# BRITISH CHEMICAL ABSTRACTS

## A., II.—Organic Chemistry

MARCH, 1937.



**Atomic interchange between water and saturated hydrocarbons.**—See A., I, 143.

**Action of oxygen in polymerisation reactions.**—See A., I, 141.

**Reversible catalytic conversion of *n*-butylenes into *iso*butylene.** A. V. Frost, D. M. Rudkovski, and E. K. Serebrjakova (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 373—376).—Quant. conversion of *n*-butylenes into *iso*butylene (I) in presence of six different catalysts is examined at about 300° and equilibrium relationships are determined between 265° and 426°. $SiO_2$ gel–$H_3PO_4$ promotes the largest yield (44·5%) of (I). F. N. W.

**Influence of structure of olefines on the iodine value.** S. Landa and M. Habada (Chem. Listy, 1937, 31, 4—10).—The I vals. obtained for $\Delta^{\alpha}$-hexadecene (I), β-methyl-$\Delta^{\beta}$-heptadecene (II), and γ-ethyl-$\Delta^{\beta}$-octadecene (III) are unaffected by varying the duration of reaction from 0·5 to 24 hr. In presence of excess of reagent normal I vals. are obtained for (I) and (II) (methods of Hübl and of Hanus), and abnormally high vals. for (III), δ-propyl-$\Delta^{\gamma}$-nonadecene, ε-butyl-$\Delta^{\delta}$-eicosene, αα-diphenyl-$\Delta^{\alpha}$-hexadecene, and δμ-diethyltetradecane-$\Delta^{\beta\nu}$-diene. The I vals. are at a max. for the freshly prepared olefines, and fall more rapidly with time for dienes than for mono-olefines. It is concluded that the I val. is not of great val. in the analysis of mineral oils. R. T.

**Carbon tetrachloride as a physico-chemical standard.** A. Zmaczynski (Svensk Kem. Tidskr., 1936, 48, 268—273; cf. this vol., 80).—The prep. of very pure $CCl_4$ is described. M. H. M. A.

**Action of elementary fluorine on organic compounds. III. Vapour-phase fluorination of hexachloroethane.** W. T. Miller, jun., J. D. Calfee, and L. A. Bigelow (J. Amer. Chem. Soc., 1937, 59, 198—199; cf. A., 1934, 62).—$C_2Cl_6$ and $F_2$ react in the vapour phase over a heated Cu-gauze catalyst, yielding 20% of *s*-$C_2Cl_4F_2$. $C_2Cl_4$ yields the same product under similar conditions. E. S. H.

**Preparation of α-chloro-γ-bromopropane, and the velocity of addition of HBr to allyl chloride.** L. I. Antzus (J. Appl. Chem. Russ., 1936, 9, 2053—2054).—In disagreement with Schostakovski (A., 1936, 819), the sole product given by $CH_2{:}CH{\cdot}CH_2Cl$ and HBr at −19° to 0° is $CHMeCl{\cdot}CH_2Br$. R. T.

**Addition of hydrogen bromide to allyl bromide in the presence of various substances. III. Elucidation of the so-called peroxide effect.** Y. Urushibara and M. Takebayashi (Bull. Chem. Soc. Japan, 1936, 11, 798—801; cf. this vol., 43).—Allyl bromide (I) and $O_2$ form peroxides in light, but not in the dark; in presence of Pd-black no peroxides are formed even in the light. Peroxides present in (I) are destroyed by Pd-black. (I) liberates Br from HBr in presence of $O_2$ and Pd-black, but not of either alone. $O_2$, HBr, and Pd-black liberate Br without the presence of (I). The proportion of isomerides in a $C_3H_6Br_2$ mixture does not change in presence of $O_2$, Pd-black, and HBr. Thus, the "peroxide effect" is probably due to liberation of $O_2$ from peroxides rather than to the presence of the latter. R. S. C.

**γ-Chloro-β-methyl-$\Delta^{\alpha}$-propene.** O. Schales (Ber., 1937, 70, [*B*], 116—121).—γ-Chloro-β-methyl-$\Delta^{\alpha}$-propene (I) is shown to be a reactive substance. When boiled with 25% KOH–MeOH for 1 hr. (I) gives a 90% yield of $CH_2{:}CMe{\cdot}CH_2{\cdot}OH$ and a 51% yield when heated with aq. $K_2CO_3$ at 100°. With Mg in $Et_2O$ it readily affords βε-dimethyl-$\Delta^{\alpha\epsilon}$-hexadiene, b.p. 136—137°/760 mm. With PhOH and $K_2CO_3$ in boiling $COMe_2$ (I) yields *Ph* β-*methyl*-$\Delta^{\beta}$-*propenyl ether*, b.p. 89°/10 mm. (yield 72%), which is isomerised in boiling $NPhEt_2$ to o-β-*methyl*-$\Delta^{\beta}$-*propenylphenol* (II), b.p. 102—103°/11 mm. (*Me ether*, b.p. 92·5—94°/11 mm.). Treatment of (II) with boiling AcOH and 48% HBr yields polymerised products, but under mild conditions *dimethylcoumaran*, b.p. 198—204°/755 mm., 82—83°/16 mm., appears to result. Addition of (I) and NaOAc in EtOH–$H_2O$ to a solution of barbituric acid at 70—73° gives 5 : 5-*di*-β-*methyl*-$\Delta^{\beta}$-*propenylbarbituric acid*, m.p. 222°, the physiological action of which does not differ considerably from that of the homologous diallylbarbituric acids. H. W.

**Allyl change : a trichloro*iso*butene.** A. Kirrmann and R. Jacob (Compt. rend., 1936, 203, 1528—1529).—ααα-Trichloro-β-methylpropan-β-ol with $P_2O_5$ at 150° affords αα*γ*-*trichloro*-β-*methyl*-$\Delta^{\alpha}$-*propene* (I), b.p. 46°/12 mm. (which with $KMnO_4$–$COMe_2$ affords $COMe{\cdot}CH_2Cl$), probably formed by the isomerisation of ααα-trichloro-β-methyl-$\Delta^{\beta}$-propene (II). Analogues of (I) and (II) are prepared; one Cl of the former is much less reactive than in the latter. (I) with NaOAc gives an *acetate*, b.p. 79°/12 mm., hydrolysed to *γγ-dichloro*-β-*methylallyl alcohol*, b.p. 78—79°/13 mm. [p-*nitrobenzoate*, m.p. 91°, obtained also from (II) directly]. J. L. D.

**Elimination of hydrogen chloride from βδ-dichloro-$\Delta^{\beta}$-butene. II.** A. L. Klebanski, K. K. Tschevitschalova, and A. P. Belenkaja (J. Appl. Chem. Russ., 1936, 9, 1985—1993).—Chloroprene is obtained in 65—70% yield by passing $CHMeCl{:}CH{\cdot}CH_2Cl$ (I) over $CaCl_2$ on Cu turnings at

350—400°, or by passing 1 : 1 steam–(I) mixtures over Cu, also at 350—400°. The inactivated catalysts are regenerated by heating in air at 500—550° for 3—4 hr. R. T.

**Chloro-derivatives of aliphatic hydrocarbons. II. Allylic isomerisation of *iso*pentenyl chlorides.** D. V. Tischtschenko. **III. Chlorination of αβ- and βγ-dichlorobutanes.** D. V. Tischtschenko and A. Tschurbakov (J. Gen. Chem. Russ., 1936, **6**, 1549—1552, 1553—1558; cf. this vol., 2).—II. $CH_2$:CMe·CHMeCl or CHMe:CMe·$CH_2$Cl yield, when hydrolysed with $H_2O$ at 70°, a mixture of $COMePr^{\beta}$, OH·CHMe·CMe:$CH_2$ (*α-naphthylurethane*, m.p. 91·5—93°), and OH·$CH_2$·CMe:CHMe (*α-naphthylurethane*, m.p. 103°). The alcohols afford isoprene when passed over $MgSO_4$ at 230—260°.

III. αβ- or βγ-Dichlorobutane and $Cl_2$ yield a mixture of $CH_2Cl$·CHCl·CHMeCl (I) and CHMeCl·$CMeCl_2$ (II). (I), when distilled from KOH, yields a mixture of cis-, b.p. 134—136°, and trans-αβ-*dichloro*-$\Delta^{\beta}$-*butene*, b.p. 101—103°, whilst (II) gives a mixture of cis-, b.p. 125—127°, and trans-βγ-*dichloro*-$\Delta^{\beta}$-*butene*, b.p. 116—118°. The position of the Cl in the dichlorobutenes is determined by examining the products of ozonolysis. R. T.

**Aliphatic chloro-derivatives. IV. Chlorination of *iso*pentane.** M. Davidova, Z. Pankina, and D. Tischtschenko. **V. Catalytic decomposition of βγ-dichlorobutane in presence of steam.** R. Gutner and D. Tischtschenko (J. Gen. Chem. Russ., 1936, **6**, 1615—1623, 1729—1735).—IV. All four possible monochloro*iso*pentanes are obtained by chlorination at 18—20° in the liquid or gaseous phase.

V. (CHMeCl·)$_2$ (I) and $H_2O$ [14 mols. of $H_2O$ per mol. of (I)] at 360—400°, in presence of $MgCl_2$– or $CaCl_2$–$SiO_2$, give butadiene (II) in 35—38, CHMe:CMeCl (III) in 21—25, and COMeEt in 6—8% yield; the yield of (II) falls with increasing concn. of (I) in the mixture. In absence of $H_2O$ the products are (III) and (CHMe:)$_2$, with >4% of (II). Under similar conditions (III), (OH·CHMe·)$_2$, or OH·CHMe·CHMeCl (IV) yields only traces of (II), which is the chief product obtained from CHMeCl·CH:$CH_2$ (V) or CHMe:CH·$CH_2$Cl (VI) and $H_2O$. The probable reactions are (III) ← (I) → (V) ⇌ (VI) → (II); or COMeEt ← (IV) ← (I) ⇄ (VI) → OH·$CH_2$·CH:CHMe ⇌ OH·CHMe·CH:$CH_2$ → (II). R. T.

**Determination of ethyl alcohol by a capillary-rise method.** F. Todd (Amer. J. Pharm., 1936, **108**, 488—497).—A method for the determination of EtOH in aq. solution is described. F. N. W.

**βββ-Tribromoethyl alcohol.** F. de Carli and A. Mangini (Atti V Congr. Naz. Chim., 1936, **14**, 741—758).—In an attempt to prepare more stable derivatives of Avertin and to establish the function of the alcohol group, the following have been synthesised, and their solubility and physiological activity on the guinea-pig determined: βββ-*tribromoethyl benzoate*, m.p. 35·5—36·5°, o-, m-, and p-*nitrobenzoates*, m.p. 117—118°, 82·5—83°, 100—101°, and *carbonate*, m.p. 112—113°; βββ-tribromoethylphenylurethane, m.p. 107—108° (Chechik, A., 1932, 367, gives m.p. 66—67°), βββ-*tribromoethyl*-p-*bromophenylurethane*, m.p. 116—117°, *di*-βββ-*tribromoethyl*-p-*phenylenedi*-, m.p. 239—240°, -*ethylenedi*-, m.p. 102—103°, and o-, m-, and p-*carboxyphenyl-urethane*, m.p. 174—176°, 185—186° (partial decomp.), and 220—222° (decomp.). The results show that the narcotic activity is a sp. function of the alcoholic OH and the derivatives prepared have not the power of regenerating, by scission in the organism, the active principle. The derivatives are markedly lipo-sol. but this is not sufficient to permit narcotic activity without $H_2O$-solubility. L. A. O'N.

**Hydrogenation of binary organic mixtures. I. Hydrogenation of mixtures of allyl alcohol and oleic acid.** V. V. Ipatiev, jun., and I. F. Bogdanov (J. Gen. Chem. Russ., 1936, **6**, 1651—1658).—Hydrogenation (Pt catalyst) of oleic acid does not commence until that of allyl alcohol is completed. R. T.

**Selective hydrogenation of unsaturated esters to unsaturated alcohols.** J. Sauer and H. Adkins (J. Amer. Chem. Soc., 1937, **59**, 1—3).—Bu oleate with $H_2$ (200 atm.) and a large amount of a Zn–Cr oxide catalyst (I) at 300° gives 65% of octadecenol, b.p. 158°/2 mm. (containing 13% of octadecanol); with less (I) at 282°, octadecenyl oleate, b.p. 272°/1 mm., is also formed. Similarly, *Bu*$^{\alpha}$ $\Delta^{\iota}$-*undecenoate*, b.p. 116°/2 mm., affords 37% of undecenol, b.p. 133°/16 mm. (containing 9% of undecanol), whilst *Bu*$^{\alpha}$ *erucate*, b.p. 211—212°/1 mm. (by butanolysis of rape-seed oil), gives 68% of docosenol, b.p. 196°/3 mm., m.p. 34—35° (containing 3% of docosanol). Zn–V oxide and Zn–Mo oxide catalysts are inferior to (I). Et oleate with $H_2$ + Cu–Mo oxide affords Et stearate; with $H_2$ + Cu–V oxide, *octadecyl stearate*, m.p. 62°, and a little octadecanol result. H. B.

**Odorous constituents of *Matsutake*.**—See A., III, 107.

**Essential oil of green tea. VIII. Linalool and acetophenone.** S. Takei, Y. Sakato, and M. Ono (Bull. Inst. Phys. Chem. Res. Japan, 1937, **16**, Abs. 3).—Oxidation of dihydrolinalool (I) gives βζ-*dimethyloctane*-βζ-*diol*-γ-*one* (2 : 4-*dinitrophenylhydrazone*, m.p. 115—117°; p-*nitrophenylhydrazone*, m.p. 168°), also obtained from methylheptenone and MgEtI. (I) is therefore CMe$_2$:CH·$CH_2$·$CH_2$·CMeEt·OH·$CH_2$Me. From green-tea oil, linalool and COPhMe have been isolated. F. R. S.

**Preparation of halogenoalkines with the triple linking as far as possible from the halogen atom. Synthesis of dehydroundecylenyl alcohol [$\Delta^{\alpha}$-undecinen-λ-ol] and dehydroundecylenyl bromide [λ-bromo-$\Delta^{\alpha}$-undecinene].** A. Oskerko (Ber., 1937, **70**, [*B*], 55—61).—Distillation of castor oil at 130—150°/75—100 mm. and passage of the vapours over heated pumice gives homogeneous $\Delta^{\iota}$-undecenoic acid, b.p. 142—145°/2—3 mm., m.p. 24° (yield 10%), transformed into ικ-dibromoundecoic acid and thence into $\Delta^{\iota}$-undecinenoic acid (I), b.p. 145°/15 mm., m.p. 42°. (I) is readily esterified to *Et*, b.p. 117°/3 mm. (*compound*, $C_{13}H_{21}O_2Ag$,$AgNO_3$), and *Me* $\Delta^{\iota}$-*undecinenoate*. The esters are reduced by Na and EtOH (BuOH) to $\Delta^{\alpha}$-*undecinen*-λ-*ol*

(II), b.p. 108—109°/2 mm., f.p. —4° (*compound*, CAg:C·$[CH_2]_8$·$CH_2$·OH,$AgNO_3$; *phenylurethane*, m.p. 51°; *acetate*), complete absence of moisture appearing essential to success. (II) is converted by $PBr_3$ in $Et_2O$ containing a little $C_5H_5N$ into *λ-bromo-Δ$^a$-undecinene*, b.p. 98—99°/2 mm., which gives an unstable compound with $AgNO_3$. $C_5H_5N$ by itself appears to lead to undesired by-products. H. W.

**Metal alkoxides and ortho-esters. II. Thermal decomposition of metal alkoxides and ortho-esters.** H. Meerwein and E. Geschke (J. pr. Chem., 1936, [ii], **147**, 203—210; cf. A., 1930, 59).—$Sn(OEt)_4$ when heated (sealed vessel; 125—170°; 2—10 hr.) in EtOH–$N_2$ (or alone) gives $Sn(OEt)_2$, MeCHO, and EtOH: crystals of the *substance* $[Sn^{IV}(OEt)_6]Sn^{II}$ separate. Above 150° further condensation of MeCHO occurs. $[Sn(OEt)_6]H_2$ and $[Sn(OEt)_6]HNa$ (I) (*loc. cit.*) decompose similarly but more rapidly owing to the accumulation of OEt on Sn. The Ca, Al, and Zn salts corresponding with (I) do not decompose so rapidly as (I), as they are split in EtOH into their components. The ethoxides of $Fe^{III}$ and $Sb^V$ readily decompose giving MeCHO and a lower ethoxide of the metal, the former also giving a black cryst. *compound* and the latter some $CHMe(OEt)_2$. The ethoxides of Cu, Co, Ni, and $Te^{IV}$ decompose to MeCHO, EtOH, and the metal, whilst those of Al, Si, $Sb^{III}$, and $Sn^{II}$ do not decompose under the above conditions but do so differently at higher temp. The yield of aldehyde from $Te(OEt)_4$ and $Te(OMe)_4$ is unexpectedly small. H. G. M.

**Reducing action of metal alkoxides. II.** H. Meerwein [with B. von Bock, B. Kirschnick, W. Lenz, and A. Migge] (J. pr. Chem., 1936, [ii], **147**, 211—225; cf. A., 1925, i, 1239).—The following alcohols have been obtained in good yield by reduction of the corresponding aldehyde or ketone with an alkoxide of Al or Mg: β-*chloro*-, b.p. 159°, and β-*bromo*-, b.p. 69—70°/13 mm., *-crotonyl*; β-*chloro*-, m.p. 14°, b.p. 147—149°/17 mm., and β-*bromo*-, m.p. 18°, b.p. 151—153°/13 mm., *-cinnamyl*; o-, m.p. 60·5—61°, m-, m.p. 51—51·5°, and p-, m.p. 127·5—128°, *-nitrocinnamyl*; *αα-αγ*-, b.p. 87—89°/14 mm., and *αα-γγ*-, b.p. 80—90°/14 mm., *-tetrachloropropan-β-ol*; *hydroxycitronellol* (OH·$CMe_2$·$[CH_2]_3$·CHMe·$CH_2$·$CH_2$·OH), b.p. 140—141°/4—5 mm. Details for the reduction of crotonaldehyde to the alcohol are given, but the formation of $Bu^aOH$ has not been confirmed (cf. A., 1934, 176). Phenolic aldehydes may also be reduced if previously methylated. Reduction of $NMe_2$·$C_6H_4$·CHO is difficult probably owing to complex formation between ·$NMe_2$ and the Al alkoxide. The yield of β-butylene glycol from aldol and $Al(OEt)_3$ is poor. Reduction of $COPh_2$ by $Al(OEt)_3$ is different from the foregoing reductions; some $CH_2Ph_2$ and AcOH are formed, and these are also obtained from $Al(OEt)_3$ and $CHPh_2$·OH, but not $(CHPh_2)_2O$. The yields of the various products obtained by reduction of PhCHO by the ethoxides of Al, Zr, $Sn^{IV}$, $Sn^{II}$, $Sb^V$, $Sb^{III}$, Te, Ti, and $Fe^{III}$ are recorded. Excellent yields of $CH_2Ph$·OH are obtained by means of the first three ethoxides only, and no reduction at all occurs with the ortho-esters of B, As, P, and Si. The mechanism is considered to involve the formation of an additive complex between the ethoxide and the aldehyde (or ketone) (cf. A., 1930, 59). H then migrates from the alcoholic to the aldehydic constituent of the complex, which immediately decomposes:
R·CHO···$Al(O·CH_2·R')_3$ → R·$CH_2$·O·$Al(O·CH_2·R')_2$ + R'·CHO (cf. preceding abstract). *p*-OMe·$C_6H_4$·CHO when heated with the benzyloxides of Al, Mg, Zn, and Ca in $CH_2Ph$·OH gives *p*-OMe·$C_6H_4$·$CH_2$·OH (I), PhCHO, and *p*-OMe·$C_6H_4$·$CO_2CH_2Ph$ (II). The yields of (I) and (II) depend on the benzyloxide used, that of (I) diminishing and that of the ester (II) increasing with the benzyloxides in the foregoing order. The relation between the mechanisms for reduction and ester formation is discussed. The results support the view that ester formation is diminished in favour of reduction with decreasing electropositive character of the metal atom (*i.e.*, increasing homopolar character of the alkoxide). H. G. M.

**Reduction products of disaccharides; maltitol, lactitol, cellobiitol.** P. Karrer and J. Büohi (Helv. Chim. Acta, 1937, **20**, 86—90).—Hydrogenation (Ni) of maltose in aq. MeOH at 130—140°/30 atm. yields *maltitol* (I), $C_{12}H_{24}O_{11}$, a colourless, hygroscopic powder, $[\alpha]_D$ about +90° in $H_2O$ (*nona-acetate*, m.p. about 86°). *Lactitol* (II), $[\alpha]_D$ about +14·84° in $H_2O$, and *cellobiitol* (III), $[\alpha]_D$ −8·8° in $H_2O$, are obtained similarly from lactose and cellobiose. The compounds are indifferent towards Fehling's solution and are hydrolysed by acids to 1 mol. of sugar and 1 mol. of sorbitol (*tribenzylidenesorbitol*, m.p. 190—191°). (I) is hydrolysed by yeast extracts and by the snail enzyme (IV). (II) and (III) are so slowly attacked by emulsin that hydrolysis appears doubtful, whereas they are readily saccharified by (IV). H. W.

**Formation of ethers by the interaction of primary alcohols and olefines at high pressures.**—See A., I, 134.

**Catalytic hydrolysis of [ethyl] ether.**—See A., I, 144.

**Action of phosphoric oxide on ether.** T. Wagner-Jauregg and H. Griesshaber (Ber., 1937, **70**, [*B*], 1—8).—Cautious hydrolysis of the "Et metaphosphate" (I) of Langheld obtained from $Et_2O$ and $P_2O_5$ in $CHCl_3$ (A., 1910, i, 536; 1911, i, 705; 1912, i, 156; also Wertyporoch *et al.*, A., 1934, 392) shows that only 20—25% of the total phosphate is readily eliminated. Fractional pptn. of the corresponding Ba salts by EtOH from dil. AcOH affords an OEt-richer portion from which $PO_4$ is obtained with difficulty and a material containing little OEt and readily hydrolysed. This fraction yields *brucine metaphosphate*, $4HPO_3,3C_{22}H_{26}O_4N_2,16H_2O$, (anhyd.) m.p. 188—190° (corr.) in sealed capillary. [A similar abnormal composition is shown by *acridinium metaphosphate*, $4HPO_3,3C_{13}H_9N,4H_2O$, m.p. 275—278° (corr.), and is ascribed to the presence of 3 primary OH in the tetrameride $PO_2$·O·PO(OH)·O·PO(OH)·O·$PO(OH)_2$; acridine pyrophosphate is $2H_4P_2O_7,3C_{13}H_9N$, whereas the corresponding *orthophosphate*, m.p. 293—294° (corr.), is $C_{13}H_9N,H_3PO_4$.] The unfractionated solution of (I) gives with brucine in EtOH–$H_2O$ the normal *salt*, $EtH_2PO_4,2C_{23}H_{26}O_4N_2$, m.p. 160° after marked soften-

ing at 140°, decomp. 185—190°, transformed by crystallisation from $COMe_2$ into the *H salt*, $EtH_2PO_4$,$C_{23}H_{26}O_4N_2$,$4H_2O$, m.p. 211—214° (corr.), also obtained from $Na_2EtPO_4$ and brucine hydrochloride. It appears therefore that $Et_2HPO_4$ is formed in very small proportion if at all by addition of $H_2O$ to (I). The hydrolysate contains $EtH_2PO_4$ and $HPO_3$ in agreement with Langheld's conception. $Ph_2O$ and $P_2O_5$ do not appear to react in $CHCl_3$. $(CH_2Ph)_2O$ and $P_2O_5$ in $CHCl_3$ yield material containing P in very small amount; after its removal a non-homogeneous polymerisate (II) remains from which after treatment with $Al_2O_3$ in $C_6H_6$ a mixture of polymeric hydrocarbons is isolated. Dry distillation of (II) gives a yellowish-red oil from which *p*-$C_6H_4Ph_2$ is isolated in small amount. H. W.

**Ethers of Δ$^{\gamma}$-butinen-α-ol.** P. A. McCusker and J. W. Kroeger (J. Amer. Chem. Soc., 1937, **59**, 213—214).—CH:C·$CH_2$·$CH_2$·OR are obtained in 60—75% yield from OR·$CH_2$·$CH_2$Br and CH:CNa in liquid $NH_3$; the following are described: δ-methoxy-, b.p. 87·5°/748 mm., δ-*ethoxy*-, b.p. 104°/747 mm., δ-*butoxy*-, b.p. 147—148°/747 mm., and δ-β′-*bromoethoxy*-, b.p. 99—100°/35 mm., -Δ$^{\alpha}$-*butinene* (*Hg* salts, m.p. 113·9°, 98·6—99°, 42·2—42·5°, and 85—86°, respectively); δ-β′-*ethoxyethoxy*-Δ$^{\alpha}$-*butinene*, b.p. 84·5—85·5°/34 mm.; *di*-Δ$^{\gamma}$-*butinenyl ether*, b.p. 164—165°/750 mm. ββ′-*Dibromodiethyl*, b.p. 115°/32 mm., and β-*bromoethyl* β-*ethoxyethyl*, b.p. 100—101°/33 mm., *ethers* are prepared from the appropriate OH-ether and $PBr_3$ in $C_5H_5N$. H. B.

**Carbohydrates and polysaccharides. LII. Preparation, separation, and identification of the isomeric propylidene-, *iso*butylidene-, *tert.*-amylidene-, and dibromoethylidene-glycerols, and general properties of glycerol cyclic acetals.** S. M. Trister and H. Hibbert (Canad. J. Res., 1936, **14**, B, 415—426).—Condensation of EtCHO, Pr$^{\beta}$CHO, Bu$^{\gamma}$CHO, and $CH_2Br$·CHO with glycerol at 90° in presence of 40% $H_2SO_4$ gave in each case a mixture of the 5- and 6-membered cyclic acetals. These were separated as benzoates by means of ligroin, and identified by hydrolysis, followed by methylation and hydrolysis to the glycerol $Me_1$ ether. In this way EtCHO gave αβ-, b.p. 70—72°/3 mm. (*γ-benzoate*, b.p. 147—149°/1 mm.; *γ-Me ether*, b.p. 67—69°/17 mm.), and α*γ-propylideneglycerol*, b.p. 50—51°/2 mm. (β-*benzoate*, m.p. 74—75°; β-*Me ether*, b.p. 89—90°/23 mm.). Pr$^{\beta}$CHO gave αβ-, b.p. 69—72°/2 mm. (*γ-benzoate*, b.p. 159—162°/5 mm.; *γ-Me ether*, b.p. 70—71°/15 mm.), and α*γ-isobutylideneglycerol*, b.p. 55—56°/2 mm. (β-*benzoate*, m.p. 73·5° β-*Me ether*, b.p. 80—81°/15 mm.). Bu$^{\gamma}$CHO gave αβ-, b.p. 83—84°/6 mm. (*γ-benzoate*, b.p. 169°/8 mm.; *γ-Me ether*, b.p. 66—68°/6 mm.), and α*γ*-tert.-*amylideneglycerol*, m.p. 45° (β-*benzoate*, m.p. 93·5°; β-*Me ether*, b.p. 79—81°/6 mm.). $CH_2Br$·CHO gave αβ-, b.p. 124—127°/3 mm. (*γ-benzoate*, b.p. 167—171°/3 mm.), and α*γ*-(*dibromoethylidene*)*glycerol*, b.p. 117—119°/3 mm. (β-*benzoate*, m.p. 67·5°); the structures of the last two benzoates were proved by direct synthesis from glyceryl α-benzoate.

Increase in the electronegative character of the aldehyde increased the ratio of 5- to 6-membered cyclic acetal produced, the ratio from Bu$^{\gamma}$CHO being 3 : 2, from Pr$^{\alpha}$CHO 3 : 1, from EtCHO 4 : 1, and from $CH_2Br$·CHO 15 : 1; Bu$^{\gamma}$CHO unites with glycerol in absence of a catalyst. High temp. also increases the proportion of 5-membered isomeride. A. Li.

**[Catalytic] synthesis of esters by dehydrogenation of alcohols.**—See A., I, 143.

**Electrolysis of mixtures of propionates with sulphates and with perchlorates.** F. Fichter and P. Sutter (Helv. Chim. Acta, 1937, **20**, 156—158).—The reactions do not yield alkyl and glycol esters (cf. A., 1935, 472). E. S. H.

**Cyclisation of geranic acid.** K. Bernhauer and R. Forster (J. pr. Chem., 1936, [ii], **147**, 199—202).—Geranic acid, best prepared (70% yield) by oxidation of citral with $Ag_2O$–NaOH–EtOH–$H_2O$, is cyclised in good yield (70—80%; cf. lit.) by refluxing (water-bath; 6 hr.) with $HCO_2H$ or with AcOH–$H_2SO_4$, which acids give yields > those obtained with other acids. H. G. M.

**Fatty acids. I. Purification of linoleic acid by crystallisation methods.** J. B. Brown and G. G. Stoner. **II. Preparation of pure oleic acid by a simplified method.** J. B. Brown and G. Y. Shinowara (J. Amer. Chem. Soc., 1937, **59**, 3—6, 6—8).—I. The acids from cotton-seed and maize oils are separated into saturated and unsaturated (*A*) by crystallisation from $COMe_2$ at −20°. Linoleic acid (80—93% pure) is isolable from (*A*) by fractional crystallisation from $COMe_2$ or MeOH at −65° to −45°, or by fractionation of the Li salts (from BuOH) or K salts (from EtOH) at −20° to 0°. Details are given.

II. Oleic acid, m.p. 13°, is isolated from the acids from olive oil by fractional crystallisation from $COMe_2$ at −60° to −20°. H. B.

**Highly unsaturated $C_{28}$-fatty acids in Hokke oil.**—See A., III, 55.

**Replacement of the hydroxyl group of ethyl (+)lactate by halogens and the molcular dissymmetry of derivatives of ethyl lactate which contain the sulphin group.** W. Gerrard, J. Kenyon, and H. Phillips (J.C.S., 1937, 153—158).—Et (−)lactate (I) with $PCl_5$ (or $PBr_5$) in presence of $K_2CO_3$ or *tert.* bases yields Et (+)α-chloro- [or (+)α-bromo]-propionate. Et (+)lactate (II) and *p*-$C_6H_4Me$·SOCl in $C_5H_5N$ afford Et (+)α-p-*toluenesulphinoxypropionate* (III), b.p. 110°/0·1 mm., $[\alpha]_{5790}^{16}$ +12·41°, which can be separated by distillation into fractions of similar composition but widely different rotations. (III) with $Cl_2$ in $H_2O$ yields Et (−)α-chloropropionate (IV), with Br in $CHCl_3$, Et (−)α-bromopropionate, and with HOCl, a mixture of (IV) and (I). *Et* (−)α-p-*toluenesulphinoxypropionate*, $[\alpha]_{5893}^{20}$ −21·5°, with KSCN in EtOH affords *Et* (−)α-*thiocyanopropionate*, b.p. 119°/20 mm., $[\alpha]_{5790}^{20}$ −7·51°, and with KSeCN in EtOH, *ethyl* (−)α-*selenocyanopropionate*, b.p. 63—64°/0·1 mm., $[\alpha]_{5790}^{17.5}$ −0·85°. (II) with $SOCl_2$ in presence of *tert.* bases yields (IV); in absence of bases, Et (+)α-chlorosulphinoxypropionate, which decomposes on distillation to (IV), with $C_5H_5N$ in $Et_2O$ affords (I) and *N-chloropyridinium* N-α-*carbethoxyethylsulphinate* (*picrate*, m.p. 95°),

and with $H_2O$ yields (II). *n*-Amyl chlorosulphinate and (I) in $C_5H_5N$–ligroin afford *α-carbethoxyethyl-n-amyl sulphite*, b.p. 140—142°/13 mm., $[\alpha]^{16}_{5893}$ −37·15°, also prepared from Et (−)α-chlorosulphinoxypropionate and *n*-$C_5H_{11}$·OH with $C_5H_5N$ in $Et_2O$. *n-Amyl sulphite*, b.p. 129·5°, is obtained from $SOCl_2$ and *n*-$C_5H_{11}$·OH, whilst (+)α-*carbethoxyethyl sulphite*, b.p. 111—112°/0·1 mm., 161°/14 mm., $[\alpha]^{15}_{5790}$ +49·60°, results from $SOCl_2$ and (II). It is deduced that the *l*-Et esters of lactic, α-chloro- and α-bromo-propionic acids, and the *d*-Et esters of α-thio- and α-selenocyanopropionic acids all have the same relative structure, and that the replacement of OH in Et lactate by Cl or Br, by means of $PCl_5$, $PBr_5$, or $SOCl_2$, either in presence or absence of a *tert.* base, results in a change of configuration. J. D. R.

**Chlorohydroxybehenic and glycidic acids from erucic and brassidic acids.** K. Hashi (J. Soc. Chem. Ind. Japan, 1936, **39**, 469—470B).—Brassidic acid and HOCl give the pure *γ-form* of *chlorohydroxybehenic acid* (I), m.p. 62·5—63·5°, converted by KOH into *glycidobrassidic acid* (II), m.p. 67·3—68·3°, which with HCl gives (I). Erucic acid and *glycidoerucic acid* (III), m.p. 62·3—63°, give, under similar conditions, a mixture of the *α-form* of (I) and a so-called *β-form*, m.p. 51·5—52° [58·3—64° when prepared from (III)], believed to be a mixture. Mixtures of (II) and (III) have depressed m.p. and (III) is more sol. than (II) in ligroin and $COMe_2$; (II) and (III) are thus *trans-* and *cis*-forms respectively. R. F. P.

**Action of hydrazine hydrate on lactones.** A. Darapsky, H. Berger, and A. Neuhaus (J. pr. Chem., 1936, [ii], **147**, 145—160).—γ-Valerolactone with $N_2H_4,H_2O$–EtOH (water-bath; 8 hr.) gives *γ-hydroxy-*n*-valerhydrazide*, m.p. 65° (:CHPh derivative, m.p. 95°), described by Blaise *et al.* (A., 1905, i, 329) as a hydrazinolactone, m.p. 61—62°. It is not converted by $HNO_2$ into the expected azide. *o*-Hydroxydiphenylacethydrazide, prepared similarly from the appropriate lactone (I), and reconverted into it by HCl or warm AcOH–$H_2O$, gives with $HNO_2$ the azide (II), which decomposes in boiling $C_6H_6$ to (I), with $NH_2Ph$–$C_6H_6$ yields the corresponding anilide, m.p. 175° (lit. 143—146°), and with hot EtOH gives (I) and a mixture which contains the expected urethane and on hydrolysis gives some *o*-hydroxybenzhydrylamine. On keeping (II) decomposes to the *compound*, $CHPh<^{C_6H_4}_{NH\cdot CO}>O$, m.p. 219° (*o-hydroxybenzhydrylcarbamic anhydride*), hydrolysed by HCl to *o*-hydroxybenzhydrylamine and *cyclo-o*-phenylenebenzylidene oxide (A., 1895, i, 537), the latter being the sole isolable product of hydrolysis with NaOH. Coumarin (III) with hot $N_2H_4,H_2O$–EtOH yields *β-hydrazino-o-hydrocoumarhydrazide* (IV), m.p. 128—129° [(:*CHPh*)$_2$ derivative, m.p. 141°], which on prolonged contact with EtOH and on hydrolysis with HCl gives (III). The constitution of (IV) is confirmed by its conversion by $HNO_2$ into 1-*nitroso-5-o-hydroxyphenyl-5-pyrazolidone*, m.p. 126° [*NH*$_4$, m.p. 132° (decomp.), and *Ag* salt], which closely resembles the known, corresponding 5-Ph compound and with Br–AcOH gives 4 : 4-*dibromo-3-o-hydroxyphenyl-5-pyrazolone*, m.p. 178°, which is readily sol. in dil. NaOH. Et *o*-hydroxybenzoylacetate could not be obtained from Et salicylate, EtOAc, and Na. H. G. M.

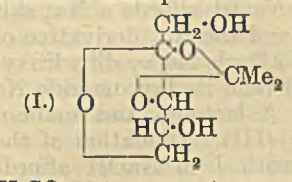
**Investigation of oxalic acid dihydrate by Fourier analysis from *X*-ray crystal data.**—See A., I, 68.

**Reaction of monosubstituted malonic esters and methylenedimalonic esters with sodium ethoxide.** J. R. Roland and S. M. McElvain (J. Amer. Chem. Soc., 1937, **59**, 132—135; cf. A., 1935, 961, 1224).—The predominant reaction occurring when $CHMe(CO_2Et)_2$ (I) (1 mol.) is heated with NaOEt (0·5 mol.) at 160° (not at 50—60° or 100—120°) is ethylation of the Na enolate of (I) by (I): $CHMe(CO_2Et)_2 + [CMe(CO_2Et)_2]Na \rightarrow CMeEt(CO_2Et)_2$ (II) + $CO_2Et\cdot CHMe\cdot CO_2Na$ (III). (II), (III) (as acid), Et α-methylbutyrate [formed from (II)], and some $EtCO_2Et$ are isolated. No intermol. condensation occurs. Similarly, $CHPr^{\beta}(CO_2Et)_2$ and NaOEt at 150—160° give Et *iso*valerate, Et α-*iso*propylbutyrate, and $CEtPr^{\beta}(CO_2Et)_2$. (I) could not be condensed with $Pr^{\beta}CO_2Et$. Et propane-αaγγ- and heptane-αaηη-tetracarboxylates do not undergo intramol. condensation with NaOEt at 110—130°; products resulting from decarboxylation and retrograde Michael reactions are isolable. Et dodecane-αaμμ-tetracarboxylate similarly affords a viscous intermol. condensation product. H. B.

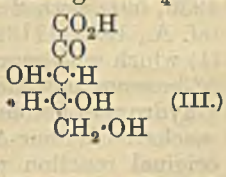
**Synthesis of αα′-diethoxy straight-chain acids.** M. Meyer (Compt. rend., 1936, **203**, 1370—1372; cf. A., 1936, 1231).—$Et_2$ sodioethoxymalonate in boiling PhMe–EtOH with $CH_2(CH_2Br)_2$, affords *Et*$_4$ *αε-diethoxypentane-αaεε-tetracarboxylate* (I), b.p. 130—131°/3 mm., and *Et*$_2$ *ethoxy-γ-bromopropylmalonate*, b.p. 170—171°/3 mm. Similarly, $(CH_2Br\cdot CH_2\cdot)_2$ and αη-dibromodecane afford *Et*$_4$ *αζ-diethoxyhexane-αaζζ-tetracarboxylate* (II), b.p. 129°/2·5 mm., *Et*$_2$ *ethoxy-δ-bromobutylmalonate*, b.p. 174—175°/3 mm., *Et*$_4$ *αμ-diethoxydodecane-αaμμ-tetracarboxylate* (III), b.p. 185°/2 mm., and *Et*$_2$ *ethoxy-μ-bromodecylmalonate*, b.p. 222°/2 mm., respectively. (I), (II), and (III) with aq. EtOH–KOH afford the corresponding tetracarboxylic *acids*, m.p. 190—191°, 218—220° (block) (+4*H*$_2$*O*, decomp. 178°), 110—112° (decomp.), respectively, decarboxylated to give diasterioisomerides of *αα′-diethoxy-pimelic*, m.p. 115° and 82°, *-suberic*, m.p. 113° and 79—81°, and *-dodecamethylenedicarboxylic acid*, m.p. 85° and 69·5°, respectively. J. L. D.

**Synthesis of *d*-xylosonic acid.** R. Prince and T. Reichstein (Helv. Chim. Acta, 1937, **20**, 101—109).—Hexosonic acids are very much more stable that pentosonic acids; it is very doubtful if the unknown tetrosonic acids are capable of existence. *d*-Arabinose is hydrogenated (Ni) to *d*-arabitol, which is transformed by oxidative fermentation into *d*-xyloketose. This passes in $COMe_2$ containing $CuSO_4$ and

(I.)



(III.)



$H_2SO_4$ at room temp. into 2 : 3-*iso*propylidene-*d*-xyloketose (I), needles, m.p. 67—68°, and (?) an

*isomeride*, rhombohedra, m.p. 81·5—83°, $[\alpha]_D^{18}$ 0°→1° in $COMe_2$. (I) is oxidised by $KMnO_4$ in alkaline solution to *K* 2 : 3-iso*propylidene*-d-*xylosonate* (+0·5$H_2O$), m.p. 264—265° (corr.; decomp.), whence 2 : 3-iso*propylidene*-d-*xylosonic acid* (II), m.p. 174—175° (corr.), $[\alpha]_D^{10}$ −12° in $COMe_2$. Hydrolysis of (II) to d-*xylosonic acid* (III) without isomerisation of the latter to *d*-erythroascorbic acid is best effected by approx. 2*N*-mineral acid at 20°, whereby syrups are produced which reduce Fehling's solution but are not immediately active towards I in acid solution; activity is readily acquired by long keeping or short warming in $H_2O$ or EtOH. H. W.

**Oxidation of ascorbic acid and its reduction *in vitro* and *in vivo*.** H. Borsook, H. W. Davenport, C. E. P. Jeffreys, and R. C. Warner (J. Biol. Chem., 1937, **117**, 237—279; cf. Herbert *et al.*, A., 1933, 1143).—Reversible oxidation of ascorbic acid (I) gives first dehydroascorbic acid (II) which, in $H_2O$ at room temp. and $p_H$ <4, undergoes spontaneous irreversible change, yielding an acid (III) (possibly αβ-diketo-*l*-gulonic acid) stronger than (II), having greater reducing power, not reduced by $H_2S$ in acid solution or by glutathione (IV) in neutral or alkaline solution, and non-antiscorbutic. This change is independent of the presence of air or oxidising agents. (III) undergoes reversible oxidation yielding *l*-threonic (V) and oxalic acids possibly by way of another intermediate. There is also a third oxidation stage which is rapid at neutrality and alkaline reaction, (V) being possibly the substance which is then oxidised. The oxidation–reduction potentials of the three stages of oxidation have been determined and the first acid dissociation consts. of (II) and (III) have been measured. The oxidation (I) ⇌ (II) is the only one which is physiologically reversible and significant for antiscorbutic action. (I) is very slowly oxidised in human whole blood and remains much longer reduced in whole blood than in plasma. Human blood does not reduce (II) or retard its conversion into (III). Erythrocytes (man, ox, cat, dog, pig, rat, sheep) are impermeable or almost so to (I). (I) and (II) have the same antiscorbutic potency, but *in vitro* at the $p_H$ and temp. of the tissues (II) is rapidly and irreversibly inactivated. In the tissues (II) is rapidly reduced, and hence retains its potency, the chief reducing agent being probably (III). Conditions affecting the reaction between (II) and (III) are described. W. McC.

**Autoxidation of ascorbic acid and its inhibition by sulphur compounds.**—See A., III, 104.

**Decomposition of double lactones of *d*-mannose sugar acids with alkali and with alkaline iodine.** K. Rehorst (Naturwiss., 1937, **25**, 13—14; cf. A., 1926, 51).—*d*-Mannosaccharodilactone (I) (A., 1936, 591) with 2 mols. of NaOH affords a $Na_2$ salt (cf. A., 1932, 1113) (50%), and the $Na_1$ derivative of (I) which with more NaOH affords Na αγ-dihydroxy-$\Delta^{\gamma}$-hexenoate βε-lactone (II) (and its tautomeride Na α-hydroxy-γ-ketohexenoate βε-lactone) and mannosaccharodilactone-$\Delta^{\alpha\alpha'}$-diene (III). Oxidation of the original reaction product with I in NaOH affords $H_2C_2O_4$ and $CHI_3$ from (II) quantitatively. The total unsaturation less that due to (II) gives (III). J. L. D.

**αα-Disulphodipropionic acid.** A. Fredga (Arkiv Kemi, Min., Geol., 1937, **12**, A, No. 13, 17 pp.).—meso-αα-*Disulphodipropionic acid* (I), m.p. 118—119° (*brucine*, +6$H_2O$ and anhyd., and *strychnine*, +5$H_2O$ and anhyd., salts), is isolated as its β-*naphthylamine* salt (not pure) from the eutectic mixture, m.p. 105°, of the *dl*- (II) (32%) and *meso*-acid which remains after crystallisation of (II) in the prep. from $K_2S_2$ and $CHMeBr{\cdot}CO_2H$. Resolution of (II) with brucine to give the *d*-acid (III) (*brucine* salt, +6·5$H_2O$ and anhyd.) is described. The solubility of (I), (II), or (III) in $H_2O$ at 25° remains const. for long periods (200 hr.) and then increases only slowly due to slight decomp., showing that no interconversion (I) ⇌ (II) occurs. In alkaline solution polarimetric measurements show that a rapid reciprocal oxidation–reduction occurs between *dl*-$SH{\cdot}CHMe{\cdot}CO_2H$ and (III) and, under these conditions, the equilibrium (I) ⇌ (II) is established. The oxidation–reduction occurs only slowly in acid solution and the results are not reproducible. The vals. $K_1 \times 10^4$ 7·3 and 7·0 are obtained for (I) and (II), respectively, by conductivity measurements. J. W. B.

**Ethylcarolic acid**, $C_{11}H_{14}O_4$, m.p. 89°, from *Penicillium terrestre*, Jensen; also ***l*-hexolactone**, b.p. 219°.—See A., III, 71.

**Influence of carriers on catalysts.**—See A., I, 143.

**Analysis of γ-fructoside mixtures by means of invertase. V. Methylated and acetylated derivatives of crystalline α-methyl- and α-benzyl-fructofuranoside.** C. B. Purves and C. S. Hudson (J. Amer. Chem. Soc., 1937, **59**, 49—56).—The cryst. γ-methylfructoside (of A., 1934, 413) is now shown to be α-methylfructofuranoside (I), new m.p. 80·5—81°, $[\alpha]_D^{20}$ +93° in $H_2O$. When (I) is treated with $Et_2O$–TlOEt in EtOH and the solvents removed in a vac. at > room temp. a $Tl_2$ derivative is obtained; this with MeI in $Et_2O$ gives a liquid *dimethyl-α-methyl-fructofuranoside* (II), $[\alpha]_D^{20}$ +94° in $CHCl_3$, hydrolysed (0·1*N*-HCl at 100°) to a liquid (? 3 : 4-)*dimethylfructose*, $[\alpha]_D^{20}$ (in $H_2O$) −10·9° → −17·2°. (II) is methylated further (as above) to the liquid *tetramethyl-α-methyl-fructofuranoside*, $[\alpha]_D^{20}$ +115·9° in $CHCl_3$, hydrolysed to tetramethylfructofuranose (III). Crude (I) (prep. from sucrose; A., 1934, 1207) is acetylated ($Ac_2O$, NaOAc) to *α-methylfructofuranoside tetra-acetate*, m.p. 48—48·5°, $[\alpha]_D^{19}$ +88·1° in $CHCl_3$. (I) and HCl (1 mol.) in dioxan give an unstable additive compound which decomposes rapidly; the reaction is studied (in dil. solution) polarimetrically and by the Cu-reducing power. The data indicate the formation of unstable reducing Cl-compounds which undergo some change prior to further reaction with the solvent; the behaviour of (I) and sucrose with MeOH–HCl (*loc. cit.*) is thus explicable. (I) and $CH_2Ph{\cdot}OH$–HCl give a reducing substance (IV), an invertase-hydrolysable benzyl derivative (V), and *α-benzylfructofuranoside* (VI), m.p. 89°, $[\alpha]_D^{20}$ +45·7° in $H_2O$, purified through its *tetra-acetate*, m.p. 84·5—85°, $[\alpha]_D^{20}$ +64·7° in $CHCl_3$; (IV) and (V) are removed from the mixture by fermentation. (VI) is hydrolysed (0·25*N*-HCl at 20°) 16·5 times as fast as sucrose. Methylation (TlOEt method) affords a liquid $Me_2$ derivative, $[\alpha]_D^{19}$ +57·1°

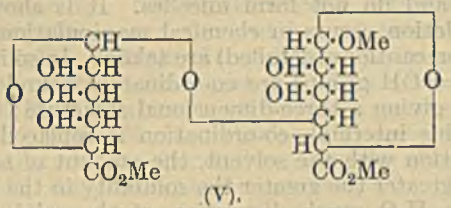
in dioxan, further methylated to the liquid $Me_4$ derivative, $[\alpha]_D^{19}$ +83·3° in $CHCl_3$, which with MeOH–HCl followed by aq. HCl gives (III). (VI) is partly converted into a $CH_2Ph$ derivative, $[\alpha]_D^{20}$ (calc.) −27±2° in $H_2O$, by $CH_2Ph$·OH–HCl. H. B.

**Anthraquinone colouring matters: galiosin; rubiadin primveroside.** R. Hill and D. Richter (J.C.S., 1936, 1714—1719).—Galiosin (I) is obtained from fresh madder root by BuOH and shown to be *purpurin-3-carboxylic acid*-1-β-*primveroside*, +6$H_2O$. *Galium verum* roots yield *rubiadin*-3-β-*primveroside* (II), m.p. 248—250° (red *Ba* and *Pb* salts), the structure of which is proved by hydrolysis to *d*(+)-xylose and rubiadin-3-glucoside. (I) is hydrolysed by cold dil. acid or alkali or in a few hr. by hot $H_2O$ to purpurin-3-carboxylic acid (III) (absorption bands in PhMe, NaOH, and $H_2SO_4$–$H_3BO_3$ detailed), also isolated from *G. verum*, *G. Mollugo*, and commercial (not fresh) madder and synthesised by condensation of $CH_2O$ and purpurin in $H_2SO_4$ to 3-*hydroxymethylpurpurin*, m.p. >300° (*Na* salt), which is oxidised to (III) by $NaNO_2$–$H_2SO_4$–$H_3BO_3$. (I) with very dil. acid gives primverose, identified by hydrolysis by 0·5*N*-$H_2SO_4$ to glucose and *d*(+)-xylose. The position of the sugar in (I) is determined by its ready hydrolysis, colour reactions, lack of reducing properties, and reduction by $Na_2S_2O_4$ and by $H_2$–colloidal Pd to munjistin. Both (I) and (II) are hydrolysed by the enzymes of *Primula officinalis* and *vulgaris*. R. S. C.

**Xylyl-β-*d*-glucoside.** T. Kitasato (J. Biochem. Japan, 1936, 24, 327—336).—The rates of hydrolysis of the xylyl- and tolyl-β-γ-glucosides by emulsin (at $p_H$ 5·0 and 30°) give an order (2 : 3-xylyl- and 2-tolyl-β-*d*-glucoside greatest, respectively) which is exactly the reverse of the order (2 : 6-xylyl- and 4-tolyl-β-*d*-glucoside greatest, respectively) given by acid hydrolysis (in 0·02*N*-HCl at room temp.). The following β-*d*-glucosides were prepared ($[\alpha]_D^{20-22}$ in $H_2O$): 2 : 3-*xylyl*-, m.p. 190—191°, [α] −65·1°; 2 : 5-*xylyl*-, m.p. 170°, [α] −68·8°; 3 : 5-*xylyl*-, m.p. 203—204°, [α] −67·7°; 3 : 4-*xylyl*-, m.p. 173—174°, [α] −66·9°. F. O. H.

**Glycyrrhizin. I.** W. Voss, P. Klein, and H. Sauer. **II. Novel disaccharide as sugar component of glycyrrhizin.** W. Voss and J. Pfirschke (Ber., 1937, 70, [*B*], 122—132, 132—137).—I. Successive crystallisations of "glycyrrhizinium ammoniacale" from AcOH and EtOH followed by extraction of the product with $Et_2O$ gives *$NH_4$ $H_2$ glycyrrhizate* (I), $C_{42}H_{65}O_{10}N$, $[\alpha]_D^{18}$ +43·3° in $H_2O$, converted by 1% $H_2SO_4$ into glycyrrhizic acid (II), $C_{42}H_{62}O_{16}$,2$H_2O$, $[\alpha]_D^{20}$ +58·5° in abs. EtOH (*$K_3$*, $[\alpha]_D^{19}$ +44·8° in $H_2O$, and *$K$ $H_2$*, $[\alpha]_D^{19}$ +43·5° in $H_2O$, salts), the composition of which is most surely deduced from analysis of the salts. (II) is hydrolysed by 1% $H_2SO_4$ at 150—155° to α-*glycyrrhetic acid* (III), $C_{30}H_{46}O_4$, m.p. 283°, $[\alpha]_D^{20}$ +140° in abs. EtOH {*Na* salt, m.p. 303—304°, $[\alpha]_D^{22}$ +130° in abs. EtOH; *K* salt, m.p. 293°, $[\alpha]_D^{20}$ +92·4° in abs. EtOH; *Ac* derivative, m.p. 308°, $[\alpha]_D^{22}$ +122° in abs. EtOH; *Me* ester (IV), m.p. 229°, $[\alpha]_D^{20}$ +106° in abs. EtOH; *Et* ester, m.p. 204°, $[\alpha]_D^{21}$ +116° in abs. EtOH, obtained from (II) and MeOH–HCl or by alcoholysis of (II). (IV) contains 1 OH and does not react with $NH_2OH$,HCl or $NH_2$·CO·NH·$NH_2$,HCl and NaOAc}. Treatment of (IV) with KOH–EtOH–$H_2O$ at room temp. gives unchanged material and β-*glycyrrhetic acid*, $C_{30}H_{46}O_4$, m.p. 296°, $[\alpha]_D^{21}$ +86° in abs. EtOH (*Me* ester, m.p. 251°, $[\alpha]_D^{20}$ +90° in abs. EtOH; *Ac* derivative, m.p. 291°, $[\alpha]_D^{20}$ +109° in abs. EtOH). H. W.

II. Hydrolysis of (II) by 1% aq. $H_2SO_4$ is accompanied by an unusually ready decomp. of the uronic acids formed, which also occurs when (I) is heated with MeOH–HCl on the water-bath. The best conditions are secured when (II) is treated with MeOH–HCl at ≯40°, whereby a *$Me_3$* 1-*methyldihexuronate*, (V), m.p. 223°, $[\alpha]_D^{18}$ +26·5° in $H_2O$, is obtained. It is converted by aq. $Ba(OH)_2$ at room temp. into the corresponding acid [*brucine* salt, anhyd. and +5$H_2O$, m.p. 206° (decomp.) after becoming yellow at 200°], also obtained by use of 2% $H_2SO_4$ at 80°. The



(V).

mother liquors from (V) contain non-cryst. substances hydrolysed by 2% $H_2SO_4$ at 80° to an acid which gives a *Ba* salt, $C_{12}H_{18}O_{14}Ba$, $[\alpha]_D^{19}$ −5·2°, and a *brucine* salt, anhyd. and +2·5 $H_2O$, m.p. 182° (decomp.) after darkening at 170°, $[\alpha]_D^{19}$ −26·9° in $H_2O$. H. W.

**Polysaccharide synthesised by a soil micro-organism.** W. Z. Hassid and W. L. Chandler (J. Biol. Chem., 1937, 117, 203—207).—A non-spore-bearing bacterium from a mud brick (A.D. 400) from the West Egyptian desert when propagated in a medium containing 0·2% of mannitol as sole org. C source produced a non-reducing, N-free *polysaccharide* (I), $[\alpha]_D$ +140° in $H_2O$ (*triacetate*, $[\alpha]_D$ +148° in $CHCl_3$, mol. wt. 2675—2980), which gave a 96·5% yield of glucose on acid hydrolysis. The I val. of (I) (cf. Bergmann *et al.*, A., 1930, 457) was 2·5. Hence it contained approx. 9—10 anhydroglucose units. W. McC.

**Highly polymerised compounds. CL. Constitution of starch.** H. Staudinger and E. Husemann (Annalen, 1937, 527, 195—236; cf. A., 1936, 710).—In starch solutions the ageing effects, the influence of electrolytes on η, and aberrations from the Hagen–Poiseuille law are due to the P content and are not observed with P-free products. The main reasons for belief in the micellar nature of starch solutions are thus invalid; only the low apparent mol. wts. are still inexplicable on the macro-mol. theory, but this is so also for other polysaccharides. P-free starch is unaffected by dissolution and repptn. The differences between different starches are due to the differing average size of the mol., but no one starch is a chemical individual; all are mixtures of polymerides, forming a polymeric-homologous series. If potato-starch is heated with 2*N*-HCl at 100° for 1·75—3·5 min., cooled for 30 sec. in ice, and poured into MeOH, the ppt. is a starch, the degree of degradation

of which depends on the time of heating. It is freed from P by addition of MeOH to its solution in cold $HCO_2H$ until the ppt. becomes granular; the P-containing amylopectin is first pptd. The final products obtained are not homogeneous, but can be fractionally pptd. The mol. wt. of the variously degraded starches, measured osmotically through an ultracellafilter in $HCO{\cdot}NH_2$, by extrapolation (van 't Hoff's law is not obeyed) are 30,000—153,000; $\eta$ is measured in $HCO{\cdot}NH_2$ and leads to the same $K_m$, $0{\cdot}63 \times 10^{-4}$, for all fractions. The triacetates (prep. by careful treatment with $Ac_2O$–$C_5H_5N$), the starches obtained therefrom by NaOMe (rigid absence of $O_2$), the Me ethers (prep. by Haworth's method; about 1·5 OMe), the Me ether acetates, and the nitrates (about 2·5 $NO_2$) are shown by the same methods, but in other solvents, to have the same mol. wt. and $K_m$. This is regarded as final proof that the products are macromols. and do not form micelles. It is shown that degradation occurs in chemical manipulations unless rigid precautions (detailed) are taken. In solid starch the free OH groups are co-ordinately bound to each other, giving a three-dimensional structure; in solution this intermol. co-ordination is replaced by co-ordination with the solvent, the amount of solvation being greater the greater the solubility in the solvent. In hot $H_2O$ much disruption of the solid linkings occurs with formation of hydrated mols., which, however, are unstable in cold $H_2O$; thus, in aq. solutions gradual decomp. of the hydrate occurs with liberation of OH and consequent formation of OH–OH linkings, leading to pptn. of solid starch. The $HCO{\cdot}NH_2$ solvate is more stable and solutions in $HCO{\cdot}NH_2$ are thus stable. These views do not apply to P-containing starch, which is heteropolar, for, firstly, the lyophilic groups increase the solubility and, secondly, several macro-mols. may be bound by one P. P-free starch is a branched-chain mol., each 2—4 glucose residues of the central chain carrying a side-chain of about 20 glucose units attached glucosidically to the O at 3 or 6. This accounts for Haworth's yields of 2 : 3 : 4 : 6-tetramethylglucose (derived from the terminal unit of each branch) and of 2 : 6-dimethylglucose (derived from the unit of the centre chain to which the branch is attached), which are thus reconciled with the macro-mol. theory. It accounts also for the fact that cellulose (a straight-chain macromol.) has about 10 times as a long a chain (as revealed by $K_m$) as has starch of the same mol. wt. and consequently has a different colloidal behaviour. The least degraded starch examined contained about 950 glucose units; natural P-free starch has a macro-mol. of >2000 units; P-containing starch is much more complex. R. S. C.

**Hydroxyethyl ethers of cellulose. II. Higher ethers.** P. P. Schorigin and J. A. Rimaschevskaja (J. Gen. Chem. Russ., 1936, 6, 1632—1638).—*Cellulose dihydroxyethyl ether* (I) is prepared by soaking the mono-ether (II) in 33% NaOH, and treating the product with $(CH_2)_2O$ in $COMe_2$; the *trihydroxyethyl ether* (III) is prepared similarly from (I). (II) is sol. in $H_2O$ but not in org. solvents, (I) is sol. in $H_2O$ and EtOH, but not MeOH, and (III) is sol. in $H_2O$, EtOH, and MeOH; all are insol. in $COMe_2$. The $\eta$ of the solutions falls in the order (II) > (I) > (III). The ethers are readily acetylated by AcOH in presence of catalysts ($H_3PO_4$, $ZnCl_2$). Various nitrates of the ethers are described. R. T.

**Preparation and properties of dideuteromethylamine.** H. J. Emeléus and H. V. A. Briscoe (J.C.S., 1937, 127—130).—$NH_2Me$,HCl treated with successive quantities of $D_2O$, followed by liberation of the base with CaO yields *dideuteromethylamine*, b.p. $-5{\cdot}2\pm0{\cdot}1°$, m.p. $-89{\cdot}2\pm0{\cdot}1°$. J. D. R.

**Poly-membered heterocyclic compounds. XI. Preparation of the 14-, 15-, and 17-membered, cyclic imines from aliphatic bromoamines. Survey of the properties of poly-membered, cyclic imines.** L. Ruzicka, G. Salomon, and K. E. Meyer [with M. Furter and H. Gysel] (Helv. Chim. Acta, 1937, **20**, 109—128).—The requisite bromoalkylamine dissolved in 30 mol.-% EtOH or $Pr^{\beta}OH$ is treated with a slight excess of alkali. With increasing concn. the yield of cyclic imine diminishes in favour of the OH-amine, whereas that of polymeric products remains const. The relationship between *d* and no. of members of cyclic imines and their *N*-Me derivatives is closely similar to that of carbocyclic compounds, and shows a max. *d* for a medium no. of C atoms. The mol. refraction of cyclic imines is normal and the m.p. of those solid at room temp. show similar variation and similar abs. vals., as do the cyclic ketones with the same no. of C atoms. The piperidine odour of cyclic imines gradually gives place to that of decay, which is very pronounced with a 9-membered ring. With the 14-membered ring a feeble basic and pronounced musk-like odour are observed. With the 15-membered ring the musk odour is very marked; it reaches a max. with the 16- and 17-rings and is weakened in the 18-ring. *N*-Me and double linking have little effect on the odour, which appears to be governed by the no. of C in the ring, one or two hetero-members of which merely cause a modification. $[CH_2]_{15}NH$ is a powerful local anæsthetic but its hydrochloride and acetate are very irritating. A similar but weaker action is shown by $[CH_2]_{14}NH$ but not by $[CH_2]_{16}NH$, $[CH_2]_{17}NH$, or $[CH_2]_{15}NMe$. αχ-Dibromotetradecane is converted by $o$-$C_6H_4{<}^{CO}_{CO}{>}NK$ under $N_2$ at 180° into *χ-bromotetradecylphthalimide*, b.p. about 250°/0·1 mm., m.p. 68—69° (corr.), hydrolysed to *χ-bromotetradecylamine hydrobromide*, m.p. 147—150° (corr.), which is transformed by NaOH in $Pr^{\beta}OH$ into *tetradecamethyleneimine*, b.p. 97—98°/0·05 mm., m.p. 47—48° (corr.) (yield 42%), *χ-hydroxytetradecylamine*, m.p. 83—84° (corr.) [*hydrochloride*; *carbamide* derivative, $C_{15}H_{32}O_2N_2$, m.p. 103—104° (corr.)] (yield 21%), and dimeric *products* [*dihydrobromide*, $C_{18}H_{60}N_2Br$, m.p. about 215° (corr.; decomp.)] (yield 24%). *ν-Bromotridecylphthalimide*, b.p. about 230°/0·1 mm., m.p. 54—55° (corr.), is hydrolysed to *γ-bromotridecylamine* [*hydrobromide*, m.p. 155° (corr.)], whence *tridecamethyleneimine*, b.p. 65°/0·05 mm., m.p. 38—39° (corr.) [*hydrochloride*, m.p. 150—151° (corr.)], *ν-hydroxytridecylamine*, m.p. 84° (corr.), and the dimeride [*dihydrochloride*, m.p. >300°; $(NO)_2$-*derivative*, m.p. 86—

87°]. λ-*Bromoundecylphthalimide*, b.p. about 200—210°/0·1 mm., m.p. about 43° (corr.), yields λ-*bromoundecylamine hydrobromide*, m.p. 154—155° (corr.), from which little if any of the corresponding cyclic imine could be obtained; λ-*hydroxyundecylamine hydrochloride*, m.p. 145° (corr.), and the *dihydrochloride*, $C_{22}H_{48}N_2Cl_2$, decomp. >250°, of the dimeric base are described. λ-*Iodoundecylamine hydrochloride* has m.p. 139—140° (corr.). π-Bromohexadecylamine hydrobromide yields hexadecamethyleneimine, m.p. 58—59° (corr.), π-*hydroxyhexadecylamine*, m.p. 90—91° (corr.) [*hydrochloride*, m.p. 152—153° (corr.)], and very little dimeride. The following substances are incidentally described: *octamethyleneimine platinichloride*, m.p. 187—188° (corr.); trimethyleneimine, b.p. 62°/730 mm.; *methyl-pentadeca-*, b.p. 93—95°/0·05 mm. [*picrate*, m.p. 93—94° (corr.); *hydrochloride*, m.p. 215—216° (corr.)], obtained by means of $CH_2O$ and $HCO_2H$, *-penta-*, b.p. 103—105°/724 mm., *-octa-*, b.p. 62—63°/16 mm., *-hexadeca-*, b.p. 124—127°/0·25 mm., and *-heptadeca-methyleneimine*, b.p. 126—129°/0·05 mm. H. W.

**Compounds of nitroprussides and hexamethylenetetramine.** E. Voyatzakis (Compt. rend., 1936, **203**, 1365—1367).—An alkali or alkaline-earth salt in conc. solution with $(CH_2)_6N_4$ and Na nitroprusside affords compounds, $M^{II}Fe(CN)_5{\cdot}NO,2(CH_2)_6N_4,xH_2O$ [$M^{II}$ = *Ca* ($x$ = 8), *Sr* ($x$ = 6), *Ba* ($x$ = 4), *Mg* ($x$ = 7), $K_2$ ($x$ = 3), $Na_2$ ($x$ = 4), and $Li_2$ ($x$ = 3)], whereas in dil. solutions $M^{II}Fe(CN)_5NO,(CH_2)_6N_4,xH_2O$ [$M^{II}$ = *Ca* ($x$ = 4), *Sr* ($x$ = 5), and *Mg* ($x$ = 6)] are formed. These compounds are stable in air and are decomposed by acids. J. L. D.

**Acetyltrideuterocholine.** H. Erlenmeyer and H. Lobeck (Helv. Chim. Acta, 1937, **20**, 142—143).—The action of K–Na on a solution of $CCl_3{\cdot}CO_2K$ in $D_2O$ gives $CD_3{\cdot}CO_2K$, whence $CD_3{\cdot}COCl$, b.p. 47—51°, and *trideuteroacetylcholine bromide*, $CD_{2\cdot 61}H_{036}{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Br$, which is distinctly less active physiologically than choline. H. W.

**Reduction products from sugars and aliphatic amines.** P. Karrer and E. Herkenrath (Helv. Chim. Acta, 1937, **20**, 83—86).—Treatment of glucose with anhyd. $NH_2Me$ at room temp. and hydrogenation (Pd on norite) of the product at 60°/23 atm. gives *N*-methyl-l-glucosamine, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}NHMe$, m.p. 126°, $[\alpha]_D^{18}$ −18·5° ±1·0° in $H_2O$, transformed by MeI in boiling EtOH into *trimethyl*-d-*sorbitylammonium iodide*, m.p. 111°, *N*-Ethyl-l-*d*-glucosamine, m.p. 137°, $[\alpha]_D^{18}$ −17·0°± 1·0° in $H_2O$, gives a *hydrobromide*, m.p. 108°. N-*Ethyl*-d-l-*galactosamine*, m.p. 145·5°, $[\alpha]_D^{18}$ −6·3°± 1·0° in $H_2O$, and N-*methyl*-d-*mannosamine*, m.p. 135°, $[\alpha]_D^{18}$ +8·2°±1·0° in $H_2O$, are obtained analogously, whereas arabinose affords *di*-l-*arabitylamine*, m.p. 172°, $[\alpha]_D^{18}$ −10·2°±1·0° in $H_2O$ (*hydrochloride*, m.p. 200°). H. W.

**Derivatives of phenylglucosamine.** P. Karrer and E. Salomon (Helv. Chim. Acta, 1937, **20**, 90—96).—Phenylglucosamine (I), $CH_2Cl{\cdot}CO_2H$, and $Na_2CO_3$ in boiling $H_2O$ give *Na phenylglucosaminoacetate*, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}NPh{\cdot}CH_2{\cdot}CO_2Na$ (+1$H_2O$), m.p. 120—130° and, after re-solidification, m.p. 210—212°. *Phenylglucosaminoacetic acid*, m.p. 139—140° (decomp.), readily loses $CO_2$ with formation of *phenylmethylglucosamine*, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}NPhMe$, m.p. 150—151°. If (I) is heated with $CH_2Cl{\cdot}CO_2H$ and only sufficient $Na_2CO_3$ to neutralise the liberated HCl, *phenylglucosaminoacetolactone*,

$$CH_2\begin{matrix}NPh{\cdot}CH_2\\CO\text{——}O\end{matrix}>CH{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}OH,$$

m.p. 205—206°, is produced. Gradual addition of I to a solution of (I) and $KHCO_3$ in $H_2O$ gives p-*iodophenylglucosamine*, which with $CH_2Cl{\cdot}CO_2H$ and $Na_2CO_3$ affords *Na* p-*iodophenylglucosaminoacetate*, m.p. 228—230°, also +1$H_2O$, m.p. (indef.) 130—140°, and +1EtOH; the corresponding free acid appears to break down immediately into $CO_2$ and p-*iodophenylmethylglucosamine*, decomp. 152° after becoming blue at 140°. H. W.

**Amino-acids, acyl-amino-acids, dipeptides, acyl-dipeptides, and derivatives of these compounds. II. Effects of irradiation with cathode rays and ultra-violet light.** A. J. Allen, R. E. Steiger, M. A. Magill, and R. G. Franklin (Biochem. J., 1937, **31**, 195—204).—By spectroscopic examination, it was found that solutions of several $NH_2$-acids, dipeptides, and derivatives in $H_2O$ or 95% EtOH undergo a change when irradiated by cathode rays or ultra-violet light regardless of whether the constituent $NH_2$-acids are primary, *sec.*, or *tert.* $NH_3$ is liberated in every case. Possible reaction mechanisms are given. The absorption curves of acetyl-dipeptides are shifted towards the red by ultra-violet light and cathode rays, and the effect of the latter on acetyl-dipeptides in which the OH of the $CO_2H$ is replaced by NHPh is usually < that on the free acid. J. N. A.

**Detection and colorimetric determination of glycine with the alloxan reagent.** G. Denigès (Bull. Trav. Soc. Pharm. Bordeaux, 1935, **73**, 161—168; Chem. Zentr., 1936, i, 2153).—Details of a colour reaction are given. H. N. R.

**Micro-crystal reaction of glycine.** G. Denigès (Bull. Trav. Soc. Pharm. Bordeaux, 1935, **73**, 168—172; Chem. Zentr., 1936, i, 2153).—A reaction with phosphotungstic acid is described. H. N. R.

**Diamino-acid, canavanine. V. Synthesis of canaline.** M. Kitagawa (J. Biochem. Japan, 1936, **24**, 107—112; cf. A., 1936, 1236).—α-Amino-γ-hydroxybutyric acid (A., 1934, 61) yields a Bz derivative, m.p. 140—144°, which in 1% HCl at 70° affords the corresponding *lactone*, m.p. 139°, $[\alpha]_D^{17}$ −28° in EtOH, which with HI–EtOH gives *Et γ-iodo-α-benzamidobutyrate*, m.p. 119—120°; with benzhydroxamic acid, this substance affords $NHBz{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NHBz){\cdot}CO_2Et$, hydrolysed (10% HCl) to canaline, which is therefore $NH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$. F. O. H.

**Heptyl carbamidoacetate**, m.p. 98—99°, and **α-carbamidohexoate**, m.p. 70—71°, and **heptyl** ester, m.p. 123—125° of **carbamidoacetylglycine**. —See A., I, 134.

**Methods of hydrolysis of protein: shortening the time for determining cystine.** M. X. Sul-

LIVAN and W. C. HESS (J. Biol. Chem., 1937, **117**, 423—428).—The protein is hydrolysed by aq. HCl in the presence of $TiCl_3$, which lessens humin formation, and decreases the time necessary for cysteine (I) liberation. (I) may be determined directly, or after oxidation to cystine. F. A. A.

**N-Substituted aliphatic amides.** G. F. D'ALELIO and E. E. REID (J. Amer. Chem. Soc., 1937, **59**, 111—112).—The following $AlkCO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, $AlkCO{\cdot}N(CH_2{\cdot}CH_2{\cdot}OH)_2$, and $AlkCO{\cdot}NH{\cdot}CH_2{\cdot}CHMe{\cdot}OH$ are prepared from $AlkCO_2Et$ and the $NH_2$-alcohols at the b.p. (lower members) or 160°: form-, b.p. 150—155°/2 mm., acet-, b.p. 155—160°/2—3 mm., m.p. 40° (lit. 63—65°), propion-, b.p. 160—168°/1—2 mm., *butyr*-, b.p. 155—162°/1—1·5 mm., *valer*-, b.p. 192°/6 mm., m.p. 32°, *hexo*-, m.p. 46°, *hepto*-, m.p. 53·6°, *octo*-, m.p. 63·2°, *nono*-, m.p. 71·6°, *deco*-, m.p. 77·1°, *undeco*-, m.p. 84·8°, *dodeco*-, m.p. 78·2°, *trideco*-, m.p. 91·8°, *tetradeco*-, m.p. 87·4°, *pentadeco*-, m.p. 97°, *hexadeco*-, m.p. 94·4°, *heptadeco*-, m.p. 99·2°, and *octadeco*-, m.p. 96·1°, -β-*hydroxyethylamides*; *undeco*-, m.p. 34·9°, *dodeco*-, m.p. 38·7°, *trideco*-, m.p. 45·3°, *tetradeco*-, m.p. 47·9°, *pentadeco*-, m.p. 50·9°, *hexadeco*-, m.p. 65·1°, *heptadeco*-, m.p. 67·9°, and *octadeco*-, m.p. 69·7°, -ββ′-*dihydroxydiethylamides*; *nono*-, m.p. 53·8°; *deco*-, m.p. 58·1°, *undeco*-, m.p. 63·1°, *dodeco*-, m.p. 66·6°, *trideco*-, m.p. 71°, *tetradeco*-, m.p. 74·2°, *pentadeco*-, m.p. 75·1°, *hexadeco*-, m.p. 78·2°, *heptadeco*-, m.p. 82°, and *octadeco*-, m.p. 86·1°, -β-*hydroxypropylamides*. H. B.

**N-Methylamides [of fatty acids].** G. F. D'ALELIO and E. E. REID (J. Amer. Chem. Soc., 1937, **59**, 109—111).—$HCO{\cdot}NHMe$, b.p. 131°/90 mm., m.p. —5·4° (*hydrochloride*, m.p. 82·8—85°), and $NHMeAc$, b.p. 140·5°/90 mm., m.p. 28° (*hydrochloride*, m.p. 67·2—69·4°); N-*Br*-, m.p. 123·5°, -*NO*-, b.p. 116·3°, m.p. —8·5°, and -Ac, b.p. 194·2°, m.p. —46·8°, derivatives), are prepared (method: A., 1931, 831) from the acid and $NH_2Me$. The following are obtained by addition of the acid chloride to conc. aq. $NH_2Me$ (3 mols.) at —20° to room temp.: propion-, b.p. 146°/90 mm., m.p. —43° (*hemihydrochloride*, m.p. 84—85°), butyr-, b.p. 156°/90 mm., m.p. —5·2° (*hemihydrochloride*, m.p. 106·4—108°), valer-, b.p. 169°/90 mm., m.p. —25·5° (*hemihydrochloride*, m.p. 17—20°), hexo-, b.p. 183°/90 mm., m.p. 13·6° (*hemihydrochloride*, m.p. —1° to 3°), hepto- (I), b.p. 151°/15 mm., m.p. 14° (lit. 9°) (*hemihydrochloride*, m.p. 32—34°), octo- (II), b.p. 161·5°/15 mm., m.p. 38·9° (*hemihydrochloride*, m.p. 38—40°), nono- (III), b.p. 175°/15 mm., m.p. 39·1°, deco-, m.p. 57·3°, undeco-, m.p. 56°, dodeco-, m.p. 68·4°, trideco-, m.p. 68·2°, tetradeco-, m.p. 78·4°, pentadeco-, m.p. 78·3°, hexadeco-, m.p. 85·5°, heptadeco-, m.p. 84·8°, and octadeco-, m.p. 92·1°, -methylamides. The m.p. alternate similarly to those of the corresponding acids. (I)—(III) are local anæsthetics. H. B.

**[Thiocyanogen and its addition to unsaturated fatty acids.]** L. BIRCKENBACH and J. GOUBEAU (Ber., 1937, **70**, [*B*], 171).—A question of priority against Kaufmann and Oetringhaus (this vol., 47). H. W.

**Determination of thiocarbamide.** R. CUTHILL and C. ATKINS (J.S.C.I., 1937, **56**, 5—8T).—The reactions of $CS(NH_2)_2$ with various oxidising agents in solution have been studied. Oxidation with I in alkaline solution, $Ce(SO_4)_2$, or $K_2Cr_2O_7$ may be utilised for determination, the $CS(NH_2)_2$ being oxidised to $CO(NH_2)_2$ and $H_2SO_4$. Another method of determination depends on the reaction of $CS(NH_2)_2$ with excess of standard $AgNO_3$ in ammoniacal solution, forming $Ag_2S$ and $CO(NH_2)_2$. After reaction, the mixture is acidified with $HNO_3$ and filtered, the excess of $AgNO_3$ in the filtrate being titrated with standard KCNS solution. R. C.

**βγ-Ethylenic nitriles and their derivatives.** R. DELABY (Compt. rend., 1936, **203**, 1521—1523).—*Vinyl-laurylcarbinol*, m.p. 27—28°, *vinyl*-iso*butyl*, -sec.-*octyl*-, and -βζ-*dimethyloctyl-carbinol* are prepared as described previously (A., 1933, 808). These and other similar compounds are converted by $PBr_3$ into allyl bromides (I) (cf. A., 1928, 1112), the straight-chain more easily than the branched, which consist mainly of the *trans*-isomerides (cf. A., 1935, 197). (I) with $Cu(CN)_2$ (cf. A., 1922, i, 817) afford allyl nitriles, converted by boiling 50% $H_2SO_4$ into γ-lactones and thence with dil. NaOH or $Ba(OH)_2$ into βγ-unsaturated acids. Acids > $C_{10}$ are not obtained pure as they are isomerised to the αβ-unsaturated form by the more severe conditions necessary for the hydrolysis. J. L. D.

**Maleo- and fumaro-nitriles.** J. JENNEN (Bull. Acad. roy. Belg., 1936, [v], **22**, 1169—1184).—When heated with CuCN at 165—170°, *cis*-$C_2H_2I_2$ affords *maleonitrile* (I), m.p. 32·2—32·6°, together with some fumaronitrile (II), m.p. 96—96·4°, obtained from the *trans*-$C_2H_2I_2$ formed by thermal isomerisation. Hydrolysis of (I) with $H_2SO_4$ (*d* 1·84) affords the corresponding diamide but (II) gives maleamic acid. At 13° 0·1*N*-NaOH eliminates 1 mol. of HCN from 2 mols. of either (I) or (II) [more rapidly from (I)], but the reaction is more complex at higher temp. The *d* and *n* vals. at various temp. are recorded: the [*M*] exaltation for (I) and (II) is approx. double that for *iso*crotono- and crotono-nitrile, respectively. J. W. B.

**Maleo- and citracono-nitriles.** P. BRUYLANTS and J. JENNEN (Bull. Acad. roy. Belg., 1936, [v], **22**, 1141—1143).—By comparison with the genuine nitriles (preceding abstract) the supposed maleo- and citracono-nitrile obtained by the action of $P_2O_5$ on the amides (de Wolf *et al.*; van de Straete, A., 1935, 737) are shown to be the *imide*, only 1 mol. of $NH_3$ being eliminated in these cases. With fumar- and mesacon-amide normal nitrile formation occurs. J. W. B.

**Pyrophosphoric ester and crystallised salts of *l*-phospholactic acid.** T. WAGNER-JAUREGG and H. GRIESSHABER (Ber., 1937, **70**, [*B*], 8—11).—*Pyrophosphoryl chloride* (I), b.p. 73°/1 mm., 88—92°/8 mm., best obtained by the action of nitrous fumes on $PCl_3$ at 0°, does not appear to react smoothly with muscle-adenylic acid (in presence of $H_3BO_3$) or $OH{\cdot}CHMe{\cdot}CO_2H$ in $C_5H_5N$; the method is unsuited to the prep. of unsymmetrical esters. Brucine hydrochloride and K *l*-phospholactate give the *salt*, $C_3H_7O_6P,(C_{23}H_{26}O_4N_2)_3,12H_2O$, m.p. 153—154° (corr.; block), whilst Ba *l*-phospholactate and brucine sul-

phate in $H_2O$ afford the *compound*, $C_3H_7O_6P,(C_{23}H_{26}O_4N_2)_2,4H_2O$, anhyd. m.p. 166° (corr.; block), $[\alpha]_D^{24}$ −29·7° in $H_2O$, transformed into the corresponding *Ba* salt, $[\alpha]_D^{23}$ −13·6° in 2*N*-HCl. *Acridinium* l-*phospholactate*, m.p. 269—271° (sealed tube), is described. H. W.

**Preparation of phosphoglyceric and glycerophosphoric acids by decomposition of hexose diphosphate by yeast.**—See A., III, 70.

**Reducing action of metal alkyls, especially of aluminium and boron alkyls.** H. Meerwein, G. Hinz, H. Majert, and H. Sönke (J. pr. Chem., 1936, [ii], **147**, 226—250).—Aldehydes (R·CHO) and ketones, when heated with $AlEt_3$ in $Et_2O$ (A., 1923, i, 289) and then treated with dil. $H_2SO_4$, are reduced to the corresponding alcohol with evolution of $C_2H_4$, or alkylated and converted into the alcohol CHREt·OH, the relative proportions of these alcohols depending on the nature of the aldehyde or ketone. Thus, chloral, bromal, COPh·$CCl_3$, mono- and tri-chloroacetone give the corresponding alcohol in good yield, benzil gives benzoin (yield 40%), but R·CHO (R = Ph, *p*-$C_6H_4Cl$, *p*-OMe·$C_6H_4$·, and CHPh:CH·) gives mainly the alcohol CHREt·OH. The colorations formed when the foregoing aldehydes and ketones are mixed with $AlEt_3$–$Et_2O$ are recorded, and their formation supports the view that additive complexes are first formed. With $BEt_3$ reaction occurs less readily, and only the corresponding alcohol is formed, no alkylation taking place. The primary product of the reaction is an ester of diethylboric acid and is readily hydrolysed by $H_2O$ to the alcohol. The following *esters* of $BEt_2$·OH have thus been prepared: ββ*β-trichloroethyl* (I), b.p. 78—79°/12 mm.; *benzyl*, b.p. 114—115°/16 mm.; and p-*chlorobenzyl*, b.p. 141·5—142°/16 mm. $BEt_3$–$Et_2O$ with bromal at 35—40° gives ββ*β-tribromoethyl diethylborate* (II), b.p. 117—119°/12 mm.; at 90°, however, the main product is *dibromovinyl diethylborate*, $BEt_2$·O·CH:$CBr_2$ (III), b.p. 98—99°/11 mm. (decomposed by $H_2O$ to $CHBr_2$·CHO,$H_2O$), and some EtBr, and with excess of bromal at 120° the main product is a mixture of *di*(*dibromovinyl*) *ethylborate*, $BEt(O·CH:CBr_2)_2$ (IV), b.p. 140—143°/3 mm., and a little *dibromovinyl* ββ*β-tribromoethyl ethylborate*, $BEt(O·CH:CBr_2)·CH_2·CBr_3$ (V). (IV) and a little (V) are also obtained from (III) and bromal at 120°, and (V) and a little *di*-(ββ*β-tribromoethyl*) *ethylborate*, $BEt(O·CH_2·CBr_3)_2$ from (II) and bromal at 135°. These reactions occur with evolution of $C_2H_2$ or EtBr. The esters (I) and (II) were also obtained directly from the appropriate alcohol and $BEt_3$. $ZnEt_2$ and *p*-$C_6H_4Cl$·CHO give *p*-$C_6H_4Cl·CH_2$·OH and some *p*-$C_6H_4Cl$·CHEt·OH, whilst MgEtBr gives the latter product only. No reaction occurs between $SnEt_4$ and chloral or bromal. The foregoing results support the view that the tendency for alkylation to occur instead of simple reduction increases with increasing electropositive character of the metal (cf. this vol., 83). H. G. M.

**Diethylboric acid.** H. Meerwein and H. Sönke (J. pr. Chem., 1936, [ii], **147**, 251—255).—Diethylboric acid (I), m.p. −51° to −48°, b.p. 35—37°/75 mm. (cf. J.C.S., 1876, 469), is best prepared by hydrolysis of its *p*-chlorobenzyl ester (see above) with $H_2O$, followed by high-vac. distillation. It is not spontaneously inflammable, and when distilled at atm. pressure decomposes partly to *diethylboron oxide*, $(BEt_2)_2O$, b.p. 142—144°, the temp. rising from about 80° to 150°. *Diethylboracetate*, m.p. 86—87°, and *diethylbor*-o-*chlorobenzoate*, m.p. 50—52°, b.p. 96—97°, are obtained when $BEt_3$ is mixed with the appropriate acid. (I) can be titrated in MeOH–$H_2O$ in presence of mannitol as a monobasic acid; a quadricovalent salt of the type $[BEt_2(OH)(OMe)]M$ (M = univalent metal) is formed, but could not be isolated. Contrary to the observations of Frankland (Ann. Chem., 1862, **124**, 137) $BEt_3$ continues to react with acids, evolving $C_2H_6$, after the first Et has been replaced; and intermediate products in the progressive autoxidation of $BEt_3$ to $B(OEt)_3$ could not be isolated. H. G. M.

**Free radicals in the dissociation of gaseous metal alkyls by light.**—See A., I, 145.

**Disymmetrical synthesis in the case of complex metallic salts. II.** I. Lifschitz (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 1192—1199).—Glutamic acid or Na monoglutamate (I) on boiling with $Co(OH)_3$ yields a mixture of the α- and β-*D*-modifications of the *acid* $[Co(d\text{-glut.})_3]H_3$ (II) (glut. = $NH_2·CH(CO_2·)[CH_2]_2CO_2$) and its Na salt. These are separable through the Ag and Pb salts of the red β-form being insol., and those of the violet α-form sol., in boiling $H_2O$. These are reconvertible into the very sol. Na salts by NaCl and $Na_2SO_4$ solutions. If, however, an aq. solution of $Co(NO_3)_2$ (1 mol.), (I) (3 mols.), and NaOH (2 mols.) is oxidised by a current of air at room temp., a similar violet solution is obtained containing the α- and β-*L*-forms of (II). These are separable through the Ag salt of the violet α-form being sol., and that of the red β-form insol., in hot $H_2O$ but yielding a dull red *compound* $[Co(d\text{-glut.})_3][Ag(C_5H_5N)_2]_3$ with aq. $C_5H_5N$. The rotatory dispersions of these compounds, which lead to the assignment of the constitutions given above, are shown in graphical form. J. W. S.

**Theory of isomerisation of cyclic compounds.** A. A. Nikolaev (J. Gen. Chem. Russ., 1936, **6**, 1587—1592).—Theoretical. R. T.

**Synthesis of mono-substituted homologues of *cyclo*pentane with branched side-chains.** B. A. Kazanski, A. F. Plate, and K. M. Gnatenko (J. Gen. Chem. Russ., 1936, **6**, 1593—1597).—*iso*Propyl-, *sec.*-butyl-, sec.-*amyl*-, b.p. 174—176°, and *benzhydryl*-cyclo*pentane*, m.p. 32·5—33°, were obtained by catalytic hydrogenation (Pt or Pd) of dimethyl-, methylethyl-, diethyl-, or diphenyl-fulvene, respectively. R. T.

**Action of aluminium chloride on di*cyclo*hexyl.** J. K. Juriev, P. J. Levina, and A. I. Kudrjavcev (J. Gen. Chem. Russ., 1936, **6**, 1500—1505).—Di*cyclo*hexyl, obtained in good yield from $Ph_2$ and $H_2$ (Ni–$Al_2O_3$ catalyst at 100°/90 atm.), when heated at 160—290° in presence of $AlCl_3$ yields a mixture of methyl*cyclo*hexane, *cyclo*pentane, $EtPr^{\beta}$, and $CMe_4$. R. T.

**Mechanism of irreversible catalysis of unsaturated cyclic hydrocarbons with a double**

**linking in the side-chain.** P. J. Levina, D. A. Petrov, and D. M. Trachtenberg (J. Gen. Chem. Russ., 1936, 6, 1496—1499).—The mixtures *cyclo*hexane–diallyl, methyl*cyclo*hexane–$\Delta^{\alpha}$-heptene, and dimethyl*cyclo*hexane–$\Delta^{\alpha}$-*iso*octene and -allylbenzene are converted by Pt–C catalyst at 200—300° into saturated products. Formation of *cyclo*hexenes as intermediate products is postulated. R. T.

**Effect of structure on the reactions of benzene derivatives.**—See A., I, 142.

**Slow combustion of benzene.**—See A., I, 141.

**Determination of small concentrations. XIII. Determination of benzene.** S. I. Siniakova (J. Appl. Chem. Russ., 1936, 9, 2109—2115).—$C_6H_6$ (≯0·6 mg.) is nitrated with Stepanov's mixture, the *m*-$C_6H_4(NO_2)_2$ (I) produced is extracted with $Et_2O$, and dissolved in 2 ml. of $COMe_2$; 5 drops of 5% NaOH are added, followed after 15 min. by 1 ml. of $H_2O$, and the violet coloration is compared with that given by standard (I). R. T.

**Cleavage of side-chains in aromatic hydrocarbons in the form of paraffins by means of aluminium chloride.** V. N. Ipatiev and H. Pines (J. Amer. Chem. Soc., 1937, 59, 56—60).—$PhPr^{\beta}$, PhBu-*sec.*, $PhBu^{\gamma}$, and *sec.*-amylbenzene with $AlCl_3$–HCl in *cyclo*hexane (I) or, better, decahydronaphthalene at 65—80° give $C_3H_8$ (also formed from *p*-$C_6H_4Pr^{\beta}_2$), *n*-$C_4H_{10}$, *iso*-$C_4H_{10}$, and *iso*pentane, respectively. The ease of fission is $Bu^{\gamma}$ > *sec.*-Bu > $Pr^{\beta}$. Similar fission does not occur with PhMe and PhEt. $Pr^{\beta}$ is eliminated more readily from $PhPr^{\beta}$ in (I) than in methyl*cyclo*hexane; fission does not occur in 4-methyl*iso*propylcyclohexane. During the above reactions (I) is probably converted into phenyl-*cyclo*hexane; side reactions also occur. H. B.

**Microcolorimetric determination of toluene.** W. P. Yant, S. J. Pearce, and H. H. Schrenk (U.S. Bur. Mines, 1936, Rept. Invest. 3323, 12 pp.).—After nitration (fuming $HNO_3$) of PhMe, dilution, and neutralisation, the $COMeEt$ extract with 50% aq. KOH develops a reddish-blue colour which is matched against standards similarly prepared. $C_6H_6$ does not interfere, and an accuracy of ±10% is obtained between 0·05 and 0·25 mg. of PhMe. Operative details are given. F. N. W.

**Electrochemical oxidation of benzene homologues. VII. ψ-Cumene.** F. Fichter and G. Schetty (Helv. Chim. Acta, 1937, 20, 150—156; 1935, 1229).—Using a Pb anode in presence of dil. $H_2SO_4$ the main reaction product is $CO_2$. Small amounts of xylylaldehyde, xylic acids, methylterephthalic acid, xylenol, toluquinone, resin, AcOH, and $HCO_2H$ are also formed. E. S. H.

**Steric influences on the phenomenon of mesomerism.** R. H. Birtles and G. C. Hampson (J.C.S., 1937, 10—15).—If the discrepancies between the observed moments of *p*-disubstituted $C_6H_6$ derivatives and those calc. by assuming vector addition are due to resonance involving quinonoid structures, then with substituents such as $NH_2$, $NO_2$, $NMe_2$, OMe there should be a tendency for the H, O, or Me of these groups to be held in the plane of the ring, but the introduction of Me in *o*-positions should exert a steric effect opposing this tendency. The dipole moments of nitro-, amino- (I), nitroamino-, bromonitro-, and dinitro-durene (II), and $C_6Me_5{\cdot}NH_2$ are < those of the corresponding $C_6H_6$ derivatives. The conclusion is reached that the lowering of the moment is due to a damping of the resonance by the steric effects of the Me groups. Bromodurene, in which no steric effect is expected, has almost the same moment as PhBr. *Bromoaminodurene* (II), m.p. 138·5—139·5°, is obtained from (I) by Br in AcOH. J. D. R.

**Mononitration of o-chloroiodobenzene.** G. Wallagh and J. P. Wibaut (Rec. trav. chim., 1936, 55, 1071—1081).—Reduction ($TiCl_3$) of 1 : 2 : 6-$C_6H_3Cl(NO_2)_2$ [from 2 : 6-$(NO_2)_2C_6H_3{\cdot}NH_2$ by Sandmeyer's method] gives 2-*chloro*-3-*nitroaniline*, m.p. 95—96°, which after diazotisation reacts with KI to form 1-*chloro*-2-*iodo*-6-*nitrobenzene*, m.p. 59·8°, whilst diazotisation of 2 : 1 : 3-$NH_2{\cdot}C_6H_3Cl{\cdot}NO_2$ followed by KI affords 1-*chloro*-2-*iodo*-3-*nitrobenzene*, m.p. 100—101°. Nitration ($HNO_3$, *d* 1·52; 1 hr. at −5° followed by 1 hr. at 0°) of *o*-$C_6H_4ClI$ gives 17·2% of 1 : 2 : 3-, 30·1% of 1 : 2 : 4-, 42·5% of 1 : 2 : 5-, and 10·3% of 1 : 2 : 6-$NO_2$-derivatives (thermal analysis). The results are discussed in connexion with Holleman and Wibaut's rule (A., 1913, i, 169). F. N. W.

**Mobility of the iodoxy-group in p-iodoxynitrobenzene.** D. Vorländer [with H. David] (Ber., 1937, 70, [*B*], 146—151).—The behaviour of *p*-$NO_2{\cdot}C_6H_4{\cdot}IO_2$ towards boiling $H_2O$, aq. $NaNO_2$, and aq. $NaN_3$ shows that in very varied reactions $IO_2$ is less firmly bound than $NO_2$ to the $C_6H_6$ nucleus. This is ascribed to the more strongly active, unsaturated character of $IO_2$ in contrast with the more turgid $NO_2$ and to the peculiar relationships of I to O which may be so pronounced that the influence of $NO_2$ on $IO_2$ is almost completely suppressed as in the reaction with alkalis. The mobility of $IO_2$ in the reaction between $NO_2{\cdot}C_6H_4{\cdot}IO_2$ and neutral salts is so increased by a second *o*-$NO_2$ that changes occur with 2 : 4-$(NO_2)_2C_6H_3{\cdot}IO_2$ at 15—20° which do not occur below 90—100° with *p*-$NO_2{\cdot}C_6H_4{\cdot}IO_2$. The chemical process here, apart from external conditions, depends on the $C_6H_6$ derivative, and on the nature of the reaction partner and the products of the change. Although the reversal of the change or the establishment of an equilibrium between the partners of org. and inorg. origin cannot be fully demonstrated, the concn. of the solution and the action of mass are influential. It is not immaterial whether $IO_3$ separates as sparingly sol. $AgIO_3$ or $Ba(IO_3)_2$ or remains in solution as freely sol. alkali iodate. The charges, however, are not ionic in character. When $NO_2$ and $IO_2$ are in the *ortho* position steric influences may come into play similar to those observed by Lock in the cases of aromatic aldehydes and alkali hydroxides. The ready mobility of $IO_2$ in 2 : 4-$(NO_2)_2C_6H_3{\cdot}IO_2$ and of 1-$NO_2$ in 1 : 2 : 4-$C_6H_3(NO_2)_3$ is probably due to co-operation of energy contrasts with steric relationships. H. W.

**Mobility of the iodoxy-group in 1-iodoxy-2 : 4-dinitrobenzene.** H. Lütgert (Ber., 1937, 70,

[*B*], 151—157).—2 : 4-$(NO_2)_2C_6H_2{\cdot}IO_2$ is best obtained by the oxidation of 1 : 2 : 4-$C_6H_3I(NO_2)_2$ with HOCl in AcOH, whereby 2 : 4-$(NO_2)_2C_6H_3{\cdot}IO$ is possibly formed intermediately. It is readily and almost quantitatively converted by aq. NaOH into *m*-$C_6H_4(NO_2)_2$ and $NaIO_3$. Aq. $AgNO_3$ reacts readily: $(NO_2)_2C_6H_3{\cdot}IO_2 + AgNO_3 + H_2O = m\text{-}C_6H_4(NO_2)_2 + AgIO_3 + HNO_3$, whereas with $H_2O$ at 15—20° the change is not appreciable after several weeks. *m*-$C_6H_4(NO_2)_2$ is not converted by $HIO_3$ in $H_2O$ or conc. $H_2SO_4$ into $(NO_2)_2C_6H_3{\cdot}IO_2$. 2 : 4-$(NO_2)_2C_6H_3{\cdot}IO_2$ and conc. aq. $NH_3$ give mainly *m*-$C_6H_4(NO_2)_2$ with some 1 : 2 : 4-$C_6H_3I(NO_2)_2$, which give an *adduct* (1 : 1), m.p. 64—67°. With aq. $NaNO_2$ at 15—20°, 2 : 4-$(NO_2)_2C_6H_3{\cdot}IO_2$ yields 1 : 2 : 4-$C_6H_3(NO_2)_3$ with some 2 : 4-$(NO_2)_2C_6H_3{\cdot}OH$; the latter is the main product in hot solution, being possibly formed by hydrolysis of 1 : 2 : 4-$C_6H_3(NO_2)_3$. $NaN_3$ and 2 : 4-$(NO_2)_2C_6H_3{\cdot}IO_2$ yield 2 : 4-$(NO_2)_2C_6H_3{\cdot}N_3$; it appears impossible to isolate the expected iodo-base, which becomes disproportionated to I′ or I and $IO_3'$. If $NaNO_2$ is replaced by $AgNO_2$ at 15—20° the product is 1 : 2 : 4-$C_6H_3(NO_2)_3$ with approx. 1 mol. of AgI and 2 mols. of $AgIO_3$. With aq. $NaNO_2$ or $Ba(NO_2)_2$ free I is liberated. 2 : 4-$(NO_2)_2C_6H_3{\cdot}IO_2$ is moderately stable towards dil. and conc. $HNO_3$ conc. $H_2SO_4$ and $H_2SO_4 + HNO_3$. HCl gives free $Cl_2$ and $C_6H_3I(NO_2)_2$. Dil. AcOH at 15—20° causes the change: $(NO_2)_2C_6H_3{\cdot}IO_2 + H_2O = (NO_2)_2C_6H_3{\cdot}OH + HIO_2$. In the acid medium $HIO_2$ becomes transformed in an involved manner into $IO_3'$ and used in iodinating $(NO_2)_2C_6H_3{\cdot}OH$ to 6-iodo-2 : 4-dinitrophenol. H. W.

**C·C linking in hexaphenylethane.**—See A., I, 67.

**Application of Ullmann's reaction to the preparation of dinaphthyls.** H. H. Hodgson and R. L. Elliott (J.C.S., 1937, 123—125).—The mechanism of the Ullmann reaction is discussed, with particular reference to the iodonitronaphthalenes, and the influence of the unsubstituted nucleus on the ease of removal of the I. With Cu in boiling $PhNO_2$, 3 : 1-$C_{10}H_6I{\cdot}NO_2$ yields 4 : 4′-*dinitro*-2 : 2′-*dinaphthyl*, m.p. 316°, but similar treatment of 3 : 2-$C_{10}H_6I{\cdot}NO_2$ affords only 2-$C_{10}H_7{\cdot}NO_2$. 4 : 2-$C_{10}H_6I{\cdot}NO_2$ in AcOH diazotised (conc. $H_2SO_4$) and treated with KI affords 1 : 4-*di-iodo*-2-*nitronaphthalene* (I), m.p. 126°, which with Cu in $PhNO_2$ yields 4 : 4′-*di-iodo*-3 : 3′-*dinitro*-1 : 1′-*dinaphthyl*, m.p. 275—280° (softening and decomp. at 220°, decomposed by slow heating to 220° to 3 : 3′-dinitro-1 : 1′-dinaphthyl), and 1 : 2-$C_{10}H_6I{\cdot}NO_2$ (II). (I) fused with Cu at 180—210° yields 1 : 2-$C_{10}H_6I{\cdot}NO_2$ and traces of (II). 1 : 2-*Di-iodo*-4-*nitronaphthalene*, m.p. 172° [from 4 : 2 : 1-$NO_2{\cdot}C_{10}H_5I{\cdot}NH_2$; prepared as (I)], with Cu in $PhNO_2$ is unchanged after 5 hr. boiling; after 10 hr., only 1-$C_{10}H_7{\cdot}NO_2$ is obtained. J. D. R.

**Dissociable anthracene oxides. Photo-oxides of 9-phenyl-10-methyl- and of 9-phenyl-10-ethyl-anthracene.** A. Willemart (Compt. rend., 1936, **203**, 1372—1374).—9-Phenyl-10-methyl- (A., 1926, 1030) and -10-ethyl-anthracene (A., 1927, 881) in $CS_2$ when insolated afford *photo-oxides*, $C_{21}H_{16}O_2$ and $C_{22}H_{18}O_2$, which at 170° and 200°, respectively, evolve 20% and 35% of their O content, unlike the oxides of *meso*-diarylanthracenes (cf. A., 1935, 1233; 1936, 197, 462), but similarly to those of anthracene (A., 1935, 1488) and of 9-phenylanthracene (A., 1936, 1101). J. L. D.

***Bz*-Monoalkylanthracenes.** H. Waldmann and E. Marmorstein (Ber., 1937, 70, [*B*], 106—108).—Clemmensen's method is unsuited to the prep. of alkylanthracenes from the acyl compounds since the hydrides so formed are not readily dehydrogenated. Good results are obtained by application of the Wolff–Kishner method. 2-*Ethylanthracene*, m.p. 150—151° (*picrate*, m.p. 92°), is obtained by treating 2-acetylanthracene with $N_2H_4{\cdot}H_2O$, NaOEt, and EtOH at 180°, or from 2-ethyl-9-anthrone by reduction with Zn dust and $NH_3$–$H_2O$. 2-Propionylanthracene affords 2-*propylanthracene*, m.p. 126° (*picrate*, m.p. 97°), oxidised by $CrO_3$ in AcOH to 2-*propylanthraquinone*. 2-iso*Propylanthracene*, m.p. 154—155° (*picrate*, m.p. 130—131°), is derived from 2-*iso*propyl-9-anthrone. 1-*Acetylanthracenesemicarbazone*, decomp. 204—208°, is converted by a short treatment with NaOEt in EtOH at 180° into 1-*ethylanthracene*, m.p. 33—34° (*picrate*, m.p. 126—127°), whence 1-*ethylanthraquinone*, m.p. 96°. H. W.

**Hydrogenation of phenanthrene.** J. R. Durland and H. Adkins (J. Amer. Chem. Soc., 1937, **59**, 135—137).—Pure phenanthrene (I) is reduced by $H_2$ and Cu–Cr oxide in EtOH at 150° to the 9 : 10-$H_2$-derivative (87%); at 220° the 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-$H_8$-derivative (II) is the main product (cf. Burger and Mosettig, A., 1936, 334). (II) is better prepared by reduction of (I) with $H_2$ + Raney Ni in methyl*cyclo*hexane at 120°; at about 200° tetradecahydrophenanthrene results. H. B.

**Synthesis of 1 : 2-benzanthracene derivatives related to cholanthrene.** L. F. Fieser and M. S. Newman (J. Amer. Chem. Soc., 1936, **58**, 2376—2382).—1 : 2-Benzanthracenes containing Me at 5 and/or 10 could not be prepared by the modified Elbs reaction but are obtained by cyclisation and subsequent reduction of the appropriate 2-benzyl-1-naphthoic acids.

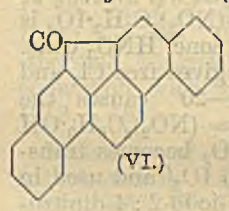
*o*-$C_6H_4Me{\cdot}MgBr$ (I) and 1 : 2-$C_{10}H_6(CO)_2O$ (II) in boiling $C_6H_6$ give 38-43% of 2-o-*toluoyl*-1-*naphthoic acid* (III), m.p. 149·5—150·5° (*Me* ester, b.p. 215—216°/2·5 mm.), and about 3% of 1-o-*toluoyl*-2-*naphthoic acid*, m.p. 210—211°, which are decarboxylated at 230—245° in presence of a little of their Cu salts to *o*-tolyl β- and α-$C_{10}H_7$ ketone, respectively. (III) and MgMeBr (excess) in $Et_2O$–$C_6H_6$ afford 86% of the *lactone*, dimorphous, m.p. 103—104° and 119—120°, of 2-α-hydroxy-α : *o*-dimethylbenzyl-1-naphthoic acid, which is reduced (modified Clemmensen; Martin, A., 1936, 1249) to 2-α : o-*dimethylbenzyl*-1-*naphthoic acid* (IV), m.p. 183·5—184°. The crude anthrone from (IV) and conc. $H_2SO_4$ at 20° is reduced (Zn dust, 10% NaOH) to 5 : 10-*dimethyl*-1 : 2-*benzanthracene* (V), m.p. 147—147·5° (*picrate*, m.p. 173·7—174·2°). MgPhBr and (II) similarly give 30% of 2-benzoyl-1- (VI), m.p. 141·8—142·8°, and some 1-benzoyl-2-, m.p. 223·5—224·5°, -naphthoic acid. *Me* 2-*benzoyl*-1-*naphthoate*, m.p. 72·5—73·5° [from (VI) and $CH_2N_2$; the "Me ester" obtained by Waldmann (A., 1931,

1063) using MeOH–HCl is probably the corresponding lactol Me ether, m.p. 156—156·5°, since it does not react with MgMeI], with MgMeI (1 equiv.) or, better, (VI) with MgMeBr affords the *lactone*, m.p. 173·8—174·2°, of 2-α-hydroxy-α-methylbenzyl-1-naphthoic acid; subsequent reduction (Clemmensen) gives 2-α-*methylbenzyl*-1-*naphthoic acid*, m.p. 128—129°, which is converted [as for (IV)] into 10-*methyl*-1 : 2-*benzanthracene* (VII), m.p. 140·2—140·8° (*picrate*, m.p. 173·5—174°). (III) is reduced by Mg octadecyl bromide to the *lactone* (VIII), m.p. 157—157·8°, of 2-α-hydroxy-*o*-methylbenzyl-1-naphthoic acid; MgEtBr (3 equivs.) affords (VIII) and some of the *lactone*, m.p. 124—125°, of 2-α-hydroxy-*o*-methyl-α-ethylbenzyl-1-naphthoic acid. Reduction (modified Clemmensen) of (VIII) yields 2-*o*-*methylbenzyl*-1-*naphthoic acid*, m.p. 144—145°, converted [as for (IV)] into 5-methyl-1 : 2-benzanthracene. Preliminary tests indicate that (V) has a carcinogenic activity of the same order as cholanthrene, methylcholanthrene, and 3 : 4-benzpyrene. (VII) is also carcinogenic.

β-$C_{10}H_7$ 2-ethyl-1-naphthyl ketone, b.p. 235—240°/2—2·5 mm. (from β-$C_{10}H_7$·COCl, 2-$C_{10}H_7Et$, and $AlCl_3$ in $CS_2$), heated at 425—430°/1·5 hr. gives 23% of 1 : 2 : 5 : 6-dibenzanthracene. *p*-Xylyl 2-ethyl-1-naphthyl ketone, b.p. 188—192°/2 mm. [from 2-$C_{10}H_7Et$ and the chloride of 2 : 5-$C_6H_3Me_2$·$CO_2H$ (prep. from 2 : 5-$C_6H_3Me_2$·COMe)], at 450—455°/15 min. afford (probably) a methylbenzanthracene, m.p. 124—126° (*picrate*, m.p. 155—156°). The carbinol from β-$C_{10}H_7$·COMe and (I) is dehydrated at 200—250° to α-*o*-*tolyl*-α-2-*naphthylethylene*, m.p. 66—66·5°, reduced ($H_2$, $PtO_2$, AcOH) to the ethane (IX), b.p. 177—179°/1·5—2 mm. Bromination (method : Cook and Haslewood, A., 1935, 1117) of (IX), subsequent treatment with $C_5H_5N$, conversion into the Grignard reagent, carbonation, and hydrogenation gives an acidic product which with 90% $H_2SO_4$ at 40° followed by Zn dust + alkali in PhMe affords a poor yield of a *hydrocarbon*, $C_{20}H_{16}$, m.p. 149—168° (*picrate*, m.p. 152—153°). Acetylation and chloroacetylation (Friedel–Crafts) of (IX) were unsuccessful. All m.p. are corr. H. B.

**Dehydrogenation and ring-transformation of *spiro*-hydrocarbons.** S. C. S. Gupta (Current. Sci., 1936, **5**, 295—296).—*cyclo*Pentane-1-carboxylic-1-acetic anhydride with $C_{10}H_8$ and anhyd. $AlCl_3$ affords α-cyclo*pentyl*-β-1-, m.p. 140—141°, and -β-2-*naphthoylpropionic acid*, m.p. 191°. The former is reduced (Clemmensen) to α-cyclo*pentyl*-γ-1-*naphthylbutyric acid*, m.p. 108—109°, cyclised (85% $H_2SO_4$) to 1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2 : 2-spirocyclo*pentane* (I), b.p. 215°/6 mm. When reduced (Clemmensen), (I) gives 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2 : 2-spirocyclo*pentane*, which with Se at 300—350° affords chrysene but no benzanthracene. Similarly are obtained α-cyclo*pentyl*-β-(4-*methyl*-1-*naphthoyl*)*propionic acid*, m.p. 176—177° and -γ-(4-*methyl*-1-*naphthyl*)*butyric acid*, m.p. 112°, 1-*keto*-9-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2 : 2-spirocyclo*pentane*, m.p. 97°, and 9-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2 : 2-spirocyclo*pentane*, m.p. 69—70°, which with Se at 300—350° gives 6-*methylchrysene*, m.p. 152—153°. J. L. D.

**Synthesis of picene.** H. Waldmann and G. Pitschak [with K. G. Hindenburg] (Annalen, 1937, **527**, 183—189).—$K_2$ *o*-*phenylenediacetate* (I), *o*-$NO_2$·$C_6H_4$·CHO, and $Ac_2O$ at 80° and finally at 130—140° yield *o*-$NO_2$·$C_6H_4$·CH:CH·$CO_2H$ and the isomeric forms of *di*-*o*-*nitrobenzylideneindan*-2-*one*, m.p. 241·5° and m.p. 199° (decomp.), respectively, also obtained from indan-2-one (II) and *o*-$NO_2$·$C_6H_4$·CHO in AcOH containing HCl. (I) and $Ac_2O$ at 80—105° afford (II). Vigorous action between *o*-$C_6H_4(CH_2·OH)_2$, *o*-$NO_2$·$C_6H_4$·CHO, and 33% NaOH in EtOH leads to *di*-*o*-*nitrobenzylidene*-*o*-*phenylenediacetonitrile*, m.p. 228°, reduced by $SnCl_2$ in AcOH–conc. HCl to *di*-*o*-*aminobenzylidene*-*o*-*phenylenediacetonitrile*, m.p. 239—240°, which is converted by conc. $H_2SO_4$ at 80° into *di*-*o*-*nitrobenzylidene*-*o*-*phenylenediacetamide*, m.p. 241°, and thence by $NaNO_2$ and $H_2SO_4$ into *di*-*o*-*nitrobenzylidene*-*o*-*phenylenediacetic acid*, m.p. 291° [*Na* salt (III)]. (III) is reduced by $Na_2S$ to *di*-*o*-*aminobenzylidene*-*o*-*phenylenediacetic acid*, m.p. 269° (decomp.) (*Na* salt), which is converted by $NaNO_2$, followed by Cu paste in $H_2SO_4$, into mainly a *substance*, m.p. 246°, containing N and *picene*-12 : 13-*dicarboxylic acid* (IV), m.p. (indef.) 320—324° (decomp.) [*anhydride* (V), m.p. 322—323°]. Ignition of (IV) with soda-lime yields picene, m.p. 356°. Sublimation of (V) at 330—340° gives unchanged material and 1 : 2 : 7 : 8-*dibenz*-4 : 5-*phenanthrylene ketone* (VI), m.p. 267°, transformed by distillation with Zn dust into 1 : 2 : 7 : 8-*dibenz*-4 : 5-*phenanthrylenemethane*, m.p. 277°. H. W.



(VI.)

**Preparation of methylcholanthrene.** L. F. Fieser and A. M. Seligman (J. Amer. Chem. Soc., 1936, **58**, 2482—2487).—The method previously described (A., 1935, 480, 853) is modified for relatively large-scale use. The mixture of ketones obtained from *p*-$C_6H_4$MeCl (I), $CH_2Cl$·$CH_2$·COCl (modified prep. of acid), and $AlCl_3$ in $CS_2$ is converted by conc. $H_2SO_4$ at 105—110° into a 2 : 1 mixture (*A*) of 4-*chloro*-7-*methyl*-, m.p. 82—82·4°, and 7-chloro-4-methyl-, m.p. 128°, -1-hydrindone (cf. Mayer and Müller, A., 1928, 65). Clemmensen reduction of (*A*) gives 7-*chloro*-4-*methylhydrindene*, b.p. 132—133°/25 mm., which with CuCN + $C_5H_5N$ at 220—230° affords the 7-*CN*-derivative (II), m.p. 72·9—73·2°, hydrolysed (conc. HCl) to the *amide*, m.p. 176—177·4°, of 4-*methylhydrindene*-7-*carboxylic acid*, m.p. 227—229°. 7-α-Naphthoyl-4-methylhydrindene [from (II) and α-$C_{10}H_7$·MgBr] is pyrolysed at 405—410° (bath)/40 min. to methylcholanthrene (III) [over-all yield from (I) 20%] and some (probably) 7-α-*naphthylmethyl*-4-*methylhydrindene*, b.p. 221—226°/4 mm. The prep. of the choleic acid, m.p. 197·5—198°, from (III) and deoxycholic acid is detailed (cf. A., 1935, 1366).

The mixture of ketones obtained [as for (I)] from *p*-$C_6H_4$MeBr with conc. $H_2SO_4$ at 100° gives a little of (probably) a *bromotolyl vinyl ketone*, m.p. 129—132°, and much oil; bromomethylhydrindones could not be obtained by cyclisation. All m.p. are corr. H. B.

**Identity of the dehydrogenation-hydrocarbons, $C_{25}H_{24}$, from cholesterol and ergosterol.** O.

Diels and H. J. Stephan (Annalen, 1937, **527**, 279—290).—The identity of the hydrocarbons, $C_{25}H_{24}$ (best prepared by Se in boiling NHPhAc and purified by crystallisation from $EtCO_2H$), from ergosterol (I) and cholesterol is confirmed by the m.p. (219—221°), mixed m.p., analysis, prep. of the $(NO_2)_2$-compound, m.p. 262° (mixed m.p.), and oxidation to the ketone (II), $C_{25}H_{22}O$, identified by the m.p. 193—194°, mixed m.p., analysis, absorption spectrum, *X*-ray diagram, and crystallo-optical data (cf. Ruzicka *et al.*, A., 1934, 398). A $NO_2$-compound is often formed as impurity in the $(NO_2)_2$-compound. A higher-boiling hydrocarbon fraction from (I) with $Na_2Cr_2O_7$–AcOH gives also a yellow *ketone*, $C_{25}H_{22}O$ or $C_{26}H_{24}O$, m.p. 174—175°, which resembles (II) closely in absorption spectrum and with $CrO_3$ gives a *substance*, (?) $C_{25}H_{18}O_3$, m.p. 230—231° (not chrysoquinone).

R. S. C.

**Separation of primary arylamines from secondary aralkylamines.** C. W. Ferry and J. S. Buck (J. Amer. Chem. Soc., 1936, **58**, 2444—2445).—Mixtures of $NH_2Ar$ (I) and NHArAlk (II) are separated by treatment with aq. PhCHO–$NaHSO_3$ [2 mols. calc. on (I) present], whereby the (II) does not react and is extracted with $Et_2O$. *o*-$C_6H_4Me{\cdot}NH_2$ can be separated from *o*-$C_6H_4Me{\cdot}NHEt$ by its preferential reaction with PhNCO. N-*Phenyl*-N′-*α*-*naphthyl*-N-*methyl*-, m.p. 99°, and -n-*butyl*-, m.p. 99°, N-o-, m.p. 85·5°, -m-, m.p. 95·5°, and -p-, m.p. 103°, -*tolyl*- and N-o-, m.p. 136·5°, and -p-, m.p. 111°, -*phenetyl*-N′-*α*-*naphthyl*-N-*ethyl*-, and N-p-*anisyl*-N′-*α*-*naphthyl*-N-iso*propyl*-, m.p. 147°, -*carbamides* are prepared from *α*-$C_{10}H_7{\cdot}NCO$ and the appropriate (II).

H. B.

**Promoter action. Oxidation of aniline sulphate by hot concentrated sulphuric acid in presence of copper and mercury sulphates.** M. M. Haring and H. H. Kaveler (J. Amer. Chem. Soc., 1936, **58**, 2595—2599).—Destructive oxidation of $(NH_2Ph)_2,H_2SO_4$ by an excess of conc. $H_2SO_4$ at 275° is accelerated by $CuSO_4$ and $HgSO_4$ (better at higher concn.). The catalytic effect increases with rise in the concn. but is not directly ∝ concn. as claimed by Bredig and Brown (A., 1904, ii, 247). Mixtures have activities > the additive val.; the most active is an approx. 2 : 1 (mol.) mixture of $HgSO_4$ and $CuSO_4$. The reaction is unimol. or pseudounimol. in the first stages (cf. *loc. cit.*).

H. B.

**Complex compounds of 4-phenylselenosemicarbazide.** K. A. Jensen and E. Frederiksen (Z. anorg. Chem., 1936, **230**, 31—33).—PhNCSe with $N_2H_4,H_2O$ in EtOH in the cold gives 4-*phenylselenosemicarbazide*, m.p. 157° (decomp.), which with $NiCl_2$ yields complex *compounds*, $[Ni(NHPh{\cdot}CSe{\cdot}NH{\cdot}NH_2)_2]Cl_2$ and $[Ni(NHPh{\cdot}CSe{\cdot}NH{\cdot}NH_2)_3]Cl_2$, the latter of which with EtOH–$NH_3$ gives $Ni(NPh{\cdot}CSe{\cdot}NH{\cdot}NH_2)_2$.

F. L. U.

**Electrolytic introduction of the thiocyanate group into aromatic amines and phenols.** F. Fichter and P. Schönmann (Helv. Chim. Acta, 1936, **19**, 1411—1415).—Anodic electrolysis using a rotating graphite anode (cf. F.P. 702,829) of the base or phenol in aq. EtOH–HCl in presence of $NH_4CNS$ (4 mols.) gives p-*thiocyano*-dimethyl- (91·7%) and -*diethyl-aniline* (68·9%), b.p. 138°/1 mm. (*picrate*, m.p. 134°), 3-*thiocyano*-NN-*dimethyl*-p-*toluidine* (21%), an oil (*hydrochloride*, cryst.), and 4-*thiocyanoguaiacol* (OH = 1) (prep. in aq. EtOH), m.p. 107° (also obtained in poor yield from 4-aminoguaiacol).

R. S. C.

**Nitration of benzylaniline and its derivatives. II.** P. van den Berg (Rec. trav. chim., 1936, **55**, 1053—1067; cf. A., 1936, 1501).—p′-*Nitrobenzyl*-p-*chloro*-, m.p. 98° (*Ac* derivative, m.p. 102°), and -*bromo-aniline*, m.p. 119° (*Ac* derivative, m.p. 100°), and -*p*-toluidine (*Ac* derivative, m.p. 85°)-are nitrated (abs. $HNO_3$) to p-*nitrobenzyl*-4-*chloro*- (I), m.p. 186°, -*bromo*- (II), m.p. 145° and -*methyl*-2 : 6-*dinitrophenylnitroamine* (III), m.p. 186° which on further nitration ($H_2SO_4$–abs. $HNO_3$) afford 2′ : 4′-*dinitrobenzyl*-4-*chloro*-, m.p. 147°, -*bromo*-, m.p. 146°, and -*methyl*-2 : 6-*dinitrophenylnitroamine*, m.p. 144°, respectively. o′-*Nitrobenzyl*-p-*chloro*-, m.p. 112°, and -bromoaniline, m.p. 87° (lit. 84—85°) [Ac derivative, m.p. 139° (lit. 137—138°)], and -*p*-toluidine on nitration ($HNO_3$, *d* 1·46) yield o-*nitrobenzyl*-4-*chloro*- (IV), m.p. 139°, -*bromo*- (V), m.p. 160°, and -*methyl*-2 : 6-*dinitrophenylnitroamine* (VI), m.p. 158°, which give 2′ : 4′-*dinitrobenzyl*-4-*chloro*-, m.p. 147°, -*bromo*-, m.p. 146°, and -*methyl*-2 : 6-*dinitrophenylnitroamine*, m.p. 144°, on further nitration (abs. $HNO_3$), whilst m′-*nitrobenzyl*-p-*chloro*-, m.p. 81° (*Ac* derivative, m.p. 120°), and -*bromo-aniline*, m.p. 72° (*Ac* derivative, m.p. 126°), -p-*toluidine*, m.p. 85° [identical with substance previously described as *p*′-tolyl-bis-(*m*-nitrobenzyl)amine] (*Ac* derivative, m.p. 101°), and -p-*nitroaniline*, m.p. 147° (*Ac* derivative, m.p. 212°), are nitrated ($HNO_3$ *d* 1·46) to m-*nitrobenzyl*-4-*chloro*- (VII), m.p. 165°, -*bromo*- (VIII), m.p. 157°, and -*methyl*-2 : 6-*dinitrophenylnitroamine* (IX), m.p. 167°, and m-*nitrobenzyl*-2 : 4 : 6-*trinitrophenylnitroamine* (X), m.p. 149°. The original substituted anilines result from the condensation (30 min.; 120—140°) of the appropriate amine and nitrobenzyl chloride. (I), (IV), or (VII) affords 4-chloro-2 : 6-dinitrophenol, (II), (V), or (VIII) affords 4-bromo-2 : 6-dinitrophenol, whilst (III), (VI), or (IX) affords 2 : 6-dinitro-*p*-cresol and (X) affords picric acid on boiling with aq. $Na_2CO_3$.

F. N. W.

**Application of Curtius degradation reaction to the synthesis of phenylethylamine.** P. P. T. Sah and C. H. Kao (Sci. Rep. Nat. Tsing Hua Univ., 1936, **3**, 525—532).—Application of the Curtius reaction to $CH_2Ph{\cdot}CH_2{\cdot}CO_2H$ has given $CH_2Ph{\cdot}CH_2{\cdot}NH_2$ [*styphnate*, m.p. 187—189° (decomp.); 3 : 5-*dinitrobenzoate*, m.p. 188—189°; 3 : 5-*dinitro*-o-*toluate*, m.p. 165—166°; β-*phenylethylcarbamide*, m.p. 115—116°].

F. R. S.

**Betaïne-like complex salts.** P. Pfeiffer [with H. Böttcher, W. Prätorius, and L. M. Kwan] (Z. anorg. Chem., 1936, **230**, 97—111; cf. A., 1933, 824).—The following are described: *Cu dianiline benzene*-, p-*toluene*-, and 1-*naphthalene-sulphonates*; *Cu aniline*-o-, -m-, -p-*sulphonates* (with $4H_2O$); *Na H* ($+2H_2O$), *Ba* ($+3H_2O$), and *Cu* ($+2H_2O$) salts of *α*-*naphthylamine*-2 : 5-*disulphonic acid*; *Cu*

*di*-1 : 2-*naphthylenediamine nitrate* and *sulphate*; *Cu di*-1 : 8-*naphthylenediamine chloride*, *nitrate*, and *sulphate*; *Ni di*-1 : 8-*naphthylenediamine sulphate*; *Cu* 1 : 2-*naphthylenediamine*-6-*sulphonate*; *Cu* and *Ni* 1 : 8-*naphthylenediamine*-4-*sulphonate*; *Na* (anhyd. and $+3H_2O$) and *Ba* salts of *Cu di*-1 : 8-*naphthylenediamine*-3 : 6-*disulphonic acid*; *Cu di*-4-α-*naphthaleneazo*-1 : 8-*naphthylenediamine nitrate* ($+2H_2O$). A dipolar structure similar to that of the betaïnes is attributed to the simpler Cu and Ni salts described. F. L. U.

***cis–trans*-Isomeric stilbenes. IV. Stereoisomeric *o*-nitro- and *o*-amino-stilbenes, *o*-aminodibenzyl, and ring-closure to phenanthrene and dihydrophenanthrene. II.** P. Ruggli and A. Staub [with, in part, O. Schmid] (Helv. Chim. Acta, 1937, 20, 37—52).—The best yields (70%) of *cis*-*o*-nitrostilbene (I), m.p. 65—66°, b.p. 187°/11 mm., are obtained by addition of *o*-$NO_2{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CO_2H$ to quinoline containing Cu chromite at 230°. (I) is not isomerised when distilled in a vac. or with superheated steam, or when boiled with HCl–$H_2O$–EtOH, and only slowly affected by insolation in $C_6H_6$ containing I. Partial isomerisation occurs at 230°, accelerated by I, but not in boiling quinoline or cymene. The most powerful reagent is $PhNO_2$ containing I at 210° whereas $PhNO_2$ alone has little effect. *trans*-*o*-Nitrostilbene has b.p. 209°/11 mm., m.p. 73°. (I) is not smoothly reduced by $SnCl_2$, whilst catalytic hydrogenation (Ni) leads to considerable amount of *o*-*aminodibenzyl* (II). Treatment with $FeSO_4$–$NH_3$ gives cis-*o*-*aminostilbene* (III), b.p. 180—181°/11 mm. (*hydrochloride*, m.p. 203°; *sulphate*, m.p. 159—161°; *Ac*, m.p. 114°, and *Bz*, m.p. 98°, derivatives; *picrate*, m.p. 145°), in 90% yield. Isomerisation of (III) occurs less readily than that of (I) and is best effected in quinoline at 250°. It occurs to some extent during the slow distillation of (III). Addition of I causes complete resinification, also observed when (III) is insolated in $C_6H_6$ containing I. *trans*-*o*-Aminostilbene (IV) gives an *Ac* derivative, m.p. 143°, a *hydrochloride*, m.p. 195—196°, *sulphate*, m.p. 204°, *Bz* derivative, m.p. 168°, and *picrate*, m.p. 156°. Diazotisation of (III) and treatment of the product with Cu paste affords phenanthrene in 61·3% yield, increased to 64% by the use of amyl nitrite in EtOH and to 80% when the diazo-product formed in EtOH is treated with $NaHPO_2$. On the other hand, (IV) gives no phenanthrene by this reaction; in $H_2O$ much resin, some PhCHO, and *trans*-*o*-hydroxystilbene, m.p. 146—147° (acetate, m.p. 55—56°), are formed, whereas in EtOH with Cu powder stilbene is obtained in 62% yield. The difference in behaviour of the two stereoisomeric forms in the Pschorr reaction is due to spatial conditions, ring-closure being impossible with the *trans*-form. (II), m.p. 33°, gives a *hydrochloride*, m.p. 198°, *sulphate*, m.p. 202°, *Ac*, m.p. 117°, and *Bz*, m.p. 166°, derivative, and a *picrate*, m.p. 167—168°. The Pschorr reaction of (II) in $H_2O$ or EtOH leads to *o*-hydroxydibenzyl, m.p. 85°, b.p. 171—172°/11 mm. (*Ac* derivative, b.p. 179°/11 mm.; 2′ : 4′-*dinitrophenyl ether*, m.p. 69°), and 9 : 10-*dihydrophenanthrene*, b.p. 158°/11 mm., m.p. 34·5—35°, dehydrogenated by S at 210° to phenanthrene and oxidised by $CrO_3$ in AcOH to phenanthraquinone; with $NaH_2PO_2$, $Ph_2$ is formed in 47% yield. H. W.

**Auxo-enoid systems. II. Colour of nitrobenzoyl derivatives of aromatic amines. III. Influence of the position of nitro- and auxo-groups on the colour of nitrobenzoylarylamides.** V. A. Ismailski and E. A. Smirnov (Bull. Soc. chim., 1937, [v], 4, 81—94, 94—111; cf. A., 1936, 1396).—II. The yellow to red colour of derivatives of the type $NO_2{\cdot}C_6H_4{\cdot}Q{\cdot}C_6H_4X$ (X = auxochrome OMe, OH, or $NMe_2$) is determined mainly by X and is of the same order if Q = ·CO·NH· instead of CH:CH, CH:N, or N:N so that conjugation between the $NO_2$- and and auxo-group is broken. The colour of these compounds cannot be due to the structure ·C(OH):N· since it is retained in derivatives containing ·CO·NR·, and even if either the $NO_2$- or the auxo-group is in a *m*-position. The theories of Burawoy (A., 1931, 144) and of Dilthey *et al.* (A., 1928, 627) are not acceptable and colour must be due to direct mutual action of isolated nitro-enoid and auxo-enoid systems. The following compounds prepared by acylation of the appropriate $NH_2$-compound, are new: m-4-, m.p. 212°, and m-3-*nitrobenzamido*-, m.p. 219°, p-4-, m.p. 214°, and p-3-*nitrobenzmethylamido*-, m.p. 224°, -*phenol*; p-3-, m.p. 174·5°, and p-4-*nitrobenzamidoanisole*, m.p. 197°; N-3-, m.p. 176°, and N-4-*nitrobenzoyl*-N′N′-*dimethyl*-m-, m.p. 188°, and N-3-, m.p. 173°, and N-4-*nitrobenzoyl*-N′N′-*dimethyl*-p-, m.p. 258·5°, -*phenylenediamine*; *p*-3-, m.p. 224° (lit. m.p. 215—216°), and *p*-4-nitrobenzamidophenol, m.p. 263° (lit. m.p. 258°), are prepared.

III. The bathochromic effect of introduction of *m*- and *p*-$NO_2$ into the Bz and of *m*- or *p*-OH and $NMe_2$ into NHPh in NHBzPh (I) is studied by spectroscopic examination (curves plotted) of the above derivatives. A bathochromic effect is produced by introduction of a single auxochrome into (I) even in absence of $NO_2$, but is greatly increased by simultaneous $NO_2$-substitution. The bathochromic effects of *p*-$NO_2$ (58 mμ) and *p*-$NMe_2$ (64 mμ) are approx. equal and are greater in the *p*- than in the *m*-position, the complete series being (*p*-$NO_2$–*p*′-$NMe_2$) > (*m*-$NO_2$–*p*′-$NMe_2$) > (*p*-$NO_2$–*m*′-$NMe_2$) > (*m*-$NO_2$–*m*′-$NMe_2$). The two chromophoric systems $NO_2{\cdot}C_6H_4{\cdot}CO$ (termed *aci*-chromophore rather than anti-auxochrome) and auxochrome $(OH)NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO$· are largely independent, colour depending on the stronger chromophore, which may be either system, *e.g.*, *p*-$NO_2{\cdot}C_6H_4{\cdot}CO$ > *m*-$OH{\cdot}C_6H_4{\cdot}NH$, but *p*-$NMe_2{\cdot}C_6H_4{\cdot}NH$ > *m*-$NO_2{\cdot}C_6H_4{\cdot}CO$. The effect of introducing a new chromophore depends mainly on the nature of the initial system, the weaker chromophore merely modifying the effect of the stronger. The group CO·NH merely modifies the condition of the two chromophores. The results are discussed on a polarity basis and Kaufmann's rule is amplified. The strongest chromophoric properties arise from the opposing polar (contra-inductive) effects of either *p*-di-auxo- or *p*-di-*aci*-chromophore groups, much weaker effects being produced by the *syn*-inductive system present in *m*-derivatives. J. W. B.

**Electrochemical properties of diphenylbenzidinesulphonic acid.** L. A. Sarver and I. M. Kolthoff (J. Amer. Chem. Soc., 1937, 59, 23—24).—Diphenylbenzidinedecasulphonic acid has been oxidised to the green and violet forms, and the subsequent reduction studied electrometrically. The green form is very stable, the violet less stable, and both are fairly sol. in $H_2O$ and dil. acids. The titration curves show that the green product is a semiquinone. E. S. H.

**Racemisation of some *d-o*-(2-dimethylaminophenyl)phenyltrimethylammonium salts.** D. E. Cook and E. E. Turner (J.C.S., 1937, 88—89).—In aq. solutions of equimol. concn. at 90° the velocity of racemisation of *d-o*-(2-dimethylaminophenyl)-phenyltrimethylammonium salts is in the order *benzenesulphonate* (half-life period 210 min.) > iodide (I) (250 min.) > *d*-camphorsulphonate (II) (310 min.). There is no simple connexion between $\mu$ of the solvent and the velocity of racemisation, the half-life periods for (II) decreasing in the order $H_2O$ > EtOH > $COMe_2$ > MeCN > $CHCl_3$. The activation energies for racemisation of (I) and (II) in $H_2O$ are 11·5 and 19 kg.-cal., respectively. J. W. B.

**Azo-dyes. II.** A. Rollett, R. Birkner, and K. R. Posselt (Monatsh., 1936, **68**, 403—406; cf. A., 1935, 1360).—Comparison is made of the colour of *o*-amino- and *o*-hydroxy-azo-dyes formed by coupling benzenoid diazo-components with 1 : 4-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ and 1 : 4-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$. *m*-Substituents ($NH_2$, NHAc, $SO_3H$, $NO_2$) bring about little deepening of shade either in solution or dyeing; *o*-substituents deepen the shade in the order $NO_2$, Cl > $CO_2H$ > OMe > Me. Methylation or acetylation of the dye 1 : 2 : 4-$NH_2{\cdot}C_{10}H_5(N_2Ph){\cdot}SO_3H$ deepens the shade but with 1 : 2 : 4-$NH_2{\cdot}C_{10}H_5(N_2{\cdot}C_6H_4{\cdot}NO_2\text{-}p){\cdot}SO_3H$ the reverse occurs. Methylation of the OH has little effect on the shade of dyes from 1 : 4- and 1 : 5-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$. The effect of *o*-, *m*-, or *p*-substituents in the benzene ring on the *p*-amino- and *p*-hydroxy-azo-dyes formed from 1 : 6- and 1 : 7-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ and $NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ is < in the *o*-azo-series and in general the survey shows that groups which cause deepening of shade when *o* or *p* are without effect when *m* and *vice versa*. No spectroscopic measurements are given. K. H. S.

**Action of hydrogen fluoride on phenyldiazomethane.** C. L. Tseng, C. H. Sze, and C. E. Sun (J. Chinese Chem. Soc., 1936, **4**, 485—489).—$CHPhN_2$ and abs. HF in $Et_2O$ give a small amount of a substance containing 35·3% of F and much stilbene. Failure to obtain $CH_2PhF$ is explained by thermal considerations: the activation energy for $CHPhN_2 + HF \rightarrow CH_2PhN_2F$ (I) is 105·5; (I) $\rightarrow CH_2PhF + N_2$ +124·8, and $2CHPhN_2 \rightarrow (CHPh)_2 + 2N_2$ +10·8 kg.-cal. R. S. C.

**Decomposition reactions of aromatic diazo-compounds. I. Evidence for non-ionic reaction.** W. A. Waters (J.C.S., 1937, 113—117).—The spontaneous decomp. of benzene*iso*(*anti*)diazoacetate (prepared as NPhAc·NO) into neutral Ph and OAc radicals and $N_2$ is indicated by the isolation of the products of further reaction with the solvent Ph + RX $\rightarrow$ PhX (X = H or halogen). Thus in *n*-$C_6H_{14}$, *cyclo*hexane, $Et_2O$, dioxan, $COMe_2$, MeCN, EtOAc, and $Ac_2O$ some $C_6H_6$ is formed; in RX and $CHX_3$ (X = halogen) PhX is isolated, and $(PhS\cdot)_2$ is formed in $CS_2$. In $Ac_2O$, $CCl_4$, and $CS_2$, $CO_2$ is liberated, indicative of the decomp. of free OAc radicals. In dry $CS_2$, Fe, Zn, Cu, Pb, and Sb are attacked even in presence of $CaCO_3$ [gives some $Ca(OAc)_2$, showing formation of some AcOH], and in $CCl_4$, Cu, Sn, Bi, and Hg (to give some HgPhCl) are attacked, diagnostic of free neutral OAc radicals. J. W. B.

**Ethyl esters of tri-iodophenoxyacetic acids and potassium tri-iodophenoxyacetate.** T. C. Daniels and R. E. Lyons (J. Amer. Chem. Soc., 1936, **58**, 2646).—*Et mono-*, m.p. 128·5°, *di-*, m.p. 160°, and *tri-*, amorphous, decomp. 208—211°, *-tri-iodophenoxyacetates* are prepared from $C_6H_2I_3{\cdot}OH$ and Et mono-, di-, and tri-chloroacetate, respectively, in EtOH–NaOEt; the first only is hydrolysed by 30% aq. KOH to the acid, m.p. 211° (*K* salt). H. B.

**Introduction of the chloromethyl group into *o*-nitroanisole and toluene.** P. P. Schorigin and S. A. Skoblinskaja (J. Gen. Chem. Russ., 1936, **6**, 1578—1582).—*o*-Nitroanisole and paraldehyde in light petroleum in presence of HCl and $ZnCl_2$ yield 3-nitro-4-methoxybenzyl chloride and 3 : 3′-dinitro-4 : 4′-dimethoxydiphenylmethane. PhMe reacts similarly, to give *o*- and *p*-methylbenzyl chloride, whilst the reaction in the gaseous phase gives ditolylmethane as sole product. R. T.

**Rearrangement of aryl allyl ethers.** C. D. Hurd and L. Schmerling (J. Amer. Chem. Soc., 1937, **59**, 107—109).—In agreement with Claisen and Tietze (A., 1925, i, 389), Ph cinnamyl ether (I) (from PhOH, $CHPh{:}CH{\cdot}CH_2Br$, and $K_2CO_3$ in $COMe_2$) heated in $NPhEt_2$ rearranges to *o*-α-phenylallylphenol (II) [phenylcarbamate, m.p. 93—94° (lit. 91°)]. The structures of (II) and *o*-cinnamylphenol (*loc. cit.*) are proved by ozonolysis. (I) heated with β-$C_{10}H_7$ allyl ether (III) at 240° (bath) gives (II) and 1-allyl-2-naphthol (IV); the non-formation of *o*-allylphenol indicates that rearrangement is not intermol. but is intramol. Similar evidence is obtained with (III) + Ph hexenyl ether; (IV) and *o*-hexenylphenol are isolable. *m*-$OH{\cdot}C_6H_4{\cdot}ONa$ and α-bromo-$\Delta^{\beta}$-hexene in EtOH give 4-hexenylresorcinol, *resorcinol hexenyl ether* (insol. in 10% NaOH), and some dihexenyl ether. The polymeric products formed when Ph allyl ether is heated at 210—240° (bath) are separable by distillation from a mol. still into a *dimeride* (probably 2-β-*o*-*allylphenoxypropylphenol*) and trimeride of *o*-allylphenol. H. B.

**Fission of benzenesulphonic esters of pyrogallol.** A. von Wacek and I. Schöpfer (Österr. Chem.-Ztg., 1937, **40**, 63—64).—Pyrogallol tribenzenesulphonate (I) is not hydrolysed by HBr, HI, or HCl–EtOH at 170°; with liquid $NH_3$ at room temp., *pyrogallol* 1 : 3-*dibenzenesulphonate*, m.p. 127°, is formed [*acetate*, m.p. 137°; *Me ether* (by $CH_2N_2$), m.p. 109° (identical with product from $PhSO_2Cl$ and pyrogallol 2-Me ether)]. Boiling $N_2H_4$ causes complete fission of (I), giving pyrogallol (60%), $Ph_2S_2$, and PhSH. J. D. R.

**Pentenyl-, hexenyl-, and heptenyl-resorcinols.** C. D. Hurd and R. W. McNamee (J. Amer. Chem. Soc., 1937, 59, 104—106).—*m*-$C_6H_4(OH)_2$ (I) and α-bromo-$\Delta^\beta$-hexene (II) in $COMe_2$ + anhyd. $K_2CO_3$ give *resorcinol dihexenyl ether* (III), 4-*hexenylresorcinol* (IV) (150; 200; 40) [*Me*$_2$ *ether*, b.p. 150—152°/10 mm., oxidised ($KMnO_4$, $COMe_2$) to 2 : 4-$(OMe)_2C_6H_3$·$CO_2H$; *di*(*carboxymethyl*) *ether*, m.p. 159—160°, prepared using $CH_2Cl$·$CO_2H$ in 10% NaOH], and 4 : 6-*dihexenylresorcinol* (V) (>200; >200; >30) (*Me*$_2$ *ether*, b.p. 158—163°/10 mm.). (III)—(V) are also obtained from *m*-$C_6H_4(ONa)_2$ and (II) in $C_6H_6$; (V) is also formed from (I) and (II) in EtOH–NaOEt. Reduction ($H_2$, $PtO_2$, EtOH) of (IV) gives a product from which 4-*n*-hexylresorcinol is isolable. (I) and α-bromo-$\Delta^\beta$-pentene (VI) in $COMe_2$ + $K_2CO_3$ afford *resorcinol dipentenyl ether* and 4-*pentenylresorcinol* [*Me*$_2$ and *di*(*carboxymethyl*), m.p. 164—165°, *ethers*], whilst α-bromo-$\Delta^\beta$-heptene (VII) gives 4-*heptenylresorcinol*, b.p. 138—143°/1 mm. [*di*-(*carboxymethyl*) *ether*, m.p. 144—145°], and 4 : 6-*diheptenylresorcinol*. The above alkenyl derivatives are mixtures since (II), (VI), and (VII) are undoubtedly admixed with the γ-bromo-$\Delta^\alpha$-alkene. Most of the compounds are purified by distillation from a Hickman mol. still. The nos. in parenthesis after (IV) and (V) are the PhOH-coeffs. towards *S. aureus*, *Strep. hæmolyticus*, and *B. typhosus*, respectively.

H. B.

**Catalytic dehydrogenation in the dibenzyl series.** J. Dewar and J. Read (J.C.S.I., 1936, 55, 347—349T).—Ordinary Pd- or Pt–C was found to be useless for the dehydrogenation of $(CH_2Ph·)_2$ at 300°, but its dehydrogenation to phenanthrene (I) at this temp. in presence of Zelinski's Pt–C was confirmed (cf. A., 1927, 47; 1930, 80). The same catalyst dehydrogenated 4 : 4′-dimethoxydibenzyl (II) slowly, and since the OMe were detached simultaneously the product was again (I). An electrically heated vertical-tube furnace suitable for the above operations is described. Rupe's activated Ni catalyst was found to convert 4 : 4′-dimethoxystilbene partly into (II) in $CO_2$ atm. at 250°. Efficient methods are described for preparing (II), anisoin, hydroanisoin, *iso*hydroanisoin, *hydroveratroin*, m.p. 210°, and iso*hydroveratroin*, m.p. 167°, the last two in approx. equal, quant. yield by electrolytic reduction of veratraldehyde.

**Nitration of 1 : 8-dihydroxynaphthalene.** F. Calvet (Anal. Fís. Quím., 1936, 34, 650—666).—1 : 8-$C_{10}H_6(OH)_2$ could not be nitrated but nitration of 1 : 8-$C_{10}H_6(OAc)_2$ yields 2 : 4-*dinitro*-1-*hydroxy*-8-*acetoxynaphthalene* (I), m.p. 200° (decomp.), which cannot be acetylated or benzoylated. (I) with $CH_2N_2$ yields 2 : 4-*dinitro*-8-*acetoxy*-1-*methoxynaphthalene* (II), m.p. 115—117°, hydrolysed by cold aq. KOH to 2 : 4-*dinitro*-8-*hydroxy*-1-*methoxynaphthalene*, m.p. 170—171°. Boiling KOH–EtOH hydrolyses (I) and (II) to the (*OH*)$_2$-compound (III), m.p. 180—182° (decomp.), from which the (*OMe*)$_2$-compound (IV), m.p. 137—139°, is obtained, converted by KOH–EtOH into the 1-*hydroxy*-8-*methoxy*-compound (V), m.p. 179—180° (decomp.). (III) and (V) are reduced to *diamines* [*hydrochlorides* (VI) and (VII) isolated]. Oxidation of (VII) with boiling dil. $HNO_3$ gives 3-methoxyphthalic acid, establishing the structure of (III). Nitration of the methylene ether of 1 : 8-$C_{10}H_6(OH)_2$ yields the 2 : 7- (?) (VIII), m.p. 198—200°, and 4 : 5-, (IX), m.p. 177—179°, -$(NO_2)_2$-derivatives. Boiling aq. KOH converts (VIII) into the (*OH*)$_2$-compound (X), m.p. 171—173° (decomp.); KOH–EtOH gives the 1-*hydroxy*-8-*methoxy*-compound (XI), m.p. 218—220°. (X) and (XI) yield the (*OMe*)$_2$-compound, darkens 250°, m.p. 278° (decomp.). (X) yields *Ac*$_1$, m.p. 125—170° (decomp.), and *Ac*$_2$, derivatives, m.p. 228° (decomp.), and is reduced to the (*NH*$_2$)$_2$-compound [*Bz*$_4$ derivative, m.p. 300° (decomp.)]. Boiling aq. KOH hydrolyses (IX) to the (*OH*)$_2$-compound, m.p. 225° (decomp.) [*Ac*$_2$, m.p. 158—160°, and (*OMe*)$_2$-derivatives, m.p. 147—150° darkening and decomp.], which is reduced to the $(NH_2)_2$-compound, the $Bz_4$ derivative of which is identical with that obtained by the reduction and benzoylation of 4 : 5-dibenzeneazo-1 : 8-dihydroxynaphthalene (Heller and Kretzschmann, A., 1921, i, 458).

L. A. O'N.

**Tetrahydroxybenzenes.** F. Mauthner (J. pr. Chem., 1937, [ii], 147, 287—292).—2 : 6-Dimethoxyphenol in EtOH is oxidised by $HNO_3$ (*d* 1·2) to 2 : 6-dimethoxy-*p*-benzoquinone (I), more conveniently obtained by similar treatment of pyrogallol $Me_3$ ether (prep. described). Reduction of (I) by $Na_2S_2O_4$ gives 2 : 6-dimethoxyquinol (II), m.p. 158°, the diacetate, m.p. 123°, of which is converted by $AlCl_3$ in $PhNO_2$ at 0° into 2 : 4-*dihydroxy*-4 : 6-*dimethoxyphenyl Me ketone*, m.p. 162—163°, which does not react with *p*-$NO_2$·$C_6H_4$·NH·$NH_2$ and is converted by $AlCl_3$ in boiling PhCl into 2 : 4 : 5 : 6-*tetrahydroxyphenyl Me ketone*, m.p. 243—244°. (II) and NaOH–$Me_2SO_4$ give 1 : 3 : 4 : 5-$C_6H_2(OMe)_4$, b.p. 271°, transformed by anhyd. $Zn(CN)_2$ and HCl in $Et_2O$ followed by treatment of the product with warm $H_2O$ into 2 : 4 : 5 : 6-*tetramethoxybenzaldehyde*, m.p. 88—89° (*p*-*nitrophenylhydrazone*, m.p. 178—179°).

H. W.

**Rearrangement of aryl alkyl sulphides.** W. H. Taylor (J. Amer. Chem. Soc., 1936, 58, 2649—2650).—ArSAlk undergo rearrangement and fission with AcOH–$ZnCl_2$ (Sprung and Wallis, A., 1934, 1097) at 135—150°. *p*-Tolyl allyl sulphide thus gives 4-methyl-2-allylthiophenol, *p*-$C_6H_4Me$·SH, and allene; Ph *sec*.-Bu sulphide, b.p. 104—105°/25 mm., affords *sec*.-Bu$C_6H_4$·SH, PhSH, and $C_4H_8$. *p*-Tolyl *sec*.-Bu sulphide has b.p. 135—138°/22 mm.

H. B.

**Rearrangement of acetylenylcarbinols.** C. D. Hurd and R. E. Christ (J. Amer. Chem. Soc., 1937, 59, 118—121).—Contrary to Rupe *et al.* (A., 1928, 640), 1-acetylenyl*cyclo*hexanol is rearranged by $HCO_2H$ to 1-acetyl-$\Delta^1$-*cyclo*hexene (also prepared from *cyclo*hexene, AcCl, and $AlCl_3$ in $CS_2$) and not to *cyclo*hexylideneacetaldehyde (cf. Fischer and Löwenberg, A., 1929, 1421). CH:C·CPhMe·OH similarly gives a little COPhMe [not CPhMe:CH·CHO (Rupe and Giesler, A., 1928, 870)] and much tar (probably arising from $CH_2$:CPh·COMe). Acetylenylbornyl alcohol, m.p. 97—98° (lit. 85°) (from camphor, Na, and $C_2H_2$ in $C_6H_6$), is rearranged by 90% $HCO_2H$ to 6-*hydroxy*-2-*acetylcamphane* (I), m.p. 77—78°; the mechanism for the rearrangement involves two Wagner rearrangements. (I) is oxidised ($O_3$ in $CCl_4$)

to 6-hydroxycamphane-2-carboxylic acid, m.p. 221° (lit. 216—220°); the *semicarbazone*, m.p. 202°, prepared from (I) appears to be that of 1-acetylcamphene. The prep. of acetylenylfenchyl alcohol is improved (cf. Rupe and Kuenzy, A., 1931, 1068). H. B.

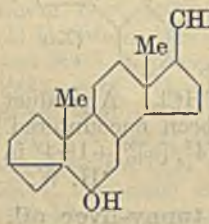
**Tetrahydronaphthalene derivatives with basic side-chains.** C. Mannich, F. Barkowsky, and W. H. Lin (Arch. Pharm., 1937, 275, 54—62).—1-Ketotetrahydronaphthalene, 30% aq. $CH_2O$ (1·1 mol.), and $NHMe_2$,HCl or piperidine hydrochloride (1·1 mol.), first at room temp. and then at 100°, give 70—75% yields of 1-*keto*-2-*dimethylamino*-, cryst. in ice–salt [*hydrochloride*, m.p. 144°; *perchlorate*, m.p. 121—123°; *oxime* (prep. in acid solution), an oil (*hydrochloride*, m.p. 188—189°)], and -*piperidino*-*methyltetrahydronaphthalene*, m.p. 37—38° [*hydrochloride*, decomp. 180°; *oxime*, m.p. 151° (*hydrochloride*, m.p. 198°)]. Reduction with 5% Na–Hg in dil. AcOH gives 1-*hydroxy*-2-*dimethylaminomethyltetrahydronaphthalene*, separable by way of the *hydrobromides*, m.p. 197° and 148°, respectively, into α- (I) (*benzoate hydrochloride*, m.p. 203°; p-*nitrobenzoate hydrochloride*, m.p. 189—190°) and β-*forms* (II) (*benzoate hydrochloride*, m.p. 171°; p-*nitrobenzoate hydrochloride*, m.p. 202°). 1-*Hydroxy*-2-*piperidinomethyltetrahydronaphthalene*, similarly prepared, gives the α- (III), m.p. 99—100° (*hydrobromide*, m.p. 180°; *benzoate hydrochloride*, m.p. 203°; p-*nitrobenzoate hydrochloride*, m.p. 185°), and β-*forms* (IV), b.p. 203—204°/14 mm. (*hydrobromide*, m.p. 193°; *benzoate hydrochloride*, m.p. 201°; p-*nitrobenzoate hydrochloride*, m.p. 191°; p-*aminobenzoate*, m.p. 142°). The isomerism of these alcohols is shown to be due to the newly formed asymmetric $C_{(1)}$, since both members of the pairs are dehydrated by an excess of HBr to yield the same 3-*dimethylamino*- (*hydrobromide*, m.p. 222°) and 3-*piperidino*-*methyl*-1:2-*dihydronaphthalene* (*hydrobromide*, m.p. 237°), hydrogenated ($PtO_2$) in AcOH to 2-*dimethylamino*- (*hydrobromide*, m.p. 180°) and 2-*piperidino*-*methyltetrahydronaphthalene* (*hydrobromide*, m.p. 231—232°). The benzoates of (I), (II), (III), and (IV) have 0·125, 0·5, 0·5, and 8 times, respectively, the local anæsthetic activity of cocaine, but are irritants. R. S. C.

**Synthesis of anisyl alcohol.** A. Ofner (Helv. Chim. Acta, 1937, 20, 53—55; cf. A., 1935, 1120).—Contrary to Quelet (A., 1936, 1505), alkaline hydrolysis of $OAc{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe$ affords $OH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe$ which is very readily dehydrated to $(OMe{\cdot}C_6H_4{\cdot}CH_2)_2O$ by technical $Na_2SO_4$ containing a trace of $NaHSO_4$. H. W.

**Deuterium abundance ratios in organic compounds. III. Cholesterol.** M. Dole and R. B. Gibney (J. Amer. Chem. Soc., 1936, 58, 2552—2555; cf. A., 1936, 667).—The D : H ratio in cholesterol is normal. On combustion there is marked fractionation of the O isotopes. E. S. H.

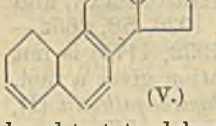
**Molecular rearrangement in sterols. I. Action of anhydrous potassium acetate on cholesteryl *p*-toluenesulphonate in acetic anhydride solution.** E. S. Wallis, E. Fernholz, and F. T. Gephart (J. Amer. Chem. Soc., 1937, 59, 137—140; cf. Stoll, A., 1932, 737; Wagner-Jauregg and Werner, *ibid.*, 844; Benyon *et al.*, A., 1936, 1105).

Reaction between cholesteryl *p*-toluenesulphonate and anhyd. KOAc in $Ac_2O$ at 70—80° is accompanied by a mol. rearrangement and gives the normal acetate together with about 43% of the *acetate* (I), m.p. 73°, $[\alpha]_D^{20}$ +47·8° in $CHCl_3$, of i-*cholesterol* (II), melts at room temp., resolidifying with m.p. 74—75°, $[\alpha]_D^{20}$ +23·9° in $CHCl_3$. (II) is considered not to contain a double linking since (I) does not react with $BzO_2H$ and neither (I) nor (II) decolorises Br in $CCl_4$. (II) is not pptd. by digitonin. (I) with $H_2$ and $PtO_2$ in AcOH gives dihydrocholesteryl acetate; reaction is slow with Pt-black and affords some cholestane. An impure ketone (*oxime*, $C_{27}H_{45}ON$, m.p. 143—144°) is obtained by oxidation ($CrO_3$, AcOH) of (II). (II) and 3:5-$(NO_2)_2C_6H_3{\cdot}COCl$ in $C_5H_5N$ at 100° (bath) give 18% of cholesteryl 3:5-dinitrobenzoate, m.p. 193° (formed only in small amount at room temp.), whilst with AcOH–conc. $H_2SO_4$ at 100° some of the normal acetate is produced. The "abnormal" ethers of Stoll (*loc. cit.*) are probably related to (II), which may have the annexed structure. H. B.



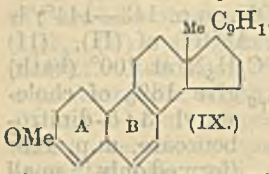

**Photochemical dehydrogenation of 7-dehydrocholesterol.** Y. Urushibara and T. Ando (Bull. Chem. Soc. Japan, 1936, 11, 802).—7-Dehydrocholesterol in EtOH in light in the presence of eosin gives a *substance*, $C_{54}H_{86}O_2$, m.p. 182—183° (corr.), possibly 7-*dehydrocholestenopinacone*. R. S. C.

**Derivatives of neoergosterol.** A. Windaus and M. Deppe (Ber., 1937, 70, [*B*], 76—84).—Reduction of tetradehydroneoergosterol (I) with Na and amyl alcohol gives epi*neoergosterol* (II), m.p. 177°, $[\alpha]_D^{19}$ +27·4° in $CHCl_3$, which differs from the tetrahydrodehydroneoergsterol of Marker *et al.* (A., 1936, 1256) since it cannot be removed from $Et_2O$ by dil. or conc. KOH and does not resemble œstrone in absorption spectrum. Its constitution is proved by its formation from neoergosterol (III) and $C_5H_{11}{\cdot}ONa$ in boiling amyl alcohol. It gives an *acetate* (II), m.p. 98°, $[\alpha]_D^{20}$ +27·2° in $CHCl_3$, and *dinitrobenzoate*, m.p. 204°, $[\alpha]_D^{19}$ +21·2° in $CHCl_3$, from which it is regenerated by hydrolysis with KOH–MeOH. Further, (II) or (III) is transformed by NaOEt–EtOH at 200° into *ergopentaene* (V), m.p. 89—90°, $[\alpha]_D^{19}$ +69·5° in EtOH. Tetradehydroneoergosteryl acetate is hydrogenated (Pt-black in EtOAc–$Et_2O$) to *tetradehydrodihydroneoergosteryl acetate* (VI), m.p. 144°, $[\alpha]_D^{21}$ +32·4° in $CHCl_3$, hydrolysed to tetradehydrodihydroneoergosterol, m.p. 140°, also obtained by dehydrogenation of dihydroneoergosterol by Pt. Reduction of (VI) with Na and PrOH yields *dihydroepineoergosterol* (VII), m.p. 167°, $[\alpha]_D^{19}$ +28·8° in $CHCl_3$, the *acetate*, m.p. 83°, $[\alpha]_D^{17}$ +24·6° in $CHCl_3$, of which is also obtained by hydrogenation (Pt-sponge in $Et_2O$) of (IV). In further attempts to prepare by direct hydrogenation a substance with aromatic ring A, tetradehydroneoergosteryl Me ether (VIII) is converted by Na and PrOH into 3:4-*de*

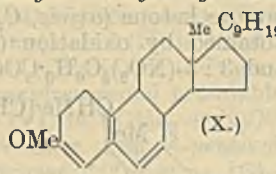


(V.)

*hydroneoergosteryl Me ether* (IX), m.p. 151°, $[\alpha]_D^{21}$ +35·6° in $CHCl_3$, the structure of which is established by its conversion into (VII) by $H_2$ in presence of Pt; ring B therefore remains unaffected. If (VIII) is cautiously hydrogenated (Pt-sponge) the double linking in the side-chain is attacked, with formation of *tetradehydrodihydroneoergosteryl Me ether*, m.p. 108°, $[\alpha]_D^{21}$ +31·5° in $CHCl_3$, also obtained by dehydrogenation (Pt) and subsequent methylation of dehydroneoergosterol and transformed by Na and amyl alcohol into *dihydro*-3 : 4-*dehydroneoergosteryl Me*



(IX.)



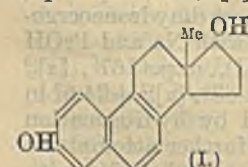
(X.)

*ether* (X), m.p. 93°, $[\alpha]_D^{18}$ +30·2 in $CHCl_3$. A product with unchanged ring A has not been encountered. epi*Neoergosteryl Me ether* has m.p. 74°, $[\alpha]_D^{20}$ +18·4° in $CHCl_3$. H. W.

**Antirachitic substance from tunny-liver oil.** E. J. H. Simons and T. F. Zucker (J. Amer. Chem. Soc., 1936, 58, 2655).—The EtOH-sol. fraction of the unsaponifiable matter is freed from hydrocarbons and cholesterol; an alcohol (I) is then isolated through its 3 : 5-*dinitrobenzoate*, m.p. 128·5°. (I) has antirachitic activity of 30 × $10^6$ I.U., shows absorption at 265 mμ, and is probably identical with the substance isolated by Brockman (A., 1936, 1161; cf. Haslewood and Drummond, *ibid.*, 1161). H. B.

**α-Sitosterol.** E. S. Wallis and E. Fernholz (J. Amer. Chem. Soc., 1936, 58, 2446—2448).—Crude "α-sitosterol" (Anderson *et al.*, B., 1927, 48, 49) with BzCl-$C_5H_5N$ gives (mainly) β-sitosteryl benzoate. Hydrolysis of the more sol. (EtOH-$C_6H_6$) fraction and subsequent 3 : 5-dinitrobenzoylation ($C_5H_5N$) affords small amounts of $\alpha_1$-*sitosterol* (I), $C_{29}H_{48}O$, m.p. 164—166°, $[\alpha]_D^{20}$ −1·7° in $CHCl_3$ [as 3 : 5-*dinitrobenzoate*, m.p. 222°, oxidised ($BzO_2H$ in $CHCl_3$) to a *dioxide*, m.p. 209—212°; *acetate*, m.p. 137°; *benzoate*, m.p. 168—172°], and $\alpha_2$-*sitosterol* (II), probably $C_{30}H_{50}O$, m.p. 156°, $[\alpha]_D^{20}$ +3·5° in $CHCl_3$ (as 3 : 5-*dinitrobenzoate*, m.p. 206°; *acetate*, m.p. 124—126°; *benzoate*, m.p. 164—166°). (I) and (II) both contain two double linkings. (I) is isomeric with stigmasterol; both are pptd. by digitonin. H. B.

**Chemical nature of δ-follicular hormone.** O. Wintersteiner, E. Schwenk, H. Hirschmann, and B. Whitman (J. Amer. Chem. Soc., 1936, 58, 2652—2653).—δ-Follicular hormone (A., 1932, 1173) is not homogeneous; fractional crystallisation gives a mol. compound, m.p. 226° (corr.), of *dihydroequilenin* (I), m.p. 215—217°, $[\alpha]_D^{25}$ −4·7° in dioxan [di-*p*-nitrobenzoate, m.p. 250—252° (corr.); benzoate, m.p. 203—205° (corr.), oxidised ($CrO_3$) to the benzoate of equilenin (II)], and an unidentified substance, which, unlike (I), does not form a picrate. The absorption spectrum of (I) coincides with that of (II). (II) is twice as œstrogenic as (I). H. B.



(I.)

**Reduction of cholic acids by Bouveault's method.** M. Vanghelovici (Bul. Soc. Chim. România, 1936, 18, 103—106).—Et cholate and Na–EtOH give 2—3% of the *alcohol*, $C_{24}H_{42}O_4$, m.p. 227°, which has a tonic action on the snail's heart. Et deoxycholate and cholanate give (no details) *alcohols*, m.p. 150° and 105°, respectively, which are difficult to purify. R. S. C.

**Vegetable heart poisons. XII. Stereochemistry of the aglucons of the heart poisons.** R. Tschesche and K. Bohle (Ber., 1936, 69, [*B*], 2443—2446).—A general review, provoked by the very slight physiological activity of uzarin, leads to the conclusion that in all the highly active and thoroughly investigated heart poisons of the digitalis group the *cis*-union of rings A and B is maintained. A mechanism is suggested for the isomerisation of strophanthidin derivatives from the α- to the β-series. H. W.

**Ethyl imido*cyclo*propanecarboxylate [α-imino-α-*cyclo*propylmethyl ethyl ether] hydrochlorides.** J. B. Cloke, E. C. Knowles, and R. J. Anderson (J. Amer. Chem. Soc., 1936, 58, 2547—2549).—α-*Imino*-α-cyclo*propyl*- (I), -α-1-*phenyl*-1-cyclo*propyl*- (II), m.p. about 110° (some decomp.), and -α-1-*phenyl*-2-*methyl*cyclo*propyl*- (III) -*methyl Et ether hydrochlorides* are prepared from the appropriate cyano*cyclo*propane, EtOH, and HCl in (usually) $Et_2O$. Pyrolysis of (I) and (II) gives *cyclo*propanecarboxylamide, m.p. 120° (lit. 124—124·5°), and 1-phenyl*cyclo*propane-1-carboxylamide, respectively; pyrrolinium salts are not produced (cf. A., 1929, 703). The rates of reaction of (I)—(III) with $H_2O$ are determined by Derby's method (A., 1908, i, 419); comparison with results for other imino-ether hydrochlorides (cf. Stieglitz, A., 1908, ii, 167) classifies *cyclo*propyl with the electronegative aryl radicals. H. B.

**Mechanism of amination by means of sodamide. II. Preparation of unsubstituted aromatic amidines by the action of sodamide on nitriles.** A. V. Kirsanov and I. M. Poljakova (J. Gen. Chem. Russ., 1936, 6, 1715—1720).—PhCN and $NaNH_2$ in PhMe (6 hr. at the b.p.) give benzamidine; the reaction also proceeds very slowly at room temp. Toluamidine (*picrate*, decomp. at 219°; *salicylate*, m.p. 210—211°) and naphthamidine were obtained analogously from *p*-tolunitrile and α-$C_{10}H_7$·CN. The reaction is represented as RCN + $NaNH_2$ → $NH_2$·CR:NNa → $NH_2$·CR:NH. R. T.

**Removal of HX from organic compounds by means of bases. III. Rates of removal of hydrogen bromide from substituted *N*-bromobenzamides and their relative ease of rearrangement in presence of alkali. Hofmann rearrangement.** C. R. Hauser and W. B. Renfrow, jun. (J. Amer. Chem. Soc., 1937, 59, 121—125).—The rates of decomp. of various *N*-bromobenzamides by a large excess of NaOH at 30° are determined by the rate of disappearance of the active Br. For the *m*- and *p*-derivatives studied, the relative rates are inversely related to the dissociation consts. of the corresponding benzoic acids, indicating that the ease of the change RCO·NHBr → RNCO is dependent on the ease of release of $Br^-$ from RCO·$NBr^-$. The yield

of the final product, *i.e.*, amine, is usually >90%; the yield from the *p*-$NO_2$-derivative is increased from 48 to 90% by carrying out the reaction at 96—100°. The following $C_6H_4R{\cdot}CO{\cdot}NHBr$, prepared by a modification of Hoogewerff and van Dorp's method (A., 1889, 981), were investigated: N-*bromo*-p-*methyl*-, decomp. 131—133°, -o-, decomp. 104—105°, -m-, decomp. 103—105°, and -p-, decomp. 170—174°, -*chloro*-, -m-*bromo*-, decomp. 122—126°, and -o-, decomp. 170—176°, -m-, decomp. 173—176°, and -p-*nitro*-, decomp. 198—202°, *benzamides*. H. B.

**Steric hindrance. I. Non-saturation index in the cinnamic series.** M. P. Duguenois (Bull. Soc. chim., 1937, [v], **4**, 193—199).—Theoretical addition occurs in 2 hr. in the dark when Br is added to $CHPh{:}CH_2$ or $CHPh{:}CH{\cdot}CH_2{\cdot}OH$ at −10° in $Et_2O$ (Volmar *et al.*, B., 1928, 236). Under such conditions addition of Br to $CHPh{:}CH{\cdot}CHO$ or $CHPh{:}CH{\cdot}CO_2H$ is incomplete but is complete in 2 hr. in diffuse sunlight. J. W. B.

**Synthesis of β-1-phenanthrylpropionic acid.** S. Natelson and S. P. Gottfried (J. Amer. Chem. Soc., 1937, **59**, 216).—Phenanthrene-1-aldehyde, $CH_2(CO_2H)_2$ (excess), and a little $C_5H_5N$ at 100° (bath) give β-1-phenanthrylacrylic acid, m.p. 259°, reduced (3% Na–Hg, dil. KOH) to β-1-phenanthrylpropionic acid, m.p. 187—188°. H. B.

**Condensation of chloral with salicylic acid.** F. Calvet and M. N. Mejuto (Anal. Fís. Quím., 1936, **34**, 641—649).—Condensation of $CCl_3{\cdot}CHO$ with *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (I) by means of conc. $H_2SO_4$ yields firstly 2-*hydroxy*-5-βββ-*trichloro*-α-*hydroxyethylbenzoic acid* (II), m.p. 180—182°, and then 4 : 4′-*dihydroxydiphenyltrichloromethylmethane*-3 : 3′-*dicarboxylic acid* (III), also obtained from (I) and (II). (II) yields an $Ac_1$ derivative, m.p. 190—192°, and *Me* ester, m.p. 97—99° ($Ac_1$ derivative, m.p. 90—92°). (II) with $H_2SO_4$ or KOH–MeOH yields 5-formyl-2-hydroxybenzoic acid, oxidised to 4-hydroxy*iso*phthalic acid (IV). (II) on oxidation yields (IV) and on reduction a *substance*, $C_9H_6O_2Cl_2$, m.p. 170—172°, probably 2-hydroxy-5-ββ-dichlorovinylbenzoic acid. (III) yields a $Me_2$ ester, m.p. 200—202° ($Ac_2$ derivative, m.p. 207—209°), hydrolysed to ββ-*dichloro*-αα-4 : 4′-*dihydroxydiphenylethylene*-3 : 3′-*dicarboxylic acid*, m.p. 295—297° ($Me_2$ ester, m.p. 120—122°). L. A. O'N.

**Electrolysis of aromatic carboxylic acids. III. Benzaldehyde-2-carboxylic acid.** V. M. Rodionov and V. V. Levtschenko (J. Gen. Chem. Russ., 1936, **6**, 1563—1566).—Electrolysis of aq. 1 : 2-$CHO{\cdot}C_6H_4{\cdot}CO_2K$ yields phthalide, α- and β-hydrodiphthalyl, and phthalic acid. R. T.

**Condensation of ethyl dichloroacetate with ketones and aldehydes by very dilute amalgams.** G. Darzens (Compt. rend., 1936, **203**, 1374—1376; cf. A., 1911, i, 6).—$CHX_2{\cdot}CO_2Et$ (X = Cl or Br) with COPhMe in dry $Et_2O$ containing Mg–, Ca–, or Zn–Hg (1 in 50) affords Et α-chloro-β-hydroxy-β-phenylbutyrate in >90% yield. The reaction is of general application to ketones or aldehydes. J. L. D.

**Degradation of *p*-hydroxydiphenylacetic acid to *p*-hydroxybenzhydrylamine.** A. Darapsky and H. Berger (J. pr. Chem., 1936, [ii], **147**, 161—166).—Et *p*-hydroxydiphenylacetate when refluxed with $N_2H_4,H_2O$–EtOH gives p-*hydroxydiphenylacethydrazide*, m.p. 194—197° (decomp.), which with $HNO_2$ gives the corresponding, unstable *azide* (I), and, unlike the corresponding *o*-compound (this vol., 85), is stable to cold conc. HCl and to boiling dil. HCl. (I) when boiled in $C_6H_6$ gives $N_2$, s-*bis*-p-*hydroxybenzhydrylcarbamide*, m.p. 215°, and p-*hydroxybenzhydrylamine* (II), m.p. 113° [*hydrochloride*, m.p. 180° (decomp.); *perchlorate*, m.p. 96°]. (I) when boiled with EtOH gives *Et* p-*hydroxybenzhydrylcarbamate*, m.p. 55° (decomp.), hydrolysed by NaOH to (II). H. G. M.

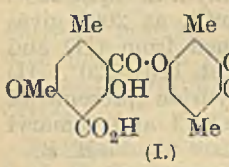
**Phthalyl chloride.** L. P. Kyrides (J. Amer. Chem. Soc., 1937, **59**, 206—208).—Phthalyl chloride (I) is obtained in good yield from *o*-$C_6H_4(CO)_2O$ (II) and $SOCl_2$ in presence of a little anhyd. $ZnCl_2$ at 220°. Passage of $SO_2$ through (I) + $ZnCl_2$ at 200° gives $SOCl_2$ and (II). (I) is also formed from (II) and $CPhCl_3$ + $ZnCl_2$ (larger amount) at 110—120°. (I) converts $PrCO_2H$ and maleic anhydride (presence of $ZnCl_2$ essential) at 140° into PrCOCl and fumaryl chloride, respectively. H. B.

**Condensations by sodium. VIII. Solvent exchange reactions, preparation of phenylmalonic acid, and mechanisms of reactions which employ sodium.** A. A. Morton and I. Hechenbleikner (J. Amer. Chem. Soc., 1936, **58**, 2599—2605).—*n*-Amyl chloride (I) and Na powder in $C_6H_6$ or $C_6H_6$–light petroleum followed by $CO_2$ give (according to conditions used) BzOH (11·5—78%), *m*- + *p*-$C_6H_4(CO_2H)_2$ (II) (0—6·5%), and $CHBu(CO_2H)_2$ (III) (trace—17·5%); use of PrCl and $(CH_2)_2O$ in place of $CO_2$ affords PhPr and $CH_2Ph{\cdot}CH_2{\cdot}OH$, respectively. In the above reactions NaPh is produced. (I) and Na with PhMe, $NPhMe_2$, PhOMe, $CH_2Ph_2$, and fluorene in light petroleum followed by $CO_2$ give varying amounts of $CH_2Ph{\cdot}CO_2H$ (IV) [accompanied by $CHPh(CO_2H)_2$ (V)], *o*-$NMe_2{\cdot}C_6H_4{\cdot}CO_2H$, *o*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$, $CHPh_2{\cdot}CO_2H$, and fluorene-9-carboxylic acid, respectively. (IV) and (V) are also formed when $Bu^{\beta}Cl$ is used instead of (I). Evidence supporting the following reactions is discussed: (i) $C_5H_{11}Na + C_6H_6 \rightarrow C_5H_{12} + NaPh$; (ii) $C_5H_{10}<$ (radical) + $C_6H_6 \rightarrow C_6H_{12} + C_6H_4<$ [whence $C_6H_4Na_2$ → (II)] or $C_5H_{10}Na_2 + C_6H_6 \rightarrow C_5H_{12} + C_6H_4Na_2$; (iii) $2C_5H_{11} \rightarrow C_5H_{12} + C_5H_{10}<$ [whence $C_5H_{10}Na_2$ → (III)]. The Wurtz–Fittig reaction is considered (cf. A., 1936, 1359) to proceed by reaction of NaAlk with AlkCl; free Alk radicals are present during the early stages and these react with Na. H. B.

**2 : 2′-Derivatives of diphenyl.** D. E. Cook and E. E. Turner (J.C.S., 1937, 117—118).—Diphenoyl chloride and excess of MgMeI give a mixture of 2 : 2′-*di*-α-*hydroxy*i*sopropyldiphenyl* (I), m.p. 138—139° (more sol. in ligroin), and 2-*acetyl*-2′-α-*hydroxy*i*sopropyldiphenyl* (II), m.p. 164—165° (less sol.). (I) is also obtained from MgMeI and 2 : 2′-diacetyldiphenyl (III), m.p. 94—95° (lit. m.p. 84°), Me diphenate, or (II). Dehydration of (I) with $PBr_3$ at 90—100° gives 2 : 2′-*di*-α-*methylvinyldiphenyl*, m.p. 97—98°: replacement of OH by halogen could not be effected. (III) with Br–AcOH gives a *substance*, $C_{24}H_{18}O_3Br_4$, m.p. 134—135°. J. W. B.

**Anthracene-1 : 2-dicarboxylic anhydride.** O. Benndorf (Monatsh., 1936, **69**, 420—423).—Reduction of anthraquinone-1 : 2-dicarboxylic acid with Zn dust and boiling dil. $NH_3$ and dehydration of the product with boiling $Ac_2O$ gives *anthracene*-1 : 2-*dicarboxylic anhydride* (I), m.p. 236°. (I) suspended in $C_6H_6$ is transformed by MgPhBr in $Et_2O$ into 1-α-*hydroxybenzhydrylanthracene*-2-*carboxylactone*, m.p. 199°, with smaller amounts of 1-*benzoylanthracene*-2-*carboxylic acid*, m.p. 239° (*Na* salt), oxidised to 1-benzoylanthraquinone-2-carboxylic acid, m.p. 302°. H. W.

**Lichen substances. LXXII. Constitution of squamatic acid.** Y. Asahina and Y. Tanase. **LXXIII. Synthesis of dimethyl squamatate.** Y. Asahina and Y. Sakurai (Ber., 1937, **70**, [*B*], 62—63, 64—66).—LXXII. Extraction of the thalli of *Cladonia bellidiflora* with $Et_2O$ followed by $COMe_2$ gives *l*-usnic acid and squamatic acid (I), m.p. 219° (decomp.) [*Me*$_2$ ester (II), m.p. 178°]. The Me$_2$ ester Me$_2$ ether of (I) is converted by boiling 95% $HCO_2H$ into Me 2 : 6-dimethoxy-3-carboxy-*p*-toluate and Me 4 : 6-dihydroxy-2 : 5-dimethylbenzoate, thus confirming the annexed structure for (I).



(I.)

LXXIII. *p*-Orsellinic acid is converted by $CH_2N_2$ into the Me ester, m.p. 98°, which with anhyd. HCN, HCl, and $AlCl_3$ in abs. $Et_2O$ followed by treatment with boiling $H_2O$ gives *Me* 2 : 6-*dihydroxy*-3-*aldehydo*-p-*toluate*, m.p. 146° (corresponding *anil*, m.p. 138°), transformed by $Ag_2CO_3$ and MeI in boiling $COMe_2$ into the corresponding *Me*$_1$ (III), m.p. 135°, and *Me*$_2$, m.p. 95·5°, *ethers*. (III) with $ClCO_2Et$ and $C_5H_5N$ at room temp. affords the *carbethoxy*-derivative, m.p. 132·5°, oxidised by $KMnO_4$ in $COMe_2$ to *Me* 6-*methoxy*-2-*carbethoxy*-3-*carboxy*-p-*toluate* (IV), m.p. 127·5. (IV) is transformed by $SOCl_2$, coupling of the chloride with Me β-orcinolcarboxylate, and subsequent decarbethoxylation into (II), identical with that derived from natural (I). H. W.

**Mellitic acid from coals, cokes, and graphites.** B. Juettner (J. Amer. Chem. Soc., 1937, **59**, 208—213).—Mellitic acid (I) is best obtained from various carbonaceous materials by successive oxidation with $HNO_3$ (*d* 1·5) (containing a little $NH_4$ vanadate) and alkaline $KMnO_4$ (excess). The g. of (I) from 100 g. of the following are quoted in parentheses: Edenborn coal (5·5), Edenborn coke prepared at 500°, 540°, 700°, and 1000° (11·9, 15·5, 24·1, and 22·5, respectively), Acheson electrode graphite (19·1), micronised Dixon graphite (natural) (21·7), "Aquadag" (dry material) (8·3). (I) is isolated from the aq. solution by electrodialysis and conversion into the $NH_4$ salt. H. B.

**Preparation of benzaldehyde from benzylidene chloride and boric acid.** J. Makarov-Semlianski and S. Prokin [with V. Ivanova and B. Ivanov] (J. pr. Chem., 1937, (ii), **147**, 317—320).—$CHPhCl_2$ and $H_3BO_3$ at 130—160° afford PhCHO in 85% yield. Similar treatment of a fraction obtained by chlorinating boiling PhMe gives PhCHO, $CH_2PhCl$, and BzOH. $CH_2PhCl$ does not react with $H_3BO_3$. PhCHO and $H_3BO_3$ at 130—140° do not appear to yield the compound $CHPh<^{O}_{O}>B\cdot OH$, the solid products being $HBO_2$ and $H_2B_4O_7$. $H_3BO_3$ can be regenerated without loss and pure HCl is evolved. H. W.

**Reducing action of potassium and sodium benzyloxide on aldehydes.** L. Palfray, S. Sabetay, and P. Mastagli (Compt. rend., 1936, **203**, 1523—1525).—Cuminaldehyde with boiling 0·5*N*-$CH_2Ph\cdot OK$ affords BzOH and cumyl alcohol. Heptaldehyde with 0·5*N*-$CH_2Ph\cdot ONa$ (I) affords BzOH (0·5 mol. per 1 mol. aldehyde), and β-*n*-amyl-*n*-nonyl alcohol (A., 1934, 1334) [*allophanate*, m.p. 120° (block)], identical with the synthetic product, together with some α-amylcinnamyl alcohol and its $H_2$-derivative. The amount of BzOH formed is sufficient to prove the hydrogenating action of (I) on the product of the aldol condensation. Similarly (I) converts α-amylcinnamaldehyde into α-amyldihydrocinnamyl alcohol. J. L. D.

**Reaction of *aci*nitro-derivatives with halogen compounds. V. Reaction of potassio-9-*aci*-nitrofluorene with halogeno-ketone derivatives.** D. A. Isăcescu (Bul. Soc. Chim. România, 1936, **18**, 63—65; cf. A., 1930, 1569).—The K salt of 9-*aci*-nitrofluorene with $COMe\cdot CH_2Br$ or $COPh\cdot CH_2Br$ in hot 96% EtOH gives 97 and 84% yields of aq. solutions of AcCHO and BzCHO, respectively. R. S. C.

**Iodination of 3-hydroxy- and of nitrated 3-hydroxy-benzaldehydes, and nitration of certain iodo-3-hydroxybenzaldehydes.** H. H. Hodgson and E. W. Smith (J.C.S., 1937, 76—78).—*m*-$OH\cdot C_6H_4\cdot CHO$ when warmed with I–aq. NaOAc gives its 6-*I*-derivative, m.p. 130° (p-*nitrophenylhydrazone*, m.p. 215°); with I–aq. $Na_2CO_3$ the 2 : 6-$I_2$-derivative (I), m.p. 144° (*Me ether*, m.p. 81°), and the 2 : 4 : 6-$I_3$-derivative, m.p. 146° [*Na* salt; *Me ether*, m.p. 162°; p-*nitrophenylhydrazone*, m.p. 237° (decomp.)], are obtained after liberation from their Na salts with $CO_2$. 2-Nitro-3-hydroxybenzaldehyde (improved prep.) [p-*nitrophenylhydrazone*, m.p. 250° (decomp.)] with aq. I gives its 4 : 6-$I_2$-derivative, m.p. 158° (II) (lit. m.p. 154·5°) [p-*nitrophenylhydrazone*, m.p. 250° (decomp.)]; 6-nitro-3-hydroxybenzaldehyde with I–$CHCl_3$–HgO gives its 2 : 4-$I_2$-derivative {p-*nitrophenylhydrazone*, m.p. 244° (decomp.); *Me ether*, m.p. 142° [p-*nitrophenylhydrazone*, m.p. 220° (decomp.)]}. 2 : 6-Dinitro-3-hydroxybenzaldehyde with I–20% NaOH affords its 4-*I*-derivative, m.p. 168° (p-*nitrophenylhydrazone*, decomp. 310°), and the corresponding 4 : 6-$(NO_2)_2$-compound gives its 2-*I*-derivative, m.p. 106·5° [p-*nitrophenylhydrazone*, m.p. 282° (decomp.)]. $HNO_3$ (30%) converts (I) into its 4-$NO_2$-derivative [*Na* salt; p-*nitrophenylhydrazone*, m.p. 218° (decomp.)], whereas $HNO_3$ (*d* 1·5) converts (II) into 6-*iodo*-2 : 4-*dinitro*-3-*hydroxybenzaldehyde*, m.p. 160°. 4-Nitro-3-hydroxybenzaldehyde is oxidised only to the acid by I–KI–$Na_2CO_3$. J. W. B.

**Synthesis of vanillin by Mottern's method.** P. P. Schorigin and K. I. Bogatscheva (J. Gen. Chem. Russ., 1936, **6**, 1567—1568).—Attempts at repeating Mottern's synthesis (A., 1934, 1354) were unsuccessful. R. T.

**Derivatives of *cyclo*pentanone.** M. C. Chang and P. P. T. Sah (J. Chinese Chem. Soc., 1936, **4**, 413—417).—The following derivatives of *cyclo*pentanone are prepared: *phenyl*-, m.p. 164—165°, p-, m.p. 180—181°, *o*-, m.p. 165—166°, and m-*tolyl*-, m.p. 192—193°, α-, m.p. 183—184°, and β-*naphthyl*-*semicarbazone*, m.p. 179—180°; p-, m.p. 173—174°, o-, m.p. 203—204°, and m-*nitro*-, m.p. 143—144°, 3 : 5-*dinitro*-, m.p. 212—214°, and m-*bromo*-*benzoylhydrazone*, m.p. 164—165°. M.p. are corr. R. S. C.

**Aldehydes and hydroxyaldehydes of the polymethylenic series. II. Condensation products of *cyclo*pentanone.** E. D. Venus-Danilova (J. Gen. Chem. Russ., 1936, **6**, 917—921; cf. A., 1936, 1109).—MgBu$^{\gamma}$Cl and *cyclo*pentanone in boiling $Et_2O$ yield a small quantity of *cyclo*pentanol and more 1-*cyclo*pentylidene*cyclo*pentan-2-one (I), b.p. 122—123°/16 mm. [*semicarbazone*, m.p. 214° (decomp.)]. Hydrogenation of (I) in presence of Pt leads to 1-*cyclo*pentyl*cyclo*pentan-2-one (II) (*oxime*, m.p. 78°; *semicarbazone*, m.p. 209—210°). *cyclo*Pentanone and Na in $H_2O$ + $Et_2O$ without EtOH give a small quantity of 1 : 1′-dihydroxydi*cyclo*pentyl and more *cyclo*pentanol and 1-*cyclo*pentyl*cyclo*pentan-2-ol, b.p. 119—120°/14 mm. (*acetate*, b.p. 121—122°/10 mm.), which is oxidised by $CrO_3$ to (II). J. J. B.

**Catalytic hydrogenation of alicyclic ketazines. Hydrogenation of *cyclo*hexanone ketazine and its methyl derivatives.** V. I. Egorova (J. Gen. Chem. Russ., 1936, **6**, 1404—1417).—The velocity of hydrogenation of ketazines of *cyclo*hexanone (I) and its Me derivatives (in AcOH or EtOH; Pt catalyst) falls in the order (I) > 4- > 3- > 2-methyl*cyclo*hexanone ketazine. The *ketazines* of (I) and 4-, b.p. 175—177°/23 mm., 3- (II), b.p. 160—167°/20 mm., and 2-methyl*cyclo*hexanone, b.p. 162°/18 mm., yield the corresponding NN-disubstituted hydrazines when hydrogenated; in the case of (II) the ketone and hydrazone are obtained, in addition. R. T.

**Autoxidation phenomena and valency tautomerism in the indone series.** A. Schönberg and R. Michaelis (J.C.S., 1937, 109—112).—The properties, especially the presence of 1 active H (Zerevitinov), show that the supposed 2-anilo- (I), 2-*p*-dimethylaminoanilo- (II), and 2-*p*-methoxyanilo- (III) -3-phenyl-α-hydrindone of Pfeiffer *et al.* (A., 1935, 1369) are actually of the type 2-anilino-3-phenylindone (I*a*, II*a*, and III*a*). (II*a*) (*methiodide*, decomp. 226°) reacts in solution in its valency-tautomeric form $C_6H_4<^{CPh}_{CO}>C(NHR)$—, and its autoxidation (A., 1936, 1511) gives actually 1-*hydroxy*-3 : 4-*diketo*-1-*phenyl*-2-p-*dimethylaminophenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (4-*monoxime*, sinters 180°, m.p. 192°). A similarly amended structure is applied to the oxidation product from (III*a*), and corresponding corrections in relation to the other reactions described by Pfeiffer *et al.* are suggested. J. W. B.

**Condensation of [aryl] propenyl ketones with ethyl oxalate.** R. C. Fuson, R. E. Christ, and G. M. Whitman (J. Amer. Chem. Soc., 1936, **58**, 2450—2452).—The Me group of Ph Δ$^{\alpha}$-propenyl ketone (I), b.p. 90—95°/2 mm. [from CHMe:CH·COCl (II), $C_6H_6$, and $AlCl_3$ at 0° in light from a Hg-vapour lamp], possesses the expected reactivity, since (I), $Et_2C_2O_4$, and KOEt in $Et_2O$ give the K salt (III) of *Et* α*ε*-*diketo*-*ε*-*phenyl*-Δ$^{\gamma}$-*hexenoate*, m.p. 106° (decomp.). (III) and BzCl in $Et_2O$ afford *Et* *ε*-*keto*-α-*benzoyloxy*-*ε*-*phenyl*-Δ$^{\alpha\gamma}$-*hexadienoate*, m.p. 123°. Similarly, *mesityl* Δ$^{\alpha}$-*propenyl ketone*, b.p. 128°/5 mm. [from (II), *s*-$C_6H_3Me_3$, and $AlCl_3$ in $CS_2$], and $Et_2C_2O_4$ give *Et* α*ε*-*diketo*-*ε*-*mesityl*-Δ$^{\gamma}$-*hexenoate*, m.p. 156° (decomp.), oxidised (3% $H_2O_2$, 10% NaOH) to β-*iso*durylic acid. (I) gives a positive $CHI_3$-test; it is cleaved by hot aq. $K_2CO_3$ to COPhMe. H. B.

**Action of alkalis on aryl and aryl alkyl ketones.** N. Kozlov, P. Fedoseev, and I. Drabkin (J. Gen. Chem. Russ., 1936, **6**, 1686—1689).—PhPr$^{\beta}$ in $CS_2$ and *p*-$C_6H_4Me$·COCl in presence of $AlCl_3$ (24 hr. at 100°) yield 4-*methyl*-4′-iso*propylbenzophenone* (I), b.p. 338—340°. *s*-$C_6H_3Ph_3$ and BzCl similarly give 2 : 4 : 6-*triphenylbenzophenone* (II), m.p. 168°. The products obtained by heating the ketones at 250—270° (1 hr.) with KOH are: from (I), *p*-$C_6H_4Me$·$CO_2H$ (III) and *p*-$C_6H_4Pr^{\beta}$·$CO_2H$; from (II), *s*-$C_6H_3Ph_3$ and BzOH; from *p*-methylbenzophenone, (III) and BzOH; from COPhMe, $CH_4$ and BzOH; from *p*-methyl-, (III) and $CH_4$, and from *p*-ethyl-acetophenone, *p*-$C_6H_4Et$·$CO_2H$ and $CH_4$. R. T.

***cyclo*Pentane derivative from αδ-dibromo-αδ-dibenzoylbutane.** R. C. Fuson, A. Lippert, R. V. Young, and H. H. Hully (J. Amer. Chem. Soc., 1936, **58**, 2633—2634; cf. this vol., 24).—3-Cyano-6-benzoyl-2-phenyl-5 : 6-dihydro-1 : 4-pyran (I) (A., 1932, 63) (from αδ-dibromo-αδ-dibenzoylbutane and NaCN) is converted by 85% $H_3PO_4$ + a little 95% EtOH (first at room temp. and then at the b.p.) into 3-benzoyl-2-phenyl*cyclo*pentanone (II). The mechanism is probably: (I) → 3-$CO_2H$ derivative → δ-hydroxy-αδ-dibenzoylvaleric acid → α-hydroxy-αδ-dibenzoylbutane → 1 : 2-dihydroxy-3-benzoyl-2-phenyl*cyclo*pentane → (II). The similar conversion of β-*benzoyloxy*-α*ζ*-*diketo*-α*ζ*-*diphenylhexane* (III), m.p. 110—111°, into (II) supports this scheme. δ-*Bromo*-δ-*benzoylvaleric acid*, m.p. 109—110° (from the CO-acid and Br in $CCl_4$) (as chloride), with $C_6H_4$ and $AlCl_3$ at 0°—room temp. gives β-*bromo*-α*ζ*-*diketo*-α*ζ*-*diphenylhexane*, m.p. 62—63°, converted by NaOBz in aq. EtOH into (III). H. B.

**Demethylations and demethyleneations.** P. Pfeiffer and W. Loewe (J. pr. Chem., 1937, [ii], **147**, 293—310; cf. A., 1928, 420).—Simple aromatic OMe-compounds are readily demethylated by $AlBr_3$ in boiling $C_6H_6$; CO, CHO, and $CO_2H$ do not influence the course of the reaction significantly except that in calculating the quantity of $AlBr_3$ it must be recognised that CO· and $CO_2H$ both react with $AlBr_3$. If $CH_2$ is interposed between CO and Ph the yield of demethylated product remains good but a chain of 2 $CH_2$ is disadvantageous; if a chain of 4 $CH_2$ is present a normal product of demethylation cannot be isolated. With unsaturated, aromatic OMe-ketones $AlBr_3$ is useful provided only one ethylenic linking is present; if two such are vicinal to CO the yield of OH-compound is minimal. In general demethyleneation resembles demethylation but the yields are poorer. The demethylation of 2-, 3-, and 4-methoxy-, 4-ethoxy-,

2 : 4- and 4 : 4'-dimethoxy-benzophenone is described. *p*-Toluenesulphonamidobenzophenone is converted by $Me_2SO_4$ and 50% KOH in MeOH into p-*toluenesulphonmethylamidobenzophenone*, m.p. 119°, hydrolysed by conc. $H_2SO_4$ at 100° to p-*methylaminobenzophenone*, m.p. 111°, which is not demethylated by $AlBr_3$ in boiling $C_6H_6$. *p*-$C_6H_4Bz{\cdot}NMe_2$ is similarly unaffected whereas *p*-$NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$-*p'* affords *p*-$NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}OH$-*p'*. *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ and *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ behave normally whereas *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ is unchanged in boiling $C_6H_6$ but converted into *p*-hydrocoumaric acid, m.p. 127—129° from boiling PhMe. 3 : 4-$(CH_2O_2)C_6H_3{\cdot}CO_2H$ and 3 : 4-$(CH_2O_2)C_6H_3{\cdot}CH_2{\cdot}CO_2H$ are demethylated but very extensive decomp. occurs with 3 : 4-$(CH_2O_2)C_6H_3{\cdot}[CH_2]_2{\cdot}CO_2H$ and 3 : 4-$(CH_2O_2)C_6H_3{\cdot}[CH_2]_4{\cdot}CO_2H$. 3 : 4-Methylenedioxybenzpiperidide is converted into *protocatechupiperidide*, m.p. 187·5°. The reaction with methylenecaffepiperidide, tetrahydropiperine, or piperine is either unsuccessful or complex. Caffeine and hydrohydrastinine are unaffected whereas papaverine gives a substance (*sulphate*, $C_{11}H_{15}O_4N,H_2SO_4$). Piperonal affords protocatechualdehyde. 2 : 4-$(NO_2)_2C_{10}H_5{\cdot}OMe$ yields 2 : 4-$(NO_2)_2C_{10}H_5{\cdot}OH$ but β-$C_{10}H_7{\cdot}OPh$ is unaffected. H. W.

**Optically active methyl- and ethyl-benzoins.** A. McKenzie and A. Ritchie (Ber., 1937, **70**, [*B*], 23—36).—Under defined conditions, *r*-atrolactamide is converted by MgPhBr in $Et_2O$ into *r*-methylbenzoin (I), m.p. 65—66°, identical with that derived from MgMeI and benzil. (+)-Atrolactic acid gives the corresponding *Me* ester, b.p. 107—108°/4 mm., $[\alpha]_{5791}^{18\cdot3}$ +32·1°, $[\alpha]_{5461}^{18\cdot3}$ +37·4°, $[\alpha]_{4358}^{18\cdot3}$ +74·8°, slowly transformed by aq. $NH_3$ at room temp. into (−)-*atrolactamide* (II), m.p. 62—63°, $[\alpha]_D^{17}$ −12·6°, $[\alpha]_{5461}^{17}$ −14·5° in $COMe_2$. (+)-Atrolactamide (III) has m.p. 62·5—63·5°, $[\alpha]_D^{17}$ +12·6°, $[\alpha]_{5461}^{17}$ +14·8° in $COMe_2$. (II) is transformed by MgPhBr into non-cryst. (−)-*benzoylphenylmethylcarbinol* (IV) (*methylbenzoin*), $[\alpha]_{5461}^{20}$ −260·1° in $COMe_2$, −176·6° in EtOH, accompanied by much $CPh_2Me{\cdot}OH$ arising thus: $OH{\cdot}CPhMe{\cdot}CO{\cdot}NH_2 \rightarrow MgBr{\cdot}O{\cdot}CPhMe{\cdot}CN \rightarrow MgBr{\cdot}O{\cdot}CPh_2Me \rightarrow CPh_2Me{\cdot}OH$. Owing to the absence of mobile H, (IV) is not racemised by KOH–EtOH at room temp. Treatment of (IV) with MgPhBr affords (+)-αα*β-triphenyl-β-methylethylene glycol*, m.p. 81—82°, $[\alpha]_{5791}^{19}$ +76·6°, $[\alpha]_{5461}^{19}$ +89° in EtOH. (−)-αα*β-Triphenyl-β-methylethylene glycol*, has m.p. 81—82°, $[\alpha]_{5791}^{20\cdot6}$ −75·9°, $[\alpha]_{5461}^{20\cdot6}$ −88·2° in EtOH. *r*-α-Hydroxy-α-phenyl-*n*-butyric acid (V), m.p. 129—131°, obtained from $BzCO_2H$ and MgEtBr in $Et_2O$, is transformed successively into the *Me* ester, b.p. 115—118°/6 mm., the *amide*, m.p. 91—91·5°, and r-*benzoylphenylethylcarbinol* (r-*ethylbenzoin*), m.p. 68—69°, also with some difficulty from benzil and MgEtBr. (V) is resolved by quinine in EtOH into (+)-α-*hydroxy-α-phenyl*-n-*butyric acid*, m.p. 128—129°, $[\alpha]_D^{20}$ +32·3°, $[\alpha]_{5461}^{20}$ +38·1° in $H_2O$, $[\alpha]_D^{20}$ +28·7°, $[\alpha]_{5461}^{20}$ +35·7° in $COMe_2$, $[\alpha]_D^{20}$ +32·7°, $[\alpha]_{5461}^{20}$ +39·9° in EtOH, which gives the *Me* ester, b.p. 127°/17 mm., $[\alpha]_D^{20}$ +24·7°, $[\alpha]_{5791}^{20}$ +26·2°, $[\alpha]_{5461}^{20}$ +31·1°, $[\alpha]_{4358}^{20}$ +65·6°, the (−)-*amide*, m.p. 91·5—92°, $[\alpha]_D^{19}$ −15°, $[\alpha]_{5461}^{19}$ −19° in $COMe_2$, and thence $CPh_2Et{\cdot}OH$, m.p. 94—95°, and (−)-*benzoylphenylethylcarbinol* [(−)-*ethylbenzoin*], m.p. 69—70°, $[\alpha]_D^{17}$ −191·3°, $[\alpha]_{5791}^{17}$ −201·5°, $[\alpha]_{5461}^{17}$ −241·4° in $COMe_2$, $[\alpha]_D^{17}$ −199·3°, $[\alpha]_{5791}^{17}$ −210·9°, $[\alpha]_{5461}^{15}$ −250·8° in EtOH, $[\alpha]_D^{17}$ +145·8°, $[\alpha]_{5791}^{17}$ +154·3°, $[\alpha]_{5461}^{17}$ +180·5° in $CS_2$, which is not racemised by KOH–EtOH. The inadequacy of the present nomenclature for substances of this type is pointed out.

In attempts to establish the configurative relationship between $OH{\cdot}CHPh{\cdot}CO_2H$ and $OH{\cdot}CPhMe{\cdot}CO_2H$, (I) is found to be reduced by Al–Hg, Zn dust and NaOH, or Na–Hg to a mixture of *r*-α- (VI) and *r*-β- (VII) -methylhydrobenzoin and by $H_2$ (Pt) to cryst. (VI) doubtless containing a small proportion of (VII). (IV) gives a lævorotatory mixture (VIII) of the two corresponding diastereoisomeric glycols when reduced by $H_2$. For these the configurations (IX) and (X) are possible and (IX) is tentatively assigned to the β-glycol. (VIII) is regarded as a mixture of (IX) and (XI) [mirror image of (X)] since it has $[\alpha]_{5893}$ −33°.

| | | |
|---|---|---|
| OH | OH | OH |
| Ph·C·Me(−) | Me·C·Ph(+) | PhC·Me(−) |
| H·C·OH(−) | H·C·OH(−) | OH·C·H(+) |
| Ph | Ph | Ph |
| (IX.) | (X.) | (XI.) |

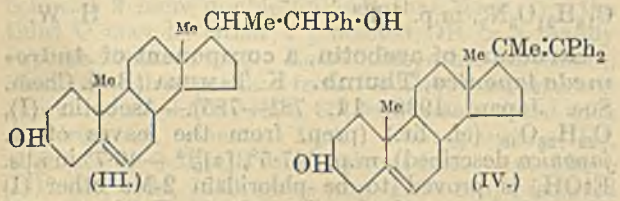
Since the prep. of (IV) from the acid does not involve change of configuration and since (−)-OH·CHPhBz and (−)-CHPhAc·OH are derived from (−)-$OH{\cdot}CHPh{\cdot}CO_2H$ without configurative change and a lævorotatory mixture of glycols is obtained from (IV) whereas the glycols from (−)-$OH{\cdot}CHPh{\cdot}CO_2H$ and (−)-CHPhAc·OH are the optically homogeneous, dextrorotatory α- or β-glycols, it appears that (+)-$OH{\cdot}CPhMe{\cdot}CO_2H$ and (−)-$OH{\cdot}CHPh{\cdot}CO_2H$ have opposite configurations in harmony with Freudenberg's views.

(I) is transformed by MgEtBr into r-αβ-*diphenyl*-β-*methyl*-α-*ethylethylene glycol*, b.p. 170—171°/5 mm. *r*-Atrolactamide and MgEtBr give COPhMe, $OH{\cdot}CPhMe{\cdot}COEt$ (2 : 4-*dinitrophenylhydrazone*, m.p. 140—141°), and $CPhMeEt{\cdot}OH$. H. W.

**Attempted syntheses of natural sterols. II. Synthesis of 7-hydroxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene.** G. Haberland and E. Blanke (Ber., 1937, **70**, [*B*], 169—171).—Interaction of $CNaMe(CO_2Et)_2$ and β-6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylethyl bromide in xylene at 150° followed by hydrolysis of the product with KOH gives *methyl*-β-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylethylmalonic acid* (I), m.p. 132—133°, which passes at 160° into γ-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*-α-*methylbutyric acid*, b.p. 160° (bath)/0·03 mm., m.p. 96° (*amide*, m.p. 106°). (I) is dehydrogenated by S to γ-6-*methoxy*-1-*naphthyl*-α-*methyl*-n-*butyric acid*, m.p. 89° (*amide*, m.p. 144°), converted by 90% $H_2SO_4$ at room temp. into 1-*keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 108°, which is demethylated (48% HBr in AcOH) to 7-*hydroxy*-1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*. H. W.

**17-*iso*-Δ$^5$-Pregnen-3-ol-20-one.** A. Butenandt and G. Fleischer (Ber., 1937, **70**, [*B*], 96—102).—3-Acetoxybisnorcholenic acid, $[\alpha]_D^{20}$ −73·5° in $CHCl_3$, exists in a stable form, m.p. 235—236°, and a labile *modification*, m.p. 224—226°, which rapidly passes

into the stable variety. The Me ester (I), $[\alpha]_D^{20}$ −61·9° in $CHCl_3$, forms leaflets, m.p. 138—139°, and stable *prisms*, m.p. 156—157°. Treatment of (I) with MgPhBr gives the corresponding diphenylcarbinol (II) and *phenyl*-3-*hydroxy*-$\Delta^5$-20-*pregnenylcarbinol* (III), m.p. 243°. (II) is converted by successive treatments with KOH–MeOH, AcOH, and $Ac_2O$ into the *acetate*, m.p. 217°, of the *alcohol* (IV), m.p. 112°, transformed by Br in $CHCl_3$ and subsequent ozonisation into pregnenolone (V). (III) (*diacetate*, m.p. 220—221°) is con-




verted by the successive action of Br and $CrO_3$ in AcOH into *Ph* 3-*keto*-20-$\Delta^4$-*pregnenyl ketone*, m.p. 227—228°, $[\alpha]_D^{20}$ +86·58° in dioxan (*oxime*, m.p. 208—209°). (V) is isomerised to the extent of about 30% by 5% KOH–MeOH to 17-iso-$\Delta^5$-*pregnen*-3-*ol*-20-*one* (VI), m.p. 172—173°, $[\alpha]_D^{20}$ −140·5° in EtOH, which cannot be separated from unchanged (V) by crystallisation. More success is obtained by employment of the acetates but iso*pregnenolonyl acetate*, m.p. 170—171°, $[\alpha]_D^{20}$ −126° in EtOH, cannot be hydrolysed without isomerisation. In contrast with (V), (VI) yields a sparingly sol., additive compound with digitonin through which its isolation is achieved. H. W.

**Corticosterone, a crystallised compound with the biological activity of the adrenal-cortical hormone.** P. DE FREMERY, E. LAQUEUR, T. REICHSTEIN, R. W. SPANHOFF, and I. E. UYLDERT (Nature, 1937, **139**, 26).—Further purification of the active substance obtained (A., 1936, 473, 1383) from the cortex of the adrenal gland yields a cryst. substance, m.p. 180—182° (corr.), $[\alpha]_D^{15}$ +223° in EtOH, *corticosterone*, a highly active cortical hormone, the biological activity of which is described. L. S. T.

**Synthesis of phenanthrene and hydrophenanthrene derivatives. VII. 1′ : 3′-Diketo-5 : 9-dimethoxy-1 : 2-*cyclo*pentenophenanthrene.** L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1936, **58**, 2382—2385).—A continuation of previous work (see this vol., 24). 1 : 5-$C_{10}H_6(OMe)_2$, $(\cdot CH_2\cdot CO)_2O$, and $AlCl_3$ in cold $C_2H_2Cl_4$–$PhNO_2$ give β-4 : 8-*dimethoxy*-1-*naphthoylpropionic acid*, m.p. 175—176° (*Et* ester, m.p. 53—53·5°), reduced (Clemmensen) to 20—25% of γ-4 : 8-*dimethoxy*-1-*naphthylbutyric acid*, m.p. 154—154·5° [*Me*, m.p. 65—65·5°, and *Et* (I), b.p. 201—203°/1 mm., m.p. 47—47·5°, esters], and some γ-8-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylbutyric acid* (II), m.p. 74·5—75·5° [oxidised (alkaline $KMnO_4$) to 3-methoxyphthalic acid]. The oxalyl derivative from (I) is cyclised (78% $H_2SO_4$) to 5 : 9-*dimethoxy*-3 : 4-*dihydrophenanthrene*-1 : 2-*dicarboxylic anhydride*, m.p. 231—232° [corresponding $Me_2$ ester (III), m.p. 151—153°], dehydrogenated (S at 250—300°) to 5 : 9-*dimethoxyphenanthrene*-1 : 2-*dicarboxylic anhydride* (IV), m.p. 289—290° [corresponding $Me_2$ ester (V), m.p. 133—134°, prepared by dehydrogenation (S) of (III)]. (V) with EtOAc+Na followed by hydrolysis (dil. HCl) of the resultant Na derivative gives 1′ : 3′-*diketo*-5 : 9-*dimethoxy*-1 : 2-cyclo*pentenophenanthrene*, m.p. 281—283° (decomp.) (softens about 265°). (IV) heated with EtOH–HCl for 24 hr. yields *Et*$_2$ 5(or 9)-*methoxy*-9(or 5)-*ethoxyphenanthrene*-1 : 2-*dicarboxylate*, m.p. 109·5—110°, converted [as for (V)] into 1′ : 3′-*diketo*-5(or 9)-*methoxy*-9(or 5)-*ethoxy*-1 : 2-cyclo*pentenophenanthrene*, m.p. 207—208°. β-2 : 6-*Dimethoxy*-1-*naphthoylpropionic acid*, m.p. 156—156·5°, is reduced (modified Clemmensen) to γ-2 : 6-*dimethoxy*-1-*naphthylbutyric acid*, m.p. 122—124°; a by-product of type (II) could not be found. The products from the above reductions are remethylated prior to separation. 4-*Methoxy*-1-*methylnaphthalene* (*picrate*, m.p. 148—149°) has b.p. 164·5—165°/21 mm. Dehydrogenation (Se) of impure (II) gives α-$C_{10}H_7$·OMe as the only identifiable product. All m.p. are corr. H. B.

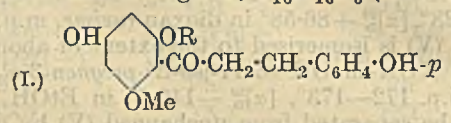
**Degradation of cholic acid to 3 : 7 : 12-trihydroxypregnan-20-one.** H. MORSMAN, M. STEIGER, and T. REICHSTEIN (Helv. Chim. Acta, 1937, **20**, 3—16; cf. Shimizu and Kazuno, this vol., 20).—Gradual addition of Me cholate (improved prep.) in $C_6H_6$ to MgMeBr in $Et_2O$ gives 3 : 7 : 12-trihydroxynorcholyldimethylcarbinol, m.p. 184—185° (corr.) [also +1$H_2O$, m.p. 126—130° (decomp.)], converted by protracted heating with $Ac_2O$ in $C_5H_5N$ at 100° into the corresponding tetra-acetate, m.p. 108—111° (corr.), and by less drastic treatment at 55—60° into the triacetate, m.p. (indef.) 60—80° (cf. *loc. cit.*). Either acetate is oxidised by $CrO_3$ (= 6 O) in AcOH at 90—95° to triacetylnorcholic acid (I), m.p. 105—108°, $[\alpha]_D^{18}$ +86·5° in abs. EtOH (*Me* ester, m.p. 70—71°), hydrolysed by KOH–$H_2O$–MeOH to norcholic acid, m.p. 188—192° (corr.) from $COMe_2$ or m.p. 200° (corr.) from $C_6H_6$. Me norcholate, m.p. (indef.) 110—125° and, after, re-solidification, m.p. 160—161°, $[\alpha]_D^{18}$ +37·5° in abs. EtOH (also +4MeOH), is transformed by MgMeBr into 3 : 7 : 12-trihydroxybisnorcholyldimethylcarbinol, m.p. 238—242° (corr.; decomp.), the tetra-acetate, m.p. 131—132°, of which is oxidised to non-cryst. *triacetylbisnorcholic acid* (II), whence *bisnorcholic acid*, m.p. 298—301° (corr.; decomp.), $[\alpha]_D^{18}$ +13·8° in abs. EtOH. *Diphenyl*-3 : 7 : 12-*trihydroxynorcholylcarbinol*, m.p. 202—205° (corr.), $[\alpha]_D^{17}$ +23·8° in abs. EtOH, is transformed into the non-cryst. *acetate*, which is oxidised to (I); it is converted by I in boiling $C_6H_6$ or by boiling mineral acid into *diphenyl*-3 : 7 : 12-*trihydroxynorcholylidenemethane*, m.p. 220—230°, $[\alpha]_D^{18}$ +52·8° in abs. EtOH, the *triacetate*, m.p. 83—85°, of which is ozonised or oxidised mainly to (I). *Diphenyl*-3 : 7 : 12-*trihydroxybisnorcholylcarbinol* gives a non-cryst. *acetate*, oxidised to (II). *Me bisnorcholate* (+0·5$H_2O$), m.p. 97—98° and m.p. 156—159° after re-solidification at about 125—140°, $[\alpha]_D^{17}$ +22·0° in abs. EtOH, is transformed by MgPhBr into the corresponding non-cryst. carbinol and thence by $Ac_2O$ in $C_5H_5N$ into *diphenyl*-3 : 7 : 12-*triacetoxyternorcholylcarbinol*, m.p. 252° (corr.), $[\alpha]_D^{18}$ +23·11° in abs. EtOH, which is dehydrated by AcOH at 165° to αα-*diphenyl*-β-*methyl*-β-3 : 7 : 12-*triacetoxyætiocholylethylene*, m.p. 182—183° (corr.), $[\alpha]_D^{20}$ +423·6° in abs. EtOH. This is converted by ozonisation in $CHCl_3$ followed by treatment with Zn

filings and AcOH into the hygroscopic 3 : 17 : 12-*triacetoxypregnan*-20-*one*, m.p. 134—135° (corr.), $[\alpha]_D^{19}$ +120·7° in abs. EtOH, whence 3 : 7 : 12-*trihydroxypregnan*-20-*one*, m.p. 120—127° (decomp.), $[\alpha]_D^{18}$ +107·75° in abs. EtOH. H. W.

**General method of preparing α-amino- and αγ-diamino-keto-compounds. II.** P. W. Neber, A. Burgard, and W. Thier (Annalen, 1936, **526**, 277—294; cf. A., 1935, 345).—The method could not be successfully applied to 3 : 4-*dihydroxyacetophenoneoxime*, m.p. 184° (decomp.), 3 : 4-*diacetoxyacetophenone*, m.p. 91°, 3 : 4-*dibenzoyloxyacetophenone*, m.p. 118°, or 3 : 4-*dimethoxyacetophenoneoxime*, m.p. 144°; the last is converted by *p*-$C_6H_4Me{\cdot}SO_2Cl$ into 3 : 4-dimethoxyacetanilide, m.p. 133°. 3 : 4-Methylenedioxyacetophenoneoxime is transformed by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in well-cooled $C_5H_5N$ into the unstable *p-toluenesulphonate*, m.p. 75° (decomp.), which is transformed by KOEt–EtOH into ω-amino-3 : 4-methylenedioxyacetophenone [hydrochloride (I), m.p. 193°]. Piperonal and $MeNO_2$ in presence of KOH–EtOH afford α-*nitro*-β-3 : 4-*piperonylethylene*, m.p. 161° (with the corresponding *nitro-alcohol*, $C_9H_9O_5N$, m.p. 94°), transformed by Br in boiling $CHCl_3$ into β-*bromo*-α-*nitro*-β-3 : 4-*piperonylethylene*, m.p. 98—99°, which is converted by KOH in boiling MeOH into ω-*nitroacetopiperone*, m.p. 172°, hydrogenated ($PtO_2$ in AcOH) to (I). OH·N:CMe·$CH_2$·$CO_2Et$ is unsuited to the isomerisation on account of its ready passage into methyl*iso*oxazolone but acetoacetanilideoxime is transformed into its *p-toluenesulphonate*, m.p. 128° (decomp.), converted by KOEt–EtOH followed by 2*N*-HCl into α-*aminoacetoacetanilide hydrochloride* (corresponding *sulphate*) which on treatment with alkali gives the *diazine*, NHPh·CO·CH<CMe:N / N:CMe>CH·CO·NHPh, m.p. 222° (decomp.). $CH_2Ac{\cdot}CO_2Et$ and *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$ at 160° give *acetoacet*-p-*dimethylaminoanilide*, m.p. 113°, the *oxime*, m.p. 137° (decomp.), of which could not be converted into the *p*-toluenesulphonate. *Acetoacet*-p-*nitroanilide*, m.p. 124°, is converted by $NaNO_2$ and $H_2SO_4$ into *oximinoacetoacet*-p-*nitroanilide*, m.p. 185° (decomp.). 1-Hydrindoneoxime gives the p-*toluenesulphonate*, m.p. 157° (decomp.), and thence 2-amino-1-hydrindone (hydrochloride, decomp. >240°; picrate, decomp. 156°) in good yield. 1-*Oximino*-1 : 2 : 3 : 4-*tetrahydronaphthalene* p-*toluenesulphonate*, m.p. 96°, yields 2-*amino*-1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, decomp. 117°, in 72% yield. 6-Phenyl-2 : 2-dimethyl-4-piperidone is transformed by $Me_2SO_4$ and anhyd. $Na_2CO_3$ into 6-*phenyl*-1 : 2 : 2-*trimethyl*-4-*piperidone*, m.p. 78°, and thence successively into its *oxime*, two (?) stereoisomeric forms, m.p. 181—182° and 164—165° respectively, its p-*toluenesulphonate*, m.p. 107° (decomp.), and the non-cryst. 5-*amino*-6-*phenyl*-1 : 2 : 2-*trimethyl*-4-*piperidone* (very hygroscopic *hydrochloride*). 2 : 6-*Diphenyl*-1-*methylpiperidone*-4-*oxime*, m.p. 190°, yields a p-*toluenesulphonate*, m.p. 98°, and 2-*naphthalenesulphonate*, m.p. 120° (decomp.), which give 5-*amino*-2 : 6-*diphenyl*-1-*methylpiperidone dihydrochloride*, decomp. 130° after softening at 90°, converted by dil. alkali into the "*dihydrodiazine*," $C_{36}H_{36}N_4$, m.p. 187° (decomp.) after becoming yellow at 160°. ε-*Methylamino*-αε-*diphenyl*-Δ$^{\alpha}$-*penten*-γ-*one*, m.p. 100°, is incidentally described.

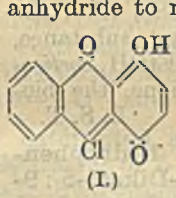
Acetoneoxime *p*-toluenesulphonate is converted by successive treatment with KOEt–EtOH and BzCl into benzamidoacetone, m.p. 85°, the *oxime* (II), m.p. 136°, of which is transformed through its unstable p-*toluenesulphonate*, m.p. 74° (decomp.), into α-*amino*-γ-*benzamidoacetone hydrochloride*, m.p. 207°. (II) is converted by 2-$C_{10}H_7{\cdot}SO_2Cl$ into a *substance*, $C_{18}H_{21}O_3N_3$, m.p. 183°. H. W.

**Structure of asebotin, a component of *Andromeda japonica*, Thumb.** K. Tamura (Bull. Chem. Soc. Japan, 1936, **11**, 781—785).—Asebotin (I), $C_{22}H_{26}O_{10}$ (cf. lit.) (prep. from the leaves of *A. japonica* described), m.p. 147·5°, $[\alpha]_D^{23\cdot5}$ −46·7° in abs. EtOH, is proved to be phloridzin 2-Me ether (I) (R = glucose residue). (I) and 5% $H_2SO_4$ at 100° give glucose and asebogenin, $C_{16}H_{16}O_5$ (cf. lit.), m.p.

(I.) 


168° ($Ac_2$ derivative, m.p. 76—77°); the aglucone and KOH at 170—180° give phloretic acid and phloroglucinol Me ether (II). (II) and phloretonitrile give (Hoesch) iso*asebogenin* (2 : 4 : 4′-*trihydroxy*-6-*methoxy*-β-*phenylpropiophenone*), m.p. 201—202°. (I) and MeI–$K_2CO_3$–$COMe_2$ give a viscous *ether*, hydrolysed by acid to 2-hydroxy-4 : 6 : 4′-trimethoxy-β-phenylpropiophenone, m.p. 109—110°. R. S. C.

**Synthesis of *ana*quinones.** H. Waldmann and H. Poppe (Annalen, 1937, **527**, 190—194).—Gradual addition of a mixture of 1 : 4-$C_{10}H_6Cl{\cdot}OH$ and maleic anhydride to molten $AlCl_3$–NaCl at 180—220° gives

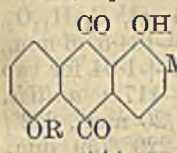


(I.)

10-chloro-1-hydroxy-4 : 9-anthraquinone (I), m.p. 205—206°, identical with that obtained from $SOCl_2$ and quinizarin. Similarly citraconic anhydride (II) and 1 : 4-$C_{10}H_6Cl{\cdot}OH$ give the isomeric 10-*chloro*-1-*hydroxy*-2(or 3)-*methyl*-4 : 9-*anthraquinones*-A, m.p. 202° (*acetate*, m.p. 210·5°), and -B (III), m.p. 174—175° [*acetate* (IV), m.p. 212°]. *o*-$C_6H_4(CO)_2O$ and toluquinol yield 1 : 4-*dihydroxy*-2-*methylanthraquinone* (V), m.p. 175° (acetate, m.p. 213°, identical with (IV)], converted by $SOCl_2$ into (III). (V) is obtained from naphthaquinol and (II). H. W.

***Aspergillus* colouring matters. I.** H. Raistrick, R. Robinson, and A. R. Todd (J.C.S., 1937, 80—88).—Flavoglaucin, $C_{19}H_{28}O_3$ (I) [2 : 4-dinitrophenylhydrazone, m.p. 179—181°, and a *form*, m.p. 186—187°; *substance*, $C_{25}H_{31}O_2N_2$, m.p. 137°, by the action of an excess of $NHPhNH_2$; *substance*, $C_{25}H_{34}O_2N_2$, m.p. 161°, by interaction with *o*-$C_6H_4(NH_2)_2$], contains 2 OH (Zerevitinov) and gives $H_2C_2O_4$, *n*-octoic acid (showing presence of a $CH_3{\cdot}[CH_2]_6{\cdot}C$: group), AcOH (?), and unidentified acids when oxidised with 4% $KMnO_4$–$C_5H_5N$ at room temp. Auroglaucin, $C_{19}H_{22}O_3$ (II), m.p. 153°, gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 223—224°, *phenylurethane*, m.p. 161°, *substance*, m.p. 108—109°,

obtained with $Ac_2O$, and a *substance*, $C_{25}H_{28}O_2N_2 + H_2O$, m.p. 185° (decomp.), by the action of *o*-$C_6H_4(NH_2)_2$. Partial hydrogenation of (I) ($3H_2$) and of (II) ($6H_2$) affords the same *product*, m.p. 111°, consisting mainly of an unsaturated alcohol, $C_{19}H_{32}O_2$ (*phenylurethane*, sinters 157°, m.p. 160—161°). Complete hydrogenation (Pt–$SiO_2$) of (I) and (II) requires $7H_2$ and $10H_2$, respectively: the product, b.p. 173—175°/12 mm., so obtained from (I) appears to be a mixture of an alcohol $C_{19}H_{38}O$ and $C_{19}H_{38}$. (II) thus contains 3 more double linkings than does (I): the third O may be either a protected OH or a readily ruptured ether linking. Emodin $Me_1$ ether (physcion), identical with a specimen from *Ventilago madraspatana* (Perkin *et al.*, J.C.S., 1894, **65**, 943), was isolated with (I) from *A. glaucus*, Link. Rubroglaucin (III), $C_{16}H_{12}O_5 + 0{\cdot}5EtOH$ and solvent-free, m.p. 180—181° (A., 1934, 1263, gives m.p. 172—173)°, isolated from *A. ruber*, *A. albidus*, and *A. glaucus alba*, gives a $Ac_2$ derivative, $+H_2O$, m.p. 226—228°, and affords 2-methylanthracene when distilled with Zn dust; (I) is therefore a dihydroxymethoxymethylanthraquinone. Demethylation of (III) with conc. $H_2SO_4$ at 140—150° gives a *substance*, $C_{15}H_{10}O_5 + H_2O$, m.p. 220° ($Ac_3$ derivative), probably (*A*) (R = H, Me at 2, 3, or 7), since it is different from 1 : 3 : 4-*trihydroxy*-2-*methylanthraquinone* $+H_2O$ (IV), m.p. approx. 268—270° (partial sublimation), synthesised as follows: resacetophenone with KOH–MeOH–MeI gives 2-hydroxy-4-methoxy-3-methylacetophenone, converted by *N*-NaOH–MeOH–3% $H_2O_2$ (under $H_2$) and subsequent methylation into 2 : 3 : 6-*trimethoxytoluene*, b.p. 145—147°/14 mm., converted by *o*-$C_6H_4(CO)_2O$–$AlCl_3$ in $CS_2$ into o-(2′ : 5′-*dimethoxy*-p′-*toluoyl*)*benzoic acid*, m.p. 205—208°, cyclised by conc. $H_2SO_4$ at 150—160° to (IV). (III) is probably *A* (R = Me). J. W. B.



(*A*.)

**Aminoanthraquinone dyes derived from tetrachloroquinizarin.** H. Waldmann (J. pr. Chem., 1937, [ii], **147**, 326—330).—5 : 6 : 7 : 8-Tetrachloro-1 : 4-dimethoxyanthraquinone is converted by *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ and KOAc in $PhNO_2$ containing $Cu(OAc)_2$ at 200—210° into 6 : 7-*dichloro*-5 : 8-*di*-p-*toluenesulphonamido*-1 : 4-*dimethoxyanthraquinone*, m.p. 255° (decomp.), transformed by conc. $H_2SO_4$ at room temp. into 6 : 7-*dichloro*-5 : 8-*diamino*-1 : 4-*dimethoxyanthraquinone*, decomp. about 290°, which is demethylated by conc. $H_2SO_4$ at 120° to 6 : 7-*dichloro*-5 : 8-*diaminoquinizarin*, decomp. 285°. 5 : 8-Di-*p*-toluenesulphonmethylamido-1 : 4-dimethoxyanthraquinone and conc. $H_2SO_4$ yield 5 : 8-*di*(*methylamino*)-1 : 4-*dimethoxyanthraquinone*, m.p. 300° (decomp.), which with $H_3BO_3$ in conc. $H_2SO_4$ at 120° gives 5 : 8-*di*(*methylamino*)*quinizarin*, m.p. >310°. 6 : 7-Dichloro-5 : 8-di-*p*-toluenesulphonamido-1 : 4-dimethoxyanthraquinone and *p*-$C_6H_4Me{\cdot}SO_3Me$ in *o*-$C_6H_4Cl_2$ containing $K_2CO_3$ at 170—180° afford 6 : 7-*dichloro*-5 : 8-*di*-p-*toluenesulphonmethylamido*-1 : 4-*dimethoxyanthraquinone*, decomp. 245°, whence 6 : 7-*dichloro*-5 : 8-*di*(*methylamino*)-1 : 4-*dimethoxyanthraquinone*, decomp. 186°, and 6 : 7-*dichloro*-5 : 8-*di*(*methylamino*)-*quinizarin*, decomp. 249°. H. W.

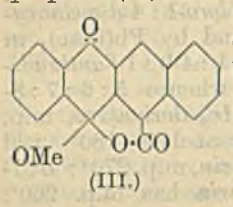
**5 : 6 : 7 : 8-Tetrachloroquinizarin and 5 : 6 : 7 : 8-tetrachloro-1 : 2-benzanthraquinone.** H. Waldmann (J. pr. Chem., 1937, (ii), **147**, 331—337).—Gradual addition of a mixture of $C_6Cl_4(CO)_2O$ and quinol to $AlCl_3$–NaCl at 130—135°, subsequently raised to 150—155°, gives 3′ : 4′ : 5′ : 6′-*tetrachloro*-2 : 5-*dihydroxybenzophenone*-2-*carboxylic acid*, m.p. 231° (yield 82%); if the temp. of the mixture is raised to 210—215°, 5 : 6 : 7 : 8-tetrachloroquinizarin (I), m.p. 247°, is obtained almost quantitatively. (I) is transformed by *p*-$C_6H_3Me{\cdot}SO_3Me$ and $Na_2CO_3$ in *o*-$C_6H_4Cl_2$ at 170° into 5 : 6 : 7 : 8-*tetrachloro*-1 : 4-*dimethoxyanthraquinone* (II), m.p. 290°, and by $Pb(OAc)_4$ in AcOH into 5 : 6 : 7 : 8-*tetrachloro*-1 : 4-9 : 10-*anthradiquinone*, m.p. 250° (decomp.), whence 5 : 6 : 7 : 8-*tetrachloropurpurin*, m.p. 265° ($Ac_3$ derivative, m.p. 208°). (I), $NH_2Ph$, and NaOAc at 170—180° yield 6 : 7-*dichloro*-5 : 8-*dianilinoquinizarin*, m.p. 270°; 6 : 7-*dichloro*-5 : 8-*di*-p-*toluidinoquinizarin* has m.p. 260°. 6 : 7-*Dichloro*-5 : 8-*dianilino*-1 : 4-*dimethoxyanthraquinone*, m.p. 265°, is obtained from (II). (I) is reduced by Sn + HCl in boiling AcOH to *tetrachlorohydroquinizarin*, $C_{14}H_6O_4Cl_4$, m.p. 254°, transformed by $NH_2Ph$ and $H_3BO_3$ at 100° into 5 : 6 : 7 : 8-*tetrachloro*-1 : 4-*dianilinoanthraquinone*, m.p. 295° after softening.

Tetrachloro-α-naphthoylbenzoic acid in $PhNO_2$ is transformed by $P_4O_{10}$ at 150—160° into 5 : 6 : 7 : 8-tetrachloro-1 : 2-benzanthraquinone, m.p. 254°, converted by *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ into 6 : 7-*dichloro*-5 : 8-*di*-p-*toluenesulphonamido*-1 : 2-*benzanthraquinone*, decomp. 245—246°, whence 6 : 7-*dichloro*-5 : 8-*diamino*-1 : 2-*benzanthraquinone*, m.p. 276°, converted by anhyd. NaOAc, Cu powder, and $C_{10}H_8$ at 220° into *dichlorodiaminodibenzindanthrone*, $C_{36}H_{18}O_4N_4Cl_2$. H. W.

**Condensations of the anhydride of 1 : 4-dihydroxyanthraquinone-2 : 3-dicarboxylic acid.** C. Marschalk (Bull. Soc. chim., 1937, [v], **4**, 184—193).—The anhydride (I) of 1 : 4-dihydroxyanthraquinone-2 : 3-dicarboxylic acid (II) reacts with $NH_2Ph$ in AcOH at room temp. to give the *$NH_2Ph$* salt of 2-*carbanilyl*-1 : 4-*dihydroxyanthraquinone*-3-*carboxylic acid* (III) which is liberated by HCl. Boiling AcOH converts (III) into a mixture of the (less sol.) *phenylimide* (IV) of (II) [best obtained by adding $NH_2Ph$ to (I) in $PhNO_2$ at 200°] and 2-*carbanilyl*-1 : 4-*dihydroxyanthraquinone*, also obtained by heating (I) with an excess of $NH_2Ph$ in $PhNO_2$, by decarboxylation of (III) with $Na_2S_2O_4$–$NaHCO_3$, or by the action of $NH_2Ph$ on 1 : 4-dihydroxyanthraquinone-2-carboxyl chloride. Similar condensation is effected between (I) and *o*-, *m*-, and *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ in AcOH to give derivatives of type (IV). Condensation of (I) with $C_6H_6$ or its appropriate derivative in presence of $AlCl_3$ affords 2-*benzoyl*-, m.p. 263—264° (V), 2-p-*toluoyl*-, m.p. 245—246°, and 2-p-*chlorobenzoyl*-, m.p. 260—261°, -1 : 4-*dihydroxyanthraquinone*-3-*carboxylic acid*, decarboxylated (boiling $C_5H_5N$ or $Na_2S_2O_4$–$NaHCO_3$) to give, respectively, 2-*benzoyl*-, m.p. 185—186°, 2-p-*toluoyl*-, m.p. 189—190°, and 2-p-*chlorobenzoyl*-, m.p. 257—258°, -1 : 4-*dihydroxyanthraquinone*. (V) is hydrolysed by boiling 5% NaOH to quinizarin. J. W. B.

**ψ-Form of methyl 2 : 3-benzanthraquinone-1-carboxylate.** H. Waldmann and R. Kretsch

(Ber., 1937, **70**, [*B*], 102—105).—1-Amino-2 : 3-benzanthraquinone is converted into 1-*cyano*-2 : 3-*benzanthraquinone*, m.p. 295·5°, hydrolysed by $H_2SO_4$ at 175° to 2 : 3-*benzanthraquinone*-1-*carboxylic acid* (I), m.p. 282°, converted by $PCl_5$ or $SOCl_2$ into the *chloride* (II), decomp. about 245°. Esterification of (I) is not readily effected by HCl–MeOH and *Me* 2 : 3-*benzanthraquinone*-1-*carboxylate*, m.p. 223°, is best obtained by heating *K* 2 : 3-*benzanthraquinone*-1-*carboxylate* with $KMeSO_4$ at 200° or from freshly-prepared (II) and boiling MeOH. At room temp. (II) and MeOH give *Me* ψ-2 : 3-*benzanthraquinone*-1-*carboxylate* (II), m.p. 193°, which is unchanged by short boiling with MeOH, partly isomerised by $H_2SO_4$–MeOH, and completely isomerised by boiling HCl–MeOH. (II) with $C_6H_6$ and sublimed $FeCl_3$ affords 9-*hydroxy*-9-*phenyl*-2 : 3-*benzoanthrone*-1-*carboxylactone*, m.p. 199°.



(III.)

H. W.

**Gland secretion of alligators (yacarol).**—See A., III, 88.

**Catalytic hydrogenation of α-ionone; ionol, dihydroionol, tetrahydroionol, dihydroionone, tetrahydroionone.** L. Palfray, S. Sabetay, and J. Kandel (Compt. rend., 1936, **203**, 1376—1378).—α-Ionone (I) with Ni–$H_2$ under pressure at 65° affords dihydro-α-ionone (A., 1934, 659) [semicarbazone, m.p. 171—172° (block)]; at 90° dihydro-α-ionol is also formed. At 150—240°, tetrahydroionol (A., 1919, i, 540) (*allophanate*, m.p. 164°) is formed, which when oxidised ($CrO_3$) affords tetrahydroionone. α-*Ionol* (II), b.p. 103°/3 mm. (*nitrobenzoyl* derivative, m.p. 62·5°), is prepared from α-ionone and $Al(OPr^{\beta})_3$ and is oxidised ($CrO_3$) to (I). (I) and (II), but not the other reduction products, give the same colour reaction with $CCl_3$·CHO and HCl. J. L. D.

**Menthylamines.** G. Vavon and I. Chilouet (Compt. rend., 1936, **203**, 1526—1528).—Since the $NH_2$ is closer in space to $Pr^{\beta}$ in neomenthylamine (I), the latter reacts more slowly than menthylamine with benzyl and trimethylbenzyl bromide, benzyl oxalate, and piperonal, and its formyl derivative is hydrolysed (alkali) more slowly (cf. A., 1926, 1147; 1927, 1080; 1931, 229; 1935, 88). This accounts for the difficulty in reducing neomenthoneoxime and for the reaction of (I) with $HNO_2$ (cf. A., 1931, 954). J. L. D.

**M.p. graphs of bornyl fumarates.** E. B. Abbot, A. McKenzie, and J. D. McB. Ross (Ber., 1937, **70**, [*B*], 163—168).—The m.p. graph of mixtures of (−)-bornyl fumarate (I) and *r*-bornyl fumarate exhibits two min. and a max. showing that the externally compensated ester is correctly described as racemic. The m.p. graph of mixtures of (+)-bornyl H fumarate and the optically inactive ester shows the racemic compound to be dissociated to the extent of 17%. The rectilinear course from 0% to 25% of (+)-ester indicates the formation of mixed crystals of (+)- and (−)-ester whereas between 25% and 50% of (+)-ester the production of a racemic compound is indicated. The graph of the m.p. of mixtures of (I) and (−)-bornyl (+)-bornyl fumarate (II) indicates the production of a partial racemate, m.p. 107·9°, which is unstable in the presence of an excess of (II) and is dissociated to a considerable extent. H. W.

**Bornylamines.** G. Vavon and I. Chilouet (Compt. rend., 1937, **204**, 53—55; see above).—Camphorimine with Pt–$H_2$ affords neobornylamine (I), isolated as the hydrochloride, in good yield, but the oxime reacts with difficulty. (I) reacts with $CH_2PhBr$, trimethylbenzyl bromide, benzyl oxalate, and piperonal less readily than does bornylamine. The formyl derivative of (I) is the less easily hydrolysed and is assigned the *cis*-structure (cf. A., 1926, 1042). J. L. D.

**Constitution of shonanic acid, one of the two characteristic volatile acids from the wood of *Libocedrus formosana*, Florin. I. Isolation of shonanic acid and its general properties.** N. Ichikawa (Bull. Chem. Soc. Japan, 1936, **11**, 759—769).—Extraction of the wood of *L. formosana* with 5% aq. NaOH, steam-distillation of the acidified solution, etc. gives 0·015% of phenols and 0·42% of acids, which (508 g.) yield by fractional distillation and crystallisation *shonanic acid* (I) (325 g.), $C_{10}H_{14}O_2$, m.p. 40—41°, b.p. 264°/754 mm., 134—134·5°/6 mm., $[\alpha]_D^{28}$ −0·75°, $[R]_D^{16}$ 47·82 (exaltation of +1·04 for two ethylenic linkings) (*amide*, m.p. 116—117°; *anilide*, m.p. 111—112°; *Me*, b.p. 113—114°/20 mm., 222°/760 mm., and *Et* ester, b.p. 228—229°/759 mm., 106—108°/7 mm.), and smaller amounts of three *acids*, (i) b.p. 139—141°/7 mm., (ii) m.p. 78—81°, and (iii) m.p. 103°. (I) and EtOH–Na (5 atoms) give *dihydroshonanic acid* (II), b.p. 142—143·5°/7 mm. (*amide*, m.p. 129—130°), hydrogenated (Pd) to *tetrahydroshonanic acid*, b.p. 142—143°/7 mm. (*chloride*, b.p. 115°/19 mm.; *amide*, m.p. 144°), which is also obtained by $H_2$–Pd–$BaSO_4$ from (I) and differs from dihydro-α-campholenic acid (prep. from camphoroxime described). With hot 50% NaOH (I) is isomerised to iso*shonanic acid*, b.p. 151—152°/7 mm., 277—278°/756 mm., m.p. 45—46° (*amide*, m.p. 107—108°; *chloride*, b.p. 107—108°/20 mm.), which gives (II) with Na–EtOH. It is concluded that (I) contains two conjugated ethylenic linkings, of which one is semicyclic and becomes endocyclic on isomerisation. R. S. C.

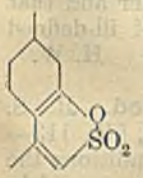
**Homologues of the camphor group. XI. 4-Methyl-3-hydroxymethylenecamphor and its tautomerides.** S. S. Nametkin and A. P. Stukov. **XII. Secondary 4-methyl-α-nitrocamphene and 4-methyl-α-camphenone.** S. S. Nametkin and A. S. Zabrodina (J. Gen. Chem. Russ., 1936, **6**, 1659—1665, 1666—1668).—XI. 4-Methylcamphor and Na in $Et_2O$ react with amyl formate at 0° to yield 4-*methyl*-3-*hydroxymethylenecamphor*, m.p. 117—120° (*Cu* salt; 3-*benzoate*, m.p. 101—101·5°; *methylanilide*, m.p. 90—91°), which gradually changes (67 days at room temp.) into 3-*formyl*-4-*methylcamphor*, m.p. 146—150°, reacts with Br to yield an unstable product, with NHPh·$NH_2$ to give a *phenylpyrazolone* derivative, m.p. 62—63°, and with semicarbazide to give a condensation *product*, m.p. 193—195° (decomp.).

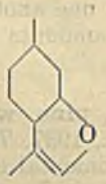
XII. 4-Methylcyclene and $HNO_3$ yield *4-methyl-α-nitrocamphene*, m.p. 40—40·5°, converted by $KMnO_4$ in aq. NaOH at 0° into *4-methyl-α-camphenone*, m.p. 129—130° [*semicarbazone*, m.p. 211—212° (decomp.)]. R. T.

**Identity of dacrene and sciadopitene with phyllocladene.** L. H. Briggs (J.C.S., 1937, 79—80).—Phyllocladene (I), isolated from the leaf oils of *Phyllocladus alpinus* and *Araucaria excelsa*, is identical with dacrene, sciadopitene, and a diterpene from *Dacrydium cupressinum*. (I) is isomerised by $H_2SO_4$–EtOH to *iso*phyllocladene, which appears to be identical with the optical antipode of a diterpene from *Sciadopitis verticcilata* (Kawamura, B., 1932, 321). (I) is hydrogenated to α- and β-dihydrophyllocladene. F. R. S.

**Caryophyllenes. V. Structure of homocaryophyllenic acid.** G. R. Ramage and J. L. Simonsen (J.C.S., 1937, 73—75).—Oxidation of caryophyllene ($HNO_3$), followed by esterification (MeOH), gives Me dimethylsuccinate, Me norcaryophyllenate (I), and Me caryophyllenate. (I) is converted through the anhydride into the *cis*-ester, which with Na–EtOH, followed by $PBr_3$, forms the $Br_2$-compound. This substance with KCN followed by hydrolysis affords *Me* dl-2-*carbomethoxymethyl*-1 : 1-*dimethyl*-cyclo*butane*-3-*acetate*, b.p. 145—155°/19 mm., $\alpha_{5461}$ +0·56°, which yields trans-, m.p. 280°, and cis-*dianilides*, m.p. 170°. Reduction (Na–EtOH) of caryophyllenic anhydride yields a lactone, converted by KCN followed by MeOH–HCl into *Me* 2-*carbomethoxy*-1 : 1-*dimethyl*cyclo*butane*-3-β-*propionate*, b.p. 145—146°/18 mm. (*dianilide*, m.p. 206°, $[\alpha]_{5461}$ −28·3° in $C_5H_5N$). Homocaryophyllenic acid (II) forms the *Me* ester, b.p. 145—147°/18 mm., $[\alpha]_{5461}$ +56·9°, which gives a dianilide, m.p. 282°, and a *cis*-dianilide, m.p. 179°, $[\alpha]_{5461}$ −57·5° in $CHCl_3$. The conclusion is reached that (II) is 2-carboxymethyl-1 : 1-dimethyl-*cyclo*butyl-3-acetic acid. F. R. S.

**Sulphonic acids of terpenes and sesquiterpenes. I. *cyclo*Pulegenolsulphonic ester and its transition into menthofuran.** W. Treibs (Ber., 1937, **70**, [*B*], 85—89).—Gradual addition of pulegone to a well-cooled mixture of conc. $H_2SO_4$ and $Ac_2O$ gives cyclo*pulegenolsulphonic ester* (I), m.p. 85°, which is insol. in $H_2O$ and cold alkalis and


(I.)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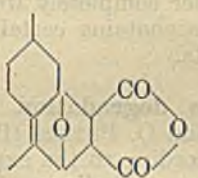
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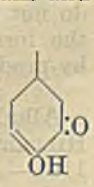

(V.)

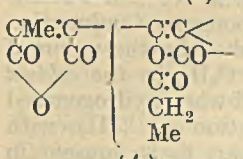
converted by hot alkali or acid or superheated steam into a stable sulphonic acid, sol. in $H_2O$. Catalytic hydrogenation (Pd–MeOH) causes absorption of 4 H with production of a strongly acidic substance. (I) with $KMnO_4$ in $COMe_2$ affords β-methyladipic acid (II). (I) can be distilled unchanged under diminished pressure but when mixed with ZnO and heated under atm. pressure breaks down almost quantitatively into $SO_2$ and menthofuran (III), b.p. 80°/18 mm., $\alpha_D$ +92°, which is stable towards Na and absorbs 4 H when hydrogenated (Pd-sponge). Conjugation of the double linkings is established by the union of (III) with maleic anhydride in $C_6H_6$ to the *adduct* (IV), m.p. 138°, which absorbs 2 H when hydrogenated (Pd-sponge in $COMe_2$). Oxidation of (III) with $KMnO_4$ affords (II). (III) appears to be present in peppermint oil (Carles, B., 1930, 740) and to give rise to the characteristic blue colour when the oil becomes autoxidised. The " acid " $C_7H_{10}O_2$, m.p. 185—186°, obtained by its oxidation with $CrO_3$ is probably (V). (I) is well adapted to the identification of pulegone or *iso*pulegone is fractions of essential oils. H. W.

**Structure of triterpenes.** L. Ruzicka (Chem. & Ind., 1937, 119).—Concerning priority (Spring, this vol., 68; Ruzicka *et al.*, A., 1936, 607). R. S. C.

**Lactucarium. II.** G. Schenck and H. Graf (Arch. Pharm., 1937, **275**, 36—44; cf. A., III, 66).—Contrary to the experience of Ludwig *et al.* (1862) lactucin (0·32%) (I) was obtained from the $H_2O$-sol., and not from the $H_2O$-insol., part of commercial lactucarium, possibly owing to difference in the starting material; its occurrence in the degraded sample is unexpected. Inositol was also isolated. The coagulated fresh juice yields (I) (0·52%), $C_{15}H_{16}O_5$ m.p. 226° (decomp.), and another bitter *substance* (C 65·5, H 5·8%), m.p. 146° (decomp.) (from EtOH) (119° in the crude state, much influenced by atm. $H_2O$). The methods (for details see original) are not suited for general analysis. R. S. C.

**Glauconin. V. Constitution of glauconic acid.** K. Kraft and H. Porsch (Annalen, 1937, **527**, 168—176).—The functions of the 6 O of glauconin (I), $C_{11}H_8O_6$, are investigated. (I) is transformed by KOH and $Me_2SO_4$ into a $Me_2$ ester, $C_{13}H_{14}O_7$, m.p. 77°, formed by the entry of 1 mol. of $H_2O$. Two of the four acidic groups must be derived from an acid anhydride or enol-lactone group. Similar relationships are found in the treatment of the $Ag_4$ salt of (I) with EtI, whereby a non-cryst $Et_2$ ester is obtained which affords a 2 : 4-*dinitrophenylhydrazone*, $C_{21}H_{22}O_{10}N_4$, m.p. 153—154°. (I) does not give a colour with $C(NO_2)_4$ and behaves negatively towards $BzO_2H$ although ozonisation establishes the presence of $\leq$2 double linkings. (I) is not hydrogenated ($PtO_2$) at room temp. and pressure but under more drastic conditions gives an acidic oil which after treatment with $Me_2SO_4$ contains 2 OMe and apparently 3 $CO_2H$ when titrated in hot solution; the ester absorbs $H_2$ readily at room temp. and atm. pressure and the product behaves as a tribasic acid even after complete esterification with $CH_2N_2$. It is therefore probable that (I) is an enol-lactone in which the acidic :C(OH)· disappears by addition of $H_2O$. This group and a neighbouring CO appear responsible for the dark blue colour given by (I) with $C_5H_5N$ and $NH_3$. The two remaining acidic groups probably involve a disubstituted maleic anhydride arrangement, one half of the mol. being probably $\begin{matrix}C\text{——}CO\\ CMe\cdot CO\end{matrix}\!>\!O$. This view is supported by the production of 1·5 mols.

of AcOH when (I) is oxidised by $CrO_3$. Enol-lactone and anhydride groups require 5 O and the remaining O is probably present as CO since (I) reacts with 2 mols. of $NH_2OH$ [cf. valerolactone and coumarin do not react with $NH_2OH$, whilst $o$-$C_6H_4(CO)_2O$ requires 1 $NH_2OH$]. The structure of (I) can therefore be partly resolved as in (*A*). H. W.


(*A.*)

**Vegetable heart poisons. XIV. Ouabain.** R. Tschesche and W. Haupt (Ber., 1937, **70**, [*B*], 43—48).—The constitutional formula assigned to ouabain (I) by Fieser *et al.* (A., 1936, 1116) is exceptional in that it contains the sugar residue involving the *tert.* OH at $C_{(5)}$ whereas in all other glucosides of this type the *sec.* OH at $C_{(3)}$ is involved. The sole exception is furnished by scillaren, but its constitution is based on analogies and colour reactions of scillaridin. Comparison of the ultra-violet absorption spectrum of the latter with that of ergosterol suggests that in this case also the sugar residue is united to O attached to $C_{(3)}$ and that the ready elimination of OH from this group is due to the double linking between $C_{(5)}$ and $C_{(4)}$. (I) is therefore considered to have the sugar residue attached to O at $C_{(3)}$. (I) is transformed into the α-lactone (II), $C_{22}H_{28}O_3$, m.p. 198—199° (Jacobs *et al.*, A., 1932, 856), accompanied by the β-*lactone*, m.p. 250—253°, $[\alpha]_D^{17}$ −108·6° in $CHCl_3$ (*Me ether*, $C_{23}H_{30}O_3$, m.p. 205—209°, $[\alpha]_D^{18}$ −85·42° in $CHCl_3$). (II) and the lactone $C_{22}H_{26}O_4$ (III) from *iso*ouabain have an absorption spectrum indicative of the presence of an aromatic system. On the basis of Fieser's formulation, ring A must be capable of becoming aromatic and (II) must be dehydrogenable in the same manner as neoergosterol (IV). The Me ether, m.p. 193—195°, is, however, stable under conditions which readily cause aromatisation of (IV). (IV) resembles *ac*-tetrahydro-β-naphthol in its inability to furnish a ketone when oxidised whereas the C·OH of (III) is readily transformed into CO. Fieser's assumption of the presence of OH in the β-position to an aromatic ring cannot therefore be correct if ring A is 6-membered. Fieser's structure of the lactones and conclusions as the positions of the OH groups in ouabagenin are therefore doubtful and all that can be stated at present is that 1 OH is attached to $C_{(14)}$ of the cholane skeleton. H. W.

**Lignin and related compounds. XXVI. Properties of spruce lignin extracted with formic acid.** G. F. Wright and H. Hibbert (J. Amer. Chem. Soc., 1937, **59**, 125—130; cf. Freudenberg *et al.*, A., 1936, 995; Staudinger and Dreher, *ibid.*, 1116).—Extraction of spruce-meal (free from resin and $H_2O$-sol. carbohydrates) with, *e.g.*, boiling 80% $HCO_2H$ gives a lignin (I) (13·5% OMe), separable by successive extraction with $CHCl_3$, $COMe_2$, and aq. $COMe_2$ (and subsequent fractional pptn. from these extracts with $Et_2O$) into fractions (12·17—14·15% OMe). (I) contains 4 OH per kg. (Zerevitinov and triphenylmethylation) and adds a small but definite amount of MgRX (thus confirming the presence of CO, which does not exist as ·O·COR). Methylation of (I) with $CH_2N_2$ indicates that 2 of the 4 OH are phenolic. Methylation of (I) and the $CHCl_3$- and $COMe_2$-sol. fractions (OMe 13·13 and 12·81%, respectively, obtained from lignin extracted with 95% $HCO_2H$, and containing 4·6 and 3·5 OH, respectively) with $Me_2SO_4$ and aq. NaOH in $N_2$ gives products (24—27% OMe) which still contain 3—4 OH, indicating that new OH groups are produced during the methylation process; lignins isolated by other methods behave similarly. The no. of OH in an unfractionated $HCO_2H$-lignin is increased from 4 to 12·5 by treatment with 1% NaOH for 45 days (during which time no absorption of $O_2$ occurs). Alkaline methylation is thus untrustworthy as a means of determining lignin structure. H. B.

**Benzylated pine wood.** R. S. Hilpert and O. Peters (Ber., 1937, **70**, [*B*], 108—113).—The reaction between $CH_2PhCl$, alkali, and pine wood appears to proceed very similarly to the corresponding reaction with cellulose and the composition of the product (I) lies within the limits established for benzylcellulose (II). The product can be separated by $C_6H_6$–EtOH or AcOH into fractions of differing C content which in each case is within the limits for (II). Since (II) is sol. in $C_6H_6$–EtOH its amount in (I) is $\gtrsim$24—30%. *Benzylalkali-lignin* (III) is sol. in warm $CH_2Ph$·OH or $C_6H_6$, sparingly sol. in AcOH, whereas *benzylacid-lignin* (IV) dissolves with difficulty in all media and only very sparingly in $C_6H_6$, $CH_2Ph$·OH, or AcOH. When the relatively high C content of (III) and (IV) is also considered their presence in either component of (I) appears excluded. The components of (I) are therefore derived from a complex material and have their own sp. properties and not those of cellulose (V). Pine wood leaves about 45% of substance resembling (V) when heated with hot alkali, towards which its $CH_2Ph$ ether is indifferent. Treatment with HCl removes about 33% of material from benzylated wood and the residue, which is partly sol. in MeOH, has neither the properties nor composition of (III) or (IV). The differing behaviour of untreated and treated wood is immediately comprehensible if it is assumed that the fission products are not components but reaction products the properties of which are modified immediately reactions are induced. (II) is dissolved by conc. HCl, leaving about 7% of residue. Protest is made against the view that alkali- and acid-lignin do not differ completely from one another and that the former contains certain amounts of ill-defined by-products. H. W.

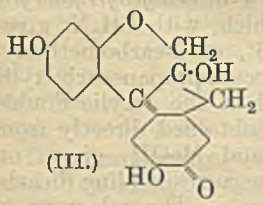
**Alkaline degradation of pine wood.** R. S. Hilpert and O. Peters (Ber., 1937, **70**, [*B*], 113—116).—According to the experimental conditions the action of conc. alkalis on pine wood occurs in widely differing manners so that the process must be regarded not as the dissolution of a portion of a heterogeneous material but as fission of a large complex. In the preformed condition cellulose and lignin are present to the extent of $<$45% and $<$30%, respectively. Lignins containing OMe are produced by the action of acids on the methoxylated carbohydrates obtained as products of fission. It must therefore be assumed that lignin is formed similarly when wood is treated with acids. H. W.

***iso*Propylidene derivative, b.p. 193·5—194·5°/712 mm., of *as*-furyl Me glycol.**—See A., III, 70.

**Dihydro-1 : 4-pyrans. V. Structure of 3-cyano-derivatives.** H. H. HULLY, F. H. BROCK, and R. C. FUSON (J. Amer. Chem. Soc., 1936, 58, 2634—2635).—3-Cyano-6-benzoyl-2-phenyl-5 : 6-dihydro-1 : 4-pyran (I) (A., 1932, 63) is reduced ($H_2$, $PtO_2$, EtOAc) to the 6-α-hydroxybenzyl derivative, m.p. 110—113° (*phenylcarbamate*, m.p. 137—138°), which is oxidised ($CrO_3$, AcOH) to (I) and converted by fuming $HNO_3$ at 0° into 3-*nitro*-2-*hydroxy*-3-*cyano*-6-*benzoyl*-2-*phenyltetrahydro*-1 : 4-*pyran* 2-*nitrate*, m.p. 139·5—140° (decomp.), also obtained from (I) and $HNO_3$ (*d* 1·42) in AcOH at 100°. Ozonolysis of (I) gives *γ-benzoyloxy-γ-benzoylbutyric acid*, m.p. 113° [*semicarbazone*, m.p. 190—195° (decomp.)], hydrolysed (aq. NaOH) to BzOH and $(\cdot CH_2 \cdot CO_2H)_2$. These results support the structure previously assigned (*loc. cit.*) to (I). γ-Bromo-γ-benzoylbutyric acid and AgOBz afford γ-benzoyl-γ-butyrolactone. H. B.

**Synthesis of tangeritin.** L. J. GOLDSWORTHY and R. ROBINSON (J.C.S., 1937, 46—49).—2 : 6-Dihydroxy-ω : 3 : 4-trimethoxyacetophenone with anisic anhydride and Na anisate gives 5-*hydroxy*-3 : 6 : 7 : 4′-*tetramethoxyflavone* (I), m.p. 171°, methylated ($Me_2SO_4$) to 3 : 5 : 6 : 7 : 4′-pentamethoxyflavone, identical with tangeritin (cf. Nelson, A., 1934, 900). (I) is hydrolysed to the $(OH)_5$-derivative, which has been characterised. F. R. S.

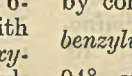
**Constitution of brazilein.** U. M. MIĆOVIĆ and R. ROBINSON (J.C.S., 1937, 43—46).—ω-Homoveratrylresacetophenone (Na salt) and EtI give 2-*hydroxy*-4-*ethoxyphenyl* β-*veratrylethyl ketone*, m.p. 97—98°, which with $HCO_2H$ and $ZnCl_2$, followed by $FeCl_3$, affords 4′ : 5′-*dimethoxy*-7-*ethoxybrazylium ferrichloride* (I), m.p. 211—212° (decomp.). 7-Methoxychromanone and *O*-ethyl*iso*vanillin yield 7-*methoxy*-3-(4′-*methoxy*-3′-*ethoxybenzylidene*)*chromanone*, m.p. 120°, reduced (Pd–$H_2$) for a short period to a *product*, $C_{20}H_{22}O_5$, m.p. 83°, and for a longer period to the *-ethoxybenzyl* compound, m.p. 87—90°. This compound is dehydrated ($P_2O_5$) to *deoxydimethylethylbrazilone*, m.p. 145—147°, closely resembling deoxytrimethylbrazilone in all characteristic properties, and converted (Br–$FeCl_3$) into 7 : 5′-*dimethoxy*-4′-*ethoxybrazylium ferrichloride* (II). Trimethyldihydrobrazileinol, EtI, and $K_2CO_3$ give O-*trimethylethyldihydrobrazileinol*, m.p. 142°, resembling the $Me_4$ derivative. Dimethoxyethoxybrazylium ferrichloride, obtained from brazilein (III) is identical with (II) and not (I). This confirms the view of the structure of (III).


(III.)

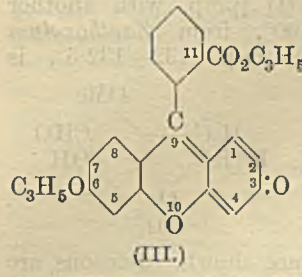
F. R. S.

**Synthesis of brazilin and hæmatoxylin. IV. Synthesis of *O*-diethylenehæmatoxylone.** W. H. PERKIN, jun., A. POLLARD, and R. ROBINSON (J.C.S., 1937, 49—53).—2 : 3-*Ethylenedioxy*-β-*phenoxypropionic acid*, m.p. 156·5—158°, prepared from 2 : 3-ethylenedioxyphenol and $CH_2Cl \cdot CH_2 \cdot CO_2H$, with $P_2O_5$ affords 7 : 8-*ethylenedioxychromanone*, m.p. 120—121°. The chromanone condenses with 3 : 4-ethylenedioxybenzaldehyde to form 7 : 8 : 3′ : 4′-*bisethylenedioxy*-3-*benzylidenechromanone*, m.p. 200—202°, converted by $FeCl_3$–$Ac_2O$ into 6 : 7 : 7′ : 8′-*bisethylenedioxychromeno*(4′ : 3′ : 2 : 3)*benzopyrylium ferrichloride*, m.p. 232—233°, and reduced (Pd–$H_2$) to 7 : 8 : 3′ : 4′-*bisethylenedioxy*-3-*benzylchromanone*, m.p. 130—132°. The benzylchromanone is dehydrated ($P_2O_5$) to *O*-diethylenedeoxyhæmatoxylone (I). O-*Diethylenehæmatoxylin*, prepared from hæmatoxylin and $C_2H_4Br_2$–$K_2CO_3$, is oxidised ($CrO_3$) to O-*diethylenehæmatoxylone*, m.p. 198—200° (decomp.), reduced ($NHPh \cdot NH_2$) to (I), m.p. 157°. F. R. S.

**Constitution of catechin.** M. NIERENSTEIN (Chem. and Ind., 1936, 1007—1008).—Isolation of pentamethyl-*dl-epi*catechin from the reduction products of pentamethylquercetin proves the correctness of Freudenberg's formula for catechin. J. W. B.

**Synthesis of benzylidenephthalan.** S. NATELSON and A. PEARL (J. Amer. Chem. Soc., 1936, 58, 2448—2449).—Phthalide (I) and $Et_2O$–$CH_2Ph \cdot MgCl$ give 2-*hydroxy*-2-*benzylphthalan*, m.p. 137°, dehydrated by conc. $H_2SO_4$ at 40° or, better, by Se at 140° to *benzylidenephthalan* (II), *o*-$C_6H_4$  O, m.p. 94°, which is readily hydrolysed (acidic or basic reagents) to (I). (I), $CH_2Ph \cdot CO_2H$ (III), and small amounts of NaOAc and pumice at 180° give PhMe and (I); (III) does not evolve $CO_2$ under similar conditions, indicating that (II) is first produced and then hydrolysed. H. B.

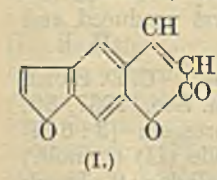
**Alkenyl derivatives of fluorescein.** C. D. HURD and L. SCHMERLING (J. Amer. Chem. Soc., 1937, 59, 112—117).—The $Na_2$ salt of fluorescein [3 : 6-dihydroxyfluoran] (I) and allyl bromide (II) (2 mols.) in aq. $COMe_2$ give 43·5% of *allyl* 6-*allyloxy*-9-*phenylfluorone*-11-*carboxylate* (III), m.p. 155°, and 30% of 6-*hydroxy*-3-*allyloxyfluoran* (IV), m.p. 205° (*acetate*, m.p. 143°), whilst (I), (II), and $K_2CO_3$ in $COMe_2$ afford (III) (42%) and smaller amounts of 3 : 6-*diallyloxyfluoran* (V), m.p. 124°, and *allyl* 6-*hydroxy*-9-*phenylfluorone*-11-*carboxylate* [*resorcinolbenzein*-11-*carboxylate*], m.p. 233°. α-Bromo-$\Delta^\beta$-pentene and (I) similarly give *γ-ethylallyl* 6-*γ-ethylallyloxy*-9-*phenylfluorone*-11-*carboxylate*, m.p. 118°, 6-*hydroxy*-3-*γ-ethylallyloxyfluoran* (VI), m.p. 220° (*acetate*, m.p. 108°), and 3 : 6-*di*-*γ-ethylallyloxyfluoran*, m.p. 131°, whilst (I) and α-bromo-$\Delta^\beta$-hexene (VII) afford *γ*-n-*propylallyl* 6-*γ*-n-*propylallyloxy*-9-*phenylfluorone*-11-*carboxylate*, m.p. 109°, 6-*hydroxy*-3-*γ*-n-*propylallyloxyfluoran*, m.p. 187° (*acetate*, m.p. 154°), and 3 : 6-*di*-*γ*-n-*propylallyloxyfluoran* (VIII), m.p. 103°. (VIII) heated at 210—220° rearranges exothermally to 2 : 7-*dihexenylfluorescein* (IX), m.p. 135—140°. Ozonolysis of (VIII) gives much $PrCO_2H$ and some $HCO_2H$ [indicating the presence of the α-propylallyl derivative and, hence, that (VII) contains γ-bromo-$\Delta^\alpha$-hexene], whilst (IX) affords mainly $HCO_2H$ (indicating inversion of the propylallyl group during rearrangement). (IV), (V), and (VI) are similarly


(III.)

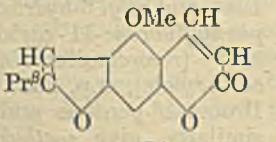
rearranged to 2-*allyl*-, m.p. 168—176°, 2 : 7-*diallyl*-, m.p. 158—161°, and 2-*pentenyl*-, m.p. 156—160°, *-fluorescein*, respectively; (III) gives *allyl* 2-*allylresorcinolbenzein*-11-*carboxylate*, m.p. 137—143°. Hydrolysis of (III) with aq. KOH affords (mainly) (I); NaOH in allyl alcohol or aq. $COMe_2$ gives (IV), whilst in MeOH and EtOH, fluorescein $Me_1$ (*acetate*, m.p. 141°) and $Et_1$ ether, respectively, result. Diacetylfluorescein is obtained from (I) and keten in $COMe_2$, whilst (I) and $SOCl_2$ give 3 : 6-dichlorofluoran, m.p. 262° (255° using $PCl_5$). *p*-Tolyl allyl and *hexenyl*, b.p. 142—146°/14 mm., ethers are readily obtained from *p*-$C_6H_4Me$·ONa and (II) and (VII), respectively, in aq. $COMe_2$ at room temp. H. B.

**Resolution of diethylaminomethylbenzdioxan (883 F).** Tréfouel, J. Tréfouel, and Y. Dunant (Bull. Sci. Pharmacol., 1935, **42**, 459—466; Chem. Zentr., 1936, i, 1220).—The *H phthalate*, m.p. 116°, of hydroxymethylbenzdioxan is converted into its *d*-ephedrine salt and resolved by fractionation with $C_6H_6$, yielding l-*hydroxymethylbenzdioxan*, m.p. 81°, $[\alpha]_D^{20}$ −31° 40′; this, with $SOCl_2$, yields l-*chloromethylbenzdioxan*, which with $NHEt_2$ affords l-*diethylaminomethylbenzdioxan*, b.p. 181°/38 mm., $[\alpha]_D^{20}$ −29° 10′ (*hydrochloride*, m.p. 129—130°, $[\alpha]_D^{20}$ −58° 20′). H. N. R.

**Identity of ficusin with psoralene.** E. Späth, K. Okahara, and F. Kuffner (Ber., 1937, **70**, [*B*], 731.—The identity of ficusin (Okahara, A., 1936, 1121), psoralene (Jois, A., 1933, 657), and the furocoumarin (I) (Späth *et al.*, A., 1936, 860) is established. The deletion of the term "ficusin" from the literature is suggested. H. W.


(I.)

**Constituent of *Zanthoxylum fraxineum*, Wild.** H. Dieterle and E. Kruta [with, in part, W. Sauter] (Arch. Pharm., 1937, **275**, 45—53).—Xanthoxylin *N* (xanthoxyletin) (I) (prep. with another *furocoumarin*, m.p. 99—100°, from *Zanthoxylum fraxineum* bark described), m.p. 132—132·5°, is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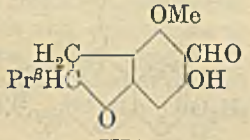
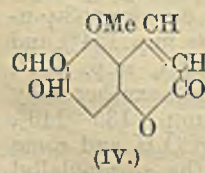

(III.)

proved to have the structure shown. Reasons are adduced against the alternative dicoumarin structure (cf. Bell *et al.*, A., 1936, 859). Hydrogenation (Pd–C) of (I) in EtOH at room temp./1 atm. gives dihydroxanthoxylin *N* (dihydroxanthoxyletin) (II), m.p. 145°, in which the coumarin ring remains unaffected, but with $PdO_2$ at 60—61°/6 atm. in AcOH gives *tetrahydroxanthoxylin* N, m.p. 134°. (I) and NaOEt–MeI give xanthoxylic-*N* acid Me ether (*O*-methylxanthoxyletinic acid), $C_{16}H_{18}O_5$, m.p. 182—183°. (II) and $O_3$ in $CHCl_3$ yield the *aldehyde* (III), $C_{13}H_{16}O_4$, m.p. 86—87° (*dinitrophenylhydrazone*, m.p. 225°; *Ac* derivative, m.p. 116—117°). (I) and $O_3$ in $CHCl_3$ give 2 : 6-*dialdehydophloroglucinol* 1-O-*Me ether*, m.p. 165—166°, volatile in steam (obtained similarly from bergapten), and the *substance* (IV), $C_{11}H_8O_5$, m.p. 220—221°. (I) and 2% $KMnO_4$ give $H_2C_2O_4$ and $OH·CMe_2·CO_2H$. R. S. C.


(IV.)

**Synthesis of diflavonols.** J. Algar and (Miss) D. E. Hurley (Proc. Roy. Irish Acad., 1936, **43**, 83—87).—Oxidation ($H_2O_2$) of dichalkones in the cold yields the corresponding diflavonol and an unidentified product: from dibenzylidenediacetoresorcinol, *diflavonol*, m.p. 323° (*diacetate*, m.p. 252°), and a *substance*, m.p. 284°; from dianisylidenediacetoresorcinol, 4′ : 4″-*dimethoxydiflavonol*, m.p. 306° (*di*-, m.p. 291°, and *tetra-acetate*, m.p. 270°), and a *substance*, m.p. 320—321° (*Ac* derivative, m.p. 263°); from dipiperonylidenediacetoresorcinol, 3′ : 4′ : 3″ : 4″-*dimethylenedioxydiflavonol*, m.p. above 330° (*diacetate*, m.p. 291—292°), and a *substance*, m.p. above 330°; and from diveratrylidenediacetoresorcinol, 3′ : 4′ : 3″ : 4″-*tetramethoxydiflavonol*, m.p. 280°, and a *substance*, m.p. 315°. F. R. S.

**Synthetic plant growth hormones.** E. M. Crook, W. Davies, and (Miss) N. E. Smith (Nature, 1937, **139**, 154—155).—*Thionaphthen-2-acetic acid* (I), m.p. 109° [synthesis: thionaphthen → 2-bromothionaphthen → thionaphthen-2-carboxyl chloride → (I)], has a much smaller growth activity (oat and pea tests) than might be expected from its similarity to 2-indolylacetic acid (II). An *isomeride* of (I), m.p. 141°, has approx. the same activity as (I) towards peas, but none towards oats. 1-Naphthylacetic acid is several times as active as (I) in both oat and pea tests. L. S. T.

**Cleavage of azlactones by diazomethane and methyl alcohol and by alkoxides. Analogy to behaviour of chlorophyll and its derivatives.** H. Fischer and H. J. Hofmann (Z. physiol. Chem., 1937, **245**, 139—151).—The azlactone (I) of 5-aldehydo-2 : 4-dimethyl-3-ethylpyrrole in MeOH gives with $CH_2N_2$ a high yield of *Me* α-*benzamido*-β-2 : 4-*dimethyl*-3-*ethylpyrrylacrylate* (II), m.p. 220°. Similarly the azlactones of PhCHO and *p*-$OAc·C_6H_4·CHO$ give the Me esters of the corresponding acrylic acids. The azlactone (III) of 3-aldehydo-5-carbethoxy-2 : 4-dimethylpyrrole in MeOH with 40% aq. KOH gives α-*benzamido*-β-5-*carboxy*-2 : 4-*dimethylpyrrylacrylic acid*, m.p. 210° (decomp.), which, with $CH_2N_2$ gives the *Me* ester (IV), m.p. 216°, of 5-carbomethoxy-2 : 4-dimethylpyrrylbenzamido*cyclo*propanecarboxylic acid, $CH_2$ having been added at the acrylic double linking. (IV), which is also obtained directly from the azlactone with $CH_2N_2$ and MeOH, gives, on hydrolysis with conc. alkali, the corresponding dicarboxylic *acid*, m.p. 176° (decomp.). The azlactone of 3-aldehydo-1-acetylindole in MeOH gives with $CH_2N_2$ the analogous *Me* ester, m.p. 243°, of acetylindolylbenzamido*cyclo*propanecarboxylic acid. (I) in abs. EtOH gives with Na or Pb–Na at ≯5° the *Et* ester, m.p. 215°, of α-benzamido-β-5-carbethoxy-2 : 4-dimethylpyrrylacrylic acid. The *Me* ester, m.p. 198°, of this acid is obtained from (I) in MeOH with Na at ≯10° and the *Me* ester, m.p. 220°, of the corresponding carbomethoxy-acid at 65°. (I) in hot PrOH and in hot *iso*amyl alcohol with Na gives the corresponding $Pr_2$, m.p. 202°, and *diisoamyl* ester, m.p. 168°.

Similarly (III) with MeOH and Na gives (IV) and with EtOH and Na the corresponding *Et* ester, m.p. 192°. Methylphæophorbide *a* in $C_5H_5N$ with MeOH and Na gives the $Me_3$ ester of chlorin $e_6$. 3-Thioaldehydo-5-carbethoxy-2 : 4-dimethylpyrrole with hippuric acid, $Ac_2O$, and $Cu(OAc)_2$ or PbO at 100° for 6 hr. gives the azlactone of 3-aldehydo-5-carbethoxy-2 : 4-dimethylpyrrole. W. McC.

**Condensation of dimethylaniline with formaldehyde and piperidine.** H. F. Tseou and Y. T. Wang (J. Chinese Chem. Soc., 1936, 4, 418—421).—Piperidine hydrochloride (I), $CH_2O$, $NPhMe_2$, and a few drops of piperidine in aq. EtOH give N-p-*dimethylaminobenzylpiperidine*, m.p. 43° (*auri-*, m.p. 120°, and *zinci-chloride*, m.p. 215°), and a little methylenebispiperidine (in strongly alkaline solution this is the main product). In strongly acid solution only di-(*p*-dimethylaminophenyl)methane is formed. No condensation occurred with $NHEt_2$ instead of (I) or with amides or PhOMe instead of $NPhEt_2$. R. S. C.

**Synthesis of 1-methyl-2-alkyl- (aryl- or arylalkyl-)3 : 4 : 5 : 6-tetrahydropyridines. Action of the Grignard reagent on amides. XI.** R. Lukeš and O. Grossmann (Coll. Czech. Chem. Comm., 1936, 8, 533—542; cf. A., 1934, 902).—*N*-Methyl-2-piperidone (1 mol.) with MgRI (3—4 mols.) free from RI in dry $C_6H_6$ affords 1-methyl-2 : 2-dialkylpiperidine, isolated as the perchlorate, and 1-methyl-2-alkyl-3 : 4 : 5 : 6-tetrahydropyridine, isolated as the picrate. The following are prepared : 1 : 2-*dimethyl-*, b.p. 40·5°/10 mm. [*perchlorate*, m.p. 228·5°; *picrate*, m.p. 156°; *aurichloride*, m.p. 169—170° (decomp.); *platinichloride*, m.p. 200° (decomp.)], 1-*methyl*-2-*ethyl-*, b.p. 58°/10 mm. (*perchlorate*, m.p. 237°; *picrate*, an oil; *aurichloride*, m.p. 131°; *platinichloride*, m.p. 213°), -2-n-*butyl-*, b.p. 85°/12 mm. [*perchlorate*, m.p. 143°; *picrate*, m.p. 144°; *platinichloride*, m.p. 182° (decomp.)], -2-n-*amyl-*, b.p. 114·5°/10 mm. [*perchlorate*, m.p. 136°; *platinichloride*, m.p. 126° (decomp.)], -2-*phenyl-*, b.p. 136°/20 mm. (*perchlorate*, m.p. 146·5°; *picrate*, m.p. 133°), -2-α-*naphthyl-* (*perchlorate*, m.p. 135°; *picrate*, m.p. 140°), -2-*benzyl-*, b.p. 169°/25 mm. (*perchlorate*, m.p. 135°; *picrate*, m.p. 151°), and -2-*phenylethyl*-3 : 4 : 5 : 6-*tetrahydropyridine*, b.p. 168°/18 mm. (*perchlorate*, m.p. 105·2°; *picrate*, m.p. 105°); 1 : 2 : 2-trimethyl- [*picrate*, m.p. 270° (decomp.)], 1-*methyl*-2 : 2-*diethyl-*, b.p. 93°/16 mm. [*picrate*, m.p. 224° (decomp.); *platinichloride*, m.p. 233° (decomp.)], and -2 : 2-dibutylpiperidine (*picrate*, m.p. 102°). J. L. D.

**Dihydropyridine compounds. IV. 1-Phenyl- and 1-*p*-anisyl-*o*-dihydropyridine.** P. Karrer, G. Schwarzenbach, and G. E. Utzinger (Helv. Chim. Acta, 1937, 20, 72—79).—Reduction of 1-phenylpyridinium chloride (I) by Na–Hg in alkaline solution gives 1 : 1-diphenyltetrahydrodipyridyl and 1-phenyl-1 : 2-dihydropyridine (II), m.p. about 48—50°. (II) is strongly reducing and can be titrated potentiometrically with $K_3Fe(CN)_6$ in alkaline medium, whereby 2 equivs. of the latter are used. The similarity of the reducing and optical properties of (II) with those of 1-methyl-1 : 2-dihydronicotinamide and 1-glucosido-1 : 2-dihydronicotinamide indicate the *ortho* structure of (II), which is confirmed by the immediate formation of a resinous product from it and maleic anhydride in $Et_2O$ or $C_6H_6$, thus establishing the presence of conjugated double linkings. Reduction of (I) by Na–Hg in more strongly alkaline solution gives a *substance*, $C_{22}H_{17}ON_2$, m.p. 160° (decomp.). 2 : 4-Dinitrophenylpyridinium chloride is transformed by anisidine in EtOH into the *hydrochloride* of glutacondialdehydedianisidide, hydrolysed by boiling HCl to 1-p-*anisylpyridinium chloride* (III) (additive *compound* with $FeCl_3$). (III) is reduced by Na–Hg to 1-p-*anisyl*-1 : 2-*dihydropyridine*, m.p. 82°, which is stable only at a low temp. in an abs. vac. It immediately reduces cold $AgNO_3$ and indigotin-tetra-, tri-, and -di-sulphonate. Spectroscopically it is closely allied to (II). H. W.

**Synthesis of pyrrolidines, piperidines, and hexahydroazepines [hexamethyleneimines].** J. H. Paden and H. Adkins (J. Amer. Chem. Soc., 1936, 58, 2487—2499).—Reduction [$H_2$ (200—400 atm.), Cu–Cr oxide, dioxan, 250—260°] of glutaramides gives 62—77% yields of piperidines and varying small amounts of other cleavage products; glutarpiperidides similarly afford the corresponding αε-dipiperidinopentanes. Thus, glutaramide gives piperidine (I); *glutarphenylethylamide*, m.p. 158·5—159·5°, affords 1-phenylethylpiperidine [*hydrochloride*, m.p. 232—233°; picrate, m.p. 147—148° (lit. 144—145°)], (I), mono- (II) and di- (III) -phenylethylamine, and PhEt; β-*methylglutarphenylethylamide*, m.p. 190—191·5°, yields 1-*phenylethyl*-4-*methylpiperidine*, b.p. 141—142°/12 mm. (*hydrochloride*, m.p. 254—256°), 4-methylpiperidine (*hydrochloride*, m.p. 186—189·5°), (II), and (III); β-*phenylglutarphenylethylamide*, m.p. 177·5—178°, furnishes 4-*phenyl*-1-*phenylethylpiperidine*, b.p. 170—174°/2 mm., m.p. 74—75° (*hydrochloride*, m.p. 270—271°), 4-phenylpiperidine (IV) (*benzenesulphonyl* derivative, m.p. 108—109°), (II), and (III); *glutar*-n-*amylamide*, m.p. 147—148°, gives 1-*n*-amylpiperidine (hydrochloride, m.p. 223—224°), and mono- and di- (V) -*n*-amylamine; β-*methylglutar*-n-*amylamide*, m.p. 149—150°, affords 4-*methyl*-1-n-*amylpiperidine*, b.p. 83—84°/10 mm. (*hydrochloride*, m.p. 239—241°), and (V); β-*phenylglutar*-n-*amylamide*, m.p. 166—167°, yields 4-*phenyl*-1-n-*amylpiperidine*, b.p. 129—130°/1 mm. (*hydrochloride*, m.p. 245—246°), (IV), and (V); ββ-*dimethylglutar*-n-*amylamide*, b.p. 210—212°/2 mm., m.p. 39—41°, furnishes 4 : 4-*dimethyl*-1-n-*amylpiperidine*, b.p. 96—97°/12 mm. (*hydrochloride*, m.p. 302°), and (V); β-*phenylglutarbenzylamide*, m.p. 159·5—160·5°, gives 4-*phenyl*-1-*benzylpiperidine*, b.p. 157—159°/1 mm. (*hydrochloride*, m.p. 212—213°), (IV), $CH_2Ph{\cdot}NH_2$, and $NH(CH_2Ph)_2$; *glutarpiperidide*, b.p. 193—197°/1 mm., m.p. 53—54°, affords αε-dipiperidinopentane (46%), b.p. 130—131°/2 mm. [*hydrochloride*, m.p. 252—253°; picrate, m.p. 188—189° (lit. 185°)], ε-piperidinoamyl alcohol (30%), and (I) (20%), whilst β-*methyl-*, b.p. 188—190°/1 mm., and ββ-*dimethyl-*, b.p. 183—187°/1 mm., *-glutarpiperidides* yield αε-*dipiperidino*-γ-*methyl-* (71%), b.p. 123—125°/1 mm. (*hydrochloride*, m.p. 246—248°), and -γγ-*dimethyl-pentane* (45%), b.p. 133—134°/1 mm. (*hydrochloride*, m.p. 314—316°), respectively. Glutarimides are similarly reduced to piperidines but fission of, *e.g.*, $>N{\cdot}CH_2Ph$ is appreciable : thus,

ββ-*dimethylglutar*-N-n-*amyl*-, b.p. 115—116°/2 mm., -*benzyl*-, b.p. 148—151°/2 mm., m.p. 63—64°, and -*phenylethyl*-, m.p. 80·5—81·5°, -*imides* give 1-n-*amyl*-, b.p. 96—97°/12 mm. (*hydrochloride*, m.p. 302°), 1-*benzyl*-, b.p. 114—115°/5 mm. (*hydrochloride*, m.p. 335—336°), and 1-*phenylethyl*-, b.p. 149—150°/12 mm. (*hydrochloride*, m.p. 252°), -4 : 4-*dimethylpiperidine*, respectively, together with 7—31% of 4 : 4-dimethylpiperidine; β-*phenylglutar*-N-*benzylimide*, m.p. 98—99°, affords 4-phenyl-1-benzylpiperidine (42%) and (IV) (32%), whilst β-methyl- and β-phenyl-glutarimide yield 4-methylpiperidine (46%) and (IV) (55%), respectively. 1-Substituted piperidines and pyrrolidines are also obtained when equimol. mixtures of $NH_2R$ with, *e.g.*, pentane-αε- (VI) and butane-αδ-diol (VII), respectively, are subjected to hydrogenolysis under the above conditions; the method is probably the most convenient of those studied. Thus, 1-benzyl- (71%) and 1-phenylethyl-piperidine (76%) are formed from (VI) with $CH_2Ph{\cdot}NH_2$ and phenylethylamine, respectively; the use of (VII) gives 1-benzyl- (*hydrochloride*, m.p. 153·5—154·5°) and 1-phenylethyl-pyrrolidine [under milder conditions δ-*phenylethylaminobutyl alcohol*, b.p. 176—178°/9 mm. (*hydrochloride*, m.p. 127—128°; O-*Bz* derivative *hydrochloride*, m.p. 153—155°), is also produced]. γ-Methylpentane-αε-diol + $CH_2Ph{\cdot}NH_2$ afford (mainly) 1-*benzyl*-4-*methylpiperidine*, b.p. 128—129°/14 mm. (*hydrochloride*, m.p. 166·5—168°); γ-phenylpentane-αε-diol + *n*-amylamine yield (mainly) 4-phenyl-1-*n*-amylpiperidine, whilst hexane-αζ-diol + $CH_2Ph{\cdot}NH_2$ give 23% of 1-*benzyl-hexahydroazepine* [-*azacycloheptane*], b.p. 130—132°/12 mm. (*hydrochloride*, m.p. 158·5—159·5°), which is cleaved by $H_2$ + Cu–Cr oxide at 275° to $[CH_2]_6NH$ and PhMe.

Adip-*n*-amylamide is reduced (as for other amides) to 1-*n-amylhexahydroazepine* (34%), b.p. 94—95°/13 mm. (*hydrochloride*, m.p. 217—218°; *picrate*, m.p. 109—110°), and (V) (41%). Similarly, 1-n-*amyl*- (VIII), b.p. 87—88·5°/1 mm., and 1-β-cyclo*hexylethyl*- (IX), b.p. 136—138°/2·5 mm., -2-*pyrrolidone* give 1-*n*-amyl- (87%) and 1-β-cyclo*hexylethyl*- (96%), b.p. 116—117°/12 mm. (*hydrochloride*, m.p. 224—225°), -*pyrrolidine*, respectively, whilst 1-β-cyclo*hexylethyl*-4-*methyl*-2-*piperidone* (X), b.p. 146—149°/2 mm., affords 1-β-cyclo*hexylethyl*-4-*methylpiperidine* (89%), b.p. 135·5—137°/12 mm. (*hydrochloride*, m.p. 277—278°). 2-Pyrrolidones and 2-piperidones are obtained from succin- and glutar-imides, respectively, by hydrogenolysis over Ni at 200—220° in dioxan. Thus, succin-*N*-β-phenylethylimide yields the -cyclo*hexylethylimide*, b.p. 145—148°/2 mm., m.p. 53—54°, and thence (IX); (VIII) and (X) are prepared from succin-*N*-*n*-amylimide and β-*methylglutar*-N-β-*phenylethylimide*, m.p. 98—100°, respectively. 2-*Methyl*-1-n-*amylpiperidine*, b.p. 92—93°/16 mm. (*hydrochloride*, m.p. 166·5—167·5°) (by amylation of the 2-Me derivative), *glutar*-N-n-*amylimide*, b.p. 105—106°/1 mm., β-*methylglutarbenzylamide*, m.p. 194—195°, and β-*phenylglutarpiperidide*, b.p. 240—248°/1 mm., are described.

The amides of glutaric and β-methyl- and β-phenyl-glutaric acids are prepared from the Et esters and the appropriate amine (4 mols.) at 175—250° under 100—150 atm. of $H_2$ (Et ββ-dimethylglutarate similarly gives amide + imide); the imides are formed from the acids and amine (1 mol.) at 250°. An improved prep. of Et glutarate is given. H. B.

**Products of the coupling of diazo-compounds with phenacylpyridinium salts.** F. Krollpfeiffer and E. Braun (Ber., 1937, 70, [*B*], 89—95).—Phenacylpyridinium bromide with $PhN_2HSO_4$ in presence of NaOAc gives a mixture of *benzeneazophenacylpyridinium bromide*, decomp. 215° (corresponding *chloride*, decomp. about 185°) (the nomenclature is provisional), and *benzeneazophenacylpyridiniumbetaine* (I) (cf. *A*), decomp. 120°; in absence of NaOAc (I) is the sole product. p-*Nitrobenzeneazophenacylpyridinium bromide*, decomp. 230—235° according to the rate of heating, the corresponding *chloride*, decomp. about 255°, and the *betaine* (II), decomp. 155—156°, are obtained analogously. Benzeneazoacetonylpyridinium chloride, decomp. 180°, and the corresponding betaine (III), decomp. 100°, are identical with the products obtained from $C_5H_5N$ and α-chloropyruvaldehyde-α-phenylhydrazone. ω-Methylphenacylpyridinium bromide gives only resinous products. When heated (I) loses $C_5H_5N$ and gives the reddish-brown *substance* (IV), $C_{28}H_{20}O_2N_4$, m.p. 200—201° (probable constitution in accordance with NPh<CAc:N / N:CAc>NPh or CAc<CAc=N / N·NPh>NPh), also obtained by protracted boiling of (I) with MeOH and converted by conc. $HNO_3$ in AcOH into the $(NO_2)_2$-compound (I), m.p. 251—252° (decomp.), identical with that derived from (II). *o*- and *m*-Nitrobenzeneazophenacylpyridiniumbetaine yield *compounds*, $C_{28}H_{18}O_6N_6$, decomp. 224—225° and 179—180°, respectively. The product from (III) is identical with that obtained by use of boiling EtOH. (IV) is transformed by short treatment with NaOEt in boiling EtOH into a colourless *substance*, $C_{14}H_{12}N_4$, m.p. 111—112°. Similar treatment of (V) affords BzOH, an *acid*, m.p. 164—165° and m.p. >335° after re-solidification (*Na* salt), and a *substance*, m.p. 214—215°. Phenacylpyridinium bromide phenylhydrazone is converted by NaOEt–EtOH into $C_5H_5N$ and a *substance*, decomp. 135—136°, converted by 48% HBr into a *compound*, m.p. 113—114°. H. W.

**Model experiments on the groups of the co-enzymes concerned with hydrogen transference.** P. Karrer, B. H. Ringier, J, Büchi, H. Fritzsche, and U. Solmssen (Helv. Chim. Acta, 1937, 20, 55—71).—Nicotinamide (I), m.p. 131—132° (improved prep. from Et nicotinate), is transformed by acetobromoglucose in dioxan at 35° into 3-*carbamyl*-1-*tetra-acetylglucosidopyridinium bromide* (II), $NH_2{\cdot}CO{\cdot}C_5H_3NBr{\cdot}CH<[CH{\cdot}OAc]_3>O>CH{\cdot}CH_2{\cdot}OAc$, decomp. 192—200°, which, like cozymase and the H-carrying co-enzyme, reduces Fehling's solution. Reduction of (II) by $Na_2S_2O_4$ in presence of $NaHCO_3$ causes absorption of 2 H with production of a dark yellow solution and formation of 1-*tetra-acetylglucosido*-1 : 2(or 1 : 6)-*dihydronicotinamide* (III), m.p. 157—158°, hydrolysed by $NH_3$–EtOH to 1-d-*glucosido*-1 : 2(or 1 : 6)-*dihydronicotinamide* (IV), decomp. 203—205°, the structure of which is established

by comparison with 1-methyl-*o*-dihydronicotinamide (V) and the reduced co-enzyme. The spectroscopic behaviour of (III) and (IV) is identical with that of the reduced form of the co-enzyme. The reducing power of (IV) is ≪ that of (V); it reduces cold $AgNO_3$ (without $NH_3$) very slowly, rapidly when heated. $K_3Fe(CN)_6$ does not dehydrogenate it in alkaline solution. It appears stable towards atm. $O_2$, but is readily oxidised thereby in the presence of flavin. 1 mol. of (IV) absorbs 1 $O_2$, and since $H_2O_2$ does not appear to be isolable it is probably destroyed by secondary changes. (III) is hydrolysed to (I) by prolonged contact with hot, very dil. $H_2SO_4$. Therefore (IV) is probably the analogue of the reduced forms of the H-transporting groups of co-enzymes from which it differs in the nature of the sugar group and the absence of the phosphate residue. (I) and acetobromoarabinose in dioxan give non-cryst. 3-*carbamyl*-1-*triacetylarabinosidopyridinium bromide*, reduced to the non-cryst. $H_2$-derivative, which is hydrolysed to 1-*arabinosido*-1 : 2(or 1 : 6)-*dihydronicotinamide* (VI); a similar sequence of changes leads to 1-*xylosido*-1 : 2(1 : 6)-*dihydronicotinamide* (VII), which, like (VI), closely resembles (IV) in reducing power and spectroscopic behaviour. 1-*d*-Tetra-acetylglucosidopyridinium bromide is reduced by $Na_2S_2O_4$–$NaHCO_3$ to 1-d-*tetra-acetylglucosido*-1 : 2-*dihydropyridine*, m.p. 154—155°, hydrolysed to 1-d-*glucosido*-1 : 2-*dihydropyridine*; both compounds reduce warm $AgNO_3$ and are stable to $K_3Fe(CN)_6$ in alkaline solution; nicotinonitrile gives 3-*cyano*-1-d-*tetra-acetylglucosidopyridinium bromide*, m.p. 156°, which absorbs 2 H but appears also to undergo secondary change during the process. 3-*Carbethoxy*-1-d-*tetra-acetylglucosidopyridinium bromide* (non-cryst.) is smoothly reduced by $Na_2S_2O_4$–$NaHCO_3$ to *Et* 1-d-*tetra-acetylglucosido*-1 : 2-*dihydropyridine*-3-*carboxylate*, m.p. 146·5°. (IV), (VI), or (VII) cannot replace cozymase in fermentation experiments. H. W.

**Action of thionyl chloride on 2-methylpyridinecarboxylic acids and 2 : 6-lutidine. New type of oxidation reaction of thionyl chloride.** R. Graf and F. Zettl (J. pr. Chem., 1936, [ii], **147**, 188—198; cf. A., 1932, 401).—6-Methylnicotinic acid (I) when warmed with $SOCl_2$ gives its *acid chloride hydrochloride*, decomp. about 120°, but when heated (closed vessel; 120°; 6 hr.) and then treated with MeOH gives *Me* 6-(*trichloromethyl*)*nicotinate* (II), m.p. 82—84°, and some $Me_2$ *iso*cinchomeronate. The latter, however, is the chief product when (I) and $SOCl_2$ are boiled (15 hr.) and then treated with MeOH. Gentle hydrolysis of (II) gives 6-(*trichloromethyl*)*nicotinic acid*, m.p. 183—184° (*Ph* ester, m.p. 87—89°), which with HI gives (I) and with boiling 80% $H_2SO_4$ gives *iso*cinchomeronic acid. 6-Methylpicolinic acid (III) when warmed with $SOCl_2$ gives its *acid chloride hydrochloride* (IV), m.p. 120° (decomp.), whilst when heated (closed vessel; 180°; 10 hr.) or boiled with $SOCl_2$ for a long time, and then treated with MeOH it gives *Me* 6-(*trichloromethyl*)*picolinate* (V), m.p. 108—110°, and $Me_2$ dipicolinate (VI). The former on gentle hydrolysis gives 6-(*trichloromethyl*)*picolinic acid*, m.p. 140—143° (*amide*, m.p. 119—122°), hydrolysed by 80% $H_2SO_4$ to pyridine-2 : 6-dicarboxylic acid. The compound, m.p. 195°, obtained by Turnau (A., 1905, i, 546) from (III) is probably a mixture of (IV) and the hydrochloride of (III). By similar methods 6-methylpyridine-2 : 4-dicarboxylic acid yields *Me*$_3$ *pyridine*-2 : 4 : 6-*tricarboxylate*, m.p. 150—152°, and *Me*$_2$ 6-(*trichloromethyl*)-*pyridine*-2 : 4-*dicarboxylate*, m.p. 114—116°. 2 : 6-Lutidine hydrochloride when heated (closed vessel; 180°; 20 hr.) with $SOCl_2$ yields 2 : 6-*di*(*trichloromethyl*)*pyridine*, m.p. 86—87°, hydrolysed according to conditions by $H_2SO_4$–MeOH to (V) or (VI). H. G. M.

**5 : 7-Dimethyloxindole.** V. Livovschi (Compt. rend., 1936, **203**, 1265—1267; cf. A., 1935, 1131).—*p*-Xylidine with $CH_2Cl$·COCl affords a compound, cyclised ($AlCl_3$) to 5 : 7-*dimethyloxindole* (I), m.p. 153°, which with the appropriate aromatic aldehyde (equimol. amount) in hot EtOH containing piperidine gives 3-*benzylidene*- (II), m.p. 195°, 3-p-*chlorobenzylidene*-, m.p. 167°, 3-*piperonylidene*-, m.p. 198°, 3-*furfurylidene*-, m.p. 246°, and the *Na* salt, decomp. at 285°, of 3-*o*-sulphobenzylidene-5 : 7-dimethyloxindole. (I) with excess of PhCHO affords, besides (II), 3 : 3′-*benzylidenedi*-5 : 7-*dimethyloxindole*, m.p. 175°, and with isatin in AcOH–HCl it affords 5 : 7-*dimethyliso*-*indigotin* (III), decomp. >360°, whereas in $Et_2O$–piperidine, 5 : 7-*dimethylisatan* results, which is converted into (III) at 185—190°. (I) with isatin chloride in anhyd. $C_6H_6$ affords 5 : 7-dimethylindirubin (A., 1919, i, 457) which dyes wool violet. (I) with *iso*amyl nitrite similarly affords 5 : 7-*dimethylisatin oxime*, m.p. 223° (decomp.). J. L. D.

**Isatincarboxylic acids.** H. Waldmann (J. pr. Chem., 1937, [ii], **147**, 338—343).—*o*-$NH_2$·$C_6H_4$·$CO_2Me$ is converted by $CCl_3$·$CH(OH)_2$, $(NH_2OH)_2$, $H_2SO_4$, and $H_2SO_4$ in boiling $H_2O$ into *Me oximinoacetanthranilate* (I), m.p. 180°. p-*Oximinoacetamidobenzoic acid*, m.p. >310°, its *Me* ester (II), m.p. 231°, and m-*oximinoacetamidobenzoic acid* (III), m.p. 228°, are obtained similarly. Gradual addition of (I) to conc. $H_2SO_4$ at 70—75° affords *Me isatin*-7-*carboxylate*, m.p. 192°, hydrolysed to isatin-7-carboxylic acid, m.p. 276—277°, which with COPhMe, EtOH, and 33% KOH gives 2-*phenylquinoline*-4 : 8-*dicarboxylic acid*, m.p. >310°. (II) is transformed similarly into *isatin*-5-*carboxylic acid*, m.p. 292—293° (decomp.) (*oxime*, decomp. 282°; *Me* ester, m.p. 264°, and its *oxime*, decomp. 280°), whence 2-*phenylquinoline*-4 : 6-*dicarboxylic acid*, m.p. >310°. (III) yields *isatin*-6-*carboxylic acid*, m.p. 292° (decomp.) (*Me* ester, m.p. 209°). H. W.

**Salts of phosphotungstic and metatungstic acids with organic bases.** E. A. Nikitina (J. Gen. Chem. Russ., 1936, **6**, 1624—1631).—The *salts* $R_6HX$, $R'_4H_3X$, $R''_7X$, $R_7H_3X'$, $R'_6H_4X'$, and $R''_7H_3X',xH_2O$ (R = quinoline, R′ = $C_5H_5N$, R″ = $NH_2Et$, X = $[P(W_2O_7)_7]_6$, X′ = $[H_2(W_2O_7)_6]$) are described. The solubility of the salts in 14% HCl at 0—100° is determined; $R_6HX$ and $R_7H_3X'$ are insol. R. T.

**Bromo-derivatives of *N*-allylquinolinium salts.** C. Candea, E. Macovski, and J. Kuhn (Atti V Congr. Naz. Chim., 1936, **1**, 330—336).—N-*Allylquinolinium bromide*, m.p. 171°, in MeOH with Br

gives successively N-β*γ*-*dibromopropylquinolinium bromide*, m.p. 192° (decomp.), and *dibromobromide*, m.p. 107—108°. The former with KI yields N-β*γ*-*dibromopropylquinolinium iodide*, m.p. 136—137°, which with Br gives the *dibromoiodide*, m.p. 123°; the last is the only product when *N*-allylquinolinium iodide is treated in MeOH with 2 or 4 Br.

E. W. W.

**Derivatives of methylcarbostyril.** H. Waldmann (J. pr. Chem., 1937, [ii], **147**, 321—325).—4-*Hydroxy*-1-*methylcarbostyril* (I), m.p. 264·5°, readily obtained from boiling $CH_2(CO_2Et)_2$ and NHPhMe, couples with *m*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ to 3-m-*nitrobenzeneazo*-4-*hydroxy*-1-*methylcarbostyril* (II), m.p. 210—211°, transformed by $SnCl_2$ and boiling HCl into 3 : 4-*dihydroxy*-1-*methylcarbostyril*, m.p. 234—235° (decomp.) (*Ac*$_2$ derivative, m.p. 185—186°). Reduction of (II) by $Na_2S_2O_4$ and alkali affords 3-*amino*-4-*hydroxy*-1-*methylcarbostyril* (III), m.p. 253° (3-*Ac* derivative, m.p. 196°). Successive treatment of (III) with $H_2SO_4$–$KNO_2$, $SnCl_2$–HCl, and $CaSO_4$ leads to 2 : 4-*diketo*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*-3-*hydrazone*, m.p. 166—167°, converted by NaOEt in abs. EtOH into (I).

H. W.

**Preparation of 2-hydroxy-4-methylquinolines.** (Signa.) L. Monti and (Signa.) V. Cirelli (Gazzetta, 1936, **66**, 723—731).—The effect of substituents (Cl, Br, Me, OMe, $NO_2$, and Ac) on the condensation of anilines with $CH_2Ac{\cdot}CO_2Et$ and on the dehydration of the product to a 2-hydroxy-4-methylquinoline is studied. *o*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ does not condense; the products from *o*-$OMe{\cdot}C_6H_4{\cdot}NH_2$, *m*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, and *p*-$C_6H_4Ac{\cdot}NH_2$ do not yield the quinoline. *m*-Bromoacetoacetanilide, new m.p. 108—110°, gives 7-*bromo*-2-*hydroxy*-4-*methylquinoline*, m.p. 286—288°. *p*-Chloro- and *p*-bromo-acetoacetanilide form respectively 6-*chloro*-, m.p. 292—294°, and 6-*bromo*-2-*hydroxy*-4-*methylquinoline*, m.p. 292—293°. m-*Acetoacetanilide*, m.p. 96—98°, is not dehydrated by $H_2SO_4$; in heavy petroleum at 300° it gives a *substance*, m.p. 230° (decomp.).

E. W. W.

**Action of formaldehyde on hydroxyquinolines.** (Signa.) L. Monti (Atti V Congr. Naz. Chim., 1936, **1**, 403—407).—6-Hydroxyquinoline and $CH_2O$ in alkaline solution yield *bis*-[6-*hydroxy*-5(or 7)-*quinolyl*]-*methane*, but in $H_2SO_4$ 6-*hydroxy*-5(or 7)-*quinolylcarbinol* cyclo*methylene ether* is formed. 4-Hydroxy-2-alkyl- or -aryl-quinolines give 4-hydroxy-2-alkyl- or -aryl-3-quinolylcarbinol *cyclo*methylene ethers.

E. W. W.

**Action of formaldehyde on hydroxyquinolines. II.** (Signa.) L. Monti and D. Dinelli (Gazzetta, 1936, **66**, 732—734; cf. A., 1936, 617).—2-Hydroxy-4 : 6-dimethyl- and 6-chloro-2-hydroxy-4-methyl-quinoline in $H_2SO_4$ with 40% $CH_2O$ give respectively 2-*hydroxy*-4 : 6-*dimethyl*-, m.p. 137—138° (*picrate*, m.p. 187°), and 6-*chloro*-2-*hydroxy*-4-*methyl*-3-*quinolylcarbinol* cyclo*methylene ether*, m.p. 169—171° (*picrate*, m.p. 187—189°).

E. W. W.

**Synthesis of phenanthridine derivatives by an application of the Stieglitz rearrangement.** L. A. Pinck and G. E. Hilbert (J. Amer. Chem. Soc., 1937, **59**, 8—13).—9-Chloro-9-phenylfluorene (I) and liquid $NH_3$ at 60° (sealed tube) give 9-*amino*-9-*phenylfluorene*, m.p. 82° [*hydrochloride*, m.p. 310° (decomp.); *Ac*, m.p. 232°, N-*Br*-, m.p. 105° (decomp.), N-*Cl*- (II), m.p. 102°, and NN-$Cl_2$-, m.p. 150° (decomp.), derivatives]; with dry $NH_3$ at 180° some *di*-(9-*phenyl*-9-*fluoryl*)*amine*, m.p. 230°, is also produced. 9-Chloro-9-α-naphthylfluorene with dry $NH_3$ at 80° and MeCN–$N_2H_4$,$H_2O$ (excess) affords 9-*amino*-9-α-*naphthylfluorene*, m.p. 186° [*hydrochloride*, m.p. 271° (decomp.); N-*Cl*-derivative (III), m.p. 133—135° (decomp.)], and 9-α-naphthyl-9-fluorylhydrazine, m.p. 98° (decomp.) (previous sintering) [*hydrochloride*, m.p. 217° (decomp.); corresponding *azide* (IV), m.p. 133°], respectively. 9-Bromo-9-methylfluorene and liquid $NH_3$ in PhMe at 75° give 9-*amino*-9-*methylfluorene* (V), m.p. 96° [*hydrochloride*, m.p. 266° (decomp.)], 9-*fluorylmethylamine* (?), m.p. 99—100° [*hydrochloride*, m.p. 294° (decomp.)], *di*-(9-*methyl*-9-*fluoryl*)*amine*, m.p. 166° [*hydrochloride*, m.p. 263—265° (decomp.)], and an appreciable amount of polymeric diphenylene-ethylene. (II), (III), and the unstable *N*-Cl-derivative of (V), which are prepared from the amine hydrochlorides and cold aq. KOCl in EtOH, are converted by NaOMe in $C_5H_5N$ into 9-phenyl- [hydrochloride, m.p. 226° (lit. 220°)], 9-α-*naphthyl*- (VI), m.p. 123·5° [*hydrochloride*, m.p. 224° (decomp.); *picrate*, m.p. 251°], and 9-methyl-phenanthridine [picrate, m.p. 250° (decomp.) (lit. 233°)], respectively. (VI) is also formed when (IV) is heated at 194°. The primary factor controlling the rearrangement of the intermediate free radical from these *N*-Cl-derivatives is considered to be the strained condition of the five-membered ring. 9-Hydroxy-9-α-naphthylfluorene and fluorenone form a mol. *compound*, m.p. 109—110°. All m.p. are corr.

H. B.

**Meso-derivatives of acridine. VI. Derivatives of 5-aminoacridine and 5-(dimethylaminophenyl)acridine.** N. S. Drozdov (J. Gen. Chem. Russ., 1936, **6**, 1641—1650).—5-Chloro-3-methylacridine and PhOH (100°; 30 min.) yield 10-*phenoxy*-2-*methylacridine* (I), m.p. 133—134°, which, when heated at 120° for 2 hr. with PhOH and $NHMe_2$,HCl, affords 5-*dimethylamino*-3-*methylacridine*, m.p. 251—252° (*hydrochloride*, m.p. >300°). (I) affords 5-(p-*arsinoanilino*)-3-*methylacridine*, m.p. 268—269°, when fused with PhOH and arsanilic acid (II), and 3-*methylacridine*-5-*glycine*, m.p. 226—228° (decomp.), with glycine and PhOH. 3-Methylacridine, $NPhMe_2$, and $POCl_3$ (100°; 2 hr.) give 5-(*dimethylaminophenyl*)-3-*methylacridine*, m.p. 231—232°. 5-Phenoxyacridine and (II) in PhOH at 100° yield 5-(p-*arsinoanilino*)-*acridine*, m.p. 264—265°. 5-Phenoxy-3-methoxyacridine similarly gives 5-*dimethylamino*-, m.p. 275—276°, and 5-(p-*arsinoanilino*)-*acridine*, m.p. 245—248°, and 3-*methoxyacridine*-5-*glycine*, m.p. 230—231° (decomp.). *o*-Chlorobenzoic acid, (II), $K_2CO_3$, glycerol, and Cu at 120—130° (3 hr.) yield 4′-*arsinodiphenylamine*-2-*carboxylic acid*, m.p. 278° (decomp.), converted by $H_2SO_4$ (100°; 1 hr.) into *acridone*-3-*arsinic acid*, m.p. >300°, and this condenses with $NPhMe_2$ in presence of $POCl_3$ to yield 5-(*dimethylaminophenyl*)*acridine*-3-*arsinic acid*, m.p. 230—232°. (I) does not react with *o*-$C_6H_4Me{\cdot}NHEt$ under the above conditions.

R. T.

**Manufacture of salts of acridinium bases.**—See B., 1937, 23.

[**Acridones.**] K. LEHMSTEDT (Ber., 1937, **70**, [*B*], 172—173).—A reply to Tănăsescu *et al.* (A., 1936, 1520). H. W.

**K salt of 4-nitrosopyrazolone-3-carboxylic acid.**—See A., III, 60.

**Reaction between Schiff's bases and pyrazolone derivatives.** M. PASSERINI and G. RAGNI [with G. CUSMANO] (Gazzetta, 1936, **66**, 684—688).—Benzylidene-aniline and -*p*-toluidine condense slowly with antipyrine in EtOH to 4-α-*anilino*-, m.p. 185—187°, and 4-α-p-*toluidino-benzyl*-2 : 3-*dimethyl*-5-*pyrazolone*, m.p. 184—186°, respectively, both hydrolysed to benzylidenebisantipyrine. Either reagent gives directly benzylidenebis-(1-phenyl-3-methyl-5-pyrazolone) when treated in cold EtOH with 1-phenyl-3-methyl-5-pyrazolone; with anisylideneaniline the last forms the corresponding anisylidene derivative. E. W. W.

**Histamine formation from histidine through ascorbic acid.** P. HOLTZ (Naturwiss., 1937, **25**, 14).—Histidine in neutral aq. solution containing ascorbic acid is converted into histamine (blood-pressure test) by $O_2$ but not by $N_2$ (cf. A., 1936, 885). J. L. D.

**Synthesis of benzoylpyrromethenes.** H. FISCHER and J. HEIDELMANN (Annalen, 1937, **527**, 115—138).—3-Benzoyl-4-phenyl-2-methylpyrrole (I) is readily condensed by 100% $HCO_2H$ and 48% HBr to 4 : 4′-*dibenzoyl*-3 : 3′-*diphenyl*-5 : 5′-*dimethylpyrromethene* (II), m.p. 212° (*hydrobromide*, m.p. 242°; *picrate*, m.p. 215°), also formed when (I) is condensed with Et 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylate (III). Analogously (I) does not react with 5-aldehydo-2 : 3 : 4-trimethylpyrrole or 2 : 4-dimethyl-3-ethylpyrrole (IV), which afford 3 : 4 : 5 : 3′ : 4′ : 5′-hexamethylpyrromethene, m.p. 295°, and 3 : 3′ : 5 : 5′-*tetramethyl*-4 : 4′-*diethylpyrromethene*, m.p. 243°, respectively. (I) in $Et_2O$ is transformed by HCN–HCl into the *imine hydrochloride* and thence into 3-*benzoyl*-4-*phenyl*-2-*methylpyrrole*-5-*aldehyde* (V), m.p. 156° (*phenylhydrazone*, m.p. 114°). 3-*Benzoyl*-2 : 4-*dimethylpyrrole*-5-*aldehyde* (VI), m.p. 170° (*phenylhydrazone*, m.p. 168°; *semicarbazone*, m.p. 215°; *aldazine*, $C_{28}H_{26}O_2N_4$, m.p. 279°), is obtained similarly, (I) and (V) readily afford (II). With 2 : 3 : 4-trimethylpyrrole and (IV), respectively, (V) smoothly gives 4-*benzoyl*-3-*phenyl*-3′ : 4′ : 5 : 5′-*tetramethylpyrromethene* (*hydrobromide*, m.p. 230°) and 4-*benzoyl*-3-*phenyl*-3′ : 5 : 5′-*trimethyl*-4′-*ethylpyrromethene*, m.p. 116° (*hydrobromide*, m.p. 213°). Attempts to condense (V) with Et 2 : 4-dimethylpyrrole-3-carboxylate in varied proportion gave mainly *Et*$_2$ 3 : 3′ : 5 : 5′-*tetramethylpyrromethene*-4 : 4′-*dicarboxylate* (*hydrobromide*, m.p. 217°) (formed by autocondensation of the ester) with small amounts of (II), m.p. 212° (also +2MeOH). Similarly (VI) could not be condensed with 3-benzoyl-4-phenyl-2-methylpyrrole the "auto product" being 4 : 4′-dibenzoyl-3 : 3′ : 5 : 5′-tetramethylpyrromethene (hydrobromide, m.p. 225°). Synthesis hampered by the heavy residues occurs only in a heated medium so that 2-free pyrroles which lead to autocondensation under cold conditions more readily lose CHO under the experimental conditions than combine with the "difficult" pyrroles. (V) and 5-phenyl-3-methylpyrrole in abs. EtOH containing 48% HBr at 100° give 4-*benzoyl*-3 : 5′-*diphenyl*-3′ : 5-*dimethylpyrromethene hydrobromide*, m.p. 232°, whilst under like conditions 2 : 4-dimethylpyrrole-5-aldehyde (VII) yields 4-*benzoyl*-3-*phenyl*-2′ : 4′ : 5-*trimethylpyrromethene*-5′-*aldehyde hydrobromide*, m.p. 210°, in which CHO is non-reactive. (IV) and (VII) in EtOH containing HBr give 3 : 3′ : 5 : 5′-*tetramethyl*-4′-*ethylpyrromethene*, m.p. 80° (*hydrobromide*, m.p. 215°; *picrate*, m.p. 179°), Et 2 : 3-dimethylpyrrole-5-carboxylate is converted by BzCl and anhyd. $AlCl_3$ in boiling $CS_2$ into *Et* 4-*benzoyl*-2 : 3-*dimethylpyrrole*-5-*carboxylate*, m.p. 178°, hydrolysed to 4-*benzoyl*-2 : 3-*dimethylpyrrole*-5-*carboxylic acid*, m.p. 203° (decomp.), which passes at 220° into 4-*benzoyl*-2 : 3-*dimethylpyrrole*, m.p. 192°. The latter is transformed by anhyd. HCN–HCl in $Et_2O$ into 4-*benzoyl*-2 : 3-*dimethylpyrrole*-5-*aldehyde*, m.p. 129°, which affords 3 : 3′-*dibenzoyl*-4 : 5 : 4′ : 5′-*tetramethylpyrromethene*, decomp. 275° after softening at 210°. Protracted chlorination of Et 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylate in $CCl_4$ leads to *Et* 2 : 4-*di*-(*trichloromethyl*)-3-*ethylpyrrole*-5-*carboxylate*, m.p. 65°, converted by conc. $HNO_3$ or conc. $H_2SO_4$ into the *pentachloromonohydroxy*-compound, $C_{11}H_{12}O_3NCl_5$, m.p. 111°. To examine the possibilities of the change $CHR{:}CH{\cdot}NH{\cdot}CO_2Me \rightarrow CH_2R{\cdot}CHO$ in the pyrrole series, Me 5-carbethoxy-2 : 4-dimethylpyrrole-3-acrylate is converted into the corresponding *hydrazide* (VIII), m.p. 235° [*hydrochloride*, m.p. 215°; *:CHPh*, m.p. 241°, and *Bz*, m.p. 253°, derivatives; condensation *products*, $C_{18}H_{25}O_5N_3$, m.p. 178°, with $CH_2Ac{\cdot}CO_2Et$ and $C_{22}H_{28}O_5N_4$, m.p. 304°, with (III)]. *Et* 2 : 4-*dimethyl*-3-ββ-*dicarboxyhydrazidoethylpyrrole*-5-*carboxylate* [*dihydrochloride*, m.p. 189°, and (*:CHPh*)$_2$ derivative, m.p. 258° (decomp.)] and *Et* 2-*methyl*-4-*ethyl*-3-ββ-*dicarboxyhydrazidoethylpyrrole*-5-*carboxylate*, m.p. 233° [*dihydrochloride*, m.p. 181° (decomp.); (*:CHPh*)$_2$ derivative, m.p. 263°], are described. *Et* 2 : 4-*dimethyl*-3-β-*carboxy*-β-*carbethoxyethylpyrrole*-5-*carboxylate* has m.p. 119°. (VIII) is converted by $NaNO_2$ and AcOH into the relatively stable *azide*, m.p. 141°, converted by $SO_2Cl_2$ in $Et_2O$ into the *compound*, $C_{12}H_{13}O_3N_4Cl$, m.p. 136° (decomp.), which with boiling MeOH gives the *substance*, $C_{13}H_{16}O_4N_4$, m.p. 130° (decomp.). With boiling *iso*-amyl alcohol, cholesterol, or $CH_2Ph{\cdot}OH$ in boiling xylene, the azide gives the respective *urethanes*, $C_{17}H_{26}O_4N_2$, m.p. 178°, $C_{39}H_{60}O_4N_2$, m.p. 217°, and $C_{19}H_{22}O_4N_2$, m.p. 200°, the last of which is transformed by $SO_2Cl_2$ in $Et_2O$ into the *compound*, $C_{19}H_{20}O_4N_2Cl_2$, m.p. 158°, converted by 10% $Na_2CO_3$ and EtOH into the *benzylurethane*,

$$CO_2Et{\cdot}C{=}CMe \\ NH{\cdot}CMe \gg C{\cdot}CH{:}CH{\cdot}NH{\cdot}CO_2CH_2Ph,$$ m.p. 90°.

H. W.

**New applications of magnesium in organic synthesis. II. Barbituric acid condensations.** H. LUND (Kong. dansk. Vidensk. Selsk., mat.-fys. Medd., 1935, **13**, No. 2, 9 pp.; Chem. Zentr., 1936, i, 2095—2096).—Mg may advantageously replace Na in such reactions, $Mg(OMe)_2$ in MeOH being superior to $Mg(OEt)_2$ in EtOH. In this manner barbituric

(86%), 5-*iso*propyl-, m.p. 214° (81%), 5-phenyl-, m.p. 258° (96%), 5 : 5-diallyl-, m.p. 170° (94%), 5-allyl-5-*iso*propyl-, m.p. 137° (81%), 5 : 5-diethyl-, m.p. 189° (81%), and 2-*thio*-5-iso*propyl*-, m.p. 178° (68%), -barbituric acids are obtained in the yields indicated. H. N. R.

**Detection of therapeutically important barbituric acids.** J. C. Jespersen and K. T. Larsen (Arch. Pharm., 1937, **275**, 28—35).—Barbituric acids are identified by their di-*p*-nitrobenzyl derivatives. The following are the corr. m.p. of the stated substituted barbituric acid, its xanthhydrol condensation *product* (prep. in hot AcOH), and the fully substituted *p*-nitrobenzyl *derivative* [prep. by *p*-$NO_2$·$C_6H_4$·$CH_2Cl$ (prep. detailed) and $Na_2CO_3$ in aq. MeOH] : 5-Me*, 206·6°, —, 208°, -Et*, 191·5°, —, 213·5°, -Pr$^\beta$, 216·7°, 207·5°, 189°, 5 : 5-$Et_2$, 188·5°, 246·5°, 193·5°, -$Pr^\alpha_2$, 146·5°, 269°, 182·3°, -ethyl-*n*-butyl, 122·5°, 250°, 148·5°, -ethyl*iso*amyl, 141°, 251°, 145·5°, -ethylallyl, 159·4°, 242°, 196·3°, -*iso*propylallyl, 139·5°, 226·5°, 192°, -*n*-butylallyl, 126·1°, 240°, 127·5°, -*iso*butylallyl*, 135·9°, —, —, diallyl, 171·5°, 242·5°, 192·5°, 5-phenyl-5-methyl, 223·7°, 282°, 197°, 5-phenyl-5-ethyl, 174·9°, 219°, 183·5°, 5-phenyl-5-allyl, 154·9°, 222·5°, 152°, *iso*propylbromopropenyl, —, —, 200·5°, 5-*cyclo*hexenyl-5-ethyl, 176·4°, 257°, 196°, 5-phenyl-1-methyl-5-ethyl, 173·2°, —, 114·5°, 5-*cyclo*hexenyl-1 : 5-dimethyl, 143·9°, —, 114·5°. The solubilities of the acids, except those marked *, in $H_2O$ at 20° and 37° are recorded. In most cases the acids are readily analysed by treatment in $CHCl_3$ with aq. KBr–$KBrO_3$ and determination of the excess of $KBrO_3$; the addition is complete in 15 min. R. S. C.

**2-Alkylbenziminazoles as derivatives for identification of aliphatic acids.** W. O. Pool, H. J. Harwood, and A. W. Ralston (J. Amer. Chem. Soc., 1937, **59**, 178—179).—2-Alkylbenziminazoles (I) are prepared from *o*-$C_6H_4(NH_2)_2$ and $AlkCO_2H$ (II) (Alk = Me—*n*-heptadecyl) by a slight modification of Seka and Müller's method (A., 1931, 600). The higher (I) have similar m.p. and are not very useful for identifying (II). The following appear to be new : 2-n-*octyl*-, m.p. 139·5—140·5° (all m.p. are corr.), -n-*decyl*-, m.p. 114—114·5°, -n-*dodecyl*-, m.p. 109—109·5°, -n-*tridecyl*-, m.p. 105—105·5°, -n-*tetradecyl*-, m.p. 98·5—99·5°, and -n-*hexadecyl*-, m.p. 93·5—94·5°, *-benziminazoles*. H. B.

**Preparation of *p*-phenanthroline and 3 : 3′-dipyridyl.** M. I. Kabatschnik and V. V. Rezon (J. Appl. Chem. Russ., 1936, **9**, 2026—2029).—*p*-$C_6H_4(NH_2)_2$, *p*-$NO_2$·$C_6H_4$·$NO_2$, glycerol, and $H_2SO_4$ (1 hr. at 130°, 1·25 hr. at 130—150°, and 1·25 hr. at 150—160°) yield *p*-phenanthroline, from which 3 : 3′-dipyridyl is prepared by known methods. R. T.

**Transformation products of some hydrazides of organic acids. I.** (Signa.) M. Freri (Atti V Congr. Naz. Chim., 1936, **1**, 361—365).—Et crotonate with $N_2H_4,H_2O$ yields crotonhydrazide, which could not be converted into the azide, but gave 1-*nitroso*-5-*methylpyrazolidone*, m.p. 173°. Et β-chloro*iso*crotonate does not give the hydrazide, but with $N_2H_4,H_2O$ forms methylpyrazolone, also obtained from Me *iso*crotonate. $Me_2$ itaconate (new prep. from Na salt and $Me_2SO_4$) yields *itacondihydrazide*, m.p. 150° (decomp.), converted into the *-diazide*, m.p. 50°. $Me_2$ mesaconate yields *mesacondihydrazide*, m.p. 215° (decomp.), converted into the *-diazide*, m.p. 113° (decomp.). *Citracondihydrazide*, m.p. 212°, with $HNO_2$ gives the *diazide*, m.p. 114°, further converted into 3 : 6-*diketo*-4-*methyl*-1 : 2 : 3 : 6-*tetrahydropyridazine*, m.p. 277°, also obtained directly from citraconic anhydride (1 mol.) and $N_2H_4,H_2O$ (1 mol.). With excess of $HNO_2$, the dihydrazide yields a *compound*, $C_4H_5O_2N_3$, m.p. 231° (coloured *Na*, *K*, and *Ag* salts; *Bz* derivative, m.p. 177°; *p-*$NO_2$·$C_6H_4$·*CO* derivative, m.p. 188°), and a *compound*, m.p. 245°. E. W. W.

**Chemiluminescent organic compounds. I. Isomeric simple and complex hydrazides of phthalic acid and mode of formation of phthalazine and *iso*indole rings.** H. D. K. Drew and H. H. Hatt. **II. Effect of substituents on the closure of phthalylhydrazides to 5- and 6-membered rings.** H. D. K. Drew and F. H. Pearman. **III. *N*-Methylated phthalaz-1 : 4-diones.** H. D. K. Drew, H. H. Hatt, and F. A. Hobart (J.C.S., 1937, 16—26, 26—33, 33—37).—I. Phthalaz-1 : 4-dione (I) is prepared by condensation of *o*-$C_6H_4(CO_2)_2O$ (II) and $N_2H_4$ in AcOH and is $C_6H_4<^{CO\cdot NH}_{CO\cdot NH}$ (cf. Curtius *et al.*, A., 1895, i, 354). With excess of (II), N-*phthalimidophthalimide* (III), m.p. 311—313°, is obtained, hydrolysed with $N_2H_4$ to (I) and with NaOH to s-*dibenzoylhydrazine*-2 : 2′-*dicarboxylic acid* (IV). Short-period reaction of (II) with $N_2H_4$ in AcOH or EtOH leads to variable amounts of N-*aminophthalimide* (V), which at its m.p. (200—205°) is changed to (I) (cf. Rothenburg, A., 1894, i, 285), and condenses with aldehydes to give N-*acetamidophthalimide*, m.p. 228—230°, and N-iso*propylidene*-, m.p. 97—100°, *-benzylidene*-, m.p. 166—167°, *-p*-anisylidene-, m.p. 189—191°, *-cinnamylidene*-, m.p. 199—200°, and *-piperonylidene-aminophthalimide*, m.p. 186·5—170°. *o*-$C_6H_4(CO)_2NH$ and $N_2H_4$ in EtOH give o-*carbamylbenzhydrazide*, m.p. 300—320°, converted into (I) and (V) in boiling EtOH. (I) with aldehydes yields the same products as from (V) but with CHPh:CH·CHO affords 3-*phenyl*-1 : 2-*phthalopyrazolone*, m.p. 224—228°, which with NaOEt–EtOH forms 5-phenylpyrazoline; these reactions show conversion from the 6- into the 5-membered ring. (V) and (II) in AcOH give (III) (N-3′-, m.p. 249—250°, and -4′-*nitrophthalimidophthalimide*, m.p. 250°). *o*-Carbomethoxybenzoyl chloride (VI) and $N_2H_4$ in $C_5H_5N$ yield *Me* s-*dibenzoylhydrazine*-2 : 2′-*dicarboxylate*, m.p. 180—200°, cyclised to (III) and hydrolysed to (IV), m.p. 260—320° (*hydrazine* and *Ag* salts), which is also partly cyclised to (III). *Me* s-*dibenzoyldimethylhydrazine*-2 : 2′-*dicarboxylate*, m.p. 171—172°, is unchanged by fusion. The formation of (V) appears not to be utilised in the production of (III).

Excess of (II) and $N_2H_4$ in AcOH, reacting for 0·5 min., give N-*phthalimidophthalamic acid*, decomp. 160—190° (*Ag* salt), cyclised to (III) (70%), (I), and (II), and also prepared from (V) and (II). *Me* N-*phthalimidophthalamate*, m.p. 166—168°, is obtained from (V) and (VI), cyclised to (III). The probable

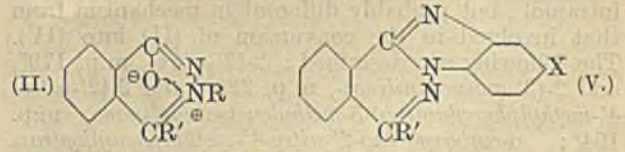
course of the reactions is discussed. (VI) and (I) condense to 2-o-*carbomethoxybenzoylphthalaz*-1 : 4-*dione*, decomp. 165—170°, cyclised to (III). (I) and *s*-phthalyl chloride in $PhNO_2$ afford 2 : 3-*phthalophthalaz*-1 : 4-*dione*, m.p. 350—360° (slight decomp.), converted by $N_2H_4$ into (I). (I) with $Ac_2O$ yields 4-*acetoxy*-2-*acetylphthalaz*-1-*one*, m.p. 139—140°, and with AcCl in $C_5H_5N$ gives an *Ac* derivative, m.p. 175—176; a second *Ac* derivative is obtained by partial hydrolysis of the $Ac_2$ compound (cf. Rowe and Peters, A., 1933, 1308). These results are in favour of the structure assigned to (I) and not the enol forms.

II. 5-Nitrophthalaz-1 : 4-dione forms two *Ac* derivatives, m.p. 221° (cf. Mihailescu *et al.*, A., 1930, 1434) and m.p. 205°. 3-*Nitro*-2-*carboxybenzhydrazide*, m.p. 298—300°, is obtained from its 2-hydrazine salt. 5-Aminophthalaz-1 : 4-dione (VII) forms 5-*acetamido*-, m.p. 325—326° (decomp.), and 5-*benzamido-phthalaz*-1 : 4-*dione*, m.p. 319° (decomp.), and a $Bz_2$ derivative, m.p. 263°. 3-Aminophthalimide and $N_2H_4$ (1 mol.) give N : 3-*diaminophthalimide*, m.p. 252° (3-*acetamido*-N-*anilinophthalimide*, m.p. 179°); with 2 mols. of $N_2H_4$ (VII) is obtained. 4-Aminophthalimide and $N_2H_4$ form only 6-*aminophthalaz*-1 : 4-*dione*, m.p. 339° (decomp.) [*Ac* derivative, m.p. 341° (decomp.)]. 3-*Nitro*-N-*anilinophthalimide*, m.p. 188°, and s-*bis*-(6-*nitro*-2-*carboxybenzoyl*)*hydrazine*, m.p. about 318° (decomp.), are described. 3-Chlorophthalimide with 1 mol. of $N_2H_4$ forms 3-*chloro*-N-*aminophthalimide*, m.p. 194—195°, but with 2 mols., 5-*chlorophthalaz*-1 : 4-*dione*, m.p. 338° (decomp.) (*azo*-compound), is obtained. 3 : 6-Dichlorophthalimide with $N_2H_4$ (1 mol.) forms 3 : 6-*dichloro*-N-*aminophthalimide*, m.p. 210° (*benzylidene* derivative, m.p. 224°), resolidifying to yield 3 : 6 : 3′ : 6′-*tetrachloro*-N-*phthalimidophthalimide*, m.p. above 350°; with 2 mols. of $N_2H_4$, it gives the *hydrazine* salt of 3 : 6-dichloro-2-carboxybenzhydrazide, dehydrated to 3 : 6-*dichlorophthalodihydrazide*. 3 : 6-Dichlorophthalic anhydride with excess of $N_2H_4$ affords 5 : 8-dichlorophthalaz-1 : 4-dione, m.p. above 350°, and with $N_2H_4$ in AcOH gives s-*bis*-(3 : 6-*dichloro*-2-*carboxybenzoyl*)*hydrazine*, m.p. above 350°, converted with $N_2H_4$ into *hydrazine* 3 : 6-*dichlorophthalate*, m.p. 206°. 4 : 5-*Dichlorophthalic anhydride* with $N_2H_4$ yields only 6 : 7-*dichlorophthalaz*-1 : 4-*dione*, m.p. above 350°. Tetrachlorophthalic acid or anhydride with $N_2H_4$ gives only 3 : 4 : 5 : 6-*tetrachloro*-N-*aminophthalimide*, m.p. 288° (decomp.) (*benzylidene* derivative, m.p. 232°), which with the anhydride forms *octachloro*-N-*phthalimidophthalimide*, m.p. above 350°. 3-*Hydroxyphthalimide*, m.p. 255—256°, with $N_2H_4$, gives only 5-*hydroxyphthalaz*-1 : 4-*dione*, m.p. 330° (decomp.) (*Na* salt). The mechanism and conditions for the reactions are discussed.

III. (II) (see above) with $(NHMe\cdot)_2$,2HCl gives 2 : 3-*dimethylphthalaz*-1 : 4-*dione*, m.p. 175—176° (+$2H_2O$), and with $NMe_2\cdot NH_2$ forms N-*dimethylaminophthalimide*, m.p. 125—126°. 3-Nitrophthalic anhydride (VIII) and $NMe_2\cdot NHMe$ yield a mixture of α-, m.p. 292° (decomp.) (*Ac* derivative, m.p. 204—205°), and β-5-*nitro*-N-*methylphthalaz*-1 : 4-*dione*, m.p. 272° (decomp.) (*Ac* derivative, m.p. 158°), reduced to the corresponding α-, m.p. 308°, and β-$NH_2$-compounds, m.p. 299° (decomp.). (VIII) and $(NHMe\cdot)_2$ form 5-*nitro*-2 : 3-*dimethylphthalaz*-1 : 4-*dione*, m.p. 194—195°, reduced to the 5-$NH_2$-derivative, m.p. 192° [*Ac* derivative, m.p. 221—222°; *azo*-compound, m.p. 312—316° (decomp.)]; with $NMe_2\cdot NH_2$, 3-*nitro*-N-*dimethylaminophthalimide*, m.p. 141—142°, is obtained. 4-Nitrophthalic anhydride with $NMe_2\cdot NHMe$ gives a mixture of α-, m.p. 307° (decomp.) (*Ac* derivative, m.p. 210°), and β-6-*nitro*-N-*methylphthalaz*-1 : 4-*dione*, m.p. 293° (decomp.) [*Ac* derivative, m.p. 195° (decomp.)], reduced to the α-, m.p. 320° (decomp.), and β-6-$NH_2$-compounds, m.p. 360° (decomp.). 6-Nitro-, m.p. 198—199°, reduced to 6-*amino*-2 : 3-*dimethylphthalaz*-1 : 4-*dione*, m.p. 262—263° [+$2H_2O$; *Ac* derivative (+$H_2O$), m.p. 269—270°; *azo*-compound, m.p. 270—272°], and 4-*nitro*-N-*dimethylaminophthalimide*, m.p. 152—153°, are similarly prepared. The conclusion is reached that the substitution of immobile groups for two of the enolisable H of phthalaz-1 : 4-diones removes the luminescence, and that such substitution of one of them greatly diminishes, if it does not entirely remove, that property. F. R. S.

**Chemiluminescence with two organic reactions.** G. Vészi (Tech. Kurir, 1937, 8, No. 2, 1—3). —A lecture. On oxidation of 10 : 10′-dimethyl-5 : 5′-diacridinium dinitrate and of 3-aminophthalhydrazide with $H_2O_2$ intense chemiluminescence is observed. E. P.

**Reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. XVII. Conversion of nitro-3-aryl- and nitro-3-aryl-4-methyl-phthalaz-1-ones into corresponding phthalaz-4-ones by migration of the nitroaryl group, and related reactions.** F. M. Rowe, D. A. W. Adams, A. T. Peters, and (in part) E. A. Gillam (J.C.S., 1937, 90—109).—The action of HCl aq. on *o*-$C_6H_4<^{C(OH)=N}_{CH_2(CH_2\cdot CO_2H)\cdot NR}$ (I) (R = $NO_2\cdot C_6H_4$ or $NH_2\cdot C_6H_4$) and the conversion of (II) (R = nitroaryl; R′ = H or Me) into the corresponding

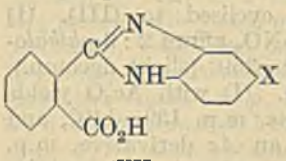


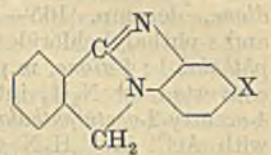

compounds $C_6H_4<^{CO-NR}_{CR':N}$ (IV) have been fully investigated and a property peculiar to 2′-$NO_2$-compounds has now been observed. Thus, 2′-amino-3-arylphthalaz-4-ones, and the corresponding 1-Me compounds, convertible into 2′ : 4-anhydro-derivatives (V) (R′ = H or Me; X = H, Me, or Cl) by aq. HCl at 180°, are obtained satisfactorily only from the corresponding compounds *o*-$CO_2H\cdot C_6H_4\cdot CR':N\cdot NHR$ (III), as reduction of (IV) (R = 2′-nitroaryl; R′ = H or Me) with $Na_2S$ (EtOH–$H_2O$) probably gives mainly hydroxylamine derivatives. Compounds (II) (R = nitroaryl; R′ = H or Me) are usually best converted into the corresponding (IV) by heating with *N*-HCl at 170—190°. The reaction is approx. unimol., whilst the rate is influenced markedly by the concn. of the acid used, the nature and position of substituents in R, and, in certain cases, by the temp. A mechanism, involving migration of R, but intramol. and not involving free

ions, is suggested. The following are described: 2′-nitro-3-phenylphthalaz-4-one, reduced ($Na_2S$) to a *substance*, m.p. 248°; 2′ : 4-*anhydro*-2′-*amino*-3-*phenylphthalaz*-4-*one*, m.p. 178°; (III) (R = 2′-*nitro*-4′-*methylphenyl*), m.p. 228°, and (IV), m.p. 195°, reduced to a *substance*, m.p. 216° (*Ac* derivative, m.p. 190°); (III) (R = 4′-*chloro*-2′-*nitrophenyl*), m.p. 237°, and (IV), m.p. 213—214°, reduced to 4′-*chloro*-2′-*amino*-3-*phenylphthalaz*-4-*one*, m.p. 236° (*Ac* derivative, m.p. 289°), or by $Na_2S$ to a *substance*, m.p. 239°; 2′ : 4-*anhydro*-4′-*chloro*-2′-*amino*-3-*phenylphthalaz*-4-*one*, m.p. 230°; (III) and (IV) (R = 2′-$NO_2$·$C_6H_4$), reduced to 2′-*amino*-3-*phenyl*-1-*methylphthalaz*-4-*one*, m.p. 241°, or with $Na_2S$ to a *substance*, m.p. 239°; 2 : 4-*anhydro*-2′-*amino*-3-*phenyl*-1-*methylphthalaz*-4-*one*, m.p. 163°; (III) (R = 2′-*nitro*-4′-*methylphenyl*), m.p. 175°, and (IV), m.p. 258°, reduced to 2′-*amino*-3-*phenyl*-1 : 4′-*dimethylphthalaz*-4-*one*, m.p. 203° (*Ac* derivative, m.p. 263°), or with $Na_2S$ to a *substance*, m.p. 264—265°; 2′ : 4-*anhydro*-2′-*amino*-3-*phenyl*-1 : 4′-*dimethylphthalaz*-4-*one*, m.p. 186°; (III) (R = 4′-*chloro*-2′-*nitrophenyl*), m.p. 185—186°, and (IV), m.p. 261°, reduced to 4′-*chloro*-2′-*amino*-3-*phenyl*-1-*methylphthalaz*-4-*one*, m.p. 222—223° (*Ac* derivative, m.p. 304°), or with $Na_2S$ to a *substance*, m.p. 212°; 2′ : 4-*anhydro*-4′-*chloro*-2′-*amino*-3-*phenyl*-1-*methylphthalaz*-4-*one*, m.p. 193°.

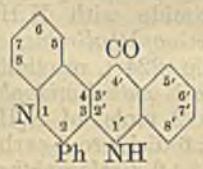
Compounds (II) (R = 2′-nitroaryl; R′ = Me) are converted by 0·8*N*-HCl into 2-(2′-nitroarylamino)-3-methylene*iso*indolinones, $o$-$C_6H_4$<CO / C(CH$_2$)>N·NHR (VI), which are hydrolysed to (III) (R′ = Me), oxidised to phthalyl-2′-nitroarylhydrazides, reduced by $Na_2S$ to (IV) (R = 2′-aminoaryl; R′ = Me), or by Fe and AcOH to (VI) (R = 2′-aminoaryl), and converted by mineral acids at 180° into (IV) (R = 2′-nitroaryl; R′ = Me). Compounds (II) (R = halogeno-4′-nitrophenyl; R′ = Me) are the only other examples capable of conversion into the corresponding (VI). The rearrangement of (II) to (VI) is also intramol., but probably different in mechanism from that involved in the conversion of (II) into (IV). The following are described: 2-(2′-*nitro*-, m.p. 179°, and 2-(2′-*amino*-*anilino*)-, m.p. 220°, and 2-(2′-*nitro*-4′-*methylphenylamino*)-3-*methylene*isoindolinone, m.p. 194°; o-*carboxybenzo*-2′-*nitro*-4′-*methylphenylhydrazide*, m.p. 260—261°; N-2′-*nitro*-4′-*methylaminophthalimide*, m.p. 263°; 2-(4′-*chloro*-2′-*nitro*-, m.p. 224°, and -2′-*amino*-*anilino*)-3-*methylene*isoindolinone, m.p. 228° (decomp.), the $NO_2$-compound oxidised to N-4′-*chloro*-2′-*nitroanilinophthalimide*, m.p. 265°, prepared from o-*carboxybenzo*-4′-*chloro*-2′-*nitrophenylhydrazide*, m.p. 263—264°; 2-(2′-*chloro*-, m.p. 164°, 2-(2′-*bromo*-, m.p. 201°, and 2-(2′ : 6′-*dichloro*-4′-*nitroanilino*)-3-*methylene*isoindolinone, m.p. 173°.

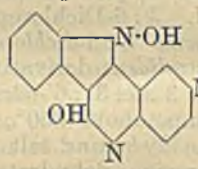
Compounds (II) (R = 4′- or 3′-$NH_2$·$C_6H_4$; R′ = H or Me) are recovered unaltered after heating with aq. HCl at 180°, but compounds (II) (R = 2′-aminoaryl; R′ = Me) or (VI) (R = 2′-$NH_2$·$C_6H_4$) are converted into (V) (R′ = Me) whilst with compounds (II) R = 2′-aminoaryl; R′ = H), $N_{(2)}$ is eliminated as $NH_3$, and (VII) and (VIII) are formed. The product of heating (I) (R = 4′-$NO_2$·$C_6H_4$) with aq. HCl is shown to be a mixture of (IV) (R = 4′-$NO_2$·$C_6H_4$; R′ = H) and (IV) (R = 4′-$NO_2$·$C_6H_4$; R′ = Me). Compound (I) (R = 2′-$NO_2$·$C_6H_4$) gives an analogous mixture, but the product from (I) (R = 3′-$NO_2$·$C_6H_4$) is only (II) (R = 3′-$NO_2$·$C_6H_4$; R′ = H). Compound (I) (R = 4′-$NH_2$·$C_6H_4$) is merely converted into (II) (R = 4′-$NH_2$·$C_6H_4$; R′ = H) by heating with aq. HCl, whereas (I) (R = 2′-$NH_2$·$C_6H_4$) is converted into $NH_3$, (VII) (X = H), and (V) (R′ = Me; X = H). The absorption spectra of some typical examples of compounds (II), (IV), and (VI) have been determined. F. R. S.


(VII.)


(VIII.)

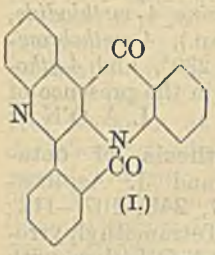
**Benzoyl derivatives of indigotin. IV.** H. DE DIESBACH and E. MOSER (Helv. Chim. Acta, 1937, **20**, 132—141; cf. A., 1934, 306).—In connexion with the constitution of Ciba-yellow (I) the following syntheses are recorded. Isatin, ω-anilinoacetophenone, and KOH in boiling EtOH–$H_2O$ afford 3-*anilino*-2-*phenylquinoline*-4-*carboxylic acid*, m.p. 250° (*Me* ester, m.p. 142°), which passes when heated above its m.p. into 3-*anilino*-2-*phenylquinoline*, m.p. 137°, and is converted by 70% $H_2SO_4$ at 100° into 4′-*keto*-2-*phenyl*-1′ : 4′-*dihydroquinolino*-2′ : 3′-3 : 4-*quinoline* (II), m.p. 266°, which could not be transformed into a Bz, Ac, or Me derivative. $CH_2Br$·COBr, *m*-xylene,


(II.)


(V.)

and $AlCl_3$ in $CS_2$ give ω-*bromo*-2 : 4-*dimethylacetophenone*, m.p. 41°, whence ω-*anilino*-2 : 4-*dimethylacetophenone*, m.p. 86°, transformed by isatin into 3-*anilino*-2-2′ : 4′-*dimethylphenylquinoline*-4-*carboxylic acid*, m.p. 245° (*Me* ester, m.p. 162°), converted into 3-*anilino*-2-2′ : 4′-*dimethylphenylquinoline*, m.p. 115°, and 4′-*keto*-2-2″ : 4″-*dimethylphenyl*-1′ : 4′-*dihydroquinolino*-2′ : 3′ : 3 : 4-*quinoline* (III), m.p. 250°. 3-p-*Toluidino*-2-*phenylquinoline*-4-*carboxylic acid*, m.p. 249° (*Me* ester, m.p. 163°), is converted into 3-p-*toluidino*-2-*phenylquinoline*, m.p. 132°, and 4′-*keto*-2-*phenyl*-6′-*methyl*-1′ : 4′-*dihydroquinolino*-2′ : 3′-3 : 4-*quinoline*, (IV), m.p. 256°. 3-o-*Toluidino*-2-*phenylquinoline*-4-*carboxylic acid*, m.p. 252° (*Me* ester, m.p. 138°), gives 3-o-*toluidino*-2-*phenylquinoline*, m.p. 93—95°, and 4′-*keto*-2-*phenyl*-8′-*methyl*-1′ : 4′-*dihydroquinolino*-2′ : 3′-3 : 4-*quinoline*, m.p. 317—320°. Decomp. of (II) by molten NaOH requires rather more drastic conditions than were used for (I) (*loc. cit.*) but yields 2-hydroxy-3 : 4-*N*-hydroxyindoloquinoline without, however, 3 : 4-indoloquinoline, whilst BzOH is destroyed at the high temp. of the reaction. Identical products are derived from (III). The main product of the alkaline degradation of (IV) is 2-*hydroxy*-6-*methyl*-3 : 4-N-*hydroxyindoloquinoline* (V), which sublimes at about 450°. It is converted by $PCl_5$ in boiling $PhNO_2$ into 2-*chloro*-6-*methyl*-3 : 4-N-*chloroindoloquin*-

*oline*, m.p. 223°, whence 2-*chloro*-6-*methyl*-3 : 4-N-*anilinoindoloquinoline*, m.p. 214° (*hydrochloride*), and 2-*anilino*-6-*methyl*-3 : 4-N-*anilinoindoloquinoline*, m.p. 256°. (V) is oxidised by $KMnO_4$ in presence of $Mn(OAc)_2$ into 2-amino-5-methylbenzoic acid and (?) 2-*N*-oxalylamino-5-methylbenzoic acid. 1 : 4-*Diketo*-2-*phenyltetrahydroisoquinoline*, m.p. 149°, and 1 : 3-*diketo*-2-*anilinohydrindene*, m.p. 215°, and the corresponding *acid*, $C_{15}H_{13}O_5N$, m.p. 137°, do not condense with isatin. The similarity of the reactions of (I), (II), (III), and (IV) supports the annexed structure for (I). H. W.



(I.)

**Aromatic nitro-derivatives. IX. 1-Bromo-3 : 4-dinitrobenzene.** A. Mangini (Gazzetta, 1936, **66**, 675—684; cf. A., 1936, 1244).—In 1 : 3 : 4-$C_6H_3Br(NO_2)_2$ (I) the 3-$NO_2$ is reactive. With NaOEt or KOH–EtOH, (I) forms 5-*bromo*-2-*nitrophenetole*, m.p. 79·5—80·5°, reduced with difficulty (Sn–HCl) to the *hydrochloride*, m.p. 199—200° (decomp.) of 5-*bromo*-2-*aminophenetole* [*picrate*, m.p. 172—173° (decomp.)]; the hydrochloride with NaOAc–$Ac_2O$ gives 5-*bromo*-2-*acetamidophenetole*, m.p. 118—119°. With piperidine followed by HCl, (I) gives 5-*bromo*-2-*nitrophenylpiperidine hydrochloride*, m.p. 152—153·5° [to a cloudy melt, clearing at 156—157° (decomp.)]; 2 : 5 : 1-$C_6H_3Br_2{\cdot}NO_2$ yields 4-*bromo*-2-*nitrophenylpiperidine hydrochloride*, m.p. 143—144° [to a cloudy melt, clearing at 153—154° (decomp.)]. With $NH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$, (I) gives, even in presence of $MgCO_3$, *bis*-(5-*bromo*-2-*nitrophenyl*) *disulphide*, m.p. 184—185°, also obtained using $CS(NH_2)_2$ or OEt·CS·SK. 5-Bromo-2-nitrophenylhydrazine hydrochloride and $NH_4SCN$ are needed to form the expected 5-*bromo*-2-*nitrophenylthiosemicarbazide*, m.p. 207—208°. The above hydrazine in boiling KOH–EtOH, or heated above its m.p., yields 5-*bromo*-1-*hydroxybenztriazole*, m.p. 201·5—202·5° (exploding); the isomeric 6-*bromo*-1-*hydroxybenztriazole*, m.p. 188—190°, is obtained from $N_2H_4.H_2O$ and 2 : 5 : 1-$C_6H_3Br_2{\cdot}NO_2$. The last with $NHPh{\cdot}NH{\cdot}CS{\cdot}NH_2$ gives bis-(4-bromo-2-nitrophenyl) sulphide. E. W. W.

**Catalytic reductions in the γ-triazine group. I. Conversion of dihydroxymethyltriazine into the "trigenic acid" of Liebig and Wöhler.** A. Ostrogovich and G. Ostrogovich (Atti V Congr. Naz. Chim., 1936, **1**, 427—431).—Dihydromethyltriazine is hydrogenated (Pt) to 2 : 4-*diketo*-6-*methyltriazidine*, m.p. 272—273° (decomp.) (*acetate*; *hemihydrochloride*; *hemiaurichloride*; *hemipicrate*; basic $Hg_2$ salt; $Ac_2$ derivative, m.p. 171—172°), identical with "trigenic acid." The reduction is also effected by Al–Hg and, less satisfactorily, by Na–Hg or Sn–HCl. E. W. W.

**γ-Triazines. XXXIII. New compounds obtained from dihydroxytriazinylformaldoxime. XXXIV. Dihydroxytriazinyl phenyl ketoxime and its salts. XXXV. Beckmann transformation of dihydroxytriazinyl phenyl ketoxime.** A. Ostrogovich and I. Tanislau (Gazzetta, 1936, **66**, 653—662, 662—671, 672—684).—XXXIII. Dihydroxytriazinylformaldoxime (I) (cf. A., 1935, 225) with $Ac_2O$ gives only an *acetate*; in presence of $C_5H_5N$ the product is the $(C_5H_5N)_2$ salt, converted over $H_2SO_4$ into the $C_5H_5N$ salt, m.p. 177—178° (decomp.), of the *Ac* derivative, m.p. 203—204° (decomp.). The $(C_5H_5N)_2$ and $C_5H_5N$ salts of the *Bz* derivative, m.p. 187—188° (decomp.), are similarly prepared. When the above are heated in $C_5H_5N$, they give the $(C_5H_5N)_2$ salt, which can be converted into the $C_5H_5N$ salt of *dihydroxytriazinylformonitrile* (*Na*, *K*, *Ag*, and *Ba* salt). (I) heated in dil. AcOH with $NHPh{\cdot}NH_2$ forms the *acetate*, decomp. 115—120°, of *dihydroxytriazinylformaldehyde phenylhydrazone* (*dihydrochloride*; *sulphate*); the corresponding *phenylmethylhydrazone* (*monohydrochloride*; *sulphate*) is also prepared. (I) is reduced ($SnCl_2$–HCl) to the *hydrochloride* of *dihydroxytriazinylmethylamine* (*stannichloride*; *sulphate*; *picrate*; *Ac* derivative), which does not give a Schiff's base. In dil. HCl with $CO_2$–$H_2S$ (I) yields *dihydroxytriazinylthioformamide* (+$H_2O$, lost at 110—115°) ($NH_4$ salt, also obtained from the nitrile and $NH_4SH$). The *Na* salt of the last, or of the nitrile, with $NH_2OH$ gives the *Na* salt, m.p. >310°, of *dihydroxytriazinylformamidoxime* (*Ag* salt). The last, or the thioamide, with $NHPh{\cdot}NH_2$ in EtOH, yields *dihydroxytriazinylformphenylhydrazidine*, $(C_3H_2O_2N_3){\cdot}C(NH_2){:}N{\cdot}NHPh$. With Br–$H_2O$, (I) gives *dihydroxytriazinylbromoformaldoxime*, $(C_3H_2O_2N_3){\cdot}CBr{:}N{\cdot}OH$ (+$2H_2O$).

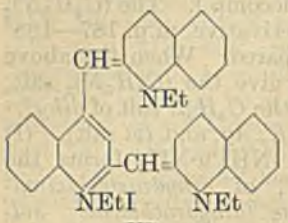
XXXIV. Dihydroxybenzyltriazine (A., 1935, 225) with $C_5H_{11}O{\cdot}NO$ in AcOH–HCl yields *dihydroxytriazinyl Ph ketoxime* [+$3H_2O$, m.p. 235—236°; +$2H_2O$, m.p. 241—242°; +$H_2O$, m.p. 255—256° (all decomp.)] [*monohydrochloride*, m.p. 226—227° (decomp.); no sulphate]. This gives *Na* (+$3H_2O$), m.p. 269—271° (decomp.); *Na* (+$H_2O$); $Na_2$ (+1·5EtOH), m.p. 264—265° (decomp.); $Na_2$; *Ag* (+$H_2O$), m.p. 300—302° (decomp.); *Ag*; *Ba* (+$3H_2O$), m.p. 252—253° (decomp.); *Ba*; $Fe^{II}$ (+$4H_2O$), greenish-grey, m.p. 228—230° (decomp.); $Fe^{II}$, yellow (formed from the last at 150°); *Cu* (+$2H_2O$); and *Cu*, m.p. 321—322° (decomp.), salts. The co-ordinated structure of the $Fe^{II}$ and Cu salts is discussed.

XXXV. Since dihydroxytriazinyl Ph ketoxime is converted by $PCl_5$–AcCl into *N-benzoylammelide* (*benzamidodihydroxytriazine*), m.p. 263—264° (hydrolysed by $NH_3$–EtOH at 110° to ammelide and $NH_2Bz$), it is presumed to have the *anti* structure (OH *anti* to triazine ring). E. W. W.

**Cyanine dye series. VII. Dyes containing three heterocyclic nuclei.** L. G. S. Brooker and L. A. Smith (J. Amer. Chem. Soc., 1937, **59**, 67—74).—2-*Iodo*-4-*methylquinoline ethiodide* (I), m.p. 218—219° (decomp.) (obtained by prolonged action of EtI on 2-chloro-4-methylquinoline in the dark), and 2-methylquinoline ethiodide (II) in EtOH–$NEt_3$ give (after treatment with $KClO_4$) 4-*methyl*-1 : 1′-*diethyl*-2 : 2′-*cyanine perchlorate*, m.p. 279—280° (decomp.); the corresponding iodide is also obtained together with 2′-methyl-1 : 1′-diethyl-2 : 4′-cyanine iodide (III) [modified prep. from (II) and EtOH–KOH] from equimol. quantities of 2-iodo- (IV) and 2 : 4-*dimethyl*- (V), m.p. 231—233°, -*quinoline ethiodide* in EtOH–

$NEt_3$. (IV) (4 mols.) and (V) (1 mol.) similarly afford 2% of 2 : 4-*di*-(1-*ethyl*-1 : 2-*dihydro*-2-*quinolylidenemethyl*)*quinoline ethiodide* (VI), m.p. 291—292° (decomp.), also obtained in 4·5% yield from (III) and (IV) (excess) and in 6·5% yield from (II) (excess) and 2 : 4-*di*-*iodoquinoline ethiodide* (VII), m.p. 235—236° (decomp.) [from 2 : 4-dichloroquinoline (modified prep.) and EtI at 100°/3 weeks]. The absorption curve of (VI) shows max. at 4550 (weak), 4800, and 6150 A.; between the two principal bands there is a region of almost complete transmission with min. absorption at about 5150 A. The unusual absorption of (VI) is ascribed to the presence in the mol. of linkings characteristic of three distinct cyanine types. 2 : 4-*Di*-(1-*methyl*- (VIII), m.p. >310° (decomp.) (shrinks from about 300°), and 2 : 4-*di*-(1-*ethyl*- (IX), m.p. 302—303° (decomp.), -1 : 2-*dihydro*-2-*quinolylidenemethyl*)*quinoline methiodides* are similarly prepared from 2 : 4-*di*-*iodoquinoline methiodide*, m.p. 236—237° (decomp.) (with 2-methylquinoline methiodide), and 2 : 4-*dimethylquinoline methiodide*, m.p. 271—272° [with (IV)], respectively. (VIII) has a stronger sensitising action than either (VI) or (IX). 1-Methylbenzthiazole etho-*p*-toluenesulphonate (X) (4 mols.) and (VII) (1 mol.) in EtOH–$NEt_3$ give a little 2 : 4-*di*-(2-*ethyl*-1 : 2-*dihydro*-1-*benzthiazolylidenemethyl*)*quinoline ethiodide*, m.p. 274—276° (decomp.), which is a better sensitiser than (VI). 2 : 4-*Di*-(2-*methyl*-1 : 2-*dihydro*-1-*benzthiazolylidenemethyl*)*quinoline methiodide*, m.p. 301—302° (decomp.), is similarly prepared. A dye containing three quinoline nuclei could not be obtained from 4-methylquinoline ethiodide and (VII); 4-*iodo*-1 : 1′-*diethyl*-2 : 4′-*cyanine iodide*, m.p. >300°, is probably formed. (I) and (X) afford 4′-*methyl*-2 : 1′-*diethylthia*-2′-*cyanine iodide*, m.p. 276—277·5° (decomp.), whilst (I) and 1-methyl-β-naphthiazole etho-*p*-toluenesulphonate give 4′-*methyl*-2 : 1′-*diethyl*-3 : 4-*benzothia*-2′-*cyanine iodide*, m.p. 272—274° (decomp.). 2′-*Iodo*-4-*methyl*-1 : 1′-*diethyl*-2 : 4′-*cyanine iodide*, m.p. 231—232° (decomp.), is obtained from (I) and EtOH–$NEt_3$.

H. B.



(VI).

**5-Anilinotetrazole.** R. Stollé and K. Heintz (J. pr. Chem., 1937, [ii], **147**, 286).—The main product of the action of $NaN_3$ on $NH_2$·CO·NHPh and white-lead in EtOH is 5-amino-1-phenyltetrazole (A., 1922, i, 689); 5-anilinotetrazole, m.p. 206°, is produced in minor amount. H. W.

**Optical sensitisers. II.** C. Gastaldi and E. Principalle (Annali Chim. Appl., 1936, **26**, 450—455).—A series of sensitisers, 3 : 3′-*diketo*-1 : 1′ : 4 : 4′ : 5 : 5′-*hexamethyl*-2 : 2′-*monostreptovinylenepyrazinecyanine* 1-*iodide*, m.p. 280°, 1-*chloride*, m.p. 277°, 1-*bromide*, m.p. 275°, and the corresponding -1 : 1′ : 5 : 5′-*tetramethyl*- 1-*iodide*, m.p. 262°, 1-*chloride*, m.p. 292°, and 1-*bromide*, m.p. 280°, and 5 : 5′-*dimethyl*-1 : 1′-*diethylpyrazinecyanine* 1-*iodide*, m.p. 272°, and 1-*bromide*, m.p. 265°, has been prepared by condensing 6-keto-1 : 2 : 5-trimethyl-1 : 6-dihydropyrazine 4-methiodide (A., 1928, 1027), 4-methochloride, and 4-*methobromide*, m.p. 258°, 6-*keto*-2 : 5-*dimethyl*-1 : 6-*dihydropyrazine* 4-*methiodide*, m.p. 248°, 4-*methochloride* (decomp.), 4-*methobromide*, m.p. 257°, 4-*ethiodide*, m.p. 230°, and 4-*ethobromide*, m.p. 250°, with $CH(OEt)_3$ in the presence of $Ac_2O$. L. A. O'N.

**Bile pigments. XVI. Synthesis of octamethylbilirubin.** H. Fischer and J. Aschenbrenner (Z. physiol. Chem., 1937, **245**, 107—112; cf. A., 1936, 346).—3 : 3′ : 4 : 4′-Tetramethylpyrromethene-5 : 5′-dicarboxylic acid in AcOH gives with Br in AcOH a mixture (I) of 5 : 5′-*dibromo*-3 : 3′ : 4 : 4′-*tetramethylpyrromethene hydrobromide* (II) and 5-*bromo*-3 : 3′ : 4 : 4′-*tetramethylpyrromethene*-5′-*carboxylic acid*, which is converted into (II) by further treatment with Br in AcOH. (I) with KOH in MeOH gives 5-*methoxy*-3 : 3′ : 4 : 4′-*tetramethylpyrromethene*-5′-*carboxylic acid* (III), m.p. 216° [*Me* ester, m.p. 152—153°; *K* salt, m.p. 292° (decomp.)], and 5′-*bromo*-5-*methoxy*-3 : 3′ : 4 : 4′-*tetramethylpyrromethene*, m.p. 144°. (III) with KOH in PrOH at 190—200° for 2 hr. gives 5-*hydroxy*-3 : 3′ : 4 : 4′-*tetramethylpyrromethene*, m.p. 290°, which, with $CH_2O$ and conc. HCl gives *octamethylbilirubin* [corresponding cryst. *ferrobilin*, m.p. 282° (decomp.)]. Similarly (III) gives *dimethoxyoctamethylbilirubin*, m.p. 245° (decomp.). (I) in MeOH with excess of $NH_2Ph$ gives 5-*anilino*-3 : 3′ : 4 : 4′-*tetramethylpyrromethene*-5′-*carboxylic acid*, m.p. 246° (*Me* ester, m.p. 199°), and similarly (II) gives 5 : 5′-*dianilino*-3 : 3′ : 4 : 4′-*tetramethylpyrromethene*, m.p. 245° (*hydrobromide*, m.p. 285°). W. McC.

**Reversible oxidation and reduction of chlorophyll.** E. Rabinowitch and J. Weiss (Nature, 1936, **138**, 1098—1099).—Et chlorophyllide in MeOH solution is reversibly oxidised by $FeCl_3$ with a change in colour to greenish-yellow and a diminution in fluorescence. Prompt addition of $FeCl_2$ restores the original colour and fluorescence. The first product of oxidation is unstable, and reacts further either with the $FeCl_3$ or possibly with dissolved $O_2$. Oxidation is favoured by illumination with red light.

L. S. T.

**Chlorophyll. LXXI. Quantitative dehydrogenation of chlorin copper salts with oxygen.** H. Fischer and K. Herrle (Annalen, 1937, **527**, 138—140).—The absorption of O by chlorin–Cu complex salts in AcOH containing $Cu(OAc)_2$ at 40° occurs with quant. formation of porphyrin Cu salts only in the cases of mesopyrro- and mesorhodo-chlorin. Other chlorins are dehydrogenated with difficulty on account of their constitution or are in part completely decomposed particularly if CH:CH is present.

H. W.

**Porphyrins. XL. Synthesis of 1 : 3 : 5 : 7-tetramethylporphin-2 : 4 : 6 : 8-tetrasuccinic acid.** H. Fischer and H. Zischler (Z. physiol. Chem., 1937, **245**, 123—138; cf. A., 1935, 363; this vol., 36).—5-Carboxy-2 : 4-dimethylpyrryl-3-succinic acid (I) in AcOH gives with 3 mols. of Br in AcOH 5-*bromo*-5′-*bromomethyl*-4 : 3′-*dimethylpyrromethene*-3 : 4′-*disuccinic acid hydrobromide*, m.p. >280°. When 2 mols. of Br are used material is obtained which, when fused with methylsuccinic acid and esterified with

HCl in MeOH, gives the $Me_8$ ester (II), m.p. 255° (*Cu* salt, m.p. 260°, *Fe* salt), of 1 : 3 : 5 : 7-tetramethylporphin-2 : 4 : 6 : 8-tetrasuccinic acid. (II) is spectroscopically but not otherwise identical with the $Me_8$ ester of natural uroporphyrin. (II) heated with dil. HCl for 3 hr. at 180° gives coproporphyrin I. (I) decarboxylated in dil. HCl at 40° gives 2 : 4-*dimethylpyrryl*-3-*succinic acid* (III), m.p. 180° (decomp.). The $Et_2$ (IV) and $Me_2$ esters of 5-carbethoxy-2 : 4-dimethylpyrryl-3-succinic acid ($Na_2$ salt) have m.p. 79° and 103°, respectively. (I) with $CH_2N_2$ gives the $Me_2$ ester, m.p. 121—122°, of 5-carbomethoxy-2 : 4-dimethylpyrryl-3-succinic acid. (IV) with Br in AcOH gives the $Et_2$ ester (V), m.p. 103°, of 5-carbethoxy-4-methyl-2-bromomethylpyrryl-3-succinic acid and with $SO_2Cl_2$ the $Et_2$ ester (VI), m.p. 105°, of the corresponding 2-$CH_2Cl$ derivative. (V) and (VI) give with MeOH the corresponding 2-$OH{\cdot}CH_2$ derivative, m.p. 57—58°. (IV) with $N_2H_4 + H_2O$ gives 5-*carbethoxy*-2 : 4-*dimethylpyrryl*-3-*succinic acid dihydrazide*, m.p. 200° [*hydrochloride* (VII), m.p. 213°]. (VII) with dil. HCl + $NaNO_2$ gives the corresponding *diazide*, which, when boiled with EtOH, yields the corresponding *diethylurethane*, m.p. 180—220° (decomp.). Pyrrole-2-aldehyde (VIII) in presence of HBr with the $Na_3$ salt of 5-carboxy-2 : 4-dimethylpyrryl-3-β-methylmalonic acid gives the *hydrobromide*, m.p. 180—205° (decomp.), of 3′ : 5′-dimethylpyrromethene-4′-β-methylmalonic acid [$Et_2$ ester (IX), m.p. 161°]. (IX) with Br in AcOH gives the corresponding 3 : 4 : 5-$Br_3$-compound, which when fused with succinic acid yields $Me_2$ 1 : 5-dimethylporphin-2 : 6-dipropionate. (III) with (VIII) in presence of HBr gives the *hydrobromide*, decomp. 180° ($Me_2$ ester, m.p. 150°), of 3′ : 5′-dimethylpyrromethene-4′-succinic acid. W. McC.

**Spectra of adsorbed porphyrin.**—See A., I, 61.

**Spectra of helicorubin and oxyhelicorubin.**—See A., III, 83.

**Pyrrole-blacks.** P. Pratesi (Atti V Congr. Naz. Chim., 1936, **1**, 463—466).—A review. Pyrrole-blacks contain linked pyrrole nuclei oxidised in the 2-position. E. W. W.

**Derivatives of quinoline. I. Nupercaine analogues. I.** M. E. Smith and C. B. Pollard (J. Amer. Chem. Soc., 1937, **59**, 131—132).—N-*Phenyl*-N′-2-*chlorocinchonylpiperazine* (I), m.p. 189·2—190·2°, and N-2-*chlorocinchonylmorpholine* (II), m.p. 173·6—174·4°, are prepared from 2-chlorocinchonyl chloride (in $C_6H_6$) and the appropriate base (in aq. $Na_2CO_3$). (I) and AlkOH–NaOAlk in $C_6H_6$ give N-*phenyl*-N′-2-*methoxy*-, m.p. 149·5—150·2°, -*ethoxy*-, m.p. 154—154·5°, -n-*propoxy*-, m.p. 102·8—103·3°, -iso*propoxy*-, m.p. 116·2—117·2°, -n-*butoxy*-, m.p. 77·2—78·2°, -*allyloxy*-, m.p. 129·5—130·5°, and -β-*methoxyethoxy*-, m.p. 91·6—92·3°, -*cinchonylpiperazines*; (II) similarly affords N-2-*methoxy*-, m.p. 134—134·9°, and -*ethoxy*- (III), m.p. 69—69·8°, -*cinchonylmorpholines*. NN′-*Di*-2-*chlorocinchonyl*-, m.p. >300°, and N-*phenyl*-N′-(2-β-N-*phenylpiperazinoethoxycinchonyl*)-, m.p. 134·7—135·2°, -*piperazines* are described. All m.p. are corr. (III) has pronounced anæsthetic activity. H. B.

**Condensation products of *s*-diphenylcarbazide and sugars.** A. Sanna (Atti V Congr. Naz. Chim., 1936, **1**, 528—530).—Either arabinose or xylose with *s*-diphenylcarbazide in boiling AcOH–NaOAc ($H_2$) yields 3-*hydroxy*-1-*phenyl*-5-α-*furyl*-1 : 2 : 4-*triazole*, m.p. 160° (decomp.) (cf. A., 1915, i, 596). E. W. W.

**Formation and reactions of substituted thiazolidones. IV.** F. A. Eberly and F. B. Dains (J. Amer. Chem. Soc., 1936, **58**, 2544—2547; cf. A., 1936, 347).—Allylthiocarbamide and $CH_2Cl{\cdot}CO_2H$ in $H_2O$ or EtOH give 2-imino-3-allyl-4-thiazolidone (*hydrochloride*, m.p. 176°), readily hydrolysed to 2 : 4-diketo-3-allyltetrahydrothiazole [5-*benzylidene* derivative (I), m.p. 88°]. Diallylthiocarbamide and $CH_2Cl{\cdot}COCl$ (II) in $COMe_2$–$C_5H_5N$ afford 2-allylimino-3-allyl-4-thiazolidone, an oil at −10°, the 5-*benzylidene* derivative, m.p. 53°, of which is hydrolysed (50% $H_2SO_4$) to (I) and allylamine. *N*-Phenyl-*N*′-allylthiocarbamide and (II) similarly give 2-*allylimino*-3-*phenyl*-4-*thiazolidone*, m.p. 151° [5-*benzylidene* derivative, m.p. 141°, hydrolysed (50% $H_2SO_4$ at 140°) to 2 : 4-diketo-3-phenyl-5-benzylidenetetrahydrothiazole (III), m.p. 208°]. The Na salt of 2-anilo-4-thiazolidone (?) with EtOH–allyl iodide yields 95% of 2-N-*allylanilino*-, m.p. 92° (5-*benzylidene* derivative, m.p. 165°), and 5% of 2-anilo-3-allyl-4-thiazolidone [5-*benzylidene* derivative, m.p. 106·5°, hydrolysed to (I) and $NH_2Ph$]. *N*-Benzoyl-*N*′-p-bromophenylthiocarbamide and (II) afford 2-*benzoylimino*-3-p-*bromophenyl*-4-*thiazolidone*, m.p. 213° [5-*benzylidene* derivative, m.p. 253°, hydrolysed (60% $H_2SO_4$ at 160°) to 2 : 4-*diketo*-3-p-*bromophenyl*-5-*benzylidenetetrahydrothiazole*, m.p. 247°], which is hydrolysed by dil. alkali to N-*benzoyl*-N′-p-*bromophenylcarbamide*, m.p. 233—234° (decomp.), and by conc. HCl to 2 : 4-*diketo*-3-p-*bromophenyltetrahydrothiazole*, m.p. 163°. Contrary to Dixon and Kennedy (J.C.S., 1920, **117**, 74), NHPh·CS·NH·$CO_2$Et and (II) in $C_6H_6$–$C_5H_5N$ give 2-*carbethoxyimino*-3-*phenyl*-4-*thiazolidone*, m.p. 256° (slow decomp. >230°) [5-*benzylidene* derivative, m.p. 225°, hydrolysed to (III)], which is hydrolysed (acid; alkali causes disruption) to 2 : 4-diketo-3-phenyltetrahydrothiazole. Contrary to Wheeler and Johnson (A., 1902, i, 760), $CHClPh{\cdot}CO_2Et$ and $NH_2{\cdot}CS{\cdot}NHPh$ furnish 2-*anilo*-5-*phenyl*-4-*thiazolidone* (IV), m.p. 185°, hydrolysed (40% $H_2SO_4$ at 140°) to a 1 : 2 mixture of 2 : 4-*diketo*-5-*phenyl*-, m.p. 130°, and -3 : 5-*diphenyl*-, m.p. 173°, -*tetrahydrothiazole*, which result thus: (IV) → thiohydantoic acid, which then loses either $NH_3$ or $NH_2Ph$ with subsequent ring closure. Methylation of the Na salt of (IV) gives 2-N-*methylanilino*-5-*phenyl*-4-*thiazolidone*, m.p. 144°, also prepared from CHBrPh·$CO_2$Et and $NH_2{\cdot}CS{\cdot}NPhMe$. $CClPh_2{\cdot}CO{\cdot}NHPh$ and $NH_4CNS$ in $COMe_2$ give (unexpectedly) 4-*keto*-2-*thion*-3 : 5 : 5-*triphenyltetrahydroglyoxaline*, m.p. 254°, which affords a S-*Me ether*, m.p. 143°, and is converted by conc. $HNO_3$ into the 2 : 4-*diketo*-derivative, m.p. 203·5°, also prepared from benzilic acid and $NH_2{\cdot}CO{\cdot}NHPh$ at 180—190°. 2-*Anilo*-5 : 5-*diphenyl*-4-*thiazolidone*, m.p. 253° [obtained (cf. Wheeler and Johnson, *loc. cit.*) from $NH_2Ph$ and $CNS{\cdot}CPh_2{\cdot}CO_2Et$ (?)], is methylated (using Na salt) to 2-N-*methylanilino*-, m.p. 191°, and

2-*anilo*-3-*methyl*- (V), m.p. 134°, -5 : 5-*diphenyl*-4-*thiazolidone*. (V) is hydrolysed to 2 : 4-*diketo*-5 : 5-*diphenyl*-3-*methyltetrahydrothiazole*, m.p. 102°. $CClPh_2$·COCl and NHPh·CS·NHMe in $C_6H_6$–$C_5H_5N$ give 25% of (V) and 75% of 2-*methylimino*-3 : 5 : 5-*triphenyl*-4-*thiazolidone*, m.p. 119° (hydrolysed to $NH_2Me$ and 2 : 4-diketo-3 : 5 : 5-triphenyltetrahydrothiazole, m.p. 150°), the only case (so far noted) of the production of two isomerides in such a reaction. H. B.

**Action of formaldehyde on cysteine.** S. Ratner and H. T. Clarke (J. Amer. Chem. Soc., 1937, **59**, 200—206).—Cysteine (I) reacts with aq. $CH_2O$ over a wide range of $p_H$ (very rapidly if >5) to give (cf. Schubert, A., 1936, 824) *thiazolidine*-4-*carboxylic acid* (II), m.p. 196—197° (decomp.), $[\alpha]_D^{20}$ −141° in $H_2O$ [*hydrochloride*, m.p. 184—185° (decomp.); *Me* ester, b.p. 75°/1 mm. (*hydrochloride*, decomp. 164—165°)], which behaves as an ampholyte. (II) is not affected to any appreciable extent by *N*-HCl at 100° [some hydrolysis to (I) and $CH_2O$ is shown by distillation], but with $CH_2I$·$CO_2H$ and $CH_2PhCl$ in aq. $K_2CO_3$ at room temp. *S*-carboxymethyl- and *S*-benzyl-cysteine, respectively, are produced. (II) is oxidised (air in a solution of $p_H$ 10·2 containing a little $FeCl_3$; aq. $H_2O_2$; I–KI) to cystine, whilst Br in aq. AcOH gives cysteic acid. (II) is also converted into (I) by $Na_2SO_3$; reaction is rapid at $p_H$ 5. *Acetylthiazolidine*-4-*carboxylic acid*, m.p. 143·5—144·5°, $[\alpha]_D^{20}$ −133·5° in $H_2O$, is oxidised by $H_2O_2$ (not I) to the *sulphoxide*, m.p. 188—190° (decomp.), or *sulphone*, m.p. 190° (decomp.). *N*-β-Thiolethylphthalimide is hydrolysed (20% HCl) to SH·$CH_2$·$CH_2$·$NH_2$,HCl, which with aq. $CH_2O$ gives *thiazolidine*, b.p. 164—165° [*hydrochloride*, m.p. 180° (decomp.); *Ac* derivative, b.p. 83—85°/0·7 mm. (*sulphone*, m.p. 122°)]; this is oxidised by I–KI to $(NH_2$·$CH_2$·$CH_2$·$S)_2$ and by Br–aq. AcOH to taurine. H. B.

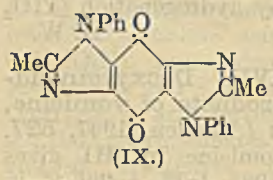
**Cyanine dye series. VIII. Dyes derived from 1-methylphenanthro-[9 : 10]-thiazole.** G. H. Keyes and L. G. S. Brooker (J. Amer. Chem. Soc., 1937, **59**, 74—79).—9-Acetamidophenanthrene, m.p. 213—215° (lit. 207—208°) (modified prep.), and $P_2S_5$ in PhMe with a little $C_5H_5N$ give 9-*thioacetamidophenanthrene*, m.p. 181—182° (decomp.), oxidised [$K_3Fe(CN)_6$, dil. NaOH] to 1-*methylphenanthro*-[9 : 10]-*thiazole*, m.p. 145—147° [*methiodide*, m.p. 206—208° (decomp.), and *ethiodide*, m.p. 202—204° (decomp.), prepared through the metho- (I) and etho- (II) -*p*-toluenesulphonate, respectively]. 2-Iodoquinoline ethiodide with (I) and (II) in EtOH–$NEt_3$ gives 2-*methyl*-1′-*ethyl*-, m.p. 244—246° (decomp.), and 2 : 1′-*diethyl*-, m.p. 248—250° (decomp.), -3 : 4 : 5 : 6-*dibenzothia*-2′-*cyanine iodide*, respectively, whilst (II) with quinoline ethiodide (III) (in EtOH–KOH) and $CH(OEt)_3$ (in $C_5H_5N$; followed by KBr) affords 2 : 1′-*diethyl*-3 : 4 : 5 : 6-*dibenzothia*-4′-*cyanine iodide*, m.p. 244—247° (decomp.), and 2 : 2′-*diethyl*-3 : 4 : 5 : 6 : 3′ : 4′ : 5′ : 6′-*tetrabenzothiacarbocyanine bromide*, m.p. 200—202° (decomp.), respectively. These new dyes are not powerful sensitisers; they show absorption nearer the red than the corresponding compounds derived from methylnaphththiazoles. 2 : 1′-*Diethyl*-3 : 4-, m.p. 248—250° (decomp.), and -5 : 6-, m.p. 285—288° (decomp.), -*benzothia*-4′-*cyanine iodides* are prepared from (III) and the requisite 1-methylnaphththiazole etho-*p*-toluenesulphonate in EtOH–KOH. Improved preps. of 2 : 1′-diethylthia-4′-cyanine and 2 : 2′-diethyl-3 : 4- and -5 : 6-benzothia-2′-cyanine iodides are given. Absorption curves of most of the above dyes are given. H. B.

**Hydrogenation of vitamin-$B_1$.**—See A., III, 103.

**Dicyclic compounds and their analogy with naphthalene. V. Benzthiodiazoles (phenylenediazosulphides).** K. Fries and H. Reitz (Annalen 1936, **527**, 38—60; cf. A., 1927, 779).—Benzthiodiazole (I) is definitely naphthoid in character. Addition of $KNO_3$ to its solution in conc. $H_2SO_4$ whereby the temp. ultimately attains 110° gives 4-*nitrobenzthiodiazole* (I), m.p. 95°, with small amounts of a *substance*, m.p. 104°; more drastic treatment causes rupture of the hetero-ring with formation of a very explosive diazonium compound which couples with *R* salt. (II) is reduced by $SnCl_2$ to 4-*aminobenzthiodiazole*, m.p. 136·5° (*Ac* derivative, m.p. 193°), which is converted in the usual manner into 4-*hydroxybenzthiodiazole*, m.p. 235° (*acetate*, m.p. 52°), transformed by Br in AcOH into 5 : 7-*dibromo*-4-*hydroxybenzthiodiazole*, m.p. 173° (decomp.) (*Na* salt; *acetate*, m.p. 157°), which is stable to light in $C_5H_5N$ or in NaOH containing $CuSO_4$. The compound therefore differs markedly from 2 : 4-$C_{10}H_5Br_2$·OH, the behaviour of which cannot therefore be attributed to peculiar modes of union in the nuclei. In attempted syntheses of (II), acet-*o*-nitroanilide (III) is converted by $P_2S_5$ at 100° into *thioacet*-*o*-*nitroanilide* (IV), m.p. 112°, which is oxidised by $K_3Fe(CN)_6$ in alkaline solution to the corresponding *disulphide*, m.p. 85°, reduced by $Na_2S$ in alkaline solution to the initial material. Reduction of (III) or (IV) by NaHS in alkaline solution gives 1-hydroxy-2-methylbenziminazole, m.p. 231°. (I) is unaffected by Br in hot AcOH but is transformed by the halogen in presence of Fe at 100° into the *perbromide* $(C_6H_4N_2S)_2$,2HBr,$Br_2$, m.p. 110° after softening at 80°. Reduction of 5-nitrobenzthiodiazole in EtOH by Sn and conc. HCl leads to 4-*chloro*-5-*aminobenzthiodiazole* (V), m.p. 169° (*Ac* derivative, m.p. 216°), whereas treatment with $SnCl_2$ and conc. HCl yields 5-aminobenzthiodiazole (VI), m.p. 95°, converted by Skraup's method into 5′ : 6′-4 : 5-*pyridinobenzthiodiazole*, m.p. 115°. 4-Aminobenzthiodiazole (VII) similarly gives 2′ : 3′-4 : 5-*pyridinobenzthiodiazole*, m.p. 141°, whereas (V) could not be caused to react, thus showing close analogy to the relationships in the $C_{10}H_8$ series. (VI) and (VII) couple directly in HCl to azo-dyes. The product from (VI) and diazotised *p*-$NH_2$·$C_6H_4$·$SO_3H$ is reduced by $Na_2S_2O_4$ to 4 : 5-*diaminobenzthiodiazole*, m.p. 158°, which with benzil in AcOH affords the *quinoxaline*, $C_{20}H_{12}N_4S$, m.p. 226° (decomp.). (VII) gives 4-*amino*-7-*benzeneazobenzthiodiazole*, m.p. >300°, whereas (V), like 1 : 2-$C_{10}H_6Cl$·$NH_2$, does not couple. 2 : 2′-Dinitro-4 : 4′ : 5 : 5′-tetramethoxydiphenyl 1 : 1′-disulphide is reduced by $Na_2S_2O_4$ in alkaline solution to 5 : 6-*dimethoxybenzthiodiazole*, m.p. 142°, converted by $H_2SO_4$ into 5 : 6-*dihydroxybenzthiodiazole*, m.p. 249° (decomp.) ($Ac_2$ derivative, m.p. 120°), which, like

the "ββ"-dihydroxynaphthalenes, could not be oxidised to an *o*-quinone by $HNO_3$ or by $PbO_2$ in $C_6H_6$ or AcOH. Acetamidoquinol $Me_2$ ether is converted by $P_2S_5$ and $K_2S$ in boiling PhMe into *thioacetamidoquinol Me₂ ether*, m.p. 101°, which is oxidised by $K_3Fe(CN)_6$ in alkaline solution to 4 : 7-*dimethoxy*-2-*methylbenzthiazole* (VIII), m.p. 101°, demethylated by $H_2SO_4$–$H_2O$ to 4 : 7-*dihydroxy*-2-*methylbenzthiazole*, m.p. 218° (*sulphate*, m.p. >300°). This is oxidised by $K_2Cr_2O_7$ and dil. $H_2SO_4$ to 4 : 7-*diketo*-2-*methyl*-4 : 7-*dihydrobenzthiazole*, m.p. 159° (decomp.). Treatment of (VIII) with KOH in abs. EtOH at 110° followed by diazotisation gives 4 : 7-*dimethoxybenzthiodiazole*, m.p. 120°, converted by conc. HCl at 100° into 7-*hydroxy*-4-*methoxybenzthiodiazole*, m.p. 101°, and by fuming HCl at 115° into 4 : 7-*dihydroxybenzthiodiazole*, m.p. 233° (*diacetate*, m.p. 114°), which is oxidised by $FeCl_3$ to *benzthiodiazole*-4 : 7-*quinone*, m.p. 132°. This, with $CaOCl_2$, possibly reacts initially in the same manner as α-naphthaquinone but the change is immediately followed by violent evolution of $N_2$. 5 : 6-*Dichloro*-4 : 7-*dihydroxybenzthiodiazole*, m.p. 205° (decomp.), is unchanged by $SnCl_2$–AcOH or $NH_2Ph$ but is oxidised by $FeCl_3$ in boiling AcOH to 5 : 6-*dichlorobenzthiodiazole*-4 : 7-*quinone*, m.p. 237° (decomp.). This resembles the corresponding dichloronaphthaquinone since it is transformed by $NH_2Ph$ in boiling EtOH into 6-*chloro*-5-*anilinobenzthiodiazole*-4 : 7-*quinone*, m.p. 216°, the *NO*-derivative, m.p. 228° (decomp.), of which is transformed by $NH_2Ph$ at 100° into 5 : 6-*dianilinobenzthiodiazole*, m.p. 130—135°.

2 : 5-Dichloro-3 : 6-diacetamido-*p*-benzoquinone is transformed by $NH_2Ph$ in boiling EtOH into 3 : 6-*dianilino*-2 : 5-*diacetamido*-p-*benzoquinone* (*trihydrate*, converted at 100° or by hot EtOH into the *semihydrate*), which when heated at 260°, boiled with NaOH–EtOH, or boiled with AcOH, $PhNO_2$, or $NH_2Ph$ passes into 1 : 1′-*diphenyl*-2 : 2′-*dimethyl*-4 : 5 : 4′ : 5′-*di-iminazolo*-p-*benzoquinone* (IX), m.p. >360°. H. W.


(IX.)

**Production of furoyl-substituted thiolbenzthiazoles.**—See B., 1937, 23.

**Synthesis of hordenine.** Y. Raoul (Compt. rend., 1937, **204**, 74—76).—Tyrosine at 250° *in vac.* gives tyramine, which with boiling 40% $CH_2O$ containing $HCO_2H$ in 10 hr. affords hordenine (50%); at room temp. the reaction takes a month and may represent the bio-mechanism. J. L. D.

**Tobacco alkaloids. X. Syntheses of *l*-anabasine and *d*-anabasine.** E. Späth and F. Kesztler (Ber., 1937, **70**, [*B*], 70—72).—Treatment of *dl*-anabasine (I) with *l*-6 : 6′-dinitro-2 : 2′-diphenic acid in boiling MeOH leads to l-*anabasine* l-*dinitrodiphenate* (I), m.p. 264·5—265° (vac.), $[\alpha]_D^{16}$ −76·92° in abs. MeOH, whence *l*-anabasine, $[\alpha]_D^{18}$ −82·45° [*dipicrate*, m.p. 198—199·5° (decomp.)]. The mother-liquors from (I) yield d-*anabasine* d-*dinitrodiphenate*, m.p. 264—265°, $[\alpha]_D^{18}$ +76·22° in abs. MeOH, whence d-*anabasine*, $[\alpha]_D^{18}$ +82·11° (*dipicrate*, m.p. 198—199°). The dipicrate of (I) has m.p. 213—214°. H. W.

**Alkaloids from *Arundo donax*, L.** J. Madinaveitia (Nature, 1937, **139**, 27).—Donaxine with EtOH–KOH and MeI in the cold, gives $NMe_4I$ and a methoxymethylindole; with EtI an ethoxymethylindole is obtained. A cryst. alkaloid, $C_{13}H_{16}O_2N_2$, and an amorphous phenolic base, both indole derivatives, have been obtained from *A. donax*, L. L. S. T.

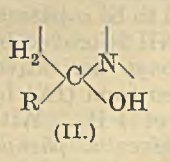
**Papaverine and Fröhde's reagent.** U. Kubli (Pharm. Acta Helv., 1935, **10**, 156—157; Chem. Zentr., 1936, i, 1263).—Cryptopine-free papaverine (I) gives a colour reaction with the reagent, which therefore cannot be used to detect cryptopine in (I). H. N. R.

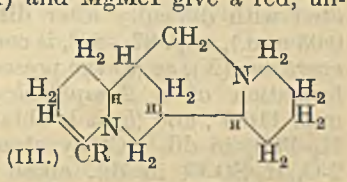
**Quinine salt, m.p. 199°, of glycerophosphoric acid.**—See A., III., 70.

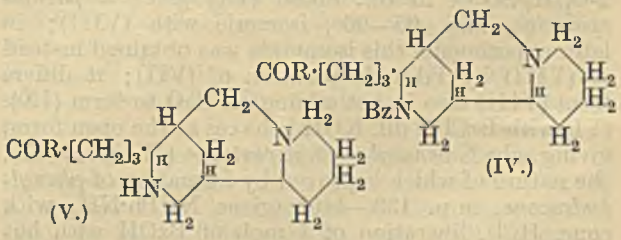
**Quinine camphorsulphonates.** L. Nobili (G. Farm. Chim., 1935, **84**, 232—239; Chem. Zentr., 1936, i, 2140).—The neutral, m.p. 210°, and basic, m.p. 192°, *salts* and their physiological action are described. H. N. R.

**Niquine and niquidine.** E. Léger (Bull. Soc. chim., 1937, [v], **4**, 180—183).—Mainly polemical against Reyman *et al.* (A., 1936, 490). The author considers that δ-cinchonine is a dihydrocinchonine and niquine and niquidine are stereoisomeric forms of a dihydroquinine (A., 1920, i, 875). J. W. B.

**Lupin alkaloids. XII. Behaviour of lupanine towards Grignard reagents.** K. Winterfeld and E. Hoffmann (Arch. Pharm., 1937, **275**, 5—27; cf. A., 1936, 216).—The presence of a lactam group in lupanine (I) is proved by quant. reaction with Grignard reagents (2—3 mols.) in $Et_2O$ to form additive products, hydrolysed to alcohols (II), which are too unstable to be isolated and readily lose $H_2O$ to give substituted dehydrosparteines (III). The presence of the C:C·N linking in the dehydrocompounds is proved by benzoylation of the Et compound, which gives (IV) by ring-fission. The crude alkyldehydrosparteines (III) undergo fission of ring 1 in acid solution, giving alkylsparteones (V). This fission is much more facile if R = Ph and various substances derived from this sparteone are prepared. Hydrogenation of (III) is the more rapid the lower is the mol. wt. of R. (I) and MgMeI give a red, un-


(II.)

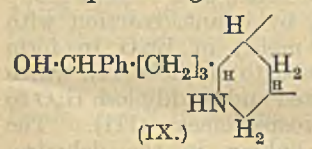

(III.)

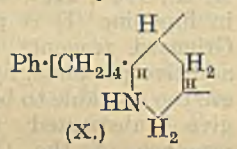

(IV.)


(V.)

saturated, uncrystallisable oil, which, when distilled at 135°/0·1 mm., gives $H_2O$ and *methyldehydrosparteine*,

an unstable oil ($HgCl_2$-compound, decomp. 257—258°; *diauri-*, decomp. 142°, and *platini-chloride*, decomp. 246—250°), hydrogenated (Pd–$CaCO_3$; $1H_2$) in abs. MeOH to *methylsparteine*, b.p. 117°/0·8 mm., m.p. 48—50° ($HgCl_2$-compound, decomp. 215°; *diaurichloride*, $+H_2O$, decomp. 178°; *picrate*, $+H_2O$, m.p. 221°; *sulphate*, m.p. 122—123°; unchanged by $H_2$–$PtO_2$ in HCl or by BzCl in dil. alkali). (I) and MgEtI give a crude oily mixture, which, when distilled at 125°/0·018 mm., gives *ethyldehydrosparteine* (VI), an oil [*picrate*, m.p. 140° (decomp.) after sintering at 132°; *platini-*, $+H_2O$, m.p. 251° (decomp.) (a fraction, decomp. 237—239°, was also obtained), and *diauri-chloride*, $+H_2O$, cryst.], hydrogenated (Pd–$CaCO_3$) to *ethylsparteine*, b.p. 109°/0·004 mm., m.p. 34—40° ($HgCl_2$-compound, $+H_2O$, decomp. 241°; *diauri-*, decomp. 186°, and *platini-chloride*, *forms*, decomp. 257—258°, 264—265°, and 261—269°, respectively; *sulphate*, m.p. 124—125°). The alkylsparteines are probably mixtures of racemic or meso-forms, owing to the new asymmetric C formed; various possible types of such isomerism are discussed. (I) and MgPhBr give a mixture, from which *phenyldehydrosparteine* (VII) [(III) (R = Ph)], m.p. 103—105°, b.p. 150—151°/0·049 mm. (*platinichloride*, decomp. 253°), gradually crystallises; with $H_2$–Pd this gives *phenylsparteine* (VIII), an oil, b.p. 160—161°/high vac. When rubbed with $H_2O$, this gives a substance, $C_{21}H_{32}ON_2$, m.p. 79—80° to a turbid liquid, clears at 139—140°, which may be a hydrate, but is probably ω-*phenylsparteol* (IX). The crude reaction product from (I) and MgMeI or its distillation product gives with HBr the *dihydrobromide*,

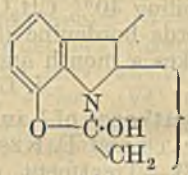

(IX.)

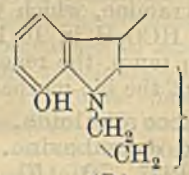

(X.)

m.p. 248°, of ω-*methylsparteone* (V) (R = Me). Neutralisation of (VII) with dil. HCl or HBr and evaporation at 100° gives the *dihydrochloride*, m.p. 189—190°, and *dihydrobromide*, m.p. 210°, respectively, of ω-*phenylsparteone* (V) (R = Ph). In presence of $PtO_2$ and dil. HCl (VII) absorbs 2 $H_2$; it probably reacts in the open form (V), giving first (IX) and then the olefine by loss of $H_2O$; the final product (isolated with difficulty after distillation at 180—181°/0·03 mm.), m.p. 87—88°, is considered to be ω-*phenylsparteane* (X), as (*a*) the presence of NH is proved by formation of a 2-*naphthalenesulphonyl* derivative, m.p. 116·5°, and (*b*) it is obtained also from (IX) by $H_2$–$PtO_2$ in dil. HCl by absorption of 1 $H_2$. With 2-$C_{10}H_7$·$SO_2Cl$ in dil. alkali (IX) gives a *phenylsparteine*, m.p. 95—96°, isomeric with (VIII); in later experiments this isomeride was obtained instead of (VIII) by Pd-hydrogenation of (VII); it differs from (VIII) also in not adding on $H_2O$ to form (IX). (VI) with BzCl in dil. KOH behaves as the open form, giving oily N-*benzoyl*-ω-*ethylsparteone* (IV) (R = Et), the nature of which is proved by formation of *phenylhydrazone*, m.p. 139—140° (gives NHPh·$NH_2$ with conc. HCl), liberation of 1 mol. of BzOH with hot 15% HCl, and formation of PhCN by the von Braun reaction with $PBr_5$. R. S. C.

***Strychnos* alkaloids. XVI. 11-Amino- and 11-hydroxy-brucine.** H. Wieland and H. Mahlerwein (Annalen, 1937, **527**, 141—151).—Reduction of oximinobrucine with Zn dust and HCl gives 11-*aminobrucine dihydrochloride* (I), decomp. about 230°, converted by aq. $NH_3$ into the unstable 11-*aminobrucine* (II), m.p. 169°. The freshly-prepared nitrosoamine of oximinodihydrobrucic acid is reduced by 2*N*-NaOH and Zn dust to 11-*aminodihydrobrucine* (III), m.p. 224° [*hydrochloride*, darkens at 196°; $Bz_2$ derivative, m.p. 225°, and its *hydrochloride*, m.p. 197° (decomp.)], also obtained by hydrogenation ($PtO_2$ in AcOH) of (II). Gradual addition of (III) to $SOCl_2$ at room temp. gives the *base*, $C_{23}H_{26}O_3N_3Cl$, m.p. >300° after darkening at 240° or (hydrated) m.p. 116° (decomp.) (*hydrochloride*). Addition of aq. $NaNO_2$ to (I) in $H_2O$ gives the very stable 11-*diazobrucine*, m.p. 189° (decomp.) after softening at about 87°, the *hydrochloride* of which passes when warmed with dil. $H_2SO_4$ into 11-*chlorobrucine* (IV), m.p. 212° (decomp.) [*dihydrochloride* (V), m.p. >300°; *methiodide*, m.p. 219° (decomp.)]. Hydrogenation of (V) ($PtO_2$ in AcOH–$H_2O$) gives *chlorodihydrobrucine*, m.p. 274° after darkening at 256°, and apparently an isomeric *base*, m.p. 212°, also obtained by hydrogenation of (IV). 11-*Methoxybrucine*, m.p. 192° (*hydrochloride methiodide*, incipient decomp. 236°), is obtained from (IV) and NaOMe in boiling NaOH, whereby the possibility of isomerisation is not completely excluded. 11-*Methoxydihydrobrucine* has m.p. 237° (decomp.). The production of 11-*hydroxybrucine*, m.p. 178° [*hydrochloride* (VI), m.p. >300° (decomp.)], from the diazo-compound is successful only in the complete absence of Cl′. 11-Hydroxydihydrobrucine, m.p. 233° (decomp.), is obtained by hydrogenation ($PtO_2$ in 50% AcOH) of (VI). H. W.

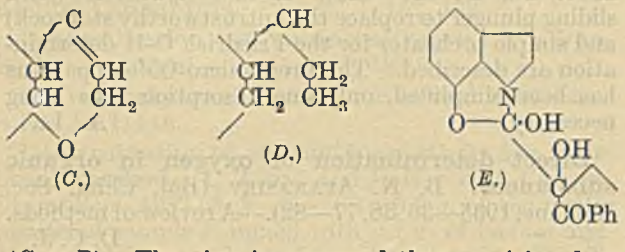
***Strychnos* alkaloids. XVII. Deoxyvomicidine and other reduction products of vomicine.** H. Wieland and J. Kimmig (Annalen, 1937, **527**, 151—159).—Reduction of vomicine by HI gives deoxyvomicine I (I), m.p. 198°, $[\alpha]_D^{20}$ + 266·4° in $CHCl_3$, isomerised by NaOH in hot $C_5H_5N$ into *deoxyvomicine* II (II), m.p. 207°, $[\alpha]_D^{20}$ + 231·4° in $CHCl_3$. (II) but not (I) is electrolytically reduced at a Pb cathode to *deoxyvomicidine* (III), m.p. 227° (*Bz* derivative, m.p. 190°), a phenolic base sol. in alkali and converted by acid oxidants into a red-violet dye, thus establishing the partial relationships


(*A*.)


(*B*.)

(*A*) and (*B*) for (I) and (III). In addition to O of OH, (III), like other *Strychnos* alkaloids, probably contains a bridge O, since it is converted by HI into *iododihydrodeoxyvomicidine*, $C_{22}H_{27}ON_2I$, decomp. >240° (*hydriodide*), from which I could not be removed in the desired manner. (I) is catalytically hydrogenated with removal of bridge O to the bases $C_{22}H_{28}O_2N_2$ (IV) and $C_{22}H_{30}O_2N_2$ (V), which are

closely related, since (IV) is transformed into (V) by hydrogenation at increased temp. and pressure. Further (IV) and (V) are electrolytically reduced to the *bases* $C_{22}H_{30}ON_2$, m.p. 217°, and $C_{22}H_{32}ON_2$, m.p. 220—222°; the remaining O is present in phenolic OH. Both bases give on oxidation the dark red-violet colour characteristic of all derivatives of vomicidine. It is therefore established that the hydrogenation of (I) to (IV) involves the saturation of the double linking and the opening of the O-bridge



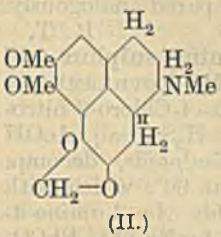

(*C* → *D*). The view is expressed that vomicine does not contain a *tert.* OH, but that the fourth O is present in a bridge.

Gradual addition of 50% KOH to a boiling suspension of dihydrovomicine and PhCHO in abs. EtOH yields *benzylidenedihydrovomicine*, $C_{29}H_{30}O_4N_2$, m.p. 285° (decomp.), which does not dissolve in dil. mineral acids and is oxidised by $KMnO_4$ in $COMe_2$–AcOH to the (?) hydrated *base*, $C_{28}H_{30}O_6N_2$ (cf. *E*), m.p. about 180° (decomp.), which passes when heated into a *substance*, m.p. 274°. H. W.

**Alkaloids of *Senecio*.** J. J. Blackie (Pharm. J., 1937, **138**, 102—104; cf. A., 1936, 1002).—To EtOH *S. isatideus* yields *isatidine*, $C_{18}H_{25}O_7N$ (hydrolysed to *isatinecic acid*, $C_{10}H_{16}O_6$, and *isatinecine*, $C_8H_{13}O_3N$), and retrorsine, also isolated from *S. glaberrimus* and *S. venosus*. *S. jacobœa* yields a *base*, $C_{18}H_{25}O_5N$, and jacobine, $C_{18}H_{26}O_6N$ (cf. Manske, A., 1932, 286), which is also isolated from *S. cineraria* and *S. erucifolius*. *S. palustris* yields a *base*, $C_{18}H_{25}O_5N$, m.p. 169°, and *S. sylvaticus*, silvasenecine. *S. saracenicus* yields three *bases*, $C_5H_9ON$, $C_8H_{13}ON$, and $C_{13}H_{21}O_3N$, and from *S. campestris*, *campestrine*, $C_{13}H_{19}ON$, m.p. 93°, and a *base*, m.p. 215°, are isolated. J. D. R.

**Chemistry of mu-fang-chi.** K. K. Chen and A. L. Chen (Chinese J. Physiol., 1937, **11**, 25—28).—*Thunbergin*, $C_{20}H_{14}O_9$, m.p. 277—277·5°, and *mufangchine*, $C_{14}H_{21}O_{11}N_{14}$, m.p. 231·5°, have been isolated from mu-fang-chi (probably the root of *Cocculus thunbergii*). E. M. W.

**Constitution and synthesis of domesticine methyl ether (*d-epi*dicentrine).** Z. Kitasato and H. Snishido (Annalen, 1937, **527**, 176—182).—6 : 7-Dimethoxy-1-piperonyl-2-methyltetrahydro*iso*quinoline, m.p. 122°, gives a *hydrochloride*, m.p. 224°, and a *picrate*, m.p. 206—208°. 6 : 7-*Dimethoxy*-6′-*nitro*-1-*piperonyl*-2-*methyltetrahydroisoquinoline* (I), m.p. 152°, its *hydroiodide*, m.p. 205—210° (decomp.), and *picrate*, m.p. 189°, are described. Reduction of (I) with $SnCl_2$ and conc. HCl in AcOH at 15° affords 6 : 7-*dimethoxy*-6′-*amino*-1-*piperonyl*-2-*methyltetrahydro*isoquinoline, m.p. 132° (*dihydrochloride*, m.p. 223°), which is diazotised and then reduced to dl-epi*dicentrine* (II), m.p. 142° [*hydrochloride*, m.p. 265—270° (decomp.) after becoming discoloured at 255°; *picrate*, m.p. 202—204° (decomp.); *methosulphate*, m.p. 238°]. By the successive use of *d*- and *l*-tartaric acid in abs. EtOH (II) is resolved into *l*- (III), m.p. 138—139°, $[\alpha]_D^{18}$ −101·31° in $CHCl_3$, and *d-epi*dicentrine, m.p. 139°, $[\alpha]_D^{18}$ +102·27° in $CHCl_3$, identical with natural domesticine Me ether (IV). Admixture of equal proportions of (III) and (IV) leads to (II). H. W.



(II.)

**Curarine from calabash curare.** H. Wieland, W. Konz, and R. Sonderhoff (Annalen, 1937, **527**, 160—168).—Prolonged fractional crystallisation of various salts of the crude material supplemented by adsorption methods leads to an amorphous but only slightly coloured *perchlorate* of greatly enhanced toxic action. The best results are obtained by fractional adsorption of the reineckates, whereby a very toxic alkaloid results which gives a cryst. *anthraquinone*-2-*sulphonate* (I) and thence a cryst. *picrate* (II). Assuming that (II) contains base : acid = 1 : 1 the formula of the former, named *toxiferine* (III) (from *Strychnos toxifera*), is $C_{25}H_{27}O_2N_3$ but (I) cannot be derived from a base of this composition. (III) gives a characteristic green colour with $HNO_3$ and blue colour with $K_2Cr_2O_7$–$H_2SO_4$. It does not appear to belong to the same alkaloidal group as tubacurarine. Phenolic OH or OMe is not present in (III) or in the crude mixtures from which it is extracted. (III) does not appear to be a quaternary $NH_4$ base since the chloride yields only a slightly alkaline solution when treated with $Ag_2O$. It is not affected by catalytic $H_2$. Protocatechuic acid is isolated from the initial material, in which the presence of succinic acid could not be established. H. W.

**Chemical incompatibility between yatrene and some mineral salts.** V. Lucas (Bol. Assoc. brasil. farm., 1935, **16**, 204—206).—Yatrene forms insol. salts with $MgCO_3$,$Mg(OH)_2$ and with Ca, Ba, and Sr salts. Ch. Abs. (*r*)

**Nitro-arsines. I. *m*-Nitrophenyldichloroarsine.** D. A. Isačescu (Bul. Soc. Chim. România, 1936, **18**, 131—134).—*m*-$NO_2$·$C_6H_4$·$AsO_3H_2$, HCl, and $SO_2$ at 100° give *m*-$NO_2$·$C_6H_4$·$AsCl_2$, m.p. 46°. R. S. C.

**Organo-arsenic compounds. II. Arsenation of aniline. Metallic arsanilates.** P. S. Yang and C. P. Lo (J. Chinese Chem. Soc., 1936, **4**, 477—484).—The prep. of arsanilic acid [*H Ag*, *H* $Mg_{\frac{1}{2}}$, *H* $Hg_{\frac{1}{2}}$, *H* $(PbOH)_{\frac{1}{4}}$, *H* $Bi(OH)_2$, and ? *H* $Sb(OH)_2$ salts] is modified. The solubilities of the salts are recorded. R. S. C.

**Aryl tin hydroxyl and halide compounds of the type $SnAr_3X$.** K. A. Kotscheschkov, M. M. Nadj, and A. P. Alexandrov (J. Gen. Chem. Russ., 1936, **6**, 1672—1675).—$SnPh_4$ and $SnCl_4$ (4 hr. at 205—210°, 3 hr. at 150—160°) yield $SnPh_3Cl$, converted by KOH in $Et_2O$ into $SnPh_3$·OH. Tri-*o*-, *m*-,

and *-p*-tolylchlorostannane, and *tri*-p-*tolylhydroxystannane*, m.p. 108—109°, were prepared analogously. R. T.

**Aromatic compounds containing sulphur and arsenic.** K. Burschkies and M. Rothermundt (Ber., 1936, **69**, [*B*], 2721—2724).—4-Chloro-3-nitrophenylarsinic acid is converted by $H_2S$ in aq. AcOH into *As* 4-*chloro*-3-*nitrophenyl disulphide*, decomp. 220° after becoming discoloured at 60°, which with $Na_2S$ in boiling EtOH–$H_2O$ yields *As* 3-*amino*-4-*thiolphenyl disulphide*, transformed by $Na_2CO_3$–$PbCO_3$ into 3-*amino*-4-*thiolphenylarsinic acid* (I). (I) dissolved in *N*-NaOH is reduced by $H_3PO_2$ or by $MgCl_2$–$Na_2S_2O_4$ at 50—60° to 3 : 3′-*diamino*-4 : 4′-*dithiolarsenobenzene*, freely sol. in alkali but insol. in acid. Passage of air through a solution of (I) in 2*N*-NaOH gives 3 : 3′-*diamino*-4 : 4′-*disulphidodiphenyl*-1 : 1′-*diarsinic acid*; the corresponding $Ac_2$ derivative is reduced by $FeSO_4$ and NaOH at 40° to 3-*acetamido*-4-*thiolphenylarsinic acid*. The products are amorphous, almost colourless powders without definite m.p. They are considerably more toxic than the corresponding OH derivatives and are therapeutically unimportant. H. W.

**Properties of proteins as a function of their fine structure.** S. J. von Przylecki (Monatsh., 1936, **69**, 243—269; cf. A., 1936, 155, 619).—The chemical properties of proteins are determined by the character and position of the active groups of the constituent $NH_2$-acids. 14 typical groups are enumerated. Compounds can be formed through these, with other substances by electrovalent, covalent, or co-ordination linkings. Of a no. of $NH_2$-acids, only arginine and tyrosine react with amylose and dextrin, whilst the proportions in which they occur in proteins determine the reactivity of the latter towards polysaccharides. The nature of the co-ordinating groups and the stoicheiometric and stereochemical relationships are discussed and the formation of electrovalent polysaccharide–protein compounds is described. Adsorption of proteins on hydrocarbons is due to attraction of the $NH_2$-acid hydrocarbon chains by the surface. The formation of compounds between proteins and fatty acids, esters, phosphatides, cholesterol, purine bases, nucleosides, and nucleotides is discussed. R. S.

**Position of constitutional investigations of proteins.** W. Grassmann (Angew. Chem., 1937, **50**, 65—72).—A lecture. J. W. S.

**Artificial "lipo-proteins."**—See A., III, 87.

***d*-Limonene tetrabromide as a reagent in Rast's micro-method for the determination of mol. wt. of organic compounds.** H. Y. Fang and P. P. T. Sah (J. Chinese Chem. Soc., 1936, **4**, 429—431).—Mol. wt. determinations of $C_{10}H_8$, camphor, 2 : 4 : 6-$C_6H_2Br_3$·OH, BzOH, and *m*-$C_6H_4(NO_2)_2$, using *d*-limonene tetrabromide (I) as solvent, gave an average cryoscopic const. for (I) of 30·70. C. R. H.

**Improved sodium fusion technique for volatile or difficultly decomposable liquids.** A. S. Miceli (J. Chem. Educ., 1936, **13**, 515).—The pellet of Na, supported on glass wool, is heated in the upper half of a 4-in. test-tube. L. S. T.

**Methods of quantitative organic analysis by hydrogenation applied to micro-analysis.** (Mlle.) A. Lacourt (Compt. rend., 1936, **203**, 1367—1369).—N, S, halogens, and O are determined with an error of ±0·21% using a modification of ter Meulen's apparatus (cf. A., 1934, 424). J. L. D.

**Microchemical technique. I. Micro-methoxyl and micro-carbon–hydrogen determination.** E. V. White and G. F. Wright (Canad. J. Res., 1936, **14**, B, 427—429).—A new flowmeter (with sliding plunger to replace the untrustworthy stopcock) and simple preheater for the Friedrich C–H determination are described. The Pregl micro-OMe apparatus has been simplified, only one absorption tube being necessary. A. Li.

**Direct determination of oxygen in organic substances.** B. N. Afanasiev (Bul. Chim. Soc. Române, 1935—36, **38**, 77—82).—A review of methods. D. C. J.

**Detection of halogens (chlorine, bromine) in organic compounds.** L. Rosenthaler (Z. anal. Chem., 1937, **108**, 22—23).—The materials are burned alone or in EtOH, and the products of combustion sucked over cotton wool impregnated with a 1% solution of *p*-$NMe_2$·$C_6H_4$·CHO + $NHPh_2$. Halogen compounds produce a yellow colour. J. S. A.

**Determination of organic iodine.** J. A. Gautier (J. Pharm. Chim., 1937, [viii], **25**, 145—156).—The I-compound with boiling *N*-NaOH or aq. EtOH–KOH and Zn affords $ZnI_2$ which, when freed from excess of Zn and org. material, is oxidised with $KMnO_4$; the liberated I is titrated. J. L. D.

**Detection of sulphur and nitrogen in organic compounds.** L. Rosenthaler (Z. anal. Chem., 1937, **108**, 24—26).—(*a*) The material is burned in a stream of air, which is passed through 1% aq. $HIO_3$. S compounds form $SO_2$, which produces a blue coloration. (*b*) The material is treated with $PbO_2$, and the gases evolved are passed into sulphanilic acid. Acid amides, $CO(NH_2)_2$ and its derivatives, and $NO_2$-compounds, but not aliphatic or aromatic amines, azo-compounds, or heterocyclic compounds, form $HNO_2$, which may be detected by adding α-$C_{10}H_7$·ONa. J. S. A.

**Application of sulphuric–perchloric acid method of destruction [of organic materials] to qualitative test for nitrogen.** H. Gauduchon-Truchot (Ann. Chim. Analyt., 1936, [iii], **18**, 316—317).—The material is heated with conc. $H_2SO_4$, and dil. (about 20%) $HClO_4$ is added until decolorisation is complete. The solution is then tested for $NH_3$. J. S. A.

**Analysis of organic compounds containing nitrogen. I. Determination of nitro-compound-nitrogen by the method of alkaline fusion.** E. V. Alexeevski and Z. E. Golbraich (J. Appl. Chem. Russ., 1936, **9**, 1535—1542).—A mixture of 0·2—0·4 g. of the $NO_2$-compound with 4 g. of NaOH and 0·8—1 g. of Zn dust is heated at a dull red heat in an Fe tube through which air is being aspirated, and the $NH_3$ evolved is absorbed in standard $H_2SO_4$. The reaction is represented: $2OH·C_6H_4·NO_2$ +

$10H_2O \rightarrow 3C + 8CO_2 + 10H_2 + CH_4 + 2NH_3$. The method is not applicable to liquid or volatile substances. R. T.

**Shortening the time required for micro-Kjeldahl determinations in the apparatus of Parnas and Wagner.** S. Z. Bartosiewicz (Biochem. Z., 1936, **289**, 55—56).—A pump is used in emptying and washing the distillation flask. P. W. C.

**Semi-micro-determination of nitrogen. Micro-Kjeldahl apparatus.**—See A., I, 152, 153.

**Determination of amino-nitrogen by Van Slyke's method.**—See A., III, 108.

**Micro-analysis of nitrous oxide and methane.**—See A., I, 148.

**Determination of organic bismuth by the Parr bomb method.** C. Tseng and L. Wang (J. Chinese Chem. Soc., 1937, **5**, 3—5).—0·1—0·2 g. of the finely powdered sample is mixed with 0·2 g. of lactose and 12 g. of $Na_2O_2$ and heated in a Parr bomb. The Bi is then determined as $Bi_2S_3$. R. S. B.

**Systematic procedure for detection and separation of anions.**—See A., I, 147.

**Determination of anhydrides of carboxylic acids.** D. M. Smith and W. M. D. Bryant (J. Amer. Chem. Soc., 1936, **58**, 2452—2454).—The anhydride (I) (alone or in MeOH or $COMe_2$) is (*a*) titrated directly with 0·5*N*-MeOH–NaOMe and a separate sample is (*b*) titrated with 0·5*N*-NaOH in presence of $C_5H_5N$ [which accelerates hydrolysis of (I)] using phenolphthalein or thymol-blue (dissolved in $COMe_2$ or dioxan; not in alcohols). The equiv. difference, $b - a$, determines the amount of (I) even if free acid is initially present. Data for $Ac_2O$, $(EtCO)_2O$, $(\cdot CH_2 \cdot CO)_2O$, $BzO_2$, and *n*-heptoic, maleic, glutaric, phthalic, camphoric, and furoic anhydrides are given. Readily hydrolysed esters and lactones (*e.g.*, $HCO_2Alk$ and δ-gluconolactone) if present lead to ambiguous results; β-methylumbelliferone (reacts as an acid), phthalide (inert), and coumarin (inert) do not interfere. H. B.

**Azides. VII. *m*-Chlorobenzazide as a reagent for the identification of amines.** P. P. T. Sah and C. S. Wu (J. Chinese Chem. Soc., 1936, **4**, 513—517; cf. A., 1936, 1006).—*m*-$C_6H_4Cl \cdot CON_3$ (modified prep.) is suitable for identification of primary amines. m-*Chlorophenylcarbamides* from the following are described: $NH_2Ph$, m.p. 187°, *o*-, m.p. 174—175°, *m*-, m.p. 247—248°, and *p*-$NO_2 \cdot C_6H_4 \cdot NH_2$, m.p. 272—273° (decomp.), *p*-$C_6H_4Br \cdot NH_2$, m.p. 237—238°, 4-aminodiphenyl, m.p. 220—221°, *o*-, m.p. 189—190°, *m*-, m.p. 236—237°, and *p*-$C_6H_4Me \cdot NH_2$, m.p. 214—215°, 3-bromo-*p*-toluidine, m.p. 228—229°, *p*-xylidine, m.p. 224—225°, *o*-, m.p. 211—212°, *m*-, m.p. 284—285°, and *p*-$NH_2 \cdot C_6H_4 \cdot CO_2H$, decomp. about 300°, benzidine, m.p. about 300°, α-, m.p. 251—252°, and β-$C_{10}H_7 \cdot NH_2$, m.p. 263—264°, $NH_2Bz$, m.p. 226—227°, and $NHPh_2$, m.p. 133—134°. R. S. C.

**3 : 5-Dinitro-*o*-toluic acid as a reagent for the identification of amines.** P. P. T. Sah and C. H. Tien (J. Chinese Chem. Soc., 1936, **4**, 490—495).—3 : 5-*Dinitro*-o-*toluates* of the following, prepared in abs. EtOH, are suitable for identification: *o*-, m.p. 157—158°, *m*-, m.p. 135—136°, and *p*-$C_6H_4Me \cdot NH_2$, m.p. 160—161°, α-, m.p. 180—181° (decomp.), and β-$C_{10}H_7 \cdot NH_2$, m.p. 136—137°, 4-aminodiphenyl, m.p. 165—166°, benzidine, m.p. 164—165°, $C_5H_5N$, m.p. 143—144°, quinoline, m.p. 135—136°, NHPhMe, m.p. 141—142°, $NH_2$, m.p. 218—219°, $CO(NH_2)_2$, m.p. 189—190°, *p*-xylidine, m.p. 145—146°, *p*-$C_6H_4Cl \cdot NH_2$, m.p. 122—123°, *p*-$C_6H_4Br \cdot NH_2$, m.p. 197—198°, *o*-, m.p. 180—181° (decomp.), and *p*-$OH \cdot C_6H_4 \cdot NH_2$, m.p. 201—202°, *o*-, m.p. 157—158°, *m*-, m.p. 150—151°, and *p*-$NH_2 \cdot C_6H_4 \cdot CO_2H$, m.p. 175—176°. $NPhMe_2$ and the nitroanilines do not form such salts. R. S. C.

**Semicarbazides. V. α-Naphthyl-, VI, β-Naphthyl-, VII, 3 - 5-Dinitrophenyl-semicarbazide as a reagent for identification of aldehydes and ketones.** P. P. T. Sah and (V) S. H. Chiang, (VI, VII) P. C. Tao (J. Chinese Chem. Soc., 1934, **4**, 496—500, 501—505, 506—512; cf. A., 1936, 1005).—α- (I) and β-*Naphthyl*- (II) and 3 : 5-*dinitrophenyl-semicarbazones* (III), respectively, of the following are prepared: MeCHO, m.p. 161—162°, 176—178°, 160—162°, EtCHO, m.p. 137—139°, 147—148°, 145—146°, $Pr^{\alpha}CHO$, m.p. 128—129°, 138—139°, 134—135°, $Pr^{\beta}CHO$, m.p. 157—158°, 137—138°, 148—149°, $Bu^{\alpha}CHO$, m.p. 124—125°, 134—136°, —, *n*-$C_5H_{11} \cdot CHO$, m.p. 112—113°, 126—128°, 135—136°, *n*-$C_6H_{13} \cdot CHO$, m.p. 133—134°, 143·5—134·5° (!), 141—142°, *n*-$C_7H_{15} \cdot CHO$, m.p. 103—105°, 135—136°, —, *n*-$C_8H_{17} \cdot CHO$, m.p. 122—123°, 150—151°, 116—117°, *n*-$C_9H_{19} \cdot CHO$, m.p. 118—119°, 148·5—149·5°, —, PhCHO, m.p. 200—201°, 222—223°, 269—270°, *m*-, m.p. 221—222°, 205·5—206·5°, —, and *p*-$NO_2 \cdot C_6H_4 \cdot CHO$, m.p. 257—258°, —, —, $CHPh{:}CH \cdot CHO$, m.p. 196—197°, 205·5—206·5°, —, *o*-$OH \cdot C_6H_4 \cdot CHO$, m.p. 213—214°, 202—203°, 244—245°, furfuraldehyde, m.p. 192—193°, 205—207°, 225—226°, $COMe_2$, m.p. 175—176°, 192—193°, 212—213°, $CHPh{:}CH \cdot COMe$, m.p. 222—223°, 198—199°, 225—226°, $COMe \cdot C_6H_{13}$-*n*, m.p. 147—148°, 144·5—145·5°, —, COPhMe, m.p. 206—207°, 207—208°, 227—228°, *p*-$C_6H_4Me \cdot COMe$, m.p. 228—229°, 255—256°, —, *m*-$NO_2 \cdot C_6H_4 \cdot COMe$, m.p. 245—246°, —, —, $COPh_2$, m.p. 174—175°, 181·5—182·5°, 121—122°, $CH_2Ac \cdot CO_2Et$, m.p. 126—127°, 159—161°, —, lævulic acid, m.p. 204° (decomp.), 214—215°, —, Et, m.p. 157—158°, —, —, and $CH_2Ph$ lævulate, m.p. 141—142°, 141—142°, —, $CHPh{:}CH \cdot COPh$, m.p. 201—202°, —, —, COMeEt, m.p. —, 169—170°, 199—200°, and *p*-$C_6H_4Br \cdot COMe$, m.p. —, 239—240°, —. (I) and (II), but not (III), are suitable for identification of CO-compounds, (II) less well in the aliphatic series. R. S. C.

***o*-Bromobenzhydrazide as reagent for identification of aldehydes and ketones.** Chung H. Kao, Cheng H. Kao, C. W. Tu, and P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1936, **3**, 555—560).—o-*Bromobenzhydrazide*, m.p. 152°, prepared from *o*-$C_6H_4Br \cdot CO_2Et$ and $N_2H_4$, gives the following *o-bromobenzoylhydrazones*: MeCHO, m.p. 156—157°, EtCHO, m.p. 174—175°, $Pr^{\alpha}CHO$, m.p. 155—157°, $Bu^{\alpha}CHO$, m.p. 153—155°, *n*-$C_5H_{11} \cdot CHO$, m.p. 130—131°, *n*-$C_6H_{13} \cdot CHO$, m.p. 140—141°, furfuraldehyde, m.p. 162—163°, PhCHO, m.p. 180—181°, *o*-, m.p. 176—178°, and *p*-$OH \cdot C_6H_4 \cdot CHO$, m.p. 253—254°, *m*-$NO_2 \cdot C_6H_4 \cdot CHO$, m.p. 195—197°, *p*-homosalicyl-

aldehyde, m.p. 183—184°, $COMe_2$, m.p. 153—154°, styryl Me ketone, m.p. 139—140°, Me hexyl ketone, m.p. 154—155°, COMePh, m.p. 146—147°, *p*-$C_6H_4Me$·COMe, m.p. 137—138°, *p*-OMe·$C_6H_4$·COMe, m.p. 165—166°, *p*-$C_6H_4Br$·COMe, m.p. 175—176°, *m*-$NO_2$·$C_6H_4$·COMe, m.p. 180—182°, Et lævulate, m.p. 96—97°, and *cyclo*pentanone, m.p. 160—161°. F. R. S.

**o-Nitrobenzhydrazide as reagent for identification of aldehydes and ketones.** P. P. T. Sah and Cheng H. Kao (Sci. Rep. Nat. Tsing Hua Univ., 1936, **3**, 461—468).—The *o-nitrobenzoylhydrazones* of the following have been prepared: EtCHO, m.p. 122—123°, $Pr^{\alpha}CHO$, m.p. 136—137°, $Bu^{\alpha}CHO$, m.p. 115—116°, *n*-$C_5H_{11}$·CHO, m.p. 119—120°, *n*-$C_6H_{13}$·CHO, m.p. 94—95°, *n*-$C_7H_{15}$·CHO, m.p. 98·5—99·5°, *n*-$C_8H_{17}$·CHO, m.p. 116·5—117·5°, *n*-$C_9H_{19}$·CHO, m.p. 103—104°, *m*-$NO_2$·$C_6H_4$·CHO, m.p. 202·2—203·2°, *p*-OH·$C_6H_4$·CHO, m.p. 257·5—258·5°, CHPh:CH·CHO, m.p. 200—201°, COMeEt, m.p. 175·4—176·4°, Me hexyl ketone, m.p. 67—68°, *p*-$C_6H_4Me$·COMe, m.p. 184—185°, *p*-$C_6H_4Br$·COMe, m.p. 228—229°, $COPh_2$, m.p. 184·4—185·4°, styryl Me ketone, m.p. 225—226°, lævulic acid, m.p. 176—177°, Et lævulate, m.p. 113·5—114·5°, and $CH_2Ac$·$CO_2Et$, m.p. 107·5—108·5°. The m-*nitrobenzoylhydrazones* of $Bu^{\alpha}CHO$, m.p. 129·5—130·5°, *n*-$C_6H_{13}$·CHO, m.p. 114·5—115·5° *n*-$C_8H_{17}$·CHO, m.p. 111—112°, and CHPh:CH·CHO, m.p. 197—198°, are also described. F. R. S.

**Phenylsemioxamazide (oxanilhydrazide) as reagent for identification of aldehydes and ketones.** P. P. T. Sah and W. P. Han (Sci. Rep. Nat. Tsing Hua Univ., 1936, **3**, 468—476).—*Phenylsemioxamazones* of the following have been prepared: MeCHO, m.p. 231—232°, EtCHO, m.p. 215—216°, $Pr^{\alpha}CHO$, m.p. 205—206°, $Bu^{\alpha}CHO$, m.p. 201—202°, $Pr^{\beta}CHO$, m.p. 204—205°, *n*-$C_5H_{11}$·CHO, m.p. 196—197°, *n*-$C_6H_{13}$·CHO, m.p. 190—191°, *n*-$C_7H_{15}$·CHO, m.p. 193—194°, *n*-$C_8H_{17}$·CHO, m.p. 185—186°, *n*-$C_9H_{19}$·CHO, m.p. 184° (decomp.), COMeEt, m.p. 219—220°, Me hexyl ketone, m.p. 163—164°, $COPh_2$, m.p. 260—261°, $CH_2Ac$·$CO_2Et$, m.p. 162—163°, lævulic acid, m.p. 236° (decomp.), and $CH_2Ph$ lævulate, m.p. 152—153°. F. R. S.

**Rapid approximate determination of aldehydes and ketones. IV. Determination of benzaldehyde and acetone.** E. K. Nikitin (J. Appl. Chem. Russ., 1936, **9**, 2098—2108).—The concn. of PhCHO is derived from the time elapsing before appearance of turbidity after addition of KOH and $COMe_2$ to various dilutions of the solution in 25% EtOH. Conversely, the method is applicable to determination of $COMe_2$. R. T.

**Determination of semicarbazones.** S. Veibel (J. Pharm. Chim., 1936, [viii], **24**, 499—502).—Modifications of Harlay's method (A., 1936, 493) are suggested and its application to certain semicarbazones is discussed. The m.p. of the semicarbazide of $AcCO_2H$ is 220—222° (slow heating), 246—248° (Maquenne block). F. O. H.

**Iodometric determination of salicylic acid, thymol, and β-naphthol.** A. Heede and S. Stensig (Dansk Tidsskr. Farm., 1937, **11**, 13—17).—Practical details are given. M. H. M. A.

**Determination of salicylates.** W. B. Bradley (Proc. Soc. Exp. Biol. Med., 1936, **35**, 1—4).—A vol. (<10 c.c.) of solution containing 1—5 mg. of *o*-OH·$C_6H_4$·$CO_2H$ is hydrolysed by heating at 100° with 1 drop of conc. aq. NaOH for 1 hr. and acidified with $H_2SO_4$. Preformed gas having been removed in the Van Slyke apparatus, 0·25—0·5 c.c. of saturated aq. NaBr saturated with Br is added and, after 1 min., 0·25—0·5 c.c. of saturated aq. KI. $C_6H_2Br_3$·OH is formed and the liberated $CO_2$ is measured. Results are accurate to ±4%. P. G. M.

**Micro-determination of menthol, menthone, and menthyl ester and of the essential oil of *Mentha*.** H. Ullrich and M. Schneider (Z. physiol. Chem., 1937, **245**, 181—184; cf. Bennet *et al.*, B., 1928, 68; Rehberg, A., 1925, i, 852).—The oil is steam-distilled from the plant (1—2 g.) and measured in a micro-burette, a correction being applied for the amount of oil remaining in the macro-burette in which the oil is first freed from $H_2O$. The menthone (I) content of the oil is determined by the $NH_2OH$ method, the menthol is oxidised to (I) with $CrO_3$ + $H_2SO_4$, and the determination repeated. The menthyl ester is determined by saponification. W. McC.

**Determination of furfuraldehyde and hydroxymethylfurfuraldehyde with *p*-nitrophenylhydrazine.** L. Maaskant (Rec. trav. chim., 1936, **55**, 1068—1070).—*p*-$NO_2$·$C_6H_4$·NH·$NH_2$ is preferred to phloroglucinol as a reagent for gravimetric determination. F. N. W.

**Cobalt colour reaction for detection of barbiturates.** F. L. Kozelka and H. J. Tatum (J. Pharm. Exp. Ther., 1937, **59**, 54—62).—The Co-barbiturate colour is due to the presence of 1 or 2 NH groups and is stable with 2 NH over a wide, and with 1 NH over a narrow, range of $p_H$. Compounds with >2 NH do not give the colour. The test can be used for determination of small amounts of barbiturates. P. W. C.

**Determination of some barbituric acid derivatives.** K. Kalinowski (Wiadom. farm., 1935, **62**, 633—635, 647—649; Chem. Zentr., 1936, i, 2391).—An argentometric method is described. H. N. R.

**Colorimetric determination of small quantities of morphine.** C. G. van Arkel (Pharm. Weekblad, 1937, **74**, 134—137).—The method of Hofmann and Popovici (A., 1935, 877) has been studied. The colour intensity must be measured within 15 min. Codeine, thebaine, and meconic acid give no coloration, whilst narcotine, papaverine, and narceine give only an extremely weak blue one. S. C.

**Potentiometric titration of proteins and amino-acids.** T. Soda and U. Tanabe (J. Chem. Soc. Japan, 1935, **56**, 672—682).—The Sb or quinhydrone–Pt electrode is used. Ch. Abs. (*e*)

**Thiol groups in proteins.** A. Todrick and E. Walker (Biochem. J., 1937, **31**, 292—296).—The ·SH content of proteins is determined by measuring the amount of dichlorophenol-indophenol required for its oxidation. No free ·SH occurs in native serum-albumin (I) or ovalbumin (II) or in denatured (I), but denatured (II) contains the ·SH equiv. of 0·63% of cysteine and native myosin the equiv. of 0·27%. W. McC.