 138—142°; *acetate*, m.p. 188—190°). 3(α)-*Hydroxyætio*allo*cholanic acid*, m.p. 282—285° (*acetate*, m.p. 208—210°), is similarly prepared from *epiallo*pregnanolone by way of the non-cryst. CHPh: derivative. 21-*Benzylidene*-Δ⁵-*pregnen*-3(β)-*ol*-20-*one* (**I**) (prep. from the OAc-ketone by PhCHO–NaOEt–EtOH at room temp.), m.p. 130—131° (gas). gives an *acetate* (**II**), m.p. 180—182°, which with, successively, Br–$CHCl_3$ at <0°, CrO_3 in 80% AcOH at 50°, Zn–AcOH at 100°, and boiling 2% KOH–MeOH gives 3(β)-*hydroxy*-Δ⁵-*ætiocholenic acid*, m.p. 273—274°. With $Al(OBu^{\gamma})_3$–$COMe_2$–PhMe, (**I**) gives 21-*benzylideneprogesterone*, m.p. 155—158°. Hydrogenation (3% Pd–$BaSO_4$; dioxan; 3 atm.) of (**II**) gives 3(β)-*acetoxy*-21-*benzyl*-Δ⁵-*pregnen*-20-*one*, *forms*, m.p. 128—129° and 143—145°, hydrolysed by $KHCO_3$ in boiling 70% MeOH to the *OH*-compound, m.p. 135—136°, which, as above, affords 21-*benzylprogesterone*, m.p. 86—88°. R. S. C.

Toad poisons. XI. Constitution of bufotalin [etc.]. H. Wieland and H. Behringer (*Annalen*, 1941, **549**, 209—237; cf. A., 1937, II, 208).—Location of the *tert.* OH and OAc of bufotalin (**I**) at $C_{(14)}$ and $C_{(5)}$, respectively, is confirmed. Substances of the series are

renamed as derived from a saturated, OH-free lactone termed bufotalane. Male and female *Bufo vulgaris* yield, per animal, respectively, moist 31 and 64, and dry secretion 16·1 and 27·3 mg., including pure bufotalin 0·55 and 1·23 mg.; each yields crude bufotoxin 1·34, pure bufotenin 0·05, and bufotenidin 0·07 mg. per animal. Bufotaliene (**II**) (prep.: A., 1913, i, 1343; ~63%), $[\alpha]_D^{28}$ +404·6° in $CHCl_3$ (acetate, $[\alpha]_D^{29}$ +366·3° in $CHCl_3$), is accompanied by 3 : 14-*dihydroxybufotalatriene* (**III**) (~5—6%), +0·5EtOH, m.p. 182—183°, $[\alpha]_D^{28}$ +79·1° in $CHCl_3$ (*acetate*), stable to cold, conc. HCl [as also is (**II**)] but resinified by HCl–MeOH at 120°. H_2–Pd-black converts (**III**) in EtOH into non-cryst. acids and 3 : 14-*dihydroxybufotalane*, m.p. 138—140°. Hydrogenation (>5 H_2; Pd-black; EtOH) of (**II**) gives acids (20%), including hydroxy*iso*bufocholanic (**IV**), m.p. 153—154°, and a *hydroxycholenic acid*, m.p. 192—193° [with H_2–PtO_2 in AcOH gives (**IV**)], and α- (**V**) (64%), m.p. 204—205° (lit. 198—199°), $[\alpha]_D^{24}$ +56·0° in $CHCl_3$, and *β-hydroxybufotalane* (**VI**) (16%), m.p. 173·5—174·5°, $[\alpha]_D^{23}$ +30·8° in $CHCl_3$ (*acetate*, m.p. 153—154°). B_2O_3 at 270—275°/vac. dehydrates (**V**) and (**VI**) to α- (**VII**) (63%), m.p. 158—160°, and *β-bufotalene*, m.p. 136—138°, respectively, hydrogenated (Pd-black; EtOH) to α-, m.p. 153·5—155·5°, $[\alpha]_D^{19}$ +55·8° in $CHCl_3$ (with 0·1N-KOH–MeOH and then CH_2N_2 gives Me 21-hydroxybufocholanate, m.p. 82—83°), and *β-bufotalane*, m.p. 131—133°, $[\alpha]_D^{19}$ +37·4° in $CHCl_3$, respectively, probably epimerides at $C_{(20)}$. OsO_4 in AcOH converts (**V**) and (**VI**) into α- (50—60%), +EtOH, sinters at 100°, m.p. 104—108° (turbid; gas at 120°), and solvent-free, m.p. 156°, and *β-bufotalene glycol*, m.p. (+solvent) 93—100° (turbid; sinters at 90°; gas at 118°) or (solvent-free) 196—198° (sinters at 190°), oxidised by $Pb(OAc)_4$–AcOH to the α-, m.p. 251—253°, and *β-lactonedicarboxylic acid*, $C_{24}H_{36}O_6$ (**VIII**), m.p. 266—267°, respectively, which at 290° (N_2)

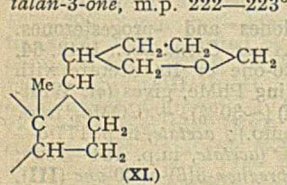


(VIII.)



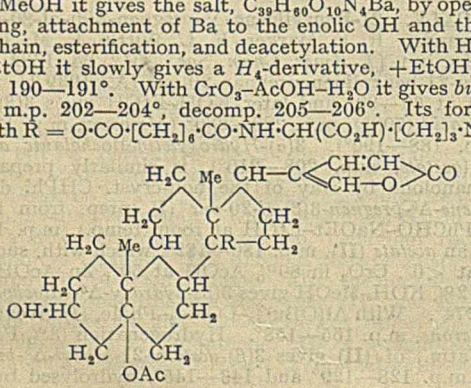
(IX.)

yield *ketones* (**IX**), $C_{23}H_{34}O_3$, m.p. 136—141° after sintering, and 177—183° (clear at 185°) after sintering, respectively. Hydrogenation (Pd-black; EtOH) of (**I**) gives α-, $[\alpha]_D^{18}$ +28·4° in $CHCl_3$, and *β-tetrahydrobufotalin*, sinters at 193°, m.p. 194—195°, $[\alpha]_D^{18}$ +35·7° in $CHCl_3$, converted by KOH–MeOH at room temp. into α-, +EtOH, foams at 149°, m.p. 217—218°, and β-3 : 5 : 14 : 21-*tetrahydrobufocholanic acid*, m.p. 188—189°, which at 150—160°/high vac. are lactonised to yield α- (**X**), m.p. 208—210°, and β-3 : 5 : 14-*trihydroxybufotalane*, respectively. CrO_3 oxidises (**X**) to 3 : 14-*dihydroxybufotalan*-3-*one*, m.p. 222—223°. H_2–PtO_2–AcOH reduces (**V**) or (**VII**) to *deoxobufotalane* (**XI**) (70%), $C_{24}H_{40}O$, m.p. 182—183° (no active H), which is also obtained from α-bufotalanone (**XII**) by Zn–Hg–HCl–EtOH and with P–HI (*d* 1·7) at 150—160° gives a *substance*, $C_{24}H_{41}OI$, b.p. 265—268°/0·001 mm. Hydrogenation (1 H_2) of (**XII**) in AcOH + HBr (little) gives a 3-*hydroxybufotalane*, m.p. 176—178°, but H_2–PtO_2 in EtOH–Et_2O (1 : 1) gives (**V**). H_2–PtO_2 in AcOH converts (**V**) into 3-*hydroxydeoxobufotalane* [as (**XI**)], m.p. 168·5—170·5° (1 active H).



(XI.)

Bufotoxin, $[\alpha]_D^{24}$ +3·9°, $[\alpha]_D^{19}$ +3·6° in MeOH, separates as $C_{40}H_{60}O_{10}N_4$, +EtOH; when dried and kept in air, it gives a *monohydrate*. It neutralises 0·22 equiv. of NaOH in 70% EtOH at once and 2·22—2·23 NaOH after 2 days and contains 1 OAc. With 0·1N-$Ba(OH)_2$–MeOH it gives the salt, $C_{39}H_{60}O_{10}N_4Ba$, by opening of the lactone ring, attachment of Ba to the enolic OH and the CO_2H of the side-chain, esterification, and deacetylation. With H_2–Pd-black in 70% EtOH it slowly gives a H_4-derivative, +EtOH, sinters at 180°, m.p. 190—191°. With CrO_3–AcOH–H_2O it gives *bufotoxinone*, +EtOH, m.p. 202—204°, decomp. 205—206°. Its formula is as shown, with R = O·CO·$[CH_2]_6$·CO·NH·CH(CO_2H)·$[CH_2]_3$·NH·C(NH_2)$_2$.



[With G. Hesse and K. Gäbelein.] Skins of *Bufo arenarum* yield bases (bufotenine and bufothionine), *arenobufogenin*, $C_{24}H_{32}O_6$ (1 mg. per skin), m.p. 252° (decomp.) (cf. Jensen *et al.*, A., 1930, 1205; 1933, 1197; 1935, 1502) (feeble Liebermann reaction; reduces Tollens' reagent immediately), and *arenobufotoxin* (**XIII**), $C_{24}H_{30}O_5$·$C_{14}H_{24}O_4N$ (2 mg. per skin), decomp. (+$3H_2O$) 204° or (anhyd.) 214°. (**XIII**) gives a positive Liebermann and strong Sakaguchi reaction, contains no Ac, neutralises 0·52 NaOH in MeOH at once and 2·1 NaOH during 2 days, and is hydrolysed by boiling 0·5N-HCl–EtOH to CO_2H·$[CH_2]_6$·CO_2H and a *substance*, (?) $C_{24}H_{26}O_3$, m.p. 195°. R. S. C.

Lactone ring of scilliroside.—See A., 1942, II, 279.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Oxidation of trans-Δ²-menthene. W. Hückel and K. Kümmerle (*J. pr. Chem.*, 1942, [ii], **160**, 74—82; cf. A., 1940, II, 227).—*trans*-Δ²-Menthene and $Pb(OAc)_4$–AcOH at 85—90° (cf. Criegee, A., 1930, 1278) afford menthenol acetate, menthanediol diacetate, and a small amount of triacetate (monoacetate monoacetylglycollate of menthanediol), hydrolysed by aq. NaOH–MeOH to *p*-menthen-1-ol [hydrogenated (Pd–$BaSO_4$–EtOH) to *p*-menthan-1-ol], *p*-menthane-2 : 3-diol (**I**) [*diphenylurethane*, m.p. 149—151°; cf. isomeride, m.p. 83—85°, obtained from menthane-2 : 3-diol (**II**) prepared from menthene oxide (*loc. cit.*)], and K glycollate, respectively. (**I**) or (**II**) is further oxidised by $Pb(OAc)_4$–AcOH to α-methyl-α′-*iso*propyladipdialdehyde (di-2 : 4-dinitrophenylhydrazone, m.p. 155—156°). Oxidation of (**II**) by $KMnO_4$ gives a lactonic acid (**III**) (*loc. cit.*) and a non-cryst. mixture which is methylated (CH_2N_2) to 90% of the Me_2 ester of α-methyl-α′-*iso*propyladipic acid, b.p. 90—92°/0·85 mm., + 10% of the ester derived from (**III**). A. T. P.

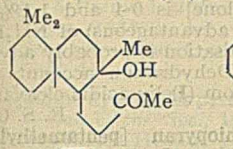
Terpinyl ethers.—See B., 1942, II, 281.

Oxidation of β-pinene by selenium dioxide. L. M. Joshel and S. Palkin (*J. Amer. Chem. Soc.*, 1942, **64**, 1008—1009).—β-Pinene and SeO_2 (0·4 mol.) in abs. EtOH give pinocarveol (29% pure) and a little (?) impure carvopinone (cf. lit.). R. S. C.

Oxidative cleavage of cyclic α-keto-alcohols by lead tetra-acetate. II. E. Baer (*J. Amer. Chem. Soc.*, 1942, **64**, 1416—1421; cf. A., 1940, II, 297).—*cyclo*Hexan-1-ol-2-one and $Pb(OAc)_4$ in AcOH containing a little H_2O yield CO_2H·$[CH_2]_4$·CHO, b.p. 144°/8 mm. (*trimeride*, m.p. 130·5—131°, formed on keeping; 2 : 4-*dinitrophenylhydrazone*, m.p. 140—141°) (cf. Treibs, A., 1939, II, 376; Harries *et al.*, A., 1908, i, 967); in AcOH–EtOH δ-*carbethoxy*-n-*valeraldehyde* (74·5%), b.p. 97—98°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 74—75°), results. 2-Hydroxy*epi*camphor and $Pb(OAc)_4$ in AcOH+H_2O yield *camphoric acid* tert.-*semialdehyde* (**I**), m.p. 76—77·5° (76—78°), $[\alpha]_D$ +112·2° (+109·5°) in C_6H_6 (cf. Bredt, A., 1917, i, 560), and in AcOH + EtOH give the *Et* ester (45·7%), b.p. 78—83°/0·2—0·3 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 183—184·5°; *semicarbazone*, m.p. 162·5—163·5°, $[\alpha]_D$ +44·9° in dry EtOH; with NaOH–EtOH gives (**I**)], of (**I**). (**I**) is indifferent to NaOI, $AgNO_3$–aq. NH_3, or dimedone, but its structure is proved by formation of a Me ester (by HCl–MeOH), b.p. 130—132°/8 mm., $[\alpha]_D^{25}$ +52·2° (homogeneous), $[\alpha]_D$ +51·4° in dry EtOH, 2 : 4-*dinitrophenylhydrazone*, m.p. 220—220·5°, semicarbazone, m.p. 204·5—206°, $[\alpha]_D$ +59·5° in EtOH, and oxime, m.p. 160—161°, $[\alpha]_D$ +62·2° in dry MeOH, neutralisation by 1 NaOH, and oxidation by HNO_3 at 100° to camphoric acid (89·3%). 3-Hydroxycamphor and $Pb(OAc)_4$ in AcOH + H_2O give *camphorič acid* sec.-*semialdehyde* (**II**) (95·2%), m.p. 126—127·5°, $[\alpha]_D$ +36·6° to +38·0° in C_6H_6 (2 : 4-*dinitrophenylhydrazone*, m.p. 223·5—224°; *oxime*, m.p. 142—143·5°, $[\alpha]_D$ −8·6° in dry MeOH; *semicarbazone*, m.p. 199—199·5°, $[\alpha]_D$ +11·9° in dry MeOH), or in AcOH + EtOH give the *Et* ester (48%), b.p. 88·5—89·5°/0·55 mm., $[\alpha]_D^{20}$ +21·2° in dry C_6H_6 (2 : 4-*dinitrophenylhydrazone*, m.p. 175—176°; reduces $AgNO_3$–aq. NH_3). R. S. C.

Dependence of optical rotatory power on chemical constitution. XIX. Stereoisomeric aminoanilino- and dimethylaminoanilinomethylenecamphors and their derivatives. B. K. Singh and B. Bhaduri (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 281—292).—The following are prepared by condensing the requisite base with hydroxymethylenecamphor (**I**) in glacial AcOH: m-*acetamidoanilino*-d-, m.p. 211—213°, -l-, m.p. 211—213°, and -dl-, m.p. 216—218°, *-methylenecamphor*; m-*aminoanilino*-d-, m.p. 64—65°, -l-, m.p. 64—65°, and -dl-, m.p. 64—65°, *-methylenecamphor*; p-*aminoanilino*-d- (**II**), m.p. 163—164°, -l-, m.p. 163—164°, and -dl-, m.p. 163—164°, *-methylenecamphor*; meso-p-*phenylenediaminomethylenecamphor*, m.p. 269—270°; p-*dimethylaminoanilino*-d-, m.p. 169—170°, -l-, m.p. 169—170°, and -dl-, m.p. 169—170°, *-methylenecamphor*. (**II**) and *d*-camphorquinone at 100° in presence of fused Na_2SO_4 afford *anilinomethylene*-d-*camphor*-4-*imino*-d-*camphor*, m.p. 269—270°. [α] is recorded for many λλ and solvents. The rotatory power of these compounds obeys the simple Drude law. For such compounds comparison of the vals. of abs. sp. rotation may be made; these are equal numerically to *k* of Drude's equation when $\lambda = \sqrt{(\lambda_0^2 + 1)}$ (always in the infra-red region). The influence of different groups in order of their decreasing rotatory power is $NH_2 > NMe_2 > H > Me > Cl > Br > I$, which agrees well, subject to minor variations, with the polar series as well as with the sequence of the dissociation consts. of the substituted anilines with which (**I**) is condensed. H. W.

Diterpenes. LIII. Oxidation of sclareol with potassium permanganate. L. Ruzicka, C. F. Seidel, and L. L. Engel (*Helv. Chim. Acta*, 1942, **25**, 621—630).—Oxidation of sclareol (**I**) with $KMnO_4$ (≡5 O) in $COMe_2$ gives an acid (**II**), $C_{17}H_{34}O_4$, m.p. 153—154°, an unstable *ketone* (**III**), m.p. 91—92° [*semicarbazone* (**IV**), m.p. 145°], and, probably, an unsaturated *oxide* (**V**), m.p. 174—176°/10 mm., formed by loss of H_2O from (**III**). (**V**) is converted by $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ into (**IV**) and by boiling aq. EtOH into (**III**). Hydrogenation (PtO_2 in AcOH) of (**V**) gives a mixture of *products*, $C_{18}H_{32}O_4$, m.p. 83—84°, and b.p. 118—120°/0·25 mm., respectively, neither of which reacts with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$. Se at 340—350° converts (**V**) into 1 : 5 : 6-$C_{10}H_5Me_3$. Ozonisation of (**V**) in *n*-C_6H_{14} leads to the *acid* (**VI**), m.p. 157—158°, hydrolysed to the (impure)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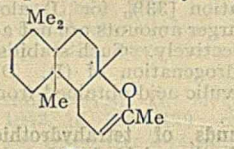
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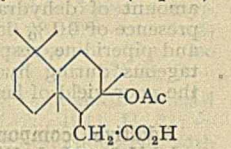
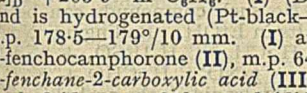
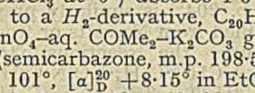

(VI.)

OH-acid, m.p. 128—129°, which passes by loss of H_2O into the lactone (**VII**), $C_{16}H_{26}O_2$, m.p. 123—124°, $[\alpha]_D$ +45·9° in $CHCl_3$, obtained previously by oxidation of (**I**) with CrO_3. (**VII**) is converted by HBr in boiling EtOH into an isomeric *lactone*, m.p. 133—134°, $[\alpha]_D$ −55·3° in $CHCl_3$, which does not contain OAlk. Energetic oxidation of (**II**) with $KMnO_4$ yields (**VII**). (**II**) gives a *Me* ester, m.p. 111—112°. (**III**) is transformed by $Mg(ClO_4)_2$ in boiling PhMe into the unsaturated *ketone*, b.p. 130—135°/0·4 mm. (*semicarbazone*, $C_{19}H_{33}ON_3$, m.p. 197—198°). H. W.

Chemistry of synthetic diterpenes. I. Dimerisation of fenchene with clay catalysts: β-difenchene. N. J. Toivonen, V. Alfthan, L. H. Böök, M. I. Erich, and E. K. Heino (*J. pr. Chem.*, 1941, [ii], **159**, 70—114).—*d*-β-Difenchene (**I**), m.p. 83°, b.p. 171°/10 mm., $[\alpha]_D^{20}$ +67·7° in C_6H_6 [HCl–AcOH at −5° gives the *hydrochloride*, m.p. 79°, $[\alpha]_{D\ c}^{21\cdot5}$ −35·7° in C_6H_6, from which (**I**) is regenerated by boiling KOH–EtOH or in quinoline at 150°; the *hydrobromide*, m.p. 76—78°, $[\alpha]_D^{20}$ −66·1° in C_6H_6, gives (**I**) with KOH–EtOH at room temp. or by air at 70°], is one of the products obtained from *cyclo*fenchene in presence of Florida earth, with or without C_6H_6 or ligroin (cf. A., 1936, 1259). A mixture of *cyclo*- and α-fenchene similarly yields polymerides and *l*-β-difenchene, m.p. 83°, $[\alpha]_D^{22\cdot2}$ −66·3° in $CHCl_3$ (*hydrochloride*, m.p. 79°, $[\alpha]_D^{21\cdot5}$ +35·7° in C_6H_6). *dl*-β-Difenchene affords a hydrochloride, m.p. 80°. (**I**) and Br in AcOH give a *Br*-derivative, $C_{20}H_{31}Br$, m.p. 48—49°, $[\alpha]_D^{20\cdot5}$ +304·6° in C_6H_6, or in $CHCl_3$ a Br_2-compound, $C_{20}H_{30}Br_2$, m.p. 108—109·5°, $[\alpha]_D^{21}$ +203·9° in C_6H_6. (**I**) (Bz_2O–$CHCl_3$ at 0°) absorbs 1·6 O, and is hydrogenated (Pt-black–AcOH) to a H_2-derivative, $C_{20}H_{34}$, b.p. 178·5—179°/10 mm. (**I**) and $KMnO_4$–aq. $COMe_2$–K_2CO_3 give β-fenchocamphorone (**II**), m.p. 64—65° (semicarbazone, m.p. 198·5°), *β-fenchane-2-carboxylic acid* (**III**), m.p. 101°, $[\alpha]_D^{20}$ +8·15° in EtOH [*anhydride*, m.p. 95°; *o-toluidide*, m.p. 163—163·5°; *chloride*, b.p. 106—106·5°/10 mm.; *amide* (**IV**), m.p. 172—173°], and a neutral


(I.)


(VI.)

product, $C_{20}H_{32\ or\ 34}O_2$, m.p. 201—202°, probably dihydroxydihydro-β-difenchene, which is decomposed by distillation at 300° or by CrO_3–AcOH at 50° to an aldehyde, $C_{11}H_{18}O$ (*semicarbazone*, m.p. 182—185°), probably corresponding with (**III**). (**I**) and O_3 yield (**II**), (**III**), a (δ-)*lactone*, m.p. 118·5°, of 4 : 4-dimethyl-3-hydroxymethyl-*cyclo*pentanecarboxylic acid or of 3-hydroxy-5 : 5-dimethyl*cyclo*pentylacetic acid [also obtained from (**II**) and Caro's acid], and β-fenchene hydrate (**V**), m.p. 67—68° (phenylurethane, m.p. 92—93°), also obtained from *iso*fenchyl chloride and aq. KOH (cf. *r*-form; Komppa *et al.*, A., 1933, 830). (**IV**) and aq. NaOBr–NaOH–Br at 0° yield *β-fenchanecarbamide* (**VI**), m.p. 285°, $[\alpha]_D^{27}$ +27·3° in $CHCl_3$, converted by distillation with KOH into 2-*amino-β-fenchane* (**VII**) (Bz_2 derivative, m.p. 159·5—160°). Distillation of the corresponding *hydrochloride*, m.p. 242—244° (decomp.) (anhyd.), or +H_2O, m.p. 74°, $[\alpha]_D^{24}$ +8·69° in EtOH, affords β- + γ-fenchene (*d*-fenchone series), as also does (**V**), obtained from the hydrochloride and aq. KNO_2. β-Fenchene is hydrogenated (Pt-black–MeOH) to β-fenchane, nitrated (HNO_3, *d* 1·075, at 130—135°) to the NO_2-compound, m.p. 111°, $[\alpha]_D^{16}$ +5·46° in EtOH, convertible by distillation into (**II**) or by reduction (Sn–HCl–EtOH) into (**VII**). α-Fenchane affords a NO_2-compound, m.p. 57—58°, $[\alpha]_D^{22}$ −84·1° in EtOH, converted by distillation into α-fenchocamphorone (*semicarbazone*, m.p. 220—221°) or by reduction into 2-*amino-α-fenchane*, m.p. 26—27·5°, b.p. 201·3—201·5°/765 mm. [*hydrochloride* (**VIII**), decomp. 270°, $[\alpha]_D^{20\cdot5}$ −25·9° in EtOH; *Bz* derivative, m.p. 155—155·5°]. Dry distillation of (**VIII**) affords terpenes, b.p. 148·5—153·5° and 153·5—157·5°/752 mm., oxidised to impure α-hydroxyfenchenecarboxylic acid (derived from α-fenchene, with no γ-compound). Isomerisation of (**I**) occurs in presence of Florida earth, and this isomeride is probably one of the by-products obtained during prep. of (**I**). A. T. P.

History of the chemistry of the terpenes. W. Hückel (*Naturwiss.*, 1942, **30**, 17—30). H. W.

Synthesis of 5-methylazulene.—See A., 1942, II, 280.

VI.—HETEROCYCLIC.

Reaction products from α-chloroketones and potassium cyanide. II. Action of potassium cyanide on chloroacetone; so-called "dimeric cyanoacetone." R. Justoni (*Gazzetta*, 1941, **71**, 41—53; cf. A., 1939, II, 406).—The product from KCN and $CH_2Cl{\cdot}COMe$ (**I**) is not "dimeric cyanoacetone," $COMe{\cdot}CH(CN){\cdot}CMe(OH){\cdot}CH_2{\cdot}CN$ (cf. Obregia, A., 1892, 324), but 5-*hydroxy*-2 : 4-*dicyano*-2 : 5-*dimethyltetrahydrofuran* (**II**), m.p. 183° [formed by cyclisation of the intermediate $COMe{\cdot}CH(CN){\cdot}CH_2{\cdot}CMe(OH){\cdot}CN$], also obtained from $CH_2Cl{\cdot}CMe(OH){\cdot}CN$ [new prep. from (**I**) and anhyd. HCN] and aq. $COMe{\cdot}CHNa{\cdot}CN$ (**III**), or by interaction of (**I**) and (**III**) in MeOH to give the *Na* derivative of *cyanoacetonylacetone*, b.p. 106—108°/3 mm. [*bis*-p-*nitrophenylhydrazone* (**IV**), m.p. 227°], which with aq. KCN and HCl gives (**II**). In boiling H_2O, (**II**) evolves HCN. In dil. NaOH, (**II**) with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ in AcOH gives (**IV**). The product from (**II**) and dil. H_2SO_4 is not the δ-lactone of $OH{\cdot}CMe{:}C(CN){\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2H$ (cf. Obregia, *loc. cit.*), but *γ-hydroxy-γ-cyano-α-acetylvaleric acid γ-lactone* (p-*nitrophenylhydrazone*, m.p. 151—152°), which is hydrolysed to $(CH_2{\cdot}COMe)_2$. E. W. W.

Furancarboxylic acid derivatives.—See B., 1942, II, 315.

Complex kojates of transition elements.—See A., 1942, I, 291.

Chemistry of vitamin-*E*. XXXVIII. α-Tocopheramine, a new vitamin-*E* factor. XXXIX. Calcium α-tocopheryl succinate. L. I. Smith, W. B. Renfrow, jun., and J. W. Opie (*J. Amer. Chem. Soc.*, 1942, **64**, 1082—1084, 1084—1086; cf. A., 1942, II, 234).—XXXVIII. 1 : 2 : 3 : 5 : 4-$OH{\cdot}C_6HMe_3{\cdot}NH_2$,HCl in boiling HCO_2Na–HCO_2H gives the *CHO* derivative, m.p. 213—214°, which with anhyd. $CuSO_4$–phytol–N_2 at 135° gives *α-tocopheramine* [5-*amino*-4 : 6 : 7-*trimethyltocol*] (**I**), b.p. 285—288°/1—2 mm. (oxalate, m.p. 153—154°), isolated after chromatography (Al_2O_3) as *hydrochloride*, anhyd. and +0·5H_2O, m.p. 155—157°. The structure of (**I**) is proved by oxidation by $FeCl_3$–HCl–MeOH–H_2O to the quinone (**II**), reduction, and cyclisation to α-tocopherol (**III**). The vitamin-*E* activity of (**I**) equals that of (**III**) but is probably not due to biological oxidation to (**II**) since (**II**) is inactive.

XXXIX. The MgBr derivative (prep. by MgRBr) of 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman (not the chroman in alkali) with $ClCO_2Et$– or $CH_2Cl{\cdot}COCl$–Et_2O at room temp. gives the Et carbonate, m.p. 50—52°, and chloroacetate, m.p. 112—114°, respectively, and with $(CH_2{\cdot}CO)_2O$–Et_2O–dioxan at room temp. and later 100° gives the *H succinate*, m.p. 138—139·5°, rapidly hydrolysed by 2% NaOH at room temp. The MgBr derivative of (**III**) gives similarly the H succinate [*Ca* salt (**IV**), m.p. various, 194—198° to 225° (softens at 220°)]. The vitamin-*E* activity of (**IV**) equals that of (**III**). R. S. C.

Antisterility factors (vitamin-*E*). X. Synthesis of nor-α-tocopherol. W. John and H. Herrmann (*Z. physiol. Chem.*, 1942, **273**, 191—198).—α-5-Hydroxy-2-methoxy-3 : 4 : 6-trimethylphenylbutan-γ-one is converted by $BaCO_3$ and boiling AcCl into its *acetate* (**I**), m.p. 80°, which gives a non-cryst., ill-defined acetal with $CH_2Cl{\cdot}OMe$. (**I**) is converted by Mg hexahydrofarnesyl bromide followed by hydrolysis (KOH–MeOH) and oxidation ($FeCl_3$) of the product into the non-cryst. quinone, which with Zn dust and HBr (*d* 1·49) in AcOH gives *nor-α-tocopherol* (**II**), $OH{\cdot}C{:}CMe{\cdot}C(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}O{\cdot}C{:}CMe{\cdot}C_{15}H_{31}$, an oil (*allophanate*, m.p. 170—172°), which is biologically somewhat less active than α- and at least as active as natural β- or γ-tocopherol. (**II**) is oxidised to nor-α-tocopherylquinone, which is reductively esterified with *p*-$C_6H_4Br{\cdot}COCl$ to the *di*-p-*bromobenzoate* of *nor-α-tocopherylquinol*, m.p. 105°. (**I**) and MgMeI in Et_2O–C_6H_6 afford β-5-hydroxy-2-methoxy-3 : 4 : 6-trimethylphenylethyldimethylcarbinol, m.p. 105°. *iso*-α-Tocopherol, m.p. 65°, is obtained by a similar series of reactions from (**I**), Mg, and cetyl chloride; it is characterised as the *di*-p-*bromobenzoate* of iso-*α-tocopherylquinol*, m.p. 102°. H. W.

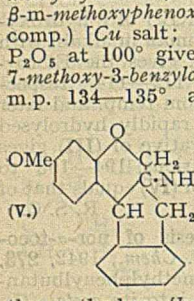
Pechmann condensation of phenols with ethyl γ-phenylacetoacetate. N. G. Kotwani, S. M. Sethna, and G. D. Advani (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 143—146).—Et γ-phenylacetoacetate condenses with phenols in presence of H_2SO_4 giving 4-benzylcoumarins. *m*-$C_6H_4(OH)_2$ yields 7-hydroxy-4-benzylcoumarin, m.p. 214—215° (*acetate*, m.p. 138—139°; *benzoate*, m.p. 180—181°; *Me ether*, m.p. 140—141°), which affords (Me_2SO_4, NaOH then HCl) 2 : 4-*dimethoxy-β-benzylcinnamic acid*, m.p. 130°. Orcinol yields 5-*hydroxy*-4-*benzyl*-7-*methylcoumarin*, m.p. 248—249° (*acetate*, m.p. 139—140°; *Me ether*, m.p. 140—141°), which affords 2 : 6-*dimethoxy*-4-*methyl-β-benzylcinnamic* acid, m.p. 153—154°. Pyrogallol yields 7 : 8-*dihydroxy*-4-*benzylcoumarin*, m.p. 192—194° (*diacetate*, m.p. 168°; *Me_2 ether*, m.p. 178—180°). Phloroglucinol yields 5 : 7-dihydroxy-4-benzylcoumarin, m.p. 274—276° [lit. 260° (decomp.)] (*diacetate*, m.p. 152—154°; *Me_2 ether*, m.p. 182—183°), which affords

2 : 4 : 6-*trimethoxy-β-benzylcinnamic acid*, m.p. 144—146°. α-$C_{10}H_7$·OH yields 4-*benzyl-α-naphthacoumarin*, m.p. 174°. PhOH, β-$C_{10}H_7$·OH, quinol, *m*-cresol, Me β-resorcylate, and resacetophenone do not condense. It appears that the Ph has a considerable inhibiting effect. W. C. J. R.

Condensation of chalkones with flavanones. B. N. Kaplash, R. C. Shah, and T. S. Wheeler (*J. Indian Chem. Soc.*, 1942, **19**, 117—120; cf. A., 1940, II, 102).—Ph (**I**) or *p*-tolyl styryl ketone condenses with flavanone (**II**) in presence of aq. NaOH–EtOH to give 3-α-*phenyl-β-benzoylethyl-*, m.p. 149—151° (2 : 4-*dinitrophenylhydrazone*, m.p. 229—230°), or -β-p-*toluoylethyl-flavanone* (2 : 4-*dinitrophenylhydrazone*, m.p. 237—239°), respectively. Ph 4′-methoxystyryl ketone and (**II**)–EtOH–NaOEt afford 3-α-p-*anisyl-β-p-toluoylethyl-flavanone*, m.p. 92—94° (+0·5H_2O), but Na–Et_2O was necessary to obtain 3-α-*anisyl-β-p-toluoylethyl-*, m.p. 90—92°, 3-α-p-*tolyl-β-benzoylethyl-* (+0·5H_2O) (2 : 4-*dinitrophenylhydrazone*, m.p. 252—255°), and 3-α-p-*tolyl-β-p-toluoylethyl-flavanone* (+H_2O) (2 : 4-*dinitrophenylhydrazone*, m.p. 244—251°), respectively, from (**II**) and the respective styryl ketone. 3′ : 4′-Methylenedioxyflavanone and (**I**) in Na–Et_2O yield 3′ : 4′-*methylenedioxy*-3-α-*phenyl-β-benzoylethyl-flavanone*, m.p. 184—185° (2 : 4-*dinitrophenylhydrazone*, m.p. 228—230°). (**II**) could not be condensed with Ph, *p*-tolyl-, *o*-hydroxy- or -methoxy-phenyl 3′ : 4′-methylenedioxystyryl ketone, 5-nitro-2-hydroxy-4-methoxyphenyl styryl ketone, or 5-nitro-2-hydroxy-4-methoxyphenyl 4′-methoxy- or -methyl-styryl ketone. A. T. P.

Isolation of hibiscitrin from the flowers of *Hibiscus sabdariffa*: constitution of hibiscetin. P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 148—153).—EtOH-extraction of the dried petals yields *hibiscitrin*, $C_{27}H_{30}O_{19}$,H_2O, m.p. 238—240° (decomp.; sinters 225°), hydrolysed (7% H_2SO_4) to hibiscetin (**I**), oxidised (*p*-benzoquinone in C_5H_5N) to the *quinone*, m.p. ∠350°, reduced by aq. SO_2 to (**I**). The Ac derivative of (**I**) with Me_2SO_4 + NaOH yields *hibiscetin Me*$_7$ *ether* (+2H_2O), m.p. 194—196°, which with 50% alkali yields 3 : 4 : 5 : 1-$C_6H_2(OMe)_3$·CO_2H. It is concluded that (**I**) is 3 : 5 : 7 : 8 : 3′ : 4′ : 5′-heptahydroxyflavone. A. Lɪ.

Synthesis of μ-amino-2-methoxychromindan. P. Pfeiffer and H. Simons (*J. pr. Chem.*, 1942, [ii], **160**, 83—94).—*m*-OMe·C_6H_4·O·CH_2·CN and CH_2Ph·MgCl–Et_2O at room temp. afford *CH_2Ph* m-*methoxyphenoxymethyl ketone*, m.p. 48—49° [*oxime*, m.p. 63—74° (mixture); *semicarbazone*, m.p. 143°], converted by aq. KCN–$(NH_4)_2CO_3$ at 100° (CO_2) into 5-*benzyl*-5-m-*methoxyphenoxymethylhydantoin*, m.p. 178·5°, and thence (25% aq. KOH) α-*amino-β*-m-*methoxyphenoxy-β-phenylisobutyric acid*, m.p. 195—200° (decomp.) [*Cu* salt; *Ac* derivative (**I**), m.p. 232°]. (**I**) and H_3PO_4–P_2O_5 at 100° give two isomeric cyclic ketones, viz., 3-*acetamido*-7-*methoxy*-3-*benzylchromanone* [-2 : 3-*dihydro*-1 : 4-*benzpyrone*] (**II**), m.p. 134—135°, and 2-*acetamido*-2-m-*methoxyphenoxymethylindan*-1-*one* (**III**), m.p. 156°. (**II**) is reduced by Na–Hg (PO_4''' buffer) to the two isomeric 3-*acetamido*-7-*methoxy*-3-*benzyl-chromanols* [-4-*hydroxy*-2 : 3-*dihydro*-1 : 4-*benzpyrans*] (**IV**), m.p. 204° and 159°, respectively, and (**III**) affords the isomeric -*indan*-1-*ols*, m.p. 205° and 108°, respectively. Ring-closure (H_3PO_4 at 90°) of (**IV**) yields μ-*acetamido*-2-*methoxychromindan* (**V**), m.p. 164°, and thence the base (*hydrochloride*, m.p. 215—217°). A. T. P.



(V.)

Cœroxan compounds.—See B., 1942, II, 281.

Synthesis of 2′-ketodihydro-1 : 2-*cyclo*pentenophenanthrene and derivatives of phenanthro[1, 2-*b*]furan.—See A., 1942, II, 318.

Behaviour of γ-diketones.—See A., 1942, II, 300.

Dioxan derivatives.—See B., 1942, II, 315.

Substituted acetylenes and their derivatives. XLIV. Catalytic addition reactions of acetylenic alcohols. G. F. Hennion and W. S. Murray (*J. Amer. Chem. Soc.*, 1942, **64**, 1220—1222; cf. A., 1940, II, 187).—In presence of BF_3–HgO at 45—55°, CH:C·CH_2·OH (prep. from CH_2O and CH:CNa in liquid NH_3; 10% yield), b.p. 54°/57 mm., CH:CHMe·OH (61% yield), b.p. 46°/50 mm., and CH:C·CHPh·OH (58% yield), b.p. 80°/4 mm., give, by addition of MeOH and ring-closure, 2 : 5-*dimethoxy*-2 : 5-*dimethyl-* (5%), m.p. 125°, -2 : 3 : 5 : 6-*tetramethyl-* (41%), m.p. 77°, and 3 : 6-*diphenyl*-2 : 5-*dimethyl-* (36%), m.p. 254—256°, -1 : 4-*dioxan*. CH:C·$[CH_2]_2$·OH (65% yield), b.p. 50°/28 mm., gives only CH_2:C(OMe)·$[CH_2]_2$·OH (47%), b.p. 45·5°/20 mm., and impure $(OMe)_2CMe·[CH_2]_2$·OH (10%), b.p. 54—56°/5 mm. 1-Acetylenyl*cyclo*hexanol (87% yield), m.p. 32°, b.p. 68°/11 mm., gives an intractable mixture. Addition of $(CH_2·OH)_2$ in presence of BF_3–HgO at 65° gives 2-*methyl*-2-α-*hydroxyethyl-* (67%), b.p. 69°/11 mm., -2-α-*hydroxyisopropyl-* (57%), b.p. 70°/12 mm., and -2-1′-*hydroxycyclohexyl-* (63%), m.p. 56°, -1 : 3-*dioxolan*. With AcOH–BF_3–HgO at 55—65° there are formed OAc·CH_2·COMe (30%), b.p. 65°/11 mm., OAc·CHMe·COMe (41%), b.p. 56°/10 mm., *phenylacetylcarbinol acetate* (50%), b.p. 65°/11 mm., and 1-*acetylcyclohexyl acetate* (35%), b.p. 109°/11 mm. A little conc. HCl in boiling EtOH hydrolyses all the products to the corresponding acyloins and MeOH or AcOH. R. S. C.

Nature [dehydration and stabilisation] of furfuryl alcohol. A. P. Dunlop and F. N. Peters, jun. (*Ind. Eng. Chem.*, 1942, **34**, 814—817).—When furfuryl alcohol (**I**) is boiled alone or with H_2O, heated at 150° or with H_2O and a trace of HCl at 80°, or kept with H_2O at room temp. (3 months), dehydration leads to some (?) 5-2′-*furfurylfurfuryl alcohol* (**II**), b.p. 131—133°/2·5 mm. (absorbs 4 Br; α-*naphthylurethane*, m.p. 107—108°; *benzoate*, m.p. 70—71°), 2-2′-*furfuryl*-5-5′′-*hydroxymethyl*-2′′-*furfurylfuran* (**III**), b.p. 199—202°/3 mm. (absorbs 6 Br), and resins. Small amounts of (**II**) or (**III**) render much (**I**) insol. in H_2O and the purity of (**I**) is best determined by its cloud point, *i.e.*, the temp. at which a mixture with an equal vol. of H_2O becomes cloudy when cooled. Dehydration is prevented by inorg. or org. bases: *e.g.*, in 10·5 hr. at 150° the amount of dehydration [33% for (**I**) alone] is 0·4 and 1·1% in presence of 0·1% (larger amounts are not advantageous) of NH_2Bu^a and piperidine, respectively. Such stabilisation is probably advantageous during hydrogenation of (**I**). Dehydration accounts for the poor yield of lævulic acid obtained from (**I**) by acidic cleavage. R. S. C.

Additive compounds of tetrahydrothiopyran [pentamethylene sulphide]. H. J. Worth and H. M. Haendler (*J. Amer. Chem. Soc.*, 1942, **64**, 1232—1233).—$[CH_2]_5S$ (*A*) (prep. from Cl·$[CH_2]_5$·Cl by Na_2S in boiling EtOH) gives additive *compounds*. (i) (*A*),X in which X = $HgBr_2$, m.p. 101—105°, CuCl (prep. from CuCl or $CuCl_2$), m.p. 154·5—160°, CuBr (prep. from CuBr or $CuBr_2$), m.p. 123—124°, CuI, m.p. 164—165° (decomp.), $AuCl_3$, m.p. 120—122° (decomp.), AuCl, m.p. 179—182° (decomp.), $AuBr_3$ (**I**), m.p. 140—145° (decomp.), and AuBr [prep. from (**I**) by an excess of (*A*) in boiling EtOH], m.p. 173—179° (decomp.), and (ii) 2(*A*),X in which X = $SnCl_4$, m.p. 149—151·5°, $SnBr_4$, m.p. 149·5—151°, PtI_2, m.p. 194·5—196° (decomp.), and $PdCl_2$, m.p. 146·5—148·5° (decomp.). R. S. C.

Thioindigos.—See B., 1942, II, 318.

Identification of organic compounds. VI. Preparation of *p*-nitrobenzylpyridinium salts of aromatic sulphonic acids. E. H. Huntress and G. L. Foote (*J. Amer. Chem. Soc.*, 1942, **64**, 1017—1020; cf. A., 1942, II, 136).—RSO_3Ag and *p*-NO_2·C_6H_4·CH_2Cl in dry C_5H_5N at 100° give C_5H_5N p-*nitrobenzyl-benzene-*, m.p. 168°, -o-*toluene-*, m.p. 170°, -4-o-, m.p. 158·5°, and -p-*xylene-*, m.p. 139·5°, -*naphthalene*-2-, m.p. 148·5°, -*anthraquinone*-2-, m.p. 187°, -p-*hydroxy-*, m.p. 162°, -p-*amino-*, m.p. 211°, and -p-*acetamido-benzene-*, m.p. 79·5°, -2-*amino*-m-*toluene-*, m.p. 200°, -2-*aminonaphthalene*-1-, m.p. 142°, and -6-, m.p. 218° (decomp.) and +H_2O (lost at 110°), -2-*acetamidonaphthalene*-6-, m.p. (anhyd.) 172° and (+xH_2O) ~115°, -1-*aminonaphthalene*-4-, m.p. 176°, -5-, m.p. 169°, and -8-, m.p. 138°, -1-*acetamidonaphthalene*-4-, m.p. 193°, -5-, m.p. 159·5°, and -8-, m.p. 85°, -*sulphonate*. $(C_5H_5N)_2$ (*di*-p-*nitrobenzyl*)*benzene*-1 : 3-*disulphonate*, m.p. 204°, is similarly prepared. No such compounds can be obtained from Na salts or from Ag salts in EtOH. Boiling aq. NaOH causes the reactions, 3*p*-NO_2·C_6H_4·CH_2·NC_5H_5}RSO_3 + 3NaOH → *p*-CHO·C_6H_4·NO:N·C_6H_4·CHO-*p* + *p*-NO_2·C_6H_4·CHO + 3C_5H_5N + 3H_2O + 3RSO_3Na; C_5H_5N benzylhydroxide is the probable intermediate, since when prepared by Ag_2O from the chloride it is similarly decomposed. R. S. C.

3 : 4-Substituted pyridines. I. Synthesis of 4-methyl-3-vinylpyridine. J. R. Stevens, R. H. Beutel, and E. Chamberlin (*J. Amer. Chem. Soc.*, 1942, **64**, 1093—1095).—OEt·$[CH_2]_2$·CHAc·CO_2Et, b.p. 115°/10 mm. (lit. 85—90°/10 mm.), CN·CH_2·CO·NH_2, and aq. NH_3 at room temp. give the NH_4 salt (34·6%) of 2 : 6-dihydroxy-3-cyano-4-methyl-5-β-ethoxyethylpyridine. α-Aceto-γ-butyrolactone, CN·CH_2·CO_2Et, and 28% aq. NH_3 give the NH_4 salt (52%), m.p. indefinite, of 2 : 6-dihydroxy-3-cyano-4-methyl-5-β-hydroxyethylpyridine, which with boiling conc. HCl at the b.p. gives 6-*hydroxy*-5-*cyano*-4-*methyl*-4′ : 5′-*dihydrofurano*-2′ : 3′-2 : 3-*pyridine*, m.p. indefinite, but with conc. HCl at 150° (sealed tube) gives 6-hydroxy-4-methyl-4′ : 5′-dihydrofurano-2′ : 3′-2 : 3-pyridine, OH-, m.p. 250°, and pyridone *form*, m.p. 177·5—179° (cf. Robinson *et al.*, A., 1934, 1373), differentiated by $FeCl_3$ and absorption spectra. With $POCl_3$ at 120° this gives a *compound*, $C_8H_9ONCl_2$, m.p. 132·8°, and at 180° gives 2 : 6-*dichloro*-4-*methyl*-3-β-*chloroethylpyridine* (57%), m.p. 68·9°, reduced (H_2–$PdCl_2$–C; HCl–MeOH–H_2O) to 4-*methyl*-3-β-*chloromethylpyridine hydrochloride* (86·5%), m.p. 170—171°, which with hot KOH–MeOH gives 4-methyl-3-vinylpyridine (*hydrochloride*, m.p. 164—166°). R. S. C.

Nitrogen compounds in petroleum distillates. XXIII. Structure of a $C_{16}H_{25}N$ base from Californian petroleum. W. Shive, S. M. Roberts, R. I. Mahan, and J. R. Bailey (*J. Amer. Chem. Soc.*, 1942, **64**, 909—912; cf. A., 1942, II, 31).—The base, $C_{16}H_{25}N$ (**I**), m.p. 24·5°, b.p. 279—281°/747 mm. (picrate, m.p. 164°), from Californian petroleum is shown by the following and earlier data to be 2-1′ : 1′ : 3′-*trimethylcyclohexyl*-4 : 6-*dimethylpyridine* and is thus related to the acids from the same source. H_2–Raney Ni at 250°/2000—6000 lb. converts (**I**) into 2-1′ : 1′ : 3′-*trimethylcyclohexyl*-4 : 6-*dimethylpiperidine*, stereoisomerides, m.p. 60·5° and liquid, converted by BzCl in dry C_5H_5N at 27—30° into the 1-*Bz* derivative (**II**), m.p. 120·5°, b.p. 208—212°/3 mm., which with PBr_3–Br at 140° gives, after distillation, $POBr_3$, PhCN, and 1 : 1 : 3-*trimethyl*-2-γ-

methyl-$\Delta^{\alpha\delta}$-*hexadienyl*cyclo*hexane* (**III**) (mixture), b.p. 109—115°/6 mm., 260—267°/746 mm. (absorbs 4 Br). With O_3 in CCl_4, (**III**) gives *trans*-2 : 2 : 6-trimethyl*cyclo*hexanecarboxylic acid (**IV**) (29%), m.p. 82—83°. O_3 converts (**II**) in CCl_4 into an oil, RCO·N:CMeR', which with NaOH–H_2O_2 (not in acid or neutral solution) gives trans-2 : 2 : 6-*trimethyl*cyclo*hexanecarboxylamide* (23%), m.p. 190—191° (isolated because so stable), unaffected by 20% NaOH at 140° or by acid, but converted by KOBr at 0°, later 70°, into the amine obtained from (**IV**) by HN_3. R. S. C.

Stearoxyalkylpyridinium salts.—See B., 1942, II, 333.

Narcotic potency of biurets containing piperidine. H. H. Anderson, C. H. Ch'eng, S. P'an, P. P. T. Sah, and C. Lu (*Science*, 1942, **95**, 255—256).—5-*Phenyl*-1-*diphenylyl*-, m.p. 134°, 1-*phenyl*-5 : 5-*pentamethylene*-, m.p. 183°, 1 : 1-5 : 5-*bispentamethylene*-, m.p. 198°, and 5 : 5-*pentamethylene*-*biuret*, m.p. 121°, have been prepared. (See also A., 1942, III, 710.) E. R. S.

Cyanine dyes of the pyridine series. II. M. Q. Doja and D. Prasad (*J. Indian Chem. Soc.*, 1942, **19**, 125—129; cf. A., 1941, II, 21).—*p*-NMe_2·C_6H_4·CHO and the respective α-picoline alkiodide give, with piperidine–EtOH, 2-p-*dimethylaminostyrylpyridine meth*-, m.p. 274°, *eth*-, m.p. 265°, *prop*-, m.p. 255—256°, and *but-iodide*, m.p. 245° (commercially, sensitin Z). Sensitisation spectra of the dyes are shown, and dyeing properties are examined. A. T. P.

Action of Grignard reagents on benzoylformanilides. R. F. Reeves and H. G. Lindwall (*J. Amer. Chem. Soc.*, 1942, **64**, 1086—1089).—BzCO·NPhEt and MgPhBr in boiling Et_2O–C_6H_6 give *N-ethylbenzilanilide*, OH·CPh_2·CO·NPhMe (75%), m.p. 97·5—98·5°, cyclised by Ac_2O, HCl–EtOH or $-H_2O$, cold conc. H_2SO_4, or, best, boiling 50% H_2SO_4 to 3 : 3-diphenyl-1-ethyloxindole, also obtained from 3 : 3-dichloro-1-ethyloxindole or CCl_3·CO·NPhEt by C_6H_6–$AlCl_3$ or from OAc·CPh_2·COCl (**I**) by NHPhEt. BzCO·NPhMe similarly gives *N-methylbenzilanilide* (81%), m.p. 106—107°, and thence (HBr–AcOH–H_2O) 3 : 3-diphenyl-1-methyloxindole, also obtained as above from (**I**) or 3 : 3-dichloro-1-methyloxindole. BzCO·NMe·C_6H_4·OEt-*p* gives *N*-methylbenzil-*p*-phenetidide (impure), b.p. 120—125°/2 mm. (decomp.), which with boiling HBr–EtOH–H_2O gives 5-*ethoxy*-3 : 3-*diphenyl*-1-*methyloxindole* (60%), m.p. 186·5—187·5°, also obtained from (**I**). β-$C_{10}H_7$·NHMe and (**I**) in boiling C_6H_6 give 3 : 3-*diphenyl*-1-*methyl*-β-*naphthoxindole* (71%), m.p. 253—254°. BzCO·NHPh and MgPhBr in Et_2O give *benzilanilide* (88%), m.p. 177—177·5°, whence red P–HI–AcOH yields $CHPh_2$·CO_2H and heating with $ZnCl_2$ at 185—190° gives 3 : 3-*diphenyloxindole*, m.p. 225—226°, also obtained from 3 : 3-dichloro-oxindole by C_6H_6–$AlCl_3$. R. S. C.

Separation of diketopiperazines and amino-acids in protein hydrolysates by ionophoresis. E. G. Antonovitsch and N. I. Gavrilov (*J. Gen. Chem. Russ.*, 1941, **11**, 763—764).—Serine, cystine, tryptophan (**I**), proline, and hydroxyproline pass towards the cathode more slowly than the acids previously studied (A., 1938, II, 351) and resemble dibasic NH_2-acids in this respect; thus, 50% of (**I**) passes towards the cathode in 103 hr.; the remaining acids require ~70 hr. ~8—10% undergo deamination. G. A. R. K.

Tetrahydroquinolines.—See B., 1942, II, 284.

Autoxidation phenomena of anils in the indandione (diketohydrindene) series. II. P. Pfeiffer and H. H. Roos (*J. pr. Chem.*, 1941, [ii], **159**, 13—35; cf. A., 1935, 1369).—β-Phenyl-β-*p*-tolylpropionyl chloride and $AlCl_3$–CS_2 afford 3-*phenyl*-6-*methyl*-1-*hydrindone* (**I**), m.p. 92—93° (not 3-*p*-tolyl-1-hydrindone; cf. von Braun *et al.*, A., 1929, 562), converted by HNO_3, *d* 1·1, at 190° in a sealed tube into benzophenone-2 : 4-dicarboxylic acid [Me_2 ester (**II**), m.p. 119—120°] or, by HNO_3, *d* 1·2, its (?-)NO_2-derivative (Me_2 ester, m.p. 129°). (**II**) is synthesised by oxidation ($Na_2Cr_2O_7$–aq. H_2SO_4) of 2 : 4-$C_6H_3Me_2$·CH_2Ph, followed by esterification. (**I**) in aq. EtOH–NaOH is converted by PhNO into its 2-*anilo*-, m.p. 155° (and a *compound*, $C_{22}H_{11}O_2N$, m.p. 230°, after becoming orange at 205° and red at 225°), or by *p*-NO·C_6H_4·NMe_2 (in N_2) 2-p-*dimethylanilo*-derivative (**III**), m.p. 146°. (**III**) is oxidised (O_2) to 1-*hydroxy*-3 : 4-*diketo*-1-*phenyl*-2-p-*dimethylaminophenyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 164—165°, converted (20% aq. NaOH) into 1-*keto*-3-*phenyl*-2-p-*dimethylaminophenyl*-6-*methyl*-1 : 3-*dihydroisoindole*, m.p. 267·5°. *p*-Tolylphthalide with NH_2Ph yields 1-*keto*-2-*phenyl*-, m.p. 190°, or with *p*-NH_2·C_6H_4·NMe_2, -2-p-*dimethylaminophenyl*-3-p-*tolyl*-1 : 3-*dihydroisoindole*, m.p. 229·5°. β-Phenyl-β-*m*-xylylpropionic acid, new m.p. 120—120·5°, gives a chloride, b.p. 180—184°/6 mm., which with $AlCl_3$–CS_2 affords 3-*phenyl*-4 : 6-*dimethyl*-1-*hydrindone*, m.p. 76·5—77°, and thence the 2-*anilo*-, m.p. 95—96° [with an *isomeride*, $C_{23}H_{19}ON$, m.p. 138° (structure suggested)], and 2-*dimethylanilo*-compound, m.p. 141·5—142° (with a *substance*, $C_{25}H_{24}O_2N_2$, m.p. 193°). β-Phenyl-β-*p*-anisylpropionic acid, new m.p. 77° (chloride, b.p. 176—182°/4 mm.), yields a ketone, b.p. 203°/6 mm., which affords the stereoisomeric α-, m.p. 166·5°, and β-*oximes*, m.p. 146·5°, both hydrolysed by HCl–EtOH to 6-*methoxy*-3-*phenyl*-1-*hydrindone*, m.p. 59° (2-*anil*, m.p. 130°). Its 2-*dimethylaminoanil*, m.p. 104—105°, is oxidised in EtOH by air to 1-*hydroxy*-3 : 4-*diketo*-6-*methoxy*-1-*phenyl*-2-p-*dimethylaminophenyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 165°. A. T. P.

Electrolytic reduction of quinoline. V. V. Levtschenko (*J. Gen. Chem. Russ.*, 1941, **11**, 686—690).—A suspension of quinoline (**I**) in 9% aq. KOH is electrolysed using a Hg cathode and a Pt anode, at 14 amp. per sq. dm./13 v., giving monomeric *dihydroquinoline* (**II**), m.p. 199—200° (yield 3%) together with tetrahydroquinoline (**III**) (0·1%) and unchanged (**I**). Reduction of (**I**) in an acid medium affords the di- and tri-merides of (**II**). Reduction of (**II**) with Sn and HCl gives (**III**). G. A. R. K.

Reaction of ethyl acetoacetate with *p*-aminoacetanilide. G. Jacini (*Gazzetta*, 1941, **71**, 53—57).—*p*-NH_2·C_6H_4·NHAc (**I**) and excess of CH_2Ac·CO_2Et (**II**) in boiling *o*-C_6H_4Me·NO_2 give p-(*acetamido*)*acetoacetanilide*, m.p. 163—164°. At 100° (bath), (**I**) and (**II**) give *Et* β-p-*acetamidoanilinocrotonate*, m.p. 182°, which at 270° (bath) gives 4-*hydroxy*-, m.p. 358°, converted by $POCl_3$ into 4-*chloro*-6-*acetamido*-2-*methylquinoline*, m.p. 206—208°. This is hydrolysed to 4-*chloro*-6-*amino*-, m.p. 170—171°, and converted by MeOH–NaOMe at 130—140° into 6-*acetamido*-4-*methoxy*-2-*methylquinoline*, m.p. 190°. E. W. W.

Quinoline- and quinaldine-6-sulphonamide from sulphanilamide. G. V. Tschelincev and V. N. Zakotin (*J. Gen. Chem. Russ.*, 1941, **11**, 729—730).—*p*-NHAc·C_6H_4·SO_2·NH_2 yields by the Skraup reaction *quinoline*-6-*sulphonamide*, m.p. 191—192° (30%), and by the Doebner–Miller reaction, quinaldine-6-sulphonamide, m.p. 212—213° (36%). G. A. R. K.

Derivatives of amino*iso*quinolines. J. J. Craig and W. E. Cass (*J. Amer. Chem. Soc.*, 1942, **64**, 783—784).—4-Bromo- (modified prep.), m.p. 38—39° (*picrate*, m.p. 195·5—197°), with aq. NH_3–$CuSO_4$ at 165—170° gives 4-amino-*iso*quinoline (70%), m.p. 108·5° [*picrate*, m.p. 231—232·5° (decomp.)], and thence 4-*acet*-, m.p. 167—168°, 4-*benz*-, m.p. 188—189°, and 4-N^4-*acetylsulphanil*-, m.p. 304—306° (decomp.), hydrolysed by boiling 12% HCl to 4-*sulphanilamido*-*iso*quinoline (**I**), m.p. 211·5—212·5°. 5- (prep. from the NO_2-compound by H_2–Raney Ni in abs. EtOH at 3 atm.), m.p. 128—129° (*Ac*, m.p. 166°, and *Bz* derivative, m.p. 158—159°), and 1-amino-*iso*quinoline (*Ac*, m.p. 148—148·5°, and Bz_2 derivative, m.p. 223·5—224·5°) give 5-, m.p. 284—288° (decomp.), and 1-N^4-*acetylsulphanil*-, m.p. 246—247°, and thence by acid 5- (**II**), m.p. 223—224·5° (decomp.), and by alkali 1-*sulphanil-amido*-*iso*quinoline (**III**), m.p. 264—267° (decomp.). (**III**) is as effective as sulphadiazine against streptococci (mice), (**I**) less so, and (**II**) ineffective. At 5—20 mg. per 20 g. body wt. only (**II**) is toxic to mice. R. S. C.

Acridines.—See B., 1942, II, 281.

Tautomeric character of the glyoxaline ring. H. Green and A. R. Day (*J. Amer. Chem. Soc.*, 1942, **64**, 1167—1173).—The theory of Roeder *et al.* (A., 1941, II, 150) as to the mode of formation of benziminazoles is confirmed. The tautomerism of glyoxalines is not explained by either prototropy or electromerism alone. 3 : 1 : 4-[prep. from 3 : 1 : 4-NO_2·C_6H_3Me·NH_2 (**I**) by Ac_2O and then H_2–Pd–C in EtOH] (*hydrochloride*, m.p. 228—230°) and 4 : 1 : 3-NH_2·C_6H_3Me·NHAc (similarly prepared), m.p. 84·9—85·5° (*hydrochloride*, m.p. 144—145°), when heated alone above the m.p. (N_2) or in boiling *p*-cymene (**II**) or 4N-HCl, gives 2 : 5(6)-dimethylbenziminazole (**III**), which is obtained from 1 : 3 : 4-$C_6H_3Me(NHAc)_2$ only at 211—213° (N_2). *m*-C_6H_4Me·NHAc and HNO_3 (*d* 1·5) in AcOH–Ac_2O at <10° give 4 : 1 : 3- (**IV**) (36%) and 6 : 1 : 3-NO_2·C_6H_3Me·NHAc, separated after hydrolysis by 1 : 1 H_2SO_4–H_2O at 100°. 3 : 1 : 4-NH_2·C_6H_3Me·NMeAc [prep. from (**I**)] and 3-*acetmethylamido*-p-*toluidine*, m.p. 142—142·5° [prep. from (**IV**) by way of its p-C_6H_4Me·SO_2 derivative, m.p. 136—137°, p-*toluenesulphon*-N-*methyl*-4-*nitro*-m-*toluidide*, m.p. 89·3—90·3°, and finally by hydrolysis and hydrogenation], are unchanged in boiling (**II**). Hydrogenation (Pd–C) of 3 : 1 : 4-NO_2·C_6H_3Me·NHMe in EtOH gives 3 : 1 : 4-NH_2·C_6H_3Me·NHMe, unstable [dihydrochloride, softens at 80°, m.p. 147° (cf. lit.)], and thence (Ac_2O–$NaHCO_3$–Et_2O) 3 : 1 : 4-NHAc·C_6H_3Me·NHMe (**V**); similarly are obtained 4 : 1 : 3-NH_2·C_6H_3Me·NHMe, unstable, and its *dihydrochloride*, decomp. 190°, and 4-*Ac* derivative (**VI**), m.p. 74—78°. Ring-closure of (**V**) and (**VI**) to 1 : 2 : 6-trimethylbenziminazole is readily effected in boiling C_6H_6 or PhMe. 3 : 1 : 4- and 4 : 1 : 3-NH_2·C_6H_3Me·NHBz, m.p. 97—98° (lit. 83°), in boiling (**II**) or 4N-HCl or when heated above the m.p. give 2-phenyl-5(6)-methylbenziminazole (**VII**), m.p. 249—250° (lit. 240°). *Benzylidene*-4-*acetamido*-m-, m.p. 74—78°, and -3-*acetamido*-p-*toluidine* (prep. from NH_2·C_6H_3Me·NHAc by PhCHO in EtOH), m.p. 122—123°, are simultaneously hydrolysed and oxidised to (**VII**) by KOH–EtOH–$PhNO_2$ at 100°. R. S. C.

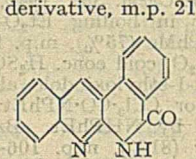
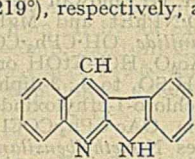
Pyrrole series. VII. Synthesis of unsymmetrical *N*-methyldipyrrylmethanes. W. M. Quattlebaum, jun., and A. H. Corwin (*J. Amer. Chem. Soc.*, 1942, **64**, 922—925; A., 1941, II, 338).—*Et* 4 : 4-*dimethyl*-2-*bromomethylpyrrole*-3 : 5-*dicarboxylate* (**I**) (prep. from the Me_3 compound by Br–AcOH at 30—40°), m.p. 82°, with the appropriate substituted pyrrole and a drop of HCl in boiling MeOH gives 3 : 5 : 4′-*tricarbethoxy*-1 : 4 : 3″ : 5′-*tetra*- (75%), m.p. 110°, and 3′-*bromo*-3 : 5 : 5′-*tricarbethoxy*-1 : 4 : 4′-*tri*-*methyldipyrrylmethane* (62%), m.p. 142°, and *Et* 3 : 5 : 5′-*tricarbethoxy*-1 : 4 : 4′-*trimethyldipyrrylmethane*-3-*propionate* (70%), m.p. 114°. Cryptopyrrole does not condense with (**I**), but the derived MgBr derivative gives 3 : 5-*carbethoxy*-1 : 4 : 3′ : 5′-*tetramethyl*-4′-*ethyldipyrrylmethane* (56%),

m.p. 126°. Replacement of (I) by *Et 5-carbethoxy*-1 : 4-*dimethyl*-2-*bromomethylpyrrole*-3-*propionate* (II) causes all condensations to fail. The reaction is thus greatly influenced by the nature of substituents in either component. Et 3-bromo-2 : 4-dimethylpyrrole-5-carboxylate with Br–AcOH and then SO_2Cl_2 at 14° and later 0·2° and finally H_2O at, first 0°, and then 60° gives 3-*bromo*-5-*carbethoxy*-4-*methylpyrrole*-2-*carboxylic acid* (40% + some aldehyde), m.p. 254° (decomp.), decarboxylated in glycerol to *Et* 3-*bromo*-4-*methylpyrrole*-5-*carboxylate* (40%), m.p. 179—183° (decomp.). Et 1 : 2 : 4-trimethylpyrrole-5-carboxylate with anhyd. HCN–HCl–Et_2O and later H_2O at 40° gives the 3-*CHO* derivative, m.p. 63—64° (also obtained by methylation of Et 3-formyl-2 : 4-dimethylpyrrole-5-carboxylate), converted by $CH_2(CO_2H)_2$–NH_2Ph in boiling EtOH into β-5-*carbethoxy*-1 : 2 : 4-*trimethyl*-3-*pyrrylacrylic acid* (68%), m.p. 184—189°, which with 3% Na–Hg in H_2O gives β-5-*carbethoxy*-1 : 2 : 4-*trimethyl*-3-*pyrrylpropionic acid*, m.p. 153—154°, and thence (Br–AcOH; room temp.) (II), m.p. 158° (decomp.). Et 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate with $CMe_2Et{\cdot}ONa$–$CMe_2Et{\cdot}OH$–Me_2SO_4 gives the 1 : 2 : 4-Me_3 compound (80%), m.p. 60°, reduced to the 3-Et compound, which with Br gives oils. Prep. of 5-carbethoxy-1 : 4-dimethyl-3-ethylpyrrole-2-carboxylic acid, m.p. 149—150° (slight decomp.), and *N*-methylation [$CMe_2Et{\cdot}ONa$–$CMe_2Et{\cdot}OH$–Me_2SO_4 or K salt + Me_2SO_4; product, b.p. 215—221° (bath)] of methylethylmaleimide are improved. R. S. C.

Pyrimidines. CLXXVII. Synthesis of derivatives of pyrimidine-5-carboxylic acid. (Miss) E. Ballard and T. B. Johnson (*J. Amer. Chem. Soc.*, 1942, **64**, 794—798; cf. A., 1942, II, 272).—Addition of $CS(NH_2)_2$ and then of $OEt{\cdot}CH{:}C(CO_2Et)_2$ (I) to NaOEt–EtOH and heating gives *Et* 6-*hydroxy*-2-*thiolpyrimidine*-5-*carboxylate* (85%), m.p. 245°, converted by hot, aq. $CH_2Cl{\cdot}CO_2H$ into uracil-5-carboxylic acid (II), also obtained with a little *Et* 6-*hydroxypyrimidine*-5-*carboxylate*, m.p. 185° after sintering, by H_2O_2–H_2SO_4–H_2O. $CH_2Ph{\cdot}S{\cdot}C(:NH){\cdot}NH_2$ gives similarly *Et* 6-*hydroxy*-, m.p. 174—179°, and thence ($POCl_3$) *Et* 6-*chloro*-, b.p. 248°/11 mm., -2-*benzylthiol*-*pyrimidine*-5-*carboxylate*. Condensation of (I) with $NH_2{\cdot}C(:NH){\cdot}SO_2H$ is unsatisfactory, but in aq. KOH (2 equivs.) gives 10% of *Et carbamidomethylenemalonate*, m.p. 207—212°. Chlorination of the Me ester of (II) is difficult, but PCl_5–$POCl_3$ gives a little Me 2 : 6-dichloro- and thence (conc. aq. NH_3) *Me* 2-*chloro*-6-*amino*-*pyrimidine*-5-*carboxylate*, m.p. 159—161°. Et 6-chloro-2-ethylthiolpyrimidine-5-carboxylate (improved prep.) is dehalogenated in 40—50% yield by Zn dust in boiling EtOH, but the method fails with the 2 : 6-Cl_2-compound (III). Red P–HI–AcOH reduces (III) to 6-*hydroxy*-*pyrimidine*-5-*carboxylic acid*, decomp. variable, 220° to 250° (decarboxylation at 250°). Et 2-ethylthiolpyrimidine-5-carboxylate (IV) and Cl_2–H_2O at 40—70° give *Et* 2-*chloro*- (V) (79%), m.p. 61°, and some *Et* 2-*ethylsulphonyl*-*pyrimidine*-5-*carboxylate*, m.p. 87—89°. NH_3–H_2O or –EtOH at 100° has no effect on (IV), but NH_3–EtOH and (V) give *Et* 2-*aminopyrimidine*-5-*carboxylate*, m.p. 147—149°, and thence the *acid*, m.p. >300°. R. S. C.

Pyridine series. V. Reactions involving the *ortho* effect in certain βγ-substituted pyridines. M. J. Reider and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 286—296).—Et 5-cyano-6-hydroxy-2-methyl*iso*nicotinate is converted by PCl_5 in $POCl_3$ into *Et* 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinate* (I), b.p. 135—136·5°/0·5 mm., m.p. 62°, converted by H_2–Pd–$BaCO_3$ in EtOH into *Et* 5-*cyano*-2-*methyl*iso*nicotinate* (II), m.p. 58° [corresponding *amide* (III), m.p. 275° (decomp.)]. (I) and aq. NH_3 at room temp. give 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinamide* (IV), m.p. 233°. The Hofmann degradation of (III) leads to *dihydroxymethylcopazoline* [3 : 6-*dihydroxy*-6′-*methylpyrido*-3′ : 4′-4 : 5-*pyrimidine*], m.p. >310° (yield 70%), and 4 : 5-*diamino*-2-*methylpyridine* [*dihydrochloride*, m.p. >250° (decomp.)]. (IV) is very readily hydrolysed by 6N-HCl at room temp. to 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinic acid* (V), m.p. 198·5° (*Me* ester, m.p. 168·5°), also obtained by the alkaline hydrolysis of (I). Boiling 5% HCl and (V) yield 6-*chloro*-2-*methylcinchomeronic acid*, m.p. 205° (*Me*$_2$ ester, m.p. 85°). (II) is very readily hydrolysed by alkali to 5-*cyano*-2-*methyl*iso*nicotinic acid*, m.p. 230°, also obtained from (III) and cold 0·1N-HCl; it is decarboxylated by Cu powder to 5-*cyano*-2-*methylpyridine*, m.p. 84—85°; 6-*chloro*-5-*cyano*-2-*methylpyridine*, m.p. 114·5—115·5°, is obtained analogously. (IV) and Br in MeOH give the *bromoamide*, m.p. 199·8°, which does not appear to rearrange with NaOMe in boiling MeOH. (II) and N_2H_4 in EtOH–Et_2O (1 : 1) yield 3-*amino*-6-*hydroxy*-6′-*methylpyrido*-3′ : 4′-4 : 5-*pyridazine*, m.p. 324° (*hydrochloride*), which does not form a derivative with PhCHO. Under similar conditions (I) affords 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinhydrazide*, sublimes at >360° (:*CHPh* derivative, m.p. 282·5°). (V) and boiling $SOCl_2$ yield 6-*chloro*-5-*cyano*-2-*methyl*-iso*nicotinyl chloride*, m.p. 98—103°. (I) is reduced (H_2–Pd–NaOAc–AcOH) to *Et* 2-*methyl*-5-*aminomethyl*iso*nicotinate* [*picrate*, m.p. 170° (decomp.)] and 2-*hydroxy*-6′-*methylpyrido*-3′ : 4′-4 : 3-*pyrrolenine*, m.p. 250° in sealed tube (*picrate*, m.p. 205·5°; *hydrochloride*, sublimes >285°). M.p. are corr. H. W.

Polynuclear condensed systems with heterocyclic rings. XIII. Polycyclic systems from 2-aminobenzylideneaniline. W. Borsche, M. Wagner-Roemmich, and J. Barthenheier (*Annalen*, 1942, **550**, 160—174; cf. A., 1939, II, 87).—2-$NH_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4Me$-4′ (I), 4 : 6-dihydro-5 : 5-dimethyl- (II) or -5-phenyl-resorcinol, and piperidine at 100° (bath) afford 4-*keto*-2 : 2-*dimethyl*-, m.p. 118° (*picrate*, m.p. 198—199°; 2 : 4-*dinitrophenylhydrazone*, m.p. 301°; *semicarbazone*, m.p. 236°), or -2-*phenyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 158°, respectively. 1 : 4-Diketo*cyclo*hexane (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 240°) similarly yields 2 : 3 : 6 : 7-*dibenzo*-9 : 10-*dihydro*-1 : 8-*diazaphenanthrene*, m.p. 256—257°; 1 : 3 : 5-$C_6H_3(OH)_3$ gives 2 : 3 : 6 : 7-*dibenzo*-9-*keto*-9 : 10-*dihydro*-1 : 5-*diazaphenanthrene*, m.p. >360°, converted by warm AcOH–HNO_3 (*d* 1·4) into 2 : 3 : 6 : 7-*dibenzo*-1 : 5-*diazaphenanthrenequinone*. (II) and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$ in MeOH yield γ-2-(4-*carboxyquinolino*)-ββ-*dimethylbutyric acid*, m.p. 156—157°. Barbituric acid and (I) or its 4 : 5-$(OMe)_2$-derivative (III) with piperidine afford 2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3-*diaza*-*acridine*, m.p. 368°, or its 6 : 7-(*OMe*)$_2$-derivative, m.p. 358—360°, respectively. Homophthalimide and (I) or (III) or *o*-aminopiperonylidene-*p*-toluidine (IV) in piperidine–$C_5H_{11}{\cdot}OH$ give 2 : 3 : 5 : 6-dibenzo-7-keto-7 : 8-dihydro-1 : 8-naphthyridine (V), new m.p. 262°, or its 2′ : 3′-(*OMe*)$_2$-, m.p. 330—332° (*picrate*, m.p. 286—288°), or -CH_2O_2-derivative, m.p. 340°, respectively. (I) and oxindole (VI) with piperidine at 150° yield quinindoline (VII), whereas (I) and (VI) in aq. NaOH–EtOH afford 2-*aminobenzylideneoxindole*, m.p. ~230° (*Ac*$_2$ derivative, m.p. 221—222°), also obtained from the corresponding 2-NO_2-compound, m.p. 227—229°, and $SnCl_2$–HCl, and convertible by heat into (VII). (V) and (III) or (IV) + piperidine at 150° yield 7 : 8-*dimethoxy*-, m.p. 302° (10-*Ac* derivative, m.p. 223°), or 7 : 8-*methylenedioxy*-*quinindoline*, m.p. 305—315° (10-*Ac* derivative, m.p. 217—219°), respectively, also obtained

(V.)  (VII.) 

by heating (170—180°) 6-*aminoveratrylideneoxindole*, m.p. 110—115° (*Ac*$_2$ derivative, m.p. 242—243°) (prepared from the 6-NO_2-compound, m.p. 261°), or 6-aminopiperonylideneoxindole (*Ac*$_2$ derivative, m.p. 221—222°), respectively. 1-Methyloxindole and *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$–EtOH–piperidine (boil for 2 days) give 3-(2′-*nitrobenzylidene*)-1-*methyloxindole*, m.p. 258—259°, reduced to the 2-NH_2-compound, m.p. 245—247° (convertible by boiling $C_5H_{11}{\cdot}OH$-glycerol–piperidine into 11-methylquinindoline). 3-(6′-*Aminoveratrylidene*)-, m.p. 208—209° (*Ac* derivative, m.p. 253—255°), and -*piperonylidene*)-1-*methyloxindole*, m.p. 315—316° (*Ac* derivative, m.p. 284—285°), are prepared. A. T. P.

Mechanism of the chemiluminescence of 3-aminophthalhydrazide. H. Kautsky and K. H. Kaiser (*Naturwiss.*, 1942, **30**, 148).—Treatment of the hydrazide (I) in pure $COMe_2$ with $Ca(OCl)_2$ gives a violet-red solution with all the properties of an azodiacyl compound (II). Addition of dil. aq. alkali to this solution causes a short, bright blue luminescence. After hydrolysis of (II) the decolorised solution contains (I) and therefore gives a temporary luminescence after addition of a suitable oxidising agent. The course of the change is:

(I) → $NH_2{\cdot}C_6H_3<^{CO{\cdot}N}_{CO{\cdot}N}$ → 3 : 2 : 1-$NH_2{\cdot}C_6H_3(CO_2H)_2$ + NH:NH →

$\left[NH_2{\cdot}C_6H_3<^{CO{\cdot}NH}_{CO{\cdot}NH}\right]^*$ + N_2 → (I) + *hν*. H. W.

Comparative reactivity of the carbonyl groups in the thionaphthenquinones. I. Constitution of certain thioindigoid dyes. J. Harley-Mason and F. G. Mann (*J.C.S.*, 1942, 404—415).—The factors determining the type of condensation of the thioindoxyls with the thionaphthenquinones (I) (*i.e.*, whether the CH_2 of the former reacts with the α-CO of the latter to give a thioindigo or with the β-CO to give a thioindirubin) have been investigated. For this purpose, thioindoxyl (II) and six substituted (II) have been condensed with the corresponding (I), and the product in each case compared with that obtained by the condensation of the (II) with the corresponding α-anil, where α-condensation must necessarily have occurred. As the compounds obtained have high or indefinite m.p. the identity of pairs of compounds has been determined by the following means: reductive acetylation (Zn–AcOH–Ac_2O) to a diacetyldihydro-derivative, *X*-ray analysis by the " powder " method, alkali fission in a few cases, dyeing tests on cotton, and, as confirmatory test, colours of H_2SO_4 solutions. The results show that the condensation in most cases is determined solely by the position of substituents in the quinone mol. and is unaffected by those in the thioindoxyl mol. Thionaphthenquinone and 5- or 6-substituted (I) always give β-condensation, 4-substituted (I) always give α-condensation, and 7-substituted (I) may give α- or β-condensation; only with the last quinones is the type of condensation affected by the (II) employed. Indoxyl and oxindole always give β- and α-condensation respectively with all the (I), the effect of the two compounds being to suppress completely the influence of substituents in the quinone mol. The significance of the results is discussed.

The following are described (temp. in parentheses are the m.p. of the *diacetyldihydro*-derivative): 3-*carboxynaphthyl*-2-*thioglycollic acid*, m.p. 175—176°, from Na 2-thiol-3-naphthoate and $CH_2Cl{\cdot}CO_2H$; 6-

ethoxythionaphthenquinone-2-p-*hydroxyanil*, m.p. 237—239°, from *p*-NO·C_6H_4·OH and 5-chloro-7-methylthioindoxyl, and the 5 : 6-*benz*-compound, m.p. 280—282° (decomp.); 6-*chloro*-4-*methylthioindirubin* (144—145°), 6-*chloro*-4-*methylthioindigo* (182—183°), 6-*ethoxythioindirubin* (131—133°), 6-*ethoxythioindigo* (162—165°), 4 : 5-*benzthioindirubin* (162—163°), 4 : 5-*benzthioindigo* (214—217°), 5 : 6-*benzthioindirubin*, 5 : 6-*benzthioindigo* (254—256°), 6 : 7-*benzthioindirubin* (178—179°), 6 : 7-*benzthioindigo* (254—256°), 5 : 6′-*dichloro*-4 : 4′-*dimethylthioindigo* (290—292°); 6′-*chloro*-6-*ethoxy*-4′-*methylthioindigo* (178—182°), 6′-*chloro*-4′-*methyl*-4 : 5-*benzthioindigo* (196—199° (decomp.)], 6′-*chloro*-4′-*methyl*-6 : 7-*benzthioindigo* [252—253° (decomp.)], 6′-*chloro*-4′-*methyl*-5 : 6-*benzthioindigo* (261—263°), 5-*chloro*-7-*methylthioindigo* (213—215°), 5 : 5′-*dichloro*-7 : 7′-*dimethylthioindigo* (308—310°), 5-*chloro*-6′-*ethoxy*-7-*methylthioindigo* (214—216°), 5′-*chloro*-7′-*methyl*-4 : 5- (269—272°), -6 : 7- (235—238°), and -5 : 6-*benzthioindigo* (258—260°), 5′-*chloro*-7′-*methyl*-6 : 7-*benzthioindirubin* (167—169°), 6-*chloro*-6′-*ethoxy*-4-*methylthioindirubin* (138—140°), 5-*chloro*-6′-*ethoxy*-7-*methylthioindirubin* (148—149°), 6 : 6′-*diethoxythio-indirubin* (144—146°) and -*indigo* (230—232°), 6′-*ethoxy*-6 : 7-*benzthio-indirubin* (166—169°) and -*indigo* (205—208°), 6′-*ethoxy*-5 : 6-*benzthio-indirubin* and -*indigo* [224—225° (decomp.)], 6′-*ethoxy*-4 : 5-*benzthioindigo* (221—225°), 4 : 5 : 4′ : 5′-*dibenzthioindigo* (>315°), 4 : 5 : 6′ : 7′-*dibenzthioindigo* (254—257°), 4 : 5 : 5′ : 6-*dibenzthioindigo* (263—265°), *ethoxy*-6′ : 7′-*benzthioindirubin* (162—165°), 4 : 5—6′ : 7′-*dibenzthioindirubin* (227—230°), 6 : 7 : 6′ : 7′- (>315°) and 5 : 6 : 6′ : 7′-*dibenzthioindigo* (251—253°), 5-*chloro*-7-*methyl*-, 6-*ethoxy*-, 4 : 5-, 6 : 7-, and 5 : 6-5′ : 6′-*dibenzthioindirubin*, and 5 : 6 : 5′ : 6′-*dibenzthioindigo* [297—300° (decomp.)]; 3-(6-*chloro*-4-*methylthionaphthen*)-2′-*indole-indigo*, 6-*chloro*-4-*methylthio-oxindole*-3-*aldehydephenylhydrazone*, m.p. 167—169°; 3-(5-*chloro*-7-*methylthionaphthen*)-2′-*indole-indigo* (-*aldehyde*, m.p. 116—118°, and *phenylhydrazone*, m.p. 194—196°), 3-(6-*ethoxy*)- (6-*ethoxy-aldehyde*, m.p. 152—154°), 3-(4 : 5-*benz*)- (4 : 5-*benz-aldehyde*, m.p. 144—145°), 3-(6 : 7-*benz*)- (*aldehyde phenylhydrazone*, m.p. 220—222°), and 3-(5 : 6-*benz*)-derivatives (5 : 6-*benz-aldehyde*, m.p. 145—146°); 2-(6-*chloro*-4-*methylthionaphthen*)-2′-*indole-indigo* (6-*chloro*-4-*methylthioindoxyl*-2-*aldehydephenylhydrazone*, m.p. 153—154°, 2-(5-*chloro*-7-*methyl*), 2-(6-*ethoxy*)-, 2-(4 : 5-*benz*)- (4 : 5-*benz-aldehyde*, m.p. 131—132°), 2-(6 : 7-*benz*)- (*aldehyde phenylhydrazone*, m.p. 197—200°), and 2-(5 : 6-*benz*)-derivatives (5 : 6-*benz-aldehyde*, m.p. 137—139°); 2-(6-*chloro*-4-*methylthionaphthen*)-3′-*indole-indigo*, 2-(5-*chloro*-7-*methyl*)-, 2-(6-*ethoxy*)-, 2-(4 : 5-*benz*)-, 2-(6 : 7-*benz*)- and 2-(5 : 6-*benz*)-derivatives; 2-*acetamido*-1-*naphthylthioglycollic acid*, m.p. 185°, and the 2-*Cl-acid*, m.p. 95—97°. F. R. S.

1 : 3 : 5-Triazines.—See B., 1942, II, 316.

Bile pigments. XXXIV. New preparation of hydroxypyrromethenes by alkaline condensation of hydroxypyrroles with pyrrole-α-aldehydes and further attempted synthesis of acetyl-substituted bile pigments; tripyrrenes. H. Plieninger and H. Lichtenwald (*Z. physiol. Chem.*, 1942, **273**, 206—224).—Condensation of the mixture (**I**) of hydroxyopsopyrroles (obtained by the oxidation of opsopyrrole with H_2O_2) with 2-formyl-3-methylpyrrole-4-propionic acid in alkaline solution yields a mixture from which, after esterification, Me *iso*-neoxanthobilirubate, m.p. 201°, is isolated. Similar condensations lead to coproneoxanthobilirubic acid and *Me* 5-*hydroxy*-4′-*acetyl*-4 : 3′ : 5′-*trimethylpyrromethene*-3-*propionate*, m.p. 218°. (**I**) and 2-formyl-4-methyl-3-bromovinylpyrrole-5-carboxylic acid yield a mixture of 5-hydroxy-4 : 4′-dimethyl-3-ethyl-3′-bromovinyl- and 5-hydroxy-3 : 4′-dimethyl-4-ethyl-3′-bromovinyl-pyrromethene-5′-carboxylic acid, m.p. >300°, darkens at 230°. Oxidation of 3-methylpyrrole by H_2O_2 in C_5H_5N affords 2-*hydroxy*-3(or 4)-*methylpyrrole* (**II**), b.p. ~145°/12 mm., m.p. 84°, from which *Me* 5-*hydroxy*-3 (or 4) : 3′-*dimethylpyrromethene*-4′-*propionate*, m.p. 183°, is derived; this is converted by successive treatments with CH_2O and HCl in MeOH, $FeCl_3$, and NaOH into *Me*$_2$ 1′ : 8′-*dihydroxy*-1(or 2) : 3 : 6 : 7 (or 8)-*tetramethylbilitriene*-4 : 5-*dipropionate*, m.p. 210°. (**II**) is condensed with 5-formyl-2 : 4-dimethylpyrrole-3-propionic acid to *Me* 5-*hydroxy*-3′ : 3(or 4) : 5-*trimethylpyrromethene*-4′-*propionate*, decomp. 278°, with cryptopyrrolealdehyde to 5-*hydroxy*-3′ : 3(or 4) : 5′-*trimethyl*-4′-*ethylpyrromethene*, m.p. 223°, with 5-formyl-3-acetyl-2 : 4-dimethylpyrrole to 5-*hydroxy*-4′-*acetyl*-3′ : 3(or 4) : 5′-*trimethylpyrromethene*, m.p. 307°, and with 2-formyl-4-acetyl-3-methylpyrrole to 5-*hydroxy*-4′-*acetyl*-3′ : 3(or 4)-*dimethylpyrromethene*, m.p. 260—262°, converted by PhN_2Cl followed by $Cu(OAc)_2$ into the *Cu* salt of 5-*hydroxy*-4′-*acetyl*-3′ : 3(or 4)-*dimethylpyrromethene*-5′-*azobenzene*, m.p. >300°. 5-*Hydroxy*-4′-*acetyl*-3′ : 4-*dimethylpyrromethene*-3-*propionic acid*, m.p. 263°, is converted into the *Cu* salt of *Me* 5-*hydroxy*-4′-*acetyl*-3′ : 4-*dimethylpyrromethene*-3-*propionate*-5′-*azobenzene*, m.p. >290°, which is reduced by Zn dust in AcOH to *Me* 5′-*amino*-5-*hydroxy*-4′-*acetyl*-3′ : 4-*dimethylpyrromethene*-3-*propionate*, m.p. 286°. Me neoxanthobilirubate (**III**) is condensed (HBr in cold MeOH) with 5-formyl-3-methyl-4-ethylpyrrole to *Me* 1′-*hydroxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-2′α : 4′β-*diene*-4-*propionate*, m.p. 143° (Kofler), which gives a red fluorescence and characteristic spectrum after addition of $Zn(OAc)_2$ in MeOH. Similarly (**III**) and Me 5-formyl-3-methyl-4-ethylpyrrole-2-carboxylate give *Me* 1′-*hydroxy*-6′-*carboxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-2′α ; 4′β-*diene*-4-*propionate* (**IV**), m.p. 208—214° (Kofler). Analogous condensations lead from (**III**) to *Me* 1′-*hydroxy*-6-*carboxy*-1 : 3 : 6-*trimethyl*-2-*ethyl*-5-*bromovinyltripyrryl*-2′α : 4′β-*diene*-4-*propionate*, no definite m.p. (*Ca* salt), and Me 1′-hydroxy-6′-carboxy-1 : 3 : 6-trimethyl-2 : 5-diethyltripyrryl-2′α : 4′α-diene-4-propionate (*Ca* salt). (**III**) and Me 5-formyl-3-methyl-4-ethylpyrrole-2-carboxylate afford *Me* 1′-*hydroxy*-6′-*carbomethoxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-2′α : 4′β-*diene*-4-*propionate* (**V**), m.p. 166—168°. Analogously obtained are *Me* 1′-*hydroxy*-6′-*carbomethoxy*-1 : 3 : 6-*trimethyl*-2-*ethyl*-5-*bromovinyltripyrryl*-2′α : 4′β-*diene*-4-*propionate* and *Me* 1′-*hydroxy*-1(or 2) : 4 : 5-*trimethyl*-2(or 1) : 6-*diethyl*-4-*bromovinyltripyrryl*-2′α : 4′β-*diene*-6′-*carboxylate*, m.p. 183°. (**IV**) is not esterified by HCl in boiling MeOH but is converted into a red *pigment*, m.p. 115°. (**V**) is converted by $Zn(OAc)_2$ and $Cu(OAc)_2$ into the *salts*, $C_{27}H_{31}O_5N_3Zn$ and $C_{27}H_{31}O_5N_3Cu$. (**V**) is reduced by Zn dust in AcOH to *Me* 1′-*hydroxy*-6′-*carbomethoxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-2′α-*ene*-4-*propionate*, m.p. 230° (Kofler). Me neobilirubinate and Me 5-formyl-3-methyl-4-ethylpyrrole-2-carboxylate condense to *Me* 1′-*hydroxy*-6′-*carbomethoxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-5′β-*ene*-4-*propionate*, m.p. 150° (Kofler). Neoxanthobilirubic acid and 2-formyl-4-acetyl-3-methylpyrrole yield *Me* 1-*hydroxy*-6-*acetyl*-1 : 3 : 5-*trimethyl*-2-*ethyltripyrrene*-4-*propionate*, m.p. 128° (*hydrobromide*, m.p. >300°). H. W.

5-Pyrazolylacetylene and 5 : 5′-dipyrazolyl. R. Kuhn and K. Henkel (*Annalen*, 1941, **549**, 279—285).—$(CH{:}C)_2$ and CH_2N_2 in Et_2O give in 1—2 days 5-*pyrazolylacetylene* (**I**) (40—50%), m.p. 45—46° [*picrate*, m.p. 122—124° (block), 126—127·5° (micro)], and after ~3 weeks also 5 : 5′-*dipyrazolyl* (**II**) (yield variable; >35%), m.p. 255—256° (block), sublimes [also obtained from (**I**) and CH_2N_2]. (**I**) gives Cu and Ag salts and is hydrogenated (PtO_2; Et_2O; ~20°) to 5-*ethylpyrazole* (**III**), b.p. ~90° (bath)/12 mm. (*picrate*, m.p. 128·5—129·5°). 5-Vinylpyrazoline (**IV**) (Müller *et al.*, A., 1932, 754) with H_2–PtO_2 in Et_2O gives 5-*ethylpyrazoline*, b.p. 59—61°/15 mm., which with Br– or $Pb(OAc)_4$–$CHCl_3$ gives (**III**), thereby proving the structure of (**III**) and (**I**). Attempts to obtain (**III**) from $(CH_2{:}CH)_2$ or (**IV**) by way of 5 : 5′-dipyrazolinyl failed owing to poor yields of the latter. R. S. C.

Enzymic degradation and structure of nucleic acids.—F. G. Fischer (*Naturwiss.*, 1942, **30**, 377—382).—A review.

Enzymic hydrolysis of ribonucleic acid and its relation to structure.—See A., 1942, III, 777.

Synthesis of biliverdin (uteroverdin) and bilirubin. H. Fischer and H. Plieninger (*Naturwiss.*, 1942, **30**, 382—387).—A review.

Light absorption and constitution of chlorophyll derivatives. II.—See A., 1942, I, 314.

Morpholinoalkyl esters and amides possessing antispasmodic activity. L. C. Cheney and W. G. Bywater (*J. Amer. Chem. Soc.*, 1942, **64**, 970—973).—Morpholine and Cl·$[CH_2]_n$·Cl give γ-morpholino-*n*-propyl (75·2%), b.p. 147—149°/21 mm., and δ-morpholino-*n*-butyl alcohol (37·5%), b.p. 127—130°/2 mm. NH_2·CMe_2·CH_2·OH, $(Cl·[CH_2]_2)_2O$, and K_2CO_3 at 170° give *β-morpholinoisobutyl alcohol* (39·1%), m.p. 59—60° (uncorr.), b.p. 110—116°/2 mm; NH_2·CH_2·CHMe·OH gives similarly *β-morpholinoisopropyl alcohol* (42%), b.p. 82—84°/1·5 mm. γ-Morpholino-ββ-dimethylpropan-α-ol, b.p. 96—97°/2 mm., is obtained (82·6%) from the aldehyde. $Fe(NO_3)_3$,$9H_2O$, Na, and xylene are added successively to liquid NH_3 in CO_2–$COMe_2$–N_2; the NH_3 is removed; CH_2Ph·CN and then at 30—40° bromo*cyclo*hexane are added; after heating at 100°, 70% of phenyl*cyclo*hexylacetonitrile, m.p. 56—57°, is obtained; KOH–MeOH at 185—195° then gives the acid (92%), m.p. 152—153·5°. The following are prepared from the appropriate acid chloride and amine or alcohol in, usually, dioxan, $CHCl_3$, or C_6H_6. Unspecified m.p. in parentheses are those of *hydrochlorides*; antispasmodic activities relative to papaverine = 100 are also given. *β-Morpholinoethyl diphenylcarbamate*, m.p. 63·5—64·5° (m.p. 160—161°, 30), diphenylacetate (m.p. 137·5—138·5°, 75; *hydrobromide*, m.p. 119—120°, 40), benzilate (**I**) (from the acid in $Pr^{\beta}OH$) (m.p. 181·5—182·5°, 25), α-acetoxydiphenylacetate [from (**I**) and NaOAc in Ac_2O at 150—160°] (m.p. 186·5—187°, 25), α-chlorodiphenylacetate (m.p. 151·5—152·5°, 75); ββ-diphenylpropionate (m.p. 127—128°, 50), ββ′-diphenyl*iso*butyrate (m.p. 117—118°, 60), α-phenyl-α-*cyclo*hexylacetate (m.p. 147—148°, 100), triphenylacetate (+EtOH, m.p. 190·5—191·5°, 25), phenylacetate (+H_2O, m.p. 137—138°, 10), cinnamate (m.p. 216·5—217°, 40), *cyclo*hexanecarboxylate (+H_2O, m.p. 144—145°, 10—20), camphene-2-carboxylate (m.p. 202·5—203·5°, 60), trimethylacetate (*picrate*, m.p. 129·5—130·5°; 5), and ββ-dimethyl-*n*-butyrate (m.p. 152—153°; 5—10). *γ-Morpholino-ββ-dimethyl*-n-*propyl diphenylacetate*, m.p. 54·5—55·5° (m.p. 149·5—150°, 200; *sulphate*, m.p. 140—141°, 200), *α-phenyl-α-cyclohexylacetate*, m.p. 77° (m.p. 127·5—128·5°, 10), *benzoate*, m.p. 55·5—56° (m.p. 161·5—162·5°, 40), and cinnamate (m.p. 140—150°, 40). γ-Morpholino-*n*-propyl (m.p. 119·5—120°, 75; *benzylobromide*, m.p. 137—138°, 50), β-morpholino*iso*propyl (m.p. 214·5—215°, 60), δ-morpholino-*n*-butyl (m.p. 118—119°, 60), and β-morpholino*iso*butyl (m.p. 124·5—125·5°, 60) diphenylacetate. *Diphenyl*-, m.p. 140—141° (m.p. 189—190°, 20), α-chlorodiphenyl- (m.p. 139—140°,

50), and *α-phenyl-α-*cyclo*hexyl-*, m.p. 152—153° (m.p. 107·5—109°, 50), *-acet-β-morpholinoethylamide*. Br·$[CH_2]_6$·Br and $CHPh_2·CO_2K$ are heated in xylene at 170—180°; addition of morpholine to the cold product and boiling gives ζ-morpholino-*n*-hexyl diphenylacetate (m.p. 113—114°; 150). In general pharmacological activity in the series requires a disubstituted Ac containing ⩽1 Ph; branching or lengthening of the alkyl chain increases activity. M.p. are corr. R. S. C.

2-Phenyloxazole and *o*-substituted derivatives [thereof]. W. E. Cass (*J. Amer. Chem. Soc.*, 1942, **64**, 785—787).—Addition of Et_2 *o-nitrobenzylideneaminoacetal*, b.p. 143—146°/2 mm., to stirred conc. H_2SO_4 at 0—5° and addition of the solution to, and heating with, P_2O_5–H_2SO_4 at 180° gives 54·5% of 2-*o-nitrophenyloxazole* (**I**), m.p. 38—39° (*picrate*, m.p. 90—92°), oxidised by $KMnO_4$ or Br–H_2O to *o*-$NO_2·C_6H_4·CO·NH_2$ and hydrogenated (Raney Ni; abs. EtOH; 3 atm.; 97%) to 2-*o-aminophenyloxazole* (**II**), m.p. 32—33° [*picrate*, m.p. 154—155°; *Ac*, m.p. 104—105°, *Bz*, m.p. 149—150°, *p-NHAc·*$C_6H_4·SO_2$, m.p. 207—208°, and thence (12% HCl) *sulphanilyl* (**III**), m.p. 172·5—173·5°, derivatives]. Similar treatment of *o*-$NO_2·C_6H_4·CO·NH·CH_2·CH(OEt)_2$ gives only 6% of (**I**) and other methods give none. Treatment of the diazonium chloride from (**II**) with HPO_2 gives 2-*phenyloxazole*, b.p. 225—228° (*picrate*, m.p. 115—116°). The antistreptococcal activity of (**III**) is about equal to that of sulphadiazine; (**III**) is not toxic in doses of 5—20 mg. per 20 g. body wt. R. S. C.

Action of ammonia, ammonium carbonate, carbamide, and dicarbamhydrazide on saccharin and thiosaccharin. (Signa.) A. Mannessier-Mameli (*Gazzetta*, 1941, **71**, 3—18).—In aq. EtOH, NH_3 converts saccharin (**I**) into NH_4 saccharinate (**II**), and thiosaccharin (**III**) into NH_4 thiosaccharinate (**IV**), with, at the b.p., saccharinimine (**V**) (cf. Mannessier-Mameli, *ibid.*, 1940, **70**, 855), previously regarded (A., 1935, 763) as *ψ*-saccharinamine. NH_4 carbonate with (**I**) at 100° gives (**II**), and at 250°, (**V**); with (**III**) at 110° it gives (**IV**), and at 300°, (**V**), with some (**I**). With $CO(NH_2)_2$ (**VI**) in aq. EtOH, (**I**) is unchanged, or at the b.p. gives (**II**). At 150°, (**I**) and (**VI**) give *carbamide saccharinate*, $C_7H_5O_3NS,2CO(NH_2)_2$, m.p. 204° (decomp.), with a product (**VII**), m.p. 365—370°; at 250°, (**V**) and (**VII**) are formed. With (**VI**) in cold aq. EtOH, (**III**) gives a small amount of a *substance*, $C_{18}H_{18}O_5N_2S_3$ (**VIII**), m.p. 215°, which may be a mixture of *N*-ethyl-saccharin and -thiosaccharin; at the b.p., some (**V**) and a mixture, m.p. 175°, of (**I**) and (**III**) are formed. $(NH·CO·NH_2)_2$ with (**I**) in aq. EtOH is unchanged, or at the b.p. gives some (**II**); with (**III**), (**IV**), or at the b.p. (**VIII**) is formed. E. W. W

Action of hydrazine on saccharin and thiosaccharin. (Signa.) A. Mannessier-Mameli (*Gazzetta*, 1941, **71**, 18—25).—With N_2H_4 in aq. EtOH, saccharin gives hydrazine saccharinate, $C_7H_5O_3NS,N_2H_4$, m.p. 145° (resolidifying at 147°, decomp. ~175°), sweet; thiosaccharin gives *saccharin hydrazone*, m.p. 257—260° [regarded by Schrader (A., 1917, i, 709) as *ψ*-saccharinhydrazide], tasteless, also obtained by hydrolysing saccharin semicarbazone. E. W. W.

Action of semicarbazide on saccharin, thiosaccharin, and acetylsaccharin. (Signa.) A. Mannessier-Mameli (*Gazzetta*, 1941, **71**, 25—40).—Saccharin (**I**) and semicarbazide (**II**) in aq. EtOH give [with, on heating, $(NH·CO·NH_2)_2$ (**III**)] o-*sulphonamidobenzsemicarbazide* (**IV**), decomp. 210—215°, hydrolysed by NaOH, and converted by conc. HCl into (**I**), and by NH_2OH into (**I**) and some *saccharin semicarbazone* (**V**), m.p. 230—235° (decomp.) [*Na* salt, m.p. 293—295° (decomp.); Ac_3 derivative, m.p. 195—198°]. In aq. EtOH, (**II**) and thiosaccharin give (**V**), with, on heating, (**III**); (**II**) and *N*-acetylsaccharin give (**I**) and (**IV**). The new compounds are tasteless. E. W. W

Thiazoles, benzthiazoles, and benzselenazoles.—See B., 1942, II, 315, 318, 319, 348.

VII.—ALKALOIDS.

Aconite alkaloids. VIII. Atisine. IX. Isolation of two new alkaloids from *Aconitum heterophyllum*, heteratisine and hetisine. W. A. Jacobs and L. C. Craig. **X. Napelline.** L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1942, **143**, 589—603, 605—609, 611—616; cf. A., 1942, II, 40).—VIII. Data of Lawson *et al.* (A., 1937, II, 527) are in part corr. Atisine (**I**), $C_{22}H_{33}O_2N$, amorphous, m.p. 57—60° [hydrochloride, m.p. 311—312° (decomp.), $[\alpha]_D^{25}$ +28° in H_2O] (prep. from the roots of *A. heterophyllum*; 98 g. from 12 kg.), is unstable in EtOH and contains 2 OH, giving a *diacetate hydrochloride*, m.p. 241—243° (decomp.), but with MgMeI giving no CH_4 at 25° and 0·472 CH_4 at 95°. In NaOH–MeOH at 100° it gives, ? by disproportionation, ? *dihydroatisine* (**II**), m.p. 156—158° (corr.) [*hydrochloride*, m.p. 261—263° (decomp.), $[\alpha]_D^{27}$ −16° in H_2O], previously (*loc. cit.*) considered to be demethylated (**I**) and obtained with other substances by boiling KOEt–EtOH–N_2. Hydrogenation (PtO_2; MeOH; 3 atm.) of (**I**) gives mixed H_4-derivatives, including a *form*, m.p. 171—174°, $[\alpha]_D^{25}$ −33° in PhMe, −23° in $CHCl_3$, stable to alkali, also obtained in an attempted dihydrogenation (Pd-black; AcOH; 3 atm.) and from (**II**). Na–EtOH converts (**I**) into a mixture whence only (**II**) was isolated. Kuhn–Roth determination shows ⩽1 CMe. With Se–N_2 at 340°, (**I**) gives *bases*, (*a*) ? $C_{21}H_{31}ON$, m.p. 180—190°, (*b*) $C_{16}H_{15}N$, tertiary, m.p. 83—85° (*picrate*, m.p. 221—223°; *methiodide*, m.p. 233—235°), (*c*) ? $C_{20}H_{29}N$ (*picrate*, m.p. 210—213°), and (*d*) ? $C_{20}H_{27}ON$ (*picrate*, m.p. indefinite), 1-methylphenanthrene, and hydrocarbons, (*a*) $C_{17}H_{16}$, m.p. 41—43° [*picrate*, m.p. 129—131°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 145—148°], and (*b*) $C_{18}H_{18}$ [*picrate*, m.p. 153—156°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 163—166°), both shown by absorption spectra to be phenanthrene derivatives. (**I**) is pentacyclic.

IX. The mother-liquors from (**I**) yield *heteratisine* (**III**), $C_{22}H_{33}O_5N$, m.p. 262—267° (decomp.), $[\alpha]_D^{27}$ +40° in MeOH [2 active H; *hydrochloride*, m.p. 265—270° (sintering and decomp. from >255°)], and *hetisine*, $C_{20}H_{27}O_3N$, sinters at >245°, m.p. 253—256°, $[\alpha]_D^{25}$ +13·7° in EtOH [*hydrochloride*, decomp. 300° (306—308°) after sintering; H_2-derivative *hydrochloride*, decomp. 333° after softening; 3 active H], stable to alkali. (**III**) contains a lactone ring, opened by NaOH which does not otherwise affect the mol.

X. Napelline (**IV**), $C_{22}H_{33}O_3N$, ? amorphous, m.p. 85—88°, contains 3 active H and 1 NMe, but no OMe. Hydrogenation (PtO_2; MeOH; 3 atm.) of its *hydrobromide*, m.p. variable, 227—230° (237—240°) after softening, gives *dihydronapelline*, m.p. (micro) 145—160° (clear at 165°) (*hydrobromide*, m.p. 256—258° after softening), and dehydrogenation (Se–N_2; 340°) gives an *alkyl-*, $C_{18}H_{18}$, m.p. 76—79° [*picrate*, m.p. 132—134°; *s*-$C_6H_3(NO_2)_3$ compound, m.p. 150—153°; structure proved by absorption spectrum], and dimethyl-(? ethyl)-phenanthrene (*picrate*, m.p. 142—146°; cf. Freudenberg *et al.*, A., 1938, II, 74, 179). R. S. C.

Argentine plants. III. Alkaloids from *Lycopodium saururus*. V. Deulofeu and J. De Langhe (*J. Amer. Chem. Soc.*, 1942, **64**, 968—969; cf. A., 1940, III, 832).—Leaves of *L. saururus* (7·4 kg., air-dry) yield to 2% HCl *tert.* bases, saururine, $C_{10}H_{19}N$, an oil [isolated as *picrate* (3·3 g.), m.p. 202°; *methiodide*, m.p. 242—244°], and *sauroxine* (0·5 g.), $C_{17}H_{26}ON_2$, m.p. 198° $[\alpha]_D^{20}$ −71·8° in EtOH (no OMe; *methiodide*, m.p. 258°]. R. S. C.

Cinchona alkaloids in pneumonia. X. *apo*Cupreine 6-*β*-alkylthiolethyl ethers. R. S. Tipson and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1942, **64**, 1162—1164; cf. A., 1942, II, 381).—Prep. of *apo*cupreine, +1·5H_2O (lost at 140°/20 mm.) (H sulphate, $[\alpha]_D^{25}$ −223° in H_2O), its Cl·$[CH_2]_2$ ether (**I**), m.p. 168° (decomp.), $[\alpha]_D^{22}$ −179·5° in abs. EtOH (dihydrochloride), and *p*-$C_6H_4Me·SO_2·[CH_2]_2$·Cl, m.p. 22·5°, b.p. 140°/1·5 mm., is modified. With RSH and KOH in boiling abs. EtOH, (**I**) gives apo*cupreine β-methyl-*, m.p. 155°, [α] −175° in EtOH ([α] −220°; this and other [α] in parentheses are those of the *dihydrochlorides* in H_2O), *-ethyl-* (**II**), m.p. 144—145°, [α] −172° in EtOH ([α], +2H_2O, −198°), *-n-propyl-*, m.p. 147—148°, [α] −165° in EtOH ([α] −210° in H_2O, −176° in EtOH), *-n-butyl-*, *forms*, m.p. 141—142° and 120—121°, [α] −153° in EtOH ([α] −182°), *-phenyl-*, m.p. 150—151°, [α] −149° in EtOH ([α] −168° in EtOH), and *-benzyl-* (**III**), m.p. 101—102°, [α] −133° in EtOH, ([α] −162°), *-thiolethyl ether*. The *in vitro* effect against pneumococcus and the toxicity (mice) increase as R changes from Me to Bu and the SMe equals the SPh compound. Oral administration (mice) of (**II**) and (**III**) has no protective effect. The effect of (**I**) equals that of the Et ether. R. S. C.

***N*-Allylnormorphine.** J. Weijlard and A. E. Erickson (*J. Amer. Chem. Soc.*, 1942, **64**, 869—870).—Normorphine, m.p. (+0·5MeOH) 272—273° or (solvent-free) 276—277°, with CH_2:$CH·CH_2Br$ in $CHCl_3$ at 110° gives *N-allylnormorphine*, m.p. 208—209° (*hydrobromide*, m.p. 258—259°) (cf. McCawley *et al.*, A., 1941, II, 111), readily converted by $NPhMe_3·OH$ into allylnorcodeine. R. S. C.

Electrolytic reduction of strychnine. B. M. G. Zwicker and R. J. Robinson (*J. Amer. Chem. Soc.*, 1942, **64**, 790—793).—Electrolytic reduction of strychnine (**I**) at a Hg cathode in 60% H_2SO_4 gives rapidly good yields, according to the conditions (mainly temp.), of strychnidine or tetrahydrostrychnine, separated by the differing solubility in H_2O after removal of (**I**) as H sulphate from 28·5% H_2SO_4. Current efficiency is 16% at 27°, 2·4% at 6°, and very low at 66°. At a Na–Hg cathode reduction is still faster but gives dihydrostrychnidine (20—30%). At PbO_2, Cu, Ta, or Pt cathodes yields are very poor. R. S. C.

Alkaloids of American hellebore.—See A., 1942, III, 723.

VIII.—ORGANO-METALLIC COMPOUNDS.

Aliphatic arsinic acids. IV. Dichloroarsinoacetic acid. A. R. Marquez (*Rev. Fac. Cienc. Quím., La Plata*, 1941, **16**, 109—116).—$AsO_3H_2·CH_2·CO_2H$ with PCl_3 gives *dichloroarsinoacetic acid*, $AsCl_2·CH_2·CO_2H$, m.p. 112°, also obtained from (·As·$CH_2·CO_2H)_3$ with dry Cl_2 at 0°. F. R. G.

Diazonium borofluorides. III. Their use in the Bart reaction. A. W. Ruddy, E. B. Starkey, and W. H. Hartung (*J. Amer. Chem. Soc.*, 1942, **64**, 828—829; cf. A., 1937, II, 406).—Use of diazonium

borofluorides in the Bart reaction gives improved yields of $RAsO_3H_2$ (14 examples). R. S. C.

Preparation of phenylarsenoxides. V. Arsenoxides of naphthalene and diphenyl. G. O. Doak, H. Eagle, and H. G. Steinman (*J. Amer. Chem. Soc.*, 1942, **64**, 1064—1066; cf. A., 1941, II, 272).—*4-Nitro-1-naphthyl benzoate* (prep. by BzCl–NaOH), m.p. 176°, with H_2–Raney Ni in $COMe_2$ gives 4-amino-1-naphthyl benzoate hydrochloride, m.p. 258—262° (decomp.), which by the Scheller–Bart (not Bart) reaction gives 2·5% of *4-hydroxy-1-naphthylarsinic acid*, m.p. >360°. 6 : 2-NH_2·$C_{10}H_6$·AsO_3H_2 by the Sandmeyer reaction [$Ni(CN)_2$] and then hydrolysis gives *6-carboxy-2-naphthylarsinic acid* (22%), converted by PCl_3–PCl_5–$CHCl_3$ and then aq. NH_3 into *6-carbamyl-2-naphthylarsenoxide* (91%), amorphous. Monodiazotisation of benzidine and then treatment with $NaAsO_2$–$CuSO_4$ gives only (3·4%) *diphenyl-4 : 4′-diarsinic acid*. 4-NH_2·C_6H_4·C_6H_4·NO_2-4′ gives (Scheller–Bart) *4-nitro-* (34%) and thence (H_2–Raney Ni) *4-amino-diphenyl-4′-arsinic acid* (80%) (*Ac* derivative), which, as above, yields *4-carbamyldiphenyl-4′-arsenoxide* (85%), m.p. 271—273°. By the Bart reaction 3-nitrobenzidine gives *3-nitro-4-aminodiphenyl-4′-arsinic* (**I**) (14·9%) and *3-nitrodiphenyl-4 : 4′-diarsinic acid* (19·4%), m.p. 249·5—250·5°. In boiling 25% KOH, (**I**) gives *3-nitro-4-hydroxydiphenyl-4′-arsinic acid* (75%). SO_2 reduces $RAsO_3H_2$ to *2-naphthyl-* (90%), *4-* (71%), m.p. 272°, and *2-acetamido-1-naphthyl-* (65%), m.p. 256·5°, and *4-aminodiphenyl-4′-* (100%), +$2H_2O$, m.p. 221—222° (*Ac* derivative, +H_2O, m.p. 297·5—298·5°), *-arsenoxide*. M.p. are corr. R. S. C.

Hexacovalent complexes of rhodous halides with diphenylmethylarsine.—See A., 1942, I, 337.

Substituted *p*-hydroxy-*m*-*N*-glycinylarsenobenzenes.—See B., 1942, II, 316.

Mercuri-alkylphenol derivatives.—See B., 1942, III, 204.

Relative reactivities of organo-metallic compounds. XLIV. Diazotisation of a lead aminoaryl compound. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1942, **64**, 1007—1008; cf. A., 1942, II, 183).—Successive addition of *p*-C_6H_4Br·NH_2, $MgBr_2$–Et_2O, $PbPh_3Cl$, and aq. NH_4Cl to $LiBu^a$ in Et_2O at room temp. gives *Pb Ph₃ p-aminophenyl* (66%), m.p. 166—167°, which by diazotisation and coupling with β-$C_{10}H_7$·OH gives *Pb Ph₃* p-*2-hydroxy-1-naphthylazophenyl* decomp. 135°, red in acid, green in alkali. R. S. C.

Organo-metallic compounds and their uses. G. N. Copley (*Ind. Chem.*, 1942, **14**, 201—205, 280—283).—A review.

IX.—PROTEINS.

Determination of the mol. wt. of degradation products of the proteins by precipitation-titration. B. Jirgensons (*J. pr. Chem.*, 1942, [ii], **159**, 303—312).—Degradation products of casein, deaminocasein, and gelatin can be determined by pptn.-titration using glycine, glycylglycine, and compounds of lower mol. wt. and non-degraded proteins as standard substances. As in other polymeric-homologous series, the precipitability has a linear relationship to the concn. of the degradation products. H. W.

Determination of the mol. wt. of degradation products of edestin by precipitation-titration. B. Jirgensons (*J. pr. Chem.*, 1942, [ii], **160**, 65—73).—Edestin is decomposed by 8M-$CO(NH_2)_2$ [4 hr. on bath (100°), 8 hr. reflux] (cf. Pauli *et al.*, A., 1935, 822), and the mean mol. wt. of the product is determined by pptn.-titration (3800—5300). Cryoscopic measurements indicate a mol. wt. of 6100. A. T. P.

Study of ovalbumin and its degradation products by precipitation-titration. B. Jirgensons (*Kolloid-Z.*, 1942, **98**, 70—75).—The relation $\gamma = a - \log c$, in which c denotes the concn. of an aq. solution of ovalbumin (**I**) and γ the concn. of $COMe_2$ needed to produce turbidity, is valid in the range 15—20° (cf. Schulz, A., 1937, I, 510). At higher temp. (40—45°) less $COMe_2$ is required for pptn. and the γ–c relation is less simple. The straight lines for different specimens of (**I**) are parallel and thus indicate a spherical shape for the (**I**) mol. A similar relation is found for lysalbic acid (**II**) and for a more degraded product (**III**) obtained by hydrolysis with NaOH, but not for a no. of physiological NH_2-acids. The mol. wts. of (**II**) and (**III**), calc. by the use of a similar formula, are 4400 and 470, respectively. F. L. U.

Viscosity and molecular decomposition of proteins. B. Jirgensons (*J. pr. Chem.*, 1940, [ii], **160**, 120—132).—Measurements of η observed during denaturing and decomp. of proteins by various agents (*e.g.*, warm aq. NaOH or HNO_2) show that in the case of proteins, *e.g.*, edestin, ovalbumin, and casein, the val. of η increases, reaches a max., and then falls, whereas with linear proteins, *e.g.*, gelatin, there is no increase, but only a lowering in the val. of η. In the former case, there is probably a loosening of the relatively compact protein to give long chain mols., whereas in the latter case, decomp. is accompanied by shortening of the chain. A. T. P.

***X*-Ray analysis of protein denaturation. II.** M. Spiegel-Adolf and G. C. Henny (*J. Physical Chem.*, 1942, **46**, 581—586; cf. A., 1941, II, 306).—Heat-denatured serum-pseudoglobulin (**I**) shows a characteristic sharpening of the backbone reflexion, but no additional rings as with serum-albumin (**II**). The *X*-ray change is irreversible and occurs even when coagulation is prevented. Thyroglobulin behaves similarly. Denaturation of (**I**) by EtOH produces the same change as does heat-denaturation. The diffraction pattern of dried (**I**) is not substantially changed by *X*-ray irradiation. Denaturation of (**II**) by adsorption at a PhMe interface does not lead to backbone sharpening, nor is this produced by subsequent heating. F. L. U.

Critical peptisation temperature of zein in concentrated ethyl alcohol.—See A., 1942, I, 327.

Tryptophan-containing acid hydrolysates of proteins suitable for intravenous administration.—See A., 1942, III, 757.

Isolation of *meso-* and *dl*-lanthionine from various alkali-treated proteins. M. J. Horn, D. B. Jones, and S. J. Ringel (*J. Biol. Chem.*, 1942, **144**, 87—91, 93—97; cf. A., 1941, II, 188).—*meso*-Lanthionine (**I**) is isolated from Na_2CO_3-treated human hair (2·5%), chicken feathers (0·25%), and lactalbumin (0·25%). 1%, 0·8%, or 0·1% of (**I**) is obtained from wool treated with boiling 0·1N-NaOH or 2% aq. Na_2S for 1 hr., or 2% aq. Na_2S at 37° for 6 days, respectively. (**I**) may probably be obtained similarly from most proteins which yield cystine on acid hydrolysis. In addition to (**I**), Na_2CO_3-treated human hair affords an equal amount of more sol. compound with similar properties to (**I**), which is most probably *dl*-lanthionine, decomp. 283—284° (Bz_2 derivative, new m.p. 195—198°). A. T. P.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Constituents of *Caucalis scabra*, Makino. I. Separation. II. Caucalol and *apo*caucalol diacetates. III. *iso*Caucalol and *apo*caucalol, saponification products of caucalol and *apo*caucalol diacetates. IV. Dehydrogenation of caucalol diacetate and *iso*caucalol. S. Mitsui (*Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 529—532, 533—539, 540—548, 549—555).—I. The C_6H_6 extracts of the seeds yields *caucalol diacetate* (**I**), $C_{19}H_{35}O_5$, m.p. 121—122°, $[\alpha]_D^{15.5}$ +33·4° in $CHCl_3$, and *apocaucalol diacetate* (**II**), $C_{19}H_{30}O_5$, m.p. 165°, $[\alpha]_D^{17.5}$ −126·4° in $CHCl_3$.

II. Both substances have 2 *tert.* OAc and 1 ether linking.

III. Saponification of (**I**) gives *isocaucalol* (**III**), $C_{15}H_{26}O_3$, m.p. 120—121°, $[\alpha]_D^{13.5}$ −99·1° in $CHCl_3$, which on re-acetylation gives *diacetates* of m.p. 58° and 86° and $[\alpha]_D^{25}$ −77·6° in $CHCl_3$. (**II**) is hydrolysed to *apocaucalol*, m.p. 139—140°, $[\alpha]_D^{21.5}$ −261·9° in $CHCl_3$.

IV. Dehydrogenation (Pd–C) of (**III**) or (**I**) yields an azulene derivative [$C_6H_3(NO_2)_3$ complex, m.p. 115—131°]. (**III**) with HI–red P, followed by dehydrogenation (Se), gives a $C_{10}H_8$ derivative [$C_6H_3(NO_2)_3$ complex, m.p. 165—168°] and, with Pd–Al_2O_3, a deoxy-derivative, m.p. 99—100°. F. O. H.

Chemical investigation of *Tinospora cordifolia* (Miers). B. V. Bhide, N. L. Phalnikar, and K. Paranjpe (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 89—92).—The following have been isolated from the stems: *bitter principle* A, $C_{22}H_{34}O_{10},3H_2O$, m.p. 226—228°, $[\alpha]_D^{26}$ +48° in $COMe_2$ (*acetate*, m.p. 213°), which does not contain OMe, OEt, CO, or CHO and cannot be methylated. It is hydrolysed by acids to a dark, amorphous material and the solution becomes fluorescent; phenyl-osazone or -hydrazone could not be obtained from the residue; *bitter principle* B, m.p. 186—188°, isolated in very small amount; a neutral substance, m.p. 82—83° (acetate m.p. 75°), probably octacosanol; a dark green oil which appears to contain glycerides of myristic and palmitic acid. H. W.

XI.—ANALYSIS.

Universal apparatus for micro- on semimicro-determination of carbon and hydrogen. G. Ingram (*J.S.C.I.*, 1942, **61**, 112—115).—The combustion apparatus described previously (A., 1939, II, 193) has been improved. The heating is now electrical and capable of very exact control; a new type of manometer which affords complete protection against loss of vapours in the event of an explosion is illustrated. A description is given of a special filling which absorbs quantitatively halogens, S, As, Sb, and Hg. 14 examples of typical results, using 3—20 mg. of substance, are given. Blumer's absorption tubes of different sizes are employed for collecting the products of micro- and semimicro-scale combustions, but the same combustion tube is retained throughout.

Semi-micro-determination of carbon using the Van Slyke–Folch oxidation mixture. R. M. McCready and W. Z. Hassid (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 525—526).—The sample is wet-oxidised with the Van Slyke–Folch reagent (CrO_3–H_2SO_4–SO_2–HPO_3–HIO_3)

and the CO_2 is absorbed on NaOH–asbestos and weighed. The method is successful with compounds which are incompletely oxidised by other wet-oxidation methods. The apparatus is described in detail. J. D. R.

Mercury azotometer for determination of organic nitrogen by the micro-Dumas method. R. G. Clarke and W. R. Winans (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 522—523).—The construction and operation are described of an azotometer, in which the N_2 produced by the Dumas method displaces Hg which is weighed. Accuracy is good. J. D. R.

Determination of fluorine and other halogens in organic compounds. P. J. Elving and W. B. Ligett (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 449—453).—The sample is heated with Na or K in a sealed tube at 400°. The solution in EtOH is neutralised (HNO_3); Cl, Br, and I are determined as the Ag salts, and F as PbClF. Apparatus is described and the technique for dealing with solids, liquids, and gases is detailed. J. D. R.

Determination of arsenic in organic compounds. Iodometric semi-micro-procedure. H. A. Slovites, W. M. McNabb, and E. C. Wagner (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 516—519).—The sample is decomposed by H_2SO_4–HNO_3, As pptd. with NaH_2PO_4, washed, and dissolved in excess of Br, and the excess titrated with $NaAsO_2$ buffered with Na_2HPO_4. The procedure is applicable in presence of halogens. J. D. R.

Electrometric titration of the carbonyl group. A. Eitel (*J. pr. Chem.*, 1942, [ii], **159**, 292—302).—The CO-compound (PhCHO, furfuraldehyde, $COMe_2$, MeCHO, *o*-C_6H_4Cl·CHO, *o*-NO_2·C_6H_4·CHO, *o*-OH·C_6H_4·CHO) is dissolved in EtOH if necessary and any acid neutralised with 0·1N-NaOH to phenolphthalein. The solution is treated with at least twice the requisite amount of NH_2OH,HCl or $(NH_2OH)_2,H_2SO_4$. After completion of oximation, the solution is diluted with H_2O, any sparingly sol. oxime is removed, and the filtrate is titrated with 0·1N-NaOH to p_H 4·1 using glass and normal HgCl electrodes. H. W.

Physical micro-methods for qualitative analysis of mixtures of organic substances. L. Kofler and M. Brandstätter (*Angew. Chem.*, 1942, **54**, 322—324).—The mixed m.p. is determined under the microscope; the component of lower m.p. is repeatedly removed with filter-paper, leaving a pure component. Examples are given, data tabulated, and procedure in presence of mol. compounds and mixed crystals is considered. A. A. E.

Conductometric titrations in non-aqueous solutions. J. T. Pinkston and H. T. Briscoe (*J. Physical Chem.*, 1942, **46**, 469—473). —Org. acids can be titrated conductometrically in NH_2·$[CH_2]_2$·OH. Complex ammine formation can also be followed. C. R. H.

Indicator method of classifying acids and bases in qualitative organic analysis. D. Davidson (*J. Chem. Educ.*, 1942, **19**, 221—226). L. S. T.

Titration of weak bases and strong acids.—See A., 1942, I, 338.

Investigation of amino-acid reactions by methods of non-aqueous titrimetry. I. Acetylation and formylation of amino-groups. J. J. Kolb and G. Teonnies. **II. Differential acetylation of hydroxy-groups, and a method for the preparation of *O*-acetyl derivatives of hydroxyamino-acids.** W. Sakami and G. Teonnies. **III. Determination of hydroxyl (and analogous) groups in amino-acids.** G. Teonnies and J. J. Kolb (*J. Biol. Chem.*, 1942, **144**, 193—201, 203—217; 219—227).—I. No large differences are noted in the rates of reaction between various NH_2-acids and Ac_2O or HCO_2H–Ac_2O in AcOH at room temp. Excess of free $HClO_4$ inhibits acylation. The course of *N*-acylation is followed by $HClO_4$ titration. During acetylation, and to a smaller extent during formylation, of cysteine, the $HClO_4$ titration val. passes through the normal min., but increases again. *N*-Acetyl-*dl*-alanine, -*dl*-methionine, -*l*-hydroxyproline, and -*dl*-tryptophan, *N*-formyl-*dl*-alanine and -*dl*-methionine, and *NN'*-diformyl-*l*-lysine, m.p. 132—133°, are prepared.

II. Reactions of hydroxy-amino-acids with Ac_2O–AcOH in presence of $HClO_4$ show that acetylation of NH_2 groups is increasingly suppressed by increasing acidity, whereas *O*-acetylation is promoted by $HClO_4$. The extent of the latter reaction can be determined by measuring the resulting decrease in Ac_2O available for reaction with NH_2-groups under basic conditions, the latter reaction being accompanied by loss of titratability of the NH_2 groups. Change from acid to basic conditions is effected by *o*-NH_2·C_6H_4·CO_2H addition, which also supplies excess of NH_2 groups. The hydroxy-amino-acid (1 mol.) is dissolved in conc. aq. $HClO_4$ (1·3 mols.)–AcOH and Ac_2O (1·4 mols.) is added carefully; after 1 hr. at room temp., H_2O is added and after a further hr., C_5H_{11}·NH_2 is added and the *O*-Ac-derivative pptd. by a suitable solvent, *e.g.*, EtOH, Et_2O, $COMe_2$, etc. Rapid hydrolysis of O-*acetyl*-l-*tyrosine*, decomp. 213—214°, and -l-*hydroxyproline*, decomp. 179—181°, occurs with aq. NaOH, but the rotation of the hydrolysed compound is almost identical with that of the parent compound; acid causes a much slower hydrolysis. O-*Acetyl*-dl-*serine*, decomp. 143—144° (evolution of gas), and -dl-*threonine*, decomp. 146—149° (evolution of gas), are prepared.

III. OH and analogous groups, *e.g.*, ·NH· of tryptophan, :NH and (less reliably) ·SH groups, are determined in dry NH_2-acids by a titrimetric method based on the acid-catalysed acetylation of these groups by Ac_2O. Under the conditions, cystine reduces $HClO_4$. Diphenylguanidine is a more suitable primary standard than glycine for $HClO_4$ titration. A. T. P.

Chromatography of aminodicarboxylic acids on alumina.—See A., 1942, II, 301.

Reaction of molybdenum. L. Rovira (*Rev. Fac. Cienc. Quím., La Plata*, 1941, **16**, 235—242).—Optimum conditions for the determination of NHPh·NH_2 with Na_2MoO_4 require a 5% solution of NHPh·NH_2 with an equal vol. of H_2O and twice the vol. of 7N-H_2SO_4, and heating for 30 min. at 100°. The reaction is inhibited by $Fe(CN)_6'''$, $Fe(CN)_6''''$, Pb'', and Sn''. The sensitivity is 5×10^{-4}. F. R. G.

Determination of *p*-toluidine in the presence of its isomerides. C. H. Benbrook and R. H. Kienle (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 427—428).—The sample of amine is diazotised and kept at 45° for 3 hr.; under these conditions, *o*- and *m*-C_6H_4Me·N_2Cl are completely decomposed, and the *p*-isomeride is almost unaffected. Measurement of the evolution of N_2 gives a measure of the *p*-content of the mixture. J. D. R.

Determination of 2-methyl-1 : 4-naphthaquinone. A. R. Menotti (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 418—420).—The quinone is treated with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 and alcoholic NH_3, and the blue-green colour is measured photo-colorimetrically. J. D. R.

Fission of phenolic ethers by pyridine hydrochloride. III. Attempted determination of methoxy-groups in phenolic ethers by pyridine hydrobromide. V. Prey (*Ber.*, 1942, **75**, [*B*], 445—446).—The ether is heated with a weighed quantity of C_5H_5N,HCl (**I**) at 220° for 3—4 hr. and unused (**I**) is titrated with 0·1N-alkali hydroxide in presence of phenolphthalein (**II**) or electrometrically. $PhOMe + 5C_5H_5N,HCl = PhOH + 4C_5H_5N,HCl + C_5H_5NMeCl$. Good results are obtained with mono- and poly-ethers. OEt can be determined under rather more drastic conditions. If CO_2H is present (**II**) must be replaced by litmus but the results are unsatisfactory. The method cannot be used for NO_2-ethers. H. W.

Performance of some distillation columns for the fractionation of terpenes. W. D. Stallcup, R. E. Fuguitt, and J. E. Hawkins (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 503—505).—Comparisons are given of the separation of α- and β-pinene with columns packed with Raschig rings, Berl saddles, and stainless steel spirals. For a loose packing, 4 × 4-mm. Berl saddles perform well, but the spiral screen packings are most economical and efficiently operated. J. D. R.

Polarographic characterisation of nicotinic acid and related compounds. I. Pyridine and nicotinic acid. P. C. Tompkins and C. L. A. Schmidt (*J. Biol. Chem.*, 1942, **143**, 643—653).—Vals. of the diffusion current *i* and of the half-wave potential are given for C_5H_5N (**I**) and nicotinic acid (**II**) in both buffered and unbuffered solutions. In the latter (**I**) is probably reduced to piperidine. The polarograph is not recommended for analysis of (**I**) solutions; if it is used, the solution should contain Na or K phosphate at ≮0·1N. concn. in the p_H range 6—8. The *i* of (**II**) depends on p_H, buffer capacity, and (**II**) concn.; no information regarding the no. of H· or electrons involved in its reduction was obtained. The anion of (**II**) is not reducible. (**II**) waves are attributed to the catalytic reduction of H· with the undissociated (**II**) mol. acting as a mild catalyst F. L. U.

Determination of quinine by absorption spectrophotometry. J. Carol (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 524—529).—For concns. ≯1·5 mg. per 100 ml. transmittance at 340 mμ. shows only slight deviation from the Beer–Lambert law. Strychnine, atropine, NHPhAc, acetylsalicylic acid, camphor, phenolphthalein, caffeine, most blue, green, and red dyes, glycerol, EtOH, sugars, and the Fe'''–H_3PO_4 complex do not interfere. A. A. E.

[Determination of] nicotine [as] silicotungstates. L. N. Markwood (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 474—476).—Although the granular nicotine salt of $4H_2O,SiO_2,12WO_3,4H_2O$ filters more rapidly than the lamellar salt of $4H_2O,SiO_2,12WO_3,22H_2O$, high accuracy cannot be attained with the former owing to incomplete recovery. A. A. E.

Quantitative spectroscopic analysis of proteins. A. M. Buswell and R. C. Gore (*J. Physical Chem.*, 1942, **46**, 575—581).—Procedure for the quant. analysis of a protein, based on the determination of the extinction coeffs. for infra-red mol. or group frequencies characteristic of various NH_2-acids, is outlined. Data for salmine, proline, arginine, and guanidine are presented and discussed. F. L. U.

INDEX OF AUTHORS' NAMES, A., II.

OCTOBER, 1942.

ERRATUM.

Page	Line	
277	20*	*For* "m.p. 332°" *read* "m.p. 132°."

* From bottom.

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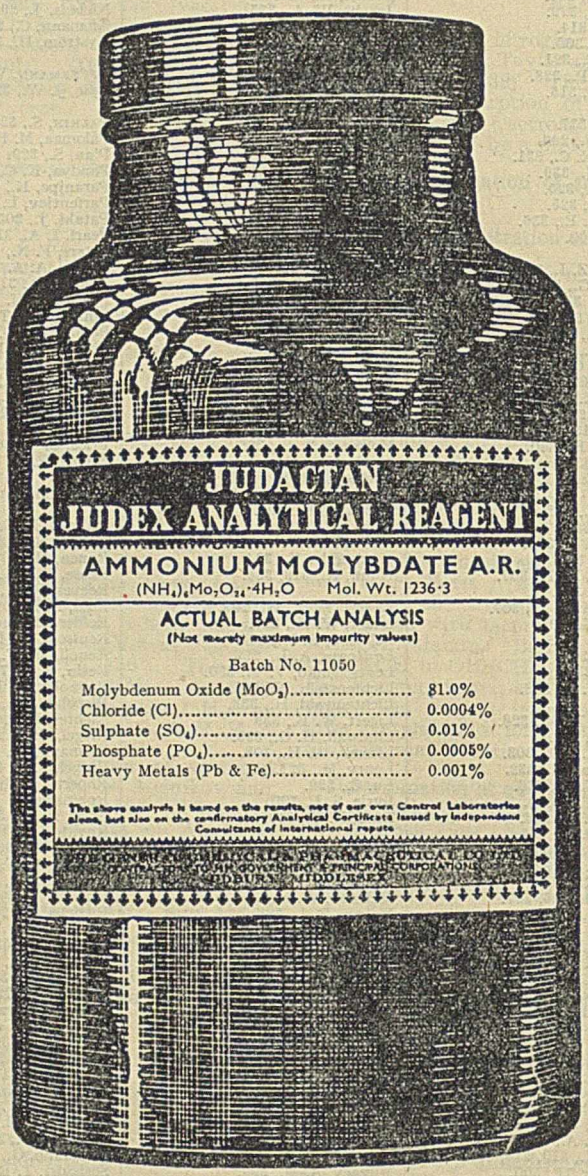

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