BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

SEPTEMBER, 1944

A II—ORGANIC CHEMISTRY

CONTENTS

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A II—Organic Chemistry.

SEPTEMBER, 1944.

I.—ALIPHATIC.

Reactions of hydrocarbons with sulphuryl chloride and with sulphur dioxide–chlorine mixtures.—See A., 1944, I, 206.

α-Methylenic reactivity in olefinic systems. I. Prins reaction with propylene. J. W. Baker (*J.C.S.*, 1944, 296—301).—$CHMe{:}CH_2$ with paraformaldehyde in 100% AcOH—100% H_2SO_4 at 35° gives the *diacetate* (I), b.p. 65°/1 mm., of $OH{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}OH$ (II) (63·5%) (*di-α-naphthylurethane*, m.p. 153°), *4-methyl-1 : 3-dioxan* (III) (14%), b.p. 25°/22 mm., and *4-acetoxytetrahydro-γ-pyran* (IV) (22·5%), b.p. 47·5°/1 mm. (III) with 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ in aq. HCl yields the hydrazone of CH_2O and (II). (IV) is hydrolysed [aq. $Ba(OH)_2$] to *4-hydroxytetrahydro-γ-pyran* (V), b.p. 60·5°/0·7 mm. (*p-nitrobenzoate*, m.p. 69°), oxidised (CrO_3) to tetrahydro-4-pyrone (VI), b.p. 73°/20 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 186—187°). Oxidation (HNO_3) of (IV), (V), and (VI) affords $CO_2H{\cdot}CH_2{\cdot}O{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 97° [*diamide*, m.p. 174°; *Me*$_2$ ester, b.p. 138°/24 mm.; *Me ester amide* (?), m.p. 73°], reduced by HI to $I{\cdot}[CH_2]_2{\cdot}CO_2H$. (II) with CH_2O in AcOH–H_2SO_4 gives (I) and (III) but no (IV). Results for a kinetic examination are given, and it is suggested that (II) and (III) are formed by acid-catalysed addition of CH_2O to the double linking but (IV) is obtained by reaction with H of Me of $CHMe{:}CH_2$ activated by conjugation. BF_3 does not catalyse the Prins reaction, but improves the catalytic efficiency of H_2SO_4. D. G.

Production of α- and β-pyronene from *allo*ocimene. L. A. Goldblatt and S. Palkin (*J. Amer. Chem. Soc.*, 1944, **66**, 655—656).—Pyrolysis (apparatus: C, 1944, Part 4) of *allo*ocimene at, best, 400° gives α- (~30%), b.p. 54—56°/20 mm., and β-pyronene (~45%), b.p. 62—64°/20 mm. R. S. C.

Conjugated systems. XXIII. Synthesis and properties of dihalogeno-derivatives of isoprene. A. A. Petrov (*J. Gen. Chem. Russ.*, 1943, **13**, 331—338).—$OH{\cdot}CMe_2{\cdot}C{:}CH$ (I), in cold $CHCl_3$, with 0·75 mol. of Cl_2, yields polychloro-derivatives and 50% of $OH{\cdot}CMe_2{\cdot}CX{:}CHX$ (II), X = Cl, *trans*-form, b.p. 61·5—62°/10 mm.; dehydration of the latter by P_2O_5, with short time of contact, gives 35% of *αβ-dichloro-γ-methyl-*$\Delta^{\alpha\gamma}$*-butadiene* (III), b.p. 60·5—61°/85 mm., and a yellow, powdery polymer. Bromination of (I) (accelerated by illumination), under similar conditions, yields 95% of *γδ-dibromo-β-methyl-*Δ^{γ}*-buten-β-ol*, [(II), X = Br], b.p. 91·5—92·5°/10 mm.; a higher-boiling form of (II), X = Br, was obtained, in one isolated experiment, together with the product described. (II), X = Br, is dehydrated over P_2O_5 at 100°/20 mm. to a mixture of cis- and trans-*αβ-dibromo-γ-methyl-*$\Delta^{\alpha\gamma}$*-butadiene*, b.p. 51·5—52°/10 mm. (IV) (probably *trans*-) and b.p. 66·5—67°/10 mm. (V). (III) and (IV), in PhMe at 100°, form sticky polymers (7—8% in 1 hr.) and, on keeping in diffused light, become viscous in 4—5 months owing to formation of soft rubber-like polymers; they do not condense with $(CH{:}CO)_2O$. In boiling 20% KOH–EtOH, (III), (IV), and (V) react in 30 min. to the extent of 8, 25, and 44% respectively, (IV) and (V) yielding $CH_2{:}CMe{\cdot}C{:}CBr$. (II), X = Cl or Br, is decomposed by alcoholic or aq. KOH to $COMe_2$, $CHX{:}CHX$, and $CH{:}CX$; *trans*-(II), X = Cl, yields *trans*-$C_2H_2X_2$. R. C. P.

Conjugated systems. XXIV. Reaction of isoprene with hypobromous acid and with alkyl hypoiodites. A. A. Petrov (*J. Gen. Chem. Russ.*, 1943, **13**, 481—490).—HOBr, as NHAcBr (I), and isoprene (II) (1 : 1·5 mol.) give *δ-bromo-γ-hydroxy-γ-methyl-*Δ^{α}*-butene* (III), b.p. 49·5°/10 mm. (33% yield on HOBr), an *isoprene dibromide*, m.p. 86° (yield <25%), besides oily dibromides and products of reaction of (II) with (I) itself. (III) affords with AcCl a *monoacetate* (IV), with Cl-compounds, whilst with Ac_2O it gives 91% pure (?) (IV), b.p. 60°—95°. Br and (III) give *αβδ-tribromo-γ-hydroxy-γ-methylbutane*, b.p. 136·5°/10 mm., which is largely unchanged on treatment with $Na_2Cr_2O_7$ in AcOH–H_2SO_4, but with aq. 80% KOH at 120° it gives *αβ*-epoxy-*β*-methyl-Δ^{γ}-butene (70% yield), b.p. 78·5—79°/715 mm., decomposed by H_2SO_4 to tiglaldehyde. Treatment of (I) with (II) (2 : 1 mol.) gives *αγ-dibromo-βγ-dihydroxy-β-methylbutane*, m.p. 86°. (II) with HgO, I, and either MeOH or EtOH gives *δ-iodo-γ-methoxy-*, b.p. 60°/10 mm., or *δ-iodo-γ-ethoxy-*, b.p. 66·5°/10 mm., *-γ-methyl-*Δ^{α}*-butene*. F. Hi.

Preparation and purification of glucose 1-phosphate with the aid of ion exchange adsorbents. R. M. McCready and W. Z. Hassid (*J. Amer. Chem. Soc.*, 1944, **66**, 650—563).—Potato starch is digested with crude potato phosphorylase in presence of Na phosphates, inorg. phosphates are then removed by $Mg(OAc)_2$–NH_3, and the filtrate is passed through a cation-absorbing resin, Amberlite IR-100. The resulting acid solution is then passed through an anion-absorbing resin, Amberlite IR-4; weak acids pass through but glucose-1-phosphoric acid is adsorbed and subsequently recovered by aq. NH_3 and pptn. as K_2 salt, $+2H_2O$, $[\alpha]_D$ +78° in H_2O. Glucose-6-, fructose-6-, and glycero-phosphoric and fructose-1 : 6-diphosphoric acids are similarly purified. R. S. C.

Carboxonium salts. I. Acetyl fluoborate. F. Seel (*Z. anorg. Chem.*, 1943, **250**, 331—351).—*Acetyl fluoborate*, $Ac[BF_4]$ (I), obtained as white crystals by direct union of AcF and BF_3, dissociates appreciably at room temp. and completely at the b.p. of AcF. It is hydrolysed by H_2O to AcOH and HBF_4. With dry KF it affords AcF and KBF_4; with other K halides in presence of ionising solvents (*e.g.*, liquid SO_2) it gives KBF_4 and Ac halide. With $NaNO_2$ it reacts: $NaNO_2 + 2(I) \rightarrow NaBF_4 + (NO)BF_4 + Ac_2O$. EtOH and AcOH give EtOAc and Ac_2O respectively. NO·OEt affords $NO{\cdot}BF_4$ and EtOAc. Warm Et_2O yields AcF and BF_3,Et_2O, which when further heated form EtOAc, BF_3, and EtF. (I) is an electrolyte in liquid SO_2, *A* at −70° being approx. that of KI, but decreasing rapidly with rising temp. Its reactions with KI and KOAc may be followed conductometrically. Its structure is ionic, $[Ac]^+[BF_4]^-$. F. J. G.

Allylic rearrangements. XV. Carbonation of magnesium butenyl bromide. J. F. Lane, J. D. Roberts, and W. G. Young (*J. Amer. Chem. Soc.*, 1944, **66**, 543—545; cf. A., 1944, I, 157).—Adding the Grignard solution from mixed $CHMe{:}CH{\cdot}CH_2Br$ (80%) + $CH_2{:}CH{\cdot}CHMeBr$ (20%) to solid CO_2 gives 75% of $CH_2{:}CH{\cdot}CHMe{\cdot}CO_2H$ (I), b.p. 95·5°/35 mm. (chloride, b.p. 55—58°/110 mm.; amide, m.p. 98°, hydrogenated to $CHMeEt{\cdot}CO{\cdot}NH_2$; *CHPhMe·NH*$_2$ salt, m.p. 119·5—120·5°). Arnold's method (A., 1942, II, 142) gives 63% of (I), 13% of *dibutenyl ketone*, b.p. 93—94°/100 mm., smaller amounts of octadienes, b.p. 52—53°/100 mm., and a fraction, b.p. 100—115°/30 mm. R. S. C.

Reduction of ester vinylogues. R. H. Baker and P. C. Weiss (*J. Amer. Chem. Soc.*, 1944, **66**, 343—345).—2-Ethylchromone is unaffected by boiling $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$, as also is $CHBz{:}CMe{\cdot}OEt$ (I), which is largely unchanged by $Al(OBu\text{-}sec.)_3$ at 100°; $OEt{\cdot}CH{:}CAc{\cdot}CO_2Et$ (II) gives a (polymerised) tar with a little dimeride. With H_2–Raney Ni, (II) at 23° gives $CHMeAc{\cdot}CO_2Et$ (50%), (I) at 118° gives $OEt{\cdot}CHMe{\cdot}CH_2{\cdot}CHPh{\cdot}OH$ (III) (57%) and at 120° gives, after absorption of only 1 H_2, 64% of (III) + $CH_2Bz{\cdot}CHMe{\cdot}OEt$; $OEt{\cdot}CMe{:}CH{\cdot}CO_2Et$ (IV) at 130° gives $OEt{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$ (V) (86%). With H_2–Cu chromite, (II) at 150° gives a tar, (I) at 180° gives $COPhPr^{\alpha}$ (58%), and (IV) at 170° gives (V) (45%). R. S. C.

Autoxidation of β-elæostearic acid. Application of the spectrophotometer to the study of the course and the kinetics of the reaction.—See A., 1944, I, 204.

Cryoscopy [and structure] of isanic acid.—See A., 1944, I, 169.

***β*-Lactones and *β*-lactonic acids. III. Condensation of citral with malonic acid.** N. S. Vulfson and M. M. Schemjakin (*J. Gen. Chem. Russ.*, 1943, **13**, 436—447).—Citral with $CH_2(CO_2H)_2$ in presence of piperidine and AcOH affords, via $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}CH{:}C(CO_2H)_2$ (I), both $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$, b.p. ~170°/15 mm., and the *βδ-dilactone* of (I), viz., $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{\cdot}CH_2{\cdot}CH{\cdot}CH{\cdot}CO$ (II), m.p. 187°. When titrated with aq. NaOH (II) behaves as a monobasic acid: with boiling aq. NaOH both rings open and on acidification the product affords the corresponding *δ-hydroxy-β-lactonic acid*, m.p. 113—114° (III), with the δ-hydroxy-β-lactone, m.p. 119·5—120·5° (IV). With boiling AcCl (III) gives (II), CO_2, (IV), and the *monoacetate* (V) of (IV) (?), whilst on long heating with H_2O or with C_6H_6 (IV) is formed. Oxidation of (III) by aq. $KMnO_4$ in alkaline solution gives $H_2C_2O_4$ but no HCO_2H; hence the lactone ring is formed at the β-position. (IV) is unattacked by boiling Ac_2O;

thus the OH is on a *tert.* C so that it is a δ-lactone; with AcCl it gives (**V**), m.p. 117—118°. F. Hi.

β-Lactones and β-lactonic acids. IV. Rate of fission of the β-lactone ring.—See A., 1944, I, 204.

Action of aromatic diazo-compounds on alkylacetoacetic esters as a method of preparing arylhydrazones of α-keto- and α-amino-acids. VII. Synthesis of *n*-valine. V. V. Feofilaktov and V. N. Zaitzeva (*J. Gen. Chem. Russ.*, 1943, **13**, 358—362).—CHPrA^{c}·CO$_2$Et (**I**) and PhN$_2$·OK, under conditions already specified (A., 1940, II, 70, 85), give NHPh·N:CPr·CO$_2$Et (**II**) (35·4%) in a *form*, m.p. 103°, not previously described; reduction of (**II**) by Zn dust and HCl–EtOH, followed by treatment with Ag$_2$CO$_3$ and H$_2$S, yield *n*-valine (**III**) (77·4%). Similarly, (**I**) and *p*-C$_6$H$_4$Me·N$_2$·OK give a mixture of two forms of *α-ketovaleric acid* p-*tolylhydrazone* (**IV**) (43·5%); crystallisation from C$_6$H$_6$ yielded the α-form, m.p. 134—135°, and an inseparable mixture of the α- and β-forms, m.p. 123—131°. Reduction of (**IV**) (α- and β-forms mixed) as above gives (**III**) (96·4%). R. C. P.

Action of aromatic diazo-compounds on substances of the type of alkylacetoacetic esters as a method for obtaining arylhydrazones of α-keto-acids and of α-amino-acids. IX. Reaction of ethyl *cyclo*hexan-2-onecarboxylate with diazobenzene. V. V. Feofilaktov and A. Ivanov (*J. Gen. Chem. Russ.*, 1943, **13**, 457—467).—The reaction of cyclic compounds allied to monoalkylacetoacetic esters with aromatic diazo-compounds has been studied partly to widen the scope of the method of obtaining α-NH$_2$-acids from monoalkylacetoacetic esters and partly to obtain α-aminodicarboxylic acids. Et *cyclo*hexan-2-one-1-carboxylate with PhN$_2$Cl in acid aq. EtOH containing NaOAc affords CO$_2$H·[CH$_2$]$_3$·C(:N·NHPh)·CO$_2$Et in 98% yield, the product beng an *α-form*, m.p. 89·5—90°, admixed with a minor proportion of a β-form (cf. Jackson and Manske, A., 1931, 363); hydrolysis of the mixture gives α-ketopimelic acid phenylhydrazone in two forms; that predominating (**I**) (from α-ester ?) has m.p. 143—144°; the other form has m.p. 131—132° (cf. Linstead and Wang, A., 1937, II, 340). With HCl in aq. EtOH and Zn dust (**I**) gives CO$_2$H·[CH$_2$]$_3$·CH(NH$_2$)·CO$_2$H. F. Hi.

Thermal decomposition of acetaldehyde.—See A., 1944, I, 204.

Preparation of ketones from nitro-olefines. (Miss) D. Nightingale and J. R. Janes (*J. Amer. Chem. Soc.*, 1944, **66**, 352—354).—AlkCHO and CH$_2$Alk′·NO$_2$ give 70—80% of OH·CHAlk·CHAlk′·NO$_2$, the acetate of which with boiling NaHCO$_3$–MeOH–H$_2$O gives 90—95% of CHAlk:CAlk′·NO$_2$, decomposed at the b.p./1 atm., reduced by Zn dust in boiling Et$_2$O–25% AcOH to CH$_2$Alk·CAlk′:N·OH (usually 50—60%), whence boiling CH$_2$O–H$_2$O–H$_2$SO$_4$ yields COAlk′·CH$_2$Alk. The following are described, m.p. in parentheses being those of the *α-naphthylurethanes*. α-, b.p. 75°/2 mm. (m.p. 118—119°), and *γ-nitrobutan-β-ol*, b.p. 78°/17 mm. (m.p. 122—123°); α-, b.p. 85°/2 mm. (m.p. 99—100°), and *γ-nitropentan-β-ol*, b.p. 78°/2 mm; (m.p. 100—101°); *β-nitropentan-γ-ol*, b.p. 79°/2 mm. (m.p. 126°). γ-, b.p. 64°/2 mm. (m.p. 137°), and *α-nitro-γ-methylbutan-β-ol*, b.p. 66°/1 mm. (m.p. 97·5—98°); *α-nitrohexan-β-ol*, b.p. 80°/1 mm. (m.p. 103°); *β-nitrohexan-γ-ol*, b.p. 82°/2 mm. (m.p. 136—137°); *γ-nitrohexan-δ-ol*, b.p. 89°/2 mm. (m.p. 113—114°); *β-nitro-δ-*, b.p. 89°/2 mm. (m.p. 112—113°), and *-β-methylpentan-γ-ol*, b.p. 75°/4 mm. (m.p. 97—98°); *α-nitroheptan-β-ol*, b.p. 105°/2 mm.; *β-nitroheptan-γ-ol*, b.p. 92°/2 mm.; *γ-nitroheptan-δ-ol*, b.p. 92°/2 mm.; *α-nitro-γ-ethyl-pentan-β-ol*, b.p. 93°/2 mm., and *-heptan-β-ol*, b.p. 110°/2 mm.; *γ-nitro-ε-methylhexan-γ-ol*, b.p. 78°/2 mm.; *β-nitro-β-methylhexan-γ-ol*, b.p. 81°/2 mm., and *-δ-ethylhexan-γ-ol*, b.p. 92°/2 mm.; *γ-nitro-γ-ethylheptan-δ-ol*, b.p. 87°/2 mm.; *β-nitro-octan-γ-ol*, b.p. 85°/2 mm.; *γ-nitro-octan-δ-ol*, b.p. 94°/2 mm., *-nonan-δ-ol*, b.p. 108°/2 mm., and *-decan-δ-ol*, b.p. 108°/2 mm.; *β-nitro-δ-ethyloctan-γ-ol*, b.p. 102°/2 mm.; *γ-nitro-ε-ethyloctan-δ-ol*, b.p. 100°/2 mm.; *β-nitro-Δ^{β}-hexene*, b.p. 53°/1 mm., *-δ-methyl-Δ^{β}-pentene*, b.p. 57°/1 mm., and *-δ-ethyl-Δ^{β}-hexene*, b.p. 84°/1 mm.; *γ-nitro-Δ^{γ}-hexene*, b.p. 53°/1 mm., *-ε-methyl-Δ^{γ}-hexene*, b.p. 53°/1 mm., *-ε-ethyl-Δ^{γ}-heptene*, b.p. 65°/1 mm., *-Δ^{γ}-decene*, b.p. 97°/1 mm., *-δ-ethyl-Δ^{β}-octene*, b.p. 84°/1 mm., and *-ε-ethyl-Δ^{γ}-octene*, b.p. 94°/1 mm.; *α-nitro-Δ^{α}-heptene*, b.p. 57°/1 mm.; *γ-oximino-ε-ethylheptane*, b.p. 75—79°/1 mm., *-decane*, b.p. 81°/1 mm., *-heptane*, b.p. 56°/1 mm., *-nonane*, b.p. 70°/1 mm., *-ε-ethylnonane*, b.p. 89—92°/1 mm., and *-ε-methylhexane*, b.p. 55°/1 mm.; *β-oximino-δ-ethylhexane*, b.bp. 69°/1 mm., and *-δ-ethyloctane*, b.p. 81°/1 mm.; *ε-ethylnonan-γ-one*, b.p. 53°/1 mm. Efforts to condense the nitro-olefines with (CH$_2$:CH)$_2$ or *cyclo*pentadiene failed. R. S. C.

Condensation of *iso*butaldehyde with aliphatic ketones. S. G. Powell and F. Hagemann (*J. Amer. Chem. Soc.*, 1944, **66**, 372—376).—Pr^{β}CHO with COMeR (R = Pr^{α}, Bu^{α}, Bu^{β}, *n*-amyl, or *n*-hexyl) in KOH–EtOH at <35° gives 35—65% of CHPr^{β}:CH·COR (*A*); only *n*-C$_5$H$_{11}$·COMe gives a little CHPr^{α}:CBu^{α}·COMe (*hydantoin* derivative, m.p. 175—176°). Na in NaHCO$_3$–Et$_2$O–H$_2$O usually converts (*A*) into CHPr^{β}:CH·CHR·OH, but reduction is sometimes incomplete; H$_2$–PtO$_2$ is always effective. *β-Methyl-Δ^{γ}-n-decen-ε-one*, b.p. 223—224° (*hydantoin* derivative, m.p. 135—136°), with Na–EtOH gives *β-methyl-Δ^{β}-n-decen-ε-ol* (42%), b.p. 129·5—131°/30 mm. (3 : 5-dinitrobenzoate, an oil), whence O$_3$ gives COMe$_2$ (no Pr^{β}CHO) and Δ^{α}-octenaldehyde [semicarbazone, m.p. 169—170° (lit. 163°)]. COEt$_2$ and Pr^{β}CHO give CHPr^{β}:CMe·COEt, b.p. 176—178° (2 : 4-dinitrophenylhydrazone, m.p. 174—175°) (cf. Franke *et al.*, A., 1924, i, 6). The following are described: m.p. prefixed by *h* are those of the derived *hydantoins*. CHPr^{β}:CH·COPr^{α}, b.p. 85—86°/25 mm.; *β-methyl-Δ^{γ}-n-nonen-ε-one*, b.p. 103—105°/25 mm. (*h* m.p. 149·5—150°); *βη-dimethyl-Δ^{ε}-n-octen-δ-one*, b.p. 199—200°; *β-methyl-Δ^{γ}-n-undecen-ε-one*, b.p. 135—136°/28 mm. (*h* m.p. 118·5—119°); COPr^{α}·CH$_2$Bu^{β}, b.p. 177—179° [semicarbazone, m.p. 144·5—145·5° (cf. lit.); *h* m.p. 175—175·5°]; *β-methyl*-n-*nonan-ε-one*, b.p. 203—204° (*h* m.p. 192—192·5°); *βη-dimethyl*-n-*octan-δ-one*, b.p. 196—198° (semicarbazone, m.p. 78—79°; *h* m.p. 216—217°); *β-methyl*-n-*decan-ε-one*, b.p. 119—121°/28 mm. [*nitroguanylhydrazone*, m.p. 78—79·5° (decomp.); *h* m.p. 192—192·5°]; *β-methyl*-n-*undecan-ε-one*, b.p. 126—128°/23·5 mm. [*nitroguanylhydrazone*, m.p. 84·5—86° (decomp.); *h* m.p. 175—175·5°]; *δζ-dimethyl*-n-*heptan-γ-one*, b.p. 170—173° (*h* m.p. 186—186·5°); *β-methyl*-n-*nonan-ε-ol*, b.p. 111·5—113°/28·5 mm. (3 : 5-*dinitrobenzoate*, m.p. 63·5—64·5°); CH$_2$Bu^{β}·CHBu^{β}·OH, b.p. 107—108°/29·5 mm. (3 : 5-*dinitrobenzoate*, m.p. 81—82°); *β-methyl*-n-*decan-ε-ol*, b.p. 122·5—123°/24 mm. (124—126°/24 mm.); *β-methyl*-n-*undecan-ε-ol*, b.p. 132—133°/24 mm. (135°/24 mm.). M.p. and b.p. are corr. R. S. C.

Synthesis of bromoacetals. P. Z. Bedoukian (*J. Amer. Chem. Soc.*, 1944, **66**, 651—652).—Adding Br to CH$_2$:CH·OAc in CCl$_4$ at 0—10° and pouring the mixture into ROH gives bromoacetaldehyde Me$_2$ (80—85%), b.p. 48—49°/14 mm., and Et$_2$ acetal (75—80%), b.p. 64—65°/16 mm. R. S. C.

Anomalous base strength of the methylamines.—See A., 1944, I, 175.

Geranylamine. D. A. Sutton (*J.C.S.*, 1944, 306).—Geranylamine hydrochloride, m.p. 145—146° (modified prep.), is a single substance, CMe$_2$:CH·[CH$_2$]$_2$·CMe:CH·CH$_2$·NH$_3$Cl. F. R. S.

Solubilities of symmetrical, normal aliphatic secondary amines of high mol. wt. C. W. Huerr, H. J. Harwood, and A. W. Ralston (*J. Org. Chem.*, 1944, **9**, 201—210).—The solubilities of dioctylamine, m.p. (α form) 14·60°, (β-form) 26·7° (lit. 36·5 and 34° respectively), f.p. 14·60°, didodecylamine, m.p. (α-form) 46·9° (lit. 51—53°), β-form 51·8°, f.p. 46·9°, *ditridecylamine*, m.p. 56·5°, f.p. 56·5°, ditetradecylamine, m.p. 60·6° (lit. 56—58°), f.p. 60·6°, *dipentadecylamine*, m.p. 63·3°, f.p. 63·3°, and dioctadecylamine, m.p. 72·3° (lit. 71—72°), f.p. 72·3°, have been determined in C$_6$H$_6$, *cyclo*hexane, CCl$_4$, CHCl$_3$, Et$_2$O, EtOAc, BuOAc, COMe$_2$, COMeEt, MeOH, 95% EtOH, Pr^{β}OH, Bu^{α}OH, and MeCN. In general, the *sec.* amines are more sol. in org. solvents than are primary amines of corresponding chain length. This behaviour is apparently due to the fact that the polar group in the centre of the paraffin chain causes the m.p. of the *sec.* amines to be considerably < those of the primary amines containing the same no. of C atoms. If a temp. correction is made for the difference in m.p., the solubility curve of any *sec.* amine can be nearly superimposed on that of the primary amine of equal chain length in any given solvent. Compared in this manner, the *sec.* amines tend to be slightly more sol. in non-polar solvents and somewhat less sol. in the highly polar solvents than the corresponding primary amines. The solubilities of the nitriles, primary and *sec.* amines, which have relatively weak polar groups, tend to suggest that the shapes of the solubility curves are probably due primarily to association of the paraffin chains with the possibility that the more polar compounds such as the acids and amides may be further associated at the polar groups. The *sec.* amines are obtained by heating the respective primary amines with Raney Ni at 200°. H. W.

Metabolism of phosphorylcholine. I. Synthesis of calcium phosphorylcholine chloride containing the radioactive isotope, ^{32}P. R. F. Riley (*J. Amer. Chem. Soc.*, 1944, **66**, 512—513).—Heating choline chloride (**I**) with P$_2$O$_5$ and 100% H$_3$PO$_4$ containing some ^{32}P at 165°/vac. and treating the product in H$_2$O with CaCl$_2$ and then Ca(OH)$_2$ to neutrality gives 63% of *Ca phosphorylcholine chloride* (**II**), C$_5$H$_{13}$O$_4$NClPCa,4H$_2$O, containing 96% of the original radioactivity. 24% of (**II**) is obtained by heating choline hydroxide [prep. from aq. (**I**) by, successively, Ag$_2$CO$_3$, Ba(OH)$_2$, and evaporation in vac. (N$_2$)] with H$_3$PO$_4$ in PhMe with removal of H$_2$O and treating the product in aq. EtOH with CaCl$_2$–Ca(OH)$_2$ as above. Ag$_3$PO$_4$ or Ag$_2$PhPO$_4$ with bromocholine bromide in boiling EtOH gives 65 and 89%, respectively, of neurine. *Phosphorylcholine reineckate* and *phosphotungstate*, the HgCl$_2$ additive *compound* of phosphorylcholine, C$_5$H$_{15}$O$_4$NP,3HgCl$_2$, m.p. 180—184° (corr.), *dicholine phosphate reineckate*, and the additive *compound*, m.p. 202—207°, of dicholine phosphate and HgCl$_2$ are prepared. R. S. C.

Nitric ester of choline perchlorate, m.p. 188—189°.—See A., 1944, III, 553.

Chromammines. III. Preparation of diacidodiethylenediaminosalts by thermal decomposition of triethylenediamine luteo-salts.—See A., 1944, I, 206.

Spectroscopic evidence for the N·H·N linking in ethyleneimine. H. W. Thompson and G. P. Harris (*J.C.S.*, 1944, 301—303).—Variation in the intensity of an absorption band at 3·1 μ. with the concn. of ethyleneimine in solution in CCl_4 suggests association through N·H·N linkings. Other evidence is adduced in support. D. G.

Polymerisation of ethyleneimine. G. D. Jones, A. Langsjoen, M. M. C. Neumann, and J. Zomlefer (*J. Org. Chem.*, 1944, **9**, 125—147).—The polymerisation of ethyleneimine (I) is indicated to involve a bimol. reaction between (I) and ethyleneimonium or substituted ethyleneimonium ions. Dimeric (I) is identical with *N-β-(aminoethyl)ethyleneimine* (II), which appears to be an intermediate in the polymerisation of (I). Polyethyleneimine is regarded as a linear poly*sec.*-amine of mean degree of polymerisation 25—100. The polymerisation of (I) is not greatly accelerated by ascaridole at 40° or 150°, Bz_2O_2 at 40°, old MeCHO at 40° or 150°, 30% H_2O_2 at 40°, $K_2S_2O_8$ at 40°, $CuSO_4$ at 40°, Cu-bronze, 5N-NaOH at 25°, Bu^tCl, *o*-, *m*-, and *p*-$C_6H_4Cl{\cdot}NO_2$. Some acceleration is caused by 30% H_2O_2 at 145°, and by H_2O at the same temp. Vigorous or explosive polymerisation is caused by $H_2S_2O_8$ at 110°, EtOAc, $EtNO_3$, $CuSO_4$ at 145°, CH_2PhCl, $CH_2{:}CH{\cdot}CH_2Cl$, and $Bu^{\gamma}Br$. The effect of HNO_3, H_2SO_4, HCl, and AcOH is detailed. The polyethyleneimines studied are obtained by use of HCl or BF_3 under varied conditions. $OH{\cdot}[CH_2]_2{\cdot}NH_2$ is converted by successive treatments with HCl and $SOCl_2$ into *β-chloroethylamine hydrochloride*, m.p. 147·5—148°; β-chloro-*n*-propylamine hydrochloride, m.p. 180—182°, and *N-phenyl-β-chloroethylamine hydrochloride*, m.p. 155—157°, are obtained similarly. $Cl{\cdot}[CH_2]_2{\cdot}NH_2$ polymerises slowly at room temp., rapidly at 40°, suddenly at 95°. Rapid addition of a dil. solution of (I) in anhyd. Et_2O to an excess of dry HCl in Et_2O gives the unstable *ethyleneimine hydrochloride*, which rapidly polymerises. *Dimeric* (I), b.p. 126—127·5°, is obtained by polymerisation of (I) in Et_2O under defined conditions and treatment of the product with NaOH. $NH_2{\cdot}[CH_2]_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}OH$ is converted by distillation under 11 mm. with aq. H_2SO_4 to incipient charring followed by 40% NaOH into piperazine hydrate, m.p. 44°, and (II), shown to be identical with dimeric (I) by prep. of the *phenylthiocarbamate*, m.p. 129—131°. A polyethyleneimine I, obtained by use of conc. HCl at −78° and then at 25° for many days, is converted (Schotten–Baumann) into the *Bz* derivative, softens (Dennis bar) 110°, which with HCl in $CHCl_3$ yields a *hydrochloride* and is converted into a *CH_2Ph* derivative (*hydrochloride*) by condensation with PhCHO and reduction of the product by Na and abs. EtOH. The *Bz* derivative, softens (Dennis bar) 111°, of a polymeride obtained by use of BF_3 and the *NO*-derivative of a polymeride obtained in H_2O are described. Triethylenetetramine and $C_2H_4Br_2$ in abs. EtOH yield *heptaethyleneoctamine* (IV), b.p. 109—110°/0·5 mm. (*Bz* derivative, m.p. 202—220°); *nonaethylenedecamine* (V), b.p. 205°/2·5 mm. (*Bz_n* derivative, m.p. 75—105°), is obtained similarly. Attempts to determine the chain length by Van Slyke NH_2-N end-group analysis, cryoscopic measurements on the polymer, and extrapolation of η data obtained with compounds of low mol. wt. are described. For this purpose $(CH_2{\cdot}NH_2)_2$, triethylenetetramine, tetraethylenepentamine, (IV), and (V) are used. Assuming no branching, the Van Slyke results indicate a degree of polymerisation of 5 units, the cryoscopic method of 42 units, and the extrapolation method of 57 units for a HCl-polymeride. Its non-distillability and relatively high η indicate the unreliability of the NH_2-N method. H. W.

Derivatives of chondrosamine. M. Stacey (*J.C.S.*, 1944, 272—274).—Chondrosamine hydrochloride (I) (new prep. from chondroitin sulphate) with Ac_2O in C_5H_5N gives (60% yield) the *α-Ac*$_5$ (II), m.p. 178°, $[\alpha]_D^{20}$ +102° in $CHCl_3$, but with Ac_2O and $ZnCl_2$ yields (30% yield) the *β-Ac*$_5$ derivative (III), m.p. 235°, $[\alpha]_D^{20}$ +7° in $CHCl_3$. (I) with AgOAc in MeOH–Ac_2O yields α-N-*acetylchondrosamine monohydrate*, m.p. 120—122°, $[\alpha]_D^{21}$ +115° → 80° after 50 hr. in H_2O. (II) with boiling 2% HCl–MeOH gives *N-acetyl-α-methylchondrosaminide*, m.p. 217—218°, $[\alpha]_D^{21}$ +170° in $CHCl_3$, which with MeI–Ag_2O gives the *Me*$_3$ derivative (IV), m.p. 185°, sublimes 187°, $[\alpha]_D^{20}$ +121° in $CHCl_3$. With Me_2SO_4 and NaOH, (II) gives (IV), (III) gives *N-acetyltrimethyl-β-methylchondrosaminide* (V), m.p. 232°, sublimes 235°, $[\alpha]_D^{20}$ +7° in $CHCl_3$, whilst a mixture of (II) and (III) gives (IV) and (V), separated by fractional crystallisation or vac.-sublimation. (V) is converted into (IV) in boiling HCl–MeOH as for the corresponding glucosamine derivative. (IV) on hydrolysis (aq. HCl) yields trimethylchondrosamine hydrochloride, m.p. 178°, $[\alpha]_D$ +114° in H_2O. A mixture of (II) and (III) with HBr–AcOH affords acetobromochondrosamine (?), m.p. 152°, which loses Br on recrystallising (EtOH), giving *triacetyl-N-acetylchondrosamine monohydrate*, m.p. 183°, $[\alpha]_D^{20}$ +60° in $CHCl_3$. D. G.

Amino-acids. III. α-Amino-*n*- and *-iso*-butyric acid. J. H. Billmann and E. E. Parker (*J. Amer. Chem. Soc.*, 1944, **66**, 538—539; cf. A., 1944, II, 152).—$NH_2{\cdot}CHEt{\cdot}CH_2{\cdot}OH$, BzCl, and Na_2CO_3 in C_6H_6 at room temp. and then the b.p. give *β-benzamido-*n*-butyl alcohol* (89—91%), m.p. 98—99°, oxidised by $KMnO_4$ in aq. NaOH at 40° [less well, by PbO_2, $Na_2Cr_2O_7$–H_2SO_4, CrO_3, $(NH_4)_2S_2O_8$, or HNO_3] to NHBz·CHEt·CO_2H (67—72%), m.p. 139—140°, whence boiling 18% HCl yields $NH_2{\cdot}CHEt{\cdot}CO_2H$ (72%). $NH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ yields similarly the *N-Bz* derivative (78—79%), m.p. 89—90°, and thence $NHBz{\cdot}CMe_2{\cdot}CO_2H$ (91—93%) and $NH_2{\cdot}CMe_2{\cdot}CO_2H$ (86%). R. S. C.

Purity of synthetic *dl*-leucine. D. M. Hegsted and E. D. Wardwell (*J. Biol. Chem.*, 1944, **153**, 167—170).—Leucine (I) and *iso*leucine (II) are essential for *Lactobacillus arabinosus* (A., 1944, III, 371). When synthetic *dl*-(I) is used it is found that (II) is no longer necessary, suggesting that natural *l*-(I) is free from (II) but that synthetic *dl*-(I) is not. 7 samples of commercial *dl*-(I) were tested by microbiological assay and 5 showed appreciable (II) activity. 3 had 10—20% of the activity of (II), and from one, (II) was isolated. Since *d*-leucine, *tert. dl*-(I), and *dl*-norleucine are all without (II) activity it is thought that the activity is due entirely to (II) or its optical isomerides. J. Ho.

Action of sulphites on cystine disulphide linkages of wool. IV. Methylation of thiol groups of bisulphited wools. S. Blackburn, R. Consden, and H. Phillips (*Biochem. J.*, 1944, **38**, 25—29; cf. A., 1942, II, 426).—SH groups formed when wool is treated with $NaHSO_3$ are methylated by MeBr or MeI. A similar reaction occurs when wool is treated simultaneously with $NaHSO_3$ and Me_2SO_4. *S*-Cysteinesulphonate groups are unaffected by these methylating agents. The isolation of *S*-methylcysteine from hydrolysates of *S*-methylated wools by partition chromatography of the *N*-acetylated NH_2-acids is described. *l-N-Acetyl-S-methylcysteine*, m.p. 73—80°, $[\alpha]_D^{18}$ −37·8° in H_2O, when heated at 100—110° in vac. is converted into dl-N-*acetyl-S-methylcysteine*, m.p. 155—156°. J. N. A.

Synthesis of homocystine and of methionine. H. R. Snyder and G. W. Cannon (*J. Amer. Chem. Soc.*, 1944, **66**, 511—512).—2 : 5-Diketo-3 : 6-di-β-chloroethylpiperazine (A., 1943, II, 72) and $CS(NH_2)_2$ in boiling EtOH give the *di-β-isothiuronium chloride* (I) (98%), darkens 250°, m.p. 255° (decomp.). Aq. NaOH at room temp. hydrolyses (I) to the $(\beta\text{-SH})_2$ compound (not isolated), converted by $FeCl_3$–O_2 into the sulphide (not isolated), which in boiling conc. HCl gives homocystine (74·5%). Gradually adding aq. NaOH to (I) and Me_2SO_4 in H_2O at 0° (not other methods) gives the $(\beta\text{-SMe})_2$ compound (75%), m.p. 226—227·5°, and thence *dl*-methionine (65%) (cf. *loc. cit.*). R. S. C.

Allylic rearrangement in the reaction of cuprous cyanide with butenyl halides. J. F. Lane, J. Fentress, and L. T. Sherwood, jun. (*J. Amer. Chem. Soc.*, 1944, **66**, 545—548).—$CHMe{:}CH{\cdot}CH_2X$ or $CH_2{:}CH{\cdot}CHMeX$ (X = Cl or Br) with CuCN at, successively, 60—70°, 95—100°, and 150—160° gives *Δ^{β}-penteno-* (91·5±0·5%) and *α-methyl-Δ^{β}-buteno-nitrile* (8·5±0·5%), both b.p. 126° (corr.); the proportions, determined by *n*, are independent of the nature of the org. halide. The reaction is thus by way of the ion, $[CHMe{=}{=}CH{=}{=}CH_2]^+$. R. S. C.

Binary systems formed from nitriles and halides of titanium, tin, and antimony. N. A. Puschin, M. Ristic, I. Parchomenko, and J. Ubovic (*Annalen*, 1942, **553**, 278—285).—HCN and MeCN with $SnCl_4$ give compounds of high m.p. at which they decompose so that the systems cannot be investigated by the method of thermal analysis. Mixtures of HCl and PhCN with $AsCl_3$, of MeCN with $SnBr_4$, PCl_3, $AsCl_3$, AsBr, and $SbBr_3$, and of EtCN or PhCN with $SnBr_4$ remain liquid at room temp. Thermal analysis shows the existence of the following *compounds*, the crystallisation temp. being given in parentheses: $TiCl_4$,EtCN (100°); $TiCl_4$,2PhCN (180°); $TiCl_4$,$2C_6H_4Me{\cdot}CN$-*p*, (153°); $SnCl_4$,2EtCN (76·5°); $SnCl_4$,2PhCN (109°); $SnCl_4$,2-$C_6H_4Me{\cdot}CN$-*o*; (73°); $SnCl_4$,$2C_6H_4Me{\cdot}CN$-*m* (97°); $SnBr_4$,$C_6H_4Me{\cdot}CN$-*o* (53°); $SbCl_3$,$C_6H_4Me{\cdot}CN$-*p* (32°). SbI_3 and PhCN do not afford a mol. compound. H. W.

Ketone series. II. Condensation of monoketones with cyanoacetic acid. D. M. Trachtenberg and M. M. Schemjakin (*J. Gen. Chem. Russ.*, 1943, **13**, 477—480).—$CN{\cdot}CH_2{\cdot}CO_2Et$ reacts with ketones in presence of piperidine for 3 hr. at 110—125°: $CN{\cdot}CH_2{\cdot}CO_2Et + CORR' \rightarrow CRR'{:}CH{\cdot}CN$. The ketones and yields of nitrile in each case are: COMePr, 70%; $COMePr^{\beta}$, 56% of *βγ-dimethyl-Δ^{α}-pentenonitrile*, b.p. 70—75°/165 mm.; COMeBu, 61% of *β-methyl-Δ^{α}-hexenonitrile*, b.p. 194—196°; $COMe{\cdot}C_6H_{13}$, 65%, b.p. 128—130°/100 mm.; mesityl oxide, 70% of *βδ-dimethyl-$\Delta^{\alpha\gamma}$-hexadienonitrile*. F. Hi.

II.—SUGARS AND GLUCOSIDES.

Interpretation of reactions in the carbohydrate field in terms of consecutive electron displacement. H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1944, **32**, 45—59).—The general viewpoint is that the peculiar properties of systems involving double linkings may be explained by the migration of electron pairs in the mol. from points of high electron density to points of lower electron density with the addition and elimination of ions. Consideration of apparently unrelated complex reactions of the carbohydrates shows that the formation of the products may be explained by a few simple reactions involving shifts of electron pairs; these include enolisation, de-enolisation,

and double decomp. Mechanisms are presented for the formation of the saccharic acids by the action of alkali on sugars, of unsaturated lactones from OH-acids, of diacetylkojic acid from acetylated glucosone hydrate, for the conversion of glucal triacetate into *ψ*-glucal diacetate, of *ψ*- into *iso*- and proto-glucal, and of tetramethyl-Δ^1-glucosene into *ω*-methoxymethylfurfuraldehyde, for the formation of lævulic acid from *ω*-hydroxymethylfurfuraldehyde and from 2-deoxypentoses and of furfuraldehyde from trimethylpentoses. H. W.

Reaction of glucose with amines. E. Mitts and R. M. Hixon (*J. Amer. Chem. Soc.*, 1944, **66**, 483—486).—Except when R = H, the rate of hydrolysis of glucosylamines, ·CH(OH)·CH(NHR)·O·, parallels the basic dissociation const. of NH_2R; when R = alkyl, equilibrium in ≯2% aq. solution is established in 20 hr. at room temp. after 40% hydrolysis, but when R = aryl, only 8% of hydrolysis has occurred after 90 hr. and when R = acyl, the amides are stable even in acid (at room temp.). The Amadori rearrangement (to ·CO·CH_2·NHR) occurs only when R = aryl, and acid conditions are ideal for prep. of glucosylalkylamines: the Bu, *n*-amyl, *n*-heptyl, and di*cyclo*hexyl derivatives are prepared from glucose (1 mol.) and amine (2 mols.) in 0·5N-HCl at 70—75°; other derivatives are prepared from 1 mol. each of glucose and base in boiling MeOH or EtOH (cf. A., 1944, II, 37). 2-Methylglucose (I) with NHPh·NH_2 and a drop of AcOH in H_2O at room temp. give *2-methylglucosylphenylhydrazine*, m.p. 176—177°, but on further reaction at the b.p. gives glucosephenylosazone; however, with *p*-toluidine in H_2O at 100° (I) gives only *2-methylglucosyl-p-toluidine*, m.p. 150—151°, which does not rearrange or condense further. Hydrogenation (Raney Ni) of the (even non-cryst.) glucosylalkylamines in MeOH, EtOH, or aq. EtOH at, usually, 70—83°/800—1300 lb. gives cryst. alkylglucamines, ·CH(OH)·CH_2·NHR (cf. *loc. cit.*), which are stable to strong acid or alkali and to heat and can be titrated electrometrically with dil. acid; the intermediate alkyl derivatives are surface-active. The following new or revised data (cf. *loc. cit.*) are recorded. Glucosyldi*cyclo*hexylamine, m.p. 97—98°, contains 1 mol. of di*cyclo*hexylamine of crystallisation, which cannot be removed without decomp. *NN'*-Diglucosylethylene diamine, m.p. 152—154° (decomp.). Glucosyl-*n*-hexa-, m.p. 106—107° after softening, and -*n*-octa-decylamine, m.p. 104—105° after softening. *N*-*n*-Butyl-, m.p. 127—128°, *N*-*n*-amyl-, $[\alpha]_D^{25}$ −13·8° in 50% EtOH. *N*-*n*-hexadecyl-, m.p. 123—124° after softening, *N*-*n*-octadecyl-, m.p. 118—119° after softening, N-iso*propyl*-, m.p. 126—127° after softening, $[\alpha]_D^{25}$ −13° in 50% EtOH, and *N*-*β*-*octylglucamine*, m.p. 107—108° after softening. NN'-*Propylenediglucamine*, m.p. 135—137°. l-Aminoglucose, m.p. 120—121°, $[\alpha]_D^{24}$ +19·1° in H_2O, is stable in H_2O at room temp. and can be titrated potentiometrically with dil. acid. R. S. C.

Large-scale preparation of *D*-altrose. *D*-Altroseoxime and its rate of mutarotation. R. C. Hockett and L. B. Chandler (*J. Amer. Chem. Soc.*, 1944, **66**, 627—628).—Prep. of cryst. *D*-altrose (*oxime*, m.p. 143—144°, $[\alpha]_D^{24\cdot9}$ −64·0° ⟶ −9·8° in H_2O, from *D*-lactose (cf. Richtmyer *et al.*, A., 1935, 1355) is modified to give 3·7% over-all yield. R. S. C.

Preparation of mannose. E. K. Narayanan (*Indian J. Med. Res.*, 1941, **29**, 1—6).—Complete hydrolysis to mannose of the polysaccharide in ivory-nut meal requires 10 hr. boiling with N-H_2SO_4 or 15 hr. heating at 105°. About 7% of the total sugar is thereby destroyed. S. E. M.

Magnitude of " unit chains " of liver-glycogen of rabbits supplied with glucose, fructose, and sucrose.—See A., 1944, III, 606.

Glycosides sensitive to alkali. Glucosides of nitro-alcohols. B. Helferich and M. Hase (*Annalen*, 1943, **554**, 261—268).—Presence of NO_2, like that of SO_3H, in immediate propinquity to the glycosidic linking renders the glycosides very sensitive to alkali and hence enables them to reduce Fehling's solution immediately. Even under mild conditions the glucose liberated by alkaline hydrolysis immediately darkens. NO_2 remote from the glycosidic linking does not cause sensitiveness to alkali. The action of Ag_2CO_3 on a solution of acetobromoglucose (I) and NO_2·$[CH_2]_2$·OH in $CHCl_3$ at room temp. leads to *β-nitroethyl-β-d-glucoside tetra-acetate*, m.p. 119—120° (corr.), $[\alpha]_D^{19\cdot5}$ −15·8° in $CHCl_3$, which could not be hydrolysed to the free glucoside; replacement of Ag_2CO_3 by Ag_2O and $CaSO_4$ gives (?) *β-nitroethyl-α-d-glucoside tetra-acetate*, m.p. 139—140° (corr.), softens at ~125°, $[\alpha]_D^{19\cdot5}$ +37·5° in $CHCl_3$. NO_2·$CH(CH_2$·OH$)_2$, (I), and Ag_2CO_3 in anhyd. Et_2O yield *β-nitropropane-αγ-dioldi-β-d-glucoside tetra-acetate*, m.p. 179·5—180·5° (corr.), $[\alpha]_D^{20\cdot5}$ −25·8° in $CHCl_3$. NO_2·$C(CH_2$·OH$)_3$, (I), and Ag_2CO_3 in EtOAc afford *β-nitroisobutanetriol-β-d-glucoside* (*nitroisobutylglycerol-β-d-glucoside*) *tetra-acetate*, m.p. (anhyd.) 132—134° (corr.), (+1H_2O), m.p. 94·5—96°, $[\alpha]_D^{18}$ −31·2° in MeOH; under similar conditions but with substitution of $COMe_2$ for EtOAc the *product* appears to be NO_2·$C(CH_2$·OH$)_2$·CH_2·O·CMe_2·O·$C_6H_7O(OAc)_4$, m.p. (very indef.) 154—156°/corr.), $[\alpha]_D^{19}$ −8·8° in $CHCl_3$; the substances are converted by Ac_2O and C_5H_5N at 0° and subsequently at room temp. into the corresponding *hexa-acetates*, m.p. 147—148° (corr.), $[\alpha]_D^{21}$ −24·1° in $CHCl_3$, and m.p. 144—146°, $[\alpha]_D^{20\cdot5}$ −18·1° in $CHCl_3$. *δ-Nitro-n-butanol-β-d-glucoside tetra-acetate* (II), m.p. 139—141° (corr.), $[\alpha]_D^{21}$ −18·7° in $CHCl_3$, is obtained from the corresponding I-compound and $AgNO_2$ in boiling C_6H_6; it reduces Fehling's solution only after hydrolysis and is converted by NaOH into the amorphous glucoside, re-acetylated to (II). H. W.

Cerebroglucoside, m.p. 185°, $[\alpha]_D^{14}$ −11·3° in C_5H_5N, from spleen, its H_2-derivative, m.p. ~188°, $[\alpha]_D^{27}$ −2·6°, and lignoceryldihydrosphingosine.—See A., 1944, III, 549.

Chemistry and biochemistry of plant materials. IX. Formation of dihydroflavonol and flavonol and synthesis of chalconeflavanone-flavonol glucosides. L. Reichel and J. Steudel (*Annalen*, 1942, **553**, 83—97).—Resacetophenone-4-glucoside (I) is used in further syntheses. Resacetopheone, α-acetobromoglucose, and 10% NaOH in $COMe_2$ at room temp. afford resacetophenone-4-glucoside tetra-acetate (cf. Müller, *Diss., Karlsruhe*, 1938), m.p. 130—131°, $[\alpha]_D^{20}$ −29·7° in $COMe_2$, hydrolysed by gradual addition of Na to its solution in abs. MeOH to (I), m.p. 198—200°, $[\alpha]_D^{20}$ −86·9° in $COMe_2$. PhCHO, (I), and 2N-NaOH give *2′ : 4′-dihydroxychalkone-4′-β-d-glucoside* (II), m.p. 195—197°, (+1H_2O), $[\alpha]_D^{20}$ −53·9° in $COMe_2$, hydrolysed by acid to 2′ : 4′-dihydroxychalkone, m.p. 147—148°. (II) is oxidised by alkaline H_2O_2 to *3 : 7-dihydroxyflavone-7-β-d-glucoside*, m.p. 223—225°, $[\alpha]_D^{20}$ −90·1° in dioxan, slowly hydrolysed by acid to 7-hydroxyflavonol, m.p. 252—254°. (II) is converted by dil. NaOH–aq. EtOH into *7-hydroxyflavanone-7-β-d-glucoside*, m.p. 184—187°, (+1H_2O), $[\alpha]_D^{20}$ −102·6° in $COMe_2$, also obtained slowly from (I), PhCHO, and NaOH in aq. EtOH at room temp. and hydrolysed by acid to 7-hydroxyflavanone, m.p. 182—184°. *iso*-Vanillin, (I), and NaOH at room temp. yield *3 : 2′ : 4′-trihydroxy-4-methoxychalkone-4′-β-d-glucoside* (*4-methylbutein-4′-glucoside*), m.p. 212—214°, (+1·5H_2O), $[\alpha]_D^{20}$ −45·2° in $COMe_2$, oxidised by alkaline H_2O_2 to *3 : 7 : 3′-trihydroxy-4′-methoxyflavone-7-β-d-glucoside*, m.p. 254—255° (decomp.), $[\alpha]_D^{20}$ −59·3° in C_5H_5N, and converted by a little NaOH in aq. MeOH into *7 : 3′-dihydroxy-4′-methoxyflavanone-7-β-d-glucoside*, m.p. 208—211°, (+1H_2O), $[\alpha]_D^{20}$ −84·3° in 50% $COMe_2$. H. W.

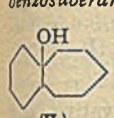
Chemistry and biochemistry of plant materials. X. Synthesis of flavanoneglucosides under physiological conditions. L. Reichel and R. Schickle (*Annalen*, 1942, **553**, 98—102).—Negative results are obtained by the attempted condensation of hydroxyacetophenones with hydroxybenzaldehydes to hydroxychalkones or hydroxyflavanones under physiological conditions so that the biosyntheses of these compounds does not occur in this manner. Since these compounds are found in plants almost exclusively as glucosides it is highly improbable that the latter are formed in the cell from aglycone and sugar under the influence of carbohydrases. The authors have therefore examined the possibility that glycosides of the OH-compounds condense with one another and that the sugar residues are partly or wholly removed from the products by sp. enzymes; glycosides may then be resynthesised from these secondary aglycones. Resacetophenone-4-*β*-*d*-glucoside (I) and PhCHO at pH 8·3 give a 20% yield of 7-hydroxyflavanone-7-*β*-*d*-glucoside, m.p. 184—187°, in 83 days; small additions of carotene are used as an antioxidant of PhCHO. 4′-Hydroxyflavanone-4′-*β*-*d*-glucoside, m.p. 218—220°, $[\alpha]_D^{12}$ −37·4° in dioxan, is obtained in 19% yield at pH 8·0 in 103 days from *o*-OH·C_6H_4·COMe and *p*-hydroxybenzaldehyde-*β*-*d*-glucoside, m.p. 156—158° (obtained by hydrolysis of the tetra-acetate, m.p. 144—145°, prep. from *p*-OH·C_6H_4·CHO and *α*-acetobromoglucose by NaOH in $COMe_2$). *o*-OH·C_6H_4·COMe and 2 : 4-*dihydroxybenzaldehyde-4-β-d-glucoside*, m.p. 218—220°, $[\alpha]_D^{12}$ −102·1° in H_2O, afford 2′ : 4′-dihydroxyflavanone-4′-*β*-*d*-glucoside, m.p. 180—183° (decomp.), (+ 2H_2O), $[\alpha]_D^{12}$ −47·1° in abs. MeOH; at pH 7·6 the yield is 23% after 40 days and at pH 8·3 it is only 12% after 63 days. (I) and *iso*vanillin-*β*-*d*-glucoside afford *7 : 3′-dihydroxy-4′-methoxyflavanone-7 : 3′-β-d-diglucoside*, m.p. 220—224°, $[\alpha]_D^{18}$ −124·3° in quinoline (also + 2H_2O); the yield is 20·4% in 83 days at pH 7·5 and 14·6% in 80 days at pH 8·4. H. W.

III.—HOMOCYCLIC.

Isomerisation of polymethylene hydrocarbons under the influence of aluminium chloride. X. Isomerisation of methyl*cyclo*heptane. M. B. Turova-Polak and P. L. Rappoport (*J. Gen. Chem. Russ.*, 1943, **13**, 353—357).—Over Pt–C at 305—310°, methyl*cyclo*heptane (I) is isomerised and dehydrogenated directly, in 94% yield, to xylene (*p*-, with a small proportion of *m*-). Bromination of (I) in the presence of $AlBr_3$ yields tetrabromoxylene, m.p. 253°. Addition of $AlCl_3$ to (I) causes a rapid rise of temp. and conversion of (I) into 1 : 4-dimethyl*cyclo*hexane, containing a very small amount of the 1 : 3- and a trace of the 1 : 2-compound. R. C. P.

Carbon rings. XXXV. Preparation of *cyclo*undecane from benzosuberane. P. A. Plattner (*Helv. Chim. Acta*, 1944, **27**, 801—810).—Gradual addition of Ph·$[CH_2]_4$·COCl in much CS_2 to $AlCl_3$ in boiling CS_2 affords benzosuberone, b.p. 138—139°/12 mm., in 87% yield. This is reduced (Clemmensen–Martin) to benzosuberane (I), b.p. 99·8—100°/13 mm., m.p. −1·5°, which is hydrogenated (PtO_2 in AcOH or Raney Ni–H_2 at 180°/145 atm.–EtOH) to *hexahydro-*

benzosuberane (*dicyclo*-[0 : 4 : 5]-*undecane*), b.p. 88·5—89°/11 mm. Ozonisation then yields mainly *dicyclo*-[0 : 4 : 5]-*undecan*-1-*ol* (II), b.p. 118—120°/13 mm., m.p. 30—31° (*dinitrobenzoate*, m.p. 201°), with minor amounts of cyclo*undecane*-1 : 6-*dione* (III), b.p. 110—115°/0·1 mm. [*dioxime* (IV), m.p. 232—234° (decomp.); *disemicarbazone*, m.p. 218°]; a *semicarbazone*, m.p. 154°, of a dicyclic monoketone is also isolated. Addition of MnO_2 favours the formation of (II) but unchanged material in considerable proportion remains. (II) is converted by anhyd. $ZnCl_2$ at 140° into *dicyclo*-[0 : 4 : 5]-*undecene* (III), b.p. 90—91°/12 mm., which when ozonised in 50% AcOH at −10° affords (III). More conveniently (III) is obtained by hydrogenation of (I) by Ca hexammine. Reduction of (IV) by Na and C_5H_{11}·OH leads to a mixture of amines from which 1 : 6-*diamino*cyclo*undecane*, b.p. 156—158°/12 mm., is readily isolated through the sparingly sol. carbamate. It gives a *dihydrochloride*, decomp. 230—260° with partial sublimation, *dipicrate*, m.p. 233—235°, and an Ac_2 derivative, m.p. 252·3—252·5°. It is methylated to 1 : 6-*tetramethyldiamino*cyclo*undecane dimethiodide*, decomp. 312—313°; the corresponding quaternary base is decomposed thermally into *cyclo*undecadiene, which is readily hydrogenated (PtO_2 in EtOH–Et_2O at room temp.) to cyclo*undecane*, b.p. 91—91·3°/12 mm., m.p. −7·3°. H. W.



(II.)

Binary system, tin tetrachloride–*m*-dinitrobenzene. E. Hertel (*Annalen*, 1942, **553**, 286—288; cf. A., 1933, 27).—In reply to Puschin *et al.* (A., 1943, II, 4) it is stated that in the examination of the system $TiCl_4$–*m*-$C_6H_4(NO_2)_2$ the authors have so worked that in the region up to 50 mol.-% of $TiCl_4$ the compound $2TiCl_4.C_6H_4(NO_2)_2$ is invariably formed in the primary crystallisation from the undercooled melt either spontaneously or by seeding. The eutectic between the phases $2TiCl_4.C_6H_4(NO_2)_2$ and *m*-$C_6H_4(NO_2)_2$ happens to be at ~50 mol.-% of $TiCl_4$. Lack of suitable seeding material has prevented the discovery of other phases. H. W.

Valency tautomerism or mesomerism with ωω′-tetraphenylpolyenes. G. Wittig and B. Fartmann (*Annalen*, 1943, **554**, 213—240).—Chemical and physical methods of discriminating between valency tautomerism and mesomerism are discussed at the instances of *p*-vinylenedi(triphenylmethyl) (I), *p*- (II) and *m*- (III) -azoditriphenylmethyl. $(p\text{-}C_6H_4Bz\cdot CH_2)_2$ is converted by Br in boiling $PhNO_2$ into *pp′*-dibenzoylstilbene, m.p. 234—235°, transformed by the successive action of LiPh in anhyd. Et_2O and H_2O into *pp′*-di(hydroxydiphenylmethyl)stilbene, m.p. 218—218·5°, which with HCl gives *pp′*-di(chlorodiphenylmethyl)stilbene, decomp. 213—216° when heated from 100° or decomp. 234° (bath preheated to nearly 234°). This with MeOH in hot dioxan gives pp′-*di(methoxydiphenylmethyl)stilbene*, m.p. 178—179°, and is dehalogenated by Cu powder (apparatus see C., 1944, Part 4) to (I), m.p. 252—255°. Its solutions are immediately decolorised by O_2 without manifestation of the Schmidlin phenomenon. *p*-$NO_2\cdot C_6H_4\cdot CPh_2Cl$, m.p. 92—93°, is converted by NaOAc and AcOH into the corresponding carbinol (IV), reduced by Zn dust and NaOH in aq. EtOH to *pp′*-di(hydroxydiphenylmethyl)hydrazobenzene (V) which, on account of its instability, is immediately oxidised to pp′-*di(hydroxydiphenylmethyl)azobenzene* (VI), m.p. 218—219°, either by Br and NaOH or, preferably, by CrO_3 in aq. AcOH. Electrolytic reduction of (IV) at a Pt cathode gives pp′-*di(hydroxydiphenylmethyl)azoxybenene*, m.p. 177—179°, and then (very slowly) (VI). (VI) is transformed by HCl in C_6H_6 containing a little AcCl into pp′-*di(chlorodiphenylmethyl)azobenzene*, decomp. 242° [corresponding $(OMe)_2$-derivative, m.p. 200—201°, softens at 198°], converted by Cu powder in C_6H_6, PhMe, or CCl_4 into (II), almost black crystals, m.p. 252—255°, which markedly depresses the m.p. of (I). Solutions of (II) are immediately and non-recurringly decolorised by air with the formation of complex peroxides $\cdot O\cdot O\cdot CR_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CR_2\cdot O\cdot O\cdot CR_2\cdots$. Formation by use of Cu powder and behaviour towards air indicate a diradical structure for (II); the possible quinonoid structure, suggested by its formation by dehydration of (V), is negatived by its prolonged stability towards dil. H_2SO_4 at 60°, which also brings evidence against a tautomerism of two valency isomerides in solution. Since the magnetic properties of the analogous (I) exclude the possibility that these polyenes exist solely in the diyl form it appears highly probable that internal valency compensation has occurred between the conjugated systems of a quinone and a diradical and therefore that the polyene mol. is in a condition intermediate between the limiting structures of a quinone and a diyl. $COPh\cdot C_6H_4\cdot NO_2$-*m* is transformed by PCl_5 at 120—130° into m-*nitrobenzophenone dichloride*, m.p. 66°, converted by $AlCl_3$ and C_6H_6 into m-*nitrotriphenylmethyl chloride*, m.p. 92—93°, which with NaOAc yields the carbinol, m.p. 75°. This is reduced electrolytically (Pb anode; Ni cathode) to mm′-*di(hydroxydiphenylmethyl)azobenzene*, m.p. 174—176°, which is converted by HCl and AcCl in $CHCl_3$ into mm′-*di(chlorodiphenylmethyl)azobenzene*, m.p. 206—208° [corresponding $(OMe)_2$-derivative, m.p. 200—201°], transformed by Cu powder in absence of air and light into (III), which could not be obtained cryst. Its solutions are pale brown with a tendency towards green resembling in shade and depth those of CPh_3. (III) behaves as a true diradical dissociated to only a slight extent; at 80° the colour becomes considerably more intense but the original shade is regained on cooling. The structure of (I), (II), and (III) is confirmed by their conversion into the corresponding dichlorides by $PhICl_2$. With Li-diphenylamine in Et_2O the dichlorides yield the corresponding diyls. From solutions of (I) and (II) mixed crystals of the compounds are obtained. (I) and (III) do not yield cryst. materials and definite products could not be isolated from (II) and (III).

The dependence of absorption spectrum on temp. opens a new way for discriminating between mesomerism and valency tautomerism. In 0·0001M. solution the varying colour of the solutions with temp. is obvious; association is excluded since the solutions obey Beer's law. The violet-blue colour of (I) passes into blue at −70° and becomes non-characteristic at 100°. (II) is more violet than (I); on cooling the colour is displaced towards shorter λ, on heating towards longer λ; at 100° it appears almost carmine-red. Difficulties due to apparatus prevent quant. measurements within such wide limits but between 15° and 55° the absorption max. [~590 mμ. for (I) and ~575 mμ. for (II)] is displaced towards shorter λ with increase of temp. Optical measurements could not be made with (III) since its max. lies at the short-wave border of the visible spectral region. H. W.

Hydrogenation of anthracene by tetrahydronaphthalene. M. Orchin (*J. Amer. Chem. Soc.*, 1944, **66**, 535—538).—In presence of Pd–C in an open tube, 1 : 2 : 3 : 4-tetrahydronaphthalene (I) at 225—230° evolves much H_2. Presence also of anthracene (II) decreases evolution of H_2, which is utilised for hydrogenation of the (II) to mainly 1 : 2 : 3 : 4-tetra- (III) with some 9 : 10-di- (IV) and *s*-octahydroanthracene. The amounts of H_2 and hydrogenated products depend on the temp. and ratio of (I) to (II). Reaction in a sealed tube is similar. The di- and octa-hydroanthracene are formed by disproportionation of the H_4-compound, a reaction which is shown to be reversible. With Raney Ni in boiling EtOH, (II) or (IV) gives a good yield of (III). In presence of Pd–C *cyclo*hexenone acts as a dihydrophenol and with (II) gives 30% of (III). These reactions show the need for caution in determining the primary products of hydrogenation of, *e.g.*, coal. Chromatographic separation of (III) and (IV) on Al_2O_3 is described. R. S. C.

Hydroanthracenes and hydrophenanthrenes. II. J. W. Cook, (Miss) N. A. McGinnis, and S. Mitchell (*J.C.S.*, 1944, 286—293; cf. A., 1939, II, 103).—*trans*-Hexahydroanthrone [$(NO_2)_1$-, m.p. 130·5—131·5°, and $(NH_2)_1$-derivative, m.p. 165—166°] is reduced (Zn–HCl) to trans-as-*octahydroanthracene* (I), m.p. 63—64°, and a little (?) *hexadecahydro*-9 : 9′-*dianthryl*, m.p. 245—250°, but with H_2–PtO_2 yields (I) and 9-*hydroxy*-trans-as-*octahydroanthracene*, m.p. 136°, giving a *hexahydroanthracene*, m.p. 63—66°, on dehydration. Sulphonation of (I) gives the *Na sulphonate*, converted by fusion with KOH into ar-*hydroxy*-trans-as-*octahydroanthracene*, m.p. 104°, affording *trans-cyclo*hexane-1 : 2-diacetic acid, m.p. 166—167°, on oxidation ($KMnO_4$). With $AlCl_3$ (I) yields a *perhydroanthracene* (II), m.p. 204°, and on catalytic hydrogenation (PtO_2) gives a *perhydroanthracene* (III), m.p. 39—40°, or (Raney Ni) at 200°/150 atm. a perhydroanthracene (IV), m.p. 89—90°. Hydrogenation of *s*-octahydroanthracene yields (Raney Ni) a mixture of (III) and (IV) and (PtO_2) a perhydroanthracene (V) (completely *cis*?), m.p. 61·5—63°. With $AlCl_3$ (V) is converted into (III) and (III) into (IV). (II) and (IV) are not dehydrogenated by Se or Pd but (V) with Se affords anthracene. $AlCl_3$ with crude *as*-octahydrophenanthrene (VI) (from cyclisation of 1-β-phenylethyl-Δ¹-*cyclo*hexene with $AlCl_3$) at 50—70° effects *cis–trans*-isomerisation, oxidation (CrO_3) of the product giving *trans*-9-keto-*as*-octahydrophenanthrene, m.p. 95—96° (oxime, m.p. 176—177°), but at 125—130° tetrahydronaphthalene, (II), and (IV) are obtained. Structures are suggested for (II), (III), and (IV). 2-β-Phenylethyl*cyclo*hexylacetyl chloride (corresponding p-*phenylphenacyl* ester, m.p. 75—77°) with $AlCl_3$ in $PhNO_2$ gives a *dibenzocyclooctanone* (2 : 4-*dinitrophenylhydrazone*, m.p. 242—244°), and with $SnCl_4$ in C_6H_6 a *lactone*, $C_{18}H_{20}O_2$, m.p. 67—68°. 2-Benzyl*cyclo*pentylacetyl chloride with $AlCl_3$ yields 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydro*-5 : 6-*benz*-7-*azulone*, m.p. 56° (2 : 4-*dinitrophenylhydrazone*, m.p. 169—170°), giving the *octahydrobenzazulol*, m.p. 128—129°, dehydration of which gives 1 : 2 : 3 : 4 : 9 : 10-hexahydrobenzazulene, m.p. 29—35°, affording 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydrobenzazulene*, m.p. 29—30°, on hydrogenation. M.p. are corr. D. G.

Influence of *n*-alkyl groups on the rate of a cyclisation reaction. E. Berliner (*J. Amer. Chem. Soc.*, 1944, **66**, 533—535).—Cyclisation of *o*-CHPhMe·C_6H_4·COR to dialkylanthracenes in boiling 48% HBr–AcOH depends on the nature of R (cf. Bradsher *et al.*, A., 1943, II, 95), *k* being R = Me 4·6, Et 1·8, Pr^{α} 0·99, Bu^{α} 0·35, *n*-amyl 0·36, *n*-C_6H_{13} 0·36, Ph 0·16, and CH_2Ph 0·91 × 10^{-2} min.$^{-1}$ With less conc. acid the rate for R = Me is greatly reduced. Ring-closure probably occurs by way of *o*-CHMePh·$C_6H_4\cdot C^+R\cdot OH$, the rate being governed by the inductive effect of R. Adding *o*-$C_6H_4Cl\cdot COCl$ in C_6H_6 to $AlCl_3$–C_6H_6, keeping at room temp., and then boiling gives *o*-$C_6H_4Cl\cdot COPh$ (85·7%), m.p. 43—44°, b.p. 178—180°/14—15 mm. (lit. an oil), whence MgMeCl yields *o*-$C_6H_4Cl\cdot CPh{:}CH_2$ (77%), b.p. 164—166°/17 mm. H_2–Raney Ni in EtOH at 1 atm. then yields *α-phenyl-α-o-chlorophenylethane*, b.p. 158°/12 mm., which with CuCN and C_5H_5N (bath at 250—260°) gives *o*-$CN\cdot C_6H_4\cdot CHPhMe$

(75·7%), b.p. 190—191°/17—18 mm. With, successively, MgRCl–C_6H_6, 20% aq. NH_4Cl, and boiling HCl–$COMe_2$–H_2O this gives o-α-*phenylethyl-aceto-* (75·5%), b.p. 184—186°/16—17 mm., *-propio-*, b.p. 189—190°/16—17 mm., *-n-butyro-*, b.p. 194—197°/14—15 mm., *-n-valero-*, b.p. 205—206°/17—18 mm., *-n-hexo-*, b.p. 209—212°/15—16 mm., *-n-hepto-*, b.p. 217—219°/14—15 mm., and *-ω-phenyl-aceto-phenone*, b.p. 195—197°/1—2 mm., and 2-α-*phenylethylbenzophenone*, m.p. 47—48°, b.p. 216—219°/7—8 mm. Cyclisation (cf. above) yields 9-*methyl*-10-*ethyl-*, m.p. 143·2—144° (*picrate*, m.p. 137·8—138·4°), -10-n-*propyl-*, m.p. 97·8—98·6° (*picrate*, m.p. 125·5—126·2°), -10-n-*butyl-*, m.p. 78·2—78·8° (*picrate*, m.p. 91·8—92·8°), -10-n-*amyl-*, m.p. 71—71·8° (*picrate*, m.p. 85·4—86·2°), and -10-n-*hexyl-*, m.p. 65·8—66·5° (*semipicrate*, m.p. 78·2—79·2°), 9-phenyl-10-methyl-, m.p. 113·5—114·5° (lit. 112°) (*picrate*, m.p. 125·2—126°), and 9-*benzyl*-10-*methyl-*, m.p. 167·8—168·6°, *-anthracene*. M.p. are corr. R. S. C.

Hydrogenolysis of abietic acid. H. B. Charmbury and C. C. Wright (*J. Amer. Chem. Soc.*, 1944, **66**, 526—532).—Hydrogenolysis of abietic acid for 2 hr. at 325°, 370°, 400°, 425°, and 450°, and for 3 discontinuous periods each of 1 hr. at 400°, is investigated. Decarboxylation to yield CO_2 accounts for almost all the loss of O_2; in 2 hr. it is incomplete at 325° but complete at 450°, and at 400° 73·9% complete in 1 hr.; some CO + H_2O are also obtained, being derived at least partly by reduction of CO_2. Loss of Pr$^\beta$ does not occur at 375° but is rapid at higher temp., being then a function of $[H_2]$ or partial pressure of H_2. The amounts of CH_4, C_3H_8, *n-* and *iso*-C_4H_{10} formed show that the C_2H_6 results partly from cracking of C_3H_8, but that loss of 1 Me begins at 325° and is also a function of time and $[H_2]$. At 370° there is some addition of H_2 to C:C or C:C·C:C, but at higher temp. dehydrogenation occurs. Ring-fission begins at 425°, thereafter becoming more rapid and being a function of $[H_2]$; products isolated include *trans*-1: 2-dimethyl-, methyl-, and ethyl-*cyclo*hexane, 3 : 5-dimethyl-Δ^1-*cyclo*hexene, and, by isomerisation of a C_6-ring, 1 : 3-dimethyl*cyclo*pentane. The H_2 consumed at lower temp. is almost all accounted for by saturation of C:C, cracking, and reduction of CO_2. The following products are isolated: at 370° 12-*methyl*-Δ$^{9(14)}$-*dodecahydroretene*, b.p. 139—142°/4 mm.; at 400° (2 hr.) 1 : 12-*dimethyl*-Δ$^{7:9(14)}$-*decahydrophenanthrene*, b.p. 122—125°/4 mm., and 12-*methyldecahydroretene*, b.p. 143—146°/5·5 mm., and by discontinuous heating two isomeric decahydroretenes, b.p. 122—128°/4 mm., and 1 : 12-*dimethyl-*, b.p. 127—130°/3 mm.; and then 1-*methyl-dodecahydrophenanthrene*, b.p. 127—131°/2 mm.; at 425° 1-*methyl*-Δ$^{7:9(14)}$-*decahydro-*, b.p. 118—120°/3 mm., and at 450° 1-*methyloctahydro-phenanthrene*, b.p. 112—116°/4 mm. R. S. C.

Aryl and aralkyl carbamides. J. S. Buck, R. Baltzly, and A. E. Ardis (*J. Amer. Chem. Soc.*, 1944, **66**, 311—312).—NH_2·CO·NH·NO_2 and NHRR′ (reaction incomplete for *o*-substituted amines) give N-*phenyl*-N-β-*hydroxyethyl-*, m.p. 110°, and N-m-4-*xylyl-*, m.p. 73—74°, N-5-*chloro*-o-*tolyl-*, m.p. 93°, N-5-*bromo*-o-*tolyl-*, m.p. 88·5—89°, N-4-*chloro*-o-*tolyl-*, m.p. 166—167°, N-3-*bromo*-p-*tolyl-*, m.p. 116°, N-4-*bromo*-2-*ethylphenyl-*, m.p. 95°, N-p-*ethylphenyl-*, m.p. 122—124°, N-2-*bromo*-4-*ethylphenyl-*, m.p. 114°, and N-5-*bromo*-o-*phenetyl*-N-*ethylcarbamide*, m.p. 124—124·5°, N-*benzyl-*, m.p. 135°, N-p-*methoxybenzyl-*, m.p. 140—141°, N-3-*chloro*-4-*methoxybenzyl-*, m.p. 169—169·5°, N-3-*bromo*-4-*methoxybenzyl-*, m.p. 178°, N-β-3-*chloro*-4-*methoxyphenylethyl-*, m.p. 117·5—118°, and N-β-3-*bromo*-4-*methoxyphenylethyl*-N-*methylcarbamide*, m.p. 116·5—117°, N-5-*bromo*-o-*tolyl*-N-n-*propyl-*, m.p. 94·5—95·5°, N-4-*chloro*-o-*tolyl*-N-n-*butyl-*, m.p. 79·5—80°, and N-*benzyl*-N-n-*butyl-carbamide*, m.p. 61—62°. EtNCO and the appropriate amine give N-5-*bromo*-o-*tolyl*-N′-*ethyl-*, m.p. 230—232°, and N-m-4-*xylyl*-NN′-*diethyl-carbamide*, m.p. 76°. *o*-C_6H_4Et·NEt·CO·NH_2 with BzCl–NaOH or –C_5H_5N gives NN-*dibenzoyl*-N′-*o-ethylphenyl*-N′-*ethylcarbamide*, m.p. 128—129°. The following amines are prepared by standard methods: NHRMe in which R = 4 : 3 : 1-OMe·C_6H_3Cl·CH_2 (*hydrochloride*, m.p. 201—201·5°), -OMe·C_6H_3Br·CH_2 (*hydrochloride*, m.p. 202—203°), -OMe·C_6H_3Cl·$[CH_2]_2$ (*hydrochloride*, m.p. 196°), and -OMe·C_6H_3Br·$[CH_2]_2$ (*hydrochloride*, m.p. 215—216°); NHREt in which R = 2 : 4 : 1-C_6H_3MeCl, b.p. 136°/13 mm., -C_6H_3MeBr, b.p. 96—99°/0·25 mm., and -C_6H_3EtBr, b.p. 135°/3 mm., 4 : 2 : 1-C_6H_3MeBr, b.p. 137°/17 mm., and -C_6H_3EtBr, b.p. 107°/3 mm., 2 : 5 : 1-C_6H_3MeCl, b.p. 141°/27 mm., and -OEt·C_6H_3Br, b.p. 111°/0·25 mm., and *p*-C_6H_4Et, b.p. 122—123°/22 mm.; 2 : 5 : 1-C_6H_3MeCl·NHBu^a, b.p. 125°/1 mm. M.p. are corr. R. S. C.

Metabolism of 2 : 4 : 6-trinitrotoluene (α-T.N.T.). H. J. Channon, G. T. Mills, and R. T. Williams (*Biochem. J.*, 1944, **38**, 70—85).—2 : 6 : 2′ : 6′-Tetranitro-4 : 4′-azoxytoluene, m.p. 215—216°, is obtained by oxidation of 2 : 6 : 1 : 4-$(NO_2)_2C_6H_2$Me·NH·OH with $K_2Cr_2O_7$ and H_2SO_4 or, preferably, of 2 : 6 : 1 : 4-$(NO_2)_2C_6H_2$Me·NH_2 (I) with $(NH_4)_2S_2O_8$. Treatment of α-T.N.T. with H_2S–NH_3–EtOH gives (I), converted into its *Bz*, m.p. 263—264°, and *PhSO*$_2$ (II), m.p. 175—177°, derivatives. Electrolytic reduction of α-T.N.T. affords a mixture of dinitroaminotoluenes (III) from which after benzoylation 2 : 4-*dinitro*-6-*benzamidotoluene*, m.p. 216—217°, is isolated. (III) is more conveniently separated into its components by treatment with $PhSO_2Cl$ and C_5H_5N, which leads to the isolation of 2 : 4-*dinitro*-6-*dibenzenesulphonamidotoluene*, m.p. 222°, and (II) (m.p. 177—178°). These are hydrolysed to 2 : 4-*dinitro*-6-*aminotoluene*, m.p. 176° (*Ac* derivative, m.p. 159—160°), and (I), respectively. (See also A., 1944, III, 606, and C., 1944, 118.) H. W.

***p*-Hydroxylaminobenzenesulphonamide, its acetyl derivatives and diazotisation reaction.** H. Bauer and S. M. Rosenthal (*J. Amer. Chem. Soc.*, 1944, **66**, 611—614).—*p*-NO_2·C_6H_4·SO_2·NH_2 and Zn dust in NH_4Cl–EtOH–H_2O at 45—52° give *p*-OH·NH·C_6H_4·SO_2·NH_2 (I) (63—88·5%), m.p. 143—144° (decomp. 148—158°) (lit. 139·5—140·5°), the mother-liquors from which with $FeCl_3$ yield p-*nitrosobenzenesulphonamide*, decomp. 155—268°. With $NaNO_2$–aq. HCl, (I) gives the N^4-*NO-*, m.p. 120°, with Ac_2O gives the N-*Ac*, m.p. 228° (cannot be diazotised), but with Ac_2O in much H_2O gives mainly the O-*Ac* derivative (II), m.p. 138° (readily diazotised). *p*-NO_2·C_6H_4·CO_2H and Zn dust in NH_4Cl–NaOH–H_2O at 15—20° give p-*hydroxylaminobenzoic acid* (III) (31%), darkens ~240°, m.p. >300° [N-*Ac*, m.p. 210° (decomp.), and *N*-NO-derivative, decomp. when heated]. In AcOH the products obtained from (I), (II), (III), and NHPh·OH by HNO_2 contain 23, 63—67, 45%, and a trace, respectively (determined colorimetrically), of diazo-compound. Addition of Ac_2O prior to treatment of (I), (III), and NHPh·OH increases these amounts to 48, 63, and 10%, respectively. Use of this reaction to determine (I) in body fluids is liable to error owing to interference by other labile compounds. R. S. C.

***N*^{4}-Benzoyl-*N*^{1}-acetylsulphanilamide.** C. P. Lo and L. J. Y. Chu (*J. Amer. Chem. Soc.*, 1944, **66**, 660).—N^4-*Benzoyl*-N^1-*acetylsulphanilamide*, m.p. 262—263°, is obtained from the *N*^{4}-Bz derivative, m.p. 285—286° (lit. 280°), by Ac_2O–C_5H_5N at 100° and from the *N*^{1}-Ac derivative by BzCl–C_5H_5N at 100°. The *N*^{1}*N*^{4}-Bz_2 derivative, m.p. 260° (decomp.) (cf. lit.), is also prepared. R. S. C.

Substituted phenols.—See B., 1944, II, 222.

Reaction of phenols with *tert.*-butyl chloride. S. C. Burket and R. Q. Brewster (*Trans. Kansas Acad. Sci.*, 1943, **46**, 133—135).—Bu$^\gamma$Cl and various *o-* and *p*-C_6H_4R·OH either do not react (in presence of C_5H_5N and, occasionally, $CaCO_3$) or give CMe_2:CH_2 and unchanged phenol (with NaOEt or $CaCO_3$). 5 : 2 : 1-C_6H_3MeCl·OH, *p*-CMe_2Et·C_6H_4·OH, and *p*-C_6H_4Bu$^\gamma$·OH (using $CaCO_3$) give their *Bu$^\gamma$ ethers*, b.p. 265—270°/740 mm., 270—275°/740 mm., and 255—260°/740 mm., respectively. M. H. M. A.

Phenylcarbamyl derivatives of alkylated phenols. M.p. and *X*-ray powder diffraction data. J. B. McKinley, J. E. Nickels, and S. S. Sidhu (*Ind. Eng. Chem.* [*Anal.*], 1944, **16**, 304—308).—*Phenylurethanes* of the following phenols are prepared: *p*-chloro-, m.p. 148·5°, *p*-nitro-, m.p. 156°, 4-chloro-2-*tert.*-butyl-, m.p. 133°, *p-tert.*-butyl-, m.p. 148·5°, 4-methyl-2-β-methylallyl-, m.p. 98·5°, *p-tert.*-amyl-, m.p. 108°, 2-methyl-4(or 6)-*tert.*-butyl-, m.p. 139·5°, 2-methyl-6(or 4)-*tert.*-butyl-, m.p. 189°, 3-methyl-4(or 6)-*tert.*-butyl-, m.p. 133°, 4-methyl-2-*tert.*-butyl-, m.p. 155°, *p*-phenyl-, m.p. 167·5°, *o-*, m.p. 111·5°, and *p-*, m.p. 145·5°, *-cyclo*hexyl-, 4-methyl-2-*tert.*-amyl-, m.p. 124°, 3-ethyl-4(or 6)-*tert.*-butyl-, m.p. 156°, 4-ethyl-2-*tert.*-butyl-, m.p. 134°, 2 : 3-dimethyl-4(or 6)-*tert.*-butyl-, m.p. 216°, 2 : 4-dimethyl-6-*tert.*-butyl-, m.p. 173°, 2 : 5-dimethyl-4-*tert.*-butyl-, m.p. 144°, 2 : 6-dimethyl-4-*tert.*-butyl-, m.p. 160°, 3 : 4-dimethyl-6-*tert.*-butyl-, m.p. 142°, 3 : 5-dimethyl-2 : 6-diethyl-, m.p. 226°, 2-methyl-3 : 5-di*iso*propyl-, m.p. 198·5°, 4-methyl-3 : 5-di*iso*propyl-, m.p. 256°, 2-methyl-4 : 6-di*tert.*-butyl-, m.p. 163·5°, 3-methyl-4 : 6-di*tert.*-butyl-, m.p. 171·5°, 4-*cyclo*hexyl-2-*tert.*-butyl-, m.p. 170°, 3-ethyl-4 : 6-di*tert.*-butyl-, m.p. 182·5°, 2 : 3-dimethyl-4 : 6-di*tert.*-butyl-phenol, m.p. 216°. *X*-Ray diffraction data (interplanar spacing) are presented for all the above, and also for the phenylurethanes of PhOH, PhSH, *o-*, *m-*, and *p*-cresol, *o-*, *m-*, and *p*-ethyl-, 2 : 3-, 2 : 4-, 2 : 5-, 3 : 4-, and 3 : 5-dimethyl-, and 2 : 4 : 6-trimethylphenol. J. D. R.

***p*-Bromoaniline salts of monoaryl sulphates.** D. H. Laughland and L. Young (*J. Amer. Chem. Soc.*, 1944, **66**, 657—658).—$KArSO_4$ with *p*-C_6H_4Br·NH_3,HCl in H_2O give p-C_6H_4Br·NH_2 *Ph*, o-*anisyl*, p-C_6H_4Br, p-*tolyl*, and α-$C_{10}H_7$ *sulphate*, which are unstable and have ill-defined m.p. R. S. C.

Dialkylstilbœstrols.—See B., 1944, III, 142.

Synthesis of two dihydroxyterphenyls. C. C. Price and G. P. Mueller (*J. Amer. Chem. Soc.*, 1944, **66**, 632—634).—Dropping *o*-C_6H_4(C_6H_4·N_2Cl-*p*)$_2$ in H_2O into boiling H_2O–steam gives 4 : 4″-*dihydroxy*-o-*terphenyl* (98%), m.p. 230·2—231·2° (corr.) [*diacetate*, m.p. 186—186·4° (corr.); *Me$_2$ ether*, m.p. 104·8—106·4° (corr.)]. *p*-C_6H_4(C_6H_4·NO_2-*p*)$_2$ with H_2–Raney Ni in C_6H_6 at 100°/2000 lb. gives the $(NH_2)_2$-compound, m.p. 240—244° [dihydrochloride, darkens 315°, m.p. 355—370° (decomp.)], whence 4 : 4″-*dihydroxy*-p-*terphenyl* (I), m.p. 375° [*diacetate*, m.p. 244·3—245·3° (corr.); *Me$_2$ ether* (II), m.p. 273—275°], is obtained as above but in very poor yield. *p*-OMe·C_6H_4·MgBr (III) and 1 : 2-dibromo*cyclo*hexane in Et_2O and later boiling Bu_2O give (II), and 4 : 4″-*dimethoxydiphenyl* (IV), m.p. 174·5—175·6°. Hydrolysis of (II) to (I) by KOH–EtOH at 200° and then oxidation by $KMnO_4$–NaOH gives

p-$C_6H_4(CO_2H)_2$ (proof of structure). (III) and (IV) in Bu_2O and then at 140° give a small amount of (II) and homologues.
R. S. C.

Selective hydrogenation of eugenol and *iso*eugenol in presence of Raney nickel. B. Gauthier (*Compt. rend.*, 1943, **217**, 28—30).—Eugenol (I) and H_2–Raney Ni at room temp. yield *dihydroeugenol* (II), b.p. 133—135°/19 mm. (*formate*, b.p. 140°/12 mm.; *acetate*, b.p. 149—150°/14 mm.; *propionate*, b.p. 154—155°/12 mm.; *iso-butyrate*, b.p. 158°/15 mm.; *butyrate*, b.p. 164°/13 mm.; *isovalerate*, b.p. 170°/13 mm.; p-*nitrobenzoate*, m.p. 76°; *cinnamate*, m.p. 88°; *phenylurethane*, m.p. 122°; *diphenylylurethane*, m.p. 104—105°); at 60—65°, hydrogenation yields (II) and a little octahydroeugenol. *iso*Eugenol is hydrogenated (as above) only slowly at 20°. EtOH accelerates hydrogenation in both cases [(I) > (II)].
A. T. P.

Condensation of vanillin substitution products with nitromethane. L. C. Raiford and D. E. Fox (*J. Org. Chem.*, 1944, **9**, 170—174).—β-Nitrostyrenes are best obtained by gently boiling a solution of vanillin or its substitution products and $MeNO_2$ in AcOH containing NH_4OAc, less frequently by keeping a solution of these reactants in abs. EtOH at room temp. for several days. *β-Nitro-3:4-dimethoxystyrene*, m.p. 140—141°, and the 2-, m.p. 134—135°, 5-, m.p. 190—191°, and 6-*Br*-, m.p. 168—169°, 5:6-Br_2-, m.p. 166—167°, 2-, m.p. 188—189°, and 5-NO_2-, m.p. 183—184°, and 5-*bromo-2-nitro*-, m.p. 169—170°, -derivatives of β-nitro-4-hydroxy-3-methoxystyrene are described. Treatment of these compounds with Br saturates the side-chain and introduces Br at $C_{(5)}$ if OH is attached to $C_{(4)}$, thus giving *αβ-dibromo-β-nitro-α-5-bromo-4-hydroxy-3-methoxyphenylethane* (I), m.p. 127°, -*α-5*:6-*dibromo-4-hydroxy-3-methoxyphenylethane* (II), m.p. 126—128° after softening, and -*α-3:4-dimethoxyphenylethane* (III), m.p. 113—114° (+0·5CS_2) (lost at ~65°/1 hr.). (I) is transformed by repeated crystallisation from EtOH or by boiling EtOH containing NaOAc into *β*:5-*dibromo-β-nitro-4-hydroxy-3-methoxystyrene*, m.p. 166—167°, whilst (II) under similar conditions gives *β*:5:6-*tribromo-β-nitro-4-hydroxy-3-methoxystyrene*, m.p. 175—176°. At room temp. NaOAc in EtOH transforms (III) into *β-bromo-β-nitro-3:4-dimethoxystyrene*, m.p. 119—120°. Oxidation of the condensation products or their Br adducts with $KMnO_4$ causes loss of Br from the side-chain and gives the related aldehyde. When veratraldehyde is used as initial material, oxidation of the condensation product gives the related acid, thus emphasising the retarding effect of *p*-OH.
H. W.

Condensation of *cyclo*hexene oxide, 1:2-dichloro*cyclo*hexane, and γδ-dichlorohexane with anisole. C. C. Price and G. P. Mueller (*J. Amer. Chem. Soc.*, 1944, **66**, 628—631).—Passing BF_3 into *cyclo*hexene oxide (I) and PhOH at 40—70° gives *trans*-1:2-dihydroxy-*cyclo*hexane (II) and a little *p-cyclo*hexylphenol (3:5-*dinitrobenzoate*, m.p. 164—166°). Passing BF_3 into (I) and PhOMe at 50° gives *p-cyclo*hexylanisole (III) (8%), 1:3-*di*-p-*anisyl*cyclo*hexane* (IV), *form*, b.p. 160—165°/1 mm., and m-*di*-p-*anisylbenzene* [4:4″-*dimethoxy*-m-*terphenyl*] (V), m.p. 197—198° (corr.), also obtained in poorer yield from (II). Similar products are obtained from 1:2-dichloro*cyclo*hexane and PhOMe by $AlCl_3$ at 5°, but an *isomeride* (VI), m.p. 102·8—104°, of (IV) is also obtained. Formation of (III), (IV), and (V) probably results by disproportionation of 3-*p*-anisyl-Δ¹-*cyclo*hexene. 10% Pd–C at 300° converts (IV) or (VI) into (V). KOH–EtOH at 200° converts (VI) into 1:3-*di*-p-*hydroxyphenyl*cyclo*hexane* (VII) (97%), m.p. 229—232° (*diacetate*, m.p. 74·5—75·5°), but (IV) gives an oil. With KOH–EtOH at 200° or HI–AcOH, (V) gives 4:4″-*dihydroxy*-m-*terphenyl* (VIII), m.p. 182—183° (*diacetate*, m.p. 130·1—131·5°), but KOH–EtOH occasionally yields a *substance*, $C_{20}H_{36}O_2$, +0·5EtOH, m.p. 66—67·5°. $KMnO_4$–NaOH oxidises (VIII) to *m*-$C_6H_4(CO_2H)_2$. Pd–C and a trace of Zn dust at 250° convert (VII) into *m*-$C_6H_4Ph_2$. $(CHEtCl)_2$ with PhOMe and $AlCl_3$ in light petroleum at the b.p. and then Me_2SO_4–20% aq. NaOH gives 1% of hexœstrol Me_2 ether, m.p. 142—143° (corr.). (VII) and (VIII) have no œstrogenic and (VII) has no androgenic activity.
R. S. C.

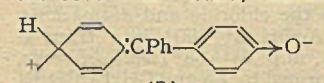
Absorption spectra of 1:2-benzenthracene and some methoxy-derivatives.—See A., 1944, I, 164.

Syntheses of compounds related to vitamin-*K*. II. 4′-Hydroxy-3′-alkylnaphthalene-1′-azobenzene-4-sulphonamides. E. J. H. Chu, Z. I. Shen, T. L. Chien, and T. S. Tuan (*J. Amer. Chem. Soc.*, 1944, **66**, 653).—α-$C_{10}H_7$·O·COR with $ZnCl_2$ or $SnCl_4$ at 140—150° gives good yields of 1:2-OH·$C_{10}H_6$·COR (formed also in minor amounts by $AlCl_3$). 2:1-$C_{10}H_6$Alk·OH and *p*-NH_2·SO_2·C_6H_4·N_2X in aq. AcOH give 4′-*hydroxy*-3′-*ethyl*- (73%), m.p. 249°, -n-*propyl*- (69%), m.p. 251°, -n- (66%), m.p. 280°, and -*iso*-butyl-, a gum, -n-*amyl*- (56%), m.p. 260°, and -*β-phenylethyl*- (51%), m.p. 261°, -*naphthalene*-1′-*azobenzene*-4-*sulphonamide*, which have no inhibitory effect on growth of *B. coli*, *Staph. aureus*, or *Strept. pyogenes*. 2:1-Ph·$[CH_2]_2$·$C_{10}H_6$·OH has m.p. 77—78° (decomp.) and gives a *picrate*, m.p. 179—180° (decomp.). 1:2-OH·$C_{10}H_6$·COR (R = Pr^β and Bu^α; not Me) are obtained from the 1:4-isomerides by boiling 35% NaOH.
R. S. C.

Aralkyl iodides and alcohols.—See B., 1944, II, 221.

Rearrangement of β-amino-alcohols with heat and alkali. B. K. Campbell and K. N. Campbell (*J. Org. Chem.*, 1944, **9**, 178—183).—Three aryl-substituted β-NH_2-alcohols rearrange to ketimines under the influence of heat and CaO; the change is shown to occur probably through the corresponding ethyleneimines. β-Amino-αα-diphenylpropan-α-ol is converted by CaO under N_2 at 270° into CPh_2:NEt (I), b.p. 154—159°/10 mm., m.p. 58—59°; at 130—230° the amine is scarcely affected. (I) is readily hydrolysed by 6N-HCl at room temp. to $COPh_2$ and NH_2Et, and is reduced by Na and abs. EtOH to $CHPh_2$·NHEt (II), b.p. 142°/8 mm. (I) is obtained by passing dry NH_2Et over CPh_2:NPh and a little NH_2Ph,HBr at 230°, and (II) from MgPhBr and CHPh:NEt. 2:2-Diphenyl-3-methylethyleneimine is transformed into (I) in presence of CaO at 250—260° or in its absence at 175—205°. β-Amino-α-phenyl-α-*p*-tolylethanol and CaO at 260° afford *Ph* p-*tolyl ketmethylimine*, b.p. 165—169°/13 mm., also obtained from NPh:CPh·C_6H_4Me-*p*, NH_2Ph,HBr, and dry NH_2Me at 200—210°; it is readily hydrolysed to COPh·C_6H_4Me-*p* and NH_2Me. It is reduced by Na and abs. EtOH to N:p-*dimethylbenzhydrylamine*, b.p. 169—172°/16 mm. [hydrochloride, m.p. 186—187° (lit. 199—201°); α-*naphthylcarbamyl* derivative, m.p. 171·5—172·5°], also obtained from CHPh:NMe and *p*-C_6H_4Me·MgBr. NH_2·CHPh·CPh_2·OH is partly rearranged by CaO at 260° to CPh_2:N·CH_2Ph, hydrolysed to $COPh_2$ and CH_2Ph·NH_2.
H. W.

Quinoidation of triaryl compounds: (A) hydroxyphenyldiphenylyl-carbinols, (B) hydroxydiphenylyldiarylmethyl cations. L. C. Anderson and W. A. Fisher (*J. Amer. Chem. Soc.*, 1944, **66**, 589—593, 594—597).—(A) Introduction of 1 or 2 *p*-C_6H_4Ph into *p*-OH·C_6H_4·CAr_2·OH (*A*) causes a high and broad absorption band at ~3800 mm.$^{-1}$, similar to that of Ph_2 and due to C_6H_4Ph; this band covers the benzenoid absorption of (*A*) (Ar = Ph). Diphenylquinomethanes do not give the 3800 mm.$^{-1}$ band, wherefore it is concluded that the C_6H_4Ph structure is different and that absorption of fuchsones in Et_2O is due largely to a structure (*B*).


(*B*.)

p-C_6H_4Ph·$CPhCl_2$ (I) and PhOH at room temp. give *p*-OH·C_6H_4·CPh(C_6H_4Ph-*p*)·OH (II) (*acetate*, m.p. 134—136°) contaminated with *p*-C_6H_4Ph·COPh and $(p$-OH·$C_6H_4)_2$CPh·C_6H_4Ph-*p*. At 130—140°/vac. (II) is dehydrated to *phenyl*-p-*diphenylquinomethane* (III), m.p. 166—167°, whence warm 70% AcOH yields the quinonoid form (IV), m.p. 139—140°, of (II). Passing CO_2 into a solution of (III) or (IV) in 2·5% NaOH gives the benzenoid form, m.p. 155—157°, of (II). $AlCl_3$ in boiling C_6H_6 converts the Me ether of (II) into (IV), m.p. 134—140°. PhOH and (I) in boiling dry C_6H_6 (1 hr.) give *diphenoxyphenyl*-p-*diphenylylmethane*, m.p. 149—150°, but PhOH and (I) alone at 100° (5 days) give 4:4′-*dihydroxytriphenyl*-p-*diphenylylmethane* (55%), softens 157°, m.p. 163—165° (*diacetate*, m.p. 168—170°, clear at 187°). By similar reactions $(p$-$C_6H_4Ph)_2CCl_2$ [prep. from $CO(C_6H_4Ph$-$p)_2$ by PCl_5] gives *p-hydroxyphenylbisdiphenylylcarbinol*, quinonoid, m.p. 106—107·5°, and benzenoid forms, m.p. 124—126° (*acetate*, m.p. 149—152°), *bis*-p-*diphenylylquinomethane*, m.p. 140—155° (slow heating) or 159—161·5° (bath preheated at 150°), *diphenoxybis*-p-*diphenylylmethane*, m.p. 118—120°, and di-*p*-hydroxyphenylbis-*p*-diphenylylmethane, m.p. 253—255·5° (*diacetate*, m.p. 256—258°).

(B) Absorption spectra are recorded for *p-p′*-OR·C_6H_4·C_6H_4·$CArAr′$·OH (*C*) (R = H or OMe; Ar and Ar′ = Ph or *p*-C_6H_4Ph) in AcOH–H_2SO_4. Comparison with the spectra of *p*-C_6H_4Ph·CPh_2·OH and *p*-C_6H_4Ph·CPh(C_6H_4·OMe-*p*)·OH (V) indicates that C_6H_4Ph is quinonoid when R in (*C*) is Me. (*C*) (Ar = Ar′ = Ph; R = H) does not exist in a quinonoid form and gives no diphenyldiphenylylquinomethane. (V) is prepared from *p*-OMe·C_6H_4·MgBr (VI) and *p*-C_6H_4Ph·COPh and from the phenol by Me_2SO_4. $CO(C_6H_4Ph$-$p)_2$ and (VI) in boiling Et_2O–C_6H_6 give *p-anisylbis*-p-*diphenylylcarbinol*, m.p. 146°. *p*-OH·C_6H_4·C_6H_4·COPh-*p* and MgPhBr in boiling C_6H_6–Et_2O give *diphenyl-4′-hydroxy-p-diphenylylcarbinol*, m.p. 224—227° (*acetate*, m.p. 154—156·5°), which is also obtained by $AlCl_3$–C_6H_6 from its *Me ether*, m.p. 108—109° (prep. from *p*-OMe·C_6H_4·C_6H_4·COPh-*p* by MgPhBr). *p*-C_6H_4Ph·COCl (prep. from the acid by $SOCl_2$), *p*-C_6H_4Ph·OMe, and $AlCl_3$ in $(CHCl_2)_2$ at −10° to room temp. give p-C_6H_4Ph *4′-methoxy-p-diphenylyl ketone* (VII) (50—65%), m.p. 246—248°, with 10—25% of p-C_6H_4Ph *6-methoxy-3-diphenylyl ketone*, m.p. 127—130°. MgPhBr and (VII) in boiling Et_2O give *phenyl*-p-*diphenylyl-4′-methoxy*-p-*diphenylylcarbinol*, m.p. 141—143°. *p*-OMe·C_6H_4·C_6H_4·CO_2H-*p′* (prep. from the *p′*-COMe compound by $KMnO_4$ or NaOI) gives, best in a Soxhlet apparatus over H_2SO_4–MeOH, its Me ester, which with an excess of *p*-C_6H_4Ph·MgBr gives *bis*-p-*diphenylyl-4′-methoxy*-p-*diphenylylcarbinol*, m.p. 130—132°.
R. S. C.

Reductions with nickel–aluminium alloy and aqueous alkali. IV. Carbon–carbon double linking. E. Schwenk, D. Papa, B. Whitman, and H. F. Ginsberg (*J. Org. Chem.*, 1944, **9**, 175—177).—Examples of the reduction of conjugated, isolated, and cyclic double linkings using Ni–Al alloy and aq. alkali are afforded by CHPh:CH·CO_2H, maleic, crotonic, oleic, and sorbic acid, *p*-OH·C_6H_4·CH:CHPh, *p*-OH·C_6H_4·CH:CPh·CO_2H, *p*-OMe·C_6H_4·CH:CPh·CO_2H, CHPh:C(C_6H_4·OMe)·CO_2H, CHPh:C(C_6H_4·OH)·CO_2H, *cyclo*hexyl-

ideneacetic (**I**), α-Δ¹-*cyclo*hexenyl- and *p*-hydroxy-Δ¹-*cyclo*hexenylcinnamic acid. Δ⁵-3(β)-Hydroxyætiocholenic acid is recovered unchanged and the reduction of Δ¹-*cyclo*hexenylacetic acid is so incomplete as to suggest a preliminary partial isomerisation to (**I**). The *cyclo*pentene ring of chaulmoogric acid is quantitatively reduced. Stilbœstrol gives the hexœstrols, m.p. 184—185° and 126—128°, in 30 and 50% yield respectively. The following appear new: α-*phenyl*-β-p-*anisylpropionic acid*, m.p. 119—120°; β-*phenyl*-α-p-*anisylpropionic acid*, m.p. 108—109°; β-*phenyl*-α-p-*hydroxyphenylpropionic acid*, m.p. 158—159°; α-p-*hydroxyphenylcinnamic acid*, m.p. 221—222°; α-cyclo*hexyl*-β-*phenyl*-, m.p. 70—71°, and -β-p-*hydroxyphenyl*-, m.p. 180—181°, -*propionic acid*. α-*p*-Anisylcinnamic acid has m.p. 152—153° (lit. 132—133°). H. W.

Steroids and sex hormones. XCVIII. Preparation of β-*trans*-4-hydroxy*cyclo*hexyl-Δ^αβ^-butenolide. E. Hardegger, P. A. Plattner, and F. Blank (*Helv. Chim. Acta*, 1944, **27**, 793—800).—$CNa_2(CO_2Et)_2$ and $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ give *Et*$_4$ *pentane-αγγε-tetracarboxylate* (**I**), b.p. 157—160°/high vac., cyclised by Na to *Et*$_3$ cyclo*hexanone*-2 : 4 : 4-*tricarboxylate* (**II**), b.p. 187—189°/water pump vac., with some *Et* cyclo*hexanone*-4-*carboxylate*, b.p. 137°/water pump vac. (**II**) in C_6H_6 is hydrolysed by aq. NaOH at room temp. to cyclo*hexanone*-4 : 4-*dicarboxylic acid*, m.p. 147·5—149·5°. (**I**) is converted by successive treatment with Na, EtOH, and C_6H_6 at 100° followed by hydrolysis into cyclo*hexanone*-4-*carboxylic acid* (**III**), m.p. 67—68°, which is reduced (H_2, Raney Ni, N-NaOH) to cis-4-*hydroxyhexahydrobenzoic acid*, m.p. 150·5—151° (*Me* ester), converted by boiling Ac_2O into the lactone, m.p. 128° (lit. 109—110°). Na–Hg, or (less well) H_2–PtO_2–AcOH, reduces (**III**) to *trans*-4-hydroxyhexahydrobenzoic acid, m.p. 119—120° (*Me* ester and its *benzoate*, m.p. 92—94°). This is converted by boiling AcCl–Ac_2O–AcOH into trans-4-*acetoxyhexahydrobenzoic acid*, m.p. 139—140° (*Me* ester, m.p. 45·5—46·5°), and thence ($SOCl_2$) into the chloride and *diazoketone*, decomp. 86—87°, which passes in AcOH at 100° into trans-4-*acetoxy*cyclo*hexyl OAc·CH*$_2$ *ketone* (**IV**), m.p. 67—68° (*semicarbazone*, m.p. 167—168°). (**IV**) is readily transformed by Zn and $CH_2Br{\cdot}CO_2Et$ followed by acetylation into β-*acetoxy*-β-trans-4-*acetoxy*cyclo*hexylbutyrolactone*, m.p. 142—142·5°, which passes at 225—240°/water pump vac. into β-trans-4-*acetoxy*cyclo*hexyl*-Δ^αβ^-*butenolide*, m.p. 88—89°, giving a positive Legal test. β-trans-4-*Hydroxy*cyclo*hexyl*-Δ^αβ^-*butenolide* has m.p. 95—95·5°. H. W.

Synthetic anthelmintics. IX. γ-6-Methoxy-*m*-tolyl- and γ-*p*-anisyl-α-alkylbutyrolactones. S. V. Mehta, J. J. Trivedi, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1944, **12**, **A**, Part 5, 33—35).—The appropriate alkylsuccinic anhydride and *o*-$C_6H_4Me{\cdot}OMe$ (Friedel–Crafts) give γ-*keto*-γ-6-*methoxy*-m-*tolyl*-α-*ethyl*-, m.p. 99° (*semicarbazone*, m.p. 179°), -α-n-*propyl*-, m.p. 96—97° (*semicarbazone*, m.p. 159°), and -α-n-*amyl*-*butyric acid*, m.p. 40—45° (purified through its *Et* ester, b.p. 260—265°/60 mm.), converted (method: A., 1942, II, 257) into γ-6-*methoxy*-m-*tolyl*-α-*ethyl*-, m.p. 63—64°, -α-n-*propyl*-, m.p. 93°, and -α-n-*amyl*-*butyrolactone*, m.p. 38—39°, b.p. 258°/28 mm., respectively. Similarly prepared from *p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CHAlk{\cdot}CO_2H$ (A., 1944, II, 78) are γ-p-*anisyl*-α-*ethyl*-, m.p. 91—92°, -α-n-*propyl*-, m.p. 98—99°, -α-n-*amyl*-, m.p. 92°, -α-n-*hexyl*-, m.p. 98°, -α-n-*tetradecyl*-, m.p. 79—80°, and -α-n-*hexadecyl*-*butyrolactone*, m.p. 95—96°. A. T. P.

Action of diazobenzene on alkylacetoacetic esters as a method of preparing phenylhydrazones of α-keto- and α-amino-acids. VIII. Synthesis of tyrosine. V. V. Feofilaktov, V. N. Zaitzeva, and K. I. Sirotkina (*J. Gen. Chem. Russ.*, 1943, **13**, 363—372).—Methods of synthesis of tyrosine are reviewed and a new procedure is described. To a stirred mixture of $CH_2Ac{\cdot}CO_2Et$ (10% excess) and NaOEt in EtOH at room temp., *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2Cl$ (prep. from PhOMe, CH_2O, and HCl in presence of $ZnCl_2$) was added dropwise, and the mixture then heated at 100° (bath) for 3 hr.; the resulting *Et* α-p-*methoxybenzylacetoacetate* (76·2%), b.p. 160—161°/3 mm., was added gradually with vigorous stirring to an equiv. of aq. $PhN_2{\cdot}OK$ and, after an additional 4 hr. stirring, the product extracted with Et_2O. Hydrolysis (aq. EtOH–KOH) of the Et_2O-sol. ester gives p-*anisylpyruvic acid phenylhydrazone* (**I**) (75·3%), dimorphic from C_6H_6–ligroin (b.p. 90—94°) (1 : 1), less sol. α-form, platelets, m.p. 158—159°, and predominating β-form, needles, m.p. 150°. (**I**) (crude or once crystallised) was reduced with Zn dust and HCl–EtOH, the EtOH evaporated in a vac., the residue ground with Ag_2CO_3, and then extracted with boiling H_2O. The aq. extracts, freed from metals with H_2S, were evaporated and crystallised from H_2O to give 55—58% of *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (**II**), m.p. 262° (sealed tube). (**II**) with boiling HI (b.p. 126°) for 5 hr. gives tyrosine (95·6%). R. C. P.

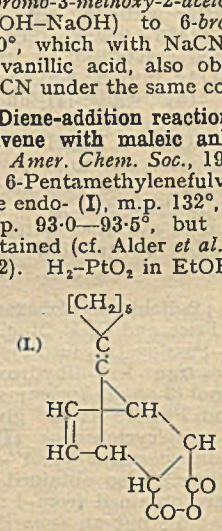
Raman spectra of salicylic acid and aspirin.—See A., 1944, I, 165.

Nitro- and nitroamino-derivatives of *o*-chlorobenzoic acid. H. Goldstein and G. Preitner (*Helv. Chim. Acta*, 1944, **27**, 612—615; cf. A., 1938, II, 13, 98).—6 : 2 : 5 : 1-$NO_2{\cdot}C_6H_2Cl(NH_2){\cdot}CO_2H$ in EtOH–conc. H_2SO_4 is converted by *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$ at −10°, followed by a little Zn dust at the b.p., into 6 : 2 : 1-$NO_2{\cdot}C_6H_2Cl{\cdot}CO_2H$ (**I**), also obtained by oxidising 1 : 2 : 6-$C_6H_3MeCl{\cdot}NO_2$; lower yields of very impure product are obtained by diazotisation in H_2O and adding EtOH. The chloride ($SOCl_2$) of (**I**) yields the Me, m.p. 94—95 (lit. 80—82°), and *Et* ester, m.p. 49—50°, the *amide*, m.p. 186—187°, and *anilide*, m.p. 176—177°. 1 : 2 : 5-$C_6H_3MeCl{\cdot}NHAc$ and HNO_3 (*d* 1·4 mixed with *d* 1·52) at ⩾15° give a mixture of mainly 2-chloro-4-nitro- (**II**), m.p. 113°, and a little 2-*chloro*-6-*nitro*-5-*acetamidotoluene* (**III**), m.p. 152—153°; the proportion of (**III**) is increased by using HNO_3 (*d* 1·52) in AcOH at 5—10°. (**II**) is oxidised (aq. $KMnO_4 + MgSO_4$) to 2-*chloro*-4-*nitro*-5-*acetamidobenzoic acid*, m.p. 214°, hydrolysed by boiling dil. HCl to the 5-NH_2-*acid*, m.p. 239—240° (decomp.). Similarly (**III**) gives 6 : 2 : 5 : 1-$NO_2{\cdot}C_6H_2Cl(NHAc){\cdot}CO_2H$. M.p. are corr. H. W.

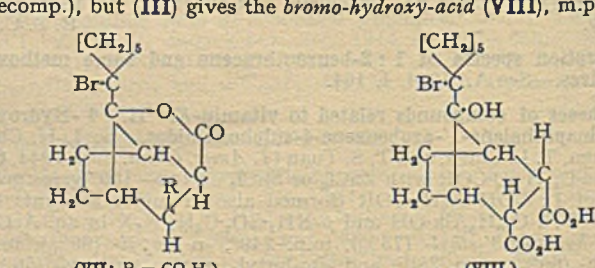
***N*-Substituted piperonylamides.** S. I. Gertler and W. F. Barthel (*J. Amer. Chem. Soc.*, 1944, **66**, 659—660).—*Piperonyl*-*ethyl*-, m.p. 87—88°, -n-*propyl*-, m.p. 86—87°, and -n-*amyl*-*amide*, m.p. 104—105°, -m-*chloro*-, m.p. 110·5—112·5°, -o-, m.p. 109·5—110°, -m-, m.p. 116—117°, and -p-*bromo*-*anilide*, m.p. 222—222·5°, are prepared. M.p. are corr. R. S. C.

Attempted syntheses of hemipinic acid from guaiacol. C. Weizmann and L. Haskelberg (*J. Org. Chem.*, 1944, **9**, 121—124).—2 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2H$, m.p. 200°, is obtained in good yield from dry *o*-$ONa{\cdot}C_6H_4{\cdot}OMe$ and CO_2 at 200° whereas at 230° it is accompanied by 2 : 3 : 1 : 4-$(OH)_2C_6H_2(CO_2H)_2$, m.p. 308°. With Br in AcOH or $CHCl_3$ at room temp. it affords 5-*bromo*-2-*hydroxy*-3-*methoxybenzoic acid*, m.p. 211° [*Me* ester, m.p. 122° (*acetate*, m.p. 95°), obtained similarly from 2 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO_2Me$]. Bromination of 3 : 2 : 1-$OMe{\cdot}C_6H_3(OAc){\cdot}CO_2Me$ in AcOH containing anhyd. NaOAc, in $CHCl_3$, or without solvent leads to *Me* 6-*bromo*-3-*methoxy*-2-*acetoxybenzoate*, m.p. 124°, hydrolysed (aq. EtOH–NaOH) to 6-*bromo*-2-*hydroxy*-3-*methoxybenzoic acid*, m.p. 150°, which with NaCN and CuCN in 50% EtOH at 180° gives *iso*vanillic acid, also obtained from 5-bromoguaiacol, NaCN, and CuCN under the same conditions. H. W.

Diene-addition reactions. II. Reaction of 6 : 6-pentamethylenefulvene with maleic anhydride. R. B. Woodward and H. Baer (*J. Amer. Chem. Soc.*, 1944, **66**, 645—649; cf. A., 1943, II, 119).—6 : 6-Pentamethylenefulvene and $(CH{\cdot}CO)_2O$ in C_6H_6 at 5° give the endo- (**I**), m.p. 132°, and some of the exo-*adduct* (**II**), $C_{15}H_{16}O_3$, m.p. 93·0—93·5°, but at higher temp. more and more (**II**) is obtained (cf. Alder *et al.*, A., 1937, II, 321; Kohler *et al.*, A., 1935, 852). H_2–PtO_2 in EtOH reduces the *cyclo*hexene CH:CH of (**I**) or



(**II**) to give the endo- (**III**), m.p. 146°, and exo-H_2-*adducts* (**IV**), m.p. 103—104°, respectively; resistance of the *cyclo*hexylidene C:C accords with the views of Linstead *et al.* (A., 1943, II, 62). Dissolving (**III**) or (**IV**) in MeOH and adding 10% aq. NaOH until alkaline to phenolphthalein gives the *Me H* endo-, m.p. 114° (Et H ester, m.p. 104·5—105°), or exo-H_2-ester, m.p. 118°, and thence the Me_2 endo- (**V**), a gum, and exo-H_2-ester (**VI**), m.p. 65°, respectively. (**II**) and EtOH similarly give the corresponding *Et H* ester, m.p. 137—137·5°. (**V**) and (**VI**) are both *cis*-esters, for both are isomerised by NaOMe–MeOH at the b.p. to the trans-Me_2 H_2-ester, m.p. 75°, whence HCl–AcOH yields the trans-*dicarboxylic acid*, m.p. 230—232° (decomp.). Hydrolysing (**IV**) by boiling AcOH–H_2O and then adding Br gives the *Br-lactone-acid* (**VII**), m.p. 146·5—147·5° (decomp.), but (**III**) gives the *bromo-hydroxy-acid* (**VIII**), m.p. 152—



(VII; R = CO_2H.) (VIII.)

153° (decomp.), this difference proving the stereochemical configurations. (**I**) dissociates in, *e.g.*, EtOAc or C_6H_6, slowly when cold and rapidly when heated, but (**II**) is stable, which accounts for the variation (above) in the ratio (**I**) : (**II**) produced. The modes of addition and the differences are discussed on electronic and energetic grounds. R. S. C.

9-Acylfluorenes and derived vinylamines. I. Von and E. C. Wagner (*J. Org. Chem.*, 1944, **9**, 155—169).—The formation of 9-

acylfluorenes by alkali-induced condensation of esters with the reactive CH_2 of fluorene (I) has been extended to the 9-Ac compound. Fluorene-9-aldehyde (II) is obtained by similar use of 1-formylpiperidine, showing the ability of the latter to function as an aquo-ammono-ester of HCO_2H. The attempted ester condensation (for the prep. of CHO-derivatives) gives tarry products when applied to *cyclo*pentadiene and indene whilst reaction does not occur with xanthene or acridan. The products from (I) and its 2 : 7-Br_2-derivative and NH_3 are shown to be enamines and di-9-fluorenylmethyleneamines. (II), b.p. 169—172°/2 mm. [prep. from (I), KOMe, and HCO_2Et or, less well, by use of Na, NaOMe, or CPh_3Na], polymerises when kept. 2 : 7-Dibromofluorene-9-aldehyde, m.p. 180—181° (corr.), is converted by BzCl and NaOH into the enol *benzoate*, m.p. 221° (corr.), and by NH_2Ph in EtOH into the *anil*, m.p. 226—227° (corr.). 9-*Acetylfluorene*, m.p. 74·5—75·5° (corr.), obtained from (I), KOMe, and EtOAc in anhyd. Et_2O, gives a somewhat unstable *phenylhydrazone*, m.p. 138—139° (corr.; decomp.), and an apparently stable *oxime*, m.p. 137° (corr.); it liquefies when kept in a desiccator at room temp. and then solidifies to the *dimeride*, m.p. 247—248° (corr.), which does not react with NHPh·NH_2. It does not condense with NH_2Ph or piperidine in dry C_6H_6 at 100°. Passage of dry NH_3 into a solution of (II) in dry C_6H_6 or Et_2O at 0° leads to 9-aminomethylenefluorene (III), m.p. 146—147° after softening, with a smaller proportion of di-9-fluorenylmethyleneamine (IV). (III) becomes discoloured when kept in a desiccator, immediately reduces $KMnO_4$, is indifferent to 10% NaOH at 100°, is immediately converted into (IV) by acid, and is monomeric in freezing C_6H_6. With dry HCl in Et_2O it yields the hydrochloride, chars without melting ~300°. (III) and Ac_2O in a vac. over NaOH and $CaCl_2$ afford 9-*acetamidomethylenefluorene*, m.p. 204·5—206° (corr.), which could not be cyclised to the *iso*quinoline derivative by P_2O_5 in PhMe. Ozonolysis of (III) in $CHCl_3$ and treatment of the ozonide with H_2O at 100° gives fluorenone (V) and HCO·NH_2 (identified by conversion by *o*-NH_2·C_6H_4·CO_2H into 3 : 4-dihydro-4-quinazolone, m.p. 212—213°). (III) is transformed by Br in $CHCl_3$ followed by H_2O into NH_4Br and 9-bromofluorene-9-aldehyde (VI). (IV) is obtained synthetically from (II) and (III) in C_6H_6. Ozonolysis of (IV) gives (V) and diformamide and brominolysis yields (VI). Not quite homogeneous 2 : 7-*dibromo*-9-*aminomethylenefluorene* (VII), m.p. 212° (Dennis bar), undergoes brominolysis to 2 : 7 : 9-*tribromofluorene*-9-*aldehyde* (VIII), m.p. 236—237° (corr.; decomp.), also obtained from the 2 : 7-Br_2-aldehyde. (VII) is converted by glacial AcOH at 100° or, readily, by dil. H_2SO_4 into *di*-2 : 7-*dibromo*-9-*fluorenylmethyleneamine*, m.p. >300°, converted by Br in $CHCl_3$ followed by hydrolysis into (VIII). 9-Acetylfluorene and NH_3 in dry Et_2O at 0° give 9-*α-aminoethylidenefluorene* or *α-methyl-*$\Delta^{9\alpha}$*-fluorenemethylamine* (IX), m.p. 124·5—126·5° (corr.; decomp.) after softening, which rapidly darkens and becomes oily in a desiccator at room temp. (IX) is hydrolysed by 4% H_2SO_4 at room temp. to a mixture of monomeric and dimeric acetylfluorene. The *Ac* derivative of (IX) has m.p. 180·5—181·5° (corr.).

H. W.

Structure of aldehydo-acids and their tautomeric transformations. M. M. Schemjakin (*J. Gen. Chem. Russ.*, 1943, **13**, 290—300).—The properties of aldehydo-acids (*A*) and their reactions are reviewed from the point of view of ionotropy. The conditions under which one or other tautomeric form of (*A*) reacts and the influence of structural and external factors are described. Evidence is adduced to support the view that isolated, cryst. (*A*) are OH-lactones. The following compounds were tested with freshly prepared fuchsin–SO_2 reagent: *o*-CHO·C_6H_4·CO_2H showed coloration in 5—10 sec. and max. intensity in 1—2 min.; opianic acid showed coloration in 5—10 sec. and max. in 2—3 min.; CHO·CBr:CBr·CO_2H showed coloration in ½—1 min. on undissolved solid but only after ½ hr. in solution and the intensity increased very slowly; CHO·CPh:CH·CO_2H showed coloration in 2—3 min. on undissolved solid and intensity again increased very slowly; nitro-opianic acid (I) showed no coloration in 24 hr. In MeOH solution, bromo-opianic acid forms the OH-lactone Me ether (*ψ*-Me ester) (low yield) at room temp. in 1½ months or at the b.p. in 4—5 hr.; CHO·CBr:CBr·CO_2H similarly forms the *ψ*-ester at room temp. in 1 month. (I) with excess of piperidine for 5 min. (water-bath), dilution with EtOH, and cooling to 0° for 1—2 hr. gives its *dipiperidide*, m.p. 160—161° (60—70%, including the less pure product recovered from the mother-liquor by evaporation at room temp.).

R. C. P.

Polyenes. I. Synthesis and absorption spectra of the ionylideneacetones and related compounds. W. G. Young, L. J. Andrews, and S. J. Cristol (*J. Amer. Chem. Soc.*, 1944, **66**, 520—524).—Absorption spectra in 95% EtOH (max. in brackets below) indicate that α- (I) and β-ionone (II) yield polyenes without isomerisation. (I) [227 (ε 12,850) and 296 mμ. (ε 1950)] and (II) [296 (ε 8600) and 222 mμ. (ε 7640)] with Zn–CH_2Br·CO_2Et give OH-esters, which distil unchanged (β-ester, b.p. 153·5—155·5°/2—3 mm.) (cf. Karrer *et al.*, A., 1932, 852) but with $KHSO_4$ at 150° give Et α-, b.p. 162·5°/5—7 mm. [272 (ε 14,700) and 236 mμ. (ε 11,800)], and β-ionylideneacetate, b.p. 162·3—164·5°/6 mm. [283 mμ. (ε 18,950)], hydrolysed by KOH–EtOH to the derived α- [267 mμ. (ε 17,650)] and β-acids (III), liquid [294 (ε 13,700) and 260 mμ. (ε 12,900)] and cryst. (m.p. 124°) form [283 mμ. (ε 17,700)] (cf. *loc. cit.*). With PCl_3 and then $CdMe_2$–Et_2O these give α- (IV), b.p. 135·5—138°/2·5 mm. [285 mμ. (ε 14,500)], and β-ionylideneacetone (V) [ζ-2 : 6 : 6-trimethyl-Δ^2-and-Δ^1-*cyclo*hexenyl-δ-methyl-$\Delta^{\gamma\epsilon}$-hexadien-β-one, respectively], b.p. 131—132°/2·5 mm. [285 mμ. (ε 11,600)]. Slowly distilling (I) and (II) with CN·CH_2·CO_2Me and a little NH_2Ac and NH_4OAc in AcOH gives *Me α-cyano*-δ-2 : 6 : 6-*trimethyl*-Δ^2-, b.p. 154·5—157·5°/1·5 mm. [292·5 mμ. (ε 16,100)], and -Δ^1-*cyclo*hexenyl-β-methyl-Δ^α-pentenoate, b.p. 165—168°/2 mm. [353 (ε 12,000) and 286 mμ. (ε 10,300)], respectively, hydrolysed to the derived α-, an oil [286 mμ. (ε 14,300)], and β-acid, m.p. 160—163° (decomp.) (lit. an oil) [332 (ε 12,500) and 275 mμ. (ε 8700)], respectively. Decarboxylation then yields δ-2 : 6 : 6-*trimethyl*-Δ^2-, b.p. 147·5—150°/3 mm. [262·5 mμ. (ε 18,900)], and -Δ^1-cyclo*hexenyl-β-methyl-*$\Delta^{\alpha\gamma}$*-pentadienonitrile*, b.p. 138—140°/3 mm. [300 (ε 12,500) and 256 mμ. (ε 14,500)] [hydrolysed to (III), m.p. 122—125°, by KOH–EtOH], also obtained from (I) and (II), respectively, by CN·CH_2·CO_2H. With MgMeI–Et_2O or LiMe, these give (IV) and (V), respectively. (IV) gives a *semicarbazone*, m.p. 162·5—164°, but (V) gives an oil with NH·CO·NH_2·NH_2 or NH_2OH, although it reacts with Girard's reagent *T*. The structures of (IV) and (V) are proved by ozonolysis to *iso*geronic and geronic acid, respectively. In presence of PtO_2 in EtOH, (IV) and (V) absorb 3 H_2. NaOCl converts (I) and (II) into α-, an oil [<212·5 mμ. (ε >10,100)], and β-cyclo*citrylideneacetic acid*, m.p. 106—108° [277 mμ. (ε 9240)] (absorbs 1·96 H_2). (V) similarly gives (III), m.p. 122—124°.

R. S. C.

Pinacols and pinacolone from *p*-methoxyacetophenone. C. C. Price and G. P. Mueller (*J. Amer. Chem. Soc.*, 1944, **66**, 634—636).—Electrolytic reduction of *p*-OMe·C_6H_4·COMe (I) in KOAc–EtOH–H_2O (in absence or presence of EtOAc) gives *βγ-dihydroxy-βγ-di-p-anisyl-n-butane* (90%), *forms*, m.p. (II) 122—123° and (III) 168—169°. (III) is also obtained by Al–Hg in moist Et_2O. $Pb(OAc)_4$–AcOH rapidly oxidises (II) to (I). A drop of H_2SO_4 in Ac_2O rearranges (II) or (III) to *αα-di-p-anisylethyl Me ketone* (IV) (63%), m.p. 69·7—71·5°, cleaved by KOH at 170—180° to (*p*-$OMe·C_6H_4)_2CHMe$, m.p. 70—72° (lit. 59·4°). The structure of (IV) is proved by conversion of its *oxime*, m.p. 192—194° (insol. in alkali), by PCl_5–Et_2O into $(p\text{-}OMe·C_6H_4)_2C{:}CH_2$, m.p. 141—143°.

R. S. C.

Lignin and related compounds. LXXIX. Synthesis and properties of γ-hydroxy-α-3 : 4-dimethoxyphenylpropan-β-one. H. E. Fisher, M. Kulka, and H. Hibbert. **LXXX. Ethanolysis of α-acetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one and its relation to lignin structure.** L. Mitchell and H. Hibbert. **LXXXI. Properties of α-bromo-α-4-acetoxy-3-methoxyphenylpropan-β-one and relation to lignin structure.** L. Mitchell, T. H. Evans, and H. Hibbert. **LXXXII. Synthesis and properties of αγ-diacetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one and γ-chloro-α-acetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one and their relation to lignin structure.** J. A. F. Gardner and H. Hibbert (*J. Amer. Chem. Soc.*, 1944, **66**, 598—601, 602—604, 604—607, 607—610; cf. A., 1944, II, 176).—LXXIX. The properties of γ-3 : 4-*dimethoxyphenylpropan-α-ol-β-one* (I) (which is synthesised) confirm the authors' views on lignin components. 3 : 4 : 1-$(OMe)_2C_6H_3$·CO_2H (prep. from the aldehyde by aq. $KMnO_4$ in 90% yield) gives ($SOCl_2$) the chloride, m.p. 70—71°, and thence (CH_2N_2) the CHN_2 ketone, m.p. 76—77° (lit. 75°), converted by Ag_2O–MeOH–CO_2 at 55—60° into *Me homoveratrate* (72%), b.p. 110—113°/3 mm. The derived acid with $SOCl_2$ and then CH_2N_2–C_6H_6 yields a CHN_2 ketone, which added (in EtOH) to H_2O at 70° gives (I), b.p. 150—160° (bath)/0·05 mm. (*semicarbazone*, m.p. 123—124°; known acetate, m.p. 55—56°). Boiling 5% H_2SO_4 in 24 hr. or 72% H_2SO_4 at room temp. in 2 hr. gives 19·5 and 62·5%, respectively, of polymer from (I). (I) is very sensitive to alkali; in 1% aq. NaOH at 100° (24 hr.) it gives 54% and in 3% aq. NaOH at room temp. gives 80%, but in 3% NaOH–EtOH–H_2O (1 : 1) gives only 17% of polymer. It is unchanged (75% recovered) by boiling 5% aq. KOAc–CO_2 (12 hr.), but in 2% HCl–EtOH–CO_2 (48 hr.) gives 3 : 4 : 1-$(OMe)_2C_6H_3$·CO·CHMe·OEt (28%) and -$(OMe)_2C_6H_3$·CH(OEt)·COMe (52%).

LXXX. Ethanolysis of *α-acetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one* (II) supports the authors' views on lignin structure. (II) is obtained (80%) from 3 : 4 : 1-OMe·C_6H_3(OAc)·CHBr·COMe by AgOAc in 1 : 1 aq. dioxan at room temp. and has m.p. 97—98°. Ethanolysis first removes the labile Ac and then causes rearrangement. Thus, 2% HCl–EtOH–CO_2 at the b.p. (48 hr.) gives 3 : 4 : 1-OMe·C_6H_3(OH)·CO·CHMe·OEt (54·6%), -OMe·C_6H_3(OH)·CH(OEt)·COMe (16·7%), -OMe·C_6H_3(OH)·CO·COMe (7·3%), and -OMe·C_6H_3(OH)·CH_2·COMe (1·3%), and polymers (10%).

LXXXI. Further evidence is provided by the properties of *α-bromo-α-4-acetoxy-3-methoxyphenylpropan-β-one* (III). *4-Acetoxy-3-methoxyphenylacetone* (prep. from the 4-OH-compound by Ac_2O–10% aq. NaOH at 0—10°), m.p. 47—48° (*semicarbazone*, m.p. 168—169°), with Br and a little Bz_2O_2 in $CHCl_3$ at <10° gives (III) (73%), m.p. 100—101° (*semicarbazone*, m.p. 180—181°), which with Ag_2SO_4 in 1 : 2 aq. dioxan–N_2 at room temp. gives 100% of AgBr, 35% of a polymer [? of 3 : 4 : 1-OMe·C_6H_3(OAc)·CH(OH)·COMe], and 60% of a mixture, whence removal of diketone as Ni glyoxime

salt and subsequent hydrolysis yields 3 : 4 : 1-$OMeC_6H_3(OH)\cdot CO\cdot COMe$ (**IV**) (44%) and -$OMe\cdot C_6H_3(OH)\cdot CH_2\cdot COMe$ (**V**) (27%). (**IV**) and (**V**) are probably formed by way of $(CHArAc)_2CO$ and, possibly, $O<\begin{matrix}CHAr\cdot CMe(OH)\\ CAr=\!=\!=CMe\end{matrix}>O$. 3 : 4 : 1-$OMe\cdot C_6H_3(OH)\cdot CO\cdot CHMe\cdot OH$ and a little (**IV**) are also obtained from (**II**) by boiling $BaCO_3$–H_2O–N_2, and from (**III**) by boiling 5% aq. KOAc.

LXXXII. Reactions described below indicate that compounds, $OH\cdot CHAr\cdot CO\cdot CH_2\cdot OH \rightleftharpoons COAr\cdot CH(OH)\cdot CH_2\cdot OH$, may perhaps form building units of lignin to a limited extent. Treatment of 3 : 4 : 1-$OMe\cdot C_6H_3(OH)\cdot CH(OH)\cdot CN$ with HCl–EtOH at −10° and subsequent hydrolysis gives the Et ester (24%), m.p. 77°, and thence (2% NaOH; N_2) *4-hydroxy-3-methoxymandelic acid*, m.p. 133°, the *diacetate*, $+H_2O$, m.p. 142°, of which with $SOCl_2$ in boiling C_6H_6 (105 min.; not longer) gives the *diacetate acid chloride*, m.p. 72°, and thence *α-acetoxy-γ-diazo-α-4-acetoxy-3-methoxyphenylpropan-β-one* (88%), m.p. 129—130°. This does not react with cold AcOH but with AcOH–Ac_2O–N_2 at the b.p. gives *αγ-diacetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one* (**VI**) (77%), b.p. 65—70°/0·025 mm., and with HCl–Et_2O–C_6H_6 at 0° gives *γ-chloro-α-acetoxy-α-4-acetoxy-3-methoxyphenylpropan-β-one* (**VII**) (81%), m.p. 110—111°. In boiling NaOAc–AcOH–CO_2, (**VII**) gives 75% of Ni glyoxime salt and thence by 12N-H_2SO_4 at room temp. (**IV**). With boiling 2% HCl–EtOH–CO_2, (**VI**) gives 66% of polymer and 8% of (**IV**), with boiling 2% H_2SO_4 gives 8·6% of (**IV**), and with 72% H_2SO_4 gives 68% of polymer. R. S. C.

Synthesis of α-mesitylpropiomesitylene. R. C. Fuson, N. Rabjohn, W. J. Shenk, jun., and W. E. Wallace [with in part, Q. F. Soper, C. H. McKeever, S. Melamed, and J. L. Marsh] (*J. Org. Chem.*, 1944, **9**, 187—192).—A synthesis from mesitylacetonitrile (**I**) with other unsuccessful attempts is recorded. *Et mesitylacetate*, b.p. 152—153°/22 mm., is obtained from the acid chloride and EtOH, from the acid and EtOH containing p-$C_6H_4Me\cdot SO_3H$, and, with a *substance*, $C_{22}H_{26}ON$, m.p. 236—237°, from (**I**) and boiling H_2SO_4–EtOH. It could not be caused to react with CH_2O or EtOAc but with $Et_2C_2O_4$ it yields a compound regarded as *Et$_2$ mesitylmalonate*, m.p. 49—80°, which could not be methylated. (**I**) fails to condense with CH_2O but is readily transformed by EtOAc in EtOH–NaOEt into *α-mesitylacetoacetonitrile*, m.p. 117—118°, converted by MeI and NaOH in EtOH into the O-*Me* derivative, b.p. 152—156°/3—4 mm. This is hydrolysed by boiling AcOH–H_2SO_4 to *mesitylacetone*, m.p. 60—61°, also obtained (impure) from *s*-$C_6H_3Me_3$, $COMe\cdot CH_2Cl$, and $AlCl_3$ or from (**I**) and a large excess of MgMeI. HCO_2Et, (**I**), and NaOEt in boiling EtOH afford *β-hydroxy-α-mesitylacrylonitrile*, m.p. 131·5—132·5° or 126·5—127·5° after several hr. (*benzoate*, m.p. 127—128°, unaffected by H_2 in presence of PtO_2), converted by NH_2Ph in boiling EtOH into *β-anilino-α-mesitylacrylonitrile*, m.p. 151·5—153°. MeCHO and Mg mesityl bromide give (?) *di(mesitylmethylcarbinyl) ether*, m.p. 94—95°; treatment of the crude condensation product with HCl in dry Et_2O followed by Mg and then 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot COCl$ lead to mesitoic acid and (?) *βγ-dimesitylbutane*, m.p. 139—140°. *s*-$C_6H_3Me_3$, $CHMeCl\cdot COCl$, and $AlCl_3$ in CS_2 at 5° yield unstable *α-chloropropiomesitylene*, b.p. 99—100°/1·5 mm. [3 : 5-$(NO_2)_2$-derivative, m.p. 127·5—128·5°]; *β-chloro-3 : 5-dinitropropiomesitylene* has m.p. 190—191·5°. Addition of (**I**) to $NaNH_2$ in Et_2O leads to α-mesitylpropionitrile, b.p. 160—165°/35 mm., hydrolysed by boiling glacial AcOH–conc. H_2SO_4 to α-mesitylpropionic acid, m.p. 102—103° (*amide*, m.p. 100—101°). This with $SOCl_2$ followed by *s*-$C_6H_3Me_3$ and $AlCl_3$ gives α-mesitylpropiomesitylene, b.p. 160—165°/1—2 mm., m.p. 74—75°. (**I**), $NaNH_2$, and CH_2PhCl yield *β-phenyl-α-mesitylpropionitrile*, b.p. 173—180°/2—5 mm., hydrolysed by boiling H_2SO_4–AcOH to the *acid*, m.p. 136—137°, with some *amide*, m.p. 119—120°. H. W.

Rearrangement of arylamides of aromatic and aliphatic acids under the action of aluminium chloride. D. N. Kursanov (*J. Gen. Chem. Russ.*, 1943, **13**, 286—289).—NHPhAc and NHPhBz with $AlCl_3$ at 200° for 1 hr. and 5 hr. respectively, give tarry products containing p-$NH_2\cdot C_6H_4\cdot COR$ [R = Me (12%), R = Ph (5%)]. NHPhAc and $AlCl_3$, in presence of PhMe at 200° in a sealed tube for 2 hr., yield 16·2% of p-$C_6H_4Me\cdot COMe$, indicating that the rearrangement proceeds through preliminary cleavage of the acyl group. R. C. P.

Volatile vegetable substances. XXIX. Isolation of a tricyclic isomeride of ionone. Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1944, **27**, 645—649).—Treatment of the portion of the products of cyclisation of ψ-ionone which does not react with $NaHSO_3$ with Girard's reagent *P* gives a mixture, b.p. 92—94°/4·6 mm., of ketones, which affords a *semicarbazone*, m.p. 209—209·5°, hydrolysed to *tricycloionone* (**I**), b.p. 90—90·5°/4 mm., the colour reactions of which are described. The tricyclic character of (**I**) is established by physical evidence. (**I**) gives a *δ-phenylsemicarbazone*, m.p. 186·5—187°, and a 2 : 4-*dinitrophenylhydrazone*, m.p. 151·1—152°. (**I**) is reduced by Na and boiling EtOH to *tricycloionol*, b.p. 98—99°/2·5 mm. (*acetate*, b.p. 95—96°/1·2 mm.), which is not hydrogenated (PtO_2 in AcOH at 60°). NaOI and (**I**) do not give CHI_3. H. W.

Three coloured isomeric forms of benzaurins and phthaleins. Structure of form *A*. P. Ramart-Lucas (*Compt. rend.*, 1943, **217**, 24—26).—The fuchsone structure for benzaurin is discussed (cf. A., 1939, II, 260, 321). A. T. P.

Nature of the isomerism of the three coloured forms of benzaurins and phthaleins. Possible metamorphosis of derivatives. P. Ramart-Lucas (*Compt. rend.*, 1943, **217**, 114—116; cf. A., 1939, II, 321).—Absorption spectra of benzaurin (**I**), its Me ether (**II**), p-$CPh_2{:}C_6H_4{:}O$, $(p\text{-}OMe\cdot C_6H_4)_3CPh\cdot OH$, $CPh_3\cdot OH$, and $CHPh_3$ are compared. (**II**), like (**I**), can exist in three forms, one of which (fuchsone, quinonoid form) exists in neutral, and one in acid, medium. A theory based on differing electronic states of the central C is suggested. A. T. P.

Synthesis of *p*-benzoquinone. J. H. Billman, B. Wolnak, and D. K. Barnes (*J. Amer. Chem. Soc.*, 1944, **66**, 652).—93—95% of p-$O{:}C_6H_4{:}O$ is obtained by adding NH_4VO_3 to quinol and $NaClO_3$ in 2% H_2SO_4 at 40—42° (30 min.) and then cooling. R. S. C.

Easy method for the preparation of dianthraquinone. Action of pyridine on dianthranol and dianthrone. A. Schönberg and A. F. A. Ismail (*J.C.S.*, 1944, 307).—Oxidation of dianthranol (**I**) with p-$O{:}C_6H_4{:}O$ in $COMe_2$ at room temp. gives dianthraquinone (approx. quant. yield) with quinhydrone. Dianthrone (**II**) or (**I**) with C_5H_5N affords a *compound*, $C_{38}H_{28}O_2N_2$, m.p. 190° (efferv.), remelts 229°, which with HCl–EtOH forms (**II**). F. R. S.

IV.—STEROLS AND STEROID SAPOGENINS.

Chromatography and mesomerism in the sterol series. Salkowski's reaction. P. Meunier (*Compt. rend.*, 1943, **217**, 78—80).—The red colour of cholesterol (**I**) in $CHCl_3$–H_2SO_4 is attributed to mesomerism. This is supported by the production of some $\Delta^{3:5}$-cholestadiene, m.p. 79° (absorption max. at 229, 235, and 245 mμ.) (cf. Schoenheimer *et al.*, A., 1936, 1105), in addition to dicholesteryl ether, from (**I**) (method : Bills *et al.*, A., 1926, 981). A. T. P.

Steroids and sex hormones. XCVII. Relationships between constitution and optical activity in the cholic acid series. P. A. Plattner and H. Heusser (*Helv. Chim. Acta*, 1944, **27**, 748—757).—The observation of Bernstein *et al.* (A., 1942, II, 177) that changes in the side-chain of the sterols have little influence on $[M]_D$ is confirmed; the effect is very small when such changes occur at a distance from the asymmetric $C_{(20)}$ and when a new centre of asymmetry is not developed. The behaviour of Me cholate on partial or complete acetylation shows that the contributions to $[M]$ of the asymmetric centres at $C_{(3)}$, $C_{(7)}$, and $C_{(12)}$ are largely independent of one another. Marked differences are found for the free, partly acetylated acids. It appears therefore that unpredictable influences also play a part. The relative independence of the asymmetric centres at $C_{(7)}$ and $C_{(12)}$ of the sterol skeleton is shown by observations of the effect of introducing OH groups into lithocholic acid. The following are described : *Me triacetylcholate*, m.p. 90·5—91°, $[\alpha]_D^{14}$ +81·8° in EtOH, $[\alpha]_D^{17}$ +76·8° in $CHCl_3$; *Me triformylcholate*, m.p. 133·5—134·5°, $[\alpha]_D^{14}$ +90·0° in EtOH, $[\alpha]_D^{17}$ +86·0° in $CHCl_3$; 3(α)-hydroxy-7(α) : 12(β)-diacetoxycholanic acid, m.p. 202—203°, $[\alpha]_D^{14}$ +71·6° in EtOH (*Me* ester, m.p. 57—59°, $[\alpha]_D^{14}$ +72·0° in EtOH, +63·7° in $CHCl_3$); 12(β)-hydroxy-3(α) : 7(α)-diacetoxycholanic acid, m.p. 261—263°, $[\alpha]_D^{17}$ +49·8° in EtOH (*Me* ester, m.p. 182—183°, $[\alpha]_D^{14}$ +35·3° in EtOH, +31·0° in $CHCl_3$); Me 7(α) : 12(β)-dihydroxy-3(α)-acetoxycholanate, m.p. 149·5—150°, $[\alpha]_D^{14}$ +52·8° in EtOH, $[\alpha]_D^{15}$ +47·6° in $CHCl_3$; 12-keto-3(α) : 7(α)-diacetoxycholanic acid, m.p. 229—230°, $[\alpha]_D^{17}$ +86·5° in $CHCl_3$ (*Me* ester, m.p. 177—178·5°, $[\alpha]_D^{17}$ +83·5° in $CHCl_3$); chenodeoxycholic [3(α) : 7(α)-dihydroxycholanic] acid, m.p. 140—141·5°, $[\alpha]_D^{17}$ +12·5° in $CHCl_3$ (*Ba* salt); 3(α) : 7(α)-diformoxycholanic acid, m.p. 132·5—133·5° and 180—182°, $[\alpha]_D^{16}$ +31·0° in EtOH. H. W.

Bile acids and related substances. XXIX. Derivative of bisnordeoxycholic acid and of 3(α) : 11(α)-dihydroxybisnorcholanic acid. A. Lardon and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 713—726).—Me 3(α) : 12(β)-dihydroxybisnorcholanate (Me bisnordeoxycholate) (**I**) is cautiously oxidised by CrO_3 in AcOH to *Me* 3 : 12-*diketobisnorcholanate*, m.p. 139—141°, $[\alpha]_D^{13}$ +82·1°±2° in $COMe_2$. Partial acetylation of (**I**) by Ac_2O in boiling C_6H_6 affords *Me* 12(β)-*hydroxy*-3(α)-*acetoxybisnorcholanate*, m.p. 198—199°, $[\alpha]_D^{19}$ +54·7°±1·5° in $COMe_2$, oxidised (CrO_3 in AcOH) to the 12-*keto*-ester, m.p. 168—170°, $[\alpha]_D^{20}$ +93·9°±1·5° in $COMe_2$. Energetic acetylation (Ac_2O–C_5H_5N at 100°) of (**I**) yields *Me* 3(α) : 12(β)-*diacetoxybisnorcholanate*, m.p. 169—170°, $[\alpha]_D^{13}$ +84·4°±1° in $COMe_2$, partly hydrolysed (1% HCl–MeOH at 16°) to *Me* 3(α)-*hydroxy*-12(β)-*acetoxybisnorcholanate*, m.p. 137—138°, $[\alpha]_D^{20}$ +73·2°±1° in $COMe_2$, oxidised to the 3-*keto*-ester (**II**), m.p. 136—137°, $[\alpha]_D^{19}$ +64·8°±1·5° in $COMe_2$, and an unidentified *by-product*, $C_{25}H_{38}O_5$, m.p. 164—165°, $[\alpha]_D^{15}$ +73·4°±1·5° in $COMe_2$. Alkaline hydrolysis and esterification (CH_2N_2) of (**II**), particularly if the conditions are not too drastic, leads mainly to *Me* 12(β)-*hydroxy*-3-*ketobisnorcholanate*, m.p. 204—206°, $[\alpha]_D^{13}$ +38·6°±1·5° in $COMe_2$, with some

Me 12(β)-hydroxy-3-ketobisnor-20-*iso*cholanate [only obtained amorphous but identified by conversion into the acetate, m.p. 169—171°, and oxidation to the 3 : 12-$(CO)_2$-compound, double m.p. 116—118° and 140—141°], and by-products, m.p. 142—144° (oxidised to a *compound*, $C_{23}H_{34}O_4$, m.p. 181—183° and m.p. 177—179° (similarly oxidised to a *substance*, $C_{23}H_{34}O_4$, m.p. 164—166°). *Me* 3-*keto*-12(β)-*benzoyloxy*-, m.p. 135—136°, $[\alpha]_D^{13}$ +46·8°±1·5° in $COMe_2$, and *Me* 3(α) : 12(β)-*dibenzoyloxy*-, m.p. 170—171°, -*bisnorcholanate* are described. (**I**) is converted by anthraquinone-2-carboxyl chloride in abs. C_5H_5N–PhMe at 100° into *Me* 3(α) : 12(β)-*dianthraquinone*-2′-*carboxybisnorcholanate*, m.p. 221—223° [accompanied under less drastic conditions by the 12(β)-*hydroxy*-3(α)-*anthraquinone*-2′-*carboxy* ester, m.p. 271—273°], hydrolysed by KOPh in boiling EtOH–dioxan to the 3(α)-hydroxy-12(β)-anthraquinone-2′-carboxy ester [*acetate* (*A*), m.p. 116—118°, becomes opaque at ~100°]. Thermal fission of the above monobenzoate or of Me 3-keto-12(β)-anthraquinone-2′-carboxybisnorcholanate, a resin, leads to *Me* 3-*keto*-Δ^{11}-*bisnorcholenate* (**III**), m.p. 122—123°, $[\alpha]_D^{13}$ +20·0°±1·5° in $COMe_2$, reduced (H_2, Raney Ni in MeOH containing NaOH) and then acetylated to Me 3(α)- (**IV**), m.p. 101—102°, new $[\alpha]_D^{15}$ +32·2°±1° in $COMe_2$ [also obtained by thermal fission of (*A*)], and *Me* 3(β)-*acetoxy*-Δ^{11}-*bisnorcholenate*, m.p. 139—140°, $[\alpha]_D^{13}$ +13·8°±1° in $COMe_2$. (**III**) and NHAcBr in aq. $COMe_2$ at 16° followed by CrO_3–aq. AcOH afford Me 12-bromo-3 : 11-diketobisnorcholanate (**V**), m.p. 198—202°, converted by Zn dust and NaOAc in AcOH at 100° into *Me* 3 : 11-*diketobisnorcholanate* (**VI**), m.p. 199—201°, $[\alpha]_D^{15}$ +47·6°±1·5° in $COMe_2$; *Me* 3 : 12-*diketo*-Δ^9-*bisnorcholenate*, m.p. 136—138°, $[\alpha]_D^{15}$ +73·1°±1·5° in $COMe_2$, and (**III**) are obtained similarly from the by-products of (**V**). (**VI**) is hydrogenated (PtO_2 in AcOH) with subsequent acetylation (Ac_2O in C_5H_5N at 60°) and re-oxidation (CrO_3 in AcOH at room temp.) to *Me* 11-*keto*-3(α)-, m.p. 148—150° (from MeOH) or 142—144° and then 153—154° (from Et_2O–light petroleum), $[\alpha]_D^{15}$ +57·6°±2° in $COMe_2$, and *Me* 11-*keto*-3(β)-*acetoxybisnorcholanate*, m.p. 163—165°, $[\alpha]_D^{13}$ +29·3°±1·5° in $COMe_2$; the former is also obtained from (**IV**). *Me* 11(α)-*hydroxy*-3(α)-*acetoxy*-, m.p. 137—139°, $[\alpha]_D^{15}$ +56·5°±1·5° in $COMe_2$, 3(α) : 11(α)-dihydroxy-, m.p. 75—85° (? hydrate), $[\alpha]_D^{16}$ +38·8°±1° in $COMe_2$, 11(α)-*hydroxy*-3(β)-*acetoxy*-, m.p. 173—175°, $[\alpha]_D^{12}$ +33·7°±1·5° in $COMe_2$, and 3(β) : 11(α)-dihydroxy-, m.p. 139—140°. $[\alpha]_D^{16}$ +34·2°±0·8° in $COMe_2$, -bisnorcholanate are described. M.p. are corr. (block); limits of error ±2°. H. W.

Degradation of bile acid derivatives. R. P. Jacobsen (*J. Amer. Chem. Soc.*, 1944, **66**, 662).—Bile acids are degraded in good yield by the following reactions. $CHRMe{\cdot}[CH_2]_2{\cdot}COCl$ [+$CdPh_2$] → $CHRMe{\cdot}[CH_2]_2{\cdot}COPh$ → mixed $CHRMe{\cdot}CH_2{\cdot}CHBr{\cdot}COPh$ → $CHRMe{\cdot}CH_2{\cdot}CH(OAc){\cdot}COPh$ → $CHRMe{\cdot}CH_2{\cdot}CH(OH){\cdot}COPh$ → ($CuSO_4$–aq. C_5H_5N) $CHRMe{\cdot}CH_2{\cdot}CO{\cdot}COPh$ (65—70%) → $CHRMe{\cdot}CH{:}C(OAc){\cdot}COPh$ → $CHRMe{\cdot}CO_2H$. The following are described: *cholophenone* [*Ph norcholyl ketone*], +0·5H_2O, m.p. 174—176·5°, $[\alpha]_D^{20}$ +26° [*triacetate*, m.p. 120·3—121°, $[\alpha]_D^{20}$ +79°; 2 : 4-*dinitrophenylhydrazone*, m.p. 221—222·5°; *oxime*, m.p. 214—217° (decomp.)]; 23(? β)-*bromocholophenone triacetate*, +H_2O, m.p. 108·5—111·5°, $[\alpha]_D^{20}$ +95°; 23(? α)-*acetoxycholophenone triacetate*, +0·5H_2O, m.p. 180—182°, $[\alpha]_D^{20}$ −10°; *Ph bisnorcholyl diketone triacetate*, m.p. 166—169° (after drying, 161·5—166°), $[\alpha]_D^{20}$ +92° (the 7 : 12-*diacetate* has m.p. 201—203·5°, $[\alpha]_D^{20}$ +80°); 3-*phenyl*-2-*bisnorcholyl*-*quinoxaline triacetate*, m.p. 217—218·5°. [α] are in $CHCl_3$. R. S. C.

Adsorption of œstrone, œstriol, and α-œstradiol on a chromatographic column. B. F. Stimmel (*J. Biol. Chem.*, 1944, **153**, 327—333).—Strongly phenolic may be separated from weakly phenolic œstrogens by means of a liquid chromatogram using activated Al_2O_3, the weakly phenolic being eluted by a 9 : 1 C_6H_6–MeOH mixture and the strongly phenolic by a 4 : 1 mixture. The Al_2O_3 is inactivated by the process and its subsequent use is inadvisable. H. G. R.

Synthesis of compounds related to sex hormones. W. E. Bachmann and R. D. Morin (*J. Amer. Chem. Soc.*, 1944, **66**, 553—557).—5 : 6 : 7 : 8-Tetrahydro-1-naphthylamine (prep. from α-$C_{10}H_7{\cdot}NH_2$ by Na and fusel oil in 84% yield) gives (diazo-reaction) the 1-I-derivative (66%), b.p. 153—158°/20 mm., and thence, successively, [Grignard; $(CH_2)_2O$] β-5 : 6 : 7 : 8-tetrahydro-1-naphthylethyl alcohol (57%), b.p. 125—135°/0·4 mm., (PBr_3) the derived bromide (62%), b.p. 113—118°/0·05 mm., [$CHNa(CO_2Et)_2$; then hydrolysis and heating at 180°] γ-5 : 6 : 7 : 8-tetrahydronaphthyl-1-butyric acid (65%), m.p. 94—95°, and (acid chloride; $SnCl_4$) 1-keto-*s*-octahydrophenanthrene (**I**) (88%), m.p. 80·5—82°. $Me_2C_2O_4$ and (**I**) give *Me* 1-*keto*-s-*octahydrophenanthrene*-2-*glyoxylate* (89%), m.p. 103—104°, converted by heating with powdered, soft glass at 180° into *Me* 1-*keto*-s-*octahydrophenanthrene*-2-*carboxylate* (88%), m.p. 83—85°, which with NaOMe and MeI in MeOH–C_6H_6 gives *Me* 1-*keto*-2-*methyl*-s-*octahydrophenanthrene*-2-*carboxylate*, m.p. 77—78° (derived *acid*, m.p. 87—88°). The Reformatsky reaction then gives *Me* 1-*hydroxy*-2-*carbomethoxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylacetate* (76—81%), m.p. 102—103° [converted by hot KOH–MeOH–H_2O into the 2-Me derivative of (**I**)], which with $SOCl_2$–C_5H_5N and then KOH–EtOH–H_2O gives 2-*carboxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylideneacetic acid* (92%), m.p. 140—141° (gas). This or an unpurified solution of it with 2% Na–Hg in aq. KOH gives 2-*carboxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylacetic acid*, α- (40—43%), m.p. 218—219°, and β-*form* (46—50%), m.p. 162—163°, the Me_2 esters (prep. by CH_2N_2), α-, m.p. 70·5—71°, and β-*form*, m.p. 81·5—82·5°, of which with hot NaOH–MeOH–H_2O give 2-*carbomethoxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylacetic acid* (95—98%), α-, m.p. 121—122°, and β-*form*, m.p. 141—142°. Arndt–Eistert reactions then yield *Me* β-2-*carbomethoxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylpropionate*, α- (75%), m.p. 63·5—64·5°, and β-form, an oil, cyclised by NaOMe in boiling C_6H_6 to *Me* 1 : 2 : 3 : 4-*tetrahydro*-17-*equilenone*-16-*carboxylate*, α- (90%), m.p. 124—125° (dark green $FeCl_3$ colour), and β-*form* (85%), m.p. 121—122° (greenish-brown $FeCl_3$ colour), which in boiling HCl–AcOH–H_2O–N_2 give 1 : 2 : 3 : 4-*tetrahydro*-17-*equilenone*, α- (88%), m.p. 72—73° (*semicarbazone*, m.p. 243—244°), and β-*form* (79%), m.p. 114—115° (vac.) [*semicarbazone*, m.p. 274—275° (vac.)] (cf. Marker *et al.*, A., 1940, II, 95), converted by S at 210° into the α- and β-forms, respectively, of 17-equilenone.

2-$C_{10}H_7{\cdot}$OMe and $(CH_2{\cdot}CO)_2O$ give 6 : 2-OMe·$C_{10}H_6{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$, m.p. 147—148°, the Et ester, m.p. 107·5—108°, of which affords (Reformatsky) the *lactone* (**II**) (84%), m.p. 121—122°, of α-Me α′-H β-hydroxy-β-6-methoxy-2-naphthyladipate. Hot N-aq. NaOH–MeOH converts (**II**) into β-6-*methoxy*-2-*naphthyl*-Δ^{α}-*butene*-αδ-*dicarboxylic acid* (**III**) (98%), m.p. 194—195°, the Me_2 ester, b.p. 190°/0·05 mm., of which yields by cyclisation 3-6′-*methoxy*- (80%), m.p. 125—126°, and thence (boiling HCl–AcOH–H_2O–N_2) 3-6′-*hydroxy*-2′-*naphthyl*-Δ^2-cyclo*pentenone* (**IV**), m.p. 252—253° (vac.) {*Me ether*, m.p. 169—170° [*semicarbazone*, m.p. 250—251° (vac.), reduced by NaOMe–EtOH at 180° to the known 1-6′-methoxy-2′-naphthyl*cyclo*pentene, m.p. 141—142°]; *semicarbazone*, m.p. 260—262° (vac.)}. 2% Na–Hg in aq. KOH reduces (**III**) to β-6-*methoxy*-2-*naphthyladipic acid*, m.p. 164—165°, the Me_2 ester, b.p. 180—190°/0·05 mm., of which by successive cyclisation, hydrolysis, decarboxylation, and demethylation affords 3-6′-*hydroxy*-2′-*naphthyl*cyclo*pentanone* (83%), m.p. 176—176·5° (*semicarbazone*, m.p. 212—213°), also obtained from (**IV**) by H_2–Pd–C in AcOH. By similar reactions β-$C_{10}H_7{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ gives the *lactone*, m.p. 111—112°, of α-Me α′-H β-hydroxy-β-2-naphthyladipate, β-2-*naphthyl*-Δ^{α}-*butene*-αδ-*dicarboxylic acid*, m.p. 179—180° (Me_2 ester, b.p. 170—180°/0·05 mm), 3-2′-naphthyl-Δ^2-*cyclo*pentenone (**V**), m.p. 126—127° [semicarbazone, m.p. 240—241° (lit. 244°)], 1-2′-naphthyl*cyclo*pentene, β-2-*naphthyladipic acid*, m.p. 153—154°, and 3-2′-naphthyl*cyclo*pentanone, m.p. 65—66° (lit. 61°) [semicarbazone, m.p. 199—199·5° (lit. 196—197°)]. 2-Chloroacetyl-5 : 6 : 7 : 8-tetrahydronaphthalene yields by similar reactions γ-keto-γ-5 : 6 : 7 : 8-tetrahydro-2-naphthylbutyric acid, β-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl*-Δ^{α}-*butene*-αδ-*dicarboxylic acid*, m.p. 185—186°, 3-5′ : 6′ : 7′ : 8′-*tetrahydro*-2′-*naphthyl*-Δ^2-cyclo*pentenone*, m.p. 82—82·5° [*semicarbazone*, m.p. 235—236°; and thence by Pd–C–N_2 at 320° (**V**)], β-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyladipic acid*, m.p. 159·5—160°, and 3-5′ : 6′ : 7′ : 8′-*tetrahydro*-2′-*naphthyl*cyclo-*pentanone*, m.p. 73—74° (*semicarbazone*, m.p. 207—208°). R. S. C.

Steroids and sex hormones. XCVI. Rearrangement products of 2-acetoxycholestan-3-one. L. Ruzicka, P. A. Plattner and M. Furrer (*Helv. Chim. Acta*, 1944, **27**, 727—737).—2-Acetoxy- (**I**) and 2-hydroxy-cholestan-3-one (**II**) are shown to be very labile compounds. Catalytic hydrogenation (Pt) of (**I**) in neutral or acidic solution affords a mixture (**III**) of compounds from which *cholestan*-1-*yl acetate*, m.p. 80—81°, $[\alpha]_D$ +9·5° in $CHCl_3$, is isolated in small amount. It is hydrolysed by boiling KOH–MeOH to *cholestan*-1-*ol* (**IV**), m.p. 165·5—166° $[\alpha]_D$ +14° in $CHCl_3$ (*benzoate*, m.p. 107—108°, $[\alpha]_D$ +0·2° in $CHCl_3$), oxidised (CrO_3 in AcOH) to *cholestan*-1-*one* (**V**), m.p. 120—120·5°, $[\alpha]_D$ +41° in $CHCl_3$, which is reduced (N_2H_4,H_2O and Na in $C_5H_{11}{\cdot}OH$ at 190°) to cholestane (**VI**). The constitution of (**V**) is based on its non-identity with any known cholestanone. The following also are isolated from (**III**): *acetoxycholestanol*-A, m.p. 168—169°, $[\alpha]_D$ +41° in $CHCl_3$ (*acetate*, m.p. 161—162°, $[\alpha]_D$ +33° in $CHCl_3$; *benzoate*, m.p. 180—182°; p-*toluenesulphonate*, m.p. 146·5—147·5°), oxidised (CrO_3) to *acetoxycholestanone*-A, m.p. 145—146°, $[\alpha]_D$ +1° in $CHCl_3$, which greatly depresses the m.p. of (**I**); *acetoxycholestanol*-B, m.p. 182·5—183·5°, and -C, m.p. 174—176°; (?) cholestane-2 : 3-diol, m.p. 196—197°, and a mixture of various diols. Reduction (Clemmensen) of (**I**) gives (**VI**) exclusively. The following are obtained by reduction (Wolff–Kishner) of (**I**): (**VI**) with smaller proportions of (**IV**), cholestan-4-ol, m.p. 189·5—190° (*acetate*, m.p. 112·5—113°, $[\alpha]_D$ +16° in $CHCl_3$; *benzoate*, m.p. 117·5—118°), oxidised to *cholestan*-4-*one*, m.p. 99—99·5°, $[\alpha]_D$ +29·5° in $CHCl_3$, a cholestan-2-ol (the presence of which is established by oxidation to cholestan-2-one), and two *azines*, $C_{54}H_{92}N_2$, m.p. 235—242° (decomp.) and 200—210° (decomp.). Hydrolysis of (**I**) in C_6H_6 with K_2CO_3 in aq. MeOH gives (**II**) in moderate yield with large amounts of a (?) 3-*hydroxycholestan*-4-*one* (**VII**), m.p. 173—175°, softens at 171°, $[\alpha]_D$ +14·5° in $CHCl_3$ [*acetate* (**VIII**], m.p. 143·5—144·5°, $[\alpha]_D$ −7·5° in $CHCl_3$], converted by HBr–AcOH–$CHCl_3$ at 100° into cholestan-4-one, m.p. 98—99°. The sole isolable product of the hydrolysis of (**I**) by KOH is a *OH-ketone* [? Δ^3-*cholestene*-3 : 4-*diol*], m.p. 125·5—127°, $[\alpha]_D$ +35° in $CHCl_3$, isomeric with (**VII**) and from which it is distinguished by its colour with $C(NO_2)_4$. It is converted by Ac_2O–C_5H_5N into (**VIII**). It and (**VII**) are converted by alkaline H_2O_2 into the dihydro-Diels' acid. Δ^3-3-

Acetoxycholesten-2-one is hydrogenated (Raney Ni in EtOH) to 3(β)-*acetoxycholestan-2-one* (**IX**), m.p. 145·5—146·5°, $[\alpha]_D$ +73° in $CHCl_3$ [*oxime* (**X**), m.p. 178—179·5° (decomp.)], reduced (Wolff–Kishner) to (**VI**). Alkaline hydrolysis (KOH–MeOH) of (**X**) yields 3(β)-*hydroxycholestan-2-oneoxime*, m.p. 207—208° (decomp.). NaOH–MeOH at 20° converts (**IX**) into 3(β)-*hydroxycholestan-2-one*, m.p. 104—105°, $[\alpha]_D$ +65° in $CHCl_3$, oxidised to the dicarboxylic acid, m.p. 193—195°, of Windaus *et al.* M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. LXVII. Attempted preparation of ætiocholane-3(α) : 12(β)-diol-17-one by systematic degradation. B. Koechlin and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 549—566; cf. A., 1944, II, 106).—Five known methods and one new one have been applied to the degradation of derivatives of ætiocholanic acid or pregnan-20-one to derivatives of ætiocholan-17-one and particularly to the prep. of ætiocholane-3(α) : 12(β)-diol-17-one (**I**). This has been obtained only from pregnane-3(α) : 12(β)-diol-20-one by the method of Marker *et al.* (A., 1942, II, 230, 264) but the yield is unsatisfactory. Unsuccessful attempts to obtain cryst. diphenyl-3(α) : 12(β)-diacetoxyætiocholanylcarbinol or the corresponding methene from Me ætiodeoxycholate (cf. A., 1941, II, 140) are described; a cryst. *by-product*, $C_{30}H_{40}O_5$, m.p. 152—153°, has been isolated. Treatment of *allo*pregnane-3(β)-ol-20-one acetate with MgMeBr and subsequent acetylation affords 20-methyl*allo*pregnane-3(β) : 20-diol 3-monoacetate (**II**), needles which pass into hexagonal plates at 185—190°, m.p. 200—202°, in good yield (cf. Butenandt *et al.*, A., 1935, 1033). (**II**) loses H_2O in boiling AcOH, giving mainly 20-*methyl*-Δ^{20}-*allopregnene*-3(β)-*ol acetate* (**III**), m.p. 111—114°, $[\alpha]_D^{15}$ ±0°±2° in $COMe_2$, with smaller quantities of an *isomeride* (**IV**), m.p. 65—67°, $[\alpha]_D^{16}$ −57·2°±1·5° in $COMe_2$, and traces of 20-methyl-Δ^{17}-*allo*pregnen-3(β)-ol acetate, m.p. 144°. (**II**) sublimes unchanged at 145° (bath)/high vac., but is partly dehydrated by repeated distillation at 210°/12 mm., whereby the main product is (**III**). This is formed almost exclusively from (**II**) and $POCl_3$–C_5H_5N at 130°, and (**IV**) is almost the sole product of the action of P_2O_5 (in C_6H_6) or of HCO_2H on (**II**). The consitution of (**III**) is deduced from its ozonisation to *allo*pregnan-3(β)-ol-20-one acetate; it is hydrogenated to 20-*methyl*allo*pregnan*-3(β)-*ol acetate*, m.p. 124—125°. (**IV**) is hydrolysed to the corresponding alcohol, m.p. 144—145° after a transformation at ~140°. Ozonisation of (**IV**) gives some acidic products but mainly neutral material from which a *substance*, $C_{24}H_{38(40)}O_{4(5)}$, m.p. 186—188°, $[\alpha]_D^{17}$ +22·1°±3° in dioxan, is isolated which does not react with NH_2·CO·NH·NH_2. Attempted chromatographic purification of this material by Al_2O_3 leads to *compounds*, $C_{24}H_{38}O_4$, m.p. 156—161°, and 202—205°. (**IV**) is hydrogenated (PtO_2 in AcOH) to a *substance*, $C_{24}H_{40}O_2$, m.p. 81—84°, which does not give a yellow colour with $C(NO_2)_4$. Ag 3(β)-acetoxyætio*allo*cholanate is largely unattacked by Br in CCl_4 at room temp. and subsequently at incipient boiling. Addition of Br–AcOH to *allo*pregnan-3(β)-ol-20-one acetate in AcOH containing HBr and treatment of the product with KOH–MeOH gives neutral products which, after acetylation, afford *Me* 3(β)-*acetoxy*-17-*methyl*ætio*allocholanate*, m.p. 200—202°, which does not give a colour with $C(NO_2)_4$ and acidic products from which after methylation, acetylation, ozonolysis, and hydrolysis androstan-3(β)-ol-17-one, m.p. 175°, is obtained in ~7% yield. A similar series of changes starting from pregnane-3(α) : 12(β)-diol-20-one diacetate leads to *Me* 3(α) : 12(β)-*diacetoxy*-17-*methyl*ætio*allocholanate*, m.p. 163—165°, and the diacetate, m.p. 160—162°, $[\alpha]_D^{16}$ +186·3°±2° in $COMe_2$, of (**I**). Gradual addition of NaOEt–EtOH to a solution of *allo*pregnane-3(β)-ol-20-one acetate and PhCHO in abs. EtOH gives 21-benzylidene*allo*pregnan-3(β)-ol-20-one acetate, m.p. 211—214° (lit. 207—209°), $[\alpha]_D^{16}$ +75·5°±2° in dioxan, and an *isomeride*, prisms, m.p. 150—152°, or hexagonal leaflets, m.p. 150—152° after transformation at 147°; either isomeride is converted by PCl_5 in C_6H_6 at 50° followed by ozonolysis into androstan-3(β)-ol-17-one. A similar change cannot be effected starting from 21-benzylidenepregnane-3(α) : 12(β)-diol-20-one diacetate, m.p. 119—121°, $[\alpha]_D^{16}$ +200·5°±2° in dioxan. H. W.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Oil of lavender. III. Monoterpene alcohols and acids present as esters in French oil of lavender. C. F. Seidel, H. Schinz, and P. H. Müller (*Helv. Chim. Acta*, 1944, **27**, 663—674).—Fractions, b.p. >100°/11 mm., of French oil of lavender have been examined. The following alcohols have been isolated: *l*-linalool (**I**), b.p. 84—85°/11 mm., α_D −16·8° (phenylurethane, m.p. 61—62°); geraniol (**II**), b.p. 115—116°/14 mm. (allophanate, m.p. 115—116°; 3 : 5-dinitrobenzoate, m.p. 60—61°); nerol (**III**), (diphenylurethane, m.p. 55—62°); *d*-citronellol (**IV**), b.p. 104—105°/11 mm. (allophanate, m.p. 105—106°, $[\alpha]_D$ +2·50° in MeOH); *d*-borneol (**V**), m.p. 203—204°; cumin alcohol (**VI**), b.p. 124°/13 mm. (allophanate, m.p. 184—185°; 3 : 5-dinitrobenzoate, m.p. 96°). (**I**), (**II**), and (**III**) are present in free and esterified forms, (**V**) and (**VI**) only as free alcohol, and (**IV**) only as ester. The identity of (**VI**) is confirmed by the prep. of it (and its derivatives) by reduction of cuminol with $Al(OPr^\beta)_3$ and by its synthesis from C_6H_6 and $Pr^\beta Br$ through *p*-$C_6H_4Pr^\beta Br$ and *p*-$C_6H_4Pr^\beta$·MgBr + CH_2O. The higher fatty acids include *d*-CHMeEt·CO_2H, b.p. 75—77°/10 mm., α_D +11° (*thiuronium* salt, m.p. 147—148°, $[\alpha]_D$ +3·6° in MeOH), *n*-C_5H_{11}·CO_2H (thiuronium salt, m.p. 154—155°; anilide, m.p. 95—96°), an incompletely identified heptoic acid (thiuronium salt, m.p. 153°), pelargonic acid (thiuronium salt, m.p. 150—151°), tiglic acid, m.p. 63—64°, probably an unsaturated C_8 acid (thiuronium salt, m.p. 150—151°), a monocyclic, singly unsaturated acid, $C_9H_{14}O_2$, hydrogenated to a saturated acid, b.p. 130—135°/10 mm., α_D +3·4° (poorly cryst. anilide; *thiuronium* salt, $C_{17}H_{26}O_2N_2S$, m.p. 154—155°), BzOH, and an unidentified acid, $C_{10}H_{12}O_2$ (possibly a phenylbutyric acid) (*thiuronium* salt, m.p. 184—185°). Coumarin and umbelliferone Me ether are also present. H. W.

New transition from camphor to homocamphor. H. Rupe and C. Frey (*Helv. Chim. Acta*, 1944, **27**, 627—645; cf. A., 1940, II, 136).—The vigorous reaction between CH_2N_2 and camphorquinone gives a mixture from which the solid 4-methoxy-3 : 4-dehydrohomocamphor (**I**), m.p. 54—55°, crystallises, leaving the liquid variety (**II**). (**I**) and (**II**) give *oximes*, m.p. 195—196° and 185—185·5° respectively. Either isomeride is converted by Br in $CHCl_3$ at room temp. into 3-bromo-4-methoxy-3 : 4-dehydrohomocamphor, m.p. 104—105°, and by an excess of Br into 3 : 3-*dibromo*-4-*ketocamphor*, $C_8H_{14}\langle_{CO}^{CO}\rangle CBr_2$ (**III**), m.p. 153—154°. (**II**) does not give homogeneous products with MgEtBr or MgPhBr. Hydrolysis of (**I**) or (**II**) leads to the strongly acidic 4-hydroxy-3 : 4-dehydrohomocamphor (**IV**), m.p. 218—222°, and since the production of a new asymmetric C is excluded it appears that (**I**) and (**II**) are *cis–trans* isomerides, (**I**) being the *trans* variety. (**IV**) and Br in $CHCl_3$ yield 3-*bromo*-4-*hydroxy*-3 : 4-*dehydrohomocamphor*, m.p. 189—191°, whilst (**IV**) and Br vapour yield (**III**). (**IV**) is transformed by *p*-NO_2·C_6H_4·COCl at 160° into the p-*nitrobenzoate*, m.p. 120—122°, and by boiling EtOH–H_2SO_4 into the *Et ether*, b.p. 142—146°/12 mm., m.p. 70—72°. With NHPh·NH_2 in EtOH (**IV**) gives a *phenylhydrazone*, m.p. 181° (colourless leaflets or red prisms into which the leaflets slowly pass), but not a di-phenylhydrazone. 4-*Ketohomocamphordioxime* has m.p. 209° (decomp.). (**IV**) is converted by EtO·NO into 4-*keto*-3-*oximinohomocamphor*, m.p. 107—109°. PhCHO (1 mol.) reacts with (**IV**) (2 mols.) in C_5H_5N containing piperidine at 100° or in NaOMe–MeOH to give the *substance*, $C_{20}H_{36}O_4$, m.p. 146—149°. In C_5H_5N–piperidine at room temp. and then at 100°, *p*-NMe_2·C_6H_4·CHO and (**IV**) afford 4-*keto*-3-p-*dimethylaminobenzylidenehomocamphor*, m.p. 152·5—153°. Under similar conditions *o*-NO_2·C_6H_4·CHO gives 4-*keto*-3-o-*nitrobenzylidenehomocamphor*, m.p. 140—142° (decomp.), and a *compound*, $C_{29}H_{35}O_6N$. With PhN_2Cl (**IV**) yields 4-*ketohomocamphor*-3-*phenylhydrazone*, m.p. 117—118°. (**IV**) is comparatively easily oxidised by $KMnO_4$ to α-*ketoepihomocamphoric acid* (**V**), m.p. 125°, which passes when distilled in a vac. into CO and camphoric anhydride (**VI**). (**V**) gives a p-*nitrobenzylthiuronium* salt, m.p. 181—182°, and a *dinitrophenylhydrazone*, m.p. 192—193° (decomp.). (**V**) is reduced (Na–Hg) to α-*hydroxyepihomocamphorolactone*, m.p. 202—204° (*monohydrate*, m.p. 171—173°, softens at 150°; p-*nitrobenzylthiuronium* salt, m.p. 171—172°). (**VI**) is obtained by oxidation of (**IV**) with CrO_3. (**IV**) is hydrogenated (Ni in dil. EtOH containing Na_2CO_3 at room temp.) to 3 : 4-*dehydrohomocamphor* (**VII**), m.p. 173—175° (*oxime*, m.p. 143·5—145°; *dinitrophenylhydrazone*, m.p. 181—184°). With Br in $CHCl_3$ (**VII**) gives 3 : 4-*dibromohomocamphor*, m.p. 103° (decomp.). Hydrogenation (Ni) of (**VII**) leads to homocamphor (**VIII**), m.p. 192—193° (oxime, m.p. 165°; dinitrophenylhydrazone, m.p. 232—233°). Hydrogenation (H_2 at 60—70°/90 atm., Ni in aq. EtOH) of (**IV**) gives (**VII**) and a dimeric *compound*, m.p. 276—279°. (**IV**) is not hydrogenated in presence of Pd–C, with Na–Hg, or with Zn and AcOH; Clemmensen reduction affords non-homogeneous products. (**IV**) is transformed by NH_2Me at 100° and later at 140—150° into 4-*methylamino*-3 : 4-*dehydrohomocamphor* [*nitrosoamine*, m.p. 167° (decomp.); *picrate*, m.p. 178—180°], obtained similarly but less advantageously from (**II**). Vals. of $[\alpha]^{20}$ in C_6H_6 for (**I**), (**II**), (**IV**), (**VII**), and (**VIII**) are recorded. H. W.

Sesquiterpenes. LXIII. Alcohols, hydrocarbons, and oxides of the sesquiterpene series from French oil of lavender. C. F. Seidel, P. H. Müller, and H. Schinz (*Helv. Chim. Acta*, 1944, **27**, 738—747).—The following have been isolated from a fraction (2·7 kg.), b.p. >100°/11 mm., from 19·25 kg. of French oil of lavender: a probably primary, possibly *sec.*, probably tricyclic *alcohol*, $C_{15}H_{24}O$, b.p. 96°/0·07 mm., occurring in the free form and giving a poorly cryst. *allophanate*, m.p. 183—187°; an unesterified monocyclic primary *alcohol*, $C_{15}H_{26}O$, b.p. 107°/0·07 mm., α_D −25·6°, hydrogenated (PtO_2 in EtOAc) to a H_4-*alcohol*, b.p. ~100°/0·04 mm., which is saturated towards $C(NO_2)_4$, oxidised to an aldehyde, b.p. 100—110°/0·04 mm. (non-cryst. semicarbazone and 2 : 4-dinitrophenylhydrazone), and gives a small amount of CH_2O when ozonised; a primary dicyclic *alcohol* (**I**), $C_{15}H_{24}O$, b.p. 100—105°/0·04 mm., α_D −66·96° (*allophanate*, m.p. 188—189°), which is hydrogenated to a H_4-compound (*allophanate*, m.p. 178—179°), oxidised to an

aldehyde, b.p. 95—100°/0·05 mm.; a tricyclic *diol*, $C_{15}H_{26}O_2$, m.p. 150—151° (present as an ester), saturated towards $C(NO_2)_4$ and Br–CS_2 and indifferent to PtO_2 in AcOH, found in the residues from (I); free cadinol (II), identified as cadinene dihydrochloride; free bisabolol containing 5% of (II); caryophyllene, identified as the dihydrochloride and as caryophyllene alcohol; cadinene (III), identified as the dihydrochloride; bisabolene (IV), identified as the trihydrochloride; a dicyclic, cryst. *oxide*, $C_{15}H_{24}O$, m.p. 62—63°, $[\alpha]_D$ −67·85° in $CHCl_3$, hydrogenated (PtO_2 in EtOAc) to a saturated *oxide*, $C_{15}H_{26}O$, b.p. 140—141°/11 mm., and separated from the hydrocarbons by adsorption on SiO_2 gel; cedrene could not be identified. Dehydrogenation of hydrocarbon fractions containing (III) and (IV) by Se at 340° gives cadalene (V) and 1 : 6-$C_{10}H_6Me_2$ (VI). To check the possibility of the production of (VI) by elimination of Pr^β from (V), *iso*zingiberene [a hydrocarbon allied to (III)] is dehydrogenated at various temp. Some (VI) is invariably produced in addition to (V), the yield increasing with increasing temp. of dehydrogenation. At 380° the elimination of Pr^β is complete so that (V) can no more be detected. H. W.

Isolation of partheniol, parthenyl cinnamate, and other constituents from guayule resin. E. D. Walter (*J. Amer. Chem. Soc.*, 1944, **66**, 419—421).—An Et_2O extract of the exudate of *Parthenium argentatum*, Gray, in 80% alcohol deposits *parthenyl cinnamate* (~20%) (photomicrograph), m.p. 125—126°, also obtained in similar yield by keeping a $COMe_2$ extract of guayule rubber (cf. Alexander, A., 1911, i, 897). Hydrolysis of the ester yields cinnamic acid and *partheniol*, $C_{15}H_{26}O$, m.p. 131° (photomicrograph), which yields no 3 : 5-dinitrobenzoate or phenylurethane and in 90% HCO_2H at room temp. gives a *formate*, b.p. 215° (decomp.)/755 mm. Crystallo-optical properties of the alcohol are reported. Air-dried foliage or the whole shrub yields to warm $COMe_2$ a resin including ~0·25% of a *wax* (C 80·18, H 13·25%), m.p. 76°, which is also obtained from rubber from the retted or unretted shrubs. The alcohol and acid are also obtained by hydrolysing $COMe_2$ extracts of the rubber from retted or whole shrubs or of the foliage, yields of the alcohol being ~2·5%, ~2%, and <1%, respectively. Steam-distilling a $COMe_2$ extract of the rubber gives an oil, b.p. 244—245°/750 mm., $[\alpha]_D^{25}$ −17·92°; distilling the resin in vac. gives cinnamic acid and fractions varying from b.p. 70—78°/1 mm., $[\alpha]_D^{22}$ −10·5°, to a *sesquiterpene*, b.p. 246—247°/755 mm., $[\alpha]_D^{22}$ −6·84°. This hydrocarbon may have been formed by dehydration of partheniol. R. S. C.

Triterpenes. LXXXVII. Transformation products of lanosterol. L. Ruzicka, E. Rey, and A. C. Muhr (*Helv. Chim. Acta*, 1944, **27**, 472—489).—Lanosterol (I) contains an unsaturated side-chain with at least 4 C which terminates in the :CMe_2 group. In structure of this side-chain and in behaviour of the part of the mol. which contains the non-reactive double linking. (I) is identical with elemadienolic acid. The unsaponifiable matter of the wool fat of sheep is extracted with $COMe_2$ and the fatty alcohols are removed chromatographically. The mixture is freed from cholesterol by repeated treatment with boiling MeOH. Chromatographic methods of separating the "*iso*cholesterol" (II) thus obtained are less satisfactory than the older acetate method, which leads to the following substances: lanosteryl acetate (III), m.p. 113·5—114·5°, $[\alpha]_D^{14}$ +55·2°, hydrolysed to (I), m.p. 140—141°, $[\alpha]_D^{15}$ +58·2° (*benzoate*, m.p. 191°; 3 : 5-*dinitrobenzoate*, m.p. 201°); dihydrolanosteryl acetate, (IV), m.p. 122—123°, $[\alpha]_D^{20}$ +60·3°, hydrolysed to dihydrolanosterol, m.p. 142·5—143·5°, $[\alpha]_D^{20}$ +60·9°; γ-lanosteryl acetate (V), m.p. 168·5—169·5°, $[\alpha]_D^{16}$ +85·9°, whence γ-lanosterol (VI), m.p. 156—157·5°, $[\alpha]_D^{16}$ +66·2°; agnosteryl acetate, m.p. 174—176°, $[\alpha]_D^{15}$ +88·3°, hydrolysed to agnosterol, m.p. 163·5—164·5°, $[\alpha]_D^{20}$ +76·9°. The main product of the dehydrogenation of (II) by Se at 350° is 1 : 7 : 8-trimethylphenanthrene; a homologue which could not be obtained pure appears to be also present with a *hydrocarbon*, (?) $C_{20}H_{20}$, m.p. 237·5—238·5°, which appears to be a homologue of chrysene according to its absorption in the ultra-violet. Ozonisation of (III) and subsequent fission of the ozonide by boiling H_2O gives $COMe_2$ (identified as the *p*-nitrophenylhydrazone) and, after methylation, *Me acetyltrinorlanosterate*, m.p. 168—170°, hydrolysed to *trinorlanosteric acid*, m.p. 257·5—259·5° (*Me* ester, m.p. 152·5—154·5°). The readily hydrogenated double linking of (I) is therefore present in :CMe_2. (IV) is oxidised by CrO_3 in AcOH at 40° to αβ-unsaturated *ketodihydrolanosteryl acetate*, m.p. 151·5—152·5°, or if introduced into a bath at 146° gives an immediate turbid melt which becomes transparent at 157°, $[\alpha]_D^{16}$ +18·2°, also obtained by ozonisation of (IV), and *diketodihydrolanosteryl acetate*, m.p. 156·5—158·8° and 160·5° after re-solidification, $[\alpha]_D^{16}$ +90·5° [also obtained from (V)], which is unaffected by N_2H_4,H_2O in EtOH at 180° or by boiling Ac_2O but is hydrolysed to *diketodihydrolanosterol*, m.p. 113—115°, $[\alpha]_D^{16}$ +78·3°. This, like (V), is oxidised to *diketodihydrolanostenone*, m.p. 105—107°, $[\alpha]_D^{16}$ +172·6°, reduced (Wolff–Kishner) to a yellow oil. A compound, m.p. 186·5—188·5°, probably *triketodihydrolanosteryl acetate*, is described. Dihydrolanostenone is transformed by NaOEt and amyl formate in MeOH into *hydroxymethylenedihydrolanostenone*, m.p. 124—126° (not const.), which gives a violet colour with $FeCl_3$ and a yellow colour with $C(NO_2)_4$. It is smoothly oxidised by H_2O_2 in alkaline solution to the dicarboxylic *acid*, $C_{30}H_{50}O_4$, m.p. 194·5—196°, $[\alpha]_D^{20}$ +86·7° (non-cryst. Me_2 ester), which passes at 280—310°/vac. of H_2O pump into *nordihydrolanostenone*, m.p. 113·5—115°, $[\alpha]_D^{20}$ +124·8° [*oxime*, m.p. 202° (decomp.)]. Dihydrolanostenone, m.p. 118—119°, $[\alpha]_D^{18}$ +70·2°, gives an *oxime*, m.p. 169—171°, and a *semicarbazone*, m.p. 236—238° (vac.; decomp.), which is converted by NaOEt–EtOH at 180° into *dihydrolanostene*, $C_{30}H_{52}$, m.p. 72·5—73·5°, $[\alpha]_D^{16}$ +104°, which gives an intense yellow colour with $C(NO_2)_4$; it is transformed by HCl in $CHCl_3$ into *isodihydrolanostene*, m.p. 79·5—80·5°, $[\alpha]_D^{15}$ +36°. (VI) is dehydrogenated (Cu powder) to γ-lanostenone, m.p. 128—129°, $[\alpha]_D^{16}$ +45·6° (oxime, m.p. 188·5—190·5°), converted through the semicarbazone, m.p. 222—225°, into *γ-lanostene*, m.p. 93—94·5° $[\alpha]_D^{15}$ +75·5°. M.p. are corr. and, unless otherwise stated, observed in open capillaries. $[\alpha]_D$ are in $CHCl_3$. H. W.

Triterpene group. XI. Non-saponifiable matter of *Lactucarium germanicum*. J. C. E. Simpson (*J.C.S.*, 1944, 283—286).—The non-saponifiable matter of *L. germanicum* is shown to be a complex mixture of triterpene alcohols; the substances, lactucerin, lactucon, α- and β-lacturerol, and α- and β-lactucol, isolated by previous workers were mixtures. Taraxasterol, β-amyrin, and a monohydric alcohol, *germanicol*, $C_{30}H_{50}O$, m.p. 176—177°, $[\alpha]_D^{17}$ +5·8° (*acetate*, m.p. 274—276°, $[\alpha]_D^{20}$ +18·1°; *benzoate*, m.p. 269—270°, $[\alpha]_D^{19}$ +39·0°), have been isolated. Rotations are in $CHCl_3$. F. R. S.

VI.—HETEROCYCLIC.

Configuration of α-βζ-epoxy-Δ$^\gamma$-heptene-γ-carboxylic [2 : 6-dimethyl-5 : 6-dihydro-1 : 2-pyran-3-carboxylic] acid. M. Delépine and G. Amiard (*Compt. rend.*, 1942, **215**, 309—312; cf. A., 1942, II, 248).—Decarboxylation of the βζ-epoxyheptane-γ-carboxylic acids could not be effected by prolonged heating alone or with Raney Ni or in quinoline containing Cu chromite at 250°, the only observed result being the transformation of the isomeride, m.p. 92°, into that of m.p. 89°. *dl*-2 : 6-Dimethyl-5 : 6-dihydro-1 : 2-pyran-3-carboxylic acid is decarboxylated by Cu chromite–quinoline at 250° to dl-2 : 6-*dimethyl*-5 : 6-*dihydro*-1 : 2-*pyran*, b.p. 115—117°/atm. pressure. Similarly the *d*-acid (I) affords (+)-2 : 6-*dimethyl*-5 : 6-*dihydro*-1 : 2-*pyran* (II), $[\alpha]_D$ +49·7° or +41·1° in Et_2O. The possibility that (I) is intermediately isomerised to 2 : 6-dimethyl-5 : 6-dihydro-1 : 4-pyran-3-carboxylic acid is excluded by the observation that this acid (*l*-form) is decarboxylated to (−)-2 : 6-*dimethyl*-5 : 6-*dihydro*-1 : 4-*pyran* (III), $[\alpha]_D$ −73·5°. (III) (*dl*-form) is transformed by H_2O at 75° into heptan-β-ol-ζ-one (*semicarbazone*, m.p. 105°, or *dihydrate*, m.p. 62°), whilst the optically active material gives an active *keto-alcohol*, $[\alpha]_D$ ~−1·6° (anhyd. *semicarbazone*, m.p. 103°, $[\alpha]_D$ −15° in H_2O). Under similar conditions there is no reaction with (II). Hydrogenation (PtO_2 in Et_2O) of the unsaturated compounds leads to dl-, b.p. 114°/762 mm., and (+)-, b.p. 113·5—115°, $[\alpha]_D$ +0·53°, -2 : 6-*dimethyltetrahydropyran*. Evidence of the reality of the optical activity is afforded. H. W.

Synthetic experiments in the benzpyrone series. VIII. Transformations of 5-hydroxycoumarin derivatives. B. Krishnaswamy, K. R. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 5—13; cf. A., 1942, II, 170).—5-Hydroxy-4 : 7-dimethylcoumarin (I), obtained from orcinol and $CH_2Ac{\cdot}CO_2Et$ in conc. H_2SO_4 at room temp. (overnight) or 100° (1 hr.) or in HCl–EtOH, is converted by $CH_2{:}CH{\cdot}CH_2Br$ and K_2CO_3 in boiling $COMe_2$ into the *allyl ether*, m.p. 127—128°, which at 160—165° gives 5-*hydroxy*-4 : 7-*dimethyl*-6-*allylcoumarin* (II), m.p. 178—179°, at 195—200° gives 4 : 7-*dimethyl*-Δ$^{2'}$-*dihydropyrano*-2′ : 3′-5 : 6-*coumarin* (III), m.p. 164—165°, and at 225—230° gives (III) and a small amount of 5-*hydroxy*-4 : 7-*dimethyl*-8-*allylcoumarin*, m.p. 239—240°. The structure of (II) is proved by conversion into (III) at 215—220°. In MeOH, (II) gives a $HgCl_2$ additive compound, m.p. 228—229°, converted by aq. KI–I at 100° into 4 : 7-*dimethyl*-5′-*iodomethyl*-, m.p. 166—167°, and thence (Na–EtOH) 4 : 7 : 5′-*trimethyl*-Δ$^{2'}$-*dihydrofurano*-2′ : 3′-5 : 6-*coumarin*, m.p. 205—206°. The difference of this compound from (III) proves the ring-structure of (III). 7-*Allyloxy*-5-*methylcoumarin* (prep. as above), m.p. 78—79°, at 200—205° or, less well, 230—240° gives 7-*hydroxy*-5-*methyl*-8-*allylcoumarin*, m.p. 174—175°. The acetate, m.p. 199—200° (lit. 195°), of (I) with $AlCl_3$ at 130—170° gives 5-*hydroxy*-6-*acetyl*-4 : 7-*dimethylcoumarin*, m.p. 177—178°. The result of Fries rearrangement in the coumarin series depends on the nature and position of substituents and on the experimental conditions. R. S. C.

Azo-dye formation by 5-hydroxycoumarins. S. Rangaswami and K. R. Rao (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 14—16).—With 1 mol. of *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ at 0° 5-hydroxy-7-methyl- or -4 : 7-dimethyl-coumarin in NH_3–EtOH–H_2O or 7-hydroxy-5-methylcoumarin in aq. Na_2CO_3 gives monoazo-*dyes*, but with >2 mols. gives mixed mono- and bis-azo-dyes. R. S. C.

Anthochlor pigments. V. Pigments of *Coreopsis grandiflora*, Nutt. II. T. A. Geissman and C. D. Heaton (*J. Amer. Chem. Soc.*, 1944, **66**, 486—487; cf. A., 1943, II, 274).—5 : 6-Dimethoxy-2-coumaranone [prep. from 3 : 4 : 5 : 1-$(OH)_3C_6H_2{\cdot}CO{\cdot}CH_2Cl$ by Me_2SO_4–

Na_2CO_3–H_2O), m.p. 122—123°, and 3 : 4 : 1-$(OMe)_2C_6H_3$·CHO (I) in warm NaOH–EtOH–H_2O give 5 : 6 : 3′ : 4′-tetramethoxybenzylidene-2-coumaranone (84%), m.p. 156—157°, identical with leptosidin Me_3 ether. 3 : 4 : 5 : 1-OH·C_6H_2(OMe)$_2$·COMe and (I) in warm NaOH–EtOH–H_2O give 2 : 3 : 4-OH·$C_6H_2(OMe)_2$·CH:CH·$C_6H_3(OMe)_2$-3 : 4, m.p. 121—122° (lit. 119°), cyclised in boiling HCl–EtOH–H_2O to 7 : 8 : 3′ : 4′-tetramethoxyflavanone, m.p. 143·5—144° (and a small amount of another substance), identical with the Me_3 ether of the naturally occurring flavanone. R. S. C.

Synthesis of hibiscetin. P. R. Rao, P. S. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 88—92).—2 : 6 : 1 : 4-$(CH_2Ph·O)_2C_6H_2(OMe)_2$ with OMe·CH_2·CN, $ZnCl_2$, and HCl in Et_2O and then H_2O at 100° gives 2 : 6-dihydroxy-3 : 6 : ω-trimethoxyacetophenone (I), m.p. 150—151°, by way of its semi-solid ketimine hydrochloride (formed with a by-product, m.p. 110—112°). The $ZnCl_2$ is responsible for the hydrolysis, since this does not occur in absence of $ZnCl_2$. 3 : 4 : 5 : 1-$(OMe)_3C_6H_2·CO_2Na$, [3 : 4 : 5 : 1-$(OMe)_3C_6H_2·CO]_2O$, and (I) at 175—180°/vac. give a moderate yield of 7-*hydroxy*-3 : 5 : 8 : 3′ : 4′ : 5′-*hexamethoxyflavone*, m.p. 238—240°, whence Me_2SO_4–NaOH yields hibiscetin Me_7 ether, hydrolysed by boiling HI–Ac_2O to hibiscetin (A., 1942, II, 327). R. S. C.

Constitution of belmacamgenin and belmacamdin. S. Wang and M. Hu (*J.C.S.*, 1944, 307).—From the powdered root of *Belmacamda*, there has been isolated belmacamdin (I), m.p. >300°, which is hydrolysed (HCl–EtOH) to belmacamgenin (II), m.p. 227°, and glucose. (II) is probably a pentahydroxymonomethoxy*iso*flavone and it forms an Ac derivative, m.p. 184—185°, and Me_2 ether, m.p. 162°. Methylation of (I) followed by hydrolysis (HCl–EtOH) yields a compound, m.p. 165°, identical with 7 : 3′-dimethylirigenin F. R. S.

Oxidation of catechin to cyanidin : applications of the reaction. J. Lavollay and M. Vignau (*Compt. rend.*, 1943, **217**, 86—88).—Oxidation of catechin (I) to cyanidin is effected, without protecting the OH groups (cf. Appel *et al.*, A., 1935, 757), by adding $Fe_2(SO_4)_3$, $K_3Fe(CN)_6$, CuO, MnO_2, $KClO_3$, $NaBO_3$, or $K_2S_2O_8$, in conc. H_2SO_4 to (I) in $COMe_2$; the diluted mixture is extracted with *iso*-C_5H_{11}·OH. Possible applications of the reaction are discussed. A. T. P.

Auroxanthin. II. P. Karrer and J. Rutschmann (*Helv. Chim. Acta*, 1944, **27**, 320).—Auroxanthin, m.p. 203°, obtained in very small amount from the blossoms of the yellow pansy, is $C_{30}H_{56}O_4$. Micro-hydrogenation indicates the presence of 9 double linkings. Acetylation (Ac_2O in C_5H_5N) appears to cause profound changes. H. W.

Dioxans.—See B., 1944, II, 157.

Reactions of anthocyanins with molybdate. H. Blaschko (*Proc. Biochem. Soc.*, 1944, **38**, xxxii—xxxiii).—Colour develops only on addition of NH_4 molybdate to solutions in 1% HCl of anthocyanins that contain free vicinal OH groups, *e.g.*, cyanidin and delphinidin. P. G. M.

Thiochroman derivatives with tocopherol structure. P. Karrer and P. Leiser (*Helv. Chim. Acta*, 1944, **27**, 678—684).—*m*-2-Xylenol is converted by H_2SO_4,H_2O at 100—110° into 1 : 2 : 6 : 4-OH·$C_6H_2Me_2$·SO_3Na, which with $ClCO_2Et$ and NaOH affords *Na* O-*carbethoxy*-2 : 6-*dimethylphenol*-4-*sulphonate*. The corresponding *sulphonyl chloride*, m.p. 127°, is reduced by Zn dust and HCl in EtOH to 4-*thiol*-2 : 6-*dimethylphenol* (I), m.p. 86°. This with phytol in boiling HCO_2H yields 6-hydroxy-5 : 7-dimethyl-2-δθμ-trimethyltridecylthiochroman (5 : 7-dimethylthiotocol), isolated as the *acetate* (II), b.p. 190—205°/0·001 mm. Condensation of (I) with CMe_2:CH·CH_2·OH [prep. from CMe_2:CH·CHO and Al(OPr$^\beta$)$_3$ described] gives 6-*hydroxy*-2 : 2 : 5 : 7-*tetramethylthiochroman* (III), b.p. 120—125°/0·002 mm. Trimethyl-*p*-benzoquinonemonoxime, m.p. 182°, is reduced ($Na_2S_2O_4$ in hot EtOH) to 4 : 2 : 3 : 6 : 1-NH_2·C_6HMe_3·OH, which affords 2 : 3 : 6 : 1-$C_6H_2Me_3$·OH when diazotised and heated with Zn dust. This yields 1 : 2 : 3 : 6 : 4-OH·C_6HMe_3·SO_3Na, converted by $ClCO_2Et$ and NaOH into *Na* O-*carbethoxy*-2 : 3 : 6-*trimethylphenol*-4-*sulphonate* (+1H_2O). The corresponding *sulphonyl chloride* gives 4-*thiol*-2 : 3 : 6-*trimethylphenol*, m.p. 87° (Pb salt), which yields 6-*hydroxy*-5 : 7 : 8-*trimethyl*-2-δθμ-*trimethyltridecylthiochroman* (IV), b.p. 215—225° (bath)/0·001 mm. (II), (III), and (IV) like the tocopherols have marked reducing power and are oxidised by $FeCl_3$, $AuCl_3$, or $AgNO_3$. With $FeCl_3$ in presence of 2 : 2′-dipyridyl they appear to require 3 equivs. of oxidising agent probably on account of the conversion of thiol into disulphide. Oxidation with $AuCl_3$ is apparently not homogeneous. (II) is without vitamin-*E* action and is not antagonistic to α-tocopherol acetate. H. W.

Pyrolysis of xanthopinacol and related compounds. A. Schönberg and A. Mustafa (*J.C.S.*, 1944, 305—306).—When heated in CO_2, xanthhydrol gives H_2O, xanthen (I), and xanthone (II); dixanthhydryl ether forms (I) and (II); xanthopinacol affords H_2O, (I) and (II), and thioxanthhydrol yields thioxanthen, thioxanthone, and dithiodixanthylen. F. R. S.

Synthesis of compounds of the indole and trimethylenepyrrole type. Buu-Hoï and P. Cagniant (*Compt. rend.*, 1943, **217**, 26—28).—ω-Δ²-cyclo*Pentenyl*-ωω-*dimethylacetophenone*, b.p. 165—168°/12 mm., or -ω-*methyl*-ω-*ethyl*-, b.p. 180—182°/10 mm., or -ω-*methyl*-ω-*benzylacetophenone*, b.p. 232—235°/10 mm. (from ω-Δ²-cyclo*pentenyl*-ω-*methylacetophenone*, b.p. 158—160°/10 mm., and BzCl), is converted by $NaNH_2$ in boiling PhMe into 4 : 5-*trimethylene*-3 : 3-*dimethyl*-, m.p. 89—90°, b.p. 158—162°/13 mm., -3-*methyl*-3-*ethyl*-, b.p. 180—182°/12 mm., and -3-*benzyl*-3-*methyl*-2-*pyrrolidone*, b.p. 232—236°/9 mm., respectively. With the last-named compound, some β-Δ²-cyclo*pentenyl*-γ-*phenylpropane*, b.p. 137—140°/10 mm., is isolable. ω-Δ²-cyclo*Hexenyl*-ωω-*dimethylacetophenone*, b.p. 182—185°/14 mm., gives 2-*keto*-3 : 3-*dimethyloctahydroindole*, m.p. 127·5—128°. Δ²-cyclo*Pentenylphenylacetonitrile*, b.p. 165—168°/10 mm., obtained from Δ²-chloro*cyclo*pentane and CH_2Ph·CN (Na), is converted (Na derivative) by Ph·$[CH_2]_2$·Br into Δ²-cyclo*pentenophenyl*-β-*phenylethylacetonitrile*, b.p. 202—205°/0·5 mm. CH_2:CH·CH_2·CO_2H gives an amide, m.p. 94°, not cyclised by $NaNH_2$ in boiling PhMe. No analyses of the compounds are given. A. T. P.

Synthetic analgesics. I. Synthesis of basic benzofuran derivatives and certain 4-phenylpiperidine compounds. F. Bergel, J. W. Haworth, A. L. Morrison, and H. Rinderknecht. **II. New synthesis of pethidine and similar compounds.** F. Bergel, A. L. Morrison, and H. Rinderknecht. **III. Action of hydrogen halides on ethers of αα-bis-(β′-hydroxyethyl)phenylacetonitrile.** F. Bergel, A. L. Morrison, and H. Rinderknecht. **IV. Synthesis of 3-substituted piperidines and pyrrolidines.** F. Bergel, N. C. Hindley, A. L. Morrison, and H. Rinderknecht (*J.C.S.*, 1944, 261—265, 265—267, 267—269, 269—272).—I. Acetylpæonol, paraformaldehyde (I), and $NHMe_2$,HCl in EtOH give *β-dimethylamino*-2-*acetoxy*-4-*methoxypropiophenone hydrochloride* (II), m.p. 175°, hydrolysed (HCl) to the -2-*OH*-compound (III), m.p. 166—167°. Similarly pæonol with $C_5H_{11}N$,HCl and (I) affords *β-piperidino*-2-*hydroxy*-4-*methoxypropiophenone hydrochloride*, m.p. 188—189°. CH_2BzBr and (III) with KOH do not form a coumarone but yield $CH_2Bz·NMe_2$ with some 2-hydroxy-4-methoxyphenyl vinyl ketone, isolated as the 2 : 4-*dinitrophenylhydrazone*, m.p. 244—245°. Et 5-methoxy-2-acetylphenoxyacetate, (I), and $NHMe_2$,HCl give *Et* 2-*β-dimethylaminopropionyl*-5-*methoxyphenoxyacetate* (IV), m.p. 149° (-*piperidino*-compound, m.p. 134°), and the corresponding *acid*, m.p. 197° (-*piperidino*-compound, m.p. 183—184°), is similarly prepared. Ac_2O–NaOAc with (IV) causes disruption of the mol. Addition of Br in AcOH to (II) leads to *α-bromo-β-dimethylamino*-2-*acetoxy*-4-*methoxypropiophenone hydrobromide*, m.p. 161°, of which the -2-*OH*-compound, m.p. 179°, with K_2CO_3–$COMe_2$ affords the unstable 2-dimethylaminomethyl-6-methoxycoumaranone hydrochloride, m.p. 144—145° (*picrate*, m.p. 123—124°; polymeric *substance*, $C_{12}H_{16}O_3NCl$). *o*-Vanillin with CH_2AcCl and KOH–EtOH gives 7-*methoxy*-2-*acetylcoumarone*, m.p. 92°, which with (I) and $C_5H_{11}N$,HCl affords 2-*β-piperidinopropionyl*-7-*methoxycoumarone hydrochloride*, m.p. 170—172° (*picrate*, m.p. 158—159°). The *azlactone*, m.p. 167—169°, of 2-benzyloxybenzaldehyde with NaOH in N_2 yields 2-*benzyloxyphenyl*-*pyruvic acid*, m.p. 119—120°, converted through the oxime into the -*acetonitrile* (V), m.p. 75—77°. *o*-CN·C_6H_4·CH_2·CN is similarly obtained from the *azlactone*, m.p. 154—156°, of 2-OMe·C_6H_4·CHO, and 2 : 3-*dimethoxyphenylacetonitrile*, b.p. 158—160°/12 mm., from the *azlactone*, m.p. 167—168°, of 2 : 3-$(OMe)_2C_6H_3$·CHO. (Cl·$[CH_2]_2)_2$NH, $NaNH_2$, and (V) in PhMe give 4-(2′-*benzyloxyphenyl*)-1-*methylpiperidine*-4-*nitrile hydrochloride*, m.p. 220—221°, which with HCl (sealed tube) affords the *hydrochloride* of 4-(2′-*hydroxyphenyl*)-1-*methylpiperidine*-4-*carboxylic acid lactone* (+0·5H_2O), m.p. 260—263°. The corresponding acetonitriles yield respectively 4-(2′ : 3′-*dimethoxyphenyl*)-1-*methylpiperidine*-4-*nitrile*, m.p. 107—110°, and 4-(2′-*hydroxy*-3′-*methoxyphenyl*)-1-*methylpiperidine*-4-*carboxylic acid lactone*, m.p. 115—117°, and 4-(2′-*methoxyphenyl*)-1-*methylpiperidine*-4-*nitrile*, m.p. 97—99°, which with MgMeI affords 4-*acetyl*-4-(2′-*methoxyphenyl*)-1-*methylpiperidine* (VI) (picrate, m.p. 197—200°). 4-Acetyl-4-phenyl-1-methylpiperidine with Na–EtOH gives 4-*phenyl*-1-*methyl*-4-(α-*hydroxyethyl*)*piperidine*, m.p. 117—119°. Na–EtOH and (VI) yield 2-*methyl*-3-4′-spiro-(1′-*methylpiperidine*)*coumaran* (*picrate*, m.p. 182—184°). 4-Phenyl-1-methylpiperidine-4-nitrile and Na–EtOH form 4-phenyl-1-methylpiperidine (*picrate*, m.p. 239—240°), identical with that obtained by decarboxylation of the corresponding -4-carboxylic acid. 4-(2′-*Hydroxyphenyl*)-, m.p. 179—181°, and 4-(2′ : 3′-*dimethoxyphenyl*)-1-*methylpiperidine*, b.p. 125—127°/1 mm. (*picrate*, m.p. 159—162°), are similarly prepared; the latter is hydrolysed to the (*OH*)$_2$-compound, m.p. 200—205°. γ-*Diethylamino*-α-*phenyl*-α-*ethylbutyronitrile*, b.p. 161—166°/10—12 mm., is similarly reduced to γ-*phenyl*-n-*amyldiethylamine*, b.p. 134°/15 mm. 4-Phenyl-1-methylpiperidine-4-nitrile is reduced (H_2–$PdCl_2$) to *bis*-(4-*phenyl*-1-*methylpiperidyl*-4-*methyl*)*amine*, m.p. 90—93°.

II. $CH_2Cl·OMe$ with $(CH_2)_2O$ and $HgCl_2$ give *Me β-chloroethyl formal*, b.p. 134—139°; *β-chloroethyl Et formal*, b.p. 62—65°/50 mm., is similarly prepared. $CH_2Ph·CN$ with $NaNH_2$ and Cl·$[CH_2]_2$·O·CH:CH_2 affords αα-*bis*-(β′-*vinyloxyethyl*)*phenylacetonitrile* (VII), b.p. 125—135°/0·15 mm., hydrolysed (HCl) to αα-*bis*-(β′-*hydroxyethyl*)*phenylacetonitrile*, m.p. 96—98° [also obtained by mild acid hydrolysis of αα-*bis*-(β′-*methoxymethoxyethyl*)*phenylacetonitrile*, b.p. 147—155°/0·05—0·1 mm.], which with $SOCl_2$ and $NPhEt_2$ yields the αα-*bis*-(β′-*chloroethyl*) compound, m.p. 52°. This nitrile

condenses with NH_2Me in EtOH (sealed tube) to 4-phenyl-1-methylpiperidine-4-nitrile, which is identical with that obtained by Eisleb's method (cf. *Ber.*, 1942, **75**, 1435), and is hydrolysed to the 4-carboxylic acid. From the acid, the *hydrochlorides* of the *Prα*, m.p. 181—183°, *Prβ*, m.p. 192—195°, *OH·[CH₂]₂*, m.p. 195—200°, *allyl*, m.p. 155—158°, and cyclo*hexyl* esters, m.p. 234—236°, are prepared; the Et ester is pethidine. A similar series of reactions leads to *αα-bis-(β'-vinyloxyethyl)-*, b.p. 135—140°/0·1 mm., and *-(β'-hydroxyethyl)-o-tolylacetonitrile*, m.p. 95—100°, 4-(*o*-tolyl)-1-methylpiperidine-4-nitrile [*hydrochloride*, m.p. 279—280°; *picrate*, m.p. 265° (decomp.)], and *Et* 4-(o-*tolyl*)-1-*methylpiperidine*-4-*carboxylate*, b.p. 175°/11 mm. (*hydriodide*, m.p. 175—176°).

III. $CH_2Ph·CN$, $NaNH_2$, and $Br·[CH_2]_2·OEt$ in PhMe give *αα-bis-(β'-ethoxyethyl)phenylacetonitrile*, b.p. 120—123°/0·05 mm., which with aq. HBr (sealed tube) forms *α-phenyl-α-(β'-bromoethyl)-butyrolactone*, b.p. 140—142°/0·2 mm. (*Cl*-compound, an oil), converted by piperidine into the *-piperidino*-compound, b.p. 154°/0·1 mm. (*hydrochloride*, m.p. 217—217°). Aq. HCl and (**VII**) afford *α-phenyl-α-(β'-hydroxyethyl)butyrolactone*, b.p. 172°/0·1 mm. 4-Phenylpentamethylene oxide-4-nitrile and aq. HBr (sealed tube) yield *phenylαα-bis-(β'-bromoethyl)acetic acid*, m.p. 118° [also obtained from (**VII**) and HBr], which with EtOH–HCl followed by NH_2Me gives pethidine.

IV. $CH_2Ph·NHMe$ and $Br·[CH_2]_3·Cl$ give *benzylmethyl-γ-chloropropylamine* (**VIII**), b.p. 137—138°/16 mm. $CH_2Ph·CN$ and bromoacetal with $NaNH_2$ in Et_2O afford *β-cyano-β-phenylpropaldehyde diacetal*, b.p. 120—121°/0·2 mm., which is hydrolysed (HCl in N_2) to *β-cyano-β-phenylpropaldehyde*, b.p. 109—111°/0·1 mm. $CH_2Ph·CN$ and benzylmethyl-β-chloroethylamine (**IX**) with $NaNH_2$ yield *γ-benzylmethylamino-α-phenylbutyronitrile*, b.p. 158°/0·1 mm. (*reineckate*, m.p. 104—107°), which is reduced (H_2–C–$PdCl_2$) to 3-*phenyl*-1-*methylpyrrolidine*, b.p. 105—110°/11 mm. (*picrate*, m.p. 155—158°). $CN·CHPh·CO_2Et$ and Na in Et_2O with (**IX**) lead to *Et α-cyano-γ-benzylmethylamino-α-phenylbutyrate*, b.p. 176—178°/0·2 mm., which is hydrogenated to *Et* 3-*phenyl*-1-*methylpyrrolidine*-3-*carboxylate*, b.p. 114°/0·4 mm. (*picrate*, m.p. 115—118°). $CN·CHPh·CO_2Et$ with (**VIII**) and $NaNH_2$ forms *Et α-cyano-δ-benzylmethylamino-α-phenylvalerate*, b.p. 180°/0·2 mm., hydrogenated to *Et* 3-*phenyl*-1-*methylpiperidine*-3-*carboxylate*, b.p. 104°/0·2 mm. (*hydrochloride*, m.p. 177—180°; *hydriodide*, m.p. 207°); the *acid* (*picrate*, m.p. 196—199°) formed by hydrolysis of the preceding ester gives a Me ester (*hydrochloride*, m.p. 177—179°), Prα ester, b.p. 110°/0·2 mm. (*hydrochloride*, m.p. 174—175°), Prβ ester, b.p. 110°/0·2 mm. (*hydrochloride*, m.p. 191—193°), and *diethylamide*, b.p. 125—128°/0·1 mm. *o*-$C_6H_4Me·CH_2·CN$ with $NaNH_2$ and Et_2CO_3 affords *Et* o-*tolylcyanoacetate*, b.p. 110—114°/0·1 mm., which with (**VIII**) and $NaNH_2$ yields *Et α-cyano-δ-benzylmethylamino-α-o-tolylvalerate*, b.p. 199—200°/0·2 mm., hydrogenated to *Et* 3-(o-*tolyl*)-1-*methylpiperidine*-3-*carboxylate*, b.p. 126—128°/0·2 mm. (*hydrochloride*, m.p. 200—201°; *hydriodide*, m.p. 178—180°). Using the appropriate reagents the following are prepared similarly: *Et α-cyano-δ-benzylmethylamino-α-benzylvalerate*, b.p. 225—235°/0·4 mm.; *Et* 3-*benzyl*-1-*methylpiperidine*-3-*carboxylate*, b.p. 125—135°/0·3 mm.; *Et δ-chloro-α-cyano-α-phenylvalerate*, b.p. 128—129°/0·1 mm.; *Et α-cyano-δ-dibenzylamino-α-phenylvalerate*, b.p. 215—217°/0·1 mm.; *Et αγ-*, b.p. 145°/0·1 mm., and *αβ-dicyano-α-phenylbutyrate*, b.p. 141—142°/0·1 mm.; *Et* 3-*phenylpiperidine*-3-*carboxylate*, b.p. 115—117°/0·1 mm. (*NO*-derivative, m.p. 88—89°); and *Et* 3-*phenylpyrrolidine*-3-*carboxylate*, b.p. 97°/0·1 mm. F. R. S.

Tetra- and hexa-hydronicotinic acid as growth-promoting factors for *Staphylococcus aureas* and *Bacillus proteus vulgaris*. H. von Euler, B. Högberg, P. Karrer, H. Salomon, and H. Ruckstuhl (*Helv. Chim. Acta*, 1944, **27**, 382—390).—The isolation of 1 : 2 : 5 : 6-tetrahydronicotinic acid (**I**), its 1-Me derivative, and arecoline from technical residues is described. Me 1 : 2 : 5 : 6-tetrahydronicotinate hydrochloride is converted by $NaNO_2$ and HCl into the NO-derivative of the ester, transformed by liquid NH_3 into 1-*nitroso*-4-*aminopiperidine*-3-*carboxylamide*, m.p. 172° (*hydrochloride*, m.p. 227—228°). (**I**), $ClCO_2Et$, and Na_2CO_3 give 1-*carbethoxy*-1 : 2 : 5 : 6-*tetrahydronicotinic acid*, m.p. 78°, converted by successive treatments with $SOCl_2$ and NH_3–Et_2O into 1-*carbethoxy*-1 : 2 : 5 : 6-*tetrahydronicotinamide*, m.p. 136—137°, from which CO_2Et could not be removed without involving $·CO·NH_2$. (See also A., 1944, III, 616.) H. W.

Heterocyclic ketones. IV. Properties of αα-dihalogeno-derivatives of heterocyclic nitrogen compounds. E. I. Elkina and M. M. Schemjakin (*J. Gen. Chem. Russ.*, 1943, **13**, 301—303).—2 : 2-Dichloro-*N*-methyldihydropyridine (**I**) and the corresponding quinoline derivative react immediately with H_2O to form *N*-methyl-2-pyridone and *N*-methylcarbostyril respectively. (**I**) is converted by liquid NH_3 into 2-imino-*N*-methyldihydropyridine, and by NH_2Ph into the corresponding anilo-derivative. R. C. P.

Oxidation of nicotine to nicotinic acid. N. A. Vasiunina, A. A. Beer, and N. A. Preobrashenski (*J. Appl. Chem. Russ.*, 1943, **16**, 206—210).—5 g. of nicotine (**I**) + 25 ml. of 27% HNO_3 are added dropwise to 180 ml. of 27% HNO_3 at 98°, and the mixture is kept at 98° for 3 hr. (yield 70%). 5 g. of (**I**) + 20 ml. of H_2O are slowly introduced into $KMnO_4$ 20 g. in H_2O 80 g. at 70°, $KMnO_4$ crystals are slowly added to the solution, and the mixture is kept for 1 hr. at 80—85° (yield 80%). 5 g. of (**I**) + 50 ml. of 35% H_2SO_4 are added within 1 hr. to 41 g. of $MnO(OH)_2$ + 100 ml. of 35% H_2SO_4 at 100—105° (yield 75%). J. J. B.

Isolation of the nicotinamide formed from asparagine and glutamic acid. M. R. Bovarnick (*J. Biol. Chem.*, 1944, **153**, 1—3; cf. A., 1944, II, 116).—Pure nicotinamide has been isolated by extraction of the mixture formed by heating solutions of asparagine and glutamic acid with Et_2O, followed by repeated recrystallisation of the extract from C_6H_6. J. Ho.

Nicotinamides.—See B., 1944, II, 157.

Sulphanilamide derivatives. F. S. Spring and E. P. H. Young (*J.C.S.*, 1944, 248—249).—Sulphanilamide derivatives with alkyl attached to N^1 are prepared, to test their tuberculocidal properties, but they are inactive. Adipamide and Br–33% aq. NaOH at 100° (bath), followed by cold *p*-$NO_2·C_6H_4·SO_2Cl$ (**I**) or *p*-$NHAc·C_6H_4·SO_2Cl$ (**II**) in Et_2O, give *NN'-di-*(p-*nitrobenzenesulphonyl*)- (**III**), m.p. 201°, or *NN'-di*(*acetylsulphanilyl*)-*tetramethylenediamine* (**IV**), m.p. 233° (sinters at 218°), respectively. (**III**) is converted by Sn in boiling HCl–EtOH into *NN'-disulphanilyltetramethylenediamine*, m.p. 205° (hydrochloride, m.p. 241°), also obtained from (**IV**) and boiling HCl–EtOH. *n*-$C_{17}H_{35}·NH_2$ and (**I**) in Et_2O yield *heptadecyl*-p-*nitrobenzenesulphonamide*, m.p. 90·5°, converted by Sn–HCl into N^1-n-*heptadecylsulphanilamide*, m.p. 118°, also prepared by hydrolysis of its N^4-*Ac* derivative, m.p. 128°, obtained from (**II**) in Et_2O. 2-*n*-Propylaminopyridine and (**II**) in dry C_5H_5N give N^1-2-*pyridyl*-N^1-n-*propylsulphanilamide*, m.p. 108°. 2-Aminopyridine (**V**) and $NaNH_2$–C_5H_5N, followed by *n*-$C_5H_{11}Br$ (2 days at room temp., then reflux for 3 hr.), yield 2-n-*amylaminopyridine*, m.p. 43°, b.p. 130—135°/12 mm. (*picrate*, m.p. 121°), converted by (**II**) in C_5H_5N into the N^4-*Ac* derivative, m.p. 83°, hydrolysed to N^1-2-*pyridyl*-N^1-n-*amylsulphanilamide*, m.p. 74—75°. 2-Cetylaminopyridine, b.p. 210—220°/12 mm., m.p. 67° (wax) (*picrate*, m.p. 84°); gives, through the N^4-*Ac* derivative, m.p. 88°, and aq. NaOH–EtOH, N^1-2-*pyridyl*-N^1-*cetylsulphanilamide*, m.p. 77°. 2-*Octadecylaminopyridine*, b.p. 180—185°/0·01 mm., m.p. 66—67° (waxy), affords N^1-2-*pyridyl*-N^1-*octadecylsulphanilamide*, m.p. 70—71°. (**V**), $NaNH_2$, and xylene at 100° (bath), then geranyl chloride at 150° for 3 hr., give 2-*geranylaminopyridine*, b.p. 185—190°/12 mm. (*picrate*, m.p. 125°), converted into N^1-*geranyl*-N^1-2-*pyridylsulphanilamide*, m.p. 75—76°. *n*-$C_{18}H_{37}Cl$, 6-amino-2-methylpyridine, and $NaNH_2$ (2 days) yield 2-*octadecylamino*-6-*methylpyridine*, b.p. 205°/0·25 mm., m.p. 46° (*picrate*, m.p. 101°), which gives, through the N^4-*Ac* derivative, m.p. 84°, N^1-2-(6-*methylpyridyl*)-N^2-*octadecylsulphanilamide*, m.p. 77—78°. A. T. P.

Synthesis of *dl*-tryptophan. H. R. Snyder and C. W. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 350—351).—$CH_2(CO_2Et)_2$ with, successively, $NaNO_2$–H_2O–AcOH at 20°, H_2–Pd–C–EtOH at 1500 lb., and Ac_2O–EtOH gives $NHAc·CH(CO_2Et)_2$, the Na derivative of which, when treated with 3-indolylmethyltrimethylammonium iodide (**I**) (A., 1944, II, 234) in xylene–dioxan at 92°, raised gradually to 125°, gives *Et α-acetamido-α-carbethoxy-β-3-indolylpropionate*, m.p. 158°. Hot aq. NaOH then gives the corresponding *NHAc-acid*, m.p. 144·5° (decomp.), which in boiling H_2O gives acetyl-*dl*-tryptophan and thence, by hot aq. acid, *dl*-tryptophan, the yield being ~45% calc. on the indole used to prepare (**I**). R. S. C.

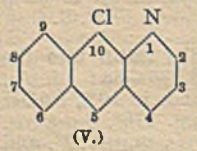
Synthesis of tryptophan. N. F. Albertson, S. Archer, and C. M. Suter (*J. Amer. Chem. Soc.*, 1944, **66**, 500).—3-Indolyldimethylethylammonium iodide with $CRNa(CO_2Et)_2$ (R = H, NHAc, or NHBz) (cf. Snyder, A., 1944, II, 234) gives Et α-carbethoxy-β-3-indolylpropionate, *α-acet-*, m.p. 157°, and *α-benz-amido-α-carbethoxy-β-3-indolylpropionate*, m.p. 142°, and thence the derived dicarboxylic *acids*, m.p. 187—189°, 135—137° (decomp.), and 85—90° (decomp.), respectively, and by decarboxylation (180—200°) thereof β-3-indolylpropionic acid, m.p. 128—130°, and its α-NHAc- and α-NHBz-derivatives, whence tryptophan is obtained in yields up to 35% calc. on the indole used. R. S. C.

Isatin and ammonia. III. Enlargement of the isatin into the quinazoline ring. G. Jacini (*Gazzetta*, 1943, **73**, 85—88; cf. A., 1944, II, 234).—Isatin-3-anil and similar compounds in 10% NaOH with 20% aq. NH_3 and H_2O_2 give 3-*phenyl-*, m.p. 276°, 3-o-*tolyl-*, m.p. 246°, 3-p-*aminophenyl-*, m.p. 311°, 3-p-*anisyl-*, m.p. 229°, and 3-α-*naphthyl*-2 : 4-*diketotetrahydroquinazoline*, m.p. 268°. *Isatin*-3-p-*anisylimide* has m.p. 229°. E. W. W.

Condensations with Michler's ketone (formation of dyes). H. L. Kehlstadt (*Helv. Chim. Acta*, 1944, **27**, 685—701).—The condensation of $CO(C_6H_4·NMe_2-p)_2$ (**I**) with 2-methylquinoline (**II**) and analogous substances and the reactions of the product with organo-metallic compounds are described. (**I**), (**II**), and $AlCl_3$ at 170° yield *αα-dipp'-tetramethyldiaminodiphenyl-β-2-quinolylethylene* (**III**), m.p. 178—179°; condensation with $ZnCl_2$ is less satisfactory. The presence of unchanged (**I**) in (**III**) can be detected by the formation of an

immediate blue colour when a solution of (I) is reduced by Na–Hg and then acidified (AcOH). (III) is yellow but becomes orange when exposed to sunlight. (III) gives strongly coloured salts involving the ring N and nearly or completely colourless salts involving the N in NMe_2. There are obtained the yellowish *triperchlorate*, decomp. 238°, red *monoperchlorate*, m.p. 238°, dark *monopicrate*, m.p. 200° (decomp.), *styphnate*, almost colourless, very unstable hydrochloride, and a dark red, non-hygroscopic, cryst. *hydrochloride*, m.p. 210°, *methiodide*, decomp. 170°, *ferrocyanide*, and an *adduct* with Me_2SO_4. (III) dyes mordanted cotton in brownish-red shades. (I), (II), and $NaNH_2$ at 140—150° give 2-*quinolylmethyldi*-pp-*tetramethyldiaminodiphenylcarbinol* (IV), m.p. 187°, becomes yellow. (IV) is not readily converted into a dye. It is stable towards cold mineral acids, gives a colourless, cryst. *perchlorate*, m.p. (indef.) 180°, and can be cryst. Short warming with org. acids, preferably HCO_2H, leads to pure (III). MgPhBr could not be added to (III). LiPh and highly purified (III) yield a product which, after decomp. with dil. acid, gives a green solution resembling malachite-green (V) and darkening when heated. It appears definite that the addition of the third Ph leads to a system in which the tenaciousness of the Ph residues is inadequate so that appreciable if not considerable hydrolysis to $OH{\cdot}CPh(C_6H_4{\cdot}NMe_2)_2$ occurs. Attempts to determine the (V) which is formed lead to the disclosure that union with LiPh is never complete. (V) cannot be separated by crystallisation and iodometric, titanometric, colorimetric, and chromatographic assays are unsatisfactory, but (V) can be determined by treatment with NH_3 in $CHCl_3$, alcoholysis of the product, and titration of the NH_3 produced. An optical method is also described. (III) is reduced (H_2 at 70—80°/120 atm.; Ni in EtOAc–EtOH–H_2O) to *αα-di*-pp′-*tetramethyldiaminodiphenyl-β*-1 : 2 : 3 : 4-*tetrahydro*-2-*quinolylethane* (VI), m.p. 106—107°, which gives colourless salts (very hygroscopic *hydrochloride*, m.p. 190°) and with $CH_2Br{\cdot}CO_2Et$ a material, decomp. 100—110°. As *sec.* base it affords a *Bz* derivative, m.p. 153—154°, and a *NO-amine*, but it could not be acetylated. The amorphous, hygroscopic *methiodide*, m.p. 154—156°, and yellow *picrate*, softens 148—158°, are described. (VI) is readily oxidised by PbO_2 or chloranil but the dark green-blue product is not a dye. (I) and $CH_2Ph{\cdot}MgCl$ in C_6H_6 afford α-phenyl-ββ-di-pp′-tetramethyldiaminodiphenylethylene (VII), m.p. 131°, which gives a dark blue-green solution in AcOH becoming colourless on addition of mineral acid. (VII) yields a colourless *hydrochloride*, m.p. 190—192°, a yellow *picrate*, m.p. 182—190° (decomp.), and a yellow *methiodide*, m.p. 195°. It is reduced (H_2 at 80—90°/115 atm.; Ni in EtOAc–EtOH–H_2O) but not by Na and EtOH to *α-phenyl-ββ-di*-pp′-*tetramethyldiaminodiphenylethane* (VIII), m.p. 131·5—132·5° [colourless *perchlorate*, m.p. 207—211° (decomp.); yellow *picrate*, m.p. 186°; pale yellow *methiodide*, m.p. 212°], also obtained in very poor yield from $CH_2Ph{\cdot}CHO$, $NPhMe_2$, and $ZnCl_2$ in boiling PhMe. (VIII) gives a green-blue or violet colour when oxidised by PbO_2 or chloranil respectively. $OH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$ (IX) and (II) in boiling AcOH afford *αα*-di-*pp′*-tetramethyldiaminodiphenyl-β-2-quinolylethane, m.p. 130—132° (colourless *triperchlorate*; brown-red *formate*, m.p. 57—58°; colourless *methiodide*, m.p. 153—155°), oxidised by PbO_2 to a dark red solution; it is hydrogenated to (VI). (IX) and phenylmethylpyrazolone in AcOH at 100° afford *tetramethyldiaminodiphenylphenylmethylpyrazolylmethane*, m.p. 185—195° (much decomp.), oxidised to a blue solution by PbO_2 and to a violet-red solution by chloranil. H. W.

Derivatives of 10-chlorobenz(*g*)quinoline [8-chloro-6 : 7-benzquinoline]. F. H. Gerhardt and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1944, **66**, 479—480).—β-$C_{10}H_7{\cdot}NHAc$ and Cl_2 give 1 : 2-$C_{10}H_6Cl{\cdot}NHAc$ (I), which with HNO_3 (*d* 1·49) at −10° gives 1-*chloro*-5- (II), m.p. 183—185°, and -8-*nitro*-2-*acetnaphthalide* (III), m.p. 188—190°, but in AcOH at room temp. some 1-*chloro*-6-*nitro*-2-*acetnaphthalide* (IV), m.p. 221—223°, is formed. (II) (80%), (III) (65%), and (IV) (76%) are also prepared by chlorinating the appropriate $NO_2{\cdot}C_{10}H_6{\cdot}NHAc$. With glycerol, H_2SO_4, and As_2O_5, (I) gives 8-chloro-6 : 7-benzquinoline [10-chlorobenz(*g*)quinoline] (V) (34%), m.p. 138—140°, which with HNO_3 (*d* 1·49) at −18° gives 10-*chloro*-6-*nitro*- (VI) (45%), m.p. 211—212°, and -9-*nitro-benz*(g)*quinoline* (VII) (12%), m.p. 209—211°. With glycerol and As_2O_5 in 70% H_2SO_4 at the b.p., (II), (III), and (IV) give (VI), (VII), and 10-*chloro*-7-*nitrobenz*(g)*quinoline* (VIII) (4%), m.p. 243—245°, respectively. With morpholine and a little KI or with piperidine, (V) at 150° yields 10-*morpholino*- (6%), m.p. 160—161°, and 10-*piperidino-benz*(g)*quinoline* (8%), m.p. 97—99°, respectively. Morpholine and a trace of Cu-bronze convert (VI) and (VIII) at the b.p. into 6- (5%), m.p. 156—158°, and 7-*nitro*-10-*morpholinobenz*(g)*quinoline* (3%), m.p. 202—204°. $NHEt_2$ does not react with (V), (VI), or (VIII). Passing Cl_2 into (V) in $CHCl_3$ gives 5 : 10-dichlorobenz(*g*)quinoline (71%), m.p. 213—215° (cf. *loc. cit.*), the structure of which is proved by oxidation (CrO_3–AcOH) to benz(*g*)quinoline-5 : 10-dione [1-aza-anthraquinone], m.p. 278—280°. With CrO_3–AcOH at the b.p. (VI) gives 6-*nitrobenz*(g)*quinoline*-5 : 10-*dione* [6-*nitro*-1-*aza-anthraquinone*] (42%), m.p. 243—245°, and with boiling Fe–AcOH–H_2O gives 10-*chloro*-6-*aminobenz*(g)*quinoline* (30%), m.p. 181—183°



(V.)

R. S. C.

Derivatives of 1 : 10-phenanthroline. F. Richter and G. F. Smith (*J. Amer. Chem. Soc.*, 1944, **66**, 396—398).—Yields in Skraup reactions (As_2O_5–H_2SO_4; 130—135°) quoted below are dependent on optimum conditions which are defined. 2 : 4 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}NH_2$ (43·1 g.) gives 6-chloro-8-nitro- (47—48 g.), m.p. 159°, and thence 6-chloro-8-amino-quinoline, m.p. 73°, and 5-chloro-1 : 10-phenanthroline (56%), m.p. 123° (cf. Kuczynski *et al.*, A., 1937, II, 116). 2 : 4 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}NH_2$ (54·3 g.) gives 6-bromo-8-nitro- (60 g.), m.p. 170°, and thence 6-bromo-8-amino-quinoline, m.p. 78°, and 5-*bromo*-1 : 10-*phenanthroline* (I) (46%), m.p. (+H_2O) 86° or (anhyd.) 119°. The so-called (I) (m.p. 215°) of F.P. 804,454 must have a different structure. 4 : 2 : 1-$NO_2{\cdot}C_6H_3Mc{\cdot}NH_2$ (38 g.) gives 8-nitro- (38—40 g.), m.p. 121—122°, and thence 8-amino-6-methylquinoline, m.p. 73°, and 5-*methyl*-1 : 10-*phenanthroline* (II) (66%), m.p. 114°, b.p. 280—282°/13 mm. (*picrate*, m.p. 203—204°). The Me of (II) facilitates nitration (HNO_3–H_2SO_4; 120°), which yields a 5-NO_2-compound, m.p. 268—270°. R. S. C.

Syntheses in the carbazine series. H. Goldstein and G. Huser (*Helv. Chim. Acta*, 1944, **27**, 616—619; cf. A., 1928, 647).—*o*-$C_6H_4Me{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$-*p* is converted by MeOH–conc. H_2SO_4 into the *Me* ester, m.p. 48·5°, which with MgPhBr in Et_2O yields 2-p-*tolylaminotriphenylcarbinol*, m.p. 164·5°; this is dehydrated by glacial AcOH containing HCl to 5 : 5 *diphenyl*-3-*methyl*-5 : 10-*dihydroacridine*, m.p. 217°. Similarly *Me* N-p-*anisylanthranilate*, m.p. 53·5°, yields successively 2-p-*anisidinotriphenylcarbinol*, m.p. 123°, and 3-*methoxy*-5 : 5-*diphenyl*-5 : 10-*dihydroacridine*, m.p. 213—214°. *Me* N-β-*naphthylanthranilate*, m.p. 53°, is converted into 2-β-*naphthylaminotriphenylcarbinol*, m.p. 132—133°, and thence into 5 : 5-*diphenyl*-5 : 10-*dihydro*-3 : 4-*benzacridine*, m.p. 260—261°. M.p. are corr. H. W.

Thiobarbituric acids.—See B., 1944, III, 119.

Pyrrole series. XI. Effect of substituents on the structure of dipyrrylmethenes. Relationships between dipyrryl- and triphenylmethane dyes. K. J. Brunings and A. H. Corwin (*J. Amer. Chem. Soc.*, 1944, **66**, 337—342; cf. A., 1943, II, 72).—By electronic influences passage of dipyrrylmethyl bromides (*A*) into dipyrrylmethene anhydro-bases or hydrobromides is favoured by substitution of the pyrryl by Me and hindered by substitution by CO_2Et. By preventing planar alignment (and thus resonance), 5-CO_2Et is much more effective than 3- or 4-CO_2Et, and 1-Me hinders the transformation. In extreme cases (*A*) exist as such and yield carbinols and carbinol ethers, but are converted into methene stannichlorides by $SnCl_4$; in less extreme cases (*A*) do not exist as such but with KOH–EtOH give the carbinol ether, though aq. KOH may give the carbinol or methene anhydro-base. (*A*) thus resemble triphenylmethyl halides; in the latter series steric reasons as above account for the lack of effect of *o*-substituents. Et_2 3 : 5 : 3′ : 5′-tetramethyldipyrrylmethene-4 : 4′-dicarboxylate hydrobromide (prep. from the methane by Br–CCl_4) with $Ca(OH)_2$ in $CHCl_3$ gives the red anhydro-base, m.p. 189—190° (decomp.). Et_2 4 : 5 : 4′ : 5′-tetramethyldipyrrylmethene-3 : 3′-dicarboxylate hydrobromide, similarly prepared, gives similarly the orange-red anhydro-base, m.p. 164—165° (decomp.). *Et*$_2$ 3 : 4 : 3′ : 4′-*tetramethyldipyrrylmethene*-5 : 5′-*dicarboxylate hydrobromide* (I) (prep. as above), decomp. 160—165°, gives no anhydro-base but with, *e.g.*, H_2O gives 5 : 5′-*dicarbethoxy*- 3 : 4 : 3′ : 4′-*tetramethyldipyrrylcarbinol*, decomp. 185—186°, and in boiling MeOH gives the *Me ether*, m.p. 169—170° (decomp.), thereof, both reconverted into (I) by HBr–CCl_4. Et_3 3 : 5 : 4′-trimethyldipyrrylmethene-4 : 3′ : 5′-tricarboxylate hydrobromide (similarly prepared) with KOH–MeOH gives the carbinol Me ether but with $Ca(OH)_2$–$CHCl_3$ gives the methene anhydro-base, m.p. 125—126° (decomp.). The appropriate methane with Br–CCl_4 gives 3 : 5 : 3′ : 5′-*tetracarbethoxy*-4 : 4′-*dimethyldipyrrylmethyl bromide*, m.p. 132—133° (decomp.), which becomes coloured in hot C_6H_6 and colourless again on cooling, colours filter-paper and textiles, becomes only weakly coloured in conc. H_2SO_4, but with $SnCl_4$ in $CHCl_3$ gives a colour (the methene stannichloride), destroyed by H_2O. The appropriate methane and Br–CCl_4 in complete absence of H_2O give 4 : 3′ : 5′-*tricarbethoxy*-1 : 3 : 5 : 1′ : 4′-*pentamethyldipyrrylmethyl bromide*, m.p. 135—136° (red), which gives brilliant colours in conc. H_2SO_4 or $HClO_4$ or with $SnCl_4$–$CHCl_3$, and in boiling MeOH gives the *carbinol Me ether*, m.p. 93—94°. R. S. C.

Molecular rearrangements of phenyl styryl ketone oxides.—See A., 1944, II, 224.

Some basically substituted derivatives of benziminazole and lupinane. G. R. Clemo and G. A. Swan (*J.C.S.*, 1944, 274—276).—4-Nitro-3-(ε-diethylamino-β-amyl)aminoanisole, prepared from 3-bromo-4-nitroanisole, is identical with the product obtained from 3 : 4-dinitroanisole (cf. Toptschiev, A., 1936, 838). 4-Bromo-3-nitroanisole with δ-amino-α-diethylaminopentane and Cu (trace) give 3-*nitro*-4-(ε-*diethylamino-β-amyl*)*aminoanisole*, b.p. 195—200°/2 mm., reduced ($SnCl_2$–HCl) to the 3-NH_2-compound (I), b.p. 180—185°/2 mm. 4-Amino-3-(ε-diethylamino-β-amyl)aminoanisole (II)

with HCO_2H affords 1-(ε-*diethylamino-β-amyl*)-6-*methoxy-benziminazole*, b.p. 190°/1·5 mm. (*dipicrolonate*, m.p. 193°), and with Ac_2O yields the -2-*methylbenziminazole*, b.p. 190°/1·5 mm. (*dipicrolonate*, m.p. 230°). Similarly, (I) with HCO_2H gives 5-*methoxy*-1-(ε-*diethylamino-β-amyl*)*benziminazole*, b.p. 195°/2 mm. (*picrate*, m.p. 161°), and with Ac_2O forms the 2-*Me* derivative, b.p. 195°/2 mm. (*dipicrate*, m.p. 198°). 11-Bromolupinane condenses similarly to give 11-(ε-*diethylamino-β-amyl*)*aminolupinane*, b.p. 165—167°/2 mm. (*tripicrolonate*, m.p. is 166—172°). Condensation of (II) with CH_2Ac_2 affords a *base*, $C_{21}H_{28}O_2N_2$, b.p. 175°/1·5 mm. F. R. S.

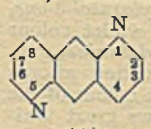
Reaction between aromatic diamines and dicarboxylic acids. I. *o*-Phenylenediamine and phthalic anhydride. B. A. Porai-Koschitz and M. M. Antoschulskaja (*J. Gen. Chem. Russ.*, 1943, **13**, 339—352). —*o*-$C_6H_4(NH_2)_2$ (I) and *o*-$C_6H_4(CO)_2O$ (II) (1 : 1 mol.) at 120—130° (oil-bath) gave 70% of benzoylenebenziminazole (III), m.p. 209·5—210° (extracted from the cooled melt with Ac_2O), diphthaloyl-*o*-phenylenediamine (IV), and *o*-di-2-benziminazolylbenzene (V); (IV) and (V) are insol. in Ac_2O and were separated by treatment with dil. HCl, crystallisation, and distillation. The use of C_6H_6 for the extraction and crystallisation of (III) leads to an impure product, indicating the presence in the melt of *o*-2-benziminazolylbenzoic acid, which is converted into (III) by Ac_2O. (IV), m.p. 296·5—297°, and diphthaloyl derivatives of other diamines are best prepared by slowly adding (I) to 7 mols. of boiling (II); the cooled melt is extracted with boiling 20% aq. Na_2CO_3, washed with H_2O, extracted with hot EtOH to remove (III), and cryst. from glacial AcOH. (V), m.p. 414—416°, was prepared in 70% yield by fusing together (I) and (II) (4 : 1 mol.) at 185—190° (oil-bath), extracting the melt with boiling aq. Na_2CO_3 and then with boiling dil. HCl; slow crystallisation of the acid extract and decomp. of the HCl salt, or direct neutralisation of the acid extract with NH_3, gave the base, which was purified by extraction with boiling polychlorobenzene, b.p. 183—187°, followed by C_6H_6, and final sublimation. Fusion of (III) with excess of (I) at 195° gave (V) in 92·6% yield; of (IV) with (I) (1 : 1 mol.) at 230—240° gave 30·9% of (III) together with (V); of (IV) with excess of (I) at 240—250° gave (V) in 89% yield. (III) with excess of (II) at 195° did not react, but addition of (III) to excess of boiling (II) gave 10% of (IV); (V) did not react with (II) under similar conditions, nor in the presence of C_5H_5N or piperidine. R. C. P.

***N*⁴-Substituted sulphonamides.** J. Finkelstein (*J. Amer. Chem. Soc.*, 1944, **66**, 407—408).—The appropriate sulphanilamido-compound and $CH_2Cl{\cdot}COCl$ in C_5H_5N give *p*-$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, m.p. 211—213°, 2-N⁴-*chloroacetylsulphanilamido-pyridine*, m.p. 192—193°, *-thiazole*, m.p. 205—206°, *-4-methylthiazole*, m.p. 231—232°, and *-pyrimidine*, m.p. 208—210°, converted by conc. aq. NH_3 at 40° into the *glycyl* derivatives, m.p. (I) 216—218°, 220—221°, 215—216°, 205—206°, and 238—240°, respectively. The substance, m.p. 260°, of Pollak *et al.* (A., 1931, 1283, m.p. 256—258°), supposed to be (I), is *iminobis*-N⁴-*acetylsulphanilamide*. 2-*N*⁴-Hexoylsulphanilamido-pyridine, m.p. 193—194°, -thiazole, m.p. 193—195°, and *-pyrimidine*, m.p. 214—215°, are also prepared. The drugs have low toxicity and may be useful therapeutically (preliminary data only are given). R. S. C.

Heterocyclic compounds containing nitrogen. LII. Pyridylisatogens. P. Ruggli and H. Cuenin (*Helv. Chim. Acta*, 1944, **27**, 649—662).—2-Methylpyridine, *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, and Ac_2O at 170—175° give 2-nitrostilbazole, m.p. 100—101° [hydrochloride, m.p. 213—215° (decomp)]; the dibromide, m.p. 181° (*picrate*, m.p. 174°), loses Br when treated with C_5H_5N, piperidine, KOH–EtOH, AgOAc, or AgOBz. The corresponding *dichloride*, m.p. 143·5—144° [*hydrochloride*, m.p. 176° (decomp.); *picrate*, m.p. 167—168° (decomp.)], is converted by prolonged boiling with C_5H_5N into *μ-chloro-2-nitrostilbazole*, m.p. 61·5—62° [*hydrochloride*, m.p. 160—165° (decomp.); *picrate*, m.p. 128—128·5°], and by boiling KOH–MeOH into 2-nitrotolazole (I), m.p. 54·5—55°, [picrate, m.p. 171—171·5°; *hydrochloride*, m.p. 158°, resinifies when kept; very hygroscopic *sulphate*, m.p. 73—76°; *dibromide hydrobromide*, m.p. 250—252° (decomp.)]. (I) is transformed into 2-2′-*pyridylisatogen* (II), m.p. 182° [also +1$CHCl_3$; *picrate*, m.p. ~177° (decomp.); *hydrochloride*, m.p. 195—196°; *sulphate*, m.p. 215° (decomp.); *oxalate*, m.p. 160°; *methiodide*, m.p. 182°; additive *compound*, m.p. 119—120°, with H_2SO_3], slowly by insolation in C_5H_5N, rapidly by PhNO (functioning at " stoicheiometric catalyst "). (II) and NH_2OH,HCl in boiling EtOH afford the C-*oxime*, m.p. 215—217° (decomp.), reduced by Zn dust in boiling AcOH to which Ac_2O is subsequently added to 3-*acetamido-2-pyridylindole* (III), m.p. 189°, or, if addition of Ac_2O is omitted, to 3-*amino-2-pyridylindole*, m.p. 240°, softens at 100° and blackens at ~170°. (II) and $NHPh{\cdot}NH_2$ in EtOH at >40° evolve N_2 and give 1 : 3-*dihydroxy-2-2′-pyridylindole* (*indolone hydrate*) (IV), m.p. 163—165° (decomp.), softens >140° (*hydrochloride*), with a small proportion of 2-2′-*pyridylindolone* (V), m.p. 186° [*picrate*, m.p. 202° (decomp.)], which is the main product from (II) and $NHPh{\cdot}NH_2$ in boiling EtOH; the *oxime*, m.p. 179—180° (blackens), is reduced by Zn dust and AcOH followed by Ac_2O to (III). (II) is reduced (Zn dust–AcOH–Ac_2O or catalytically in presence of Raney Ni and Ac_2O) to 3-*acetyl-2-pyridylindoxyl* (VI), m.p. 129·5—130·5°, also obtained from (IV) and (V). In absence of Ac_2O (II) affords *indoloneindoxyl*, $C_6H_4\langle{CO \atop NH}\rangle CR{\cdot}O{\cdot}C\langle{C_6H_4 \atop CR}\rangle NH$ (R = C_5H_4N), decomp. (indef.) 210—230° [*picrate*, m.p. 205—207° (decomp.)], also obtained by reduction of (II) with KI–HCl. (II), (IV), or (V) yields with piperidine in boiling EtOH an *adduct*, $C_{18}H_{19}ON_3$, m.p. 184—185°; when treated with NaOH it gives piperidine, with 2N-HCl at 40° it gives (IV), and in cold dioxan it slowly yields (V) and a red resin. It is reduced (Zn dust–AcOH–Ac_2O) to (VI). (II) is transformed by H_2SO_4–EtOH at 100° into (?) 2-*pyridylisoisatogen*, m.p. 105—107°. H. W.

Hydrogenation-dehydrogenation reactions involving compounds of ammono-aldehyde, ammono-acetal, and aquo-ammono-aldehyde types. P. J. McLaughlin and E. C. Wagner (*J. Amer. Chem. Soc.*, 1944, **66**, 251—254).—The mechanism proposed by Simons (A., 1937, II, 185) for the conversion of $CH_2(NH{\cdot}C_6H_4Me\text{-}p)_2$ (I) into the dihydroquinazoline (II) is confirmed and extended. Conversion of the intermediate tetrahydroquinazoline (III) into (II) is a crossed Cannizzaro reaction in which (I) or the trimer of *p*-$C_6H_4Me{\cdot}N{:}CH_2$ (IV) functions as proton-acceptor; this function is exercised by dissociation into (IV) or, in acid at a lower temp., the cation thereof. The reaction is shown to be irreversible and independent of H_2O, air, or picric acid (used as precipitant). The proton-acceptor may also be CHPh:NPh, methylenebispiperidine, NPh:CH·NHPh, *p*-$C_6H_4Me{\cdot}NH{\cdot}CHO$, or $HCO{\cdot}NH_2$ (*i.e.*, substances of aldehydic or ammono-aldehydic type), but not NPh:CMe·NHPh, NHPhAc, or NH_2Ac. Sources of acid may be, in order of decreasing efficiency, *p*-$C_6H_4Me{\cdot}NH_2$,HCl, NMe_3,HCl, the hydrochloride of (II), piperidine hydrochloride, or NH_4Cl, which, except for NH_4Cl, accords with their activities as proton donors. R. S. C.

Heterocyclic compounds containing nitrogen. LI. New linear benzodipicoline, 2 : 6-dimethyl-1 : 5-anthrazoline. P. Ruggli and F. Brandt (*Helv. Chim. Acta*, 1944, **27**, 274—291; cf. A., 1938, II, 460).—Derivatives of 2 : 6-dimethyl-1 : 5-anthrazolone (cf. *A*) are described. 1 : 4 : 2 : 5-$C_6H_2Me_2Cl_2$ (I) (prep. from *p*-xylene and Cl_2 in presence of Fe powder and absence of light described) is converted by dry Cl_2 in strongly irradiated $C_6H_3Cl_4$ at 120—130° into 2 : 5 : 1 : 4-$C_6H_2Cl_2(CHCl_2)_2$, b.p. 313°, m.p. 72·5—74°, converted by NH_2Ph at 100° into the *tetraanilino*-compound, darkens >260°, and hydrolysed by conc. H_2SO_4 at 170° to 2 : 5 : 1 : 4-$C_6H_2Cl_2(CHO)_2$ (II), m.p. 157—158° (*dianil*, m.p. 213—214°). Chlorination of (I) at 130—140° in light in absence of solvent or catalyst affords 1 : 4 : 2 : 3 : 5 : 6-$C_6Me_2Cl_4$, m.p. 217·5°, and in strongly illuminated, technical $C_6H_3Cl_3$ at 120—130° gives 2 : 3 : 5 : 6-*tetrachloro*-1 : 4-*dichloromethylbenzene*, m.p. 174·5—175° (*dianilino*-compound, m.p. 170°). 2 : 5-*Dichloro*-1 : 4-*di*(*trichloromethyl*)*benzene*, m.p. 193°, is obtained by chlorinating (I) in illuminated C_2HCl_5 at 130—145°. Gradual addition of Br to (I) at 120—180° and finally at 210° yields 2 : 5 : 1 : 4-$C_6H_2Cl_2(CHBr_2)_2$, hydrolysed to (II). Gradual addition of Br to illuminated 1 : 4 : 2 : 5-$C_6H_2Me_2Br_2$ (prep. from *p*-xylene described) containing I at 120° and finally at 170° gives 2 : 5-*dibromo*-1 : 4-*di*(*dibromomethyl*)*benzene*, m.p. 162—163°, hydrolysed by H_2SO_4,H_2O at 130—140°/25 mm. to 2 : 5-*dibromoterephthalaldehyde* (III), m.p. 189—190·5° (corresponding *dianil*, m.p. 234·5—235°). (III) is converted by NH_2Ac at 135—140° into 2 : 5-*dibromoterephthaltetra-acetamide*, darkens at 305° and carbonises at a higher temp., and by *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$, Cu powder, CuBr, and K_2CO_3 in $PhNO_2$ according to conditions into 5-*bromo*-2-p-*toluenesulphonamido*-, m.p. 183—185°, or 2 : 5-*di*-p-*toluenesulphonamido*- (IV) *-terephthalaldehyde*, m.p. 241—243° (decomp.) [*dipiperidine* salt, decomp. 140°, reddens at 110°; *dianil*, m.p. 297° (decomp.)]. (IV) is transformed by $CH_2Ac{\cdot}CO_2Et$ in presence of piperidine at 70° into Et_2 2 : 5-*di*-p-*toluenesulphonamidoterephthalylidenediacetoacetate* (V), m.p. 216—217° (decomp.), becomes discoloured at 210°, which with NH_2Ph at 100° affords a *compound*, $C_{54}H_{48}O_6N_6S_2$, m.p. 299—301° (decomp.). (V) with conc. H_2SO_4 at 27—32° suffers one-sided ring-closure to *Et* 6-*amino*-3-*carbethoxy*-2-*methylquinoline*-7-*methenylacetoacetate* (VI), m.p. 219—220° (*picrate*, decomp. 215—220°, softens at 200°), hydrolysed to the dicarboxylic *acid* (VII), decomp. >280° (*Na*₂ salt). Under more drastic conditions conc. H_2SO_4 causes two-sided ring-closure of (V) to 2 : 6-*dimethyl*-1 : 5-*anthrazoline*-3 : 7-*dicarboxylic acid* (2 : 6-*dimethyl*-lin-p-*benzodipyridine*-3 : 7-*dicarboxylic acid*), decomp. ~320°, becomes brown at 280°, also obtained from (VI) and (VII). This is decarboxylated by Cu powder and Cu chromite in quinoline at 215° to 2 : 6-*dimethyl*-1 : 5-*anthrazoline*, needles, m.p. 238—239° (decomp.), or apparently hydrated leaflets, which give solutions in dil. HCl or H_2SO_4 from which it is repptd. by Na_2CO_3 but not by NaOAc. It gives a cryst. oxalate, perchlorate, chromate, and *picrate*, decomp. ~263°, becomes discoloured at 250°, a (*CHPh*:)₂, m.p. 267°, and a *di*-p-*dimethylaminobenzylidene*, decomp. 340°, derivative. (IV) is transformed by COPhMe at 190—197° into 2 : 6-*diphenyl*-1 : 5-*anthrazoline*, m.p. 284—285° (*picrate*, m.p. 283°). H. W.


(A.)

Tetrahydrotriazines.—See B., 1944, II, 158.

Morpholinomethylurea.—See B., 1944, II, 157.

αβ-Diamino-ketones. II. Reactions of thalline and open-chain *sec.* amines with α-bromo-β-amino-ketones. N. H. Cromwell, J. A. Caughlan, and G. F. Gilbert (*J. Amer. Chem. Soc.*, 1944, **66**, 401—403; cf. A., 1944, II, 171).—Interaction of α-bromo-β-heterocyclic amino-β-phenylpropiophenone (or the COMe compound) with open-chain *sec.* bases gives poor yields of mixed diamino-ketones, mainly owing to steric reasons. *p*-OMe·C_6H_4·NH_2, $FeSO_4$, *p*-OMe·C_6H_4·NO_2, glycerol, and H_2SO_4 at the b.p. give 6-methoxyquinoline (53%), m.p. 18—20°, b.p. 182—184°/34 mm., which with H_2–Cu chromite in EtOH at 180°/1800 lb. gives 6-methoxy-1 : 2 : 3 : 4-tetrahydroquinoline (93%), m.p. 42—43°, b.p. 127—130°/1 mm. (picrate, m.p. 164—165°). α-Bromo-β-piperidino-β-phenylpropiophenone (I) with the appropriate amine in EtOH at 70° gives *α-piperidino-β-6-methoxy*-1 : 2 : 3 : 4-*tetrahydroquinolino-β-phenylpropiophenone* (85%), m.p. 159—160°; similarly are prepared *α-morpholino-β-6-methoxy*-1 : 2 : 3 : 4-*tetrahydroquinolinopropiophenone* (68%), m.p. 143°, *α-piperidino-* (39%), m.p. 124°, and *α-morpholino-β-6-methoxy*-1 : 2 : 3 : 4-*tetrahydroquinolino-β-phenylethyl Me ketone* (40%), m.p. 126°. CH_2Ph·NHMe and (I) in 1 : 3 EtOH–Et_2O at room temp. (12 hr.) and then 0° (2 days) give *β-N-methylbenzylamino-α-piperidino-β-phenylpropiophenone* (36%), m.p. 138—140°, hydrolysed by 15% H_2SO_4 at 100° to ω-piperidinoacetophenone; similarly are prepared *α-piperidino-β-N-methyl-N-β′-hydroxyethylamino-β-phenylpropiophenone* (10%), m.p. 108°, *α-piperidino-β-N-methylbenzylamino-* (14%), m.p. 111°, and *-β-N-methyl-N-β′-hydroxyethylamino-β-phenylethyl Me ketone* (5%), m.p. 132°. $NH(CH_2Ph)_2$ with (I) at room temp. and then 0° gives *α-piperidino-β-dibenzylamino-β-phenylpropiophenone* (13%), m.p. 173—175° (decomp.), and with α-bromo-β-piperidino-β-phenylethyl Me ketone in 37 : 63 EtOH–Et_2O at room temp. and then 0° gives *α-piperidino-β-dibenzylamino-β-phenylethyl Me ketone* (4%), m.p. 158—160° (decomp.). R. S. C.

Further 2-*p*-nitrophenyl-4-alkyloxazol-5-ones. P. Karrer and C. Christoffel (*Helv. Chim. Acta*, 1944, **27**, 622—623; cf. A., 1943, II, 187).—*dl*-Phenylalanine in 2N-NaOH is converted by *p*-NO_2·C_6H_4·COCl in Et_2O into 2-p-*nitrophenyl-4-benzyloxazol-5-one*, m.p. 162°, which with NaOH–Et_2OH gives a dark violet colour becoming blue on addition of C_5H_5N; N-p-*nitrobenzoylalanine*, m.p. 168·5°, is obtained as by-product. Similarly, *dl*-valine affords 2-p-*nitrophenyl*-4-iso*propyloxazol-5-one*, m.p. 92°. The colour of the alkali salts of the oxazolones in different media shows great variations which do not appear related to the dielectric const. of the liquids. H. W.

Chemotherapy of bacterial infections. IX. Synthesis of some sulphathiazole derivatives. K. Ganapathi. **X. 2-Acetsulphanilimido-3-acetsulphanilylthiazolone and 2-diacetsulphanilylamidothiazole. New route to sulphathiazole.** C. V. Deliwala, K. Ganapathi, and M. V. Shirsat (*Proc. Indian Acad. Sci.*, 1943, **18**, **A**, 355—359, 360—363).—IX. The Na salt of sulphathiazole condenses with the appropriate alkyl bromide or iodide in EtOH to give 2-(p-*aminobenzenesulphonimido*)-3-*methyl-*, m.p. 244—246°, *-ethyl-*, m.p. 183—185°, -n-*butyl-*, m.p. 186—188°, -iso*amyl-*, m.p. 201—203°, -n-*hexyl-*, m.p. 156°, *-β-hydroxyethyl-*, m.p. 154—156°, *-β-ethoxyethyl-*, m.p. 150—152°, *-acetonyl-*, m.p. 202°, and *-carboxymethylthiazolone*, m.p. 184—185°. Of these compounds only the Me derivative shows good therapeutic activity.

X. 2-Aminothiazole condenses with acetylsulphanilyl chloride in H_2O or suspension in presence of $NaHCO_3$, $CaCO_3$, or $BaCO_3$ to yield 2-diacetsulphanilylamidothiazole, m.p. 128—129°, which in boiling EtOH isomerises to 2-acetsulphanilimido-3-sulphanilylthiazolone. These two products are hydrolysed by acid or alkali to sulphathiazole in good yield. F. R. S.

Synthesis of the aluminium and the magnesium salts of thiolbenzthiazole. K. D. Petrov and A. M. Fedortschenkova (*J. Appl. Chem. Russ.*, 1943, **16**, 211—213).—The *salt*, $Al(OH)(C_7H_4NS_2)_2,H_2O$, from $Al_2(SO_4)_3$ and a saturated solution of thiolbenzthiazole (I) in NaOH, is easily hydrolysed. The *salt*, $Mg(C_7H_4NS_2)_2$, is prepared from (I) and MgO at 160—170°. J. J. B.

Preparation of the zinc salt of thiolbenzthiazole and its transformation during vulcanisation of rubber. K. D. Petrov (*J. Appl. Chem. Russ.*, 1943, **16**, 214—218).—A saturated solution of thiolbenzthiazole (I) in 1% NaOH with a 2·5% solution of $Zn(OAc)_2$ yields the *salt*, $Zn(C_7H_4NS_2)_2$ (II), which with 0·05 part of S in boiling xylene gives ZnS, (I), and a little dibenzthiazolyl disulphide (III), and with H_2S in C_6H_6 gives ZnS and (I). From rubber vulcanised by means of (II) and S, $COMe_2$ extracts (I). Probably, during vulcanisation (II) reacts with S, giving (III), which with H_2S forms (I) and active S, causing vulcanisation. J. J. B.

Synthesis and constitution of vitachrome. P. Karrer and M. C. Sanz (*Helv. Chim. Acta*, 1944, **27**, 619—621).—$(CS{\cdot}NH_2)_2$ and COMe·$CHCl{\cdot}[CH_2]_2$·OH at 120° afford 4 : 4′-dimethyl-5 : 5′-di-β-hydroxyethyl-2 : 2′-dithiazolyl (vitachrome) (I), m.p. 180°, which when pure forms completely colourless needles with pure blue fluorescence in ultra-violet light. Its formation by irradiation of 2-chloro-4-methyl-5-β-hydroxyethylthiazole is due to dissociation of this compound into Cl atoms and residual radicals which become dimerised. Similarly $COMe{\cdot}CHCl{\cdot}[CH_2]_2{\cdot}OAc$ affords vitachrome diacetate, m.p. 116—116·5°. The destruction of the fluorescence of (I) by aq. $Na_2S_2O_4$ (restored by shaking with air) is not due to the formation of a non-fluorescent reduction product since Na_2 4 : 4′-dimethyl-2 : 2′-dithiazolyl-5 : 5′-dicarboxylate does not evolve CO_2 when treated with $Na_2S_2O_4$. H. W.

Structure-chemical investigations. X. Reactive behaviour of dithioamides of aliphatic dicarboxylic acids. H. Lehr and H. Erlenmeyer (*Helv. Chim. Acta*, 1944, **27**, 489—493).—$(CS{\cdot}NH_2)_2$ and $(CH_2{\cdot}NH_2)_2,H_2O$ (1 : 2) in boiling EtOH yield 2-*β-aminoethylaminothioformyl-iminazoline* [*-glyoxalidine*], decomp. 250—255° (*picrate*, m.p. 284—285°), readily transformed by an excess of $(CH_2{\cdot}NH_2)_2,H_2O$ into di-2-Δ²-iminazolinyl, $\begin{matrix}CH_2{\cdot}NH\\CH_2—N\end{matrix}\!>\!C{\cdot}C\!<\!\begin{matrix}NH{\cdot}CH_2\\N—CH_2\end{matrix}$, m.p. 290—298° (cf. Forssel, A., 1891, 1003). Adipdithioamide (I) and $(CH_2{\cdot}NH_2)_2,H_2O$ in EtOH or in absence of solvent afford *αδ-di-2-Δ²-iminazolinylbutane*, m.p. 209—210° (*picrate*, m.p. 207°); the monomeric character of the products is remarkable. (I) and $(CO{\cdot}CH_2Br)_2$ in abs. EtOH at room temp. give the chain *polymer*, $(C_{10}H_{10}N_2S_2)_n$, softens at 230° and then decomposes gradually. (I) and CH_2BzBr readily yield *αδ-di-4-phenyl-2-thiazolylbutane*, m.p. 89° (*hydrobromide*, m.p. 288°). CH_2BzBr and $(CS{\cdot}NH_2)_2$ yield 4 : 4′-*diphenyl*-2 : 2′-*dithiazolyl*, m.p. 222°, from which a picrate or hydrobromide could not be obtained. H. W.

2 : 2′-Dithiazolyl compounds. P. Karrer, P. Leiser, and W. Graf (*Helv. Chim. Acta*, 1944, **27**, 624—625).—$(CS{\cdot}NH_2)_2$ and $COMe{\cdot}CH_2Cl$ in boiling EtOH afford 4 : 4′-*dimethyl*-2 : 2′-*dithiazolyl*, m.p. 136°. Similarly $(CS{\cdot}NH_2)_2$ and $CHAcCl{\cdot}CO_2Et$ at 120° give *Et*$_2$ 4 : 4′-*dimethyl*-2 : 2′-*dithiazolyl*-5 : 5′-*dicarboxylate*, m.p. 186°, hydrolysed to the *acid*, decomp. >310°. $(CS{\cdot}NH_2)_2$ and $(CO{\cdot}CH_2Br)_2$ in EtOH yield a polythiazole compound of high mol. wt. The compounds resemble vitachrome in giving a very pronounced fluorescence in ultra-violet light; in conc. H_2SO_4 the fluorescence is intense in daylight. H. W.

Cyanine type dyes.—See B., 1944, II, 160.

VII.—ALKALOIDS.

Synthesis of *dl*-heliotridane (1-methylpyrrolizidine). V. Prelog and E. Zalán (*Helv. Chim. Acta*, 1944, **27**, 531—534).—Addition of $OPh{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CN$ (I) to Mg γ-ethoxypropyl bromide in Et_2O leads to *α-phenoxy-η-ethoxy-γ-methylheptan-δ-one*, b.p. 100—110°/0·2 mm., the *oxime*, b.p. 150°/0·1 mm., of which is reduced by Na and abs. EtOH to *δ-amino-α-phenoxy-η-ethoxy-γ-methylheptane*, b.p. 190—191°/12 mm. The hydrobromide is transformed by 66% HBr at 100° into *αη*-dibromo-δ-amino-γ-methylheptane hydrobromide, which with dil. aq. NaOH affords dl-1-*methylpyrrolizidine* (dl-*heliotridane*) [*picrate*, m.p. 234—236°; *styphnate*, m.p. 196—197°; *picrolonate*, m.p. 162—163°; *aurichloride*, m.p. 200—201° (decomp.)]. The salts resemble closely those of the natural *l*-heliotridane. Only one of the two possible racemates appears to be produced. $OMe{\cdot}[CH_2]_2{\cdot}Br$, $CHMe(CO_2Et)_2$, and NaOEt–EtOH yield Et_2 methyl-β-methoxyethylmalonate, b.p. 111—126°/11 mm., hydrolysed and decarboxylated to *γ-methoxy-α-methylbutyric acid* (II), b.p. 114—120°/11 mm., which is less suitable than (I) as initial material for the above synthesis. (II) is converted ($SOCl_2$) through the chloride into the *amide*, m.p. 45—47°, and *anilide*, m.p. 102—103°. H. W.

Alkaloids. I. Oxidation of papaverine to papaveraldine (xanthaline) by selenium dioxide. K. N. Menon (*Proc. Indian Acad. Sci.*, 1944, **19**, **A**, 21—22).—This oxidation is readily effected by SeO_2 in AcOH at 100°. R. S. C.

Isolation of lupinine from technical anabasine sulphate. A. Sadikov and G. Lazurevski (*J. Gen. Chem. Russ.*, 1943, **13**, 319—321).—Anabasine (I) and lupinine (II) in the fraction of b.p. 136—139°/12 mm., obtained by Orekhov's method (A., 1931, 498; 1932, 405) from *Anabasis aphylla*, were separated by stirring and heating the mixture, dissolved in PhMe or light petroleum, with Na. When reaction was complete (1½—2 hr.), the mixture was cooled and the yellow Na lupinate filtered off and washed with PhMe or light petroleum. This may be used directly for synthesis or decomp. with H_2O to regenerate (II) (yield 97%). The mother-liquor after distillation yields (I). Light petroleum gave better results than PhMe. R. C. P.

Alkaloids of *Ammothamnus lehmanni*, Bge. A. Sadikov and G. Lazurevski (*J. Gen. Chem. Russ.*, 1943, **13**, 314—318).—Stems and leaves were extracted with EtOH containing 2% of NH_3. The extract, after evaporation, acidification, and removal of tar, was saturated with KOH and extracted first with Et_2O and then $CHCl_3$ (extracts *A* and *B* respectively). Evaporation of extract *A* gave 0·45% (on dry plant) of pachycarpine + sophocarpine (I). Evaporation of extract *B* and extraction of the residue with $COMe_2$ left a yellow powder (0·05%), from which was separated, by fractional pptn. from acid solution and recrystallisation from $COMe_2$, an

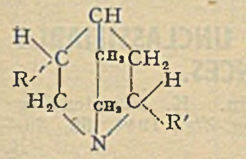
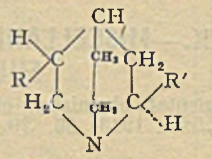
alkaloid, *ammothamnine*, $C_{15}H_{24}O_3N_2$, m.p. 199—201°, α' = 0° [*picrate*, m.p. 212—214° (decomp.); *hydriodide*, m.p. 183—189°]. The total yield of crude alkaloids from the roots was 0·12%; 0·8% of $H_2C_2O_4$ was also separated from the plant. (I) is a good insecticide.
R. C. P.

Alkaloids of *Lycopodium* species. V. *L. obscurum*, L. R. H. F. Manske and L. Marion (*Canad. J. Res.*, 1944, **22**, **B**, 53—55).—The following have been isolated from *L. obscurum* var. *dendroideum* (Michx.) D. C. Eaton: lycopodine, obscurine, alkaloid *L*13 (cf. Marion *et al.*, A., 1944, II, 147), *alkaloid L*16, $C_{16}H_{25}ON$ (*perchlorate*, m.p. 221°), and *alkaloid L*17, $C_{16}H_{27}O_3N$ (*perchlorate*, m.p. 296°). All m.p. are corr.
F. R. S.

Synthesis of possible degradation products of metathebainone. I. H. L. Holmes and L. W. Trevoy (*Canad. J. Res.*, 1944, **22**, **B**, 56—65).—7-*Methoxy*-3 : 4-*dihydro*-2-*naphthoic acid* (I), m.p. 149·5—150° (improved general method of prep.), is dehydrogenated (S) to 7-*methoxy*-2-*naphthoic acid*, m.p. 195—196°, and condenses with $(CH_2{:}CH)_2$ to 3-*methoxy*-, m.p. 126—127°, and with $(CH_2{:}CMe)_2$ to 3-*methoxy*-6 : 7-*dimethyl*-5 : 8 : 9 : 10 : 13 : 14-*hexahydrophenanthrene*-14-*carboxylic acid* (II), m.p. 137·5—138·2°. The Et ester of (I) with $(CH_2{:}CMe)_2$ gives the Et ester of (II), b.p. 187°/2 mm. The acid chloride of (II) could not be converted into the corresponding aldehyde. The relationship of these hydrophenanthrenes to possible degradation products of morphine and metathebainone is discussed. M.p. are corr.
F. R. S.

***Cinchona* alkaloids. VI. Configuration of (−)-γ-methyl-δ-ethylhexane.**—See A., 1944, II, 209.

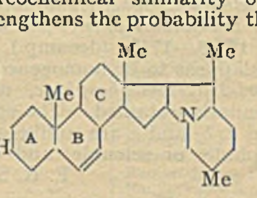
***Cinchona* alkaloids. V. Configuration of the asymmetric carbon atoms 3, 4, and 8 of the *Cinchona* alkaloids.** V. Prelog and E. Zalán (*Helv. Chim. Acta*, 1944, **27**, 535—545).—The configuration (*A*) [R = CH:CH_2, R' = $OMe{\cdot}C_9H_5N{\cdot}CH(OH){\cdot}$] with the two hydrocarbon residues in the *endo* position is assigned to the dextrorotatory

(*A*.)   (*B*)

alkaloids, cinchonine and quinidine, and the structure (*B*) [R = ·CH:CH_2; R' = $C_9H_6N{\cdot}CH(OH){\cdot}$] to the lævorotatory cinchonidine and quinine. Cincholoipone Et ester (I), b.p. 81·5—84°/0·04 mm., 137—138°/11 mm., $[\alpha]_D^{17}$ +16·75° to 16·85°±0·05° (cf. Kaufmann *et al.*, A., 1917, i, 50), obtained by the degradation of cinchonine or by hydrogenation of meroquinine Et ester, is converted into its *hydrochloride*, m.p. 159—160°, $[\alpha]_D^{23}$ −9·3°±1° in EtOH, $[\alpha]_D^{22}$ −7·0° ±1° in H_2O; the hydrochloride of the free base has m.p. 202—203°, $[\alpha]_D^{18}$ −4·6°±1° in H_2O. The ester is reduced by Na and abs. EtOH to 3-ethyl-4-β-hydroxyethylpiperidine, b.p. 103—108°/0·02 mm., $[\alpha]_D^{17}$ +13·1°±0·4° in EtOH, which with fuming HBr at 110° gives 3-ethyl-4-β-bromoethylpiperidine hydrobromide, m.p. 115—117°, $[\alpha]_D^{18}$ −16·9°±0·5° in EtOH. This is converted by Zn dust and AcOH at 80—90° into cis(+)-3 : 4-*diethylpiperidine*, b.p. 70°/12 mm., $[\alpha]_D^{22}$ +26·0±0·6° in EtOH, +37·7°±0·6° in $CHCl_3$ (*picrate*, m.p. 110·5—111°). The N-*Bz* derivative, b.p. 136°/0·2 mm., is transformed by PBr_5 into (+)-*αε-dibromo-βγ-diethylpentane* (I), b.p. 127—134°/12 mm., $[\alpha]_D^{21}$ +11·64°±0·02° in substance, $[\alpha]_D^{19}$ +11·8° ±0·3° in EtOH, converted by H_2 (Raney Ni in alkaline solution) into (−)-γ-*methyl*-δ-*ethylhexane*, a liquid, $[\alpha]_D^{18}$ −11·70° to −12·05° ±0·05° in substance, $[\alpha]_D^{17}$ −9·1°±0·6° in $CHCl_3$. The space arrangement of this methine can be transferred therefore to $C_{(3)}$ of the cinchona alkaloids. (I) is converted by $CH_2(CO_2Et)_2$ and NaOEt in EtOH at 120° into Et_2 (−)-cis-3 : 4-*diethyl*cyclo*hexane*-1 : 1-*dicarboxylate*, b.p. 116—121°/0·1 mm. The corresponding *acid*, m.p. 163—164°, $[\alpha]_D^{16}$ −11·2°±1° in $CHCl_3$, is decarboxylated at 180° to the non-cryst. cis-3 : 4-*diethyl*cyclo*hexanecarboxylic acid*, $[\alpha]_D^{16}$ −2·13° ±0·05°, the Ag salt of which is converted by Br in dry, boiling CCl_4 into 1-*bromo*-cis-3 : 4-*diethyl*cyclo*hexane*, b.p. 136—156° (bath)/12 mm., $[\alpha]_D^{16}$ −1·41°±0·5° in EtOH. This is converted by H_2 (Raney Ni in EtOH containing NaOEt) into cis-1 : 2-*diethyl*cyclo*hexane*, $[\alpha]_D$ = 0°. Since the two asymmetric C are not disturbed during these reactions and could not have been racemised the Et groups are in the *cis* position to one another. The *cis* relationship of the residues R and R' at $C_{(3)}$ and $C_{(4)}$ of the products of the degradation of the cinchona alkaloids is thus established. The configuration at $C_{(8)}$ follows the observation (on models) that only compounds in which the hydrocarbon residues at $C_{(3)}$ and $C_{(8)}$ are in the *endo* relationship can give compounds with ether rings. M.p. are corr.
H. W.

Partial Hofmann degradation of emetine and its dehydrogenation to emetamine. A. Ahl and T. Reichstein (*Helv. Chim. Acta*, 1944, **27**, 366—381).—The results are compatible with but do not establish the constitutional formulæ proposed for emetine (I) by Späth *et al.* (A., 1927, 471) and Brindley *et al.* (*ibid.*, 682) but cannot be reconciled with the formula of Staub (*Diss., Zürich*, 1927). (I) in Et_2O is transformed by 10% KOH and Ac_2O at room temp. into N-*acetylemetine*, m.p. 97—99° [*methiodide* (II), m.p. 213—216°; *methochloride*, m.p. 192—195°; *methoaurichloride*, m.p. 127—129°; *methoplatinichloride*, m.p. 213—217° (decomp.)]. (II) is converted by Ag_2O and solid KOH followed by cautious thermal decomp. and reacetylation into the amorphous methine *base*, $C_{32}H_{44}O_5N_2$ [*methiodide* (III), m.p. 239—240°; *methochloride*, m.p. 217—225°; *methoaurichloride*, m.p. 137—141°]. Hofmann degradation of (III) followed by reacetylation leads to a base (*methoaurichloride*, m.p. 111—118°), the *methiodide*, $C_{34}H_{49}O_5N_2I$, m.p. (indef.) 165—175°, of which is degraded under strictly defined conditions into NMe_3 and a neutral *compound* (IV), $C_{31}H_{39}O_5N$, in which the originally *tert.* N is completely absent whilst the *sec.* N remains unchanged as its Ac derivative. Oxidation of (IV) by $KMnO_4$–$COMe_2$ gives *m*-hemipinic acid (V) as sole isolable compound whereas with $KMnO_4$–dil. H_2SO_4 the products are (V) and 4 : 5-dimethoxyphthalonimide (VI), needles, m.p. 269—275° (decomp.), or occasionally granules which are converted into needles at 200°, obtained by Hermanns (*Diss., Freiberg i. Br.*, 1915) by the oxidation of (I) with CrO_3. The structure of (VI) is confirmed by its prep. by oxidation of 6 : 7-dimethoxytetrahydro*iso*quinoline or its *Ac* derivative, m.p. 104—105°. Dehydrogenation (Pd–C) of (I) at 190—200° gives considerable amounts of amorphous products, 6 : 7-dimethoxy-1-methyl*iso*quinoline, m.p. 106—107° (picrate, m.p. 266—267°), and emetamine, 2 forms m.p. 138—139° and 153—154°, $[\alpha]_D^{20}$ +11·1° in abs. EtOH (picrate, m.p. 149—151°). M.p. are corr. (block); limit of error ±2°.
H. W.

Steroids and sex hormones. XCII. Stereoisomeric dihydrosolanidines. V. Prelog and S. Szpilfogel (*Helv. Chim. Acta*, 1944, **27**, 390—400).—The isolation of four stereoisomeric dihydrosolanidines and of the two corresponding saturated parents emphasises the stereochemical similarity of solanidine (I) and cholesterol and strengthens the probability that (I) is (*A*). (I) is hydrogenated (PtO_2 in AcOH) to solanidan-3(β)-ol (II), m.p. 220°, $[\alpha]_D^{18}$ +28·2°±4° {acetate, m.p. 196°, $[\alpha]_D^{18}$ +16·5°±2°; p-*toluenesulphonate* (III), m.p. 169·5—170°}. (II) is oxidised [$Al(OPh)_3$–$COMe_2$–C_6H_6] to solanidan-3-one, m.p. 210—212°, $[\alpha]_D^{17}$ +45·8°±2°, hydrogenated (PtO_2–AcOH) to (II) but converted by similar

(*A*.) 

hydrogenation with addition of HBr into a solanidanol acetate, m.p. 190°, $[\alpha]_D^{17}$ +18·0°±2°, hydrolysed by boiling KOH–MeOH to *solanidan*-3(α)-*ol* (IV), m.p. 211—212·5°, $[\alpha]_D^{18}$ +31·9°±4° (*acetate*, m.p. 174—176°, $[\alpha]_D^{15}$ +21·9°±3°), which does not give a ppt. with digitonin. The proof that (IV) is epimeric with (II) with respect to $C_{(3)}$ is furnished by the production of (IV) by treatment of (III) with NaOAc and subsequent alkaline hydrolysis. (II) and (IV) are converted by B_2O_3 at 290—200°/high vac. into Δ^2- (or Δ^3-)solaniden, m.p. 165°, $[\alpha]_D^{13}$ +67·9°±1°, which is hydrogenated to solanidan, m.p. 161·5—162·5°, $[\alpha]_D^{17}$ +33·1°±2°. (I) is transformed by $Al(OBu^\gamma)_3$ in boiling $COMe_2$ into Δ^4-solaniden-3-one, m.p. 213—216·5°, $[\alpha]_D^{20}$ +89·0°±1°, also obtained by use of $Al(OPh)_3$. This is hydrogenated (platinised Raney Ni in an alkaline medium) to allo*solanidan*-3(β)-*ol*, m.p. 216—217·5°, $[\alpha]_D^{17}$ +27·9°±2° (*acetate*, m.p. 140—141°, $[\alpha]_D^{18}$ +31·4°±3°), and allo*solanidan*-3(α)-*ol*, m.p. 212—214°, $[\alpha]_D^{18}$ +34·5°±3° (*acetate*, m.p. 140—141·5°, $[\alpha]_D^{18}$ +45·2°±3°). Further cryst. products could not be obtained from the residues but the presence of one of the solanidan-3-ols is established by epimerisation (Na in boiling xylene) followed by pptn. with digitonin, whereby (II) is isolated. B_2O_3 at 300°/high vac. transforms the *allo*-alcohols into Δ^2- (or Δ^3-)allo*solaniden*, m.p. 145·5—146·5°, $[\alpha]_D^{20}$ +34·0°±3°, hydrogenated (PtO_2 in AcOH) to allo*solanidan*, m.p. 140—142°, $[\alpha]_D^{18}$ +34·8°±4°. M.p. are corr. $[\alpha]_D$ are in $CHCl_3$.
H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

Stereochemistry of organic derivatives of phosphorus. I. Synthesis of acidic and basic dissymmetric tertiary phosphines. Optical resolution of phenyl-*p*-(carbomethoxy)phenyl-*n*-butylphosphine sulphide. W. C. Davies and F. G. Mann (*J.C.S.*, 1944, 276—283).—*p*-$C_6H_4Br{\cdot}PCl_2$ and $HgPh_2$ in N_2 give *phenyl*-p-*bromophenyl*-*chlorophosphine* (I), b.p. 203—204°/11 mm., which with Cl_2 followed by H_2O affords the -*phosphonic acid*, m.p. 174·5°, and with MgEtBr yields the -*ethylphosphine*, b.p. 136—138°/0·05 mm. $MgBr{\cdot}C_6H_4{\cdot}NMe_2$ (special conditions of prep.) with (I) leads to *phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine* (II), m.p. 107—108° (also obtained by using the Li derivative), which with S in CS_2 forms the *sulphide*, m.p. 126°. The *methiodide*, m.p. 158—159°, of this sulphide is produced with difficulty and reacts to give the *metho*-d-*camphorsulphonate*, m.p. 224—226° (decomp.), *methobromide Me alcoholate*, m.p. 145°, and *metho*-d-α-*bromocamphorsulphonate*, m.p. 198—199°, which could not be resolved. *Phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine selenide* has m.p. 135·5—136·5°. Mg 2-bromopyridine with (I) affords *phenyl*-p-*bromophenyl*-2-*pyridylphosphine*, m.p. 90—91° (*picrate*, m.p. 132°), converted into the *sulphide*, m.p. 109° [*methiodide*, m.p. 132—134° (decomp.)], which is too weakly

basic for salt formation, as is also the *sulphide*, m.p. 115—116°, of the *-3-pyridyl* derivative [*picrate*, m.p. 143—144° (decomp.)]. *p*-OMe·C_6H_4·PCl_2 (**III**) with MgEtBr gives *p*-anisyldiethylphosphine (methiodide, m.p. 132—133°, lit. 91°), which is hydrolysed (HI) to the p-*hydroxyphenyl* compound, b.p. 168—176°/19 mm. (*methiodide*, m.p. 168—169°). $HgPh_2$ and (**III**) yield *phenyl*-p-*anisyl-chlorophosphine* (**IV**), b.p. 137°/0·03 mm., which with $MgBu^aBr$ leads to the *-n-butylphosphine*, b.p. 139—141°/0·025 mm. This after hydrolysis (HI) with BzCl gives *phenyl*-p-*benzoyloxyphenyl*-n-*butylphosphine*, m.p. 91° (*oxide*, m.p. 136°), which forms the *sulphide*, m.p. 66—67°, hydrolysed to the *hydroxysulphide*, m.p. 97—98°. This sulphide condenses with $CH_2Br·CO_2Et$ to phenyl-*p*-(carboxymethoxy)phenyl-*n*-butylphosphine sulphide, which with *d*-CHPhMe·NH_3Cl gives the salt, cryst. to the d-α-*phenylethylamine* salt of the *sulphide*, m.p. 209—210°, decomposed (H_2SO_4) to the *l*-sulphide, $[M]_D^{16}$ −9·7° in C_6H_6 (l-NH_3 salt). From the mother-liquor is obtained the l-*amine* d-*acid* salt, m.p. 209—210°, decomposed to the *d*-sulphide, $[M]_D^{16}$ +9·6° in C_6H_6 (d-NH_4 salt, $[M]_{5461}^{16}$ +12·2° in H_2O).

MgEtBr and (**IV**) give *phenyl*-p-*anisyl-ethylphosphine*, b.p. 137°/0·1 mm. (*methiodide*, m.p. 114—115°), hydrolysed to the -p-*hydroxyphenyl* compound, b.p. 160—175°/0·1 mm. (*Bz* derivative, m.p. 79—80°; *benzoyloxyphosphine sulphide*, m.p. 83—84°), which with S followed by $CH_2Br·CO_2Et$ leads to *phenyl*-p-(*carboxymethoxy*)*phenylethylphosphine sulphide*, m.p. 84° (*Na* salt; l-*phenylethylamine* salt, m.p. 206—207°; d-sec.-*butylamine* salt, m.p. 189—190°; d-*aminocamphor* salt, m.p. 166—168°), which could not be resolved. $MgPr^aBr$ and (**IV**) yield *phenyl*-p-*anisyl*-n-*propylphosphine*, b.p. 163·5°/0·3 mm. (*methiodide*, m.p. 114°), which with $MgBr·C_6H_4Me$ affords the -p-*tolylphosphine*, m.p. 116—118° (p-*chlorophenacyl bromide*, m.p. 199°). *Phenyl*-p-*bromophenyl*-p-*anisylphosphine*, m.p. 71°, is similarly prepared. NH_4 palladochloride and (**II**) give *dichlorobis*(*phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine*)-*palladium*, partial m.p. 247—249°. *Dichlorobis*(*phenyl*-p-*bromophenylethylphosphine*)*palladium*, m.p. 172·5—174° (decomp.), is similarly prepared and both compounds appear to be homogeneous. PCl_3 and Mg 2-bromopyridine give *tri*-2-*pyridyl-phosphine*, m.p. 113—114°; the *-arsine*, m.p. 85°, is similarly obtained. The compounds are formulated *abc*P→X, where *a*, *b*, and *c* are unlike aryl or alkyl groups, and X is oxide, sulphide, or selenide, and one compound has been resolved. F. R. S.

Sulphides and sulphones derived from *p*-thiolphenylarsonic acid. J. F. Morgan and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1944, **66**, 874—875).—*p*-$NH_2·C_6H_4·[CH_2]_2·OH$ (prep. from the NO_2-compound by H_2–Raney Ni in $COMe_2$), m.p. 43—44°, b.p. 232—235° (decomp.)/38 mm. (*hydrochloride*, m.p. 170°), gives (Bart) p-β-*hydroxyethylthiolphenylarsonic acid*, dimorphic, m.p. 120·5—121° and 132—133°. *p*-$AsO_3H_2·C_6H_4·SCN$ in boiling 10% NaOH gives an acid, ? *p*-$SH·C_6H_4·AsO_3H_2$, which with the appropriate halide in boiling NaOH–H_2O or –EtOH yields p-*γ-hydroxy*-n-*propyl*-, m.p. 116·3—117·5°, p-β-*ethoxyethyl*-, m.p. 121—122°, p-β-β′-*hydroxyethoxyethyl*- (*Na* salt, m.p. >250°), p-*acetonyl*-, m.p. 172·5°, *p*-carboxymethyl- (**I**), m.p. 192° (lit. 187°, 248—250°). p-*carbethoxymethyl*-, m.p. 123° [some (**I**) is also obtained], and *p*-2′-*amino*-4′-*pyrimidyl*-(**II**), m.p. 131·5—132°, *-thiolphenylarsonic acid* and 4-*nitro*-, m.p. 183°, and thence (H_2–Raney Ni in aq. $NaHCO_3$) 4-*amino*-4′-*arsonodiphenyl sulphide*, m.p. 211·5° (decomp.). 27·5% H_2O_2 oxidises these compounds [except (**II**), which decomposes] to p-β-*hydroxyethane*-, m.p. 177°, p-γ-*hydroxypropane*-, m.p. 160·5°, p-β-*ethoxyethane*-, m.p. 182·5—184·5°, *p*-β-β′-hydroxyethoxyethane- (*Na* salt, m.p. 180·5°), p-*acetone*-, m.p. 202·5—203·5°, p-*carboxymethane*-, m.p. 188—189°, and p-*carbethoxymethane*-, m.p. 165—166°, *-sulphonylphenylarsonic acid* and 4-*nitro*-, m.p. >250°, and 4-*amino*-4′-*arsonodiphenyl sulphone*, m.p. 229—230° (decomp.). M.p. are determined in a preheated bath to minimise anhydride formation. R. S. C.

Factors determining the course and mechanism of Grignard reactions. XIV. Replacement of halogen atoms of aromatic halides with hydrogen atoms by the action of Grignard reagents and cobaltous chloride. M. S. Kharasch, D. C. Sayles, and E. K. Fields (*J. Amer. Chem. Soc.*, 1944, **66**, 481—482; cf. A., 1944, II, 223).—In presence of 5 mol.-% of $CoCl_2$, dihalogenated C_6H_6 derivatives are reduced by MgRBr (R = Me, Et, or Ph) in Et_2O to the monohalogenated compound (usually 40—55%) or, if a large excess of MgRBr is used, to the hydrocarbon; polymerides are also formed. Polycyclic aryl bromides with $MgBu^aBr$ give 44—62% of hydrocarbon, but *p*-C_6H_3PhBr gives also 1·3% of dixenyl. Use of MgPhBr gives also much Ph_2. Mg *p*-xenyl or 9-phenanthryl bromide with EtBr and $CoCl_2$ gives 100% of dixenyl and diphenanthryl, respectively. A free radical mechanism is postulated. R. S. C.

Gallium trimethyl—See A., 1944, I, 182.

IX.—PROTEINS.

Methylation and acetylation of wool, silk fibroin, collagen, and gelatin. S. Blackburn and H. Phillips (*Biochem. J.*, 1944, **38**, 171—178; cf. B., 1941, II, 338).—Acetylation of wool with Ac_2O diminishes the extent of subsequent methylation of free CO_2H by Me_2SO_4, MeBr, or MeI. When wool and silk fibroin are treated with Ac_2O in MeOH, methylation of free CO_2H groups and *N*- and *O*-acetylation occur simultaneously. Peptide methylation of wool and esterification of its free CO_2H are not prevented by previous treatment with borax, HNO_2, or CH_2O. Esterification is increased if amide groups are removed by acid hydrolysis. Me_2SO_4 esterifies free CO_2H and causes peptide methylation of collagen, H_2SO_4 becoming covalently linked to proteins. When MeBr or MeI replaces Me_2SO_4, esterification occurs but peptide methylation takes place slowly or not at all. W. McC.

Reaction of casein with formaldehyde. V. Behaviour of the ε-amino-group of lysine and of the peptide groups. H. Nitschmann and H. Hadorn (*Helv. Chim. Acta*, 1944, **27**, 299—312).—The ε-NH_2 of lysine (**I**) is primarily involved in the action of CH_2O on casein (**II**) at pH 5·6 and room temp. Comparison of the abilities of deaminated and ordinary (**II**) to unite with CH_2O and the diminution of the Van Slyke N caused by CH_2O tanning indicate that CH_2O and the free NH_2 of (**I**) react in the ratio 1 : 1. It is established that the amount of H_2O formed is equiv. to the CH_2O which reacts with (**I**). In addition to the NH_2 of (**I**), other groups are present in (**II**) which react with CH_2O in a weakly acid medium. These are probably peptide groups but their reaction with CH_2O is not accompanied by condensation, at any rate in the cold. The tanning action of CH_2O (loss of solubility; diminution of the ability to swell) appears to depend on the formation of CH_2 bridges between the NH_2 of (**I**) and the peptide groups whereby the protein mols. are united by main valencies. H. W.

Blue chromo-protein of eggs of goose-barnacle.—See A., 1944, III, 537.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Fundamental chemistry of lignin. K. Freudenberg (*Svensk Kem. Tidskr.*, 1943, **55**, 20; *Chem.-Ztg.*, 1944, **68**, 39—42).—A lecture. R. S. C.

Colour reactions of lignin and their use in analytical chemistry. P. M. Isakov (*J. Appl. Chem. Russ.*, 1943, **16**, 234—240).—Drop reactions on newspaper paper (containing lignin) are different from those on filter-paper. Solutions of $AuCl_3$ give a black and of NH_4VO_3 a greenish-black spot. $SnCl_2$ and H_2PtCl_6 produce a stable orange spot. $SnCl_2$ and $AgNO_3$ form first AgCl and then Ag which is dissolved by $Hg(NO_3)_2$ solution. Picric acid and $SnCl_2$ form picramic acid. $Co(NO_3)_2$ gives a stable blue spot with KCNS and an azure spot with picric acid. $Fe(NO_3)_3$ and $K_3Fe(CN)_6$ give Turnbull's blue. Aq. NH_2Ph gives a yellow and aq. benzidine an orange coloration. Dil. HNO_3 can be used as a sympathetic ink. J. J. B.

Constitution of shellac. Increased yield of aleuritic acid. B. S. Gidvani (*J.C.S.*, 1944, 306).—By a new method of separation, the yield of aleuritic acid has been increased to nearly 43%. The previous formulæ for shellac resin may not be correct and shellolic acid is possibly not a primary product of hydrolysis. F. R. S.

Dyes from *Ammothamnus lehmanni*, Bge. A. Sadikov and G. Lazurevski (*J. Gen. Chem. Russ.*, 1943, **13**, 309—313).—The crude dye from this Central Asiatic plant (obtained by extraction with alkali and acidification of the extract, in 14% yield from roots, 4% from stems and leaves), after fractional extraction with alkali, was divided into two parts by extraction with EtOAc. The sol. part, after purification by pptn. from EtOH, yielded an orange-red amorphous *compound*, $C_{16}H_{22}O_4$ (**I**), m.p. 96—98° (*Ac*$_3$ derivative, m.p. 107—109°); the insol. portion, recryst. from EtOH, yielded dark red plates, decomp. >360°, of an acidic *compound* (**II**), probably $C_{16}H_{22}O_7N_2$. (**I**) is pptd. from faintly alkaline solution by CO_2 and gives a dark green coloration with $FeCl_3$; distillation of (**I**) with Zn dust gave no recognisable products, oxidation with alkaline $KMnO_4$ gave $H_2C_2O_4$, and fusion with NaOH yielded phloroglucinol and AcOH. The similarity of (**I**) and tetrahydro-α-mangostene is indicated. (**I**) and (**II**) are acid dyes, satisfactory for silk. R. C. P.

Chemical examination of root of *Centaurea behen* (Linn.). P. N. Bhargava and S. Dutt (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 163—166).—Extraction of the root of *C. behen* (" behman ") with EtOH affords " *behmin*," $C_{23}H_{45}O_2·OMe$, sinters 72°, m.p. 79—80° (*tetrabromide*, m.p. 67°), which has properties of a $\Delta^{\alpha\beta}$-unsaturated lactone. D. G.

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SEPTEMBER, 1944.

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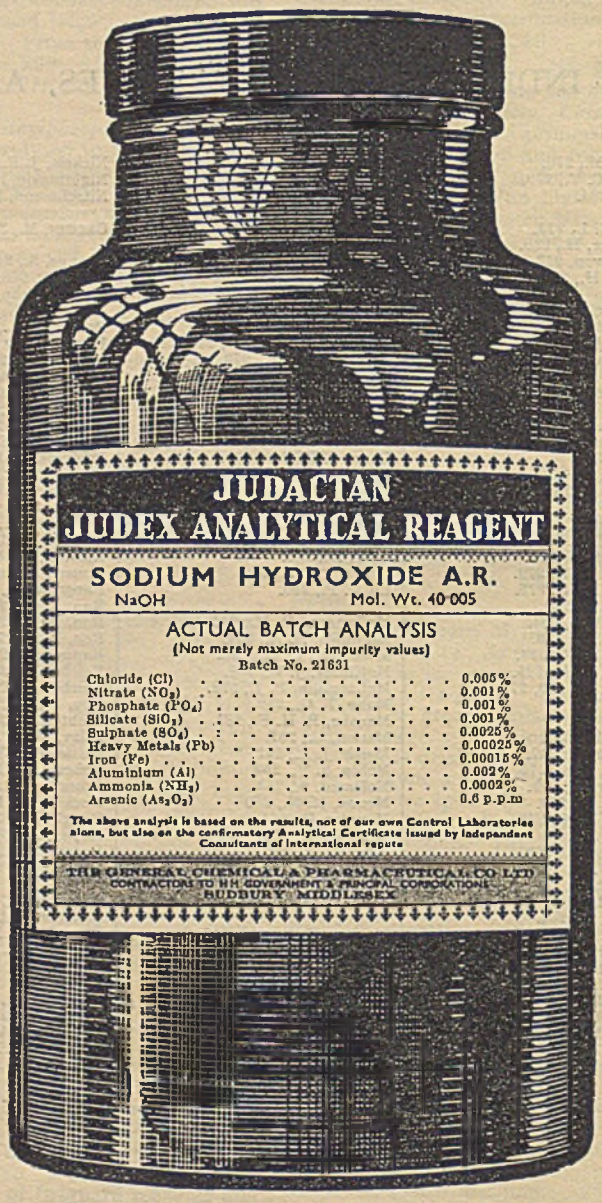

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