BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

DECEMBER, 1941.

I.—ALIPHATIC.

Dehydrogenation of *n*-heptane and *cyclo*hexane on cerium, vanadium, and thorium catalysts.—See A., 1941, I, 478.

Thermal decomposition of ethylidene bromide.—See A., 1941, I, 473.

Reaction of olefines with solid cuprous halides. E. R. Gilliland, H. L. Bliss, and C. E. Kip (*J. Amer. Chem. Soc.*, 1941, **63**, 2088—2090).—C_2H_2 and butadiene with solid CuCl give compounds X,2CuCl (X = olefine). Isoprene yields a compound of the approx. formula C_5H_8,3CuCl but this may be due to incomplete reaction. Amylene and *cyclo*pentadiene do not give detectable compounds with CuCl. W. R. A.

Polymerisation of olefines. V. Isomerides [contained] in tri*iso*butylene. F. C. Whitmore, C. D. Wilson, J. V. Capinjola, C. O. Tongberg, G. H. Fleming, R. V. McGrew, and J. N. Cosby. **VI. Dimerides obtained from tetramethylethylene.** F. C. Whitmore and P. L. Meunier. **VII. Isolation and oxidation of αα-dineopentylethylene.** F. C. Whitmore and J. D. Surmatis (*J. Amer. Chem. Soc.*, 1941, **63**, 2035—2041, 2197—2199, 2200—2201; cf. A., 1941, II, 237).—V. Efficient fractionation (75, later 90—100, theoretical plates) of tri*iso*butylene gives fractions, (*A*) (75%), b.p. 177·7°, (*B*) (15%), b.p. 179·0°, and (*C*) (10%), b.p. 183—185°, unchanged by further fractionation, extraction with NH_2Ph or MeOH, or equilibrium melting. (*A*) is a mixture of $CH_2{:}C(CH_2Bu^{\gamma})_2$ (**I**) and the lower-boiling isomeride of $CHBu^{\gamma}{:}CMe{\cdot}CH_2Bu^{\gamma}$ (**II**), since ozonolysis in AcOH (less well, saturated hydrocarbons, b.p. 0—30°, and not other solvents) gives $Bu^{\gamma}CHO$, $COMe{\cdot}CH_2Bu^{\gamma}$ (**III**), CH_2O, $CO(CH_2Bu^{\gamma})_2$ (**IV**), m.p. −10°, b.p. 63°/11 mm. (*oxime*, m.p. 78°), and $Bu^{\gamma}CO_2H$. (*B*) is similarly shown to contain mainly the higher-boiling isomeride of (**II**) and less (**I**). By ozonolysis of (*A*) and (*B*) $(CH_2Bu^{\gamma})_2CH{\cdot}CO_2H$ and $CH_2Bu^{\gamma}{\cdot}CMeBu^{\gamma}{\cdot}CO_2H$, both known to be derived from (**I**) and (**II**), are also obtained. (*C*) contains $CH_2{:}CMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2Bu^{\gamma}$ and $CMe_2{:}CH{\cdot}CMe_2{\cdot}CH_2Bu^{\gamma}$, since ozonolysis yields CH_2O, *ααγγ-tetramethyl*-n-*valeric acid* (**V**), m.p. 40—45°, b.p. 123°/15 mm. (*amide*, m.p. 70—71°; *β-keto*-n-*propyl* ester *semicarbazone*, m.p. 155°), *δδζζ-tetramethyl*-n-*heptan-β-one* (**VI**), b.p. 75°/10 mm. (*semicarbazone*, m.p. 149°), and usually $Bu^{\gamma}CO_2H$, (**IV**), and (by a side-reaction) $CH_2Bu^{\gamma}{\cdot}CMe_2{\cdot}OH$ (**VII**), b.p. 143—145°. The structure of (**VII**) is proved by dehydration by 20% H_2SO_4 to di*iso*butylene, identified by oxidation (CrO_3). That of (**V**) is proved by Curtius degradation to $CH_2Bu^{\gamma}{\cdot}CMe_2{\cdot}NH_2$ (*phenylcarbamide* derivative, m.p. 137°; *Ac* derivative, m.p. 98—99°), also prepared from $CH_2Bu^{\gamma}{\cdot}CMe_2Cl$ by AgCNO, followed by KOH. Oxidation of (**VI**) by CrO_3 in dil. H_2SO_4 gives ~21% of (**V**) and 20% of AcOH. (**VI**) gives no CHI_3, but with MgPhBr gives an alcohol, b.p. 139°/5 mm., converted by dehydration into (**I**) and then ozonolysis into COPhMe and CH_2O. Ozonolysis of (**II**) is more rapid than that of (**I**). (**IV**) is synthesised in 60% yield from $CH_2Bu^{\gamma}{\cdot}MgCl$ and $CH_2Bu^{\gamma}{\cdot}COCl$ in Et_2O. Polymerisation of $CH_2{:}CMe_2$ by H_2SO_4 proceeds by reversible formation of $Bu^{\gamma}HSO_4$, the electronically deficient so-called carbonium "ion" $Bu^{\gamma+}$ and HSO_4^-, and related more complex products; its exact course is in doubt.

VI. The dimeride, b.p. 70—100°/100 mm., obtained in 62% yield from $(CMe_2{:})_2$ by 80% H_2SO_4 at 0°, contains $CHMePr^{\beta}{\cdot}CH{:}CMeBu^{\gamma}$ (50), $CMe_2{:}CMe{\cdot}CHMe{\cdot}CH_2Bu^{\gamma}$ (10) (cf. Brunner *et al.*, A., 1937, II, 395), $CHBu^{\gamma}{:}CMe{\cdot}CH_2Bu^{\gamma}$ (25), and $CH_2{:}C(CH_2Bu^{\gamma})_2$ (0·2%), since fractionation and then ozonisation in saturated light petroleum yields pinacolone, $CHMePr^{\beta}{\cdot}CHO$, $COMe_2$, (**III**), $Bu^{\gamma}CHO$, $COMe{\cdot}CHMe{\cdot}CH_2Bu^{\gamma}$, CH_2O, and (**IV**). The mechanism of the reaction, discussed in detail and shown to differ fundamentally from that of polymerisation by BF_3, combines rearrangement and polymerisation.

VII. Oxidation of tri*iso*butylene by $Na_2Cr_2O_7$ in aq. H_2SO_4 at 50—60° gives 18% of unattacked, pure $CH_2{:}C(CH_2Bu^{\gamma})_2$ (**VIII**), b.p. 112—113°/100 mm., which on further oxidation at 50—60° and later 80° gives $(CH_2Bu^{\gamma})_2CH{\cdot}CO_2H$ (24·7), m.p. 93—94°, unchanged (**VIII**) (46), (**IV**), (1·9), ketones (~9%) of higher b.p., and smaller amounts of (**III**), $Bu^{\gamma}CO_2H$, and $CH_2Bu^{\gamma}{\cdot}CO_2H$. R. S. C.

Mechanism of photochemical change of acetylene.—See A., 1941, I, 480.

Polymerisation of hydrocarbons of the C_nH_{2n-4} series with vicinal double and triple linkings. II. Cyclic dimerisation of *iso*propenylacetylene. A. I. Zacharova and V. A. Bezel-Sitscheva (*J. Gen. Chem. Russ.*, 1941, **11**, 67—69).—. $CH_2{:}CMe{\cdot}C{:}CH$ in MeOH is converted by heating for 12 hr. at 120° into *m-iso*propenyltoluene. R. T.

High-temperature chlorination of saturated, aliphatic monochlorides. Vicinal effect. F. F. Rust and W. E. Vaughan (*J. Org. Chem.*, 1941, **6**, 479—487).—Investigation of the vapour-phase chlorination of EtCl, $Pr^{\alpha}Cl$, $Pr^{\beta}Cl$, $Bu^{\alpha}Cl$, and $Bu^{\beta}Cl$ shows that the C·Cl group in a straight-chain aliphatic monochloride markedly retards substitution on the adjacent (once-removed) C atoms, the effect becoming increasingly pronounced with progressively higher temp. This "vicinal" effect extends in a smaller degree to the C twice removed from the C·Cl group. In this type of chlorination substitution of H on C linked to Cl is mildly retarded, the effect decreasing with increasing temp. Thus the small amount of $CH_2Cl{\cdot}CHEtCl$ formed from $Bu^{\alpha}Cl$ at 202° decreases when the chlorination is performed at a higher temp. At the same time, the relative reactivity of the H atoms of CH_2Cl steadily increases in comparison with those of the uninfluenced Me; the reactive *sec.* H at $C_{(\gamma)}$ are seemingly not greatly affected. In the chlorination of $Pr^{\alpha}Cl$ a progressive decrease in the proportion of $CHMeCl{\cdot}CH_2Cl$ is observed with rise of temp. while the relative reactivities of the H at $C_{(\alpha)}$ and $C_{(\gamma)}$ are enhanced. Examination of the chlorination of EtCl, $Pr^{\alpha}Cl$, and $Bu^{\alpha}Cl$ at 310—320° shows that the "vicinal" effect of Cl in the monochloride is not confined to the C·H linking on the once-removed C atoms but extends at least to those twice removed. Substitution into Me of $Pr^{\alpha}Cl$ does not occur as readily as it does into CH_2Cl. Only when Me is sufficiently removed from Cl, as in $Bu^{\alpha}Cl$, do its H atoms approach the reactivity of those in C_2H_6. H. W.

Reaction of halogens and iron with alcohols and esters. IV. Reaction of iron and bromine with ethyl alcohol. M. T. Dangjan (*J. Gen. Chem. Russ.*, 1941, **11**, 108).—EtBr is obtained in 81% yield when Br is added to a suspension of Fe in EtOH. R. T.

Allylic rearrangements. XI. Action of magnesium and zinc on crotyl and methylvinylcarbinyl chlorides. W. G. Young and M. Eisner (*J. Amer. Chem. Soc.*, 1941, **63**, 2113—2115; cf. A., 1940, II, 148).—86% of $C_4H_7{\cdot}MgCl$ is obtained from 30 : 15 : 1 Et_2O–Mg–C_4H_7Cl. The butenes obtained from mixtures of $CHMe{:}CH{\cdot}CH_2Cl$ (**I**) and $CH_2{:}CH{\cdot}CHMeCl$ by Mg–Et_2O or activated Zn in boiling 80% EtOH are independent of the nature of the mixture [8—93·5% of (**I**)], but depend on the metal + solvent; *e.g.*, Mg gives ~54·5% of Δ^{α}-, ~20·5% of *cis*-Δ^{β}-, and ~25% of *trans*-Δ^{β}-C_4H_8, and Zn–EtOH gives 67·4, 32·6, and <2%, respectively. With Mg, C_4H_7Br gives the same butenes (56·4 ± 2·0,

17·2±3·3, and 25·5±1·4%, respectively), but with Zn–EtOH gives a different mixture (62, 30, and 7, all ±2—3%, respectively). Use of abs. EtOH or $Pr^{\beta}OH$ instead of 80% EtOH with Zn and C_4H_7Br has no effect on the ratio of products. R. S. C.

Preparation of tetradeuteroethylene dibromide by direct union of dideuteroacetylene and deuterium bromide. Route to tetradeuteroethylene. C. L. Wilson and A. W. Wylie (*J.C.S.*, 1941, 596—601).—C_2H_2 and HBr, thoroughly mixed, and a C catalyst (granular charcoal activated in HBr at 450°) at ~200° give 70% yields of $(CH_2Br)_2$, with some $CHMeBr_2$, $CH_2{:}CHBr$ (I), and EtBr; the walls of the glass reaction tube probably catalyse union between (I) and HBr; higher temp. gives increased yields of (I). When a change to D compounds is made, it is necessary first to replace the exchangeable H in the catalyst by D, which is carried out by prolonging the activation process using DBr at 450°. An all-glass apparatus for producing a continuous supply of DBr by combination of electrolytic D and Br is described. DBr and C_2D_2 at 180° give products of similar composition to that obtained with "light" materials, and yield isomeric dibromotetradeuteroethanes (D content = ~99 at.-%), with a little $CD_2{:}CDBr$ and C_2D_5Br. C_2D_4 is prepared from the mixed isomerides by reaction with Zn in moist dioxan (+D_2O) and combination with Br affords the pure dibromide. A. T. P.

Promoting action of mercury on aluminium oxide in the dehydration of ethyl alcohol.—See A., 1941, I, 478.

Vapour-phase catalytic conversion of methyl*tert.*-butylcarbinol. E. A. Kelso, G. Wash, J. T. Horeczy, B. Shive, and W. A. Felsing (*J. Amer. Chem. Soc.*, 1941, **63**, 2273—2274).—In presence of commercial Al_2O_3 at 293—305°, $CHMeBu^{\gamma}{\cdot}OH$ gives $(CMe_2{:})_2$ 52, $CH_2{:}CMePr^{\beta}$ 32, and $CH_2{:}CHBu^{\gamma}$ 16%. The proportion of isomerides thus depends on the activity of the Al_2O_3 (cf. Brooks *et al.*, A., 1940, I, 201; Cramer *et al.*, A., 1939, II, 136). R. S. C.

Dehydration of *tert.* carbinols containing the neopentyl group. F. C. Whitmore and E. Rohrmann (*J. Amer. Chem. Soc.*, 1941, **63**, 2033—2035).—When $CH_2Bu^{\gamma}{\cdot}CR_2{\cdot}OH$ is dehydrated by anhyd. $CuSO_4$ and pumice, the CH_2Bu^{γ} is barely affected. The structure of the products below is proved by ozonolysis. $CH_2Bu^{\gamma}{\cdot}CEt_2{\cdot}OH$ (prep. from $Bu^{\gamma}{\cdot}[CH_2]_2{\cdot}CO_2Et$ and MgEtBr), b.p. 32°/3 mm., at 180—190° gives ~9 parts of $CHMe{:}CEt{\cdot}CH_2Bu^{\gamma}$ and 1 part of $CEt_2{:}CHBu^{\gamma}$. $CH_2Bu^{\gamma}{\cdot}CMeBu^{\alpha}{\cdot}OH$ (prep. from $COMe{\cdot}CH_2Bu^{\gamma}$ and $MgBu^{\alpha}Br$), b.p. 55—56°/5 mm., at 193—198° gives >8 parts of $CHPr^{\alpha}{:}CMe{\cdot}CH_2Bu^{\gamma}$, 1 part of $CH_2{:}CBu^{\alpha}{\cdot}CH_2Bu^{\gamma}$, and a trace of $CHBu^{\gamma}{:}CMeBu^{\alpha}$. R. S. C.

***cis*- and *trans*-Forms of βε-dimethyl-Δ^γ^-*n*-hexene-βε-diol.** (A) J. Salkind. (B) J. R. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 2282).—(A) Bourguel's substance, m.p. 101°, was shown (Salkind *et al.*, A., 1938, II, 123) to be a form of $(\vdots C{\cdot}CMe_2{\cdot}OH)_2$ (cf. Johnson *et al.*, A., 1941, II, 1).

(B) This correction is confirmed by hydrogenation of the substance by $2H_2$–PtO_2 to $(CH_2{\cdot}CMe_2{\cdot}OH)_2$, m.p. 88·5°, and by $1H_2$–Pd to $(\vdots CH{\cdot}CMe_2{\cdot}OH)$, m.p. 68—69°. The structure, *trans*-$(\vdots CH{\cdot}CMe_2{\cdot}OH)_2$, for Salkind's substance, m.p. 75°, requires confirmation. R. S. C.

Aliphatic sulphonic acids. Synthesis and properties of acylamides of aliphatic sulphonic acids. A. G. Kostzova (*J. Gen. Chem. Russ.*, 1941, **11**, 63—66).—The following have been prepared by standard methods: *chloromethanesulphonyl chloride*, b.p. 60°/10 mm., *chloromethanesulphon-acetamide*, m.p. 146°, and *-benzamide* (I), m.p. 118°, *α-chloroethanesulphon-acetamide*, m.p. 114°, and *-benzamide* (II), m.p. 123°, *benzylsulphon-acetamide*, m.p. 129°, and *-benzamide*, m.p. 148°. (I) and (II) are intensely sweet. R. T.

Reactions of carboxylic esters. M. P. Balfe and J. Kenyon (*Nature*, 1941, **148**, 196).—Although acid- or alkali-catalysed hydrolysis or esterification, and alkoxy-interchange, take place usually by mechanisms in which the linkings of the alkoxyl C are not disturbed, the alternative mechanism involving rupture between O and Alk occurs, to a greater extent than has been recognised, when the OAlk has electron-releasing properties. Reactions which can be explained on the assumption that the esters dissociate according to the second manner are quoted. L. S. T.

Acylals. C. D. Hurd and F. O. Green (*J. Amer. Chem. Soc.*, 1941, **63**, 2201—2204).—Compounds, $CHR(O{\cdot}COR')_2$ and $OR''{\cdot}CHR{\cdot}O{\cdot}COR'$ (*A*) (R, R′, and R″ = alkyl or aryl), are termed acylals. Acylals, exemplified by $CHMe(OAc)_2$, react with NH_2Ph, thus: → NHPhAc + [OH·CHMe·OAc] → MeCHO + AcOH; with $3NH_2OH$, thus: → NHAc·OH + $CHMe{:}N{\cdot}OH$ + $OH{\cdot}NH_2{\cdot}OAc$ + H_2O (method of analysis detailed); and with Cl_2 at 90—100° (no reaction at room temp.) to give $CCl_3{\cdot}CHO$, $CHCl_2{\cdot}CHO$, AcOH, and $CH_2Cl{\cdot}CO_2H$ with some $CH_2Cl{\cdot}CH(OAc)_2$ and $CHCl_2{\cdot}CH(OAc)_2$. RCHO, HCl, and R′OH give ~80% of $CHRCl{\cdot}OR'$, which with $R''CO_2Na$, first at 0° and then warm, gives 40—74% of (*A*) and a higher-boiling residue. Thus are obtained: *α-methoxyethyl acetate*, b.p. 24—25°/15 mm., *propionate*, b.p. 41—43°/18 mm., and *butyrate*, b.p. 44—45°/11 mm.; *α-ethoxyethyl propionate*, b.p. 51—51·5°/18 mm., and *butyrate*, b.p. 55—56°/11 mm.; *α-propoxyethyl acetate*, b.p. 54—55°/20 mm., *propionate*, b.p. 54·8—55·2°/11 mm., and *butyrate*, b.p. 67·8—69°/11 mm.; *α-butoxyethyl acetate*, b.p. 69·5—70°/21 mm., *propionate*, b.p. 70—71°/11 mm., and *butyrate*, b.p. 80—81°/11 mm.; *α-ethoxypropyl acetate*, b.p. 46·3—46·8°/14 mm.; *α-ethoxybutyl acetate*, b.p. 53—54°/10 mm., and *propionate*, b.p. 66—67°/10 mm. *n* and *d* are recorded. R. S. C.

Tracer studies using radioactive carbon. Oxidation of propionic acid. P. Nahinsky and S. Ruben (*J. Amer. Chem. Soc.*, 1941, **63**, 2275—2276).—Using radioactive C*, it is shown that EtC^*O_2H, prepared from MgEtBr and C^*O_2, with $KMnO_4$ gives C* in both $H_2C_2O_4$ and CO_2 but with $K_2Cr_2O_7$ gives only AcOH and C^*O_2, both oxidations being quant. R. S. C.

Reliability of reactions used to locate assimilated carbon in propionic acid. H. G. Wood, C. H. Werkman, A. Hemingway, A. O. Nier, and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1941, **63**, 2140—2142).—When $Et^{13}CO_2H$, prepared from MgEtBr and $^{13}CO_2$ (4·92% of the CO_2 used), is oxidised by $KMnO_4$–NaOH, the ^{13}C is obtained partly in the $Na_2C_2O_4$ and partly in the Na_2CO_3. At 460° reaction occurs strictly according to $(Et^{13}CO_2)_2Ba$ → $^{13}COEt_2$ + $Ba^{13}CO_3$. R. S. C.

Migration of acyl groups during hydrogenation of triglycerides. D. Atherton and T. P. Hilditch (*J.C.S.*, 1941, 527—535; cf. B., 1938, 79).—During the hydrogenation of mixtures of glycerides at 180° in presence of Ni on kieselguhr, interchange of acyl groups between the mols. of the triglycerides is slow; ~5% of the total glycerides are involved per hr. of exposure to hydrogenation conditions. Interchange of acyl groups proceeds between completely saturated glycerides, *i.e.*, is not dependent on concurrent hydrogenation. The change appears to occur more readily between simple triglycerides than when one component is a mixed triglyceride, *e.g.*, oleodipalmitin or palmitodiolein (I). Appreciable interchange occurs between tripalmitin (II) and triolein (III) or tristearin (IV), but is much less evident in mixtures of oleo- or stearo-dipalmitin and (III) or (IV), and occurs only slightly during hydrogenation of mixtures of (I) and (III). Conclusions from analytical data in these cases, however, are only of qual. significance. The presence of unresolved ternary mixtures in the final crystal fractions is less likely to occur in the case of hydrogenation of a mixture of (III) and (V), and this allows a more reliable estimation of (IV) and (V). After 3 hr. 20 min., ~14% of the glycerides undergo acyl interchange, and after 12·5 hr., 37% of interesterification is noted. The mixed triglycerides produced in both cases are probably almost wholly dilaurostearin, and laurodistearin is formed in small amounts only. When hydrogenation of a mixture of (III) and (II) is interrupted before completion (105 min.; I val. of 18·3), or when a similar mixture is heated at 180° in presence of catalytic Ni in CO_2 for 9 hr., the product contains a small proportion of mixed glycerides containing both palmitic and oleic acids. Results are considered in relation to the procedure adopted for determining the proportion of tri-C_{18} glycerides in fats by hydrogenation, followed by estimation of (IV) in the products; when this procedure is essential, hydrogenation should be rapid at 65—70° using Raney Ni, Pd, or Pt catalysts. The possible effect of time of hydrogenation, involving variations in degree of acyl interchange, on the texture and other properties of technically hydrogenated fats is indicated. A. T. P.

Polymerisation and drying of oils and esters of fatty acids. I. Theory of polymerisation. A. J. Drinberg. **II. Heat of polymerisation and nature of polymerides of oils.** A. J. Drinberg and A. I. Schepelev. **III. Heat of drying of linseed oil.** A. J. Drinberg and V. G. Juschin (*J. Gen. Chem.*

Russ., 1940, **10**, 2052—2058, 2059—2064, 2065—2072).—I. Polymerisation of drying oils involves reactions between C:C groups and of carbalkoxy-groups. Possible modes of polymerisation are reviewed, and methods of calculating polymerisation coeffs. are discussed.

II. The heat of polymerisation, Q, of oils is determined as the difference between the heat of combustion of the oil and of the polymeride. Derived formulæ for calculating Q give results in satisfactory agreement with experimental vals. for linseed (**I**), sunflower seed (**II**), and cottonseed oils (**III**) polymerised at 300° in an atm. of N_2. The results indicate that the ratio of intra- to inter-mol. reaction of reactive groups is 2 : 1 in the case of (**I**) and (**II**) oil, and 3 : 2 in that of (**III**).

III. The velocity and the heat of drying of (**I**) rise with increasing temp. from 20° to 98°. At 20° the reaction is of an auto-oxidative type, but with rising temp. direct oxidation becomes increasingly important. R. T.

Photolysis of some chloronitroso-compounds. S. Mitchell, K. Schwarzwald, and G. K. Simpson (*J.C.S.*, 1941, 602—605; cf. A., 1939, I, 89).—*γ-Chloro-γ-nitrosovaleric acid* (**I**) and *β-chloro-β-nitroso-αδ-diphenylbutane* (**II**) have been prepared by the action of Cl_2 on the oximes of lævulic acid and of αδ-diphenylbutan-β-one, respectively. Both (**I**) and (**II**) form blue crystals, m.p. 33° and 46°, respectively. (**I**) decomposes slightly when kept. The absorption spectra of (**I**) and (**II**) in MeOH solution are recorded from 7460 to 6590 A. The quantum efficiencies, γ, of the decomp. in MeOH solution of (**I**) and (**II**) and of 1-chloro-1-nitroso*cyclo*hexane (**III**) and β-chloro-β-nitroso-γγ-dimethylbutane (**IV**) have been measured at the λ of max. absorption in each case. γ for (**I**) and (**II**) is ~1 at this λ, whilst for (**II**) and (**IV**) vals. are 0·78 and 0·62, respectively. At shorter λ, γ for (**II**) and (**IV**) becomes ~1. The products of decomp. in all cases contain 90—100% of the theoretical HCl. Other products are: for (**I**), the oxime hydrochloride of Me lævulate, $C_6H_{12}O_3NCl$, and a small amount of Me lævulate; for (**II**) the oxime of αδ-diphenylbutan-β-one and CH_2O. O. D. S.

Acyloins. IX. Non-enzymic decarboxylation of pyruvic acid and acetoin formation. W. Dirscherl and H. Nahm (*Z. physiol. Chem.*, 1940, **264**, 41—56; cf. A., 1931, 1457).—$AcCO_2H$ is decarboxylated by various NH_2-acids [*e.g.*, *l*(−)-tyrosine (**I**), *dl*-alanine, *dl*-serine, *l*(−)-proline, and *l*(+)-arginine at 100°; *dl*-tyrosine at 120° (not at 54°); reaction generally accelerated in presence of C_5H_5N], aneurin (**II**) at 120° (not particularly active), or quinine at 100° (unaffected by C_5H_5N). Formation of acetoin (**III**) thereby occurs with, *e.g.*, *dl*- or *l*(+)-alanine, *dl*- or *l*(−)-asparagine or -aspartic acid, and *dl*-NH_2·CHPh·CO_2H, but not with, *e.g.*, (**I**), (**II**), *dl*-cystine, or *dl*-leucine. Use of (−)-NH_2·CHPh·CO_2H or *l*(−)-asparagine leads to optically inactive (**III**), whereas a mixture of (−)- and *dl*-(**III**) is formed during decarboxylation by yeast carboxylase (cf. A., 1938, III, 442). The significance of these results in connexion with the "carboligase" question is discussed. *l*(+)-Alanine, *l*(−)-aspartic acid, and (+)-NH_2·CHPh·CO_2H are more or less rapidly racemised by hot AcOH or $AcCO_2H$; *l*(−)-leucine is more stable. H. B.

Hydrogenation of acetylenic compounds. XXXIII. Synthesis and catalytic hydrogenation of acetylenic hydroxy-acids. J. S. Salkind and B. I. Michantiev (*J. Gen. Chem. Russ.*, 1941, **11**, 92—98).—A solution of (:C·MgBr)$_2$ when saturated with CO_2–$COMe_2$ mixture yields *γ-hydroxy-γ-methyl-*Δ^{α}*-pentinene-α-carboxylic acid*, an oil (*amide*, m.p. 72—73°), converted by hydrogenation (Pd and Pt) into *γ-iso*hexolactone. When $COPh_2$ replaces $COMe_2$ in the above reaction the product is *γ-hydroxy-γγ-diphenyl-*Δ^{α}*-butinene-α-carboxylic acid*, m.p. 78—80° (*amide*, m.p. 96—97°), hydrogenated to OH·CPh_2·$[CH_2]_2$·CO_2H. R. T.

Alkyl carbonates in synthetic chemistry. II. Condensation with ketones. Synthesis of β-keto-esters. V. H. Wallingford, A. H. Homeyer, and D. M. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 2252—2254; cf. following abstract).—The reaction, COMeR + Et_2CO_3 (or Me_2CO_3) + NaOEt → COR·CHNa·CO_2Et + 2EtOH, is realised in yields up to 74% by heating COMeR in an excess of Et_2CO_3 with NaOEt, NaOEt–EtOH, or NaOMe with continuous removal of EtOH. The method is limited by (*a*) self-condensation of very reactive ketones and (*b*) formation of ethers and $NaEtCO_3$ at >100° when reaction is "forced" for non-reactive ketones. *O*-Carboxylation and subsequent decarbomethoxylation may occur; thus COPhEt, COPhPr, and *cyclo*hexanone give 25%, 15%, and only (20%) esters of type CO_2Et·O·CPh:CR. In examples R = Pr^{β}, Bu^{γ}, Bu^{β}, *n*-amyl, CH_2Bu^{γ}, Ph, *p*-C_6H_4Me, -C_6H_4Cl, -C_6H_4·OMe, and -C_6H_4·OEt; $COEt_2$, $COPr^{\alpha}_2$, COPhEt, COPhPr, COPh·CH_2Ph, $CO(CH_2Ph)_2$, and *cyclo*hexanone are also used. The following are incidentally described. *Et β-keto-δδ-dimethyl*-n-*hexoate*, b.p. 104—105°/15 mm.; *Et* p-*ethoxybenzoylacetate*, m.p. 53—54°; 1-*phenyl*-3-iso*propyl*-, m.p. 81—83°, -*neopentyl*-, m.p. 138—140°, and -*p*-chlorophenyl-5-pyrazolone, m.p. 161° (lit. 140°); 3-p-*ethoxyphenyl*-5-iso*oxazolone*, m.p. 135—136°. When KOPr–PrOH is used, *n*-C_6H_{13}·COMe gives Pr^{α} *β-keto*-n-*nonoate*, b.p. 104—105°/15 mm. When KOBu–BuOH is used, COPhMe gives Bu^{α} *benzoylacetate*, b.p. 120—125°/1 mm. R. S. C.

Alkyl carbonates in synthetic chemistry. I. Condensation with organic esters. Synthesis of malonic esters. V. H. Wallingford, A. H. Homeyer, and D. M. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 2056—2059).—The reaction, CH_2R'·CO_2R + R_2CO_3 + NaOR (or NaOR–ROH) ⇌ CR′Na$(CO_2R)_2$ + 2ROH, is forced to the right by heating under reflux in an excess of R_2CO_3 with continuous removal of the alcohol formed and then becomes preparative for CHR′$(CO_2R)_2$. The method is particularly good if R′ = aryl, but succeeds in the purely aliphatic series up to Et and Bu stearate and Et oleate. In examples, R = Et, Pr, or Bu. In the aliphatic series *C*-alkylation by R_2CO_3 may also occur; thus, $Pr^{\alpha}CO_2Et$ gives CHEt$(CO_2Et)_2$ 45 and CEt$_2$$(CO_2Et)_2$ 10, *n*-C_5H_{11}·CO_2Et gives CHBu$^{\alpha}$$(CO_2Et)_2$ 26 and CEtBu$^{\alpha}$$(CO_2Et)_2$ 34, $Bu^{\beta}CO_2Et$ gives CHPr$^{\beta}$$(CO_2Et)_2$ 30 and CEtPr$^{\beta}$$(CO_2Et)_2$ 10, and *iso*-C_5H_{11}·CO_2Et gives *iso*-C_5H_{11}·CO_2Et 30 and *iso*-C_5H_{11}·CEt$(CO_2Et)_2$ 45%. Acylation or alkylation of the CR′Na(CO_2Et_2) produced can be effected without isolation of the CHR′$(CO_2Et)_2$. CHR′R″·CH_2·CO_2Et reacts, but not CR′$_3$·CO_2Et (*e.g.*, $Bu^{\gamma}CO_2Et$) or CHR′R″·CO_2Et (CHPhEt·CO_2Et, CHEt$_2$·CO_2Et). EtOAc gives $CH_2(CO_2Et)_2$ 25 and $CH(CO_2Et)_3$ 10, $CH_2(CO_2Et)_2$ gives $CH(CO_2Et)_3$ 10, and Et_2 sebacate gives CO_2Et·$[CH_2]_7$·$CH(CO_2Et)_2$ (b.p. 185—198°/1·5 mm.) 60%. n-*Decylmalonic acid*, m.p. 118—119·5°, *Et*$_2$ p-*iodo*-, b.p. 165°/1·5 mm., and 3 : 4-*dimethoxy-phenylmalonate*, b.p. 170°/1 mm., are incidentally described. R. S. C.

Grignard synthesis of glucosaccharic acid from *l*-arabinose. A. M. Gachokidze (*J. Gen. Chem. Russ.*, 1941, **11**, 109—116).—*l*-Arabinosazone and HCl yield l-*arabosone*, a syrup, oxidised by aq. Br to *α-keto*-l-*arabonic acid*, a syrup, $[\alpha]_D$ −61·2° in H_2O (*Ca* and *Ba* salts; *phenylhydrazide-phenylhydrazone*, m.p. 131°; *Ac*$_2$ derivative, m.p. 165°), which with Me_2SO_4 affords *Me α-keto-γδε-trimethylarabonate*, a syrup, $[\alpha]_D$ −59·8° in $CHCl_3$. With MgMeI in Et_2O–$CHCl_3$ this gives *Me γδε-trimethylsaccharate*, a syrup, $[\alpha]_D$ −10·5° in $CHCl_3$, hydrolysed by 8% H_2SO_4 to the *acid*, a syrup, $[\alpha]_D$ −21·4° (*Ca* and *Ba* salts), reduced by HI to *δ-hydroxypentane-β-carboxylic acid*, m.p. 139° (*Ba* salt). R. T.

Identification of carbonyl compounds by the use of 3-carbohydrazido-1-methylpyridinium *p*-toluenesulphonate. C. F. H. Allen and J. W. Gates, jun. (*J. Org. Chem.*, 1941, **6**, 596—601).—3-*Carbohydrazido*-1-*methylpyridinium* p-*toluenesulphonate* (**I**), m.p. 160° (metastable variety, m.p. 130—131°), is obtained by the successive action of *p*-C_6H_4Me·SO_3Me and N_2H_4,H_2O on Et nicotinate in boiling EtOH. It reacts with many CO compounds (**II**) in boiling EtOH, giving well-cryst. products which are usually crystallised from boiling EtOH and from which (**II**) are smoothly regenerated by warm dil. acids. They may be readily converted into other derivatives of (**II**); *e.g.*, the 2 : 4-dinitrophenylhydrazone may be made by warming the compound with dil. mineral acid and adding 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH·NH_2 directly to the resulting solution. The *-hydrazones* of the following -aldehydes have been characterised: *acet*-, m.p. 187°; *prop*-, m.p. 171°; n-*but*-, m.p. 168°; iso*but*-, m.p. 173°; n-, m.p. 142°, and iso-, m.p. 159°, *-valer*-; n-*hex*-, m.p. 153°; n-*hept*-, m.p. 160°; n-*oct*-, m.p. 154°; n-*non*-, m.p. 152°; n-*dec*-, m.p. 152°; n-*undec*-, m.p. 142°; n-*dodec*-, m.p. 145°; n-*tetradec*-, m.p. 142°; *α-methyl*-n-*non*-, m.p. 132°; *α-ethyl*-n-*but*-, m.p. 137°; *α-ethyl*-n-*hex*-, m.p. 131°; *croton*-, m.p. 193°; *α-methyl-β-ethylacr*-, m.p. 182°; *α-ethyl-β*-n-*propylacr*-, m.p. 197°; *citronellal*, m.p. 142°; n-Δ^{ω}-*undecylen*-, m.p. 145°; *furfur*-, m.p. 164°; *benz*-, m.p. 211°; *cumin*-, m.p. 259°; *phenylacet*-, m.p. 165°; *hydratrop*-, m.p. 125°; *β-phenylprop*-, m.p. 160°; *cinnam*-, m.p. 235°; p-iso*propylcinnam*-, m.p. 241°; *α*-n-*propylcinnam*-, m.p. 187°; *α*-n-*butylcinnam*-, m.p. 163°; *α*-n-*amylcinnam*-, m.p. 126°;

α-n-*hexylcinnam-*, m.p. 113°. The *-hydrazones* of the following ketones are described: cyclo*pentanone*, m.p. 181°; cyclo*hexanone*, m.p. 146°; cyclo*pentadecanone*, m.p. 144°; 2-*heptyl*cyclo*pentanone*, m.p. 136°; iso*phorone*, m.p. 156°; *COMe*$_2$, m.p. 166°; *Me octyl*, m.p. 109°, *Me nonyl*, m.p. 110°, and *Me decyl*, m.p. 111°, *ketone*; β-*ionone*, m.p. 147°; *Ac*$_2$, m.p. 264°; *CH*$_2$*Ac*$_2$, m.p. 212°; *COPhMe*, m.p. 191°; p-sec.-*amylacetophenone*, m.p. 143°; *CH*$_2$*BzCl*, m.p. 120°; 2 : 4-*dimethylphenacyl chloride*, m.p. 196°; *COMe·CH*$_2$*Cl*, m.p. 135°; *COMe·CHCl*$_2$, m.p. 115°; *CH*$_2$*Cl·COEt*, m.p. 137°; *CH*$_2$*Ac·CH*$_2$*·CO*$_2$*Et*, m.p. 136°; *CH*$_2$*Ac·CH*$_2$*·CO*$_2$*Me*, m.p. 160°; β-*chloropropiophenone*, m.p. 171°. (I) does not react or gives non-cryst. products with the following: CH_2O, CH_2BzBr, α-ionone, technical ionone, Me and Ph vinyl ketone, heptylideneacetone, 2-heptylidene*cyclo*pentadecanone, mesityl oxide, diacetone alcohol, hydroxycitronellal, glucose, COMe·CH:CHPh, $CH_2Ac·CH_2·CO_2H$, phorone, fenchone, $COBu^{\alpha}_2$, $COBu^{\beta}_2$, chloral, and 2 : 5-dimethylfuran. M.p. are corr. H. W.

Catalysis of aldol condensation of acetaldehyde by amino-acids. E. V. Budnitzkaja (*Biochimia*, 1941, **6**, 146—154).—At 35—37° and neutral reaction, NH_2-acids catalyse the conversion of MeCHO into aldol (I), glycine being more active than alanine, which is more active than aspartic acid. The rate of conversion increases with increase in p_H and NH_2-acid concn. Products of higher mol. wt. than (I) are also produced. Org. N compounds other than NH_2-acids (*e.g.*, amines, amides, and to a small extent peptones, diketopiperazine, and ovalbumin) also catalyse the conversion. The action depends on the enolisation of MeCHO by the catalysts. NH_2-acids or analogous substances possibly catalyse the synthesis of C chains in the living cell. W. McC.

Semicarbazone of the methyl ester of azelaic half-aldehyde. F. Bergmann (*J. Amer. Chem. Soc.*, 1941, **63**, 2279).—$CO_2Me·[CH_2]_7·CHO$, b.p. 159—164°/26 mm. (*semicarbazone*, m.p. 107°), is obtained from Me θι-dihydroxystearate by $Pb(OAc)_4$. R. S. C.

Effect of structure on reactivity of carbonyl compounds; temperature coefficients of rate of formation of semicarbazones.—See A., 1941, I, 474.

Catalytic hydrogenation of organic compounds. I. Hydrogenation of acetone. K. Akashi (*Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 422—430).—The composition of Ni catalysts exercises a marked influence on the reaction products. The following substances are obtained by hydrogenating $COMe_2$ with the catalysts and at the temp. indicated: Ni (110°) $Pr^{\beta}OH$, (300°) CH_4; Ni + B_2O_3 (210°) C_3H_8, (290°) C_3H_8, CH_4; Ni + ThO_2 + kieselguhr (200°) C_3H_8; Ni + Al_2O_3 + kieselguhr (165°) $Pr^{\beta}OH$, CH_4; Ni + Al_2O_3 (1 : 5) (200°), Cu + Al_2O_3 (1 : 5) (200°), or Ni + TiO_2 (230°) $COMeBu^{\beta}$, $COBu^{\beta}_2$. F. L. U.

Photo-decomposition of gaseous acetone.—See A., 1941, I, 480.

Keto-ethers. VIII. Preparation of γ-chloro-α-ethoxypropyl alkyl ketones. R. C. Wilson with H. R. Henze (*J. Amer. Chem. Soc.*, 1941, **63**, 2112—2113; cf. A., 1939, II, 403).—CH_2:CH·CHO and HCl–EtOH give $Cl·[CH_2]_2·CHCl·OEt$ (66%), b.p. 64—65°/18 mm., converted by AgCN (not CuCN) in Et_2O into *γ-chloro-α-ethoxybutyronitrile* (70%), b.p. 68—70°/3 mm., which with MgRBr in Et_2O gives 40—75% of *Me*, b.p. 68°/4 mm., *Et*, b.p. 86—87°/8 mm., Pr^{α} (I), b.p. 95—96°/6 mm., Pr^{β}, b.p. 90—91°/8 mm., Bu^{α} (II), b.p. 96—98°/4 mm., Bu^{β}, b.p. 94—95·5°/5 mm., *CHMeEt*, b.p. 90—91°/4 mm., n-, b.p. 112—113°/6 mm., and iso-*amyl*, b.p. 98—100°/5 mm., *γ-chloro-α-ethoxy-n-propyl ketone*. Of these ketones, only (I) and (II) give *semicarbazones* [m.p. 130° (corr.; decomp.) and 104° (corr.; decomp.), respectively]. Physical consts. of the products are given. R. S. C.

Anomalous reactions of α-bromo-ketones. II. Methyl α-bromohexyl ketone. T. I. Temnikova and V. I. Veksler (*J. Gen. Chem. Russ.*, 1941, **11**, 3—8).—$COMe·C_6H_{13}$-*n* in CCl_4 and Br yield *Me α-bromohexyl ketone*, b.p. 92—92·5°/11 mm. [*semicarbazone*, m.p. 116—118° (decomp.)], which with KOAc or KOBz in EtOH (4—12 hr. at the b.p.) affords *γ-acetoxy-*, b.p. 109—110°/11 mm., or *γ-benzoyloxy-β-keto-octane*, b.p. 148·5—149·5°/1·5 mm. With MgMeBr in Et_2O these esters yield *β-methyloctane-βγ-diol*, b.p. 119—120°/12 mm. R. T.

Structure of diketen from spectroscopic evidence. M. Calvin, T. T. Magel, and C. D. Hurd (*J. Amer. Chem. Soc.*, 1941, **63**, 2174—2177).—Absorption spectra of ββδ-trimethylpentane solutions of diketen (I), β-butyrolactone, CH_2:CH·OAc, and dehydroacetic acid show that the most probable structure of (I) is $\begin{matrix} CMe{:}CH \\ O{-}{-}CO \end{matrix}$ with easy transformation into CHAc:CO. W. R. A.

Acyl exchanges between esters and 1 : 3-diketones and β-keto-esters. S. M. McElvain and K. H. Weber (*J. Amer. Chem. Soc.*, 1941, **63**, 2192—2197).—The reaction RCO_2R' + COR″·CHNa·COR‴ → COR″·CHNa·COR + R‴CO_2R' is effected by heating the pure enolate and ester with continuous removal of the more volatile constituent (20° rise of temp.); interaction is incomplete owing to solidification of the product; formation of some R′OH indicates presence of ONa·CR(OR′)·CH(COR″)·COR‴ as intermediate. The similar exchange, COR·CR′Na·CO_2R″ (*A*) + R‴CO_2Et → COR‴·CR′Na·CO_2R″ + RCO_2Et, is more facile and has preparative val.; an intermediate of the type, COR‴·CH_2·C(ONa)(OEt)·CHR′·CO_2R″ [from (*A*; R = Me)], is probable. COPh·CHNa·COMe with EtOBz at 150° gives EtOAc (49) and CH_2Bz_2 (48%), with *p*-$C_6H_4Cl·CO_2Et$ (I) at 145° gives EtOAc (33%), *p*-$C_6H_4Cl·CO·CH_2Bz$, and much *di-p-chlorobenzoylmethane*, m.p. 158—159° [formed by a reversed Tischtschenko reaction; also obtained from (I) by NaOEt at 160—180°], with $CH_2Ph·CO_2Et$ at 150° gives EtOAc (43%), COPh·CH_2·CO·CH_2Ph, $CH_2(CO·CH_2Ph)_2$, and EtOBz (40%), and with Et 2-furoate (II) at 140° gives EtOAc (51) and ω-2-furoylmethylacetophenone (47%). $CHAc_2Na$ and (II) at 135° give EtOAc (72), 2-furoylacetone (32), and difuroylmethane (34%). $CHNaBz_2$ does not react with EtOAc at 125° or with (I) at 180°. CHAcNa·CO_2Et and EtOBz at 100—155° give EtOAc (46—56) and CHBz·CO_2Et (33—49%). CEtAcNa·CO_2Et and EtOBz at 140° give EtOAc (10), $Pr^{\alpha}CO_2Et$ (60), and CHBzNa·CO_2Et (61%). *Et α-isobutyryl-n-butyrate* (III) and EtOBz at 145° give $Pr^{\beta}CO_2Et$ (72) and CHEtBz·CO_2Et (50%). CHAcNa·CO_2Et with (II) at 135° gives EtOAc (66) and Et 2-furoylacetate (38%), and with Et 3-pyridylacetate at 160° gives EtOAc (73), 3-ω-carbethoxyacetylpyridine (4%), and much tar. $CHNa(CO_2Et)_2$ and EtOBz at 135° give Et_2CO_3 (10) and $CH_2Bz·CO_2Et$ (16%). (III), b.p. 105—107°/18 mm., is obtained from $Pr^{\beta}CO_2Et$ and $Pr^{\alpha}CN$ by way of α-iso*butyryl*-n-*butyronitrile*, b.p. 89—90°/11 mm. R. S. C.

Action of hydrogen peroxide in *tert.*-butanol on *d*-glucal and its triacetate in presence of osmium tetroxide. R. C. Hockett, A. C. Sapp, and S. R. Millman (*J. Amer. Chem. Soc.*, 1941, **63**, 2051—2053).—*d*-Glucal triacetate, 2—3 mols. (1 mol. causes incomplete reaction) of 5·63% H_2O_2–$Bu^{\gamma}OH$, and a trace of OsO_4 give 55—60% of *d*-glucose (I) (isolated as β-*d*-glucose penta-acetate), a trace of mannose (II), and 5% of volatile acids (III). *d*-Glucal gives similarly (1—2 mols. of H_2O_2) (I) (8—18%), (II) (2%), and (III) (8%). R. S. C.

***D*-Galactosan<1 : 5>β<1 : 3>, a new anhydride of *D*-galactose.** R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **63**, 2241—2242).—Pyrolysis (cf. A., 1941, II, 242) of α-*D*-galactose gives D-*galactosan*<1 : 5>β<1 : 3> (I), m.p. 174—175° (corr.), $[\alpha]_D^{20}$ +54·9° in H_2O, and a small amount of *D*-galactosan<1 : 5>β<1 : 6> (isolated as CMe_2: derivative). The structure of (I) is proved by formation of a 2 : 4 : 6-*triacetate*, m.p. 79—80° (corr.), $[\alpha]_D^{20}$ +144·9° in $CHCl_3$ (correct mol. wt. in camphor), failure to react with Fehling's solution or $NaIO_4$, and hydrolysis by 0·2N-HCl at 100° (not 20°) to *D*-galactose. R. S. C.

Isolation of crystalline cardiac glucoside from *Adonis vernalis* and its identification as cymarin.—See A., 1941, III, 819.

Synthesis of glucosido-2-glucose. A. M. Gachokidze (*J. Gen. Chem. Russ.*, 1941, **11**, 117—126).—1-Chloroglucose 3 : 4 : 6-triacetate in Et_2O and AgOAc yield *glucose* 1 : 3 : 4 : 6-*tetra-acetate*, m.p. 138°, a solution of which in $CHCl_3$ when shaken with glucose 2 : 3 : 4 : 6-tetra-acetate and $ZnCl_2$ affords glucosido-2-glucose 2′ : 3′ : 4′ : 6′ : 1 : 3 : 4 : 6-octa-acetate (I), hydrolysed by NaOMe in MeOH to (1 : 5)-glucosido-2-(1 : 5)-glucose (*phenylhydrazone*, m.p. 178°). This is oxidised by aq. Br to *glucosido-2-gluconic acid*, a syrup, which is methylated (Me_2SO_4) to *Me* 2 : 3 : 4 : 6-*tetramethylglucosido*-α-(1 : 3 : 4 : 6-*tetramethyl*)*gluconate*, a syrup, $[\alpha]_D$ +95·9° in $CHCl_3$. (I) is heated with NH_2OH in EtOH and the solution is evaporated to a syrup, which is heated at 110° with NaOAc and

Ac_2O, yielding *glucosido-2-gluconitrile* 2′ : 3′ : 4′ : 6′ : 1 : 3 : 4 : 6-*octa-acetate*, m.p. 149—151°. This is heated with NaOEt in EtOH, the solution is diluted with H_2O, extracted with $CHCl_3$, and the extract is shaken with AgOAc in Ac_2O, yielding glucosido-2-arabinoside (*Ac*$_8$ derivative, m.p. 168—180°, $[\alpha]_D$ −21·5° in $CHCl_3$). R. T.

Glucosides of the œstrone series. A. Hagedorn, F. Johannessohn, E. Rabald, and H. E. Voss (*Z. physiol. Chem.*, 1940, **264**, 23—30; cf. A., 1939, II, 358).—Acetobromoglucose (**I**), œstrone (**II**), and 2N-KOH in $COMe_2$ at room temp. for 12 hr. give 10% of *œstrone glucoside tetra-acetate*, m.p. 214°, $[\alpha]_D^{17}$ +64·64° in $CHCl_3$ [also obtained in 63% yield from (**I**), (**II**), and Ag_2CO_3 in quinoline at 60°], which when reduced (H_2, PtO_2, EtOH) affords *œstradiol glucoside*, m.p. 234°. The physiological activity of these and related compounds is studied (see A., 1941, III, 1010.) H. B.

Polysaccharides synthesised by *Streptococcus salivarius* **and** *S. bovis*.—See A., 1941, III, 804.

Synthesis of *N*-substituted choline carbamates and trimethyl-β-anilinoethylammonium chloride. D. B. Sprinson (*J. Amer. Chem. Soc.*, 1941, **63**, 2249—2251).—$ClCO_2\cdot[CH_2]_2\cdot Cl$ (1 mol.) with the appropriate amine (2 mols.) in C_6H_6 or amine hydrochloride (1 mol.) and Na_2CO_3 (1·05 mol.) in H_2O at <0° gives β-chloroethyl methyl-, b.p. 100—102°/11 mm., *dimethyl-*, b.p. 80—81°/9 mm., ethyl-, b.p. 102—104°/11 mm., *diethyl-*, b.p. 66—68°/1 mm., *n*-propyl-, b.p. 83—85°/1 mm., n-*butyl-*, b.p. 97—99°/1 mm., *pentamethylene-*, b.p. 91—93°/2 mm., and -phenyl-carbamate, b.p. 133—135°/2 mm. With NaI in dry $COMe_2$ or MeOH at <0° these give *β-iodoethyl dimethyl-*, b.p. 109—110°/4 mm., n-*propyl-*, m.p. 50°, b.p. 98°/0·07 mm., n-*butyl-*, m.p. 46°, b.p. 106—108°/0·07 mm., *pentamethylene-*, b.p. 115—117°/2 mm., and *phenyl-carbamate*, m.p. 77—79°. The chloroethyl carbamates with NMe_3 at 50—70°, usually in $COMe_2$, give trimethyl-β-methyl-, m.p. 178—180° (corr.) (lit. 171—173°), *-dimethyl-*, m.p. 185—187° (corr.), *-ethyl-*, m.p. 198—200° (corr.), and *-diethyl-*, m.p. 131—133° (corr.), *-carbamylethylammonium chloride*. The I-compounds at room temp. give similarly *trimethyl-β-diethyl-*, m.p. 121—123° (corr.), -n-*propyl-*, softens at 85—87°, m.p. 87—89° (corr.), -n-*butyl-*, m.p. 101—103° (corr.), *-pentamethylene-*, m.p. 200—201° (corr.), and *-phenyl-*, m.p. 131—132° (corr.), *-carbamylethylammonium iodide*. *Triethyl-β-diethyl-*, m.p. 99—101° (corr.), and *-pentamethylene-carbamylethylammonium iodide*, m.p. 95—97° (corr.), are similarly obtained, but $NHPh\cdot CO_2\cdot[CH_2]_2\cdot I$ and NEt_3 in $COMe_2$, even at −10° to −5°, give NEt_3,HI and 3-phenyloxazolid-2-one. $NHPh\cdot[CH_2]_2\cdot Cl$ was not obtained from $NHPh\cdot[CH_2]_2\cdot OH$ by $SOCl_2$; its *hydrochloride*, m.p. 157—159°, with NMe_3 in $COMe_2$ at room temp. and later 70—75° gives *β-anilinoethyltrimethylammonium chloride hydrochloride*, m.p. 221—222° (corr.; decomp.). *N*-Substitution of choline carbamate abolishes the muscarine, but does not affect the stimulating nicotine, activity. R. S. C.

Aryl and alkyl ethers of β-methylcholine. A. R. Goldfarb (*J. Amer. Chem. Soc.*, 1941, **63**, 2280—2281).—Passage of $NHMe_2$ into propylene oxide and MeOH at 60° gives *β-dimethylamino*iso*propyl alcohol* (70%), b.p. 124·5—126°/758 mm., converted by $SOCl_2$ in $CHCl_3$ at −5° to 0° into the cryst. *chloride hydrochloride* (>70%), which with anhyd. NaOR (2·2 mols.) in ROH or NaOMe–MeOH–ArOH at 100° gives *dimethyl-β-methoxy-*, b.p. 113—116° (*methiodide*, m.p. 155·5—156°), *-ethoxy-*, b.p. 133—135° (*methiodide*, m.p. 144·5°), -iso*propoxy-*, b.p. 140—145°/758 mm. (*methiodide*, m.p. 145·5°), -n-*butoxy-*, b.p. 55—58°/18 mm. (*methiodide*, m.p. 156·5—157°), *-phenoxy-*, b.p. 143—144°/18 mm. (*methiodide*, m.p. 139·5—140°), -o-, b.p. 132—135°/18 mm. (*methiodide*, m.p. 141—142°), -m-, b.p. 136—140°/12 mm. (*methiodide*, m.p. 130—131°), and -p-*tolyloxy-*, b.p. 140—143°/15 mm. (*methiodide*, m.p. 140—141°), -n-*propylamine*. $OH\cdot CHMe\cdot CH_2\cdot NEt_2$ (modified prep.), b.p. 62·5—63·5°/22 mm., gives similarly the *chloride hydrochloride* and thence *diethyl-β-methoxy-*, b.p. 46—47°/12 mm., *-ethoxy-*, b.p. 70—72°/18 mm', -iso*propoxy-*, b.p. 60—63°/10 mm. (*ethiodide*, m.p. 129—130°), -n-*butoxy-*, b.p. 63—65°/10 mm., *-phenoxy-*, b.p. 125—126°/11 mm., -o-, b.p. 141°/12 mm. (*ethiodide*, m.p. 128°), -m-, b.p. 141—142°/10 mm. (*ethiodide*, m.p. 129—130°), and -p-*tolyloxy-*, b.p. 144—146°/14 mm. (*ethiodide*, m.p. 138—139°), -n-*propylamine*. R. S. C.

Production and properties of additive compounds of amino-acids with sugars. A. Kuzin and O. Poljakova (*Biochimia*, 1941, **6**, 113—121).—In conc. solutions at alkaline reaction, NH_2-acids yield additive compounds, isolated as Ca and Ba salts, with monosaccharides. The compounds, which readily hydrolyse in acid and neutral media, are of the *N*-glucoside type. W. McC.

Ammonolysis. II. Ammonolysis of α-halogeno-acids in liquid ammonia. H. H. Sister and N. D. Cheronis (*J. Org. Chem.*, 1941, **6**, 467—478; cf. A., 1941, II, 243).—For all except very high mol. ratios of acid to NH_3 the yield of glycine (**I**) from $CH_2Cl\cdot CO_2H$ and NH_3 is < that from the reaction in aq. NH_3 using the same mol. ratio. The extent of conversion into (**I**) remains practically const. in the anhyd. system until the ratio acid : NH_3 is decreased to >0·05, whereas in aq. NH_3 a steady rise in % conversion with decreasing ratio of acid : NH_3 is obtained throughout. The yield of (**I**) is definitely increased by use of 2 mols. of an NH_4 salt and there is a further increase when 4 mols. are used. 6 mols. of NH_4NO_3 produce no further increase, whilst 6 mols. of NH_4Cl cause only a slightly larger effect than 4 mols. The effect of 2 mols. of NH_4NO_3 is confirmed by observations with $CH_2Br\cdot CO_2H$ and $CHMeCl\cdot CO_2H$. Appreciable increase in the yield of (**I**) is not caused by the presence of NaCl or $NaNO_3$, showing that the effect is not due to electrolytes in general but to NH_4^+. Liquid NH_3 is more basic than H_2O and hence has a higher affinity for protons, thus favouring the existence of the ion $NH_2\cdot CHR\cdot CO_2^-$ (*A*) rather than the zwitterion $^+NH_3\cdot CHR\cdot CO_2^-$ (*B*). Since (*B*) has a free pair of electrons on N it is open to further reaction with the halogen compound, thus leading to the formation of *sec.* and *tert.* ammonolytic products. If, however, $[NH_4^+]$ is very high the equilibrium is somewhat forced from (*B*) towards (*A*), thus reducing (*B*) concn. and inhibiting the *sec.* and *tert.* ammonolytic changes. NH_4 salts are acids in liquid NH_3 and their effect on the ammonolysis of halogen acids in liquid NH_3 is analogous to the p_H effect observed in aq. systems. The pronounced increase in % conversion by $NH_2\cdot CO_2NH_4$ is difficult to explain. Experiments with $CH_2Br\cdot CO_2H$, $CHMeBr\cdot CO_2H$, $CHEtBr\cdot CO_2H$, $CHPr^{\alpha}Br\cdot CO_2H$, and $CHPr^{\beta}Br\cdot CO_2H$ show that ammonolysis in liquid NH_3 is more promising with the less reactive acids (**II**) of higher mol. wt. than with $CH_2Cl\cdot CO_2H$, as there is less tendency towards the formation of *sec.* and *tert.* products. With (**II**) liquid NH_3 is superior to aq. NH_3, since the reaction is faster and temp. may be raised without fear of hydrolytic side reactions. With $CH_2Br\cdot CO_2H$ and $CH_2Cl\cdot CO_2H$ a change in the ratio acid : NH_3 from 1 : 12 to 1 : 20 does not affect the % conversion into (**I**). With $CHMeBr\cdot CO_2H$ a marked improvement in the yield of NH_2, derivative is obtained with use of 1 : 20 rather than 1 : 12, and a still greater effect is produced with this change of ratio with $CHEtBr\cdot CO_2H$. $CHPr^{\beta}Br\cdot CO_2H$ gives an 84·5% conversion at a ratio 1 : 8, and an almost quant. conversion at 1 : 20. H. W.

Microscopy of the amino-acids and their compounds; silver salts. K. Inouye, R. Sunderlin, and P. L. Kirk (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 587—588; cf. A., 1939, II, 470).—Cryst. NH_2-acids dissolved in H_2O, and a small crystal of $AgNO_3$, give cryst. Ag salts. Cryst. form of *Ag* salts of the following is given (nearly all are needles): alanine, arginine, aspartic acid, glutamic acid (**I**), glycine, histidine (**II**) (2 forms of Ag salt), hydroxyvaline, *iso*leucine, leucine, norleucine, norvaline, phenylalanine, hydroxyproline, serine, tryptophan, tyrosine (**III**), and valine [anisotropic with parallel extinction and elongation (−)], and di-chloro-, -bromo-, and -iodotyrosine [elongation (+)]. Characteristic crystals are those from (**I**), (**II**), (**III**), and the dihalogenotyrosines. Cystine, cysteine, lysine, *iso*serine, proline, and methionine do not give Ag salts. A. T. P.

New method for isolating *l*(+)-lysine. A. C. Kurtz (*J. Biol. Chem.*, 1941, **140**, 705—710).—*l*(+)-Lysine is isolated from protein hydrolysates by conversion of the NH_2-acids into their Cu salts by $CuCO_3,Cu(OH)_2$, and subsequent benzoylation by BzCl–aq. NaOH at 0°. The ε-benzoyl-*l*-(+)-lysine–Cu complex is decomposed by aq. H_2S to ε-benzoyl-*l*(+)-lysine, m.p. 247—260° (impurities remain in mother-liquor), converted by refluxing with aq. HCl into *l*(+)-lysine dihydrochloride, m.p. 192—193°. Yields of lysine from various proteins are recorded. No insol. derivative is obtained when solutions of arginine–Cu chloride or hydroxyproline–Cu are treated with BzCl–aq. NaOH. A. T. P.

Special lability of serine and threonine towards alkali, when in peptide combination. B. H. Nicolet and L. A. Shinn (*J. Biol. Chem.*, 1941, **140**, 685—686).—Serine and threonine are destroyed by alkali when in peptide combination but not when free. It is suggested that seryl peptide first loses H_2O and is then hydrolysed. E. M. W.

Deuteromethionine and deuterocholine.—See A., 1941, III, 899.

Palmitoyl- and stearoyl-glycylglycine and -diglycylglycine. A. Koebner (*J.C.S.*, 1941, 564—566).—Palmitoylglycine Me ester, m.p. 104—105°, and 5% NH_3–MeOH at room temp. give *palmitoylglycinamide*, m.p. 161—162°. Stearoylglycine, new m.p. 125—126°, affords the Me ester, m.p. 75—76°, and thence the *amide*, m.p. 157—158°. Glycine anhydride and palmitoyl (**I**) or stearoyl chloride (**II**) in 2N-NaOH–Et_2O yield *palmitoyl-*, m.p. 171—172° (decomp.) [and thence (HCl–MeOH) the *Me* ester, m.p. 139°, and (MeOH–NH_3 in sealed tube) *amide*, m.p. 199—200°], or *stearoyl-glycylglycine*, m.p. 168° (softens at 160°) (*Me* ester, m.p. 135—136°; *amide*, m.p. 196°), respectively. Diglycylglycine and (**I**) or (**II**) in 2N-NaOH–Et_2O afford *palmitoyl-*, m.p. 209° (decomp.), or *stearoyl-diglycylglycine*, m.p. 210°, respectively, which have not been esterified. A. T. P.

Formation of betaine from hydroxyamino-acids on methylation. H. D. Dakin (*J. Biol. Chem.*, 1941, **140**, 847—852).—Serine, threonine, *cis-* and *trans*-phenylserine, and hydroxyaspartic (**I**) and hydroxyglutamic acids form varying amounts of betaine on methylation, whereas cystine and cysteine produce considerable quantities of NMe_4·OH. N of (**I**) and, to a smaller extent, the phenylserines is also partly converted into NMe_4 salts. H. G. R.

Stereoisomeric forms of lanthionine. G. B. Brown and V. Du Vigneaud (*J. Biol. Chem.*, 1941, **140**, 767—771; cf. A., 1941, II, 188).—*p*-Nitrobenzoyl-*l*-serine, $[\alpha]_D^{20}$ +43·8° in aq. NaOH, is hydrolysed in 16% HBr and then esterified to *l*-serine Me ester hydrochloride, which is converted into *l*-β-chloro-α-aminopropionic acid hydrochloride (**I**) (free acid, $[\alpha]_D^{20}$ −15° in H_2O). *l*-Cystine when treated with Na in liquid NH_3 and then with aq. KOH under N_2 and (**I**) affords l(+)-*lanthionine* (**II**), decomp. 293—295° (darkens at 245°), $[\alpha]_D^{20}$ +8·6° in dil. NaOH (*Bz*$_2$ derivative, m.p. 202—204°). Benzyl-*d*-cysteine is reduced in liquid NH_3 with Na, and the *d*-cysteine produced is condensed with (**I**) to give d(−)-*lanthionine* (**III**), decomp. 293—295° (darkens at 245°), $[\alpha]_D^{21}$ −8·0° in dil. NaOH (*Bz*$_2$ derivative, m.p. 202—203°). Equal quantities of (**II**) and (**III**) in aq. NH_3 afford dl-*lanthionine*, decomp. 286—292° (darkens at 240°) (*Bz*$_2$ derivative, m.p. 183—184°). The *meso*-form assigned to the inactive isomeride prepared previously (*loc. cit.*) and also by Horn *et al.* (A., 1941, II, 188), is confirmed. A. T. P.

Reaction of arsenic trichloride with diazomethane. G. I. Braz and A. J. Jakubovitsch (*J. Gen. Chem. Russ.*, 1941, **11**, 41—44).—$AsCl_3$ and CH_2N_2 in Et_2O at 0° yield *chloromethylarsine dichloride*, b.p. 57—58°/16 mm., and *di(chloromethyl)-arsine chloride*, b.p. 86—88°/16 mm., from which *chloromethyl-*, sinters at 133—135°, and *di(chloromethyl)-arsinic acid*, m.p. 117—126° (decomp.), are prepared. R. T.

II.—HOMOCYCLIC.

Investigation of the *cyclo*hexane–methyl*cyclo*pentane equilibrium by the Raman effect.—See A., 1941, I, 467.

Dipole moments of some nitro- and amino-derivatives of benzene and naphthalene.—See A., 1941, I, 400.

Preparation of styrene by catalytic dehydrogenation of ethylbenzene. A. A. Balandin, N. D. Zelinski, G. M. Marukian, and O. K. Bogdanova (*J. Appl. Chem. Russ.*, 1941, **14**, 161—172).—Styrene is obtained in 50—55% yield by passing 1 : 2 PhEt–CO_2 or –N_2 mixtures over 1 : 4 Cu–CrO_3 catalyst at 650°, or over 1 : 19 V_2O_5–Al_2O_3 catalyst at 625°. ~15% of the PhEt is used up in side reactions involving production of CH_4, C_2H_6, and C_6H_6. R. T.

Pyrolysis of αaγ-triphenyl-Δ^{α}-propene. C. F. Koelsch and P. R. Johnson (*J. Org. Chem.*, 1941, **6**, 534—542).—Pyrolysis of CPh_2:CH·CH_2Ph (**I**) is scarcely observed at 450—460° under reduced pressure, but at atm. pressure the following are produced: PhMe, CPh_2:CH_2, $CHPh_2Me$, CH_2Ph_2, 1 : 2- (**II**) and 2 : 3-diphenylindene (**III**), identified by conversion into pure (**III**) by warming with KOH–EtOH and into 2 : 3-diphenyl-1-benzylideneindene by treatment with PhCHO and alkali. Oxidation (CrO_3) of the oils remaining after removal of the indenes gives BzOH, CH_2Ph·CO_2H, *o*-C_6H_4Bz·CO_2H, $COPh_2$, and *o*-$C_6H_4Bz_2$, indicating the presence of 1 : 3-diphenylindene (**IV**) and (**I**). The distillation residue contains a minute amount of a cryst. material, m.p. 280°, (**II**), and (**III**); oxidation of the non-cryst. remainder gives *o*-$C_6H_4Bz_2$ [indicating (**IV**)], BzOH, and anthraquinone (origin uncertain). Of compounds possible through coupling of radicals formed by cracking during pyrolysis only (**I**) is isolated. This is not regarded as evidence against the formation of free radicals, since coupling between two energy-rich fragments probably requires the assistance of a third body for the dissipation of energy. Further, the concn. of the radicals is low, so that their most likely fate is to become hydrogenated at the expense of the relatively abundant (**I**). Cyclisation of (**I**) probably results from the dehydrogenation of the acyclic hydrocarbon by the free radicals formed through cracking; this hypothesis is supported by a semi-quant. survey of all the pyrolysis products, which shows that a mol. is cyclised for every mol. which is cracked. Direct cyclisation should lead to 1 : 1-diphenylindene, which is not found, or to (**IV**), present only in small amount. The main cyclisation products are (**II**) and (**III**), easily interconvertible substances the formation of which from (**I**) necessitates the migration of Ph. Probably migration occurs after and not before cyclisation, since rearrangement before cyclisation would lead to CHPh:CPh·CH_2Ph, and either this substance or its cracking products, stilbene or $(CH_2Ph)_2$, would be isolated. Apparently the breaking of an open propylene chain is more readily effected than is displacement of Ph. To avoid the cleavage, the C chain along which Ph migrates must be part of a ring, and a cyclic structure thus appears essential for this type of rearrangement. Since C_6H_6 is not produced the migrating Ph does not separate as a free radical. H. W.

Attempted synthesis of αβγ-triphenyl-$\Delta^{\alpha\gamma}$-butadiene. Synthesis and properties of αβγ-triphenylallyl alcohol. F. Bergmann (*J. Org. Chem.*, 1941, **6**, 543—549).—CHPh:CPh·CHPh·OH (**I**) is obtained when the product of the action of MgPhBr on CHPh:CPh·CHO is decomposed with NH_4Cl, whereas when dil. H_2SO_4 is used and the residue is distilled in vac. 1 : 2-diphenylindene, m.p. 177°, results. (**I**) is also obtained from $Al(OPr^{\beta})_3$ and benzylidenedeoxybenzoin in $Pr^{\beta}OH$ and is converted by boiling Ac_2O into its *acetate* (**II**), m.p. 129°, and by MeOH containing a little conc. H_2SO_4 at room temp. into its *Me ether* (**III**), m.p. 96°. (**II**) and conc. H_2SO_4 afford 2 : 3-diphenylindene. Boiling HI with subsequent distillation under 5 mm. transforms (**I**), (**II**), or (**III**) into 1 : 2-diphenylhydrindene, m.p. 126°. With Na powder in Et_2O (**I**) appears to give a C·Na compound decomposed by EtOH to benzyldeoxybenzoin, m.p. 120°, and the α-form, m.p. 92°, of CH_2Ph·[CHPh]$_2$·OH. This with the β-variety, m.p. 86—89°, is obtained by the reduction (H_2–Pd–$BaSO_4$ in AcOH) of (**I**). (**III**) and Na in Et_2O give the product CHPh:CPh·CHPhNa (**IV**), transformed by CH_2O into *βγδ-triphenyl-Δγ-buten-α-ol* (**V**), m.p. 106°, which does not decolorise Br. It could not be satisfactorily dehydrated to CHPh:CPh·CPh:CH_2 (**VI**). (**V**) and boiling AcCl give an *acetate*, m.p. 94°, stable at 350°/atm. pressure. When (**V**) is boiled with Na in xylene and the filtered solution is treated successively with CS_2, MeI, and Ag powder, a liquid, b.p. 155°/0·2 mm., results which does not give satisfactory analytical results but may contain (**VI**), since it strongly decolorises Br; it does not give a picrate or an additive compound with maleic anhydride. The structure of (**III**) is established by its conversion by CH_2PhCl into CHPh:CPh·CHPh·CH_2Ph, m.p. 147—148°. H. W.

Preparation of chloromethylindenes and determination of their reactivities towards sodium iodide. C. F. Koelsch and R. V. White (*J. Org. Chem.*, 1941, **6**, 602—611).—The reactivity of a substituted 2- or 3-chloromethylindene towards NaI exceeds that of an alkyl chloride and lies in the range of reactivities of the substituted benzyl chlorides. Since the rate consts. are so highly dependent on apparently insignificant structural features of the chloromethylindenes, it is not possible to make a precise summarising statement. Gradual addition of Br to α-methylstilbene in AcOH at 60° followed by boiling the mixture gives *α-bromo-αβ-diphenyl-Δ^{α}-propene*, b.p. 153—156°/0·001 mm., the Grignard reagent from which is carbonated by solid CO_2 to *αβ-diphenylcrotonic acid*, m.p.

124—126°, which does not appear to be cyclised by $POCl_3$ in C_6H_6. Fluorenone (I) is converted by this Grignard reagent followed by boiling AcOH containing a few drops of conc. H_2SO_4 into *βγ-diphenyl-α-diphenylene-Δ^αγ-butadiene*, m.p. 197—198°, transformed by more prolonged action of AcOH–H_2SO_4 into *2-phenyl-1-diphenylene-3-methylindene* (II), m.p. 152·5—153·5°, oxidised by CrO_3 in AcOH at room temp. to BzOH and diphenylenephthalide, m.p. 220—222°. (II) is transformed by Br in $CHCl_3$ in direct sunlight and subsequent treatment with KOAc in boiling AcOH into *1-diphenylene-2-phenyl-3-acetoxymethylindene*, m.p. 172—173°, which is unchanged by HCl in boiling AcOH but converted by AcOH–conc. HCl at 150° into *2-phenyl-1-diphenylene-3-chloromethylindene*, m.p. 145·5—146·5°. (I) is transformed by the Grignard reagent (III) from CPh_2:CMeBr, b.p. 169—173°/13 mm., into the non-cryst. carbinol, converted by boiling AcOH–H_2SO_4 into *3-phenyl-1-diphenylene-2-methylindene*, m.p. 173—174·5°, which is transformed through the 2-CH_2Br and 2-*OAc·CH*$_2$ compound, m.p. 148·5—150°, into *3-phenyl-1-diphenylene-2-chloromethylindene*, m.p. 134—136°. $COPh_2$ is converted by (III) and subsequent treatment with boiling AcOH–H_2SO_4 into 1 : 1 : *3-triphenyl-2-methylindene*, m.p. 157—159·5°, oxidised by CrO_3 in hot AcOH to *o*-benzoyltriphenylacetic acid, m.p. 129° (decomp.), and *o-benzoyl-ααα-triphenylacetone*, m.p. 172—173·5°, and transformed by the usual steps into 1 : 1 : *2-triphenyl-2-bromomethyl-*, m.p. 154—156°, *-2-acetoxymethyl-*, m.p. 178·5—180°, and *-2-chloromethyl-*, m.p. 154—155·5°, *-indene*. spiro-*3-Phenyl-2-methylindene-1 : 9-xanthene*, m.p. 153·5—155°, is obtained from (III) and xanthone and converted successively into the *-2-OAc·CH*$_2$, m.p. 203·5—205°, and *-2′-CH*$_2$*Cl*, m.p. 144—145°, compounds. 1-Bromo-1 : 2 : 3-triphenylindene and MgMeI in boiling Et_2O–C_6H_6 afford *1-methyl-1 : 2 : 3-triphenylindene* (IV), m.p. 96—98°, which with 1 equiv. of Br in AcOH affords a *substance*, $C_{28}H_{21}Br$, m.p. 170—171° after softening at 162°, which fails to react with $AgNO_3$ in EtOH. Triphenylacrylophenone (V) and MgMeI give CPh_2:CPh·CPhMe·OH (VI), m.p. 96—98°, transformed by NaOAc and boiling Ac_2O into *ααβγ-tetraphenyl-Δ^αγ-butadiene*, m.p. 118·5—120°. This is oxidised by powdered $KMnO_4$ in $COMe_2$ to (V) and converted by H_2SO_4–AcOH into (IV), also obtained directly from (VI).

H. W.

Synthesis of growth-inhibitory polycyclic compounds. III. G. M. Badger (*J.C.S.*, 1941, 535—538).—1- and 2-$C_{10}H_7$·CHO [from $C_{10}H_7$·CH_2Br and $(CH_2)_6N_4$ in boiling AcOH] with 1- and 2-$C_{10}H_7$·CH_2·CO_2Na in Ac_2O at 130—140° yield *α-1-naphthyl-β-2-*, m.p. 215—216° (after sintering), *α-2-naphthyl-β-1-* (I), m.p. 213—214° (after sintering), and *αβ-di-1-naphthylacrylic acid*, m.p. 227—228°. (I) with Cu-bronze in quinoline at 240—250° yields *α-1-naphthyl-β-2-naphthylethylene*, m.p. 103—105°. 1-$C_{10}H_7$·CO·CH_2Ph with MeI in EtOH–NaOEt yields *1-α-phenylpropionylnaphthalene*, b.p. 172—173°/0·5 mm., which with MgMeI and MgEtI followed by dehydration (PBr_3 in $CHCl_3$) yields respectively *β-phenyl-γ-1-naphthyl-Δ^β-butene*, m.p. 68·5—70° (via *γ-phenyl-β-1-naphthylbutan-β-ol*, m.p. 97—99°), and *-Δ^β-pentene*, b.p. 161—164°/0·6 mm. 2-$C_{10}H_7$·CO·CH_2Ph similarly yields *2-α-phenylbutyrylnaphthalene*, m.p. 116—118°, *γ-phenyl-δ-2-naphthyl-Δ^γ-hexene*, b.p. 165—168°/0·5 mm., and *-Δ^γ-pentene*, b.p. 178—180°/1 mm. Fluorene and 1 : 2-benz- and 1 : 2 : 5 : 6-dibenz-fluorene are oxidised (SeO_2 in H_2O at 230—240°) to fluorenone (II) and 1 : 2-benz- (III) and 1 : 2 : 5 : 6-*dibenz-fluorenone*, m.p. 164—165°, respectively. (II) and (III) with MgMeI yield respectively 9-methyl-fluoren-9-ol and *-1 : 2-benzfluoren-9-ol*, m.p. 170·5—171·5°, dehydration (boiling AcOH) and hydrogenation (PtO_2) of which yields 9-methyl-fluorene and *-1 : 2-benzfluorene*, m.p. 120·5—122·5° (*bis*-s-*trinitrobenzene* complex, m.p. 109—111°).

A. Lt.

Cyclisation of dienines. XI. Ring closures with di-Δ²-octahydro-2-naphthylacetylenes. Synthesis of perhydro-9-phenanthrone. C. S. Marvel and L. A. Paterson (*J. Amer. Chem. Soc.*, 1941, **63**, 2218—2220; cf. A., 1941, II, 15).—The Grignard reagent of 2-hydroxy-2-acetylenyl-*trans-* and *-cis*-decahydronaphthalene with 2-keto-*trans*-decahydronaphthalene gives 2 : 2′-*dihydroxydi*-trans-*decahydronaphthylacetylene*, m.p. 151·5—152·5°, and the cis–trans-*isomeride*, m.p. 136·5—137°, dehydrated to *di-Δ²-*trans-*octahydronaphthylacetylene* (I), m.p. 80—82°, and the cis–trans-*isomeride* (II), b.p. 211°/3 mm., respectively. Cyclisation of (I) gives a glassy *product* (III), $C_{22}H_{32}O$, and a trace of a substance, m.p. 112—115°; that of (II) gives a *product* (IV), b.p. 225—245°/6 mm. Dehydrogenation of (III) or (IV) gives a small amount of the hydrocarbon, $C_{22}H_{18}$, m.p. 179—181°, but other derivatives could not be obtained. *o*-CO_2H·C_6H_4·C_6H_4·CO_2Me-*o*, $SOCl_2$, and a little C_5H_5N in C_6H_6 at 45—50° give the *Me* ester *chloride*, m.p. 63—64°, converted by CH_2N_2 and then Ag_2O–MeOH into *Me*$_2$ *diphenyl-2-carboxylate-2′-acetate*, m.p. 71—71·5°. The derived (10% NaOH) *dicarboxylic acid*, m.p. 171—172°, is hydrogenated (Raney Ni; 215°/2000 lb.) as Na_2 salt in H_2O to *2-carboxyhexahydrodiphenyl-2′-acetic acid*, m.p. 261—263°, and then to a glassy H_{12}-acid, cyclised at 200°, later 300—320° (CO_2), to the known 9-ketotetradecahydrophenanthrene, m.p. 57° (oxime, m.p. 218—219·5°).

R. S. C.

2-Nitro-2′-aminodiphenyl. D. Purdie (*J. Amer. Chem. Soc.*, 1941, **63**, 2276).—(*o*-NO_2·C_6H_4)$_2$ and boiling aq. EtOH–Na_2S_x give *2-nitro-2′-aminodiphenyl*, m.p. 94—95° [Ac derivative, m.p. 159—160° (lit. 158°)].

R. S. C.

***p*-Dialkylaminoalkylaminobenzenesulphonamides.**—See B., 1941, III, 296.

Synthesis of lipophilic chemotherapeutics. V. *N*⁴-Acylsulphanilamides. F. Bergmann and L. Haskelberg (*J. Amer. Chem. Soc.*, 1941, **63**, 2243—2245).—*p*-NH_2·C_6H_4·SO_2·NH_2 (I) with RCOCl in C_5H_5N–$CHCl_3$ at 0° (later, room temp.) or NaOAc–AcOH–H_2O at −5° (later, room temp.) gives N⁴-*chloroacetyl-*, m.p. 214°, *-dichloroacetyl-*, m.p. 218°, *-trichloroacetyl-*, m.p. 205°, *-bromoacetyl-*, m.p. 218° (decomp.), *-trichloroacryl-*, m.p. 258°, -stearyl-, m.p. 245° (lit. 201°), *-oleyl-*, m.p. 204°, *-Δ^θ-octadecinenoyl-* (*-stearolyl-*), m.p. 189°, *-undecoyl-*, m.p. 205° (decomp.), *-undecenoyl-*, m.p. 194—196°, *-dibromoundecoyl-*, m.p. 173—175°, *-cinammoyl-*, m.p. 255—257°, -trans-*αβ-dibromocinnamoyl-*, m.p. 266°, and *-phenylpropiolyl-*, m.p. 254°, N⁴N⁴′-iso*phthalyldi-*, m.p. >360°, N⁴N⁴′-*adipyldi-*, m.p. >300°, and N⁴N⁴′-*sebacyldi-*, m.p. >300°, *-sulphanilamide*. The acid anhydride and (I) at 150° give N-p-*sulphamyl-phthal-*, m.p. 338°, *-tetrachlorophthal-*, decomp. 322°, and -succin-anilic acid, m.p. 212·5—213·5°. p-*Sulphamyldiphenanilic acid*, m.p. 278—279° (decomp.), is obtained from (I) and (·C_6H_4·CO)$_2$O in boiling PrOH (not alone at 150°). Citraconic anhydride and (I) at 25°, later 100°, give p-*citraconimidobenzenesulphonamide*, m.p. 210—213°. Stearolyl chloride, b.p. 210°/15 mm., CPh:C·COCl, b.p. 103—105°/3·5 mm., and *trans*-CPhBr:CBr·COCl, b.p. 205—208°/7 mm., are prepared by $SOCl_2$.

R. S. C.

Preparation of xylidinesulphonamides and of xylidinesulphonyl derivatives of 2-aminopyridine. A. J. Savitzki and E. I. Rodionovskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 2091—2094).—1 : 3 : 4-$C_6H_3Me_2$·NHAc and $ClSO_3H$ (1 hr. at 80°) yield *4-acetamido-*m-*xylene-6-sulphonyl chloride*, m.p. 133—134° (decomp.), which with aq. NH_3 affords the *-sulphonamide*, m.p. 258—259° (corresponding 4-*NH*$_2$-compound, m.p. 187—188°), and with 2-aminopyridine gives 2-(4′-*acetamido-*m-*xylene-6′-sulphonamido*)*pyridine*, m.p. 260·5—261° (corresponding 4-*NH*$_2$-compound, m.p. 244—245°). 2-*Amino-*, m.p. 189—190°, and 2-*acetamido-*p-*xylene-5-sulphonamide*, m.p. 242—243°, and 2-(2′-*amino-*, m.p. 217—218° (decomp.), and 2-(2′-*acetamido-*p-*xylene-5′-sulphonamido*)*pyridine*, m.p. 243·5—244·5°, were prepared similarly from 2 : 1 : 4 : 5-NHAc·$C_6H_2Me_2$·SO_2Cl.

R. T.

Synthesis of lipophilic chemotherapeuticals. VI. Lipophilic substitutions in azo-dyes. E. Bergmann, L. Haskelberg, and F. Bergmann (*J. Amer. Chem. Soc.*, 1941, **63**, 2245—2248).—Treatment of the dye with, usually, RCOCl in C_5H_5N–$CHCl_3$ at 0° or boiling K_2CO_3–C_6H_6 gives *acet-*, m.p. 241°, *chloro-*, m.p. 221°, *dichloro-*, m.p. 214°, and *trichloro-acet-* (I), m.p. 153·5°, *trichloroacryl-*, m.p. 143—144°, *undeco-*, m.p. 150°, *undeceno-*, m.p. 84°, *dibromoundeco-*, m.p. 111—112°, *cinnam-*, m.p. 236—237°, *phenylpropiol-*, m.p. 221°, trans-*αβ-dibromocinnam-*, m.p. 215°, *toluenesulphon-*, m.p. 209°, N⁴-*acetylsulphanil-* (II), m.p. 270°, *-4-benzeneazo-1-naphthylamide*. *Phthal-*, m.p. 224—225°, and *tetrachlorophthal-4-benzeneazo-1-naphthylimide*, m.p. 296°, are obtained by the anhydride at 120° and 100—130°, respectively. The following are also prepared. *Di-*, m.p. 214°, and *tri-chloroacet-*, m.p. 130°, *trichloroacryl-*, m.p. 174°, *undeceno-*, m.p. 82—84°, *undeco-*, m.p. 98°, *phenylpropiol-*, m.p. 170°, and N⁴-*acetylsulphanil-* (III), m.p. 206—207°, *-1-benzeneazo-2-naphthylamide*; 1-*o*-C_6H_4Cl·N_2·$C_{10}H_6$·NH_2-2, m.p. 158° (lit. 151°) (*CCl*$_3$·*CO* derivative, m.p. 171°, and +*x*BuOH, m.p. 133°); 1-*p*-carboxy-, m.p. 265° (*CCl*$_3$·*CO* derivative, m.p. 246°), 1-*carbethoxy-*, m.p. 183° [*CCl*$_3$·*CO* (IV), m.p. 206°, *C*$_{10}$*H*$_{19}$·*CO*, m.p. 106°, *C*$_{10}$*H*$_{21}$·*CO*, m.p. 110—111°, *C*$_{10}$*H*$_{19}$*Br*$_2$·*CO*, m.p. 124°, and *CCl*$_3$:*CCl·CO*

derivative, m.p. 193°], and 1-p-*carbamyl-benzeneazo-2-naphthylamine*, m.p. 243—244° [CCl_3·*CO* derivative, m.p. 230° (decomp.)]; 4-*o*-$C_6H_4Cl·N_2·C_{10}H_6·NH_2$-1, m.p. 141° (lit. 129°); 4-p-*carbethoxybenzeneazo-1-naphthylamine*, m.p. 164° (CCl_3·*CO*, m.p. 149°, and *undecenoyl* derivative, m.p. 164—165°); *trichloroacet-4-p-chlorobenzeneazo-1-naphthylamide*, m.p. 184°; 4 : 3 : 1-$NH_2·C_6H_3Me·N_2Ph$, m.p. 101° (lit. 118—119°); 4-*trichloroacetamido-azobenzene*, m.p. 149°, -2-*methylazobenzene*, m.p. 137°, and -3-*methoxyazobenzene*, m.p. 132°. Hydrolysis of (**II**) regenerates the basic dye, but boiling 15% HCl–EtOH converts (**III**) into *sulphanil-1-benzeneazo-2-naphthylamide*, m.p. 221—222°. (**I**) and (**IV**) are definitely active against leprosy in hamsters and (**I**) for tuberculosis in guinea-pigs. R. S. C.

p-Aminodimethylaniline. I. Properties of its diazonium compounds. E. E. Ayling, J. H. Gorvin, and L. E. Hinkel (*J.C.S.*, 1941, 613—620).—Diazotisation of *p*-$NH_2·C_6H_4·NMe_2$ proceeds slowly but quantitatively below 5°, and solutions of *p*-$NMe_2·C_6H_4·N_2Cl$ (**I**) are stable at p_H <3·5 (the stability, measured by the incipient decomp. temp., decreases with increasing p_H) but are rapidly decomposed by Cu-bronze in the cold (whereby $NPhMe_2$ is formed). Coupling reactions with amines are very slow, the yield being almost independent of p_H or temp. Coupling with phenols is best at low temp. and at a p_H just high enough to give a conveniently rapid rate of reaction. The yields of azo-compounds depend mainly on the substance coupled. (**I**) behaves normally with CuCl and KI. A. Li.

Oxidation of hydrocarbons to phenols.—See B., 1941, II, 373.

Effect of temperature and light on 2 : 6-dichlorophenol-indophenol solutions. W. Lojander (*Suomen Kem.*, 1941, **14, A**, 26).—The solutions (0·0005—0·001M.) are practically unchanged after 2 months at 6° in the dark, and are only slightly decomposed after 1 month at 20° in daylight and artificial light, but at 30° they are appreciably decomposed after 10 days in the dark. M. H. M. A.

Aquo-ammonophosphoric acids. I. Preparation of phenyl esters of amido- and diamido-phosphoric acids. L. F. Audrieth and A. D. F. Toy (*J. Amer. Chem. Soc.*, 1941, **63**, 2117—2119).—The products formed from $POCl_3$, PhOH, and C_5H_5N in $CHCl_3$ depend on the mol. ratios of the constituents and on temp. A complex equilibrium is established and ammonolysis gives mixtures of Ph diamidophosphate (**I**), Ph_2 amidophosphate (**II**), and Ph_3PO_4. (**I**) and (**II**) are readily separable and this procedure is recommended for their prep. W. R. A.

Synthetic œstrogenic substances. II. Hexœstrol and its esters. E. L. Foreman and C. O. Miller (*J. Amer. Chem. Soc.*, 1941, **63**, 2240).—(*p*-$OH·C_6H_4·CHEt)_2$ (**I**) (prep. from the Me_2 ether improved) and $(RCO)_2O$ in boiling C_5H_5N give the *dipropionate*, m.p. 127—128°, *dibutyrate*, m.p. 106—107°, *dibenzoate*, m.p. 236—237°, *di*-n-*hexoate*, m.p. 96—97°, and *H₂ disuccinate* (**II**), m.p. 150—153°. The oil-sol. esters have low but prolonged œstrogenic effect. The activity of (**II**) in aq. solution is about the same as that of (**I**). R. S. C.

4 : 4′-Dihydroxystilbene and related compounds.—See B., 1941, II, 372.

Antimonial and thioantimonial derivatives of pyrocatechol. H. P. Brown and J. A. Austin (*J. Amer. Chem. Soc.*, 1941, **63**, 2054—2055).—*o*-$C_6H_4(OH)_2$ (**I**), $SbCl_3$, and Na_2CO_3 in aq. NaCl give the *hydroxide* (**II**), *o*-$C_6H_4<^{O}_{O}>Sb·OH$ (70%), unchanged at 300°. SbF_3 and (**I**) in H_2O give the *fluoride*, *o*-$C_6H_4<^{O}_{O}>SbF$ (55%), converted into (**II**) by Na_2CO_3. Moist (**II**) and *o*-$SH·C_6H_4·CO_2Na$ in H_2O give the *salt* (**III**), *o*-$C_6H_4<^{O}_{O}>Sb·S·C_6H_4·CO_2Na$-*o*, m.p. >300°, decomposed by acid. *o*-, *m*-, and *p*-$OH·C_6H_4·CO_2H$ give similarly *salts*, *o*-$C_6H_4<^{O}_{O}>Sb·O·C_6H_4·CO_2Na$-*o*, -*m*, and -*p*, all m.p. >300°, decomposed by acid. *o*-$C_6H_4(SH)_2$ (**IV**) with SbF_3 in H_2O gives *trisdithiopyrocatecholdistibine*, $(o\text{-}C_6H_4S_2)_2Sb_2$, unchanged at 250°, but with $SbCl_3$ or $SbBr_3$ in boiling C_6H_6 gives *salts*, *o*-$C_6H_4S_2SbCl$, m.p. 174—175° (decomp.), or *o*-$C_6H_4S_2SbBr$, m.p. 162—163° (decomp.), respectively, and with Sb_2O_3 in boiling EtOH gives the corresponding *hydroxide*, m.p. >300°, but with *o*-$OH·C_6H_4·CO_2Na$ etc. gives indefinite products. K SbO tartrate and (**IV**) in aq. EtOH give the *acid*, *o*-$C_6H_4S_2>Sb·O·CH(CO_2H)·CH(OH)·CO_2H$ (K_1 salt, m.p. >250°). *o*-$OH·C_6H_4·SH$ and freshly pptd. Sb_2O_3 in boiling EtOH give the *compound*, *o*-$C_6H_4<^{O}_{S}>Sb·S·C_6H_4·OH$-*o*, m.p. >250°, but other derivatives could not be obtained. (**III**) is a useful agent for the treatment of heartworms in dogs. R. S. C.

Choline tolyl ethers. A. R. Goldfarb (*J. Amer. Chem. Soc.*, 1941, **63**, 2280).—Addition of 50% NaOH (1 mol.) to cresol (1 mol.) and $C_2H_4Br_2$ (2 mols.) in boiling H_2O gives β-o-, b.p. 142—145°/18 mm., -m-, b.p. 146·5—147°/18 mm., and -p-*tolyloxyethyl bromide*, b.p. 136—138°/18 mm., converted by NMe_3 (at 40°) or NEt_3 (at 60°) in PhMe into β-o-, m.p. 157·5°, -m-, m.p. 145·4°, and -p-*tolyloxyethyltrimethyl*-, m.p. 144°, β-o-, m.p. 152—152·5°, -m-, m.p. 136·4°, and -p-*tolyloxyethyltriethyl*-, m.p. 134·5°, -*ammonium bromide*. R. S. C.

Direct synthesis of many-membered ring compounds from two ωω′-difunctional molecules. R. Adams and L. N. Whitehill (*J. Amer. Chem. Soc.*, 1941, **63**, 2073—2078).—The effect of dilution on interaction of two ωω′-difunctional mols. is discussed. High-dilution technique is used in cyclisations described below. Quinol (**I**), $Br·[CH_2]_3·Br$, and K_2CO_3 in boiling aq. $COMe_2$ give *quinol di-γ-bromopropyl ether* (**II**) (28·9%), m.p. 78—79°, b.p. 174—177°/4 mm., which (2 mols.) with (**I**) (1 mol.) and KOH (0·3 mol.) in boiling EtOH gives α-p-*hydroxyphenoxy-γ-p-γ′-bromo*-n-*propoxyphenoxypropane* (23·7%), m.p. 100—101°, cyclised by addition to K_2CO_3 in boiling *iso*-$C_5H_{11}·OH$ to 1 : 1′ : 4 : 4′-*bistrimethylenedioxydibenzene*, *p*-$C_6H_4<^{O·[CH_2]_3·O}_{O·[CH_2]_3·O}>C_6H_4$-*p* (**III**) (59·2%), m.p. 195—195·5°. Direct intermol. condensation of (**I**) and (**II**) to (**III**) is also effected, yields up to 18% being recorded. $Br·[CH_2]_6·Br$ and (**I**) give similarly *quinol di-ζ-bromo*-n-*hexyl ether* (63·2%), m.p. 96—97°, and thence 1 : 1′ : 4 : 4′-*bishexamethylenedioxydibenzene* (15%), m.p. 141°. Attempts to condense quinol di-β-bromoethyl, m.p. 114°, b.p. 145—147°/2 mm., and the insol. *di-κ-bromo*-n-*decyl*, m.p. 88·5—89·5°, and *di-θ-bromo*-n-*octyl ether*, m.p. 78·5—79·5°, with (**I**) failed. Quinol mono-θ-bromo-*n*-octyl ether, m.p. 76—77°, is also described. M.p. are corr. R. S. C.

Synthesis of 5-methoxy-10-methyl-1 : 2-benzanthracene and related compounds. M. S. Newman and P. H. Wise (*J. Amer. Chem. Soc.*, 1941, **63**, 2109—2111).—*o*-$OMe·C_6H_4·MgBr$ (**I**) and 1 : 2-$C_{10}H_6(CO)_2O$ in boiling C_6H_6–Et_2O give 13% each of o-*anisyl* 1-*carboxy*-2- (**II**), m.p. 193·8—194·6°, and 2-*carboxy*-1-*naphthyl ketone* (**III**), m.p. 193—194·4°, with 17% of 2-α-*hydroxy*-2′ : 2″-*dimethoxybenzhydryl*-1-*naphtholactone* (**IV**), m.p. 232·2—232·5°. The structure of (**II**) and (**III**) is proved by decarboxylation to o-*anisyl* 2- (62%), m.p. 74·5—76° (74·6—75·6°), and 1-*naphthyl ketone* (21%), m.p. 75—76° (76—76·5°), respectively, also obtained from 2- and 1-$C_{10}H_7·CN$, respectively, by condensation with (**I**). The structure of (**IV**) is proved by synthesis from (**II**) and (**I**). Condensation of (**II**) and MgMeBr in boiling C_6H_6–Et_2O gives 78% of 2-α-*hydroxy*-α-o-*anisylethyl*-1-*naphtholactone*, m.p. 129·6—130·6°, reduced by Zn dust (Cu-activated) in NaOH–aq. EtOH to 2-α-o-*anisylethyl*-1-*naphthoic acid* (90%), m.p. 188·8—189·6°. Ring-closure by 90% H_2SO_4 and subsequent reduction by Zn–Cu–NaOH–H_2O then gives 5-*methoxy*-10-*methyl*-1 : 2-*benzanthracene* (**V**) (40%), m.p. 131—132·2° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 204·6—205·2°; *picrate*, m.p. 187—188·4°], and a little 5-*methoxy*-10-*methyl*-1 : 2-*benz*-9-*anthrone* (**VI**), m.p. 158—159°. Me_2SO_4–KOH–EtOH converts (**VI**) into 5 : 9-*dimethoxy*-10-*methyl*-1 : 2-*benzanthracene*, m.p. 136·2—137·2° [*picrate*, m.p. 128·8—130°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 146·2—146·8°]. (**V**) is not carcinogenic. M.p. are corr. R. S. C.

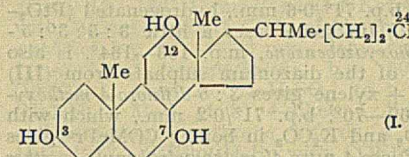
Synthetic experiments in the group of sympathomimetics. II. Poly- and hetero-cyclic ring systems. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 566—572).—2 : 3 : 4 : 1-$NO_2·C_6H_2(OMe)_2·CHO$, 1-$C_{10}H_7·CH_2·CO_2K$, and Ac_2O at 105—110° (oil-bath) afford 2-*nitro*-3 : 4-*dimethoxy*-α-1′-*naphthylcinnamic acid*, m.p. 238—239° (decomp.), reduced by aq. NH_3–$FeSO_4$ to the 2-*NH₂*-compound, m.p. 201° (decomp.), which with *iso*-$C_5H_{11}·O·NO$ and conc. H_2SO_4 in $(iso\text{-}C_5H_{11})_2O$, followed by aq. NaH_2PO_2 (+ a little active Cu) at 40—50°, then at 80—90°, yields 11 : 12-*dimethoxychrysene*-7-*carboxylic acid*, m.p. 201—202° (decomp.), decarboxylated (Cu, quinoline) to 11 : 12-*dimethoxychrysene*, b.p. 210—220°/

1—2 mm. [*picrate*, m.p. 153—155° (decomp.)]. Glycerol, 3 : 1 : 2-$NH_2 \cdot C_6H_3(OMe)_2$ (**I**), conc. H_2SO_4, and $PhNO_2$ at 100° (bath), then at 130—135°, afford 7 : 8-*dimethoxyquinoline*, b.p. 148—150°/3—4 mm. [*picrate*, m.p. 182—184° (softens at 180°); *methiodide*, m.p. 182° (decomp.)]. (**I**), conc. HCl, $ZnCl_2$, and paraldehyde at 100°, then at 130—135°, give 7 : 8-*dimethoxy*-2-*methylquinoline*, b.p. 147—148°/2—3 mm. [*picrate*, m.p. 155—156° (decomp.); *methiodide*, m.p. 176—177° (decomp.)]. β-2 : 3-*Dimethoxyphenylethylacetamide*, m.p. 64—66°, and $POCl_3$–PhMe give 5 : 6-*dimethoxy*-1-*methyl*-3 : 4-*dihydro*isoquinoline, b.p. 141—143°/3 mm. [*hydrochloride*, m.p. 202—203° (decomp.); *picrate*, m.p. 214° (decomp.) (sinters at 210°); *methiodide*, m.p. 106—107° (decomp.)], reduced [Zn–aq. H_2SO_4 at 100° (bath)] to 5 : 6-dimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, an oil [*hydrochloride*, m.p. 213—214° (decomp.); *picrate*, m.p. 196—198° (decomp.) (sinters at 194°)]. Aminoacetal (**II**), α-$C_{10}H_7 \cdot OH$, and AcOH–conc. HCl at room temp. afford *ββ-bis*-(4-*hydroxy*-1-*naphthyl*)*ethylamine hydrochloride*, m.p. 237—238° (decomp.). The product obtained from 1 : 2-$C_{10}H_6(OH)_2$ is unstable, and reaction does not occur using 8-hydroxyquinoline. (**II**), 3 : 4-dihydroxyphenanthrene, and AcOH–conc. HCl yield the unstable β-hydroxy-β-3 : 4-dihydroxy-*x*-phenanthrylethylamine (*picrate*, decomp. 195—197°). 3 : 4-Dimethoxyphenanthrene and hippuryl chloride in CS_2–HCl yield 3 : 4-*dimethoxy*-x-*phenanthryl benzamidomethyl ketone*, m.p. 268—269° (decomp.), in poor yield. A. T. P.

Preparation of a pregnane-3(α) : 17 : 20-triol. H. Hirschmann (*J. Biol. Chem.*, 1941, **140**, 797—806).—Pregnane-3(α) : 20(α)-diol and boiling AcOH give the 3-*acetate* (**I**), m.p. 131·5—132·5° (solvent-free specimen obtained only by sublimation in high vac.), the 20-acetate, new m.p. 175·5° (cf. Butenandt *et al.*, A., 1935, 215), and the diacetate, which are separated by chromatographic analysis. (**I**) and *p*-$C_6H_4Me \cdot SO_2Cl$–C_5H_5N at room temp. yield *pregnanediol* 3-*acetate* 20-p-*toluenesulphonate*, m.p. 112—115° (decomp.), converted by $CaCO_3$–C_5H_5N, then aq. NaOH–MeOH, into Δ^{17}-*pregnen*-3(α)-*ol*, m.p. 118—120°, hydroxylated by OsO_4–Et_2O, then aq. Na_2SO_3–EtOH, to a *pregnane*-3(α) : 17 : 20-*triol* (**II**), m.p. 215—218°, purified through the *diacetate*, m.p. 193—196°, $[\alpha]_D^{20}$ +71° in EtOH (chromatographic separation), and hydrolysis with aq. NaOH–MeOH. (**II**) is not identical with 3(α) : 17 : 20-triol described by Butler *et al.* (A., 1938, II, 368); the difference is attributed to different spatial arrangement at $C_{(17)}$ or $C_{(20)}$ or both. (**II**) and aq. MeOH–H_2SO_4 give ætiocholan-3(α)-ol-17-one. M.p. are corr. A. T. P.

Toad bile. VII. Pentahydroxybufostane, $C_{28}H_{50}O_5$. T. Kazuno (*Z. physiol. Chem.*, 1940, **266**, 11—30; cf. A., 1937, II, 420).—The neutral portion of toad bile was fractionated by addition of NaCl (concn. 3%, 10%, and finally saturation). The first fraction gave a substance, m.p. 197°, yielding on hydrolysis 1 mol. of H_2SO_4 and cryst. *pentahydroxybufostane* (**I**), $C_{28}H_{50}O_5$, m.p. 172°, $[\alpha]_D^{24}$ +33·49° in EtOH. (**I**) is saturated (Br, $KMnO_4$, and H_2) and gives no ketone reaction. It therefore contains four rings (the *cyclo*pentanoperhydrophenanthrene nucleus). With AcOH–CrO_3 at 20°, (**I**) affords *dihydroxytriketobufostane* (**II**), m.p. 198·5—199° (*trioxime*, decomp. 234°), and *tetraketo*isobufostane (**III**), $C_{28}H_{42}O_4$, m.p. 245—248° (250°) (*tetraoxime*, m.p. 244°). (**II**) is reduced (H_2, PtO_2, AcOH) to (**I**), whilst (**III**) takes up 4 H_2 to yield *tetrahydroxy*isobufostane (**IV**), $C_{28}H_{50}O_4$, m.p. 204°. Incomplete hydrogenation (2 H_2) affords *dihydroxydiketo*isobufostane, m.p. 221—224°. (**IV**) shows a positive Hammarsten reaction indicating OH at positions 3, 7, and 12, yields no oxime or semicarbazone, and is converted by CrO_3 into (**III**). Similarly in dehydrocholic acid the CO at 3 and 7 are more easily hydrogenated than is that at $C_{(12)}$. Partial hydrolysis of the 3 : 7 : 12-*triacetate* (**V**), m.p. 117—119°, $[\alpha]_D^{24}$ +5·55° in MeOH, of (**I**) affords a *diacetate*, m.p. 165—166°, oxidised by CrO_3 to *dihydroxyketodiacetoxybufostane*, m.p. 149—150°, which is hydrolysed to *tetrahydroxy*-3-*ketobufostane*, m.p. 161° (*oxime*, m.p. 211°), giving a positive Jaffé reaction. (**III**) is probably formed from (**II**) by a pinacolic rearrangement; thus (**II**) can be rearranged to (**III**) by CrO_3 in AcOH. The same rearrangement occurs at 80—90° with (**V**), which yields (cf. below) (after hydrolysis) *trihydroxyketo*isobufostane (**VI**), m.p. 161°, isolated as the semicarbazone. CrO_3 converts (**VI**) into (**III**). The assumption that the side-chain contains a glycol group is confirmed by the conversion (cf. above) by CrO_3 of (**V**) into cholic acid triacetate, which was hydrolysed to cholic acid. By Clemmensen reduction, (**III**) gives isobufostane (**VII**), $C_{28}H_{50}$, m.p. 72°, and by partial reduction *triketo*isobufostane (**VIII**), m.p. 163°. (**VII**) is not identical with coprostane; it is probably 25-methylcoprostane. (**VIII**) shows no Jaffé reaction, indicating that the CO at $C_{(3)}$ is reduced. Thus the CO groups are at 7, 12, and 24.

The neutral *substance* (**IX**), $C_{24}H_{40}O_4$, m.p. 175°, $[\alpha]_D^{28}$ +30·27° in EtOH, from the fourth fraction occurs free in bile. With CrO_3 it gives a *triketone*, (**X**), $C_{24}H_{34}O_4$, m.p. 242°. It must thus belong to the cholane series and is named tetrahydroxycholane. As the Hammarsten reaction is positive and NaOH does not cause rearrangement of (**V**), 3 OH are at positions 3,



(I.

7, and 12. (**IX**) is thus regarded as an oxidation product of (**I**). The formation of the C_{24} bile acids from C_{27} and C_{28} sterols in the animal organism may proceed either by glycol oxidation coupled with ω-oxidation or by ω-oxidation together with β- or glycol oxidation. J. H. B.

Synthesis of *dl*-"*o*"-thyronine. H. E. Ungnade (*J. Amer Chem. Soc.*, 1941, **63**, 2091—2093).—*p*-$NO_2 \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot OMe$-*o* (prep. by Ullmann reaction; 64% yield) and H_2–Raney Ni at 100°/2000 lb. give *p*-$NH_2 \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot OMe$-*o* (**I**) (86%), m.p. 96—97°, b.p. 149—150°/1 mm. [Ac derivative, m.p. 115—115·5° (lit. 118°)], converted (diazo-reaction) into the *p*-I-compound, b.p. 150—151°/2 mm., and thence (CuCN; 250°) o-*anisyl* p-*cyanophenyl ether* (**II**), m.p. 93—94°, b.p. 145—150°/1 mm., also obtained less well from (**I**) by a diazo-reaction. *o*-$OMe \cdot C_6H_4 \cdot OK$, *p*-$C_6H_4MeBr$, and Cu powder at 150° give o-*anisyl* p-*tolyl ether*, m.p. 51·8—52·5°, converted by HI–AcOH–Ac_2O into 2-*hydroxy*-4′-*methyl*-, m.p. 63—63·8°, and by $KMnO_4$ in aq. C_5H_5N into 4′-*carboxy*-2-*methoxy*- (**III**), m.p. 159—160°, which with HI–AcOH gives 2-*hydroxy*-4′-*carboxy*-*diphenyl ether*, m.p. 139—139·5° [also obtained from (**II**) by HI–AcOH]. Stephen reduction of (**II**) gives only a trace of aldehyde [whence 2-*phenyl*-4-p-o′-*anisyloxybenzylidene*-5-*oxazolone* (**IV**), m.p. 184—185°]. *p*-$OK \cdot C_6H_4 \cdot CO_2Et$, *o*-$C_6H_4Br \cdot OMe$, and Cu powder at 240—260° give *o*-$OMe \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot CO_2Et$-*p*, b.p. 145—147°/1 mm. [with a little (**III**) and *o*-$OMe \cdot C_6H_4 \cdot OPh$]. This yields p-o′-*anisyloxybenzhydrazide*, m.p. 130·5—131·5° [also prepared starting from (**III**)], the p-$C_6H_4Me \cdot SO_2$ derivative, m.p. 205—206°, of which with Na_2CO_3 in $(CH_2 \cdot OH)_2$ at 160° (1·5 min.) gives p-o′-*anisyloxybenzaldehyde*, m.p. 56—56·5°, and thence (**IV**) and α-*amino*-β-p-o′-*hydroxyphenoxypropionic acid* [o-*thyronine*] (**V**), m.p. 240° (decomp.) (sinters at 238°; bath pre-heated to 200°). An impure I_2-derivative of (**V**) has no thyroid activity (tadpole), but di-iodotyrosine has some activity. Mixtures of "*p*"-thyronine and (**V**) can be analysed by means of the absorption spectra, which are given for both. R. S. C.

Synthesis of 3′ : 5′-difluoro-*dl*-thyronine and 3 : 5-di-iodo-3′ : 5′-difluoro-*dl*-thyronine. C. Niemann, A. A. Benson, and J. F. Mead (*J. Amer. Chem. Soc.*, 1941, **63**, 2204—2208).—Crude 4 : 3 : 1-$OMe \cdot C_6H_3(NO_2) \cdot CO_2H$ (prep. from oil of anise by conc. HNO_3 and V_2O_5 first at 90° and then at the b.p.) and HCl–MeOH give the ester (86%), m.p. 108—109°, hydrogenated (PtO_2–MeOH) to 4 : 3 : 1-$OMe \cdot C_6H_3(NH_2) \cdot CO_2Me$ (91%), m.p. 85—86°. Addition of HF–BF_3 to the derived diazonium chloride at −25° gives the diazonium fluoroborate (88%), decomposed by dry distillation at 50 mm. to *Me* 3-*fluoro*-4-*methoxybenzoate* (**I**) (56%), m.p. 70—71°, b.p. 116°/5 mm. With HNO_3 (*d* 1·5) at 0—5° this gives 4 : 3 : 5 : 1-$OMe \cdot C_6H_2F(NO_2) \cdot CO_2Me$ (72%), m.p. 49·3—49·5°, hydrogenated (PtO_2–MeOH) to the NH_2-ester (92%), m.p. 51—54°, b.p. 117°/0·1 mm., which yields (diazo-reaction as above) *Me* 3 : 5-*difluoro*-4-*methoxybenzoate* (**II**) [30% and some (**I**)], m.p. 37·5°, b.p. 55°/0·2 mm. The derived (KOH–EtOH) acid (98%), m.p. 164—165°, with $SOCl_2$ and then NH_3–Et_2O gives the *amide* (91%), m.p. 158—160°, converted by NaOBr–NaOH at, successively, −10°, 25°, and 100° into 3 : 5-*difluoro*-p-*anisidine* (**III**) (77%), m.p. 78·5—79°, b.p. 80°/0·1 mm. (p-$NO_2 \cdot C_6H_4 \cdot CO$ derivative, m.p. 207—207·5°). Nitration of *o*-$C_6H_4F \cdot OMe$ (**IV**) (prep. improved to give 64% yield) yields only 4 : 2 : 1-$NO_2 \cdot C_6H_3F \cdot OMe$ (cf. Holmes *et al.*, A., 1926, 831). With conc. H_2SO_4 at room temp. and then aq.

NaCl, (**IV**) gives *Na* 3-*fluoro*-4-*methoxybenzenesulphonate*, converted by HNO_3 (*d* 1·5) in H_2SO_4 at 0° followed by aq. NaCl into *Na* 3-*fluoro*-5-*nitro*-4-*methoxybenzenesulphonate* or, after keeping and then distillation in steam at 170°, into 2-*fluoro*-6-*nitrophenol* (37%), m.p. 90—91°. The Na salt thereof with Me_2SO_4 and PhMe at 110—120° gives 2-*fluoro*-6-*nitroanisole* (86%), m.p. 9°, b.p. 93°/3 mm., hydrogenated (PtO_2) to 2-*fluoro*-6-*aminoanisole* (84%), b.p. 94°/10 mm. (p-$NO_2{\cdot}C_6H_4{\cdot}CO$ derivative, m.p. 147—148·5°), which affords (diazo-reaction) 2 : 6-*difluoroanisole* (56%), b.p. 62°/40 mm. H_2SO_4–HNO_3 (*d* 1·5) then gives 2 : 6-*difluoro*-4-*nitroanisole* (88%), m.p. 37—38°, b.p. 71°/0·6 mm., hydrogenated (PtO_2–MeOH) to (**III**) (93%) (in some cases a little 3 : 5 : 3′ : 5′-*tetrafluoro*-4 : 4′-*dimethoxyazobenzene*, m.p. 163—164°, is also formed). Treatment of the diazonium sulphate from (**III**) with hot aq. $CuSO_4$ + xylene gives 3 : 5-*difluoro*-4-*methoxyphenol* (86%), m.p. 69—70°, b.p. 71°/0·2 mm., which with 3 : 4 : 5 : 1-$C_6H_2I_3{\cdot}NO_2$ and K_2CO_3 in boiling $COMePr^{\alpha}$ gives 2 : 6-*di-iodo*-3′ : 5′-*difluoro*-4-*nitro*-4′-*methoxydiphenyl ether* (73%), m.p. 127—128°, reduced by $SnCl_2$–AcOH to the amine (*hydrochloride*, m.p. 185—200°; *Ac* derivative, m.p. 219—220°). Treatment with *sec.*-BuO·NO in AcOH at 20—25° and then with aq. KCN–$CuSO_4$ at 90° gives 3 : 5-*di-iodo*-4-3′ : 5′-*difluoro*-4′-*methoxyphenoxybenzonitrile* (66%), m.p. 129—134°, converted by HI–AcOH into 3 : 5-*di-iodo*-4-3′ : 5′-*difluoro*-4′-*hydroxyphenoxybenzoic acid*, m.p. 232—234°, and by $SnCl_2$–HCl–Et_2O into 3 : 5-*di-iodo*-4-3′ : 5′-*difluoro*-4′-*methoxyphenoxybenzaldehyde* (72%), m.p. 124—126° [p-*nitrophenylhydrazone*, m.p. 280—281° (decomp.)], which yields 2-*phenyl*-4-3′ : 5′-*di-iodo*-4′-3″ : 5″-*difluoro*-4″-*methoxyphenoxybenzylidene*-5-*oxazolone*, sinters at 214·5°, m.p. 216—217°, and thence (Ac_2O–HI–red P) dl-3 : 5-*di-iodo*-3′ : 5′-*difluorothyronine* (60%), m.p. 248° (decomp.). This is converted by H_2–Pd–$CaCO_3$–NaOH into dl-3′ : 5′-*difluorothyronine*, m.p. 242—244°. 85% N_2H_4,H_2O and (**I**) give 3-*fluoro*-4-*methoxybenzhydrazide*, m.p. 178—179° (decomp.), the *PhSO*$_2$ derivative, m.p. 176—177°, of which with Na_2CO_3 in $(CH_2{\cdot}OH)_2$ at 155° gives crude 4 : 3 : 1-OMe·C_6H_3F·CHO (67%) and thence the azlactone, 3-*fluoro*-α-*benzamido*-4-*methoxycinnamic acid*, m.p. 221—222°, and *dl*-3-fluorotyrosine (12% over-all), decomp. 275—278° (rapid heating). (**II**) yields similarly 3 : 5-*difluoro*-4-*methoxybenzhydrazide*, m.p. 189—190° (decomp.) (*PhSO*$_2$ derivative, m.p. 179—180°), and thence as above *dl*-3 : 5-difluorotyrosine (13% over-all), decomp. 280° (rapid heating; lit. 265°). R. S. C.

Reduction of amines and substituted amides. II. Kinetics and mechanism of electro-reduction of amides. A. V. Koperina and M. M. Kliutschareva (*J. Gen. Chem. Russ.*, 1941, **11**, 51—62).—The chief product of reduction of NH_2Bz in aq. EtOH (Pb cathode, c.d. 0·024 amp. per sq. cm., at 10°) is $CH_2Ph{\cdot}NH_2$ (95%), with PhCHO and $CH_2Ph{\cdot}OH$ as by-products. The velocity of electro-reduction falls in the order $NH_2Br > NHBz{\cdot}CH_2{\cdot}CO_2H > NHMeBz > NMe_2Bz$. Reduction of $NHBz{\cdot}CH_2{\cdot}CO_2H$ in aq. EtOH involves production of $NHBz{\cdot}CH_2{\cdot}CO_2Et$, owing to which *N*-benzylglycine is not obtained in quant. yield. R. T.

Chemically marked antigens. II. Reactivity of oxazolones. H. Lettré and M. E. Fernholz (*Z. physiol. Chem.*, 1940, **266**, 37—40).—See A., 1941, III, 1078. The following esters of *dl*-benzoyl-α-alanine (**I**) have been prepared by heating 2-phenyl-4-methyloxazolone (**II**) with the appropriate alcohol: *Pr*$^{\beta}$, m.p. 79—80°, *CH*$_2$*Ph*, m.p. 88—89°, l-*menthyl*, m.p. 104—105°, *Ph*, m.p. 131—132°, β-$C_{10}H_7$, m.p. 164—165°, o-*carboxyphenyl*, m.p. 152—153°, and the *Ph thio*-ester (from PhSH), m.p. 130—131°. The *ethylamide*, m.p. 136—137°, *methylanilide*, m.p. 119—120°, and *piperidide*, m.p. 114—115°, of (**I**), and dl-*benzoylalanyl*-l-*proline*, m.p. 228—230°, have also been prepared. α-Terpineol, NH_2Bz, NHPhBz, and indole did not react with (**II**). J. H. B.

Relative directive powers of carboxyl and quaternary ammonium group. A. Zaki and W. Tadros (*J.C.S.*, 1941, 562—564).—*p*-CHO·$C_6H_4{\cdot}NMe_3Cl$ with boiling fuming HNO_3, conc. HNO_3–H_2SO_4 at 100° (bath), or $KMnO_4$ yields (after suitable treatment) the following p-*carboxyphenyltrimethylammonium* salts: *picrate*, m.p. 207°; *iodide*, m.p. 238°; *perchlorate*, m.p. 284°; *chloride perbromide*, m.p. 200°; the *chloride* (**I**), m.p. 240—241°, with EtOH–NaOEt gives *p*-$NMe_2{\cdot}C_6H_4{\cdot}CO_2H$. Fuming HNO_3–conc. H_2SO_4 at 100° (bath) etc. converts (**I**) into the following 3-*nitro*-4-*carboxyphenyltrimethylammonium* salts: *picrate*, m.p. 198°; *iodide*, m.p. 236°; *perchlorate*, m.p. 259°; *chloride perbromide*, m.p. 158—159°; the *chloride*, m.p. 230—231°, with EtOH–NaOEt gives 2-*nitro*-4-*dimethylaminobenzoic acid*, m.p. 242° (darkens at 225°), decarboxylated to *m*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$. MeI could not be added to 3 : 4 : 1-$NO_2{\cdot}C_6H_3(NMe_2){\cdot}CO_2H$. A. Lt.

Hydrogen bonds involving the C–H link. XV. Non-bonding of triphenylmethane hydrogen atoms. C. S. Marvel and J. Harkema (*J. Amer. Chem. Soc.*, 1941, **63**, 2221—2222).—*o*-, m.p. 84° (prep. from the acid by $SOCl_2$ at room temp. and removal of excess in N_2), and *p*-$CHPh_2{\cdot}C_6H_4{\cdot}COCl$ with $NHMe_2$ in Et_2O give o-, m.p. 146°, and p-*benzhydrylbenzdimethylamide*, m.p. 89—90°, respectively. Infra-red absorption spectra of the amides and corresponding Me esters (*p*-, new m.p. 78—79°) show max. only at 3·20 (aromatic C–H) and 3·32 μ. (aliphatic C–H), and the compounds are not associated (f.p.) in C_6H_6. H-bonding thus does not occur by chelation. R. S. C.

***n*-Amyl, m.p. 58°, *n*-hexyl, m.p. 52—53°, and *n*-octyl orsellinate, m.p. 61°.**—See A., 1941, III, 925.

Action of semicarbazide hydrochloride on β-*p*-anisylglutaconic anhydride. R. Y. Shahane (*Rasāyanam*, 1941, **1**, 222—223; cf. Limaye *et al.*, A., 1931, 1055).—The action of $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ on an aq. suspension of β-*p*-anisylglutaconic anhydride at 100° gives an additive *compound*, $C_{13}H_{15}O_5N_3$, which gives a colour with $FeCl_3$. The semicarbazone structure (Dixit, A., 1936, 847) cannot be accepted. H. W.

Constitution of tetrahydroxynorsterocholanic acid. H. Isaka (*Z. physiol. Chem.*, 1940, **266**, 117—122).—Tetrahydroxynorsterocholanic acid (**I**), $C_{27}H_{46}O_6$, is partly acetylated by AcCl–AcOH at room temp. to the *diacetate*, m.p. 230—231°, which is oxidised by CrO_3–AcOH to 12-*keto*-3 : 6-*diacetoxycholanic acid* (**II**), m.p. 210°. This is hydrolysed by KOH–EtOH to 3 : 6-*dihydroxy*-12-*ketocholanic acid*, $C_{24}H_{38}O_5$, m.p. 188—190°. By the same method iso*cholic acid diacetate*, m.p. 240°, affords (**II**). The semicarbazone of (**II**) by Wolff–Kishner reduction yields hyodeoxycholic acid. Thus the two *sec.*-OH of (**I**) and of *iso*cholic acid are at $C_{(3)}$ and $C_{(6)}$. On distillation in a high vac. (**I**) gives 12-*ketocholadienic acid*, $C_{24}H_{34}O_3$, m.p. 193—195°, reduced (H_2, Pd-black, AcOH) to 12-ketocholanic acid. This indicates another *sec.*-OH at $C_{(12)}$ in these acids. (**I**) is thus 3 : 6 : 12 : 24-tetrahydroxynorsterocholanic acid, confirming Ohta (A., 1939, II, 371). (**I**) gives the Hammarsten reaction, which is therefore positive not only with OH at $C_{(3)}$, $C_{(7)}$, and $C_{(12)}$, or $C_{(3)}$ and $C_{(12)}$ with double linking in ring B, but also with bile acids with OH at $C_{(3)}$, $C_{(6)}$, and $C_{(12)}$. J. H. B.

Action of hydrogen and Raney nickel on aromatic aldehydes. A. Albert and B. Ritchie (*J. Proc. Roy. Soc. N.S.Wales*, 1940, **74**, 373—376; cf. A., 1941, II, 39).—PhCHO is not reduced (H_2, Raney Ni; method, *loc. cit.*) at 25°, but at 70° yields 100% of $CH_2Ph{\cdot}OH$. *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ or *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ is reduced (25°) to *o*-$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ (7 hr., 25°) to *p*-$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, or (11 hr., 70°) to a mixture of *p*-$C_6H_4Me{\cdot}NH_2$ and poly-*p*-aminobenzyl alcohol, 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}CHO$ (2 hr., 25°, coarse catalyst) to 2 : 2′-dinitro-4 : 4′-azoxytoluene (**I**), m.p. 165°, or (6 hr., 25°, coarse catalyst) to 2 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}NH_2$, and (**I**) (8 hr., 50°) to 1 : 2 : 4-$C_6H_3Me(NH_2)_2$. A. Lt.

Preparation of *o*-hydroxyaldehydes from phenols and hexamethylenetetramine. J. C. Duff (*J.C.S.*, 1941, 547—550; cf. A., 1934, 1213).—When heated at 150—155° with $(CH_2)_6N_4$ in glycerol previously heated at 170° with H_3BO_3, and the product hydrolysed (dil. H_2SO_4), PhOH, *o*-, *m*-, and *p*-cresol, *o*- and *p*-$C_6H_4Cl{\cdot}OH$, 2 : 4 : 1-$C_6H_3Cl_2{\cdot}OH$, 1 : 6 : 3-$C_6H_3MeCl{\cdot}OH$, *m*-5-xylenol, 1 : 3 : 2 : 5-$C_6H_2Me_2Cl{\cdot}OH$, *p*-$C_6H_4Ph{\cdot}OH$, β-$C_{10}H_7{\cdot}OH$, carvacrol, and thymol yield respectively (without isolable intermediate products) *o*-$OH{\cdot}C_6H_4{\cdot}CHO$, 2 : 1 : 3- [with 3 : 5-*dialdehydo*-*o*-*cresol*, m.p. 123° (*dioxime*, m.p. 199°)], 3 : 1 : 4-, and 4 : 1 : 3-$OH{\cdot}C_6H_3Me{\cdot}CHO$, 2 : 3 : 1- and 2 : 5 : 1-$OH{\cdot}C_6H_3Cl{\cdot}CHO$, 2 : 3 : 5 : 1-$OH{\cdot}C_6H_2Cl_2{\cdot}CHO$, 3 : 1 : 6 : 4-$OH{\cdot}C_6H_2MeCl{\cdot}CHO$ [with 6-*chloro*-2 : 4-*dialdehydo*-m-*cresol*, m.p. 113° (*dioxime*, m.p. 148°) (not obtained in the Reimer–Tiemann prep.)], 5 : 1 : 3 : 4-$OH{\cdot}C_6H_2Me_2{\cdot}CHO$, 2-*chloro*-4-*aldehydo*-m-5-*xylenol*, m.p. 96° (*oxime*, m.p. 197°) (also prepared by the Reimer–Tiemann method), 4 : 1 : 3-$OH{\cdot}C_6H_3Ph{\cdot}CHO$, 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}CHO$ [better prepared in AcOH alone (*loc. cit.*)],

o-carvacrolaldehyde, b.p. 130°/15 mm. (*phenylhydrazone*, m.p. 150°), and *o*-thymolaldehyde, b.p. 130°/15 mm. (*oxime*, m.p. 123°). A possible intermediate is $CH_2Ar{\cdot}N{:}CH_2$, which isomerises to $CHAr{:}NMe$; hydrolysis then gives ArCHO and NH_2Me.
A. LI.

p-Bromophenacyl esters. D. T. Mowry and W. R. Brode (*J. Amer. Chem. Soc.*, 1941, **63**, 2281).—*Di*-p-*bromophenacyl oxalate*, m.p. 242° (decomp.), and p-*bromophenacyl Me succinate*, m.p. 104·6—104·8°, and *glutarate*, m.p. 46·6—46·8°, are described. R. S. C.

Syntheses of 2-acylresorcinols by the "Nidhon" process. VII. Use of 7-hydroxycoumarin. D. B. Limaye and M. C. Joshi (*Rasāyanam*, 1941, **1**, 225—227).—Umbelliferone acetate is converted by anhyd. $AlCl_3$ at 160—165° into 8-*acetylumbelliferone* (**I**), m.p. 167° (*Me ether*, m.p. 126°; *semicarbazone*, m.p. 250°; *benzoate*, m.p. 145°), and 6-*acetylumbelliferone* (**II**), m.p. 177° (*semicarbazone*, m.p. >270°; *acetate*, m.p. 149°). (**I**) is hydrolysed by boiling N-NaOH to MeCHO, an *acid*, $C_{11}H_{10}O_5$, m.p. 184—210°, which loses CO_2 when heated above its m.p., and a very small proportion of $2:1:3\text{-}C_6H_3Ac(OH)_2$ (**III**). (**II**) is very resistant towards NaOH, giving a very small yield of an acid, m.p. 220° (decomp.), but no (**III**). 7-Hydroxycoumarin (umbelliferone) can thus be used in the "Nidhon" process, but the method is not suitable for the prep. of (**III**) by reason of the small yield.
H. W.

Extension of the "Nidhon" process for the syntheses of 2-acylresorcinols to 2-acyl-4-alkylresorcinols. I. 2-Acetyl-4-ethylresorcinol. S. D. Limaye and D. B. Limaye (*Rasāyanam*, 1941, **1**, 201—207; cf. A., 1934, 298).—$4:1:3\text{-}C_6H_3Et(OH)_2$ (**I**), $CH_2Ac{\cdot}CO_2Et$, and conc. H_2SO_4 at room temp. give 4-methyl-6-ethylumbelliferone (**II**), m.p. 213° [*acetate* (**III**), m.p. 145°; *benzoate*, m.p. 155°; *Me ether*, m.p. 165°], hydrolysed by boiling 2N-NaOH to $COMe_2$ and (**I**). (**II**) is also obtained by reduction (Clemmensen) of 6-acetyl-4-methylumbelliferone. (**III**) and anhyd. $AlCl_3$ at 160° yield 8-*acetyl*-4-*methyl*-6-*ethylumbelliferone* (**IV**), m.p. 137° (*Me ether*, m.p. 95°; *semicarbazone*, m.p. >290°; *benzoate*, m.p. 139°), identified by reduction (Clemmensen) to 4-methyl-6:8-diethylumbelliferone, m.p. 137°, also obtained from 6-acetyl-4-methyl-8-ethylumbelliferone (**V**). (**IV**) is converted by boiling N-NaOH into $COMe_2$ and 2-acetyl-4-ethylresorcinol (**VI**), m.p. 130° (lit. 127°) (*Et*$_1$ *ether*, m.p. 84°), which with $CH_2Ac{\cdot}CO_2Et$ and $POCl_3$ affords (**V**). Reduction of (**VI**) by Zn–Hg and HCl affords $2:4:1':3\text{-}C_6H_2Et_2(OH)_2$, m.p. 96—97°. H. W.

Condensation of β-arylglutaconic anhydrides with phenolic ethers. V. M. Bhave (*Rasāyanam*, 1941, **1**, 224).—β-*p*-Anisylglutaconic anhydride, PhOMe, and anhyd. $AlCl_3$ afford (probably) δ-keto-βδ-di-*p*-anisyl-Δ^{α}-pentenoic acid, m.p. 132° (decomp.), and its δ-enol-lactone, m.p. 174°.
H. W.

Naphthalene series. V. Properties of 2-stearyl-, -palmityl-, and -lauryl-1-naphthols and synthesis of 2-octadecyl-, -hexadecyl-, and -dodecyl-1-naphthols. R. D. Desai and W. S. Waravdekar (*Proc. Indian Acad. Sci.*, 1940, **12**, **A**, 507—512; cf. A., 1940, II, 252).—α-$C_{10}H_7{\cdot}OH$, stearic acid, and $ZnCl_2$ at 180° yield 2-*stearyl*-1-*naphthol* (**I**), m.p. 81—82° (*Me ether*, m.p. 42—43°; p-*nitrophenylhydrazone*, m.p. 89—90°), and some α-$C_{10}H_7$ *stearate*, m.p. 125° [with $AlCl_3$ at 140° gives (**I**)]. (**I**) and Br–AcOH at room temp., or HNO_3 (*d* 1·5)–AcOH, afford the 4-*Br*-, m.p. 84—85°, or 4-NO_2-compound, m.p. 71—72°, respectively. (**I**) is reduced (Clemmensen) to 2-*octadecyl*-1-*naphthol*, m.p. 119—120°. (**I**)–Ac_2O–NaOAc at 175—180° yield 2-*methyl*-3-*hexadecyl*-1 : 4-α-*naphthapyrone*, m.p. 73—74°, hydrolysed by 5% aq. NaOH (reflux) to (**I**). Similarly prepared are: 2-*palmityl*-1-*naphthol*, m.p. 83—84° (p-*nitrophenylhydrazone*, m.p. 94—95°; *Me ether*, m.p. 41—42°; 4-*Br*-, m.p. 86—87°, and 4-NO_2-derivative, m.p. 76—77°); 2-*hexadecyl*-1-*naphthol*, m.p. 124—125°; 2-*methyl*-3-*tetradecyl*-1 : 4-α-*naphthapyrone*, m.p. 89°; 2-*lauryl*-1-*naphthol*, m.p. 74—75° (p-*nitrophenylhydrazone*, m.p. 135—136°; *Me ether*, m.p. 37—38°; 4-*Br*-derivative, m.p. 65—66°); 2-dodecyl-1-naphthol, m.p. 150—151°. A. T. P.

Synthesis of substances related to sterols. XXXVI (continuation of Part XXII). A. Koebner and (Sir) R. Robinson [with (in part) H. M. E. Cardwell]. **XXXVII. Derivatives of chrysene.** L. Golberg and (Sir) R. Robinson. **XXXVIII. Ethyl *cyclo*hexane-1 : 4-dione-2-carboxylate and other intermediates.** (Sir) R. Robinson and E. Seijo [with (in part) F. Litvan]. **XXXIX. (A) Derivatives of hydrindene. (B) Reduction of 1-γ-ketobutyl-2-naphthol.** F. J. McQuillin and (Sir) R. Robinson (*J.C.S.*, 1941, 566—575, 575—582, 582—586, 586—590).—XXXVI (cf. A., 1939, II, 75). 3-β-Naphthyl-*cyclo*pentanone-2-acetic acid (**I**) with $SnCl_4$ in CS_2 yields the isomeric *hydroxy-lactone*, m.p. 60° [*acetate* (Ac_2O containing HI, 15 min.), m.p. 157—158°, hydrolysed to (**I**)], which affords the semicarbazone of (**I**). Acetonyl-lævulic acid with 2% aq. KOH at 100° (bath) yields 3-*methyl*-Δ^2-cyclo*pentenone*-2-*acetic acid*, m.p. 109—110°. Difurfurylidene*cyclo*hexanone is hydrogenated (Pd–$SrCO_3$, EtOAc) to 2 : 6-*di*-α-*furyl*cyclo*hexanol*, b.p. 169°/2·5 mm., further reduced to a H_4-derivative, b.p. 180°/1 mm. *trans*-1-Ketodecahydronaphthalene with MgMeI in Et_2O–C_6H_6 yields trans-1-*methyldecahydro*-1-*naphthol*, b.p. 83—88°/2 mm., dehydrated (SO_2 in $COMe_2$) to 1-*methyloctahydronaphthalene*, b.p. 60°/0·4 mm., oxidised $[Pb(OAc)_4]$, then AcOH–H_2SO_4] to a ketone. Methylation ($NaNH_2$ + MeI) of 3′ : 4-diketo-1 : 2 : 3 : 4-tetrahydro-1 : 2-*cyclo*pentenophenanthrene affords a *Me* derivative, m.p. 191—192°. $COPh{\cdot}CH_2Br$ with $COEt{\cdot}CHNa{\cdot}CO_2Et$ in Et_2O yields a product hydrolysed (aq. EtOH–NaOH) to 3-phenyl-2-methyl-Δ^2-*cyclo*pentenone, new m.p. 50—51° (2 : 4-*dinitrophenylhydrazone*, m.p. 232—233°) (with some $Bz{\cdot}[CH_2]_2{\cdot}CO_2H$), reduced ($H_2$, Pd–$SrCO_3$, EtOH) to the -*cyclo*pentanone, b.p. 112—114°/0·4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 203—204°). Bromination of $2:6\text{-}OMe{\cdot}C_{10}H_6{\cdot}COMe$ in $CHCl_3$ yields 5-*bromo*-6-*methoxy*-2-*naphthacyl bromide* (**II**), m.p. 134—135°, and some Br_3-derivative, m.p. 162—163°. (**II**) with excess of C_5H_5N at 100° gives the *pyridinium bromide*, m.p. 255—256° (decomp.), hydrolysed (NaOH) to $6:5:2\text{-}OMe{\cdot}C_{10}H_5Br{\cdot}CO_2H$. (**II**) with $CHNaAc{\cdot}CO_2Et$ in Et_2O yields *Et* 5-*bromo*-6-*methoxy*-2-*naphthacylacetoacetate*, m.p. 78—80°, hydrolysed (aq. EtOH–NaOH) to 5-*bromo*-6-*methoxy*-2-*naphthacylacetone*, m.p. 176—177° (2 : 4-*dinitrophenylhydrazone*, m.p. ∢300°), which with NH_4OAc in AcOH gives a *pyrrole* derivative, $C_{16}H_{14}ONBr$, m.p. 173—175°. (**II**) with $COEt{\cdot}CHNa{\cdot}CO_2Et$ yields *Et* β-5-*bromo*-6-*methoxy*-2-*naphthacylpropionylacetate*, m.p. 89—91°, converted by hot aq. EtOH–NaOH into β-5-*bromo*-6-*methoxy*-2-*naphthoylpropionic acid*, m.p. 204—205°, and 3-(5′-*bromo*-6′-*methoxy*-2′-*naphthyl*)-2-*methyl*-Δ^2-cyclo*pentenone* (**III**), m.p. 177—178° [2 : 4-*dinitrophenylhydrazone*, m.p. 292—293° (decomp.)]. (**III**) and AcOH–HI (*d* 1·7) give 3-(6′-*hydroxy*-2′-*naphthyl*)-2-*methyl*-Δ^2-cyclo*pentenone*, m.p. 204—205°, whilst reduction (H_2, Pd–$SrCO_3$, EtOH, 60°) affords the *Me ether* (**IV**) (two forms), m.p. 116—117° and 84—86°, of 3-(6′-*hydroxy*-2′-*naphthyl*)-2-*methyl*cyclo*pentanone*, m.p. 143—144°. (**III**) with $(CH{\cdot}CO)_2O$ in boiling xylene yields (?) 8-*bromo*-3′-*keto*-7-*methoxy*-2-*methyltetrahydro*-1 : 2-cyclo*pentenophenanthrene*-3 : 4-*dicarboxylic anhydride*, m.p. 147—148°. $6:5:2\text{-}OMe{\cdot}C_{10}H_5Cl{\cdot}COMe$ (modified prep.; cf. A., 1941, II, 295) with Br in $CHCl_3$ yields 5-*chloro*-6-*methoxy*-2-*naphthacyl bromide*, m.p. 116—117°, from which are obtained (as above) *Et* β-5-*chloro*-6-*methoxy*-2-*naphthacylpropionylacetate*, m.p. 87—89°, and 3-(5′-*chloro*-6′-*methoxy*-2′-*naphthyl*)-2-*methyl*-Δ^2-cyclo*pentenone*, m.p. 165—166° [2 : 4-*dinitrophenylhydrazone*, m.p. 296—297° (decomp.)] (with the naphthoylpropionic acid), reduced to the -cyclo*pentanone*, m.p. 137—139°, and (mainly) (**IV**), m.p. 84—86°. *x*-Norequilenin Me ether (**V**) is demethylated (HI) and acetylated to the *acetate*, m.p. 135—136° (picrate), a weak œstrogenic agent. Reduction (H_2, Pd–C + aq. $PdCl_2$, EtOH) of 3′ : 4-diketo- (**VI**) yields 3′-*keto*- (**VII**), m.p. 111—112° (2 : 4-*dinitrophenylhydrazone*, m.p. 255—256°), the 4′-*piperonylidene* derivative, m.p. 173—174°, of which is methylated (KOBu$^{\gamma}$–Bu$^{\gamma}$OH, MeI) to 3′-*keto*-4′-*piperonylidene*-2-*methyl*-, m.p. 158—159°, -1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*. The 16-*piperonylidene* derivative, m.p. 187—188°, of (**V**) is similarly methylated to 16-*piperonylidene*-*x*-*equilenin Me ether* [3′-*keto*-7-*methoxy*-4′-*piperonylidene*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*], m.p. 180—181°, which, like the stereoisomeric 16-*piperonylidene*-*equilenin Me ether*, m.p. 208—209°, cannot be further methylated. 1-*Keto*-6-*methoxy*-2-*piperonylidene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 171—172°, is not methylated by MeI in Bu$^{\gamma}$OH–KOBu$^{\gamma}$, which converts 5-*methoxy*-2-*piperonylidene*-α-*hydrindone*, m.p. 226—227°, into an *isomeride* (or dimeride), m.p. 253—254°. (**VI**) with boiling $PhNO_2$–EtOH–aq. NaOH followed by Ac_2O yields 3′-keto-4-acetoxy-1 : 2-*cyclo*pentenophenanthrene. (**V**) when boiled with PhCHO–EtOH–aq. NaOH and then exposed to air yields 3′-*keto*-7-*methoxy*-4′-*benzylidene*-1 : 2-cyclo*pentenophenanthrene* (also $+0{\cdot}5H_2O$), m.p. 224°. 3′-Keto-4 : 7-dimethoxy- is partly

reduced (H_2, PtO_2, aq. $FeCl_3$, AcOH) to 4 : 7-*dimethoxy*-1 : 2-cyclo*pentenophenanthrene*, m.p. 119—122° (shrinking at 114°). The *oxime*, m.p. 244—246° (*acetate*, m.p. 209—210°), of 3′-keto-7-methoxy-4-ethoxy-1 : 2-*cyclo*pentenophenanthrene is partly reduced (H_2, PtO_2, Ac_2O) to the 3′-*acetamido*-compound, m.p. 219—221°, which could not be hydrolysed to the base. Hydrolysis and re-esterification of Me (*cis*-)3-6′-methoxy-2′-naphthyl*cyclo*pentanone-2-acetate (**VIII**), m.p. 61° (A., 1939, II, 75) gives probably the trans-*isomeride*, m.p. 101—102°. The *trans*-acid, m.p. 147°, when hydrogenated in AcOH yields a gummy acid which reverts to the original when heated with aq. NaOH and acidified; both acids on cyclisation give the same result. Methylation ($Bu^{\gamma}OH$–$KOBu^{\gamma}$–MeI) and hydrolysis of (**VIII**) yields 3-6′-*methoxy*-2′-*naphthyl*-2 : 5 : 5-*trimethyl*cyclo*pentanone*-2-*acetic acid*, m.p. 193—195°. (**VII**) with MgMeI yields 3′-*hydroxy*-3′-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 112—113°.

XXXVII (cf. A., 1933, 828). *Et* 4 : 4′-*dimethoxydesylacetate*, b.p. 220—225°/0·14 mm. (from deoxyanisoin, $CH_2Br{\cdot}CO_2Et$, and EtOH–NaOEt) (free *acid*, m.p. 110°), with $CH_2Br{\cdot}CO_2Et$ and Zn in C_6H_6 yields *β-hydroxy-βγ-dianisyladipolactone*, m.p. 186° (decomp.). δε-Dianisyl-βη-dimethyloctane-βη-diol-*a* (Dodds *et al.*, A., 1939, II, 312) with AcOH–HI at 150° yields 5 : 14-*dimethoxy*-2 : 2 : 11 : 11-*tetramethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 219° (which yields no picric acid when boiled with AcOH–HNO_3), dehydrogenated (Se) to 5 : 14-*dimethoxy*-2 : 11-*dimethylchrysene*, m.p. 199° [*picrate*, m.p. 190° (sinters 169—171°)], also obtained from 2 : 11-diketo-5 : 14-dimethoxy-1 : 2 : 9 : 10 : 11 : 18-hexahydrochrysene-*a* and MgMeI. $(CO_2Me{\cdot}CH_2{\cdot}CHPh)_2$-*a* (*meso*) with MgMeI yields δε-*diphenyl-βη-dimethyloctane-βη-diol*-a, m.p. 125°, cyclised (AcOH–HI at 90°) to 2 : 2 : 11 : 11-*tetramethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 173°, dehydrogenated (Se) to 2 : 11-dimethylchrysene. δε-*Dianisyl-βη-dimethyloctane-βη-diol*-b (prepared as above), m.p. 120°, could not be cyclised. 4 : 3′ : 4′-Trimethoxychalkone, m.p. 80° (lit. 80—81°; 90°; 137—138°) [from 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}COMe$, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, and NaOH in aq. EtOH] with MeOH–NaCN yields *γ-keto-α-cyano-α-anisyl-γ*-3 : 4-*dimethoxyphenylpropane*, m.p. 112—114°, hydrolysed (AcOH–conc. H_2SO_4) to *β-veratroyl-α-anisylpropionamide*, m.p. 174—175°, and thence (aq. EtOH–NaOH) to the *acid*, m.p. 184—185°, reduced (Clemmensen) to *α-anisyl-γ*-3 : 4-*dimethoxyphenylbutyric acid*, m.p. 77—79° (*Me* ester, b.p. 220—222°/1 mm., m.p. 41—43°). This with boiling $POCl_3$ affords 1-*keto*-6 : 7-*dimethoxy*-2-*anisyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**IX**), m.p. 141—142° (p-*nitrophenylhydrazone*, m.p. 205—207°), reduced (Na + PrOH) to 1-*hydroxy*-6 : 7-*dimethoxy*-2-*anisyl*-1 : 2 : 3 : 4-*tetrahydro*-, b.p. 214—215°/0·23 mm., dehydrated (PBr_3 in Et_2O) to 6 : 7-*dimethoxy*-2-*anisyl*-3 : 4-*dihydro-naphthalene*, m.p. 155—156°. (**IX**) with $CH_2{:}CH{\cdot}CH_2{\cdot}MgBr$ in Et_2O–C_6H_6 gives 6 : 7-*dimethoxy*-2-*anisyl*-1-*allyl*-3 : 4-*dihydronaphthalene*, b.p. 207—210°/0·5 mm., and with $CH_2Br{\cdot}CO_2Et$ and Zn in C_6H_6 affords (after hydrolysis with aq. EtOH–KOH) a mixture of γ-(1-*hydroxy*-6 : 7-*dimethoxy*-2-*anisyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*)*acetoacetic acid lactone* (**X**), m.p. 237—238° (*Me ether*, m.p. 209—210°; p-*nitrophenylhydrazone*, m.p. 203—205°), and 6 : 7-*dimethoxy*-2-*anisyl*-3 : 4-*dihydro*-1-*naphthylacetic acid*, m.p. 169—171° (which gives no turbidity with Br in aq. Na_2CO_3), hydrogenated (Pd–$SrCO_3$, EtOH) to the 1 : 2 : 3 : 4-*tetrahydro-acid*, m.p. 192—194° (with a small amount of an acid, m.p. 180—183°). This is cyclised (P_2O_5 in C_6H_6) to 2-*keto*-5 : 14 : 15-*trimethoxy*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*, m.p. 166—168° (*semicarbazone*, m.p. 220°), reduced (Clemmensen) to a saturated (non-homogeneous) *substance*, m.p. 193°. (**X**) is sol. in alkali and repptd. on acidification, and when heated at 250° yields 6 : 7-*dimethoxy*-2-*anisyl*-1-*acetonylidene*-, m.p. 214—215° (2 : 4-*dinitrophenylhydrazone*, m.p. 228—230°), hydrogenated (Pd–$SrCO_3$, EtOH) to -1-*acetonyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 142—145°. 3 : 4 : 3′-*Trimethoxychalkone*, m.p. 66—68° [from *m*-$OMe{\cdot}C_6H_4{\cdot}COMe$, 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CHO$, and aq. EtOH–NaOH], yields (as above) β-m-*anisoyl-α*-3 : 4-*dimethoxyphenyl-propionitrile*, m.p. 98—99°, and -*propionamide*, m.p. 177—178°, γ-m-*anisyl-α*-3 : 4-*dimethoxyphenylbutyric acid*, m.p. 78° (*Me* ester, m.p. 64—65°), and 1-*keto*-6 : 3′ : 4′-*trimethoxy*-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 145—146°.

XXXVIII. The keto-acetal from $CO(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, $CH(OEt)_3$, and AcCl with NaOEt in Et_2O, then dil. HCl, yields *Et* cyclo*hexane*-1 : 4-*dione*-2-*carboxylate* (**XI**), b.p. 116—120°/0·5 mm., which with $Ph{\cdot}[CH_2]_2{\cdot}Br$ and EtOH–KOEt gives a *β-phenylethyl* derivative, b.p. 175—185°/0·7 mm., hydrolysed to the *acid*, m.p. 129—130° (*Me* ester 2 : 4-*dinitrophenylhydrazone*, m.p. 113—114°). (**XI**) is hydrolysed (H_2O at 190° under pressure) to *cyclo*hexane-1 : 4-dione. $CO(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$ with paraformaldehyde and ~20% aq. HCl yields after esterification (EtOH–H_2SO_4) *β-(β′-carbethoxypropionyl)butyrolactone*, b.p. 179—183°/0·5 mm. (*semicarbazone*, m.p. 171—173°; 2 : 4-*dinitrophenylhydrazone*, m.p. 148—152°), which when treated with $CH_2Ac{\cdot}CO_2Et$ (NaOEt), hydrolysed (conc. HCl), and re-esterified yields *Et* 4-*carbethoxy*-3-*methyl*-Δ^2-cyclo*hexenone*-2 : 6-*diacetate*, b.p. 189—191°/0·15 mm., with *substances*, b.p. 150—151°/0·2 mm., 155—156°/0·2 mm., and 161—163°/0·2 mm. $CO(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$ is reduced (Na–Hg + H_2O) to β-(β′-carboxyethyl)butyrolactone. *cyclo*Hexanone (**XII**) and $CH_2(CH_2{\cdot}CO_2Me)_2$ with Na in C_6H_6 at successively 0°, room temp., and the b.p. yield *Me* δ : 2-*diketo*-δ-cyclo*hexylvalerate*, b.p. 132—143°/0·2 mm. (? *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 247°), which with cold conc. H_2SO_4 gives the *enol lactone*, b.p. 120—123°/0·1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 189°), of δ : 2-diketo-δ-*cyclo*hexylvaleric acid. (**XII**) and $(CH_2{\cdot}CO_2Me)_2$ with MeOH–NaOMe at 0° yield *Me pentamethyleneparaconate*, m.p. 73·5—74·5° (no colour with $FeCl_3$); the distilled product, b.p. 145°/0·5 mm. (colour with $FeCl_3$), in EtOH + aq. $FeCl_3$ (1 drop) affords ? *Me H* cyclo*hexylidenesuccinate*, m.p. 99—101°, and is hydrolysed (aq. NaOH or cold conc. HCl) to cyclo*hexylidenesuccinic acid*, m.p. 186—187°; these three substances are oxidised ($KMnO_4$) to (**XII**). $CMeNaAc{\cdot}CO_2Me$ with $CO_2Me{\cdot}[CH_2]_2{\cdot}CO{\cdot}Cl$ in Et_2O yields Me β-keto-α-acetyl-α-methyladipate, hydrolysed (anhyd. NH_3 in Et_2O) to Me β-keto-α-methyladipate, which when treated with $COMe{\cdot}[CH_2]_2{\cdot}NMe_3I$ and NaOMe in C_5H_5N yields (2 hr. at 0°, 2 hr. at 100°) 3-*β-carbomethoxyethyl*-4-*carbomethoxy*-4-*methyl*-, b.p. 164°/0·3 mm., or (2 hr. at 0°, 8 hr. at the b.p.) 3-*β-carboxyethyl*-4-*methyl*-Δ^2-cyclo*hexenone*, m.p. 80—83°.

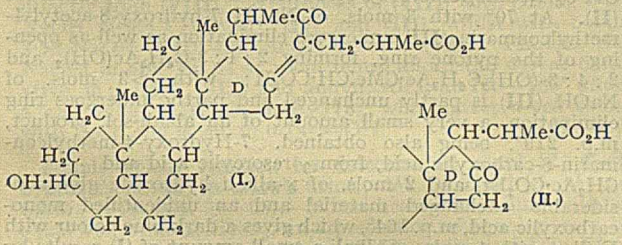
XXXIX (cf. A., 1938, II, 411). Hydrindene, $(CH_2{\cdot}CO)_2O$, and $AlCl_3$ in $PhNO_2$ yield *γ-keto-γ-5-hydrindylbutyric acid*, m.p. 123°, oxidised (NaOCl) to hydrindene-5-carboxylic acid, and reduced (Clemmensen) to *γ-5-hydrindylbutyric acid*, m.p. 48°, which is cyclised (H_2SO_4) to 8-*keto*-5 : 6 : 7 : 8-*tetrahydro*-2 : 3-cyclo*pentenonaphthalene* (**XIII**), b.p. 128—130°/0·2 mm. The *semicarbazone*, m.p. 245°, of (**XIII**) when heated with solid KOH at 20 mm. and the product dehydrogenated (Pd–C at 300°) yields 5 : 6-*benzhydrindene*, m.p. 94° (*picrate*, m.p. 118°). (**XIII**) with MgMeI followed by dehydrogenation yields 3′-*methyl*-5 : 6-*benzhydrindene*, b.p. 170—172°/20 mm. (*picrate*, m.p. 109—110°). Hydrindan-5-one with $NaNH_2$ in Et_2O followed by $COEt{\cdot}[CH_2]_2{\cdot}NMeEt_2I$ in C_5H_5N yields 6-*keto*-5-*methyl*-7 : 8-*dihydro*-1 : 2(or 2 : 3-)cyclo*pentenonaphthalene*, b.p. 153—155°/1·6 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 174—175°), which when dehydrogenated (Se) gives a *phenol*, $C_{14}H_{14}O$, m.p. 162—163°, and when reduced (H_2, Pd, EtOH, then Clemmensen) and dehydrogenated gives a substance; m.p. 38—42° (? 3′-methyl-4 : 5-benzhydrindene, *loc. cit.*). β-$C_{10}H_7{\cdot}OH$ with $COMe{\cdot}[CH_2]_2{\cdot}Cl$ in EtOH–KOEt at 0° yields 1-*γ*-ketobutyl-2-naphthol (**XIV**) (*semicarbazone*, m.p. 179—180°). This, its *oxime*, m.p. 168—169°, or *acetate*, b.p. 174—176°/0·2 mm., is reduced (H_2, PtO_2, AcOH) to a *methyltetrahydrobenzchroman*, m.p. 69°, dehydrogenated (Pd–C) to 2-*methyl*-5 : 6-*benzchroman*, m.p. 90—91°. $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ reduces (**XIV**) to 1-*γ-hydroxybutyl*-2-*naphthol*, m.p. 135—136°, which is reduced (H_2, PtO_2, AcOH, 60°) to some *methyldecahydrobenzchroman*, b.p. 123—126°/0·5 mm. Et *cyclo*hexanone-2-carboxylate in EtOH–NaOEt yields with $COEt{\cdot}[CH_2]_2{\cdot}NEt_2$, *Et* 3-*keto*-4-*methyl*-$\Delta^{4:10}$-*octahydronaphthalene*-9-*carboxylate*, b.p. 135—136°/0·2 mm. (*semicarbazone*, m.p. 166—167°), and with $COMe{\cdot}[CH_2]_2{\cdot}NEt_2$, *Et* 2-*γ-ketobutyl*cyclo*hexanone*-2-*carboxylate*, b.p. 176—180°/12 mm., which with Mg and a trace of I in Et_2O–C_6H_6 gives Et 4-keto-$\Delta^{5:10}$-octahydronaphthalene-9-carboxylate, with no pinacol. A. Lt.

Preparation of dibenzpyrenequinone. II. Structure of isomeride of benzoylbenzanthrone. N. K. Moschtschinskaja (*J. Gen. Chem. Russ.*, 1941, **11**, 45—50; cf. A., 1939, II, 555). —2-Benzoylbenzanthrone (prep. Schaarschmidt, A., 1917, i, 274) has m.p. 237·8° (lit. 206°). The chief product of condensation of BzCl with benzanthrone in presence of $AlCl_3$ is 3-benzoylbenzanthrone, with 9-*benzoylbenzanthrone*, m.p. 206·2°, as a by-product. This is oxidised by CrO_3 in AcOH to 6-*benzoylanthraquinone*-1-*carboxylic acid*, m.p. 349°. R. T.

16-Hydroxymethyleneœstrone.—See B., 1941, III, 296.

Conjugation of œstrogens with proteins. I. L. F. King and W. R. Franks (*J. Amer. Chem. Soc.*, 1941, **63**, 2042—2045).—The K salt of œstrone [2 : 4-*dinitrophenylhydrazone*, m.p. 278—280° (decomp.) (darkens at 268°)] with, best, *p*-$C_6H_4F{\cdot}NO_2$ and Cu dust at 200—210° gives *œstrone* p-$NO_2{\cdot}C_6H_4$ *ether* (65%), m.p. 192—194°, reduced ($SnCl_2$) to the p-$NH_2{\cdot}C_6H_4$ *ether* (**I**), m.p. 166·5—168·5° [*picrate*, m.p. ~160° (decomp.) (darkens at 120°); *semicarbazone*, m.p. ~295°; 2 : 4-*dinitrophenylhydrazone*, m.p. 238—240° (decomp.); N-*Ac* derivative (+xH$_2$O), softens at 100° and 170°, resolidifies, m.p. 201—202°, or (anhyd.) softens at 170—172°, resolidifies, m.p. 202—204°]. The product, m.p. 138—143°, from (**I**) and $COCl_2$ in C_6H_6–PhMe with boiling MeOH and EtOH gives the corresponding *Me*, m.p. 210—212° (softens at 207°), and *Et carbamate*, m.p. 163—165° (softens at 160°), respectively. Diazotisation of (**I**) and coupling with casein at p_H 8—10 then gives an orange-yellow conjugated azoprotein (**II**). The œstrogenic activity of (**I**) is fairly high and 10 times that of (**II**). *Ph* p-*aminobenzyl ether*, m.p. 71—73° (vac.) (*picrate*, m.p. 80·5—82·5°), is obtained by reducing ($SnCl_2$, AcOH–HCl) the NO_2-ether at 0°, but is unstable; conjugation with casein gives an azoprotein, which cannot be extracted by cold org. solvents. *Œstrone* p-*nitrobenzyl ether*, m.p. 176·5—178·5° (semicarbazone, m.p. 273—275°), and 4 : 4′-*di*-p-*nitrobenzyloxy*-$\alpha\beta$-*diethylstilbene*, m.p. 183—185°, are prepared but cannot be reduced to amines. Coupling of *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ with œstrogens failed. Micro-Kjeldahl analysis of the œstrone derivatives is modified to give correct results. R. S. C.

Sterols. CXXII. Sapogenins. LXIX. Structure of the side-chain of sarsasapogenin. Anhydrosarsasapogenoic acid. R. E. Marker, A. C. Shabica, and D. L. Turner (*J. Amer. Chem. Soc.*, 1941, **63**, 2274—2275; cf. A., 1941, II, 199, 257).—Anhydrosarsasapogenoic acid is (**I**) (cf. Fieser *et al.*, A., 1939,



II, 31, 437), since with O_3 in $CHCl_3$ at 0° it gives 3(β)-*hydroxy*-16-*ketobisnorcholanic acid* (**II**), m.p. 285° (decomp.), reduced by Na–EtOH to sarsasapogeninlactone. R. S. C.

Antihæmorrhagic activity of sulphonated derivatives of 2-methylnaphthalene. M. B. Moore (*J. Amer. Chem. Soc.*, 1941, **63**, 2049—2051).—The following relative antihæmorrhagic activities are reported, the salts being sol. in H_2O. 1 : 2 : 4-O:$C_{10}H_5$Me:O (**I**), Na (**II**), or $CH_2Ph{\cdot}NH_3$ (**III**) 1 : 4-dihydroxy-2-methylnaphthalene-3-sulphonate 100, 3-β-dimethylaminoethylamino-2-methyl-1 : 4-naphthaquinone hydrochloride ~25 (free *base*, a glass, prepared from 2-methyl-1 : 4-naphthaquinone 2 : 3-oxide and $NMe_2{\cdot}[CH_2]_2{\cdot}NH_2$ in abs. EtOH at room temp.), *K* 2-*methyl*-1 : 4-*naphthaquinone*-3-*sulphonate* (**IV**) 1·25, 2 : 1- 0·0013, 2 : 6- and 2 : 8-$C_{10}H_6Me{\cdot}SO_3Na$ 0, 2 : 1-$C_{10}H_6Me{\cdot}NO_2$ (m.p. 81—82°) 0·0016, and 1-*amino*-2-*methylnaphthalene*-4-*sulphonic acid* 0·002. (**II**), (**III**), and similar salts are obtained (but could not be isolated in a cryst. condition) from (**I**) and the appropriate $RHSO_3$ in H_2O or EtOH; the K salt is oxidised to (**IV**). R. S. C.

Dynamics of oxidation of alkyl-substituted organic compounds by chromic acid. I. Oxidation of 2-methylanthraquinone and its 1-nitro- and 1-chloro-derivatives to anthraquinone-2-carboxylic acids. M. A. Iljinski and V. A. Kazakova (*J. Gen. Chem. Russ.*, 1941, **11**, 16—22).—The velocity of oxidation of 2-methylanthraquinone (**I**) or its 1-NO_2- (**II**) or 1-Cl-derivative (**III**) (CrO_3 in AcOH at 70°) falls rapidly with rising [H_2O] of the systems, being practically nil in 80% AcOH. The velocity of oxidation of (**I**) is considerably > of (**II**). Both (**III**) and 1-chloroanthraquinone-2-carboxylic acid undergo profound decomp. under the reaction conditions. Directions for the prep. of anthraquinone-2-carboxylic acid and its 1-NO_2- and 1-Cl-derivative, in 98, 88, and 87% yield, respectively, are given. R. T.

III.—TERPENES.

Mutarotation of ethyl-alcoholic solutions of *l*-menthyl benzoylformate. M. M. Jamison and E. E. Turner (*J.C.S.*, 1941, 538—542).—In anhyd. EtOH at 18·8°, the mutarotation of *l*-menthyl benzoylformate is too rapid to be measured, $[\alpha]^{18\cdot8}_{5461}$ being −60·8° (unaffected by addition of traces of H_2O), but at 0° is measurable, follows a first-order law, and gives final $[\alpha]^{0}_{5461}$ −64° to −65°. The mutarotation observed by McKenzie *et al.* (A., 1929, 877) was due to the (unsuspected) presence of traces of H_2O in their abs. EtOH. It is suggested that mutarotation is caused by hemiacetal formation, an ionic mechanism occurring in presence of traces of H_2O. A. Li.

Bornyl chloride and its isomerides. G. A. Rudakov and I. G. Eroschevski (*J. Gen. Chem. Russ.*, 1940, **10**, 1958—1960).—The hydrocarbon, b.p. 157·8—158·5°, obtained by Liubomilov *et al.* (A., 1940, II, 228) by elimination of HCl from the liquid fraction of the additive product from pinene and HCl, is identified as α-fenchene. R. T.

Dehydrogenation of borneol in the vapour phase, using activated nickel catalyst. B. N. Rutovski and P. A. Muliar (*J. Appl. Chem. Russ.*, 1941, **14**, 173—180).—Camphor is obtained in 62—88% yield by passing borneol vapour over Raney Ni activated with alkali or alkaline-earth oxides, at 350°; the activating action of these oxides rises with increasing at. wt. of the metals. The activity of $CuCO_3$ at 350° is very considerably raised by adding 0·25% of KOH. R. T.

***p*-Aminobenzenesulphonamide camphorate.**—See B., 1941, III, 296.

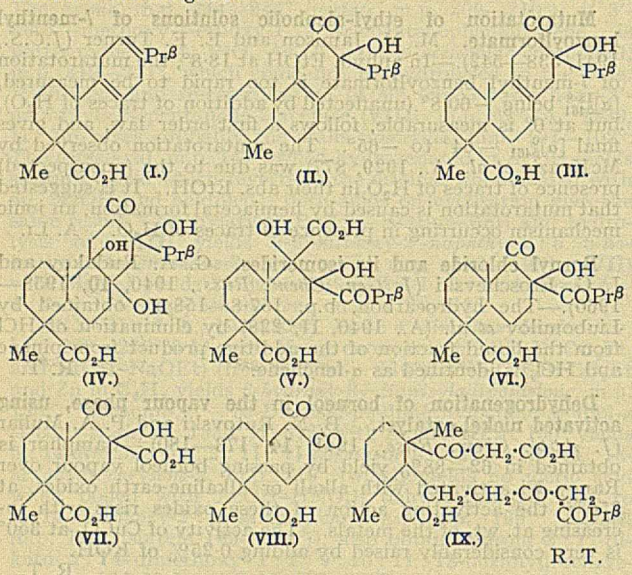
Sesquiterpenes from *Lansium annamalayanum*.—See B., 1941, III, 268.

Sapogenins. XI. Constitution of quillaic and oleanolic acids. P. Bilham and G. A. R. Kon (*J.C.S.*, 1941, 552—561).—Deoxyquillaic (**I**) and echinocystic acid (**II**) are identical [comparison of the acids and various derived CO-compounds (cf. White *et al.*, A., 1939, II, 333)]. (**I**) or (**II**) with 50% AcOH–HBr and Ac_2O at room temp. yields the same iso*diacetyl-lactone*, m.p. 275°. Quillaic acid diacetyl-lactone (A., 1939, II, 436) or its *semicarbazone*, m.p. 256—258°, is reduced (N_2H_4,H_2O and EtOH–NaOEt at 200° under pressure) to the *lactone*, m.p. 272° (*Ac*$_2$ derivative, m.p. 282—283°), of (**I**). Hydrogenation (PtO_2, AcOH) of the *trans*-monoketone previously described (A., 1941, II, 19) yields α-*norechinocystenol*, m.p. 210—211°, $[\alpha]_D$ −26·5° in $CHCl_3$ (acetate, m.p. 170—171°); the β-form (*loc. cit.*) has $[\alpha]_D$ −23° in $CHCl_3$. *trans*-Norhederabetulene, new m.p. 157°, when boiled with Zn–Hg in AcOH–HCl yields *norhederabetulene-III*, m.p. 166—167°, $[\alpha]_D$ +31·4° in $CHCl_3$. Me oleanonate is reduced (N_2H_4,H_2O and NaOEt under pressure) to pure γ-oleananic acid, or (Zn–Hg in AcOH–HCl) to the Me ester, m.p. 170—172°, of β-*oleananic acid* (+H_2O), m.p. 234°. Both acids on heating yield oleanene-II. Measurements on unimol. films of these acids, hedraganic acid, and their esters suggest that the CO_2H group is attached to one of the end rings, probably to $C_{(20)}$; $OH^{(2)}$ would then be on $C_{(19)}$. A possible new formulation for sapogenins of the β-amyrin group is discussed. A. Li.

Saponins and sapogenins. XIX. Decarboxylation of echinocystic acid. C. R. Noller and J. F. Carson (*J. Amer. Chem. Soc.*, 1941, **63**, 2238—2239).—At 280° (later 300—320°)/~10 mm. echinocystic acid (**I**) gives by loss of CO_2 and H_2O *norechinocystadienol* (**II**), m.p. 192—195°, $[\alpha]_D^{24}$ +81·8° in dioxan (*benzoate*, shrinks at 230°, m.p. 231—233°), which contains two conjugated ethylenic linkings in adjacent rings (absorption max. at 2410 A.) and does not react with (:CH·CO)$_2$O, H_2–catalyst, or Na–BuOH. Distillation of the monoacetate of (**I**) in a vac. and hydrolysis of the resulting product also gives (**II**). Structures are suggested for (**I**) and (**II**). R. S. C.

Resinic acids of conifers. V. Structure of γ-sapinic acid. V. N. Krestinski, E. V. Kazeeva, and N. F. Komschilov (*J. Appl. Chem. Russ.*, 1941, **14**, 229—238).—The following products were obtained by oxidation ($KMnO_4$ in 1% NaOH) of α-sapinic acid (**I**): a ketone (**II**), $C_{19}H_{30}O_2$, and the acids $Pr^{\beta}CO_2H$, $C_{20}H_{30}O_4$ (**III**), m.p. 201—204°; $C_{20}H_{32}O_6$ (**IV**), m.p. 131—134°, $C_{20}H_{32}O_7$ (**V**), $C_{18}H_{28}O_5$ (**VI**), $C_{14}H_{20}O_6$ (**VII**), and $C_{13}H_{18}O_4$ (**VIII**). With O_3 (**I**) yields a diozonide, which

decomposes at 100° to the acid $C_{20}H_{30}O_7$ (**IX**). The following structures are assigned :



R. T.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin and related compounds. LI. Solvent fractionation of maple ethanol-lignin. R. F. Patterson, K. A. West, E. L. Lovell, W. L. Hawkins, and H. Hibbert. **LII. Fractionation of lignin and other polymerides.** E. L. Lovell and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 2065—2070, 2070—2073; cf. A., 1940, II, 378).—LI. The amorphous material obtained by ethanolysis of maple wood is separated by fractional pptn. into C_5H_5N-sol., Et_2O-sol. and -insol., and H_2O-sol. products, and low-boiling oils, mol. complexity (determined by η) decreasing in the order named. Analysis and the relation of η and precipitability by H_2O indicate that the Et_2O-sol. and -insol. and H_2O-sol. fractions are chemically similar. The method is probably generally applicable.

LII. Lignin is fractionated by varying the proportions of solvents in its solution in two-layer mixtures of MeOH, H_2O, $CHCl_3$, and CCl_4. R. S. C.

Pigments from marine muds.—See A., 1941, I, 487.

V.—HETEROCYCLIC.

Vinylfuran. M. M. Koton [with A. P. Votinov and F. S. Florinski] (*J. Appl. Chem. Russ.*, 1941, **14**, 181—186).—2-Vinylfuran (**I**) is obtained in 42% yield by distilling β-2-furylacrylic acid at 250—275°. A hard, insol., infusible polymeride of (**I**) is obtained by heating at 100° with 1% of HCl, $SnCl_4$, $SiCl_4$, $SbCl_5$, or AcCl, or at 175° with 5% of linseed oil. R. T.

Carbonyl compounds of the furan series. II. Certain derivatives of furylacraldehyde. G. E. Rudtschenko (*J. Gen. Chem. Russ.*, 1940, **10**, 1953—1957).—Furylacraldehyde and arylamines in EtOH (3 hr. at the b.p.) yield the anils CHR:CH·CH:NR′ (R = *furyl*, R′ = *Ph*, m.p. 65·5°, o-*tolyl*, b.p. 180—181°/6 mm., m-*tolyl*, b.p. 188—189°/8 mm., p-*tolyl*, m.p. 74·5—75°, o-*xylyl*, m.p. 49·5—50°, *mesityl*, m.p. 77—77·5°, o-*anisyl*, m.p. 77·5—78°, p-*anisyl*, m.p. 66°). With p-$C_6H_4(NH_2)_2$ or benzidine the products are p-C_6H_4(*N:CH·CH:CHR*)$_2$, m.p. 188°, or (C_6H_4·N:CH·CH:CHR)$_2$, m.p. 197—198° (decomp.). R. T.

1 : 2-Pyrone-5-carboxylamides.—See B., 1941, III, 269.

Derivatives of coumaran. VIII. Reductions in the coumaranone series. Synthesis of dihydrotubanol. R. L. Shriner and M. Witte (*J. Amer. Chem. Soc.*, 1941, **63**, 2134—2137; cf. A., 1941, II, 201).—4-Hydroxy-2-*iso*propylidenecoumaran-3-one (**I**) and H_2–PtO_2 in abs. EtOH at 45 lb./room temp. give 4-*hydroxy*-2-iso*propylcoumaran*-3-*one* (**II**) (98·5%), m.p. 92° (*ketazine*, m.p. 220°), which with (*a*) boiling Ac_2O, (*b*) BzCl and Na_2CO_3 in boiling 1 : 1 H_2O–$COMe_2$, or (*c*) PhNCO at 100° gives (*a*) the 4-*acetate*, b.p. 147°/3 mm., of (**II**) and 3 : 4-*diacetoxy*-, m.p. 72—74°, b.p. 175°/3 mm., and (*b*) 3 : 4-*dibenzoyloxy*-2-iso*propylbenzfuran*, m.p. 132°, and (*c*) the corresponding 3 : 4-*bisphenylurethane*, m.p. 220°. However, in presence of a little HCl, (**I**) absorbs 5 H_2 and gives 4-*hydroxy*-2-iso*propylhexahydrocoumaran*, b.p. 130°/4 mm. (*phenylurethane*, m.p. 181—182°, obtained only at 100°). With H_2–Raney Ni at 60°/1300 lb. in abs. EtOH, (**I**) gives 3 : 4-*diethoxy*-, b.p. 115°/3 mm., or in dry dioxan at 100°/2700 lb. 3 : 4-*dihydroxy*-2-iso*propyloctahydrobenzfuran*, m.p. 134° (*bisphenylurethane*, m.p. 192°). 4-Benzoyloxy-2-*iso*propylidenecoumaran-3-one and H_2–PtO_2 in HCl–EtOH at 25°/42 lb. similarly give *dihydrotubanol hexahydrobenzoate* (68%), b.p. 170°/2 mm., hydrolysed by NaOH–EtOH–H_2O to dihydrotubanol (*phenylurethane*, m.p. 137°). R. S. C.

Coumarone derivatives.—See B., 1941, II, 408.

Effect of substitution in 7-hydroxycoumarin on the elimination of the pyrone ring by caustic alkali. D. B. Limaye and K. M. Kulkarni (*Rasāyanam*, 1941, **1**, 208—214).—7-Hydroxycoumarin is converted by NaOH at 70° into 2 : 4 : 1-$C_6H_3(OH)_2$·CH:CH·CO_2H; m-$C_6H_4(OH)_2$ (**I**) does not appear to be produced, indicating the absence of ring elimination. Similar results are obtained at 100°, whereas a small proportion of (**I**) results from the use of 30% alkali. 7-Methoxycoumarin is hydrolysed to a small proportion of 2 : 4 : 1-OH·C_6H_3(OMe)·CH:CH·CO_2H, but no m-OH·C_6H_4·OMe (**II**). 7-Hydroxy-4-methylcoumarin is unchanged by 1 mol. of N-NaOH; with 2 mols. there is a small and with 4 mols. a complete elimination of the ring. Similar results are obtained with 2N-alkali, showing the reaction to depend on the proportion and not on the concn. of alkali. 7-Methoxy-4-methylcoumarin is hydrolysed to 2 : 4 : 1-OH·C_6H_3(OMe):CMe:CH·CO_2H with a small proportion of (**II**). At 70° with 3 mols. of NaOH 7-hydroxy-8-acetyl-4-methylcoumarin (**III**) undergoes elimination as well as opening of the pyrone ring, forming 2 : 1 : 3-$C_6H_3Ac(OH)_2$ and 2 : 4 : 3-$(OH)_2C_6H_2$Ac·CMe:CH·CO_2H; with >3 mols. of NaOH (**III**) is partly unchanged and partly undergoes ring elimination, a very small amount of an alkali-sol. product, m.p. 219°, being also obtained. 7-Hydroxy-4-methylcoumarin-8-carboxylic acid, from γ-resorcylic acid and CH_2Ac·CO_2Et, and 2 mols. of N-alkali hydroxide give considerable unchanged material and an unidentified monocarboxylic acid, m.p. 164°, which gives a dark blue colour with $FeCl_3$; with 4 mols. of alkali a small amount of (**I**) results by elimination of the pyrone ring. Hydrolysis of 7-methoxy-4-methylcoumarin-8-carboxylic acid with 4—5 mols. of N-alkali hydroxide yields 3 : 2 : 1-CO_2H·C_6H_3(OMe)·CMe:CH·CO_2H but no β-resorcylic acid Me_1 ether. 7 : 8-Dimethoxy-4-methylcoumarin is very resistant to alkaline hydrolysis. Elimination of the pyrone ring is not observed with 7-hydroxycoumarin-4-acetic acid and 1 mol. of N-alkali hydroxide; it is evident when 2 mols. are used and almost complete with a large excess of alkali. Ring elimination does not take place when 7-methoxycoumarin-4-acetic acid is acted on by an excess of alkali. 7 : 8-Dihydroxycoumarin-4-acetic acid suffers ring elimination when boiled with 4 mols. of NaOH but the 7 : 8-$(OMe)_2$-compound is resistant to boiling alkali hydroxide. H. W.

***iso*Coumarin derivatives. I. Synthesis of *iso*coumarin-3-carboxylic acid.** N. N. Voroshcov, jun., and L. N. Bogusevitsch (*J. Gen. Chem. Russ.*, 1940, **10**, 2014—2016).—Me_2 homophthalate is condensed with $Me_2C_2O_4$ in Et_2O in presence of Na (48 hr. at room temp.); the oily product, heated at 100° for 2 hr., yields *Me*$_2$ iso*coumarin*-3 : 4-*dicarboxylate*, m.p. 134°. This with conc. HCl (2 hr. at the b.p.) gives *iso*coumarin-3-carboxylic acid. R. T.

Chemical investigation of Indian lichens. II. Synthetic uses of some lichen acids. V. V. K. Sastry and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1940, **12, A**, 498—506).—Atronorin, extracted from the lichen, *Parmelia abessinica* (Kremp.) (**I**) with light petroleum, is hydrolysed to Et hæmotommate (**II**), m.p. 113—114°, which is obtained in better yield from Et orsellinate (**III**) [from lecanoric acid obtained from (**I**)] and $Zn(CN)_2$–$AlCl_3$–Et_2O–HCl at 0°. (**II**) and $CH_2(CO_2Et)_2$ (**IV**) + piperidine at room temp. afford *Et*$_2$ 5-*hydroxy*-7-*methylcoumarin*-3 : 8-*dicarboxylate*, m.p. 141—142°, hydrolysed by 5% aq. KOH at room temp. to the 8-*carboxylic acid* (+0·5H_2O),

m.p. 270—271° (decomp.), which is decarboxylated by Cu-bronze and quinoline at 150—160° to 5-*hydroxy*-7-*methylcoumarin* (V), m.p. 215—216° (decomp.), also obtained from (II), (IV), and H_2SO_4. 5-Hydroxycoumarins, unlike the 7-OH-compounds, do not exhibit fluorescence. (III) with $CH_2Ac{\cdot}CO_2Et$–H_2SO_4 at 0°, or (less efficient) $AlCl_3$–$PhNO_2$ at 120—130°, affords *Et* 5-*hydroxy*-4 : 7-*dimethylcoumarin*-6-*carboxylate*, m.p. 179—180°, converted into the *acid*, m.p. 247° (decomp.), and thence 5-hydroxy-4 : 7-dimethylcoumarin, m.p. 258°, also obtained from (III), $CH_2Ac{\cdot}CO_2Et$, and H_2SO_4 at 90—95°. (III) or lecanoric acid, malic acid, and H_2SO_4 at 90—95°, yield (V). Orcinol reacts in the β-position with malic acid to give 7-hydroxy-5-methylcoumarin (cf. Sen *et al.*, A., 1930, 219). A. T. P.

5-Hydroxybenzopyrone group. III. 5-Hydroxy-2 : 3-dimethyl- and 5-hydroxy-2-methyl-3-ethyl-chromone. D. B. Limaye, G. S. Shenolikar, and S. S. Talwalkar. **IV. 5-Hydroxy-2-methyl-3-propylchromone.** V. K. Bhagwat and R. Y. Shahane (*Rasāyanam*, 1941, **1**, 217—220, 220—222).—III. 2-Propionylresorcinol (I) is converted by Ac_2O at 165—170° into its *diacetate*, m.p. 80°, and by Ac_2O and fused NaOAc at 165—170° into 5-*hydroxy*-2 : 3-*dimethylchromone* (II), m.p. 130° (*benzoate*, m.p. 194°), and its *acetate*, m.p. 112—113°. (I) is hydrolysed by boiling N-NaOH to COMeEt, CO_2, and m-$C_6H_4(OH)_2$ (III), by 2·5N-NaOH to (I) and AcOH, and by 0·5N-NaOH to γ-resorcylic acid (IV). 2-*n*-Butyrylresorcinol (V) is transformed by Ac_2O at 150—160° into a liquid *diacetate* and by Ac_2O and NaOAc at 150—155° into 5-*hydroxy*-2-*methyl*-3-*ethylchromone* (VI), m.p. 97° (*benzoate*, m.p. 158°), and its *acetate*, m.p. 107°. (VI) is hydrolysed by boiling 2·5N-NaOH to $COMePr^a$, (V), and (III) and by 0·5N-NaOH to (IV).

IV. 2-*n*-Valerylresorcinol (VII), NaOAc, and Ac_2O at 165—170° afford 5-*hydroxy*-2-*methyl*-3-n-*propylchromone* (VIII), m.p. 67°, and its *acetate*, m.p. 109°, also obtained directly from (VIII). Hydrolysis of (VIII) with boiling 0·5N-NaOH yields $COMeBu^a$, (IV), and (III), whilst with boiling 2·5N-NaOH (VII) and AcOH result. (VIII), PhCHO, and NaOEt in abs. EtOH at room temp. afford the *styrene* derivative, m.p. 158°. (IX) and anhyd. $AlCl_3$ at 160—165° afford a *compound*, $C_{15}H_{16}O_4$, m.p. 118°, which gives a red colour with $FeCl_3$ and is sol. in 0·1N-NaOH. H. W.

Simple colour reaction for detection of equol [7 : 4′-dihydroxy*iso*flavan] in mare's urine. W. Dirscherl (*Z. physiol. Chem.*, 1940, **264**, 57—63).—When heated to boiling with an equal vol. of 25% HNO_3, an aq. solution of equol gives a N-containing red ppt. ["equol-red" (I)], which is sol. in Et_2O, $C_5H_{11}{\cdot}OH$, aq. NaOH, or aq. NH_3. The reaction appears to be sp. (HNO_3 cannot be replaced by HNO_2, HCl, or H_2SO_4). It is inhibited by EtOH. The reaction is given only by the acidic fraction of the urine which is non-volatile in steam; acetylation of this fraction prevents the reaction but subsequent hydrolysis causes it to occur. Œstrone, œstradiol, equilin, and equilenin give yellow colours, as do many other phenols; 7 : 4′-dihydroxy*iso*flavone and its 4′-Me ether do not give the reaction. Various tocopherols give usually yellow, and occasionally red, colours; in the latter case no ppt. results and reaction occurs in presence of EtOH. Reduction ($Na_2S_2O_4$ in aq. AcOH) of (I), which is probably a nitrated quinone, gives a yellow substance (with $FeCl_3$ becomes red). H. B.

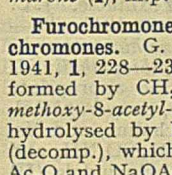
Methylation of hydroxyflavonols using methyl iodide and potassium carbonate. P. S. Rao, P. P. Reddy, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1940, **12, A**, 495—497).—Quercetin, refluxed with MeI–K_2CO_3–$COMe_2$ (action is similar to CH_2N_2) for 60 hr., gives the 3 : 5 : 7 : 3′ : 4′-Me_5 derivative, m.p. 150—151°, whilst herbacetin affords the 3 : 7 : 8 : 4′-Me_4, m.p. 158—160° (sinters at 115—120°), and gossypetin yields the 3 : 7 : 8 : 3′ : 4′-Me_5 compound, m.p. 166—168°. A. T. P.

Pyrylium salts derived from 4-*o*-methylresorcylic aldehyde. L. R. Row and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 510—518).—7-Methoxy-2-phenylbenzopyrylium chloride (I), m.p. 105—106° (cf. Perkin *et al.*, *J.C.S.*, 1908, **93**, 1098), prepared from 4-methoxysalicylaldehyde (II) and COPhMe–HCl–dry EtOAc, is converted by addition of NaOAc to a solution in dil. HCl, or by pouring a solution in AcOH into much H_2O, into *Ph* 2-*hydroxy*-4-*methoxystyryl ketone*, m.p. 126—128°; the latter is synthesised from (II) and COPhMe–KOH–MeOH. Prepared similarly to (I), or in EtOH–EtOAc, using ω : 4-dihydroxy-, ω : 3 : 4-triacetoxy-, or ω : 3 : 4 : 5-tetra-acetoxy-acetophenone, are 3 : 4′-*di*- (III), m.p. 250—251°, 3 : 3′ : 4′-*tri*- (IV), m.p. 258—260° (decomp.), or 3 : 3′ : 4′ : 5′-*tetra-hydroxy*-7-*methoxy*-2-*phenylbenzopyrylium chloride* (V), does not melt at 340°, respectively. All the pyrylium salts exhibit strong greenish fluorescence in conc. H_2SO_4, persisting on addition of H_2O in cases of (I) and (III). Numerous colour reactions are recorded, using a range of buffered solutions. (III), (IV), and (V) in general resemble pelargonidin, cyanidin, and delphinidin, although they show a marked poverty of colour in reactions. A. T. P.

Structure of cannabidiol. XII. Isomerisation to tetrahydrocannabinols. R. Adams, C. K. Cain, W. D. McPhee, and R. B. Wearn (*J. Amer. Chem. Soc.*, 1941, **63**, 2209—2213; cf. A., 1941, II, 331).—Isomerisation of cannabidiol (I) by p-$C_6H_4Me{\cdot}SO_3H$ in boiling C_6H_6 or by a drop of H_2SO_4 in boiling *cyclo*hexane gives *tetrahydrocannabinol* (II), b.p. 169—172°/0·03 mm., $[\alpha]_D^{28}$ ~−265° in 95% EtOH or $COMe_2$. Boiling, dry 0·5M-HCl–EtOH gives an *isomeride* (III), b.p. 157—160°/0·05 mm., $[\alpha]_D^{26}$ −130±5° in 95% EtOH. Seven other acids effected partial cyclisation or none. (II) and (III) are considered to be pure isomerides, products of intermediate [α] (A., 1940, II, 379) being mixtures. In dry Et_2O at 0°, (III) adds HCl to give an oil, $[\alpha]_D^{26}$ −82° in 95% EtOH, unaffected by dil., aq. $NaHCO_3$ but decomposed, when distilled, to HCl and an oil, $[\alpha]_D^{26}$ −196° to −203° in 95% EtOH. (II) gives no such adduct, which confirms the view that isomerism is due to the position of the ethylenic linking. Isomerisation of (III) or other material of low [α] by p-$C_6H_4Me{\cdot}SO_3H$ gives products of intermediate [α], indicating that shift of the nuclear C:C of (I) takes place during or before cyclisation. Absorption spectra of (I), (II), and (III) are very similar but differ from that of the H_4-derivative in which the ethylenic linking is conjugated with the C_6H_6 ring. Cannabidiol Me_2 ether and 2·5% O_3 in AcOH give an ozonide, which in warm H_2O yields CH_2O (confirmation of the CMe:CH_2) and indefinite aldehydes and with CrO_3–AcOH gives 2 : 6-dimethoxy-4-*n*-amylbenzaldehyde (2 : 4-*dinitrophenylhydrazone*, m.p. 228—230°); with 8% O_3 (excess) n-$C_5H_{11}{\cdot}CO_2H$ is obtained. Dihydrocannabidiol and p-$C_6H_4Me{\cdot}SO_3H$ in boiling C_6H_6 give *olivetol Me₂ ether*, b.p. 100—103°/0·05 mm., and a resin (? polymerised menthadiene). Hydrogenation (PtO_2) of H_4-derivatives of any [α] gives the H_6-compound, $[\alpha]_D$ −70°. Attempts to prepare cryst. derivatives of (II) or OH-derivatives of dihydrocannabidiol Me_2 ether failed. The marihuana effect of (II) on dogs is approx. equal to that of (III). (II) has typical marihuana effect on humans, thus confirming the validity of tests on dogs. R. S. C.

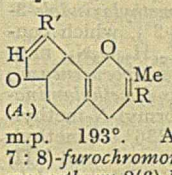
Aminoeuxanthic acid.—See A., 1941, III, 930.

Furocoumarone group. I. Synthesis of 3 : 3′-dimethyl-6′ : 7′-furocoumarone. D. B. Limaye and T. B. Panse (*Rasāyanam*, 1941, **1**, 231—232).—The dry Na salt of 6-hydroxy- is converted by $CH_2Br{\cdot}CO_2Et$ and NaOEt in boiling EtOH into 6-*carboxymethoxy*-7-*acetyl*-3-*methylcoumarone*, m.p. 167° (decomp.) (*Et* ester, m.p. 48°), converted by NaOAc and Ac_2O at 150—155° into 3 : 4′-*dimethyl*-(2′ : 3′-6 : 7)-*furocoumarone* (I), m.p. 27°, b.p. 270°. H. W.



(I.)

Furochromone group. I. Furochromones from hydroxychromones. G. R. Kelkar and D. B. Limaye (*Rasāyanam*, 1941, **1**, 228—230).—The dry Na salt of 7-hydroxy- is transformed by $CH_2Br{\cdot}CO_2Et$ at 160—165° into 7-*carbethoxymethoxy*-8-*acetyl*-2 : 3-*dimethylchromone*, m.p. 137—139°, hydrolysed by boiling 0·1N-NaOH to the *acid*, m.p. 240° (decomp.), which passes when heated above its m.p. or with Ac_2O and NaOAc at 160—170° into 2 : 3 : 4′-*trimethyl*-(2′ : 3′-7 : 8)-*furochromone* (cf. *A*), m.p. 245°. Similarly 6-*carboxymethoxy*-8(6)-*benzoyl*-2-*methylchromone*, m.p. 260° (decomp.), passes at 260—265° or 150—165° in presence of NaOAc and Ac_2O into 4′-*phenyl*-2′-*methyl*-(2′ : 3′-7 : 8)-*furochromone* (cf. *A*), m.p. 193°. Analogously, 4′-*phenyl*-2 : 3-*dimethyl*-(2′ : 3′-7 : 8)-*furochromone*, m.p. 153—155°, is derived from 7-*carboxymethoxy*-8(6)-*benzoyl*-2 : 3-*dimethylchromone*, m.p. 225° (decomp.), and 2 : 4′-*dimethyl*-(2′ : 3′-7 : 8)-*furochromone* from 7-*carboxymethoxy*-8-*acetyl*-2-*methylchromone*, m.p. 273° (decomp.). H. W.



(A.)

Absorption spectra of derride, *iso*rotenone, malaccol, toxicarol, and sumatrol.—See A., 1941, I, 446.

Saponins and sapogenins. XVIII. Non-identity of chlorogenonic, digitogenic, and digitoic acids. C. R. Noller and S. Lieberman (*J. Amer. Chem. Soc.*, 1941, **63**, 2131—2134; cf. A., 1941, II, 264).—The dibasic CO-acid (termed *chlorogenonic acid*) (**I**), $C_{27}H_{40}O_7$, +AcOH, m.p. 235—237° or (usually) 229—230° (shrinks at 225°), $[\alpha]_D^{25}$ −40·6°, $[\alpha]_{5461}^{25}$ −51·3° in dioxan (Me_2 ester, new m.p. 159·5—160·5°, $[\alpha]_D^{23}$ −45·1°, $[\alpha]_{5461}^{23}$ −54·0° in dioxan; fairly sol. Mg salt does not crystallise from 95% EtOH), obtained (A., 1937, II, 346) by oxidation of chlorogenin, is stable towards alkali and differs from digitogenic, +AcOH, m.p. 215·5—217·5° (sinters at 170—175°) or (preheated bath) 183°, $[\alpha]_D^{23}$ −41·2°, $[\alpha]_{5461}^{23}$ −47·6° in dioxan (Me_2 ester, sinters at 153°, m.p. 154·4—159·5°, $[\alpha]_D^{23}$ −49·4°, $[\alpha]_{5461}^{23}$ −54·8° in dioxan), and digitoic acid (anhyd.), sinters at 205°, m.p. 207—209°, $[\alpha]_D^{25}$ −85·7°, $[\alpha]_{5461}^{25}$ −130·9° in dioxan (cryst. Mg salt from 95% EtOH) (cf. Marker *et al.*, A., 1940, II, 99). Na–EtOH–N_2H_4,H_2O at 200° converts (**I**) into gitogenic acid, thus confirming oxidative fission of the $C_{(2-3)}$ linking. The positions of the OH are in doubt. Digitogenin is obtained having m.p. 289—293° (shrinks at 285°). R. S. C.

Thiophen series. LIII. 2 : 2′-Di-α-thiophanthrenequinonyl, the thiophen isologue of 2 : 2′-dianthraquinonyl. W. Steinkopf and M. Kühnel (*Annalen*, 1940, **545**, 33—37).—2 : 2′-Dithienyl, *o*-$C_6H_4(CO)_2O$, and $AlCl_3$ in boiling CS_2 give 5-o-*carboxybenzoyl*-, m.p. 176·5°, and 5 : 5′-*di*-o-*carboxybenzoyl*-2 : 2′-*dithienyl* (**I**), m.p. 300°, separable owing to the insolubility of (**I**) in boiling PhMe. $AlCl_3$–NaCl and (**I**) at 210° afford 3—4% of 2 : 2′-*di*-α-*thiophanthrenequinonyl* [4 : 5 : 4′ : 5′-*diphthalyl*-2 : 2′-*dithienyl*] (**II**), sublimes at >360°/high vac., m.p. 498° (uncorr.), 507° (corr.), which gives a wine-red vat (alkaline $Na_2S_2O_4$), is luminescent (golden-orange) in Hg-light, and is largely unaffected by Zn dust–$ZnCl_2$–NaCl at 370°/45 min. Conversion of (**I**) into (**II**) could not be effected with conc. H_2SO_4, PCl_5, or $AlCl_3$. 5 : 5′-Dimethyl-2 : 2′-dithienyl and *o*-$C_6H_4(CO)_2O$ give (as above) the 3 : 3′-*di*-o-*carboxybenzoyl* derivative (+H_2O), m.p. 147°, ring-closure of which could not be effected. 5-*Phenyl*-2-2′-*quinolylthiophen*, m.p. 144—145·5°, is obtained by distillation of its 4′-CO_2H-derivative (A., 1940, II, 232) with soda-lime. H. B.

Theory of hydrolysis of amines. 2 : 6-Diaminopyridine and 2-amino-6-hydroxypyridine. A. I. Titov and B. B. Levin (*J. Gen. Chem. Russ.*, 1941, **11**, 9—15).—The velocity of hydrolysis by 70% H_2SO_4 at 100° falls in the order 2 : 6-diamino- (**I**) > 2-amino-6-hydroxy- > 2-amino-pyridine. This is explained on lines of resonance mesomerism. The first product of hydrolysis of (**I**) is 2 : 6-dihydroxypyridine (*Ac*$_2$ derivative, m.p. 69°). Rupture of the C_5H_5N ring also takes place during hydrolysis, with production of glutaconic acid. R. T.

2-Picolinoylanilides.—See B., 1941, II, 408.

Preparation of nicotinic acid from pyridine. S. M. McElvain and M. A. Goese (*J. Amer. Chem. Soc.*, 1941, **63**, 2283—2284).—Nicotinic acid is readily prepared from 3-bromopyridine by the action of CuCN (1·5 mol.) at 165—170°, and hydrolysis (90%) of the 3-cyanopyridine (50%) by boiling NaOH (4 g.) in 70% EtOH (40 ml.). R. S. C.

N-**4-Nicotinylsulphanilamide.**—See B., 1941, III, 296.

Monothiophthalimide and some derivatives of oxindole. J. C. Porter, (Sir) R. Robinson, and M. Wyler (*J.C.S.*, 1941, 620—624).—*o*-$C_6H_4(CN)_2$ and NaSH give o-*cyanothiobenzamide*, decomp. ~218°, which with HCl affords *monothiophthalimide* (**I**), m.p. 175°. Condensation of (**I**) with the appropriate reagent affords *anilophthalimidine*, m.p. 170°, *anhydrophthalimide*-N-*methyloxindole*, m.p. 242°, β-quinophthaline, and bismetaindolone (with α-$C_{10}H_7$·OH), and with NH_2·SO_3NH_4 and $CuCl_2$ a *phthalocyanine* is obtained. *N*-Methyloxindole (**II**) and $Et_2C_2O_4$ with Na–EtOH yield *Et* N-*methyloxindole*-3-*oxalate*, m.p. 81° (*phenylhydrazone*, m.p. 158·2°), which condenses with *p*-C_6H_4Me·NH_2 to a *compound*, $C_{20}H_{20}O_3N_2$, m.p. 97°, and with the appropriate reagent to p-*nitrobenzeneazo*-, m.p. 272°, 3-*vanillylidene*-, m.p. 180·5°, and 3-p-*dimethylaminobenzylidene*-N-*methyloxindole*, m.p. 155°. 3-Formyl-*N*-methyloxindole and $NPhMe_2$ give a *compound*, m.p. 236° (*N*-methyloxindolylmethyleneoxindole?). 6-Aminopiperonal and (**II**) with KOH give 3-(6′-*aminopiperonylidene*)-N-*methyloxindole*, m.p. 186°, which with NH_2·SO_3H and quinoline yields 2 : 3-*methylenedioxy*-10-*methylquinindoline*, m.p. 225°. Nitration (KNO_3–H_2SO_4) of (**II**) leads to 6(or 5)-*nitro*-N-*methyloxindole*, m.p. 196°, reduced ($SnCl_2$–HCl) to the -NH_2-compound, m.p. 112·5°. Cotarnine and (**II**) give *anhydrocotarnine*-N-*methyloxindole*, m.p. 154·5° (decomp.), and with isatin-α-anil, *N*-methylindirubin, m.p. 283°, is obtained. The Me derivative of acet-*p*-anisidide with CH_2Cl·COCl, followed by $AlCl_3$, yields 5-*hydroxy*-N-*methyloxindole*, m.p. 186·5°, which is methylated to the *OMe*-compound, m.p. 92°. (**II**) and OPh·$[CH_2]_2$·Br give a *substance*, $C_{20}H_{24}O_4N_2$, m.p. 233°. 5-Hydroxy-*N* : 3-dimethyloxindole and OPh·$[CH_2]_2$·Br afford 5-methoxy-1 : 3-dimethyl-3-β-phenoxyethyl-2-indolinone. F. R. S.

Quinoline derivatives. W. S. Emerson and J. W. Davis (*J. Amer. Chem. Soc.*, 1941, **63**, 2279).—1 : 2-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline zincichloride*, m.p. 152—154°, and *hydriodide*, m.p. 138·5—140°, and 2 : 6 : 8-*trimethylquinoline zincichloride*, m.p. ~200°, are prepared. R. S. C.

Sympathomimetics. II.—See A., 1941, II, 360.

Separation of Acriquin [Atebrine] into optical antipodes. G. V. Tschelincev znd E. D. Osetrova (*J. Gen. Chem. Russ.*, 1940, **10**, 1978—1980).—6-Chloro-9-(δ-diethylamino-α-methylbutyl)amino-2-methoxyacridine (**I**) in EtOH and bromocamphorsulphonic acid yield a 1 : 2 *salt*, m.p. 170—172°, $[\alpha]_D$ −195·5° in EtOH, from which the *l*-isomeride of (**I**), an oil, $[\alpha]_D$ −194·5° in EtOH, is isolated as the *dihydrochloride*, m.p. 243° (decomp.), $[\alpha]_D$ −357° in H_2O. The *d*-isomeride, an oil, $[\alpha]_D$ +197° in EtOH [*dihydrochloride*, m.p. 243° (decomp.), $[\alpha]_D$ +358·6° in H_2O)], is isolated from the mother-liquor from the *l*-salt. R. T.

Synthesis of *ms*.[4 : 5]-benzacridan. H. Waldmann and S. Back (*Annalen*, 1940, **545**, 52—58).—N-o-*Nitrophenyl*-α-*naphthylamine*, m.p. 155° (from *o*-C_6H_4Br·NO_2, α-$C_{10}H_7$·NH_2, and anhyd. NaOAc at 222—226°), is reduced (EtOH–Na_2S or EtOH–conc.HCl–$SnCl_2$) to the o-NH_2-derivative, m.p. 135°, which with $NaNO_2$ in aq. AcOH–H_2SO_4 at −8° followed (after 10 min.) by H_2O at ≯−3° gives 1-α-*naphthylbenztriazole* (**I**), m.p. 114°. Thermal decomp. of (**I**) affords α-naphthocarbazole; no decomp. occurs in boiling $NHPh_2$. 1 : 8-$C_{10}H_6(NH_2)_2$, NH_2Ph, and a little I at 230°/6 hr. and then at 250°/2 hr. give N-*phenyl*-1 : 8-*naphthylenediamine*, b.p. 253°/14 mm., m.p. 133°, converted by $NaNO_2$ in aq. AcOH at ≯−2° into 1-*phenyl*peri*naphthtriazole*, m.p. 134°, which decomposes in boiling $C_{10}H_8$ or (explosively) at 180° alone yielding ms.[4 : 5]-*benzacridan*, m.p. 123°. 1-2′ : 4′-*Dinitrophenyl*peri*naphthtriazole*, decomp. 163°, in boiling $PhNO_2$ yields 7 : 9-*dinitro*-ms.[4 : 5-]*benzacridan*, decomp. 293°, whilst 1-2′ : 4′-dinitrophenylbenztriazole in $PhNO_2$ at 300° (sealed tube) gives 1 : 3-*dinitrocarbazole*, m.p. 266°. *peri*Naphthtriazole decomposes at 236—237° (rapid heating). H. B.

Preparation of 5-phenylhydantoin-5-acetates and -acetamides. B. G. Rogers and H. R. Henze (*J. Amer. Chem. Soc.*, 1941, **63**, 2190—2191).—CH_2Bz·CO_2Et, KCN, and $(NH_4)_2CO_3$ in 60% EtOH at 58—60° give *Et* 5-*phenylhydantoin*-5-*acetate* (60%), m.p. 139—140°, hydrolysed by boiling 20% HCl to the corresponding *acid* (**I**), m.p. 261·5—262·5° (decomp.), and with aq. NH_3 or NH_2Et at room temp. (7—10 days) giving the *amide* (77%), m.p. 255·5—256·5° (decomp.), and *ethylamide* (33%), m.p. 247—248° (decomp.), respectively. Attempts to prepare other amides similarly failed, but the *diethylamide* (65%), m.p. 223—223·5°, *morpholide* (70%), m.p. 168—170°, resolidifies, remelts at 255·5—257°, and *anilide* (62%), m.p. 269—270°, are obtained by way of the acid chloride ($SOCl_2$). With boiling HCl–ROH, (**I**) gives the *Me*, m.p. 223—224°, *Pr*$^{\alpha}$, m.p. 105·5—107°, iso*amyl*, m.p. 126·5—127·5°, *allyl*, m.p. 112·5—113·5°, *OH*·$[CH_2]_2$, m.p. 127—128°, and *CH*$_2$*Ph* ester, m.p. 160—161°. The *Ph* ester, m.p. 226—227°, is obtained from the acid chloride and PhOH in C_5H_5N–$(CCl_2{:})_2$. CH_2Bz·CN, KCN, and $(NH_4)_2CO_3$ in 65% EtOH react incompletely at 58—62°, giving 9% of 5-*phenylhydantoin*-5-*acetonitrile*, m.p. 251·5—252·5° (decomp.). No product was obtained from CHMeBz·CN. CHMeBz·CO_2Et gives 32% of *Et* 5-*phenylhydantoin*-5-α-*propionate*, m.p. 241—242°, hydrolysed by 1 : 1 aq. HCl to the corresponding *acid*, m.p. 271·5—273°. M.p. are corr. R. S. C.

Ultra-violet absorption spectra of 5-methoxy-1-phenyl-3-methylpyrazole and 1-phenyl-3-methyl-5-pyrazolone.—See A., 1941, I, 446.

Action of copper compounds on 5-methyl-2-thiobarbituric acid. T. Nisikawa (*Mem. Ryojun Coll. Eng.*, 1940, **13**, 195—235).—5-Methylthiobarbituric acid (**I**) (1 mol.) and $Cu(OAc)_2$ (1·2 mols.) or $Cu(OH)_2$ in boiling H_2O give a red ppt. converted by boiling ~2N-HCl into a yellow *complex* (**II**), $(C_5H_5O_2N_2S)_2$,$(C_5H_4O_2N_2SCu)_2$,2HCl. Boiling H_2O resolves

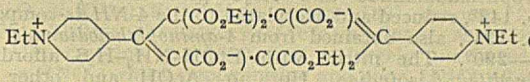
(II) into the sol. *di-(4 : 6-diketo-5-methyl-3 : 4 : 5 : 6-tetrahydro-2-pyrimidyl) disulphide* (III), m.p. 298° (decomp.) (sinters and darkens at 285°) (no colour with $FeCl_3$; contains 6·6% of enolic form in ? 0·005N-MeOH solution), and its red insol. *Cu* salt [also formed from (III) and Cu_2O in boiling EtOH; stable to H_2SO_4 and 3N-NaOH; converted by conc. HCl at room temp. into (II); oxidised by HNO_3 to *di-(2 : 4 : 6-triketo-5-methyl-hexahydro-5-pyrimidyl) ether*, chars at >300°]. The reactions etc. of (III) and its Cu^I salt indicate that they are resonance hybrids. Oxidation (H_2O_2; aq. EtOH–I) of (I) gives no (III) but affords *5-hydroxy-5-methylthiobarbituric acid*, m.p. 233·5°, obtained pure only with difficulty. Cu^I 4-imino-5-methylthiobarbiturate and NaOH form a complex (IV), $C_5H_6ON_3SCu,NaOH$, which with (I) in warm ~2N-HCl yields a *complex* (V), $C_5H_6ON_3SCu,C_5H_6O_2N_2S,HCl$, also obtained in a less pure condition by the direct action of aq. HCl on (IV), whereby an intermediate *complex*, $C_5H_6ON_3SCu,C_5H_7ON_3S,HCl$, can be isolated. Boiling 8N-HCl hydrolyses (IV) to *Cu^I 5-methylthiobarbiturate hydrochloride* (VI), $(C_5H_5O_2N_2SCu,HCl)_2$, best prepared from (I) and Cu_2O in 0·8N-aq. NH_3 at ~43° followed by aq. HCl (final concn. ~2N.), which with 4-imino-5-methylthiobarbituric acid in aq. NaOH followed by 2N-HCl gives (V). Aq. NaOH converts (V) into (IV) and (I). Titration of (VI) with NaOH (phenolphthalein) shows that it functions as a dibasic acid and is thereby converted into Na Cu^I 5-methylthiobarbiturate, which when dried at 115° undergoes oxidation to *Na hydroxy-cupric 5-methylthiobarbiturate* (VII), $[C_5H_4O_2N_2SNaCu(OH)]_2$. Suitable treatment of (VII) with aq. HCl affords a complex, $(C_5H_5O_2N_2ClSCu)_2,xH_2O$ [also formed together with the Cu^I salt of (III) from (I), $Cu(OAc)_2$ or $Cu(OH)_2$, and dil. HCl], which is converted by boiling ~2N-HCl (whereby some O_2 is evolved) or by drying at 115° into *Cu^{II} 5-methylthiobarbiturate hydrochloride* (VIII), $(C_5H_5O_2N_2SCu,HCl)_2$; in the former case (VIII) may be accompanied by some of the *complex*, $(C_5H_5O_2N_2SCu)_2S,2HCl$. (VIII) is also obtained from (I) and $Cu(OH)_2$ or Cu_2O in 10N. aq. NH_3 followed by aq. HCl; in 0·8N. aq. NH_3 (cf. above) (VI) is the ultimate product, whilst in 3·6N. aq. NH_3 a mixture of (VI) and (VIII) results. When kept in contact with H_2O at 40°, (VI) gives *Cu^I 5-methylthio-barbiturate hydrate* (IX), $(C_5H_5O_2N_2SCu,H_2O)_2$ [regenerates (VI) with aq. HCl], which undergoes oxidation and dehydration at 127° to *Cu^{II} 5-methylthiobarbiturate* (X) [*hydrate*, $(C_5H_5O_2N_2SCu,H_2O)_2$, obtained by exposure of (X) to H_2O vapour at 65° or from (VIII) in contact with H_2O at 42°]. (IX) is also prepared from (I) and Cu_2O in dil. aq. NH_3 followed by H_2SO_4. (VIII) appears to exist in orange and brown forms. Prolonged heating of (VII) and (X) at 145° gives the *substances*, $(C_5H_4O_2N_2SNaCu)_2O$ and $(C_5H_5O_2N_2SCu)_2O$ (impure), respectively. The f.p., p_H, and conductivities of aq. solutions of the Na Cu complexes are determined. Constitutions are assigned to many of the complexes. H. B.

Thiobarbituric acids.—See B., 1941, III, 270.

Pyrimidines. CLXXIII. Interaction of chloromethyl ether with 4-methyluracil. II. (Miss) M. M. Endicott and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 2063—2065; cf. A., 1941, II, 270).—4-Methyluracil and $CH_2Cl·OMe$ at 100° (much less well 80—85° or 125—130°) give variable yields of *4-methyl-5-chloromethyluracil* (I), decomp. 330—335° (yellow at 225°), with small amounts of an insol. mixture of di-4-methyl-2 : 6-dihydroxy-5-pyrimidylmethane (II) and (?) a polymeride of 4-methyl-5-hydroxymethyluracil. The structure of (I) is proved by conversion by AgOAc in boiling AcOH into the 5-$CH_2·OAc$ compound. The Cl of (I) is ionic, reacting with aq. $AgNO_3$. With NaOR–ROH at the b.p., (I) gives *4-methyl-5-ethoxy-*, sinters at 195—200°, decomp. 312—315°, and *-methoxy-methyl-uracil*, decomp. >330°, and with H_2O or, better, NaOH (1 mol.) gives *4-methyl-5-hydroxymethyluracil*, m.p. 314—315° (decomp.). Conc. HCl converts (I) into (II), but 4-chloro-methyl- and 5-methyl-4-chloromethyl-uracil are unaffected. R. S. C.

Substituted 2-sulphanilamidopyrimidines. W. T. Caldwell, E. C. Kornfeld, and C. K. Donnell (*J. Amer. Chem. Soc.*, 1941, **63**, 2188—2190).—COR·CH₂R′, HCO_2Et, and Na in Et_2O give good yields of COR·CR″:CH·OH, which with guanidine carbonate in boiling Et_2O give 2-amino- (from *cyclo*hexanone; 23%), 2-amino-5-methyl-8-*iso*propyl- (from menthone; 32%), and 2-amino-8-methyl-5 : 8-*endoiso*propylidene- (from camphor; 64% obtained by condensation in $C_5H_{11}·OH$ with continuous removal of H_2O) -5 : 6 : 7 : 8-tetrahydroquinazoline, 2-amino-4 : 5-dimethyl- (from COMeEt; 6·1%), *-4-methyl-5-n-amyl-* (I), m.p. 92—93° (from $COMe·C_6H_{13}$-*n*; 4·4%; 20% of impure product formed in Pr^{β}_2O with removal of H_2O), and -4 : 5-trimethylene-pyrimidine (from *cyclo*pentanone; very poor yield). The structure of (I) follows from its oxidation by HNO_3 (*d* 1·6) in H_2SO_4 at 0°, without nitration, to *2-amino-5-n-amylpyrimidine-4-carboxylic acid*, m.p. 191—192°. Condensation of the products with *p*-$NHAc·C_6H_4·SO_2Cl$ in C_5H_5N at 60° and later hydrolysis by boiling 0·5—1·0N-NaOH gives *2-sulphanilamido-*, m.p. 255—256° (N^4-*Ac* derivative, m.p. 258—260°), *2-sulphanilamido-5-methyl-8-isopropyl-*, m.p. 185—187° (N^4-*Ac* derivative, m.p. 227·5—228·5°), and *2-sulphanilamido-8-methyl-5 : 8-endoiso-propylidene-*, m.p. 276—277° (N^4-*Ac* derivative, $+3H_2O$, m.p. 261·5—262°), *-5 : 6 : 7 : 8-tetrahydroquinazoline*, *2-sulphanil-amido-4 : 5-dimethyl-*, m.p. 225·7—226·3° (N^4-*Ac* derivative, m.p. 276—277°), *-4-methyl-5-n-amyl-*, m.p. 188—190° (N^4-*Ac* derivative, m.p. 208·3—209°), and *-4 : 6-dimethyl-*, m.p. 178—180° (N^4-*Ac* derivative, m.p. 246·8—247·4°), *-pyrimidine*. These products are moderately to very sol. in H_2O and form sol. hydrochlorides and Na salts. M.p. are corr. R. S. C.

Condensation of α-picoline and quinaldine with active ketones. S. M. McElvain and H. G. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 2213—2217).—2-Methylpyridine with $CO(CO_2Et)_2$ at 140° gives *Et_2 2-pyridylmethyltartronate* (I) (33%), m.p. 38—39°, b.p. 148—150°/1 mm., with $COBz_2$ gives *αα-dibenzoyl-β-2-pyridylethyl alcohol* (16%), m.p. 115—116°, with $COBz·CO_2Et$ (modified prep.), b.p. 106—110°/1 mm., gives *Et α-hydroxy-α-benzoyl-β-2-pyridylpropionate* (74%), m.p. 100—101°, with Bz_2 (at 175°) gives *α-benzoyl-α-phenyl-β-2-pyridylethyl alcohol* (54%), m.p. 110—111°, and with alloxan hydrate gives *5-hydroxy-5-2′-pyridylmethylbarbituric acid* (30%), m.p. 230—231°. Quinaldine gives similarly *Et_2 2-quinolylmethyltartronate* (47%), m.p. 70—71°, *αα-dibenzoyl-β-2-quinolylethyl alcohol* (24%), m.p. 258—260°, *Et α-hydroxy-α-benzoyl-β-2-quinolylpropionate* (II) (4%), m.p. 80—81°, and *5-hydroxy-5-2′-quinolylmethylbarbituric acid* (24%), m.p. 238—240°, but with Bz_2 (at 175°) gives *Ph α-phenyl-β-2-quinolyl-vinyl ketone* (38%), m.p. 187—188°. Low yields are due to formation of other (tarry) condensation products. Thus, 54% of (II) is obtained in boiling dioxan, and (I) is accompanied by 40% of *Et β-2-pyridylacrylate*, m.p. 26—27°, b.p. 104—105°/0·7 mm., and 8% of the dibetaine (? III), m.p. 258—260° (decomp.) (method of formation discussed). The


(III.)

structure of (III) is supported by cryoscopy in C_6H_6, failure to react with EtI, formation of a *ferricyanide*, $+2H_2O$, m.p. >320°, decolorisation of aq. $KMnO_4$ and Br, interaction with conc. aq. NH_3 at room temp. to give a *Et_2 ester diamide*, $C_{30}H_{32}O_{10}N_4$, m.p. 282—284°, formation in boiling dry HCl–EtOH of a *dihydrochloride*, m.p. 129—130°, and later of an ester dihydrochloride, and absorption in presence of Raney Ni at 100°/112 atm. of 2 H, at 155°/112 atm. of a further 9 H, and at 160°/112 atm. of a final 9 H (hydrogenolysis to H_2O-sol. products). R. S. C.

Dithio-β-*iso*indigo (dithiodiphthalimidine) from phthalonitrile. I. Condensation reaction of *o*-dinitriles. II. Mechanism of its formation from phthalonitrile. Derivatives. III. Further members of the series. H. D. K. Drew and D. B. Kelly (*J.C.S.*, 625—630, 630—637, 637—641).—I. o-$C_6H_4(CO)_2NH$ and P_2S_5 in xylene give *mono-*, m.p. 174°, and *di-thiophthalimide*, m.p. >350°. o-$C_6H_4(CN)_2$ in EtOH–NH_3 with H_2S yields *dithio-β-isoindigo* (I),

$\left(o\text{-}C_6H_4{<}\begin{smallmatrix}C\\C(SH)\end{smallmatrix}{>}N\right)_2$ and tautomeric forms, m.p. >350°, which forms metallic *compounds*, $C_{16}H_8N_2S_2Hg$; $C_{16}H_8N_2S_2Hg,HgCl_2,4C_5H_5N$; $C_{16}H_8N_2S_2Cu$; $C_{32}H_{16}N_4S_4Cu,4H_2O$; $C_{32}H_{18}N_4S_4Co,2H_2O$; and $C_{16}H_8N_2S_2Cd,2H_2O$. Methylation of (I) affords *SS′-dimethyl-dithio-β-isoindigo*, m.p. 258° (*Et_2* compound, m.p. 162°), which with HCl gives the *S-methylthio*-compound, m.p. 297° (*Et* compound, m.p. 252°), further converted (HCl–EtOH) into *β-iso*indigo. (I) may also be obtained by condensing phthalimidine with S, dithiophthalimide (II) with H_2S–NH_3, and heating (II) with Ag. N_2H_4 and (I) give *β-isoindigodi-hydrazone*, decomp. 260°. 3 : 6-Dihydroxyphthalonitrile and NH_3–EtOH afford *3 : 6-dihydroxyphthalodiamidine*, decomp. 210—270°.

II. In the formation of (I), *o-cyanothiobenzamide* (III) and (II) are intermediates, generated initially as the NH_4 or alkali salts. The production of (III) from *o*-$C_6H_4(CN)_2$ requires the presence of a hydroxylic solvent and is greatly facilitated by the presence of a base (NH_2Ph can take the place of both together). NaSH in EtOH with *o*-$C_6H_4(CN)_2$ gives (III), chars at 221—224°, and at room temp. and on boiling the Na_2 salt ($+4H_2O$) of (I) is obtained. This salt is methylated to S-*methyldithio-β-*iso*indigo*, m.p. 245°, which with EtI affords S-*methyl*-S′-*ethyldithio-β-*iso*indigo*, m.p. 152—153°. NH_2Ph–EtOH and (II) yield *thiophthalimidemonophenylimine*, m.p. 209°, and *phthalimidemonophenylimine*, m.p. 161°, is prepared from NH_2Ph and monothiophthalimide. Reduction ($SnCl_2$–HCl) of (II) gives *thiophthalimidine*, m.p. 159°. P_2S_5 and phthalimidine afford a *substance*, $C_{16}H_8O_2N_2S$, m.p. >350°, and very little of the thio-compound, which with S at 200° gives (I) and H_2S. The following derivatives of (I) are prepared by using the appropriate reagent: *thio-β-*iso*indigomonophenylhydrazone* [S-*Me* derivative, m.p. 220° (decomp.)], *thio-β-*iso*indigomonophenylimine*, m.p. 265° (S-*Me* derivative, m.p. 212°), and *β-*iso*indigophenylimine*, m.p. 306°; and from the hydrazone are obtained *β-*iso*indigo-dibenzylidene-*, m.p. 272°, *-di-*p*-anisylidene-*, m.p. 259°, and *-tetra-acetyl-dihydrazone*, m.p. 262°. Br and (I) give 1-*bromo*-3-*phthalimidyl*iso*indolenine*, m.p. 297°, which with NH_2Ph affords *monoanilo-β-*iso*indigo*, m.p. 279° (+EtOH, m.p. 280°), and with C_5H_5N yields a *pyridinium bromide* derivative, decomp. ~295° ($+H_2O$ or $+3H_2O$). *SS′*-Dimethyldithio-*β-iso*indigo and Br give a *dibromide*, m.p. 152—154°, in which the Br may be added on to the double bond. *β-iso*Indigo and Br in a sealed tube at 100° afford 6 : 6′-*dibromo-β-*iso*indigo* (?), mixed with other derivatives. Monothiophthalimide with NH_3 does not yield (I) but *iminophthalimidine*, m.p. 205°. HCl and (III) give a hydrochloride.

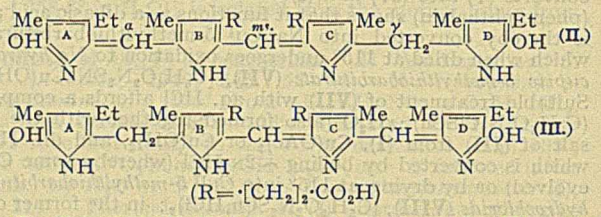
III. *Monothio-β-*iso*indigo* is obtained from EtOH–NH_3 and H_2S with the residues from the purification of *o*-$C_6H_4(CN)_2$; with $NHPh{\cdot}NH_2$ it forms *β-*iso*indigomonophenylhydrazone*, m.p. 273° (slight decomp.). 1 : 2-$C_{10}H_6(CN)_2$ and EtOH–NH_3–H_2S give 6 : 7 : 6′ : 7′-*dibenzdithio-β-*iso*indigo*, m.p. >350°, which with MeI affords the SS′-Me_2 derivative, m.p. 321°. With HCl–EtOH, the Me_2 compound yields the S-*Me* derivative, m.p. >350°, and with H_2SO_4 it forms 6 : 7 : 6′ : 7′-*dibenz-β-*iso*indigo*, m.p. >350°. 4-Nitrophthalodiamide and Ac_2O give 4-*nitrophthalonitrile*, m.p. 142°, reduced and acetylated to the 4-*NHAc*-compound, m.p. 194°, also obtained from 4-*aminophthalodiamide*, m.p. 280—290°. The nitrile with EtOH–NH_3–H_2S affords *diaminodithio-β-*iso*indigo*. Hot aq. AcOH and other org. acids with the dihydrazone of *β-iso*indigo give a blue *substance*, decomp. ~300°, which is probably a hexahydrated form of a tetrapolymeride of *o*-$C_6H_4(CN)_2$. H_2S and *o*-$C_6H_4(CN)_2$ alone give phthalocyanine. F. R. S.

Preparation of free crystalline biotin. V. Du Vigneaud, K. Hofmann, D. B. Melville, and J. R. Rachele (*J. Biol. Chem.*, 1941, **140**, 763—766; cf. A., 1941, II, 188; III, 896).—Biotin Me ester (I) and 0·1N-NaOH at room temp. give free *biotin* (II), $C_{10}H_{16}O_3N_2S$, m.p. 230—232° (decomp.), $[\alpha]_D^{22}$ +92° in 0·1N-NaOH, reconverted by CH_2N_2 into (I). The titration curve for (II) corresponds with that of a monocarboxylic acid. No sp. absorption in the ultra-violet and near ultra-violet region was found. A. T. P.

***N*-Glyoxaline derivatives. II.** S. I. Lurie (*J. Gen. Chem. Russ.*, 1940, **10**, 1909—1914).—The Ag salt of benziminazole, shaken with *p*-NHAc·C_6H_4·SO_2Cl (I) or *o*-$C_6H_4(CO_2)N{\cdot}[CH_2]_2{\cdot}Br$ (II) in EtOH, yields 2-(p-*acetamidobenzenesulphonyl*)*benziminazole* (III), m.p. 197—200°, or 2-(*β-phthalimidoethyl*)*benziminazole*, m.p. 214—215°. The Na salt of theophylline and (I) or (II) in $COMe_2$ yield 7-(p-*acetamidobenzenesulphonyl*)*theophylline* (IV), m.p. 200—203°, or 7-(*β-phthalimidoethyl*)*theophylline*, m.p. 255—257°, which when heated under reflux with N_2H_4,HCl in EtOH yields 7-(*β-aminoethyl*)*theophylline* (*dihydrochloride*, m.p. 187—190°). This condenses with (I) to 7-[*β*-(p-*acetamidobenzenesulphonamido*)*ethyl*]*theophylline*, m.p. 248—250° (+H_2O, m.p. 159—160°), hydrolysed by 9% HCl in 40% EtOH to 7-[*β*-(p-*aminobenzenesulphonamido*)*ethyl*]*theophylline*, m.p. 250—251°. Lysidine and (I) yield 1-(p-*acetamidobenzenesulphonyl*)-2-*methylglyoxaline*, similarly hydrolysed to 1-(p-*aminobenzenesulphonyl*)-2-*methylglyoxaline*, m.p. 228—230°. Hydrolysis of (III) or (IV) gives sulphanilic acid. R. T.

Dibenziminazoles from dibasic acids. R. L. Shriner and R. W. Upson (*J. Amer. Chem. Soc.*, 1941, **63**, 2277—2278).—*o*-$C_6H_4(NH_2)_2$ (2 mols.) and $CO_2H{\cdot}[CH_2]_{2-8}{\cdot}CO_2H$ (1 mol.) in 4N-HCl at 125—135° (bath) give 28—63% of 2 : 2′-*ethylene-*, decomp. 325—330° (312—315°), 2 : 2′-*tri-*, decomp. 258—259° (270—273°), *-tetra-*, decomp. 259—260° (305—309°), *-penta-*, decomp. 225—226° (270—272°), *-hexa-*, decomp. 263—266° (296—299°), *-hepta-*, decomp. 273—275° (269—272°), and *-octa-methylene-bisbenziminazole*, decomp. 277—279° (263—265°) (temp. in parentheses are those of decomp. of the *dihydrochlorides*). $H_2C_2O_4$ gives 2 : 3-dihydroxyquinoxaline. $CH_2(CO_2H)_2$ gives 80% of ? a *polyamide*, $C_9H_8O_2N_2$, decomp. 345—349°, insol. in acid. R. S. C.

Mesobiliviolins. I. Constitution of mesobiliviolin; syntheses of mesobiliviolins IXa and XIIIα; ψ-mesobiliviolin and ketourobilin. W. Siedel and H. Möller (*Z. physiol. Chem.*, 1940, **264**, 64—90).—The mesobiliviolin obtained by Fischer *et al.* (A., 1924, i, 1092) from mesobilirubinogen IXa (= urobilinogen) (I) and hot aq. HCl–$FeCl_3$ can be separated chromatographically into the violet-red mesobiliviolin IXa (II) and the brownish-red mesobilirhodin IXa (III), both of which are isomerides of mesobilirubin differing from this in the position of the ·CH_2· bridge. The primary dehydrogenation product



(R = ·$[CH_2]_2$·CO_2H)

of (I) [*i.e.*, the $N_AN_CC_\alpha C_{ms.}$-H_4-derivative of (II) = the $N_CN_DC_{ms.}C_\gamma$-H_4-derivative of (III)] is urobilin IXα (formed by loss of 2H between $C_{ms.}$ and N_C), which then loses 2 H to give (II) and (III). *Mesobiliviolin* XIIIα *Me*$_2$ ester [*Me*$_2$ 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 8-*tetramethyl*-2 : 7-*diethyl*-(2′α, ms.-5′)-4 : 5-*di-β-propionate*] (IV), m.p. 164° (corr.) (*hydrochloride*, m.p. 170°; forms Zn and Cu complex salts), is synthesised from neobilirubic (V) and formylneoxanthobilirubic acid (VI) in MeOH–48% HBr and N_2. *iso*Neobilirubic acid and (VI) similarly give the less stable Me_2 1′ : 8′-dihydroxy-1 : 3 : 6 : 7-tetramethyl-2 : 8-diethyl-(2′α, *ms.*-5′)-4 : 5-di-β-propionate [*i.e.*, the Me_2 ester of (II)] [hydrochloride, m.p. ~165° (corr.)]. Oxidation of (I) with boiling MeOH–25% HCl–$FeCl_3$ also affords the Me_2 ester (hydrochloride, m.p. 150—160°) of (II), which is separated chromatographically from other products. Formyl*iso*neoxanthobilirubic acid, (V), and MeOH–HBr give the unstable *iso*mesobiliviolin IXα Me_2 ester (VII), which changes rapidly (in $CHCl_3$) to a green substance, converted by dil. HNO_3 or HCl into (III); the production of (III) from (VII) probably involves migration of H from N_C to N_B. Reduction of (IV) with Na–Hg in aq. MeOH affords mesobilirubinogen XIIIα, m.p. 205°; Zn dust and AcOH yield mesobilirubin XIIIα Me_2 ester [dihydrochloride, m.p. 238·5° (corr.)], whilst H_2–PtO_2–MeOH give dihydromesobililrubin XIIIα Me_2 ester (oxidised by air to the mesobilirhodin). Reduction (Na–Hg) of bilirubin or the Me_2 ester of (II) affords the less stable mesobilirubinogen IXα, m.p. 200—205° or 195—200° (mixed m.p. 195—202°), which is readily oxidised (air) to urobilin. The "mesobiliviolinogen" of Fischer *et al.* (*loc. cit.*) is thus a mesobilirubinogen. Oxidation [$Pb(OAc)_4$–AcOH at 60° or Br–$CHCl_3$ on Zn complex salt] of (IV) gives ketourobilin XIIIα Me_2 ester (probably contains C_α:O), which is dehydrogenated by MeOH–25% HCl–$FeCl_3$ to (probably) ketomesobilirhodin XIIIα. Glaucobilin Me_2 ester is formed from (IV) and excess of $FeCl_3$ in MeOH–25% HCl. When kept for some time (IV) partly isomerises to ψ-mesobiliviolin XIIIα Me_2 ester (separated chromatographically), which behaves as (IV) towards Na–Hg, Zn–AcOH, or $Pb(OAc)_4$ but is degraded by $FeCl_3$ to colourless substances. Debye–Scherrer diagrams of the various bilirubinoids are appended. H. B.

Porphyrins. XLIV. Conversion of hæmin into deuteroporphyrin-2 : 4-dicarboxylic acid tetramethyl ester and of hæmatoporphyrin into diacetyldeuteroporphyrin. H. Fischer and K. O. Deilmann (*Annalen*, 1940, **545**, 22—27).—Oxidation of hæmin (1 g.) with $KMnO_4$ in aq. C_5H_5N at room temp. (shaking for 42 hr.), removal of Fe from the residue

obtained after evaporation in a vac. by $Fe(OAc)_2$–HCl, subsequent fractionation with Et_2O and aq. HCl, and final esterification (CH_2N_2) gives *deuteroporphyrin-2 : 4-dicarboxylic acid* Me_4 ester (30—35 mg.), m.p. 185° (*Zn* salt, m.p. 274—280°). Similar oxidation of protoporphyrin affords a small amount of a cryst. substance which forms an oxime. Hæmatoporphyrin is oxidised by $Na_2Cr_2O_7$ in C_5H_5N at 100° (bath) to diacetyldeuteroporphyrin (13%) (Me_2 ester, m.p. 239°). H. B.

Morpholine derivatives.—See B., 1941, II, 407.

Thiazolinyl sulphides.—See B., 1941, II, 335.

Preparation of phenthiazine. E. P. Belokvinitzki (*J. Appl. Chem. Russ.*, 1941, **14**, 187—191).—Phenthiazine is obtained in theoretical yield by heating a mixture of $NHPh_2$ 100, S 38, and I 0·5 g. for 10—15 min. at 190—200° (cf. A., 1914, i, 519). R. T.

4-Thienyl-2-methylthiazole.—See B., 1941, II, 374.

Vitamin-B_1. XX. Analogues of aneurin. Their physiological activity. G. A. Stein, W. L. Sampson. J. K. Cline, and J. R. Stevens (*J. Amer. Chem. Soc.*, 1941, **63**, 2059—2062; cf. A., 1940, II, 285).—CHO·CNa(CH_2·OEt)·CO_2Et, prepared *in situ* from OEt·[CH_2]$_2$·CO_2Et, HCO_2Et, and Na in light petroleum at 30—35°, is treated with NH_2·CEt:NH_2,HCl in H_2O at −5° and then with NaOH and kept at 0°. 4-*Hydroxy*-2-*ethyl*-5-*ethoxymethylpyrimidine*, m.p. 146—146·5°, sublimes at 120°/0·5 mm., thus obtained (55%), with $POCl_3$ at 80° gives the 4-Cl-compound, which with NH_3–EtOH at 120° yields 4-*amino*-2-*ethyl*-5-*ethoxymethylpyrimidine*, m.p. 64·5—65·5°. This is converted by HBr–AcOH at 100° into the 5-CH_2Br compound hydrobromide, m.p. 175—178°, which with 4-methyl-5-β-hydroxyethylthiazole (**I**) in light petroleum gives 4-methyl-5-β-hydroxyethyl-5′-4′-amino-2′-ethylpyrimidylmethylthiazolinium bromide hydrobromide (**II**), m.p. 235·5—236° (decomp.). 4-Hydroxy-2-methyl-6-ethoxymethylpyrimidine, m.p. 158°, and $POCl_3$ at 80° give oily 4-chloro- and thence (NH_3–MeOH; 125°) 4-*amino*-2-*methyl*-6-*ethoxymethylpyrimidine*, m.p. 95·5—96°, which could not be converted into the CH_2·OH compound. 4-*Hydroxy*-5-*methyl*-6-*ethoxymethylpyrimidine* (prep. from its 2-SH derivative by 8% H_2O_2 at 75—80°), m.p. 118°, is similarly converted into the 4-NH_2-compound, m.p. 137—138°, whence HBr–AcOH at 80° gives 4-amino-5-methyl-6-bromomethylpyrimidine hydrobromide. With (**I**) at 115—120° this gives 4-*methyl*-5-β-*hydroxyethyl*-6′-4′-*amino*-5′-*methylpyrimidylmethylthiazolinium bromide hydrobromide* (**III**), m.p. 233—234° (decomp.). In vitamin-B_1 activity (prophylactic and curative) (**II**) equals aneurin, but (**III**), 4-methyl-5-β-hydroxyethyl-5′-4′-amino-6′-methyl- and -6′-4′-amino-2′-methyl-pyrimidylmethylthiazolinium bromide hydrobromide are inactive (cf. lit.). R. S. C.

Thiazyl sulphides.—See B., 1941, II, 374, 404.

Alkaloidal substance from *Carica papaya* seeds. T. B. Panse and A. S. Paranjpe (*Rasāyanam*, 1941, **1**, 215—216).—Extraction of the dried seeds with Prollius' fluid leads to an oil and *carpasemine* (**I**), $C_8H_{10}O_2N_2$, m.p. 165° (*Ac*, m.p. 132°, and *Bz*, m.p. 125°, derivatives). (**I**) is a weak base, neutral to litmus. It gives positive tests with the usual alkaloidal reagents and forms an additive compound with $PtCl_4$. H. W.

Cinchona alkaloids in pneumonia. IX. Quaternary salts. (Miss) M. A. Clapp, (Miss) A. G. Renfrew, and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1941, **63**, 2169—2171; cf. A., 1941, II, 79).—Interaction of β-hydroxyethyl*apo*cupreine with CH_2Cl·CO·NHAr in boiling, dry $COMe_2$ gives β-*hydroxyethyl*-apo*cupreinium carbo*-β-p-*hydroxyethylanilido*-, $[\alpha]_D^{26}$ −59·4° in H_2O, *carbo*-p-*hydroxyanilido*-, $[\alpha]_D$ −87·6° in H_2O, and *carbanilido*-, $[\alpha]_D$ −89·2° in H_2O, -*methochloride hydrochloride*, which have very low antipneumococcic activity. *Cinchonidinium carbo*-p-*hydroxyanilidomethochloride*, $[\alpha]_D^{21}$ −30·3±0·5° in C_5H_5N (*hydrochloride*, $[\alpha]_D^{21}$ −47·0° in H_2O), also has very slight activity. R. S. C.

Aconitum **alkaloids. XIV. Formation of ketones from** *Aconitum* **alkaloids.** R. Majima and K. Tamura (*Annalen*, 1940, **545**, 1—21).—Mesaconitine (Morio, A., 1930, 228) and aq. CrO_3 in cold $COMe_2$ for 10 days give ~80% of *mesaconitinone* (**I**), $C_{33}H_{43}O_{11}N$, decomp. 173°, $[\alpha]_D^{20}$ −35° in $CHCl_3$ [*semicarbazone*, decomp. 214°; *aurichloride*, decomp. 226°; *perchlorate*, decomp. 215°; *Ac*$_2$ derivative, decomp. 215°, prepared by AcCl at 35° (sealed tube)/5 days, readily oxidised by $KMnO_4$ to non-cryst. products], which contains 2·7—2·8 active H (excess over 2 probably due to an enolic OH). Boiling dil. H_2SO_4 (1 equiv.) hydrolyses (**I**) to AcOH (1 equiv.) and benzmesaconinone, $C_{31}H_{41}O_{10}N$ [*hydrochloride* (+4H_2O), m.p. ~230° (decomp. ~221°)]. At 175°/15 mm. in H_2, (**I**) loses 1 mol. each of MeOH and H_2O to give the alkali-insol. *demethanolanhydromesaconitinone* (**II**), $C_{32}H_{37}O_9N$, m.p. 194—194·5°, $[\alpha]_D^{20}$ +26·24° in $CHCl_3$ [*Ac*$_2$ derivative (**III**), decomp. 157°], which contains 2 active H, does not react with CH_2N_2, decolorises Br slowly, and does not give Liebermann's reaction. At 219° (**II**) loses 1 mol. of AcOH and yields a little of a *substance*, decomp. 252°. Dissolution of (**II**) in dil. HCl and pptn. with aq. NH_3 affords *demethanolmesaconitinone*, $C_{32}H_{39}O_{10}N$ (*hydrobromide*, decomp. 212°; *perchlorate*, decomp. 226°; *picrate*, decomp. 194°), which loses H_2O only at high temp./vac. over P_2O_5. Hydrolysis of (**II**) with dil. H_2SO_4 gives *benzdemethanolmesaconinone*, $C_{30}H_{37}O_9N$, decomp. 247—249°, whilst with boiling aq. EtOH–KOH *demethanolmesaconinone*, $C_{23}H_{33}O_8N$, decomp. 250—252°, $[\alpha]_D^{21}$ +76·5° in H_2O [*hydrochloride* (+H_2O), decomp. 267°], results. Reduction (H_2, Pd, EtOH) of (**III**) affords *dihydrodiacetyldemethanolmesaconitinone*, $C_{36}H_{45}O_{12}N$, m.p. ~204°, $[\alpha]_D^{30}$ −31·2° in $CHCl_3$, hydrolysed (aq. EtOH–KOH) to *dihydrodemethanolmesaconinone*, $C_{23}H_{35}O_8N$, decomp. 263°, which is reduced (H_2, PtO_2, AcOH) to tetrahydrodemethanolmesaconinone (*hydrochloride*, decomp. 235°). An aromatic nucleus is not present in (**II**). Oxidation (CrO_3, AcOH) of aconitine gives aconitinone (**IV**), $C_{30}H_{33}O_7N(OMe)_4$, m.p. ~150° (decomp.) (rapid heating), resolidifying with m.p. 212° (decomp.) [*perchlorate*, decomp. 197° (sinters ~185°)], and not aconitoline (Lawson, A., 1936, 351). Loss of MeOH from (**IV**) occurs gradually at room temp. and rapidly when heated, yielding *demethanolaconitinone* (**V**), $C_{33}H_{41}O_{10}N$, m.p. 220° (decomp.), $[\alpha]_D^{20}$ +69·28° in $CHCl_3$ [also isolable from the mother-liquor after crystallisation of (**IV**) from MeOH; *aurichloride*, m.p. ~177°; *picrate*, decomp. 197—198°], which is hydrolysed (aq. EtOH–KOH) to demethanolaconinone, $C_{24}H_{35}O_8N$ [*hydrochloride* (+3H_2O), decomp. 224°]. At 219° (**V**) loses AcOH and passes into pyrodemethanolaconitinone, $C_{31}H_{37}O_8N$, amorphous, m.p. 115—130° [*aurichloride*, decomp. 196°; *perchlorate* (+ H_2O) (**VI**), decomp. 257°; *hydrochloride*, decomp. 224°; the base recovered from the EtOH mother-liquor of (**VI**) affords a *hydrochloride*, decomp. 196° (sinters ~189°)]. Oxidation of (**II**) or (**V**) with HNO_3 (*d* 1·43) in AcOH at 80° gives nitronitrosoaconitic acid (**VII**), $C_{28}H_{24}O_{10}N_3(OMe)_3$,EtOH,$H_2O$, softens 180°, decomp. 282°, $[\alpha]_D^{14(15)}$ −31·94° (−33·92°) in EtOAc (cf. Suginone, A., 1938, II, 74). Hypaconitine (A., 1930, 228) is largely unaffected by CrO_3 or HNO_3, whilst hypoxonitine and conc. HNO_3 afford a non-cryst. product. *iso*-C_5H_{11}·O·NO and (**I**) in AcOH–HCl give *oximinomesaconitinone*, decomp. 236°, $[\alpha]_D^{30\cdot5}$ −98·9° in $CHCl_3$ (*aurichloride* and *picrate*, both soften at 203° and then gradually blacken), oxidised (N_2O_3 in cold $CHCl_3$) to the nitrite, decomp. 205°, of *nitromesaconitinone* (**VIII**), m.p. 215° (sinters ~161°; decomp. 175°), $[\alpha]_D^{30\cdot5}$ −41·4° in $CHCl_3$ (hydrochloride, decomp. 181°). Oxidation (HNO_3) of (**VIII**) affords (**VII**). Mesaconitine probably contains the group ·CH_2·CH(OH)·CH_2·C(OMe)·CH_2·NMe· in addition to 2 OH, OMe, OAc, and OBz. H. B.

Strychnos **alkaloids. XXII. Degradation of quaternary salts of the vomicine group.** H. Wieland and O. Müller. **XXIII. Vomicine.** H. Wieland and O. Schmauss. **XXIV. Oxidation of derivatives of vomicidine.** H. Wieland and R. G. Jennen (*Annalen*, 1940, **545**, 59—71, 72—85, 86—98).—XXII. Vomicine (**I**) and Me_2SO_4 in boiling C_6H_6 (pure, dry reagents must be used under strictly anhyd. conditions) give (cf. A., 1929, 708) the quaternary *methosulphate* (+2H_2O; crystallisation from H_2O) (**II**), m.p. 272° (decomp.), whence *methylvomicinium iodide* (+2H_2O), m.p. ~220°, bromide, m.p. 221°, chloride, m.p. 265° (decomp.), and perchlorate, decomp. ~315°, are obtained. Electrolytic reduction (Pb cathode) of (**II**) in 40% H_2SO_4, removal of H_2SO_4 with $Ba(OH)_2$, and subsequent treatment with KI gives methylvomicidinium iodide, m.p. >300° [corresponding perchlorate, m.p. 280° (decomp.)]. The quaternary hydroxide from (**II**) and $Ba(OH)_2$ or from the halides and TlOH (not Ag_2O owing to its reduction) is unstable and isomerises to *vomicinemethylbetaine* (**III**), $C_{23}H_{28}O_5N_2$ (+3H_2O), m.p. 224°, which does not add MeI and is reduced (H_2, PtO_2, H_2O) to a H_2-derivative, m.p. 260° (decomp.). Solutions of (**III**) in aq. NaOH are sensitive to air, but a Na salt can be obtained by evaporation in a vac. Concn. of a solution of (**III**) in aq. HBr at low

temp. gives the hydrobromide, decomp. ~300° [with aq. Na_2CO_3 affords (**III**)], solutions of which slowly (more rapidly when heated) pass into those of the quaternary salt. Dihydrovomicine (**IV**) and MeI at 100° (sealed tube) afford the methiodide, m.p. 261°; the methosulphate [prep. as for (**II**)] with Na–Hg in warm 0·5N-AcOH regenerates (**IV**). Catalytic reduction (PtO_2) of the quaternary salts of (**I**) gives those of (**IV**). Reduction of (**II**) with 5% Na–Hg in N-AcOH + N-NaOAc at 60—70° yields 30—40% of "*methylvomicine*" (**V**), $C_{23}H_{28}O_4N_2$, m.p. 236·5° [hydrochloride, m.p. 308° (decomp.); perchlorate, decomp. >300°], which contains OMe and NMe, and is reduced (H_2, PtO_2, 2N-AcOH) to a H_4-derivative [*picrate*, m.p. 220° (decomp.)]. Demethylation [AcOH–HI (*d* 1·7) and red P; aq. HBr] of (**V**) gives an impure *base*, $C_{22}H_{26}O_4N_2$, m.p. 294°. The methiodide, m.p. 244—245° (decomp.) (formed readily in the cold), of (**V**) is reduced (Na–Hg, aq. AcOH–NaOAc) to "*dimethylvomicine*" (**VI**), $C_{24}H_{32}O_4N_2$, m.p. 114° [obtained cryst. through the perchlorate, m.p. 274° (decomp.)], further reduced (H_2, PtO_2, 2N-AcOH) to a H_2-derivative, m.p. 139°. The methiodide, m.p. 261°, of (**VI**) is unaffected by Na–Hg or boiling aq. NaOH; the quaternary hydroxide (prep. by Ag_2O) decomposes at 160° to NMe_3 and a non-cryst. substance. Deoxyvomicine methobromide is reduced (Na–Hg) to a *base* (**VII**), $C_{23}H_{30}O_3N_2$, m.p. 221°, $[\alpha]_D$ +99·6° in $CHCl_3$, which contains 2 NMe but no OMe; the *methiodide*, m.p. 248° (decomp.), of (**VII**) with Ag_2O in cold H_2O (reduction occurs if warmed) gives the hydroxide (loses NMe_3 at 150°). Reduction (H_2, PtO_2, 2N-AcOH) of (**VII**) affords a 3 : 1 mixture of isomeric H_4-derivatives, m.p. 150° and 214°.

XXIII. Deoxyvomicidine (**VIII**) [*methiodide* (+$2H_2O$), m.p. 175°, obtained in poor yield] is prepared *in situ* by electrolytic reduction (Pb electrodes) of colourless deoxyvomicine (**IX**), m.p. 207°, $[\alpha]_D^{20}$ +209° in $CHCl_3$ [*methiodide*, m.p. 270° (decomp.)], in dil. H_2SO_4, and then oxidised (CrO_3) at 0°—room temp. to a *base*, $C_{16}H_{20}ON_2$, m.p. 70°, $[\alpha]_D^{20}$ +341° in $CHCl_3$ [*dihydrochloride* (+H_2O) (**X**), m.p. 256° (decomp.); perchlorate, m.p. 263° (decomp.)]. Reduction (H_2, PtO_2, H_2O) of (**X**) gives a base, $C_{16}H_{24}N_2$ (*methiodide*, m.p. 178°), whilst (**VIII**) (in AcOH) affords a base, $C_{22}H_{30}ON_2$ [*hydrochloride* (+0·5EtOH), m.p. 250—254° (decomp.)]. Vomicine with AcOH–HI (*d* 1·96) and red P yields (cf. A., 1929, 708) (**IX**) and a small amount of an I-containing base, decomp. 225°, which with Zn dust and AcOH affords a *dihydrodeoxyvomicine*, m.p. 194°, $[\alpha]_D^{20}$ +173° in $CHCl_3$; the primary product of the HI reduction is not (**IX**) but the yellow modification (**XI**), new m.p. 211°, $[\alpha]_D^{22}$ +242° in $CHCl_3$ (cf. A., 1937, II, 126), which when heated for a long time with $CHCl_3$ (used for extraction of the crude reduction product) or EtOH passes into (**IX**). The absorption spectra of (**IX**) and (**XI**) are different. Furthermore, (**IX**) absorbs ~8 H on catalytic reduction (PtO_2, AcOH) to give two *bases*, $C_{22}H_{30}O_2N_2$, m.p. 177°, $[\alpha]_D^{21}$ −94·4° in $CHCl_3$, and m.p. 143° (may not be pure), in addition to the isomeride, m.p. 211°, $[\alpha]_D^{21}$ +73° in $CHCl_3$, previously described (A., 1933, 1312); (**XI**) similarly slowly absorbs 4 H forming the base, $C_{22}H_{28}O_3N_2$, m.p. 220° (*loc. cit.*), which may also be produced from (**IV**). The acid, $C_{17}H_{22}O_7N_2$ (A., 1929, 708), is now shown to be $C_{16}H_{20}O_6N_2$ (+$5H_2O$); with CH_2N_2 it gives a *compound*, $C_{18}H_{24}O_6N_2$, and it is decarboxylated at 200° to a *base*, $C_{15}H_{20}O_4N_2$, m.p. 264—266°, $[\alpha]_D^{18}$ −51·3° in $CHCl_3$, which contains NMe (does not add MeI) and 1 active H, and does not give the CHI_3 reaction.

XXIV. Electrolytic reduction (Pb electrodes) of dihydrodeoxyvomicine in 60% H_2SO_4 and subsequent neutralisation (conc. aq. NH_3 at ≯5°) gives the unstable *dihydrodeoxyvomicidine*, decomp. 264° (darkens from 240°) [*methiodide* (+$3H_2O$), m.p. 204° (decomp.)], which is oxidised (CrO_3, aq. H_2SO_4) to a *base*, $C_{16}H_{22}ON_2$, m.p. 88° [*dihydrochloride* (+H_2O) (**XII**), m.p. 255° (decomp.); in some cases an anhyd. *dihydrochloride*, m.p. 282°, is obtained]. With Pd at 220°, (**XII**) affords a NMe-free base, $C_{15}H_{20}N_2$ (as *dihydrochloride*, decomp. 300°). Oxidation (CrO_3, dil. H_2SO_4) of dihydrovomicidine (prep. *in situ* by electrolytic reduction of dihydrovomicine in 60% H_2SO_4) gives a poor yield of an *acid*, $C_{16}H_{20}O_4N_2,3H_2O$, decomp. 264° (darkens from 220°) (*hydrochloride*, decomp. >300°; Me_1 ester *dihydrochloride*, decomp. 286°). Electrolytic reduction of *iso*dihydrovomicine affords *iso*dihydrodeoxyvomicidine (*dihydrochloride*, decomp. ~215°), oxidised (CrO_3 ≡ 30 O; dil. H_2SO_4) to a base, $C_{16}H_{20}O_3N_2$ (*dihydrochloride*, decomp. 295°, absorbs 4 H on catalytic reduction). Partial structures are suggested for many of the compounds. H. B.

VI.—ORGANO-METALLIC COMPOUNDS.

Arsinoanilinotriazines.—See B., 1941, III, 270.

Preparation of *p*-aminobenzenephosphonic [phosphanilic] acid. H. Bauer (*J. Amer. Chem. Soc.*, 1941, **63**, 2137—2138).—*p*-$C_6H_4Cl\cdot PO_3H_2$ (modified prep.), m.p. 188° (lit. 184—185°) (NH_4 salt), and freshly prepared Cu_2O (1 mol.) in 28% aq. NH_3 at 150° give 62% (Cu gives only 5—15%) of *phosphanilic acid*, m.p. 245° (decomp.), resolidifies, remelts at ~285° [*Ac* derivative, m.p. 229° (decomp.)]. R. S. C.

Thiophen series. LIV. Mercuration of nitrated thiophens. W. Steinkopf (*Annalen*, 1940, **545**, 38—45).—3-Nitrothiophen (**I**) (1 g.) and HgO (6 g.) in boiling AcOH (50 c.c.) for 1 hr. give the *tri*(*acetoxymercuri*)-derivative (**II**), amorphous, darkens >270°, converted by aq. KI–I into 2 : 4 : 5-*tri-iodo*-3-*nitrothiophen* (**III**), m.p. 169·5—170·5°. $Hg(OAc)_2$ (4 g.) and (**I**) (1 g.) in 50% AcOH (40 c.c.) first at 55—60° (30 min.) and then at 95° (1 hr.) afford the 2 : 5-*di*(*acetoxymercuri*)-derivative, decomp. ~220° (preheated bath), and thence 2 : 5-*di-iodo*-3-*nitrothiophen*, m.p. 108·5—110°. The product obtained from a nitrothiophen, m.p. 42—43° [mixture of (**I**) and 2-nitrothiophen (**IV**) obtained by nitration of thiophen], and HgO in boiling AcOH is converted into (**III**) and 2 : 3-*di-iodo*-5-*nitrothiophen* (**V**), m.p. 98—99°. The compound, m.p. 79—80°, obtained by nitration of 2 : 3-di-iodothiophen and previously described (A., 1937, II, 163) as (**V**), is now shown to be a mixture of impure (**V**) and 3-*iodo*-2-*nitrothiophen*, m.p. 131—134°. Nitro-2-thiophenic acid, m.p. 130—135° (Römer, A., 1887, 362), and HgO in boiling AcOH give mainly (**II**) [and thence by distillation with dil. HCl pure (**I**), m.p. 78—79° (lit. 67—69°, 75—77°); this method is recommended for the prep. of small amounts of (**I**)]; the product from the mother-liquors similarly affords a mixture of (**I**) and (**IV**). 5-Nitro-2 : 2′-dithienyl and $Hg(OAc)_2$ in AcOH at 100° (bath) give the 3 : 3′ : 5′-*tri*(*acetoxymercuri*)-derivative, yellow, becomes orange-red and amorphous at 140°, converted by boiling H_2O into the red 3 : 3′-*di*(*hydroxymercuri*)-5′-*acetoxymercuri*-derivative and by aq. KI–I into 3 : 3′ : 5′-*tri-iodo*-5-*nitro*-2 : 2′-*dithienyl*, m.p. 187—189°. H. B.

Thiophen series. LV. 2-Methyl-3-ethyl- and 3-methyl-2-ethyl-thiophen and derivatives. W. Steinkopf, A. Merckoll, and H. Strauch (*Annalen*, 1940, **545**, 45—51).—*Et₂ α-acetyl-α-ethylsuccinate*, b.p. 143—145°/14 mm. (from Et_2 sodioacetosuccinate and EtI in boiling C_6H_6), is hydrolysed (dil. HCl) to *β-ethyl-lævulic acid*, b.p. 144—146°/14 mm., which with P_2S_5 at 130—140° gives 2-*methyl*-3-*ethylthiophen* (**I**), b.p. 156—157°. With $HgCl_2$ and NaOAc in aq. EtOH, (**I**) affords the 5-*ClHg*-derivative (**II**), m.p. 150—151°, converted by NaI (2 mols.) in $COMe_2$ into *Hg di*-2-*methyl*-3-*ethyl*-5-*thienyl*, m.p. 85—85·5°, which with $HgHal_2$ in $COMe_2$ gives 5-*bromomercuri*-, m.p. 165·5—166·5°, and 5-*iodomercuri*-2-*methyl*-3-*ethylthiophen*, m.p. 157·5—158°. 2-*Methyl*-3-*ethyl*-5-*acetothienone*, b.p. 132—134°/16 mm. (p-*nitrophenylhydrazone*, m.p. 189·5°), is obtained from (**I**), AcCl, and $AlCl_3$ in light petroleum. 5-*Iodo*-2-*methyl*-3-*ethylthiophen*, b.p. 103—103·5°/4 mm. [from (**II**) and aq. NaI–I], with Cu-bronze at 210—225° affords 5 : 5′-*dimethyl*-4 : 4′-*diethyl*-2 : 2′-*dithienyl*, m.p. 48·8—49·4° [3 : 3′-*di*(*acetoxymercuri*)-derivative, decomp. 225—230°]. Clemmensen reduction of 3-methyl-2-acetothienone gives 3-*methyl*-2-*ethylthiophen* (**III**), b.p. 160—161·5° (5-*ClHg*-derivative, m.p. 172—173° after sintering, converted by NaI in $COMe_2$ into the 5-*IHg*-derivative, m.p. 156—157°, and *Hg di*-3-*methyl*-2-*ethyl*-5-*thienyl*, m.p. 99—100°). Excess of aq. $Hg(OAc)_2$ converts (**III**) into the 4 : 5-*di*(*acetoxymercuri*)-derivative, m.p. 248—250° (decomp.). 3-*Methyl*-2-*ethyl*-5-*acetothienone*, b.p. 140—143·5°/14 mm. [p-*nitrophenylhydrazone*, m.p. 186—187°; *semicarbazone*, m.p. 228·5—229° (decomp.)], is prepared. H. B.

Phenyl- and 3-pyridyl-mercuri salts.—See B., 1941, III, 270.

Relative reactivities of organo-metallic compounds. XXXIX. Addition reactions of organo-metallic compounds with conjugated systems. H. Gilman and R. H. Kirby (*J. Amer. Chem. Soc.*, 1941, **63**, 2046—2048; cf. A., 1941, II, 273).—1 : 4-Addition to COPh·CH:CHPh (**I**) occurs with the less reactive $BePh_2$, $ZnPh_2$, $AlPh_3$, and MnPhI, and 1 : 2-addition with more reactive CaPhI, KPh, LiPh, and NaPh. LiPh gives 13% of $CHPh_2\cdot CH_2\cdot COPh$ as well as, mainly, $CHPh{:}CH\cdot CPh_2\cdot OH$ (cf. lit.). Similarly, with *p*-$NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot COPh$ (**II**), MgPhBr and $BePh_2$ give *p*-

$NMe_2 \cdot C_6H_4 \cdot CHPh \cdot CH_2 \cdot COPh$ (**III**) (66 and 71%, respectively) (cf. lit.), CaPhI gives *diphenyl-p-dimethylaminostyrylcarbinol* (**IV**), m.p. 117° (64%), and LiPh gives (**III**) 14 and (**IV**) 76%. CPh_2:NPh with NaPh or KPh gives $CPh_3 \cdot NHPh$ by 1 : 2-addition. Interaction with (**I**) is used to show the interconversions, $BeCl_2 + 2LiPh \rightarrow BePh_2 + 2LiCl$, $MnI_2 + LiPh \rightarrow MnPhI + LiI$, and $MgI_2 + p\text{-}NMe_2 \cdot C_6H_4Li \rightarrow LiI + p\text{-}NMe_2 \cdot C_6H_4 \cdot MgI$. $p\text{-}NMe_2 \cdot C_6H_4 \cdot MgI$ with (**I**) gives (**III**). $p\text{-}NMe_2 \cdot C_6H_4Li$ with (**I**) gives *phenyl-p-dimethylaminophenylstyrylcarbinol* (75%), m.p. 131°, and (**III**) (12%). R. S. C.

VIII.—ANALYSIS.

Rapid preliminary determination of m.p.—See A., 1941, I, 484.

Advances in microchemistry. I. Quantitative organic micro-analysis. H. Roth (*Angew. Chem.*, 1940, **53**, 441—450).—Recent work (145 references) on micro-balances and on the following determinations is summarised briefly: C, H, O, N, halogens, S, P, As, metals in org. compounds, equiv. wt., active H; the CO, OMe, OEt, NHAlk, OAc, and CMe_2 groups and double linkings; the sap., I, and diene vals.; and of mol. wt. by the b.p. elevation, f.p. depression, osmotic pressure, and v.p. methods. J. G.

Systematic qualitative organic micro-analysis. Improved apparatus for micro-preparative work. H. K. Alber (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 656—658).—The construction and operation of the following are described: an improved balance for micro-preparative work, sensitive to 0·1 mg., based on the Friedrich torsion spring micro-balance; a micro-mortar and pestle for grinding small quantities of material (data are presented on recoveries of materials of varying hardness); a combined separatory and sedimentation funnel, which has a small sediment collector in the stopcock. J. D. R.

Removal of nitrogen oxides in semi-micro-determination of carbon and hydrogen. P. J. Elving and W. R. McElroy (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 660—663).—The defects in the use of PbO_2 in org. combustions are discussed, and suggested substitutes are described. Various metals and oxides remove N oxides satisfactorily but are excluded as they give low C and H vals. The use of a solution of $KMnO_4$ in H_2SO_4 between the H_2O and CO_2 absorption tubes gives improved results, and is considered to be better and cheaper than PbO_2; this also simplifies the tube filling. J. D. R.

Report on recommended specifications for microchemical apparatus. Carbon–hydrogen and Dumas nitrogen. G. L. Royer, H. K. Alber, L. T. Hallett, W. F. Spikes, and J. A. Kuck (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 574—580).—Specifications for various units for the C–H and Dumas N determinations by the Pregl technique are illustrated fully. L. S. T.

Modifications in the combustion micro-method for carbon and hydrogen. G. L. Royer, A. R. Norton, and O. E. Sundberg (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 688—690).—A detailed description is given of an automatic combustion furnace controlled by time switches, and of modifications in the H_2O and CO_2 absorption tube assembly which adapt the normal C and H determination apparatus to the new automatic furnace. The use of one-rate automatic combustion, ground-glass joints for connecting the absorption tubes, weighing the tubes filled with O_2, simplification of filling, elimination of preheater, and shorter intervals for the weighing of the absorption tubes make the procedure applicable to routine industrial analysis. J. D. R.

Effect on selenium on the Kjeldahl digestion. R. B. Bradstreet (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 657).—In the Kjeldahl determination of N, the use of Se catalyst, alone or with $FeSO_4$ or $CuSO_4$, causes a loss of N, and quantities >0·25 g. should not be used. J. D. R.

Micro-Kjeldahl determination of nitrogen. E. P. Clark (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 641—647).—Apparatus (digester; Parnas–Wagner type still) and standard procedure are recommended. The sample is weighed on tared cigarette paper, which is digested with the sample, Hg is removed by addition of $Na_2S_2O_3$ with the alkali, and the NH_3 is collected in 4% aq. H_3BO_3 and titrated (Me-red) with 0·02N-HCl. By using Friedrich's modification (A., 1933, 621) N in compounds containing N·N, NO, and NO_2 groups may be determined with precision. A. A. E.

Micro- and semi-micro-Kjeldahl method for the determination of nitrogen. F. Acree, jun. (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 648—651).—Satisfactory results were obtained by using Clark's procedure (preceding abstract) for the determination of N in 15 compounds, employing 5—20-mg. samples. A. A. E.

Direct determination of oxygen in organic compounds by hydrogenation. III. Reduction mechanism on the nickel–thoria catalyst. K. Morikawa, T. Kimoto, and R. Abe (*Bull. Chem. Soc. Japan*, 1941, **16**, 229—232; cf. A., 1941, II, 157).—$CO + CO_2$ produced in the cracking zone at 950° are reduced on the $Ni\text{–}ThO_2$ catalyst in H_2 at 350°; relations between temp. and equilibrium consts. of the reactions $CO + 3H_2 = CH_4 + H_2O$ and $CO_2 + 4H_2 = CH_4 + 2H_2O$ are discussed. Sucrose, cellulose, lignin, and brown coal of Jarahinohl mine (Manchoukuo) are decomposed at various temp. in H_2 and % O evolved as volatile O compound is measured; little change resulted from varying the time of reaction between 10 and 30 min. Classification of O bonds in the samples is recorded; *e.g.*, sucrose affords 72·73% of alcoholic O, 18·18% of pyran- or furan-O, and 9·09% of etheric O, of the total O (51·43%). A. T. P.

Analytical investigation of hydrocarbon mixtures by means of Raman spectra. Detection of paraffins and olefines with straight and branched chains. J. Goubeau and (Frl.) V. von Schneider (*Angew Chem.*, 1940, **53**, 531—535).—The method previously described (cf. A., 1938, II, 120) has been applied to the analysis of 12 hydrocarbon fractions. The data are presented in detail and include a table comparing the Raman frequencies of the fractions with those of 18 pure hydrocarbons. C. R. H.

Determination of alcohols in dilute aqueous solution. R. Skrabal (*Z. anal. Chem.*, 1940, **119**, 222—226).—Modifications of and improvements in the Fischer–Schmidt method (A., 1926, 632) are described. It can then be extended to unsaturated alcohols. Cylinder N_2, freed from O_2, replaces CO_2, and the absorption flasks are fitted with sintered-glass discs to facilitate absorption. Details of procedure, and data for PrOH and allyl alcohol, are given. L. S. T.

Distinction and identification of *n*- and *iso*-propyl alcohol with mercuric sulphate. G. Denigès (*Bull. Trav. Soc. Pharm. Bordeaux*, 1938, **76**, 72—77; *Chem. Zentr.*, 1938, ii, 3960).—On warming, $HgSO_4$ solution and $Pr^{\beta}OH$ give a white ppt. (spherical and radial aggregates under the microscope), which turns brown on addition of NH_3. Under similar conditions $Pr^{\alpha}OH$ gives pale yellow needle crystals in 4—5 min. Addition of 2—3 drops of Br before warming accelerates and inhibits pptn. with $Pr^{\beta}OH$ and $Pr^{\alpha}OH$, respectively. A. J. E. W.

Potentiometric determination of mercaptans in aqueous alkaline solution. M. W. Tamele, L. B. Ryland, and V. C. Irvine (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 618—622).—The mercaptan in N-NaOH—0·05N-aq. NH_3 is titrated with standard $AgNO_3$ with a Ag electrode, and the e.m.f. of the cell formed by this solution in contact with a standard reference electrode (*e.g.*, Hg–0·1N-NaOAc) is plotted against ml. of $AgNO_3$. The method is sp. for mercaptans; usual impurities accompanying these in petroleum products do not interfere. J. D. R.

Cerate oxidimetry. Determination of glycerol. G. F. Smith and F. R. Duke (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 558—560).—The procedure detailed depends on the reaction $C_3H_8O_3 + 8H_2Ce(ClO_4)_6 + 3H_2O = 3HCO_2H + 8Ce(ClO_4)_3 + 24HClO_4$. The excess of $H_2Ce(ClO_4)_6$ is determined by titration with $Na_2C_2O_4$ (nitro-*o*-phenanthroline). A potentiometric end-point is thus avoided. Other advantages over the $K_2Cr_2O_7\text{–}FeSO_4$ method are that the time required for oxidation of the glycerol (**I**) is reduced from 180 to 15 min., and the reaction temp. from 90—100° to 50—60°. Oxidation of (**I**) can also be effected by means of $(NH_4)_2Ce(SO_4)_4.2H_2O$ in 0·5M-H_2SO_4. The two methods compare favourably with existing procedures. L. S. T.

Determination of α-glycerophosphates in aqueous solution by lead tetra-acetate. D. J. Wormith and J. J. Rae (*J. Amer. Chem. Soc.*, 1941, **63**, 2523—2524).—Optimum amounts of HCl and H_2O are described for determination of mixtures of Ca or Ba α- and β-glycerophosphates by $Pb(OAc)_4\text{–}AcOH$. R. S. C.

Methyl esters of the higher fatty acids. Separation of small quantities by fractional distillation. F. W. Wyman and C. Barkenbus (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 658—661).—Details are given of the construction and operation of a spinning band fractionating column. Me octoate, decoate, laurate, myristate, palmitate, and stearate have been purified by this column, 1—5 g. of material being used. Separation is good, and n_D^{45} vals. are given for the esters. The method can be used for analysis of mixed esters formed from fatty acids from natural oils, even when only 1—2 g. of the acid is available. J. D. R.

Polarographic determination of ascorbic acid. M. M. Kirk (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 625—626).—The determination of ascorbic acid at a dropping Hg electrode using a 2% HPO_3 solution as extractant is described. J. D. R.

Errors of Munson and Walker's reducing-sugar tables and the precision of their method. R. F. Jackson and E. J. McDonald (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 767—788, and *J. Res. Nat. Bur. Stand.*, 1941, **27**, 237—255).—Discrepancies between Munson and Walker's (A., 1906, ii, 634) and Hammond's (B., 1940, 889) reducing-sugar tables are attributed to contamination of the Cu_2O with org. matter; Hammond's vals. are confirmed. For the determination of Cu the iodometric method was principally used, NH_4CNS being added near the end of the titration. Schoorl and Regenbogen's modification of the $KMnO_4$ method (A., 1917, ii, 222) gives accurate results. Determination of Cu_2O by dissolution in HCl–aq. $K_2Cr_2O_7$ and titration with $FeSO_4$ (*o*-phenanthroline) approaches in precision the iodometric method very closely at the median and lower concns. of sugar. A. A. E.

Micro-determination of glucose, free and conjugated glucuronic acid. Use of *Saccharomyces sake* No. 6 as fermentative yeast.—See A., 1941, III, 947.

Detection and determination of mono- and di-ethanolamine. I. S. Shupe (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 754—757).—The colour tests described are modifications of Rimini's and Simon's tests for primary aliphatic and *sec.* amines, using Na nitroprusside, $NaHCO_3$, and $COMe_2$ or MeCHO, respectively. Determination is accomplished by prep. and weighing of the p-$C_6H_4Br{\cdot}SO_2$ derivatives, extracting that of $NH([CH_2]_2{\cdot}OH)_2$ from an alkaline (NaOH) liquid with $CHCl_3$, and extracting that of $NH_2{\cdot}[CH_2]_2{\cdot}OH$ similarly from the acidified residual liquid. Blank determinations are made with the reagent. The procedure is designed to minimise formation of the disulphonylmonoethanolamine, which is insol. in alkali. An aq. extract of cosmetic creams is first extracted with $CHCl_3$ after addition of acid or alkali (not NH_3). A. A. E.

Micro-determination of betaine and choline. I. Reifer (*New Zealand J. Sci. Tech.*, 1940, **22**, **B**, 111—116; cf. Blood and Cranfield, B., 1937, 174).—A neutral solution (3 c.c.) of choline (**I**) (0·1—5·0 mg.) is treated with 10% KI_3 (5 c.c.) at <10°. After 3 hr. at 0° the ppt. is centrifuged and a suspension of $Al(OH)_3$ (0·5 c.c.) introduced as a top layer. After centrifuging, the supernatant fluid is removed and the reagent washed from the walls of the tube. $Al(OH)_3$ is removed with cold 5% H_2SO_4 (2 c.c.), the fluid removed after centrifuging, and the ppt. dissolved in 90% EtOH (1—3 c.c.). I is determined titrimetrically. Glycine betaine (**II**) (0·3—5·0 mg. in 3 c.c. of 10% NaCl) is treated with H_3PO_4 (0·5 c.c.) and KI_3 (1 c.c.). After 3 hr. at −5° to −10° the ppt. is freed from periodide and H_3PO_4 and titrated as above. In mixtures, only (**I**) is determined by the former procedure whereas both (**I**) and (**II**) are pptd. quantitatively in the latter. Error ±2%. The method is applied to the determination of (**I**) and (**II**) in plants and is limited by the facts that $NHMe_2$, NMe_3, some cyclic bases, and alkaloids are pptd. by KI_3, that the composition of the ppt. depends on the betaine, and that some betaines are pptd. in neutral solution with (**I**). J. L. D.

Determination of leucine and valine by the method of Fromageot and Heitz. E. D. Stacheeva-Kaverzneva (*Biochimia*, 1940, **5**, 513—520; cf. A., 1940, II, 269).—The method is applicable to the determination of valine and leucine, separately, in pure solutions, but not to mixtures of the acids such as occur in protein hydrolysates even after fractionation of the Cu salts. W. McC.

Determination of amino-acids with ninhydrin. A. I. Virtanen, T. Laine, and T. Toivonen (*Z. physiol. Chem.*, 1940, **266**, 193—204; cf. Abderhalden, A., 1938, II, 212).—Free alanine (**I**), valine (**II**), leucine (**III**), *iso*leucine (**IV**), phenylalanine (**V**), and methionine (**VI**) but not the other NH_2-acids of protein or peptides rapidly give theoretical yields of corresponding N-free aldehydes when heated in aq. solution with KH_2PO_4, NaCl, and ninhydrin, $NH_2{\cdot}CHR{\cdot}CO_2H$ yielding $R{\cdot}CHO$. The aldehydes are distilled into aq. $NaHSO_3$ and determined iodometrically. In mixtures of NH_2-acids (protein hydrolysates), (**I**) is separately determined because of the volatility of MeCHO, (**V**) by Kapeller-Adler's method (A., 1933, 1094), and (**VI**) by Baernstein's method (A., 1932, 1149). Application of the procedure to the analysis of zein gives results in agreement with those obtained by other methods, but N contents from (**I**), (**II**), (**III**), and (**IV**) of ovalbumin (7·3 and 15·9% of total N) and caseinogen (5·6 and 14·3% of total N) are > those otherwise determined. W. McC.

Determination of sulphanilamide derivatives.—See A., 1941, III, 1043.

Determination of benzocaine and its separation from acetanilide. E. H. Wells (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 736—739).—Washed $CHCl_3$ extracts of the aq. mixture are shaken with successive portions of 6N-H_2SO_4, combined, and evaporated nearly to dryness; the NHPh·OAc is hydrolysed and titrated by the A.O.A.C. bromide–bromate method. The H_2SO_4 solution and washings are treated with aq. Br in excess, the excess being determined iodometrically and the wt. of p-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$ calc. Recoveries were 98·9—100·3 and 98·2—108·0%, respectively. A. A. E.

Detection and estimation of dihydrorotenone in the hydrogenation products of rotenone. L. D. Goodhue and H. L. Haller (*Ind. Eng. Chem.* [*Anal.*], 1941, **12**, 652—654).—The detection and determination depend on the red colour produced by dihydrorotenone with a reagent of $NaNO_2$–EtOH–KOH followed by H_2SO_4. The colour produced is compared photometrically with a standard of similar and known concn. Rotenone interferes, but the non-toxic by-products of catalytic reduction, rotenonic acid, dihydrorotenonic acid, and dihydrorotenol, do not interfere. J. D. R.

Photo-electric estimation of indole. C. B. Allsopp (*Biochem. J.*, 1941, **35**, 965—966).—The transient colour produced by indole solutions in presence of acidified, alcoholic p-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ is measured in a Hilger "Absorptiometer." It is employed for concns. up to 0·002% of indole and the colour is fully developed by heating rapidly just to the b.p. H. G. R.

Colorimetric determination of indolyl-3-acetic acid.—See A., 1941, III, 939.

Determination of piperazine. II. A. Castiglioni (*Z. anal. Chem.*, 1940, **119**, 118—120; cf. A., 1939, II, 398).—Alcoholic solutions of piperazine (**I**) are treated with excess of CS_2–Et_2O (1 : 1), warmed slightly, and kept. (**I**) in $CHCl_3$ is treated with CS_2 alone. The ppt. is washed repeatedly with small quantities of EtOH–Et_2O or $CHCl_3$, according to the solvent used, dried at 105°, and weighed as $C_4H_{10}N_2,CS_2$. The method can be used to determine (**I**) in presence of $(CH_2)_6N_4$, which gives no ppt. with CS_2. Owing to the excessive time required for the complete pptn. of (**I**), Dragendorff's reagent (KI + BiI_3) is unsatisfactory. L. S. T.

Influence of concentration and acid content on crystal form. L. Rosenthaler (*Pharm. Acta Helv.*, 1940, **15**, 257—265).—The influence of concn. of base and HCl on the form of the ppts. obtained by adding (solid) $K_4Fe(CN)_6$ to solutions of 15 bases (synthetic drugs) is described. E. H. S.

Colorimetric determination of pilocarpine and its separation from other alkaloids. I. S. Shupe (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 757—766).—Pilocarpine (**I**), after hydrolysis of the lactone group with alkali in presence of $NaHSO_3$ to avoid oxidation, is retained in aq. solution and separated from other alkaloids by extraction of the latter with $CHCl_3$, followed by acidification and extraction of (**I**) with $CHCl_3$. It may then be determined volumetrically (1 ml. of 0·02N-acid = 4·16 mg.) or colorimetrically. Helch's reaction involving the formation of (**I**) perchromate, which, unlike $HCrO_5$, is sol. in C_6H_6 and $CHCl_3$, is employed, colour intensity measurements being made, *e.g.*, by means of a Clifford type neutral wedge photometer. The colour is stable for ≯2 hr. when protected from light. AcOH is most suitable for acidification during development and extraction of the colour. Recoveries were: 97·0—98·6% (volumetric); 97·6—99·0% (colorimetric). A. A. E.

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ERRATA.

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Page	Line	
263	25*	*For "* **(II)** *" read "* **(V)**.*"*
264	—	*Following line 2, in formulæ* **(VI)** *and* **(IX)** *the vertical bond at the left of ring* (A) *should be omitted.*
328	—	*In formula* (*A*) *the single bond in the central ring at the lower right side should be a double one.*

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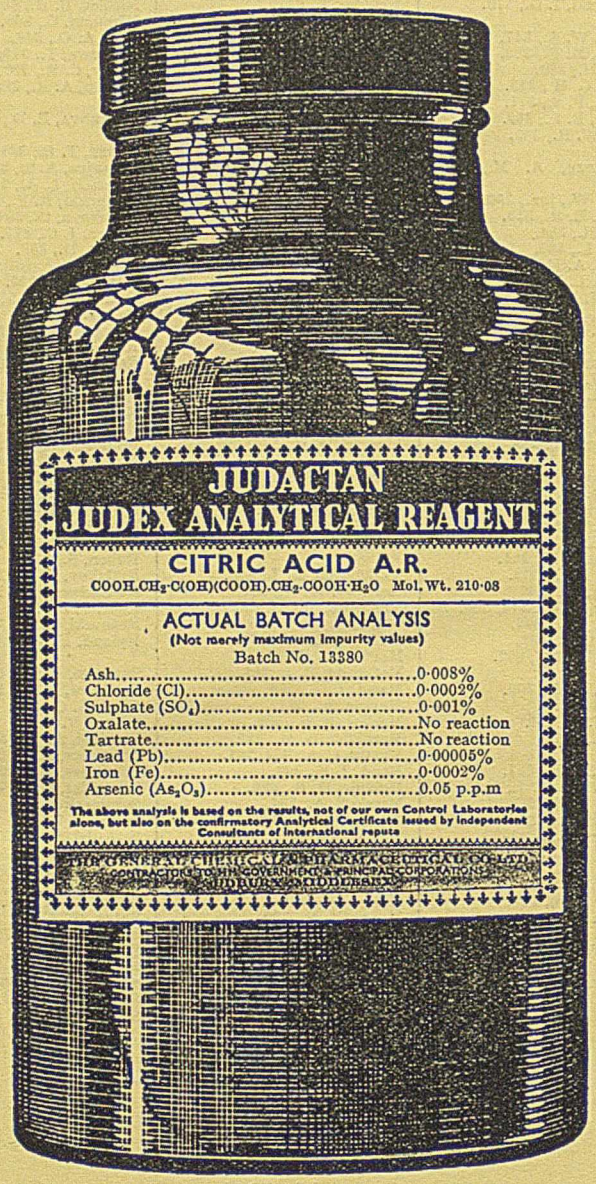

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