BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

OCTOBER, 1937.

Crystal behaviour of hydrocarbons.—See A., I, 448.

Mechanism of polymerisation. I. Dimeric tetramethylethylene. H. BRUNNER and E. H. FARMER (J.C.S., 1937, 1039—1046).—$CMe_2{:}CMe_2$ polymerised with BF_3 at −10° affords a mixture of dimeric products. With O_3 in light petroleum, the fraction of b.p. 54·9—56·5°/12 mm. yields an *acid* (I), probably *dl*-methyl*iso*propylacetic acid (*amide*, m.p. 121—122°); the fraction of b.p. 71—82°/11·5 mm. gives CH_2O, a *ketone*, $C_9H_{18}O_2$ (2 : 4-*dinitrophenylhydrazone*, m.p. 114—115°), and (I). Similarly, the fraction of b.p. 54·9—58·5°/10·5 mm. on ozonolysis yielded pinacolone and $CHMePr^{\beta}{\cdot}CHO$. Six of the eight theoretically possible hexaldehydes are synthesised by improved methods, and the m.p. of their 2 : 4-dinitrophenylhydrazones, semicarbazones, and dimedon derivatives are recorded below in that order (— signifying no variation from the literature): *iso*butyl- (99°, 126·5—127·5°, 133°), *sec.*-butyl- (93·5—94·5°, —, 144°), diethyl- (94·5—95°, 97·5—99·5°, 102—102·5°), dimethylethyl- (145°, —, 118—120°) -acetaldehyde. $COMePr^{\beta}$ with Na and $CH_2Cl{\cdot}CO_2Et$ yields β-methyl-β-*iso*propylglycidoacrylate, hydrolysed (NaOEt–H_2O) to dl-*methyl*iso*propylacetaldehyde*, b.p. 115—117°/770 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 121—123·5°; *semicarbazone*, m.p. 110—111°; *dimedon* derivative, m.p. 162°). J. D. R.

Formation of diene hydrocarbons. I. Principles relating to the course of reaction in the dehydration of unsaturated alcohols. The co-formation of αα- and αγ-dimethylbutadiene. R. G. R. BACON and E. H. FARMER (J.C.S., 1937, 1065—1077).—δ-Methyl-Δ^{α}-penten-δ-ol dehydrated with Br or I yields β-*methyl*-$\Delta^{\alpha\delta}$-*pentadiene*, b.p. 57—58°/766 mm., and αγ-dimethylbutadiene (I). Similarly, ε-methyl-Δ^{β}-hexen-δ-ol gives hydrocarbons of b.p. 99—112°, which with maleic anhydride afford 3-iso*propyl*-Δ^{4}-*tetrahydrophthalic anhydride*, m.p. 90°, and on oxidation ($KMnO_4$) give $Bu^{\beta}CO_2H$ and $COMe_2$, whilst δ-methyl-Δ^{β}-penten-δ-ol affords (I) (about 95%) and αα-dimethylbutadiene (about 5%), both of which are dehydration products of β-methylpentane-βδ-diol. β-Methyl-Δ^{β}-penten-δ-ol (from β-methylcrotonaldehyde and MgMeI), b.p. 137—138°, is dehydrated by HBr to a hydrocarbon, probably containing (I), oxidised to $COMe_2$, $H_2C_2O_4$, HCO_2H, and AcOH whilst δ-methyl-Δ^{α}-penten-γ-ol (improved prep.) is unaffected by HBr or I, but is dehydrated by PhNCO to unidentified conjugated and non-conjugated hydrocarbons. J. D. R.

Synthesis of higher polyenes. R. KUHN (Angew. Chem., 1937, **50**, 703—708).—The synthesis of the following substances is described in historical outline: $Ph{\cdot}[CH{:}CH]_n{\cdot}Ph$ (n = 1—8), $CO_2H{\cdot}[CH{:}CH]_n{\cdot}CO_2H$ (n = 1—5, 7), $CO_2H{\cdot}CH_2{\cdot}[CH{:}CH]_n{\cdot}CO_2H$ (n = 1—4), $Me{\cdot}[CH{:}CH]_n{\cdot}Me$ (n = 1—4, 6), $Me{\cdot}[CH{:}CH]_n{\cdot}CHO$ (n = 1—5, 7), $Me{\cdot}[CH{:}CH]_n{\cdot}CO_2H$ (n = 1—6, 8). ζ-Phenylpentadecaheptaenal is converted into the corresponding thioaldehyde and thence into the greenish-black *hydrocarbon*, $Ph{\cdot}[CH{:}CH]_{15}{\cdot}Ph$.

H. W.

Recent acetylene chemistry. H. VOGL (Österr. Chem.-Ztg., 1937, **40**, 373—377).—A review.

Solubility of halogenated hydrocarbon refrigerants in organic solvents. G. F. ZELLHOEFER (Ind. Eng. Chem., 1937, **29**, 548—551).—The solubility of CCl_2F_2, EtCl, CH_2Cl_2, $C_2Cl_2F_4$, and $CFCl_3$ in a few, and of MeCl and $CHFCl_2$ in a large no. of, org. solvents at 32°, under the pressure exerted by the solute at 4·5°, has been determined and the results are discussed. Among the solvents used, the following are new: *triethylene glycol* Me_2 *ether*, b.p. 216°; *tetraethylene glycol* Me_2 *ether*, b.p. 115—118°/2 mm., and Et_2 *ether*, b.p. 132—134°/12 mm.; *tetrahydrofurfuryl ether* of $OH{\cdot}[CH_2]_2{\cdot}OBu$, b.p. 246°; *diethylene glycol ditetrahydrofurfuryl ether*, 199—203°/14 mm.; *hexaethylene glycol* Me_2 *ether*, b.p. 195—199°/14 mm.; 2 : 3-*di*-β-*ethoxyethoxydioxan*, b.p. 161—166°/2 mm.; 2 : 3-*di*-β′-*methoxy*-β-*ethoxyethoxydioxan*, b.p. 210—220°/2 mm.; *Bu carbitol chloride*, b.p. 215°; *ethylene glycol* $(C_2H_4Cl)_2$ *ether*, b.p. 80—85°/2 mm.; *triethylene glycol chloride Me ether*, b.p. 116—117°/12 mm.; *carbitol methoxyacetate*, b.p. 128—132°/7 mm., *ethoxyacetate*, b.p. 155—160°/15 mm., and *lævulate*, b.p. 175—182°/14 mm.; *diethylene glycol dimethoxyacetate*, b.p. 204—208°/17 mm., and *diethoxyacetate*, b.p. 210—215°/15 mm.; *Me carbitol acetate*, b.p. 79°/10 mm., and *methoxyacetate*, b.p. 145—149/15 mm.; *triethylene glycol dimethoxyacetate*, b.p. 230—234°/15 mm., and *methoxyacetate*, b.p. 244°; *trimethylene glycol dimethoxyacetate*, b.p. 180—184°/20 mm.; *tetrahydrofurfuryl methoxyacetate*, b.p. 136—140°/18 mm.; *ethylene glycol diethoxyacetate*, b.p. 163—165°/14 mm.; *ethylene glycol* Bu_1 *ether methoxyacetate*, b.p. 136—140°/18 mm., *n-butyrate*, b.p. 220°, *acetate*, b.p. 192°, and *laurate*, b.p. 188°/8 mm.; *triethylene glycol acetate Me ether*, b.p. 253°; *ethylene glycol* Et_1 *ether succinate*, b.p. 159—162°/5 mm.; *ethylene glycol* CH_2Ph *ether acetate*, b.p. 122—125°/5 mm.; *ethylene glycol tetrahydrofurfuryl ether acetate*, b.p. 112°/6 mm.; *glycerol-αγ-dichlorohydrin adipate*, b.p. 235—240°/8 mm.; *di*-β-*chloroethyl phthalate*, b.p. 198°/5 mm.; Bu^{α}_2 *dichlorophthalate*, b.p. 200—210°/7 mm.; *benzenesulphonyl*-n-*butylaniline*, b.p. 190—200°/6 mm. R. C. M.

Determination of tetranitromethane. C. K. Krauz and J. M. Štěpánek (Chem. Obzor, 1937, **12**, 81—85).—In neutral aq. solution 1 mol. of $C(NO_2)_4$ reacts with 2KI exactly, and the I is titrated with standard $Na_2S_2O_3$. About 5 hr. are required for a determination. In an acid medium secondary reactions cause a higher separation of I, so that 1 mol. of $C(NO_2)_4 \rightarrow 2KI + k$, where k increases linearly with the acidity of the solution titrated. The acidity must be determined by a separate titration. In presence of $NaHCO_3$, owing to secondary reactions the separation of I never reaches the theoretical and results of titrations must be corr. from a graph constructed from empirical results. The time of reaction in a neutral medium may be reduced to 10—15 min. with an accuracy of determination of $\pm 0{\cdot}2\%$ by using EtOH solutions, where, owing to partial oxidation of EtOH by $C(NO_2)_4$, a correction must be applied. F. R.

Catalytic dehydrogenation of a tertiary alcohol to a ketone. L. Martineau and C. Prévost (Compt. rend., 1937, **205**, 154—156).—$Bu^{\gamma}OH$, freed from ketonic substances, is dehydrogenated by Cu–ThO_2 at 130° to $CMe_2{:}CH_2$ and a small amount of COMeEt. A theoretical explanation of the reaction is suggested. J. L. D.

Ethoxides and *iso*propoxides of manganese and rhenium. J. G. Druce (J.C.S., 1937, 1407—1408).—Addition of $MnCO_3$ or $Re_2(CO_3)_2$ to HCl or HBr in EtOH or $Pr^{\beta}OH$ yields the following *compounds*: $MnCl_2$,EtOH; $MnCl_2$,$Pr^{\beta}OH$; $MnBr_2$,EtOH; $MnBr_2$,$Pr^{\beta}OH$; $ReCl_3$,EtOH; $ReCl_3$,$Pr^{\beta}OH$. Treatment of the appropriate halide-alcoholate with NaOEt or $NaOPr^{\beta}$ affords $Mn(OEt)_2$, *Mn* iso*propoxide*, *Re triethoxide* and *tri*iso*propoxide*. J. D. R.

Stereochemistry of deuterium compounds of the type $RR'CX_EX_D$: ethyl-d_4-ethylcarbinol. F. C. McGrew and R. Adams (J. Amer. Chem. Soc., 1937, **59**, 1497—1500).—Na and a little Fe [prepared by addition of Na to hydrated $Fe(NO_3)_2$] in liquid NH_3, treated at −50° to −60° first with C_2H_2 and then with EtCHO, give Δ^{α}-pentinen-γ-ol, b.p. 121—124°/750 mm. (3 : 5-*dinitrobenzoate*, m.p. 91°); the *H phthalate*, m.p. 72°, thereof is partly resolved by brucine to yield an impure l-Δ^{α}-*pentinen-γ-ol*, $[\alpha]_D^{25}$ −15·25°. This with H_2–PtO_2 in EtOAc gives $CHEt_2{\cdot}OH$, $[\alpha]_D$ $0 \pm 0{\cdot}01°$ [3 : 5-*dinitrobenzoate* (II), m.p. 99—99·5°]. D_2–PtO_2 gives *ααββ-tetradeutero-n-pentan-γ-ol*, $[\alpha]_D$ $0 \pm 0{\cdot}01°$ [3 : 5-*dinitrobenzoate*, m.p. 98·5—99°, not depressed by admixture with (II)]. This makes it improbable that compounds CRR'R''R''', in which R and R' are alkyl and R is substituted by D, will show measurable [α]. Calculation by Boys' method, admittedly untrustworthy, gives an expected [α] 0·01° for $C_6D_5{\cdot}CHPh{\cdot}NH_2$; the val. of Clemo *et al.* (−5·7°) may be erroneous. R. S. C.

Free radicals in organic decomposition reactions. I. Thermal decomposition of mixtures of methyl ether and deuteroacetone. E. W. R. Steacie and W. A. Alexander (Canad. J. Res., 1937, **15**, B, 295—304).—The H_2 produced by heating an equimol. mixture of Me_2O and $CO(CD_3)_2$ at 590° for 5 min. contains the same amount (3%) of D_2 as that obtained by decomp. Me_2O and $CO(CD_3)_2$ separately, mixing the products, and heating at 590° for 5 min., indicating that no at. H is produced during the decomp. of Me_2O or of its primary decomp. product, CH_2O. The D_2 is determined by freezing out all but CO and H_2, burning these, and distilling and analysing the H_2O. A. Li.

Drying of ether. N. Schoorl (Pharm. Weekblad, 1937, **74**, 1108—1109).—"Wet" Et_2O when dried with Na_2SO_4 or $CaSO_4{\cdot}0{\cdot}5H_2O$ contains about 0·6% of H_2O (test: turbidity with 2 vols. of CCl_4) and <0·35% when dried with $MgSO_4$ (test: no turbidity with 2 vols. of CS_2). S. C.

Molecular structure of βγ-epoxybutanes.—See A., I, 448.

Mono- and di-hydroxymethylene dimethyl ether. J. Löbering and A. Fleischmann (Ber., 1937, **70**, [*B*], 1680—1683).—$CH_2(OMe)_2$ obtained from MeOH, $(CH_2O)_n$, and HCl at 100° is contaminated with about 33% of MeOH, from which it can be freed by p-$NO_2{\cdot}C_6H_4{\cdot}COCl$ but not by distillation. It can be obtained pure by repeated passage of CH_2Cl_2 over NaOMe on pumice at 200° or by heating NaOMe and $CH_2Cl{\cdot}OMe$ (1 : 1 mol.). $(OMe{\cdot}CH_2)_2O$ is best obtained by gradual addition of $(CH_2Cl)_2O$ to NaOMe free from MeOH. H. W.

Sulphonic and sulphuric esters as alkylating agents in liquid ammonia. A. L. Kranzfelder and F. J. Sowa [with (in part) K. J. Schueppert] (J. Amer. Chem. Soc., 1937, **59**, 1490—1492).—Slow addition of p-$C_6H_4Me{\cdot}SO_3R$ (R = Me, Pr^{α}, or Bu^{α}), sometimes in Et_2O, to the Na derivatives of PhOH, C_2H_2, CuOH, or $C_5H_{11}{\cdot}OH$ in liquid NH_3 gives 37—47% of the appropriate ether or acetylene; $Pr^{\alpha}{}_2SO_4$, $Pr^{\beta}{}_2SO_4$, and $(n\text{-}C_5H_{11})_2SO_4$ give 29—50% yields; $NaPhSO_4$ gives 60—88% yields of Ph alkyl ethers, but only 25% of Ph_2O. Best yields are obtained by using 2 mols. of ester. Cryst. esters insol. in liquid NH_3 (*e.g.*, p-$C_6H_4Me{\cdot}SO_3C_5H_{11}$ and p-$C_6H_4Me{\cdot}SO_3Ph$) do not react, neither does NaOPh or $NaHC_2$ with n-$C_5H_{11}{\cdot}OAc$, or Bu_3PO_4 with $Bu^{\alpha}OH$. *γ-Methyl-Δ^α-butinene* is prepared, but not described. Prep. of p-$C_6H_4Me{\cdot}SO_3Bu^{\alpha}$, b.p. 170—172°/10 mm. (98% yield), $Pr^{\alpha}{}_2SO_4$, b.p. 120°/20 mm. (quant. yield from *cyclo*propane and H_2SO_4), and $Pr^{\beta}{}_2SO_4$ (50% yield from $CHMe{:}CH_2$ and H_2SO_4) is described. R. S. C.

Tribromoethyl borate. A. Mangini (Riv. Biol., 1937, **22**, 457—462).—$CBr_3{\cdot}CH_2{\cdot}OH$ (I) (avertin) with BBr_3 in light petroleum yields *tribromoethyl borate* (II), m.p. 179—182°, sol. in fats and readily hydrolysed by H_2O. (II) resembles (I) in narcotic properties. The lack of narcotic action in other derivatives of (I) is due to non-liberation of the alcoholic OH of (I) in the organism (cf. this vol., 82). F. O. H.

Synthesis of the biological *l*(−)-glyceryl-α-phosphoric acid. H. O. L. Fischer and E. Baer (Naturwiss., 1937, **25**, 589).—d(+)-*iso*Propylideneglycerol and $POCl_3$ in quinoline give the *Ba* α-*phosphate* and thence the natural *l*(−)-glyceryl-α-phosphoric acid, $[\alpha]_D$ −1·45° in 2N-HCl (Me_2 ether Me_2 ester, $[\alpha]_D$ −4·78°; Ag salt, $[\alpha]_D$ +1° in dil. aq. NH_3). Embden's mechanism for the disproportion-

ation of triosephosphoric acids is thus proved. The following mechanism is probable: $CO_2H{\cdot}C(OH){:}CH_2 + OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}PO_3H_2 \rightarrow OH{\cdot}CHMe{\cdot}CO_2H + OH{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}PO_3H_2$. R. S. C.

Synthetic optically active glycerides. H. O. L. Fischer and E. Baer (Naturwiss., 1937, **25**, 588—589).—Ni-hydrogenation of *iso*propylidene-*d*-glyceraldehyde (from 1 : 2 : 5 : 6-di*iso*propylidenemannitol) gives d(+)-αβ-iso*propylideneglycerol* (I), b.p. 80—80·5°/12 mm., $[\alpha]_D^{20}$ +12·6° (homogeneous), −1·6° in H_2O, +11·09° in C_5H_5N, and thence the *α-benzoate*, b.p. 159—160°/10·5 mm., $[\alpha]_D^{18}$ +12·3°, *-acetate*, b.p. 85—86°/10—11 mm., $[\alpha]_D$ +3·24°, *-laurate*, b.p. 130—131°/0·002 mm., $[\alpha]_D^{21}$ +3·42°, *-stearate*, m.p. 43·5°, $[\alpha]_D^{50}$ +3·0 to 3·5° (molten), $[\alpha]_D$ +1·9° in C_5H_5N, and *-palmitate*, m.p. 33—35°, $[\alpha]_D$ +2·48° in C_5H_5N, +4·38° (molten), hydrolysed to d(+)-*glycerol* α-*laurate*, m.p. 53—54°, $[\alpha]_D$ −3·76° in C_5H_5N, *-stearate*, m.p. 76—77°, $[\alpha]$ −3·58° in C_5H_5N, *-palmitate*, m.p. 71—72°, $[\alpha]_D$ −4·37°, and -p-*toluenesulphonate*, m.p. 63—64°, $[\alpha]_D$ −7·3° in C_5H_5N, which afford d(+)-*glycerol* α-*laurate* α′β-*distearate*, m.p. 67—68°, $[\alpha]_D$ 0° in C_5H_5N, α-*stearate* α′β-*dipalmitate*, m.p. 62·5°, $[\alpha]_D$ 0° in C_5H_5N or $CHCl_3$, α-*palmitate* α′β-*dilaurate*, m.p. 44°, $[\alpha]_D$ 0° in C_5H_5N, and α-p-*nitrobenzoate* α′β-*dibenzoate*, m.p. 77—78°, $[\alpha]_D$ −19·9° in $C_2H_2Cl_4$. d(+)-αβ-iso*Propylideneglycerol* α′-*Me ether*, b.p. 43—44°/10·5 mm., $[\alpha]_D$ +20·14°, is prepared. The p-*nitrobenzoate* of (I) gives d(+)-*glycerol* α-p-*nitrobenzoate*, m.p. 88—89°, $[\alpha]_D$ −17·1° in EtOH, and thence the α′-*CPh*$_3$ *ether* α-p-*nitrobenzoate*, m.p. 138—139°, $[\alpha]_D$ −5·06° in $C_2H_2Cl_4$, and α′-*CPh*$_3$ *ether*, m.p. 97—98°, $[\alpha]_D$ +2·8° in $C_2H_2Cl_4$, d(+)αβ-iso*propylideneglycerol* α′-*CPh*$_3$ *ether*, $[\alpha]_D$ −10·8° in $C_2H_2Cl_4$, and l(−)-iso*propylideneglycerol*, $[\alpha]_D$ −12·6°. Unless otherwise stated, [α] are for the homogeneous substance. R. S. C.

Amorphous and crystallised oxide hydrates and oxides. XXXIII.—See A., I, 528.

Amplified distillation of binary aliphatic acid mixtures. W. N. Axe and A. C. Bratton (J. Amer. Chem. Soc., 1937, **59**, 1424—1425).—By amplified distillation (*i.e.*, dilution with 10 vols. of hydrocarbon oil prior to distillation) 1 : 1 mixtures give 72% of pure $Et^{\alpha}CO_2H$ with 73% of pure $Pr^{\alpha}CO_2H$ or 45·5% of pure $pr^{\alpha}CO_2H$ with 16·5% of pure $CH_2Pr^{\beta}{\cdot}CO_2H$, the corresponding figures for ordinary distillation being 13·5, 50·4, 0, and 13·2%, respectively. The Dyer method of analysing the acids is modified. R. S. C.

Preparation of acetic anhydride and homologues. V. M. Rodionov, A. I. Smarin, and T. A. Abletzova (Chim. Farm. Prom., 1935, No. 2, 102—106).—A new method is based on the reaction $2NaOAc + N_2O_4 \rightarrow Ac_2O + NaNO_2 + NaNO_3$. Ch. Abs. (*r*)

Preparation of methyl methacrylate from *iso*butyric acid. J. S. Salkind and I. F. Markov (J. Appl. Chem. Russ., 1937, **10**, 1042—1044).—$Pr^{\beta}CO_2H$ and Cl_2 (60-watt lamp illumination) at an initial temp. of 50° yield $CMe_2Cl{\cdot}CO_2H$ (*Me* ester, b.p. 64—65°/55 mm., 128—129·5°/753 mm.) and $CH_2Cl{\cdot}CHMe{\cdot}CO_2H$ (*Me* ester, b.p. 85—90°/60 mm., 151—155°/750 mm.). These esters yield $CH_2{:}CMe{\cdot}CO_2Me$ when boiled with quinoline in presence of quinol, and the acids give $CH_2{:}CMe{\cdot}CO_2H$ when distilled from active C. R. T.

Determination of oleic, linoleic, and linolenic acids in mixtures. E. Delvaux (J. Pharm. Belg., 1936, **18**, 101—105, 131—139, 153—159; Chem. Zentr., 1936, i, 3769).—The H_2 uptake of oleic acid (I), Me linoleate, linoleic acid (II), and mixtures with Et linoleate (III) in presence of a catalyst has been measured. The prep. of pure (I), (II), and linolenic acid is described and the absorption spectra of their pure Me esters and of pure (III) recorded. A method of determination based on $(CNS)_2$ addition, hydrogenation, and absorption spectra is described. H. N. R.

***X*-Ray and thermal examination of the glycerides. III. αα′-Diglycerides.** T. Malkin, M. R. el Shurbagy, and (in part) M. L. Meara (J.C.S., 1937, 1409—1413; cf. A., 1934, 666; 1937, 17).—The αα′-diglycerides from αα′-didecoin to αα′-dipentadecoin exist in three solid forms (α, β′, and β) and from αα′-dipalmitin to αα′-distearin in two solid forms (α and β). The β-form is stable and high-melting, and separates from solvents; the lower-melting, metastable α-form separates first from the molten diglyceride, and rapidly changes into the β′-form (lower members) or the β-form (higher members), the β′-form rapidly changing to the β. The β′-form has m.p. intermediate between the α- and the β-forms. *X*-Ray examination shows that the crystals are built up of layers of double mols., with the hydrocarbon chains lying parallel on the same side of the glyceride mol. Suitable esterification of the monoglyceride with acid in presence of p-$C_6H_4Me{\cdot}SO_3H$, or with the acid chloride in C_5H_5N, yields the following (the m.p. given is that of the stable β-form): αα′-*di-*, m.p. 44·5°, *-un-*, m.p. 49°, *-tri-*, m.p. 56·5°, *-penta-*, m.p. 68·5°, and *-hepta-decoin*, m.p. 74·5°. J. D. R.

Association of certain fatty acids on the basis of their molecular polarisation. K. Hrynakowski and A. Żochowski (Ber., 1937, **70**, [*B*], 1927—1743).—The dielectric polarisation of the higher fatty acids increases with increasing concn. of their solutions in C_6H_6 in consequence of an increase in the mutual action of the hydrocarbon residues which diminishes with the increasing length of the hydrocarbon chain. The higher fatty acids do not show dipole character since their mols. associate in pairs to complexes of which the total moment is zero. The proportion of at. polarisation to displacement polarisation diminishes with lengthening of the chain. The elasticity of the mol. diminishes with increasing chain length in the homologous series of the fatty acids; the effect is probably a parallel to diminution in the mutual influence of the hydrocarbon residues. H. W.

Oxidation of fats by per-acids. H. Böhme and G. Steinke (Ber., 1937, **70**, [*B*], 1709—1713).—A weighed quantity of the fat or fatty acid in Et_2O is treated with the per-acid (usually $CO_2H{\cdot}C_6H_4{\cdot}CO_2OH$) (I) in Et_2O at the required temp. After given intervals the mixture is cooled to 0° and

an aliquot portion is mixed with KI; the liberated I is determined by $Na_2S_2O_3$. Oleic acid is oxidised somewhat more rapidly than elaidic acid. With octadecadienoic acid an inflexion in the graph occurs after consumption of about 50% of the calc. quantity of (I) owing to the presence of the conjugated double linking. The consumption of (I) corresponds quantitatively with the I val. for triolein, olive oil, and cacao butter. Sesamé and poppy-seed oil require < and linseed oil considerably < the amount of (I) indicated by the I val. As far as can be judged at present, a parallelism appears between the diene and per-acid nos. H. W.

Wax of white pine chermes. B. K. Blount, A. C. Chibnall, and H. A. El Mangouri (Biochem. J., 1937, **31**, 1375—1378; cf. A., 1936, 1137).—The wax consists of ι-*keto*-n-*triacontanoic acid*, m.p. 103·3—103·6° [*oxime* (I), m.p. 62·5°], esterified with ρ-*keto*-n-*hexatriacontanol* (II), m.p. 102—102·5° (*acetate*, m.p. 84·2°; *oxime*, m.p. 78·5°), and a small amount of a *substance*, m.p. 78°, possibly a *n*-fatty acid. (I) with H_2SO_4 (100°; 1 hr.) gives a mixture of amides which with conc. HCl at 180° for 4 hr. yields arachidic acid (III), *n*-nonane-αι-dicarboxylic acid, *n*-nonadecanamine hydrochloride (IV), and θ-amino-*n*-decoic acid hydrochloride. (II) with CrO_3 gives the corresponding keto-acid, the oxime of which, as in the case of (I), yields (III), (IV), *n*-pentadecane-αω-dicarboxylic acid, and a trace of ξ-aminopalmitic acid hydrochloride. W. McC.

Wool fat. A. Heiduschka and E. Nier (J. pr. Chem., 1937, [ii], **149**, 98—106).—Wool fat is hydrolysed by KOH–EtOH and the saponifiable and unsaponifiable (I) matter are separated from one another by Et_2O. Cerotic acid, m.p. 78°, is obtained by fractional pptn. from the mixture of fatty acids and is purified through the Et ester and the Li salt. The *Pr*$^{\alpha}$, m.p. 65·5°, *Pr*$^{\beta}$, m.p. 75°, *Bu*$^{\beta}$, m.p. 65·5°, and *amyl*, m.p. 63°, esters are new. Lanoceric acid, m.p. 102·5° (*Ag* salt; *Et* ester, m.p. 78°), is isolated by using its sparing solubility in Et_2O. Evidence of the presence of lanocerolactone was not obtained. (I) is separated by crystallisation and pptn. from MeOH and EtOH or their mixtures into a no. of fractions from which ceryl alcohol, *iso*cholesterol, and cholesterol but not carnaubyl alcohol are isolated; other substances are present which could not be identified since they are smeary or resinous and retain these characteristics when oxidised. H. W.

Racemiase, an enzyme which catalyses racemisation of lactic acid.—See A., III, 311.

Polar group orientation in linear polymeric molecules. ω-Hydroxydecoic acids. W. B. Bridgman and J. W. Williams (J. Amer. Chem. Soc., 1937, **59**, 1579—1580).—Certain classes of polymerides of high mol. wt. do not give a measurable dispersion of ϵ in a frequency interval where this is expected from the chemical mol. wt. μ are determined for six polymerides of ω-hydroxydecoic acid (*M* 905—13,900). It appears that the μ is due mainly to rotation of the regularly spaced ester groups, for $\mu \propto \sqrt{M}$ and polarisation per g. of polymeride is independent of *M*. The polymerides probably consist of flexible chains. R. S. C.

Chemical constituents of lichens found in Ireland. *Lecanora sordida*, Th. Fr. G. Kennedy, J. Breen, J. Keene, and T. J. Nolan (Sci. Proc. Roy. Dublin Soc., 1937, **21**, 557—566).—Extraction of the lichen with Et_2O followed by treatment with light petroleum gave a mixture of 65% of atranorin and 35% of chloratranorin, *roccellic acid* (I), m.p. 131°, $[\alpha]_D$ +17·4° in EtOH, and an *acid*, $C_{21}H_{20}O_9Cl_2$, m.p. 258—260°, which gave a greenish-blue colour with EtOH–$FeCl_3$ (? thiophanic acid). Mannitol was also obtained from the residue. (I) is shown synthetically to be *α-methyl-β-dodecylsuccinic acid*, two forms, m.p. 131° and m.p. 81—82°, respectively. It gives a *Me*$_2$ ester, m.p. 28—29°, an *anil*, m.p. 57—58°, and a *derivative*, $C_{23}H_{35}O_4N_3$, m.p. 113—114°, with *p*-NO_2·C_6H_4·NH·NH_2. P. G. M.

Structure of glutaconic acid. A. I. Vogel, W. L. German, and G. H. Jeffery (Chem. and Ind., 1937, 804).—Determinations of the thermodynamic primary dissociation const. of glutaconic acid (I), m.p. 138°, at 25° by conductivity and of the two thermodynamic dissociation consts. by potentiometric titration with the quinhydrone electrode at 25° show the similarity of (I) and fumaric acid and provide evidence for the *trans* structure of the acid of m.p. 138°. H. W.

Ethyl α-formyl-α-α′-hydroxyethylglutaconate. H. Gault and M. Cogan (Compt. rend., 1937, **205**, 151—153; cf. A., 1901, i, 361).—CHO·CH_2·CO_2Et (as Na derivative) (1 mol.) with conc. HCl (1 mol.) and excess of MeCHO at −15° affords Et_2 α-formyl-α-α′-hydroxyethylglutaconate which cannot be distilled (*Ac* derivative, b.p. 160—163°/0·7 mm.). J. L. D.

Experiments towards the synthesis of *iso*fenchone. I. Synthesis of βδ-dimethylpentane-βδε-tricarboxylic acid. S. K. Ranganathan (J. Indian Chem. Soc., 1937, **14**, 264—267; cf. this vol., 4).—β-*Hydroxy*-ββδ-*trimethyladipolactone*, m.p. 128—129°, is obtained by hydrolysis of the corresponding Et ester, which with KCN at 220° gives βδ-dimethylpentane-βδε-tricarboxylic acid, m.p. 185—186° (cf. *loc. cit.*). The Et_3 ester of this when cyclised with Na-C_6H_6 and subsequently hydrolysed and decarboxylated gives *iso*fenchocamphoronic acid [semicarbazone, m.p. 212—213° (decomp.) (cf. Bardhan *et al.*, this vol., 67)]. H. G. M.

Production of phosphoglyceric acid.—See A., III, 395.

Mol. wt. of racemic acid. E. W. Blank (J. Chem. Educ., 1937, **14**, 393).—This mol. wt. is twice that of the other forms of tartartic acid, and racemic acid should be represented by $2C_4H_6O_6 + 2H_2O$, not $C_4H_6O_6 + H_2O$. L. S. T.

Enzymic determination of ascorbic acid.—See A., III, 406.

Stability of ascorbic and dehydroascorbic acids.—See A., III, 364.

Catalysis of Cannizzaro's reaction by active nickel and platinum. Application to aldoses.

M. Delépine and A. Horeau (Compt. rend., 1937, **204**, 1605—1608).—CH_2O, $Pr^{\alpha}CHO$, and PhCHO with NaOH and Ni at room temp. rapidly undergo the Cannizzaro reaction (cf. A., 1897, i, 504). Galactose similarly affords dulcitol and galactonic acid in good yield but not without Ni; glucose and arabinose also react. With Pt as catalyst, the H_2 liberated in the oxidation reaction destroys some of the initial aldehyde. The reaction with Ni probably proceeds similarly although H_2 is not liberated, for crotonic acid added to the reaction mixture is partly reduced. J. L. D.

Determination of formaldehyde and formic acid in the presence of one another. L. Spitzer (Annali Chim. Appl., 1937, **27**, 292—296).—CH_2O is determined iodometrically by the Romijn method (A., 1897, ii, 166) and the total CH_2O and HCO_2H, bromometrically, by the Meulen (A., 1930, 1392) or a modified Oberhauser method (A., 1927, 475). L. A. O'N.

Kinetics of polymeric aldehydes. VII. Velocity of hydrolysis of formaldehyde acetals. J. Löbering and A. Fleischmann (Ber., 1937, **70**, [*B*], 1713—1719).—Increase in size of the alkyl residue causes increase in the temp. coeff. of the hydrolysis of $CH_2(OMe)_2$, $CH_2(OEt)_2$, and $CH_2(OPr^{\beta})_2$. It appears therefore that the acetal yields a mol. of alcohol and a mol. of semiacetal which immediately, possibly owing to a very rapid intramol. process, gives CH_2O and a second mol. of alcohol. The coeffs. of these two reaction stages obey the Arrhenius law. The temp.-dependence of the dimeric product can be expressed by the same simple formula. Dimethoxydimethyl ether must therefore decompose thus: $O(CH_2{\cdot}OMe)_2 + H_2O \rightarrow OMe{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}OH$ (I) + MeOH; (I) + $H_2O \rightarrow CH_2(OH)_2 + OMe{\cdot}CH_2{\cdot}OH$ (II); (II) + H_2O = MeOH + $CH_2(OH)_2$. Since these three stages are alike in character their summation coeff. must be determined by the same simple law. The rate of reaction is governed by that of the first step in a degree which increases with temp. Examination of the velocity coeff. of the initial members of the polymeric homologous series of Me_2 ethers shows that $CH_2(OMe)_2$ decomposes most slowly and the dimeride has the highest hydrolysis const. At first the terminal group suddenly loses its influence on the total reaction. With increasing degree of polymerisation other influences make themselves felt; these cause a continuous decrease in the rate of depolymerisation with increasing chain length. H. W.

Magnetism and polymerisation. II. Oxymethylene diacetates and polyoxymethylenes.—See A., I, 451.

Kinetics of polymeric aldehydes. VI. Formation and decomposition of polyoxymethylene. J. Löbering (Z. Elektrochem., 1937, **43**, 638—643; cf. this vol., 228, 274).—The polymerisation of aq. CH_2O reaches an equilibrium state, and the degree of polymerisation of the pptd. polymeride, characteristic for the temp. and initial concn., increases with the temp. and with diminished initial concn. If the pptd. polymeride is removed from the solution it can be redissolved partly to form the equilibrium solution with the depolymerised form, but the velocity of dissolution decreases with increasing degree of polymerisation. If the filtrate after removing the polymeride is kept at a lower temp. a further ppt. of a lower polymeride is formed. Catalysts increase the chain length of the polymeride, the effects being in the order $H_2SO_4 > HCl > NaOH$. Polymerisation probably occurs exclusively in solution and all polymerides are slightly sol. J. W. S.

Hydration of unsaturated compounds. VI. Rate of hydration of *trans*-crotonaldehyde. Equilibrium between *trans*-crotonaldehyde and aldol in dilute aqueous solution. S. Winstein and H. J. Lucas (J. Amer. Chem. Soc., 1937, **59**, 1461—1465).—*trans*-CHMe:CH·CHO (I) is reversibly hydrated to aldol (II) in 0·5N-HNO_3 or -$HClO_4$, equilibrium at 25° being with hydration of 47% of (I) and at 35° with hydration of 39% of (I). Energies of activation are 18·23 and 24·48 kg.-cal. for hydration and dehydration, respectively. Hydration and dehydration are first-order reactions, the former with respect to concns. of acid and (I), the latter with respect to concns. of acid and (II). The reactions in $HClO_4$ are 6—7% slower than in HNO_3. CHMe:CH·CH_2·OH and *trans*-CHMe:CH·CO_2H are not appreciably hydrated in aq. HNO_3 at 25°. R. S. C.

Detection and determination of small amounts of glucose in mixtures containing maltose. M. Somogyi (J. Biol. Chem., 1937, **119**, 741—747).—The fermentation rate of a sugar solution at p_{H} 7·2—7·4 is compared with that of a 1% maltose solution. In presence of glucose the fermentation proceeds faster than that of maltose. A quant. method is described, together with an alkaline reagent for the determination of slowly oxidised sugars. J. L. C.

Disintegration of methylated glucoses in alkaline medium. N. Ariyama and T. Kitasato (J. Biochem. Japan, 1937, **25**, 357—373).—The reducing properties of various mono- and poly-methylglucoses to various reagents and under various conditions were examined. The results of Sobotka (A., 1926, 1026) are generally confirmed. With mild treatment by alkaline $K_3Fe(CN)_6$ at 70°, the velocity of oxidation of 3- and 3 : 5 : 6-derivatives is higher initially but diminishes more rapidly than that of glucose (I); a similar relationship exists between the 2 : 3 : 4 : 6- and 2-derivatives. Transformation of 2-methylglucose occurs more readily than that of (I). With HIO_4, production of aldehyde decreases with proximity of Me to $C_{(6)}$ and with the increase in no. of Me groups. Data for the equilibrium potentials of Me derivatives of (I) are given. F. O. H.

Emulsin. XXX. Enzymic hydrolysis of 6-halohydrin-β-*d*-glucosides and of related compounds. B. Helferich, S. Grünler, and A. Gnüchtel (Z. physiol. Chem., 1937, **248**, 85—95; cf. A., III, 313).—The rate of hydrolysis by the emulsin (I) of sweet almonds of 6-substituted β-*d*-glucosides of vanillin decreases as the vol. of the substituent, as deduced by the methods of Biltz (A., 1931, 895) (OMe an exception) and Stuart (A., 1935, 432) (OH and OMe exceptions) and from the parachor (OH an exception), increases; thus H > OH

> F > Cl > Br > OMe > I. Acetobromoglucose 6-chlorohydrin with vanillin and KOH gives the *triacetate*, m.p. 141°, $[\alpha]_D^{21}$ −53·0° in $CHCl_3$, of *vanillin*-β-d-*glucoside* 6-*chlorohydrin*, m.p. 162—164°, $[\alpha]_D^{21}$ −85·5° in C_5H_5N. The 6-*bromohydrin*, m.p. 181—182°, $[\alpha]_D^{19}$ −110° in aq. EtOH [*triacetate* (II), m.p. 146—148°, $[\alpha]_D^{19}$ −58·1° in $CHCl_3$], and *vanillin*-β-d-iso*rhamnoside* (III), m.p. 162—165°, $[\alpha]_D^{20}$ −85·2° in H_2O (*triacetate*, m.p. 179—181°, $[\alpha]_D^{18}$ −31·5°), are obtained in the same way, and (II) at 100—120° for 3 hr. with NaI in $COMe_2$ gives the *triacetate*, m.p. 136—138°, $[\alpha]_D^{16}$ −67·3° in $CHCl_3$, of the 6-*iodohydrin*, m.p. 205—207° (decomp.), $[\alpha]_D^{20}$ −116° in C_5H_5N. (III) is less rapidly hydrolysed by (I) than is the corresponding glucoside. *Phenol*-β-d-*glucoside* 6-*fluorohydrin* has m.p. 148—149°, $[\alpha]_D^{21}$ −79° in H_2O.

W. McC.

Ketone sugar series. VIII. Structure of *l*-sorbose penta-acetate. F. B. Cramer and E. Pacsu (J. Amer. Chem. Soc., 1937, **59**, 1467—1469; cf. this vol., 325).—Sorbose tetra-acetate has m.p. 100—101·5°, $[\alpha]_D^{20}$ −19·4°, and contains no solvent. With Ac_2O and $ZnCl_2$ at room temp. or 50° it gives the penta-acetate (I), which is a derivative of keto-sorbose, since with H_2–Pt, best in Et_2O at 4 atm., it yields a syrup, whence by acetylation 60% of *l*-iditol and 40% of *d*-sorbitol hexa-acetates are obtained. *l*-Iditol is readily prepared by this method. Ketone reagents are without effect on (I); addition of a little NaOH to (I) in $COMe_2$ gives a deep yellow solution, which after neutralisation reduces $KMnO_4$.

R. S. C.

History of the rotatory power of sucrose. D. Sidersky (Bull. Assoc. Chim. Sucr., 1937, **54**, 413—424).—An account is given of the more important determinations, and results are summarised in a table showing vals. of $[\alpha]_D^{20}$ for different concns. of sucrose. J. H. L.

Sugar osazones and their anhydrides. E. E. Percival and E. G. V. Percival (J.C.S., 1937, 1320—1325).—Lactosephenylosazone is acetylated (Ac_2O–C_5H_5N) to the *hepta-acetate*, m.p. 105—110°, $[\alpha]_D^{20}$ +27° in $CHCl_3$, which with NaOH in aq. $COMe_2$ affords anhydrolactosephenylosazone, m.p. 231—232°, identical with that of Diels and Meyer (A., 1935, 1225), converted by acetylation into *anhydrolactosephenylosazone penta-acetate*, m.p. 115—117°, $[\alpha]_D^{20}$ −102° in $COMe_2$. Similar acetylation of maltose-phenylosazone yields the *hepta-acetate*, m.p. 162°, $[\alpha]_D^{20}$ +41° in $CHCl_3$, deacetylated (NaOH in aq. $COMe_2$) to two *products*, $C_{24}H_{30}O_8N_4$ (I), m.p. 245—246°, $[\alpha]_D^{20}$ +58° in C_5H_5N, and $C_{24}H_{34}O_{10}N_4$ (II), m.p. 194°, $[\alpha]_D^{20}$ +160° in C_5H_5N. Acetylation of (I) yields an amorphous *penta-acetate*, $[\alpha]_D^{20}$ +90·7° in $COMe_2$, whilst (II) affords an amorphous *penta-acetate*, m.p. 110—112°, $[\alpha]_D^{20}$ +150° in $COMe_2$. By acetylation (Ac_2O–C_5H_5N) of the appropriate osazone, d-*xylosazone triacetate*, m.p. 116—117°, $[\alpha]_D^{16}$ −46° in $CHCl_3$, l-*arabinosazone triacetate*, m.p. 114°, $[\alpha]_D^{16}$ +5° in $CHCl_3$, and l-*rhamnosazone triacetate*, m.p. 75°, $[\alpha]_D^{18}$ +52° in $CHCl_3$, are produced; attempted deacetylation of these led to non-cryst. products. Monoanhydro-glucosazone and -galactosazone when acetylated afford *monoanhydroglucosazone diacetate*, m.p. 70°, $[\alpha]_D^{17}$ −125° in $CHCl_3$, and *monoanhydrogalactosazone diacetate*, m.p. 86°, $[\alpha]_D^{16}$ +64° in $CHCl_3$, respectively. *Fructose-phenylmethylhydrazone*, m.p. 170°, $[\alpha]_D$ −253° in C_5H_5N–EtOH (4 : 6) (from fructose and NPhMe·NH_2 in EtOH–aq. AcOH), when acetylated yields a *penta-acetate*, m.p. 121°, $[\alpha]_D^{17}$ +86·5° in $CHCl_3$, whilst the phenylmethylosazone affords a *tetra-acetate*, m.p. 128°, $[\alpha]_D^{17}$ −435° in $CHCl_3$, −236° in 95% EtOH. Glucosephenylhydrazone yields a *penta-acetate*, m.p. 152°, $[\alpha]_D^{17}$ −10·4° in C_5H_5N, and glucosephenylmethylhydrazone a *penta-acetate*, m.p. 113—114°, $[\alpha]_D$ +157° in $CHCl_3$. There is little evidence to differentiate between the *N*-Ac and the *O*-Ac structures in the acetates formed. J. D. R.

Titrimetric determination of sugar.—See A., III, 410.

***d*- and *l*-Borneolglucosides.** W. Lipschitz and E. Büding (Compt. rend., 1937, **205**, 58—60; cf. A., 1909, i, 365).—Acetobromoglucose, m.p. 87—89°, $[\alpha]_D^{20}$ +195·5° in Et_2O (cf. A., 1917, i, 467), with Ag_2CO_3 and *d*-borneol affords *d*-borneolglucoside tetra-acetate, m.p. 131·5° (lit., 119—120°), $[\alpha]_D^{20}$ −20·9° in C_6H_6, hydrolysed by 0·4N-$Ba(OH)_2$ at 60° to *d*-borneol-β-glucoside, m.p. 154—155° (lit., 134—136°), $[\alpha]_D^{20}$ −15·2° in EtOH, H_2O content, 5·4% (lit., 4·54%), but after crystallisation from H_2O it was 4·35%. Similarly prepared, *l*-borneolglucoside tetra-acetate has m.p. 118—119·5°, $[\alpha]_D^{21}$ −52·7° in C_6H_6, and *l*-borneol-β-glucoside, m.p. 135—136°, $[\alpha]_D^{21}$ +55·6° in 95% EtOH, H_2O content 4·45%.

J. L. D.

Soluble dextrins and the constitution of starch. K. Myrbäck (Current Sci., 1937, **6**, 47—50).—A review.

Are dextrins fermentable? H. Haehn, M. Glaubitz, and W. Gross (Z. Spiritusind., 1937, **60**, 197—198, 206, 208).—A detailed account of work already noted (this vol., 370). I. A. P.

Molecular structure of canna starch. W. Z. Hassid and W. H. Dore (J. Amer. Chem. Soc., 1937, **59**, 1503—1508).—Hydrolysis of the fully methylated starch, followed by quant. separation of the cleavage products into 2 : 3 : 4 : 6-tetramethyl- and 2 : 3 : 6-trimethyl-glucose, shows the starch mol. to contain about 27 anhydroglucose units. These probably form chains, which are bound by primary valencies, and are associated by secondary valencies to form a colloidal unit, $[(C_6H_{10}O_5)_m]_n$, where n is the no. of associated chains and m the no. of glucose units in the chain (26—30). A starch triacetate, containing a single unaggregated mol., has been prepared directly from canna starch without special preliminary disaggregation. E. S. H.

Glycogen. VI. Molecular structure of horse muscle-glycogen. D. J. Bell (Biochem. J., 1937, **31**, 1683—1691; cf. A., 1937, III, 7).—Acetylation followed by simultaneous deacetylation and methylation of the glycogen (I) affords a methylated (I), $[\alpha]_D$ +208° in $CHCl_3$, +207° in H_2O, org. P 0·018%, which, on hydrolysis and fractional distillation of the methylated hydrolysate, afforded 10% of 2 : 3 : 4 : 6-tetramethylmethylglucoside and nearly 15% of dimethylmethylglucoside (II). Hence (I) has a min.

chain length of 11—12 glucose units. The bearing of the production of (II) on the possible aggregation of relatively small "unit-chains" is discussed. F. O. H.

Action of liquid ammonia on cellulose fibres. Formation of ammonia-cellulose I, ammonia-cellulose II, and cellulose III. K. Hess and J. Gundermann (Ber., 1937, 70, [*B*], 1788—1799).—In contact with liquid NH_3 cellulose forms two ammoniates dependent on temp.; these are mutually interconvertible between −20° and −30°. *Ammonia-cellulose* II (I), the form stable at the lower temp., has a fibre period of 15·20 A. = 3 × 5·07 A. and trigonal symmetry. Probably the fibre axis is a trigonal screw axis. The dimensions of the usually-hexagonal, elementary cell are $a = c = 14{\cdot}50$, b 14·20 A., β 60°, cell vol. = 2764 A.^{3} The probable composition is $C_6H_{10}O_5(NH_3)_6$. *Ammonia-cellulose* I (II), the variety more stable at the higher temp., has fibre period 10·30 = 2 × 5·15 A. A satisfactory interpretation of its Röntgen diagram cannot yet be given. It is not yet possible to decide whether (I) and (II) are different modifications with the same chemical composition or ammoniates with different NH_3 content. Decomp. of (I) or (II) leads to a new modification, *cellulose* III (III). Its Röntgen diagram resembles that of hydrocellulose (IV), having, as has natural cellulose (V), a fibre period of 10·3 A. In contrast with (IV), (III) passes at 200° largely into (V) of which it is regarded as an unstable modification. Except for small differences the changes above described occur similarly with natural or mercerised cellulose fibres. It is therefore possible through (III) to effect a re-conversion of (IV) into (V). H. W.

Available surface of cellulose.—See A., I, 442.

Reaction metal hydroxide solution–cellulose fibre. III. Transformation reactions in 0—10% sodium hydroxide solutions of sodium celluloses obtained in highly concentrated sodium hydroxide solutions. W. Schramek and O. Succowsky (Kolloid-Z., 1937, 80, 129—138; cf. A., 1935, 1074).—Published work is critically discussed and supplementary data have been obtained by *X*-ray analysis of the products. The product of direct reaction of cellulose with 10—20% aq. NaOH is Na-cellulose I (period 10—20 A.), and with >20% NaOH is Na-cellulose II (15 A.). By dilution of these liquors the products are Na-cellulose IV (10 A.) and Na-cellulose IIh (15 A.), respectively, both of which can be further transformed into cellulose hydrate. Na-cellulose III is an intermediate, unstable modification (10 A.). The conditions of interconversion of these products are described. E. S. H.

Oxycellulose. J. Dumas (Rev. Gén. Mat. Col., 1937, 41, 381—382).—The intensity of colour and its tendency towards grey produced by the action of Nessler's reagent on cellulose increases with the proportion of oxycellulose; the aldehydic group of the latter causes the production of Hg_2I_2 which passes into HgI_2 + Hg. H. W.

Polyamines. III. Preparation of unsymmetrical amines of the type NHR·C_2H_4·NH·C_2H_4·NH_2 and NH_2·C_2H_4·NH·C_3H_6·NH_2, and the action of ammonia on di-*p*-toluenesulphonylbis-(β-chloroethyl)ethylenediamine. D. H. Peacock and Y. S. Gwan (J.C.S., 1937, 1468—1471; cf. A., 1934, 1207; 1936, 1493).—*p*-Toluenesulphonbenzyl-β-hydroxyethylamide with $SOCl_2$ in C_5H_5N yields p-*toluenesulphonbenzyl*-β-*chloroethylamide* (I), m.p. 69°, which with $(CH_2{\cdot}NH_2)_2$ (II) affords a mixture of the *dihydrochloride*, m.p. 149—150°, of N-p-*toluenesulphonbenzylamidoethylethylenediamine*, and the *hydrochloride* m.p. 141—142°, of NN′-*bis*-(β-p-*toluenesulphonbenzylamidoethyl*)*ethylenediamine* [p-$C_6H_4Me{\cdot}SO_2{\cdot}N(CH_2Ph){\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}]_2$. *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NEtNa$ and $Cl{\cdot}[CH_2]_2{\cdot}OH$ or $(CH_2)_2O$ yield p-*toluenesulphon*-(β-*hydroxyethyl*)*ethylamide*, converted ($SOCl_2$–C_5H_5N) into p-*toluenesulphon*-(β-*chloroethyl*)*ethylamide*, m.p. 67°, which, treated successively with (II) in $C_5H_{11}{\cdot}OH$ and *p*-$C_6H_4Me{\cdot}SO_2Cl$, gives the *tri*-p-*toluenesulphonyl* derivative, m.p. 203°, of N-β-*aminoethyl*-N′-*ethylethylenediamine*. *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NHNa$ with $Cl{\cdot}[CH_2]_3{\cdot}OH$ yields crude p-*toluenesulphon*-γ-*hydroxypropylamide*, converted ($SOCl_2$–C_5H_5N) into p-*toluenesulphon*-γ-*chloropropylamide*, m.p. 53°, which with (II) affords the *dihydrochloride*, m.p. 202°, of N-(γ-p-*toluenesulphonamidopropyl*)*ethylenediamine*, and NN′-*bis*-(γ-p-*toluenesulphonamidopropyl*)*ethylenediamine dihydrochloride*. (I) with $NH_2{\cdot}[CH_2]_3{\cdot}NH_2$ gives the *trihydrochloride*, m.p. 205°, of β-(p-*toluenesulphonamidoethyl*)*trimethylenediamine*, and the *dihydrochloride*, m.p. 215°, of NN′-*bis*-(β-p-*toluenesulphonamidoethyl*)*trimethylenediamine*. (*p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot})_2$ and $(CH_2)_3O$ with EtOH–NaOEt–C_6H_6 afford a mixture of NN′-*di*-p-*toluenesulphonyl*-NN′-*bis*-(β-*hydroxyethyl*)*ethylenediamine* (IV), m.p. 144°, and *di*-p-*toluenesulphonyl*-N-β-*hydroxyethylethylenediamine* (V), which is converted ($SOCl_2$) into *di*-p-*toluenesulphonyl*-N-β-*chloroethylethylenediamine*, m.p. 111°, transformed by Na in EtOH or by (II) into 1 : 4-di-*p*-toluenesulphonylpiperazine, m.p. 291° (cf. A., 1934, 1207). With $SOCl_2$–C_5H_5N–CCl_4, (IV) yields NN′-*di*-p-*toluenesulphonyl*-NN′-*bis*-(β-*chloroethyl*)*ethylenediamine*, m.p. 145°, which with NH_3–EtOH gives NN′-*di*-p-*toluenesulphonyl*-NN′-*bis*-(β-*aminoethyl*)*ethylenediamine* (VI), m.p. 134° (*dihydrochloride*, m.p. 243°), and 1 : 4-*di*-p-*toluenesulphonyl*-1 : 4 : 7-*triazacyclononane*, m.p. 218° (*hydrochloride*, m.p. 289°). Hydrolysis of (VI) (conc. H_2SO_4) affords *NN′*-bis-(β-aminoethyl)ethylenediamine. *p*-Toluenesulphon-β-chloroethylamide and $NH(CH_2{\cdot}CH_2{\cdot}NH_2)_2$ in EtOH yield the *trihydrochloride*, m.p. >360°, of p-*toluenesulphonyl*-NN′-*bis*-(β-*aminoethyl*)*ethylenediamine*. J. D. R.

***iso*Propylmethyleneimine, b.p. 220°.**—See A., I, 501.

Synthesis of amino-acids by condensation of amines with aldehydes and hydrocyanic acid. Mechanism of synthesis, and application to synthesis of alkamino-acids. B. A. Raschkovan (Trav. Inst. Chim. Charkov, 1936, **2**, 41—79).—The mechanism of the Strecker reaction is discussed, and an electronic mechanism is proposed. Published work (this vol., 309) is described. R. T.

Combination of sugars with amino-acids in a current of oxygen. B. Bauminger and F. Lieben (Biochem. Z., 1937, 292, 92—97).—At initial p_H 8 and 70° the amount of CO_2 liberated by a current of

O_2 from a mixture of glucose (I) and glycine (II) is > that liberated from (I) alone, whilst the amount of acid (partly an increased amount of lactic acid) produced and the amount of (I) decomposed are increased, the effects being most pronounced when the mol. ratio (I) : (II) is 1·5 : 1. Liberation of CO_2 is favoured by alkaline media in the case of the mixture and by acid media in that of (I), so that when the initial p_H is 7·2 the reverse holds. The magnitude of the changes is increased by addition of $Fe^{\cdots}$ but the total amount of (I) decomposed remains small. (II) alone is but slightly affected (deaminated) by the O_2 current. Probably combination of (I) with (II) occurs. W. McC.

Interaction of α-amino-acids and peptides with sugars in aqueous solution. M. Frankel and A. Katchalsky (Biochem. J., 1937, **31**, 1595—1604).—The interaction of α-NH_2-acids and peptides with various monoaldoses and aldodisaccharides is followed by the lowering of p_H consequent on the disappearance of NH_2-groups during the reaction. The α-NH_2 appear to be the dominating factor. The reaction takes place over a p_H range of 4·5—11 and has an optimum zone. In a strongly alkaline medium (p_H >10) a second reaction predominates, the nature of which is discussed. P. W. C.

Alkamino-acids (hydroxyalkamino-acids); their synthesis and reactions. A. I. Kiprianov (Trav. Inst. Chim. Charkov, 1935, **1**, 39—51).—A review of published papers. R. T.

Amino-acids and related compounds. X. Electrolytic oxidation of aspartic acid and malonic acid. Y. Takayama and S. Miduno. XI. Formation of aldehydes by the electrolytic oxidation of α-amino-acids. Y. Takayama, T. Harada, and S. Miduno (Bull. Chem. Soc. Japan, 1937, **12**, 338—341, 342—349).—X. Aspartic acid in N-H_2SO_4 oxidised at a PbO_2 anode gives, at 35°, HCO_2H, $CH_2(CO_2H)_2$, $(\cdot CH_2\cdot CO_2H)_2$, NH_3, and CO_2 and at 100° the same products with MeCHO instead of $CH_2(CO_2H)_2$, which is similarly oxidised at 35° to HCO_2H and CO_2 and at 100° to HCO_2H and a little CH_2O. The mechanism of the oxidation is presumed to be through $CHO\cdot CH_2\cdot CO_2H$.

XI. The oxidation of glycine, alanine, valine, and leucine (cf. A., 1933, 1127), repeated at 100°, the volatile products being distilled off during electrolysis, gives rise to the corresponding aldehydes ($NH_2\cdot CHR\cdot CO_2H \rightarrow R\cdot CHO$). MeCHO can be isolated from the oxidation products of alanine at 35° when the volatile products are removed by bubbling air through the cell. F. R. G.

Formation of histamine from histidine by catalytic oxido-reduction. P. Holtz (Naturwiss., 1937, **25**, 589).—Alternate passage of O_2 (0·5—1 min.) and H_2 (2—3 min.) into 10 c.c. of neutral buffered 0·1% aq. *l*-histidine (I) hydrochloride in the presence of 1—2 mg. of Pd-black for 30 min. gives 2×10^{-5} g. of histamine (II), determined biologically. The formation of (II) from (I) in the presence of ascorbic acid and SH-compounds is due to oxidation by peroxidic intermediates, decarboxylation, and finally reduction. R. S. C.

Peptides of aminomalonic acid and of *l*(+)-αβ-diaminopropionic acid. F. Schneider (Biochem. Z., 1937, **291**, 328—339; cf. this vol., 233).—The hydrochloride of Et_2 aminomalonate (I) with $CH_2Ph\cdot COCl$ in presence of MgO gives the corresponding *carbobenzyloxy*-derivative, which with KOH in EtOH gives the *Et* ester, m.p. 66° [*chloride* (II), m.p. approx. 37°], of carbobenzyloxyaminomalonic acid. (II) with the Et ester of glycine (III) gives the Et_2 ester, m.p. 114°, of the *carbobenzyloxy*-derivative, m.p. 145° (decomp.), of the corresponding *peptide*, m.p. 181° (decomp.). (I) with the chloride (IV) of carbobenzyloxyglycine gives the Et_2 ester, m.p. 99°, of the *carbobenzyloxy*-derivative, m.p. 136° (decomp.), of *glycylaminomalonic acid*, decomp. >220°, and, with the chloride of carbobenzyloxy-*l*-alanine, the Et_2 ester (V), m.p. 121°, of the *carbobenzyloxy*-derivative, m.p. 140° (decomp.), of *l-alanylmalonic acid*, decomp. >225°, $[\alpha]_D^{21}$ +13·79°±0·3° in H_2O. (V) with NH_3 in MeOH gives the *carbobenzyloxy*-derivative, m.p. 220°, of the *diamide*, m.p. 171° (decomp.), $[\alpha]_D^{22}$ +3·96°±0·3° in H_2O. (II) with (III) gives the *Et* ester, m.p. 133°, of the *carbobenzyloxy*-derivative (*amide*, m.p. 175°) of aminomalonylglycine (*amide*, decomp. 201°). Me β-carbobenzyloxydiaminopropionate hydrochloride with (IV) in presence of MgO gives the *Me* ester, m.p. 91°, of *α-carbobenzyloxyglycyl-β-carbobenzyloxydiaminopropionic acid*, converted in the usual manner into the *sulphate*, $[\alpha]_D^{21}$ −16·50°±0·3° in H_2O, of α-glycyl-*l*-diaminopropionic acid. Me *l*-diaminopropionate with (IV) gives the *Me* ester, m.p. 133°, of *αβ-dicarbobenzyloxydiglycyl-l-diaminopropionic acid*, which yields the *sulphate*, $[\alpha]_D^{21}$ −1·09°±0·15° in H_2O, of αβ-diglycyl-*l*-diaminopropionic acid in the usual manner. Dicarbobenzyloxy-*l*-diaminopropionyl chloride with (III) Et ester gives the *Et* ester, m.p. 145—146°, of *dicarbobenzyloxy-l-diaminopropionylglycine*, m.p. 160°, converted in the usual way into *l-diaminopropionylglycine sulphate*, $[\alpha]_D^{22}$ + 30·90°±0·3° in H_2O. W. McC.

Diamino-acid, canavanine, and monoamino-acid, canaline. M. Kitagawa (J. Biochem. Japan, 1937, **25**, 23—41; cf. A., 1936, 320, 1236).—The prep. and properties of canavanine (I), $C_5H_{12}O_3N_4$ [*picrate*, m.p. 220°; *dipicrate*, m.p. 163—164°; *sulphate*, m.p. 172° (decomp.), $[\alpha]_D^{17}$ +19·41° in H_2O; Bz_3 derivative, m.p. approx. 86°; *Cu* salt, $(I)_2Cu$, m.p. 205—207° (decomp.); $CuSO_4$ derivative, $(I)_2CuSO_4$, m.p. approx. 190° (decomp.); *Me* ester *dihydrochloride*, m.p. 166—167° (decomp.)], are described. Hydrolysis by canavanase (pig's liver) affords (75% yield) canaline (II), $C_4H_{10}O_3N_2$ (A., 1934, 61), $[\alpha]_D^{21}$ −8·31 in H_2O [*flavianate*, m.p. 211° (decomp.); *dipicrate*, m.p. 193—194° (decomp.); *hydrochloride*, (II),1·5HCl, m.p. 166° (decomp.); sulphate, (II),0·75H_2SO_4, m.p. 97° (decomp.); *Cu* salt, $(II)_2Cu$; Et ester hydrochloride, m.p. 172—173° (decomp.)], the synthesis and constitution of which are discussed. The distribution and biological properties of (I) are reviewed. F. O. H.

Canavanine. VIII. M. Kitagawa and J. Tsukamoto (J. Agric. Chem. Soc. Japan, 1937, **13**, 601—612).—Canavanine when heated in aq. EtOH easily

loses NH_3 giving *deaminocanavanine*, $C_5H_9O_3N_3$. This gives a Sakaguchi reaction for guanido-fatty acids, forms a *Cu* salt and an *ester* with EtOH, gives a negative ninhydrin reaction, and on prolonged hydrolysis with acid yields canaline. A provisional structure is given. J. N. A.

α-Guanidoglutaric acid, a possible precursor of creatine. K. Thomas and A. Akao (J. Biochem. Japan, 1937, **25**, 339—356).—α-Guanidoglutaric acid, m.p. 150—152° (cf. Kapfhammer and Müller, A., 1934, 876) [*anhydride*, m.p. 245° (decomp.); *Me* ester *hydrochloride*, m.p. 135°; *oxalate*, m.p. 209° (decomp.); *Me* ester *oxalate*, m.p. 144—146°; *phenacyl* ester, m.p. 246°], and the following related compounds were prepared: *diphenacyl* ester, *anhydride*, and *phenacyl* ester *anhydride* of α-ureidoglutaric acid, m.p. 136·5° (decomp.), 186°, and 145°, respectively, and *phenacyl ureidoacetate*, m.p. 162°. The constitutions of some of these compounds and their bearing on the formation of creatine in the organism are discussed. F. O. H.

Constitution of octopine, a nitrogenous substance from the muscle of *Octopoda*. I. Properties and degradation. II. Synthesis. III. Stereochemistry. S. Akasi (J. Biochem. Japan, 1937, **25**, 261—280, 281—290, 291—298).—I. Octopode muscle yields arginine and 0·036% of *octopine* (I), $C_9H_{18}O_4N_4$, m.p. 281—282°, $[\alpha]_D^{17}$ +20·94° in H_2O [*picrate*, m.p. 225°; *flavianate*; $Cu(NO_3)_2$ salt, m.p. 247°]. (I) gives negative Jaffé and ninhydrin reactions and contains no NH_2-N. Hydrolysis with aq. $Ba(OH)_2$ affords $CO(NH_2)_2$ and *octopinic acid* (II), $C_8H_{14}O_4N_2$, m.p. 270—271° (decomp.), $[\alpha]_D^{20}$ +18·48° in H_2O (*Cu* salt, m.p. 237°; *Bz* derivative, m.p. 213—214°), containing 2 CO_2H and NH_2. Oxidation of (I) by $BaMn_2O_8$ yields γ-guanidobutyric acid. Condensation of $CN{\cdot}NH_2$ with (II) affords (I).

II. *d*-Arginine (III) with *dl*- or *l*-$CHMeBr{\cdot}CO_2H$ in dil. aq. NaOH at 37° for 72 hr. affords (I). Thus (I) is $NH_2{\cdot}C(:NH){\cdot}NH{\cdot}[CH_2]_3{\cdot}CH(CO_2H){\cdot}NH{\cdot}CHMe{\cdot}CO_2H$ and (II) $NH_2{\cdot}[CH_2]_3{\cdot}CH(CO_2H){\cdot}NH{\cdot}CHMe{\cdot}CO_2H$. (III) with $CH_2Br{\cdot}CH_2{\cdot}CO_2H$ yields the isomeride δ-guanido-α-(β-carboxyethylamino)valeric acid (IV), m.p. 275—276°, $[\alpha]_D^{14}$ +23·18° in H_2O (*picrate*, m.p. 225°).

III. (III) with *dl*- or *d*-$CHMeBr{\cdot}CO_2H$ yields iso*octopine* (V), $C_9H_{18}O_4N_4,2H_2O$, m.p. 158—159° [mixture with (I), m.p. 158°], $[\alpha]_D^{20}$ +25·77° in H_2O (*picrate*, m.p. 198°), oxidised to (II). Application of the method of Lutz and Jirgensons (A., 1931, 943) to (I), (IV), and (V) is described and the configuration of the substances discussed. F. O. H.

Relations of thiocarbamide, cysteine, and the corresponding disulphides. G. Toennies (J. Biol. Chem., 1937, **120**, 297—313).—Cysteine (I) oxidised by dithioformamidine (II) gives, contrary to Pirie (A., 1933, 1018), *S*-(guanylthio)-*l*-cysteine, $NH{:}C(NH_2){\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (III), isolated as its *hydrochloride*, decomp. 150—155°, $[\alpha]_{Hg}^{26}$ −110°. Cystine (IV) with (II) also yields (III) when $CS(NH_2)$ is present. The influence of varying amounts of $CS(NH_2)_2$ on the phosphotungstate determination of (I) and (IV) is tabulated. F. R. G.

Oxidation of thiol compounds by hydrogen peroxide in presence of inorganic catalysts. II. Oxidation of cystine by means of hydrogen peroxide in presence of vanadic acid sol. J. C. Ghosh and B. C. Kar (J. Indian Chem. Soc., 1937, **14**, 249—253).—Cysteic acid is the main product. The effects of varying temp., concn. and p_H on the velocity of the reaction have been studied. F. J. G.

Synthesis of hexocystine and hexomethionine and their physiological availability. C. B. Jones and V. du Vigneaud (J. Biol. Chem., 1937, **120**, 11—20).—The condensation product of Et sodiophthalimidomalonate with $Br{\cdot}[CH_2]_4{\cdot}Br$ in 95% EtOH with H_2S in NaOH and subsequent hydrolysis gives *εε′-dithio-αα′-diaminodihexoic acid* (*hexocystine*) *hydrochloride* (I), the solution of which with Na in NH_3 gives with CH_2PhCl, *S-benzylcysteine*, m.p. 240—242° (decomp.) (*N-formyl* derivative, m.p. 103—104°), and with MeI, *ε-methylthiol-α-aminohexoic acid* (*hexomethionine*) (II), m.p. 276—278° (decomp.) (*benzenesulphonyl* derivative, m.p. 86—87°). Neither (I) nor (II) produced any alteration in the growth curves of rats on a cystine-deficient diet (cf. A., 1935, 389). F. R. G.

Condensation of cyanoacetamide with formaldehyde. II. Rate of reaction under differing conditions. T. Enkvist (J. pr. Chem., 1937, [ii], **149**, 65—84).—The reaction between $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ and CH_2O at 20° (followed by periodical determination of CH_2O) is bimol. and in absence of any sp. catalyst the rate is $\propto [OH']$. In alkaline solutions the change proceeds very rapidly. NH_4Cl, C_5H_5N,HCl, peroxides, and HCO_2K have no appreciable catalytic action whereas semicarbazide hydrochloride appears to cause an initial and transient acceleration. Piperidine hydrochloride produces such marked acceleration that its effect can scarcely be ascribed to the different change of the position of mesomerism in the anion induced by a different cation. A more probable explanation is indicated by the scheme: $C_5H_{10}NH + CH_2O = C_5H_{10}N{\cdot}CH_2{\cdot}OH$ (I); (I) $= C_5H_{10}N{\cdot}CH_2^+$ (II) + OH; $CN{\cdot}\dot{C}H{\cdot}CO{\cdot}NH_2^- +$ (II) → $NH_2{\cdot}CO{\cdot}CH(CN){\cdot}CH_2{\cdot}NC_5H_{10}$ (III); (III) + $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2 = CH_2[CH(CN){\cdot}CO{\cdot}NH_2]_2 + C_5H_{10}NH$. H. W.

Limits and velocity of formation of pyromucanilide. B. Z. Amitin and S. A. Litkevitsch (Trav. Inst. Chim. Charkov, 1935, **1**, 33—37).—The velocity of reaction of pyromucic acid with NH_2Ph is > with NH_3, and the yield of anilide is > that of amide. The reaction is favoured by high temp. R. T.

Applications of the nitro-ferrocyanide [nitroprusside] reaction: new formula for carbamide. W. R. Fearon (Analyst, 1937, **62**, 586—589).—Carbamide (I) is oxidised at room temp. with neutral aq. Br to a substance (II) which gives a reaction with Na nitroprusside given by ketonoid compounds containing an NH linked on both sides to C. (II) may be $\begin{matrix}NH\\NH\end{matrix}>CO$, or hydrazi-ketone, since it is decomposed into N_2H_4 and CO_2 by warming with aq. $Ba(OH)_2$. Possibly (I) exists in aq. solution as $\begin{matrix}NH\\NH\end{matrix}>CH{\cdot}OH$ (hydrazi-carbinol). E. C. S.

Asymmetrical arylalkylcarbamides. II. Preparation, physical properties, and hypnotic effects. J. S. Buck, A. M. Hjort, E. J. de Beer, C. W. Ferry, and W. S. Ide (J. Pharm. Exp. Ther., 1937, **60**, 369—386; cf. A., 1935, 1488).—The following new *as*-carbamide derivatives have been prepared from the corresponding *sec.* amines by the method of Buck and Ferry (A., 1936, 829): o-, m.p. 95°, m-, m.p. 86°, and p-*anisyl*-, m.p. 116°, o-, m.p. 63°, m-, m.p. 88·5°, and p-*phenetyl*-, m.p. 110°, -n-*propyl*-; m-*tolyl*-, m.p. 66°, o-, m.p. 90°, and p-*anisyl*-, m.p. 106°, o-, m.p. 56°, and p-*phenetyl*-, m.p. 90°, -n-*butyl*-; m-*tolyl*-, m.p. 67°, o-, m.p. 53°, and p-*anisyl*-, m.p. 94°, and p-*phenetyl*-, m.p. 84°, -n-*amyl*; *phenyl*-, m.p. 126°, o-, m.p. 141°, m-, m.p. 92°, and p-*tolyl*-, m.p. 127°, o-, m.p. 127°, m-, m.p. 119°, and p-*anisyl*-, m.p. 165°, o-, m.p. 105°, m-, m.p. 126°, and p-*phenetyl*-, m.p. 165°, -iso*propyl*; *phenyl*-, m.p. 100°, m-, m.p. 91°, and p-*tolyl*-, m.p. 94°, o-, m.p. 88°, m-, m.p. 100°, and p-*anisyl*-, m.p. 142°, m-, m.p. 76°, and p-*phenetyl*-, m.p. 122°, -iso*butyl*-; *phenyl*-, m.p. 68°, m-*tolyl*-, m.p. 71°, o-, m.p. 104°, and p-*anisyl*-, m.p. 126°, and p-*phenetyl*-, m.p. 102°, iso*amyl*-. The following amines are new: iso*propyl*-o-, b.p. 108—116° (23 mm.), -m-, b.p. 100—104° (11 mm.), iso*butyl*-m-, b.p. 97—100° (1 mm.), and iso*amyl*-m-*toluidine*, b.p. 108—110 (1 mm.), iso*propyl*-o-, b.p. 111—115° (10 mm.), -m-, b.p. 130—132° (12 mm.), -p-, b.p. 125—129° (10 mm.), iso*butyl*-o-, b.p. 108—114° (4 mm.), -m-, b.p. 148—153° (10 mm.), -p-, b.p. 138—152° (10 mm.), iso*amyl*-o-, b.p. 118—124° (1·2 mm.), and -p-*anisidine*, b.p. 137—141° (1·2 mm.), iso*propyl*-o-, b.p. 119—122° (12 mm.), -m-, b.p. 137—143° (14 mm.), -p-, b.p. 138—142° (13 mm.), iso*butyl*-m-, b.p. 135—139° (1·6 mm.), -p-, b.p. 135—149° (4 mm.), and iso*amyl*-p-*phenetidine*, b.p. 154—164° (4 mm.). With homologous carbamides the min. hypnotic dose and min. lethal dose vary inversely with m.p. and H_2O solubility, and directly with mol. wt., heptane : H_2O distribution coeff., and power for lowering γ of H_2O. The *iso*-compounds are generally less active physiologically than the *n*-alkyl isomerides. The anisyl compounds are the least active. J. N. A.

Co-ordination compounds of semicarbazide, phenylsemicarbazide, *m*-tolylsemicarbazide, and aminoguanidine. G. S. Smith (J.C.S., 1937, 1354—1358).—Semicarbazide or its hydrochloride in H_2O with the appropriate metal salt yields the following co-ordination compounds; *disemicarbazido-Fe*^{II} *sulphate*, *-Zn sulphate*, *-Co sulphate*, *-Co chloride*, *-Ni chloride*, *-Ni sulphate*, and *-Ni oxide*; *semicarbazido-Cd chloride*; *trisemicarbazido-Ni chloride trihydrate*, *-Ni sulphate*, *-Ni nitrate*, and *-Co nitrate*. With 4-phenylsemicarbazide the following are formed: *di-4-phenylsemicarbazido-Fe*^{II} *sulphate*, *-Cd chloride*, and *tri-4-phenylsemicarbazido Ni chloride*, *-Ni sulphate*, *-Co chloride*; with 4-*m*-tolylsemicarbazide, *di*-4-m-*tolylsemicarbazido-Cd chloride* and *tri*-4-m-*tolylsemicarbazido-Ni nitrate* are obtained, and from aminoguanidine, *diaminoguanidino-Ni nitrate* and *chloride*. J. D. R.

Addition of thiocyanic acid to olefinic double bonds. M. S. Kharasch, E. M. May, and F. R. Mayo (J. Amer. Chem. Soc., 1937, **59**, 1580).—HCNS adds to $CMe_2{:}CH_2$, $CMe_2{:}CHMe$, $CHPh{:}CH_2$, Δ^{β}-pentene, and camphene. $CMe_2{:}CH_2$ gives 32% of Bu$^{\gamma}$CNS and 62% of Bu$^{\gamma}$SCN. The prep. of Bu$^{\gamma}$CNS (42% pure), b.p. 53—54°/25 mm., is modified. R. S. C.

Simple compounds of cyanogen. IV. Dibromomalononitrile and its conversion into sodioazidomalononitrile and a bimolecular cyanoazide, C_2N_8. E. Ott and H. Weissenburger (Ber., 1937, **70**, [*B*], 1829—1834).—$CBr_2(CN)_2$, obtained by bromination of $CH_2(CN)_2$ in H_2O, sometimes decomposes spontaneously into $CHBr_2{\cdot}CO_2H$ when its solution in Et_2O is dried; this can be avoided by addition of CCl_4. The compound from KI and $CBr_2(CN)_2$ regarded previously (A., 1922, i, 643) as $CI_2(CN)_2$ is an additive *compound*, $[CBr_2(CN)_2]_4$,KI; the *substances* $[CBr_2(CN)_2]_4$,NaI, $[CBr_2(CN)_2]_4$,$NaClO_3$, $[CBr_2(CN)_2]_4$,NaCl, $[CBr_2(CN)_2]_4$,NaBr, and $[CBr_2(CN)_2]_4$,KBr are obtained analogously. These can be washed thoroughly with cold H_2O without loss of alkali salt but are decomposed by warm H_2O with separation of $CBr_2(CN)_2$ which is thus readily purified. NaN_3 and $CBr_2(CN)_2$ in H_2O–Et_2O at 0° give the very unstable bimol. *cyanazide* (I), C_2N_8, decomp. 127°, explosion temp. 143—144°. The *Ag* compound of (I) differs from the similarly obtained *substance* from the azide, m.p. 40·5°. Treatment of NaN_3 with $CBr_2(CN)_2$ (3 : 1) and evaporation of the solution at 35°/vac. gives the *Na* derivative of azidomalononitrile which explodes at 179—180° when rapidly heated and affords (I) when treated with acid. *Sodioazidocyanoacetamide* (corresponding *Ag* and *Cu* salts) is described. H. W.

Ultra-violet isomerisation of fumaronitrile. J. Jennen (Bull. Soc. chim. Belg., 1937, **46**, 258—261).—Irradiation of fumaronitrile in $COMe_2$ with ultra-violet light for about 100 hr. (temp. 40—50°) gives maleonitrile and an additive *compound*, m.p. 40—40·4°, considered to be CN·CH:C(CN)·CMe_2·OH. It is hydrolysed by conc. HCl to hydroxy*iso*terebic acid (Fittig, A., 1904, i, 418). H. G. M.

Itacononitrile. J. de Wolf (Bull. Soc. chim. Belg., 1937, **46**, 256—257).—Attempts to prepare itaconitrile by heating the amide with P_2O_5, and alone, failed, a small amount of *itaconimide*, m.p. 103·2—103·6°, being produced. H. G. M.

Relative and absolute spatial configurations of optically active tri-diamine complexes of chromium, cobalt, and rhodium.—See A., I, 445.

Transformations of *cyclo*pentadiene. J. von Braun, E. Kamp, and J. Kopp (Ber., 1937, **70**, [*B*], 1750—1760).—*cyclo*Pentenyl chloride (I) and MgEtBr give Δ^2-*ethyl*cyclo*pentene* (II), b.p. 99—103°/758 mm., in 30% yield. The corresponding *dibromide*, b.p. 98—100°/12 mm., like its homologues, does not readily lose HBr under the action of *tert.* bases. (II) and fuming HBr afford 3-*bromoethyl*cyclo*pentane*, b.p. 84—86°/42 mm., which with Mg and CO_2 gives 3 : 3′-*diethyl*dicyclo*pentyl*, b.p. 125°/15 mm., and *ethyl*cyclo*pentane*-3-*carboxylic acid* (III), b.p. 132—134°/15 mm. PCl_5 transforms (III) into the *chloride*, b.p. 76—78°/11 mm., converted by Br at 125° into 3-*bromo*-1-*ethyl*cyclo*pentane*-3-*carboxyl chloride*, b.p.

110°/11 mm.; this is transformed by NaN_3 followed by EtOH and KOH and then by HCl into 1-*ethyl*cyclo*pentan*-3-*one*, b.p. 150° (*semicarbazone*, m.p. 175°; *product* $C_{20}H_{18}O_5N_2$, m.p. 142°, with *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$). Δ^2-iso*Amyl*cyclo*pentene*, b.p. 86—87°/59 mm., is converted into 3-*bromo*iso*amyl*cyclo*pentane*, b.p. 109—110°/15 mm., and thence into *di*iso*amyldi*cyclo*pentyl*, b.p. about 190°/19 mm., and iso*amyl*cyclo*pentane*-3-*carboxylic acid*, b.p. 160°/20 mm. (I) and Mg dodecyl chloride afford Δ^2-n-*dodecyl*cyclo*pentene* (IV), b.p. 172°/15 mm., whence 3-*bromo*-n-*dodecyl*cyclo*pentane*, b.p. 163°/0·1 mm. This with Mg followed by CO_2 yields n-*dodecyl*cyclo*pentane*-3-*carboxylic acid*, m.p. 29°, n-*dodecyl*cyclo*pentane*, b.p. 175°/15 mm., also obtained by hydrogenation (Pd) of (IV), and 3:3′-*didodecyldi*cyclo*pentyl*, b.p. about 260°/0·2 mm. (IV) gives a *dibromide*, b.p. about 180°/0·2 mm. Δ^2-cyclo*Pentenyl*cyclo*pentane*, b.p. 63°/9 mm., from (I) and Mg *cyclo*pentyl bromide in 60% yield, affords 3-*bromodi*cyclo*pentyl*, b.p. 115°/9 mm., which gives di*cyclo*pentyl, b.p. 67°/9 mm., *tetra*cyclo*pentyl*, b.p. 205—207°/9 mm., and cyclo*pentyl*cyclo*pentane*-3-*carboxylic acid*, b.p. 172°/13 mm. The corresponding acid *chloride*, b.p. 125°/10 mm., is transformed into the *Br*-derivative, b.p. 128—132°/0·3 mm., which affords 1-cyclo*pentyl*cyclo*pentan*-3-*one* [*oxime*, b.p. 145—146°/10 mm., m.p. 46° (1-cyclo*pentyl*cyclo*pentan*-2-*oneoxime*, m.p. 78—79°); *semicarbazone*, m.p. 184°; *derivative* $C_{24}H_{22}O_5N_2$, m.p. 172°, with *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$]. Δ^2-cyclo*Pentenyl*cyclo*hexane*, b.p. 80—85°/12 mm., is converted by fuming HBr at 100° into 3-*bromo*-1-cyclo*hexyl*cyclo*pentane*, b.p. 132—136°/11 mm., which gives cyclo*pentyl*cyclo*hexane*, b.p. 86—88°/11 mm., 3:3′-*di*cyclo*hexyldi*cyclo*pentyl*, b.p. about 180°/0·1 mm., and 1-cyclo*hexyl*cyclo*pentane*-3-*carboxylic acid*, b.p. 180°/11 mm. The acid *chloride*, b.p. 142—144°/11 mm., is transformed into the α-*bromo*-derivative, b.p. 140—142°/0·05 mm., whence cyclo*hexyl*cyclo*pentan*-3-*one* (*semicarbazone*, m.p. 186°; *compound* $C_{25}H_{24}O_5N_2$, m.p. 122°, with *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$). *Et* Δ^2-cyclo*pentenylacetate*, b.p. 81°/12 mm., best obtained from the acid, EtOH, and H_2SO_4, is reduced by Na and EtOH to β-Δ^2-cyclo*pentenylethyl alcohol* (V), b.p. 82—83°/15 mm., readily hydrogenated (Pd) to β-cyclo*pentylethyl alcohol*, b.p. 84—85°/11 mm., also obtained by reduction of Et *cyclo*pentylacetate and smoothly transformed by HBr at 100° into β-cyclo*pentylethyl bromide*, b.p. 70—71°/11 mm. (V) and fuming HBr at >70° give a mixture (VI) of unchanged alcohol and the corresponding unsaturated bromide and β-3-*bromo*cyclo*pentylethyl bromide* (VII), b.p. 100°/0·4 mm. (VI) and $NHMe_2$ in C_6H_6 at 100° give *dimethyl*-β-cyclo*pentenylethylamine*, b.p. 66—68°/13 mm. (*picrate*, m.p. 136—138°; *platinichloride*, m.p. 148°; *methiodide*, m.p. 223°). (VII) is converted by Na in Et_2O containing a little EtOAc into a mixture of hydrocarbons $(C_7H_{12})_n$. When treated with Mg followed by CO_2 (VII) gives a mixture of acids. $CHNa(CO_2Et)_2$ and (VII) in EtOH afford *Et*$_2$ dicyclo-(1:2:3)-*octanedicarboxylate*, b.p. 155—160°/12 mm., hydrolysed by conc. KOH to the corresponding *dicarboxylic acid*, m.p. 189—190° (decomp.), which, when distilled, gives dicyclo-[1:2:3]-*octanecarboxylic acid*, b.p. 150—152°/13 mm. H. W.

[Biological] dehydrogenation of the *cyclo*hexane ring.—See A., III, 384.

Oxidation of *cyclo*hexene and Δ^γ- and Δ^δ-nonenes with selenium dioxide. A. Guillemonat (Compt. rend., 1937, **205**, 67—68).—Oxidation (cf. A., 1936, 51) of *cyclo*hexene affords only Δ^1-*cyclo*hexen-3-ol, whereas oxidation of Δ^γ- or Δ^δ-nonene leads to a mixture of alcohols as each C next to the double linking is oxidised. J. L. D.

Isomerisation of carotenes by chromatographic adsorption. II. Neo-α-carotene. A. E. Gillam, M. S. El Ridi, and S. K. Kon (Biochem. J., 1937, **31**, 1605—1610).—A new pigment, *neo-carotene* (I), is produced by repeated adsorption of α-carotene (II) on Al_2O_3. The absorption max. are at 501 and 470 mμ. in CS_2, compared with 508 and 477 for (II). On crystallisation *neo-α-carotene* (III), m.p. 172°, $[\alpha]_{Cd}$ +220° in C_6H_6, is obtained. Biologically (III) has 0·7 of the potency of β-carotene (IV), ψ-α-carotene is at least as potent as (IV), and (I) has >1/10 the potency of (IV). (III) is probably a geometrical isomeride of (II). P. G. M.

Condensation of alcohols with benzene in presence of aluminium chloride. S. Ishikawa and G. Maeda (Sci. Rep. Tokyo Bunrika Daigaku, 1937, **3**, **A**, 157—164).—$CH_2Cl{\cdot}CH_2{\cdot}OH$, C_6H_6, and $AlCl_3$ at 100° but not at 50—60° give dibenzyl (I) in 39·8% yield; dilution of the mixture with CS_2 diminishes the yield. It appears probable that $CH_2Ph{\cdot}CH_2{\cdot}OH$ is first formed and in part condenses with C_6H_6 to (I) and in part yields styrene which passes into resinous matter. *l*-Menthol, C_6H_6, and $AlCl_3$ afford *p*-menthene, b.p. 166—167°, and 3-*phenylmenthane*, b.p. 275°/760 mm., $[\alpha]_D^{17}$ −3·898° in C_6H_6, which does not decolorise Br in $CHCl_3$ and is converted by fuming HNO_3 into a resin and thence into *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$. *cyclo*Hexanol, C_6H_6, and $AlCl_3$ yield *cyclo*hexene, phenyl*cyclo*hexane, b.p. 238°/761 mm., oxidised to *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, and small amounts of 1:2-diphenyl*cyclo*hexane, m.p. 173° (corr.; Berl). Definite products could not be obtained by condensation of $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ or $(CH_2{\cdot}OH)_2$ with C_6H_6 and $AlCl_3$. H. W.

Dealkylation of dialkylbenzenes. V. N. Ipatiev and B. B. Corson (J. Amer. Chem. Soc., 1937, **59**, 1417—1418).—$FeCl_3$ in C_6H_6 at 83° dealkylates di*tert.*-alkylbenzenes, but not the primary or *sec.* alkyl compounds. This is proved for *p*-di*tert.*-butyl- (I) and -amyl-benzene, *p*-$C_6H_4Pr^\beta_2$, -$C_6H_4(CHMeEt)_2$ (II), -$C_6H_4MePr^\beta$, and -$C_6H_4Et_2$. A mixture of (I) and (II) yields $PhBu^\gamma$ and unchanged (II). (I) and H_2SO_4 in C_6H_6 at 15° give $PhBu^\gamma$ and *p*-$C_6H_4Bu^\gamma{\cdot}SO_3H$, formation of the acid indicating that dealkylation precedes substitution. (I) and H_3PO_4 in C_6H_6 at 90°, 150°, 200°, 250°, and 300° give 0, 0, 2, 19, and 23%, respectively, of $PhBu^\gamma$. 71% $HClO_4$ in C_6H_6 at 85° is without effect on (I). R. S. C.

Reactions in the presence of metallic halides. II. Behaviour of fluorides and the reactivity of the halogens. N. O. Calloway (J. Amer. Chem. Soc., 1937, **59**, 1474—1479; cf. this vol., 293).—C_6H_6, AcF, and $AlCl_3$ give 41·6% of COPhMe, and $Bu^\gamma F$ gives $PhBu^\gamma$. ZnF_2 gives 1·3% of

p-OMe·C_6H_4·COMe from AcCl and PhOMe, and 30·6% of *p*-$C_6H_4Bu^{\gamma}$·OMe from BuCl and PhOMe, but only 0·06% of 2-acetylfuran with much tar from furan and AcCl. In all cases both HCl and HF are evolved, owing to reaction between the HHal and the halide. AlF_3 does not cause reaction of C_6H_6 with AcF or $Bu^{\gamma}F$, or of PhOMe with AcCl. ZnF_2 does not cause reaction of PhOMe with AcF, $Bu^{\alpha}Cl$, or $Bu^{\alpha}Br$, or of furan with AcCl. $Bu^{\alpha}I$, C_6H_6, and $AlCl_3$ at 29° give no HHal. As judged by the temp. at which evolution of HHal is approx. the same, the order of activity for acyl halides is I > Br > Cl > F, but for alkyl halides F > Cl > Br > I. The validity of this method of assessment is discussed and upheld. The change, the ease of which is measured, is probably $RX,AlCl_3,C_6H_6 \rightarrow RPh,AlCl_3,HX$. R. S. C.

Diazonium borofluorides. II. Their use in the preparation of nitro-compounds. E. B. Starkey (J. Amer. Chem. Soc., 1937, **59**, 1479—1480; cf. this vol., 39).—Difficultly accessible aromatic NO_2-compounds are obtained by treating the diazonium borofluorides with Cu and aq. $NaNO_2$ at room temp. The following yields were obtained: $PhNO_2$ 20, *o*- 33, *m*- 43, and *p*-NH_2·C_6H_4·NO_2 64, *o*- 32, and *m*-C_6H_4Cl·NO_2 15, *p*-C_6H_4Me·NO_2 10, *p*-NO_2·C_6H_4·CO_2Et 50, and *p*-NO_2·C_6H_4·OMe, *p*-NO_2·C_6H_4·N:NPh, *p*-C_6H_4Ph·NO_2, and 1-$C_{10}H_7$·NO_2 <10%. R. S. C.

Preparation of *m*-dinitrobenzene. S. V. Shah (J. Chem. Educ., 1937, **14**, 322).—A correction (cf. this vol., 182). L. S. T.

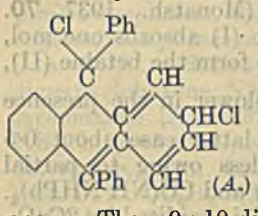
Radicals with several tervalent carbon atoms. M. Leo (Ber., 1937, **70**, [*B*], 1691—1694).—Me_3 trimesate is connverted by LiPh in Et_2O into 1 : 3 : 5-*trihydroxybenzhydrylbenzene*, m.p. 188—189°, transformed by AcCl into 1 : 3 : 5-*trichlorobenzhydrylbenzene*, m.p. 203—204°; 2% solutions of this in C_6H_6 are colourless and are dehalogenated by Cu powder to solutions which do not show a dark, characteristic colour coupled with the development of absorption bands. Only partial decolorisation occurs when the solution is shaken with air. The free radical (I) is freely sol. in most media but appears mainly unimol. in solution. It appears therefore that the free valencies saturate one another within the mol., at any rate in some degree. 2 : 7-$C_{10}H_6Bz_2$ and LiPh afford 2 : 7-*dihydroxybenzhydrylnaphthalene*, m.p. 141—145°, converted into 2 : 7-*dichlorobenzhydrylnaphthalene*, m.p. 176—178°, dehalogenated solutions of which behave like those of (I). H. W.

Dehydrogenation. I. Catalytic dehydrogenation of hydronaphthalenes with and without an angular methyl group. R. P. Linstead, A. F. Millidge, S. L. S. Thomas, and A. L. Walpole (J.C.S., 1937, 1146—1157).—1-Ketodecahydronaphthalene with MgMeI yields 1-*hydroxy*-1-*methyldecahydronaphthalene*, b.p. 112—113°/10 mm., dehydrated ($H_2C_2O_4$) to 1-*methyl*-3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-*octahydronaphthalene*, b.p. 81—83°/10 mm., reduced (Pt–H_2) to 1-*methyldecahydronaphthalene*, b.p. 80—81°/12 mm. *trans*-2-Methyloctahydronaphthalene affords a *nitrosochloride*, m.p. 138°. In the liquid phase at the b.p. of the hydrocarbon, tetra- and decahydronaphthalene with Pt–asbestos or 30% Pd–C yield $C_{10}H_8$ whilst octahydronaphthalene with 25% Pd–C gives a mixture of $C_{10}H_8$ and tetra-, octa-, and deca-hydronaphthalene. 1- and 2-Methyloctahydronaphthalene yield with Pd–C, 1- and 2-$C_{10}H_7Me$, respectively, the latter also affording some *trans*-2-methyldecahydronaphthalene; 9-methyloctahydronaphthalene is unchanged, and 1 : 10-dimethyloctahydronaphthalene affords 1 : 5-$C_{10}H_6Me_2$. In the vapour phase *cis*-decahydronaphthalene over Pt or Pd yields $C_{10}H_8$; 1-methyloctа- and 1-methyldecahydronaphthalene give 1-$C_{10}H_7Me$, and 9-methyldeca- or -octa-hydronaphthalenes over Pt–C affords chiefly $C_{10}H_8$ and a trace of 1-$C_{10}H_7Me$, over 30% Pd–C a mixture of $C_{10}H_8$ and 1-$C_{10}H_7Me$, and over Pt–asbestos chiefly 1-$C_{10}H_7Me$. 4 : 9-Dimethyloctahydronaphthalene over Pt–asbestos yields 1 : 5-$C_{10}H_6Me_2$ and a *dimethylnaphthalene* (I) (*picrate*, m.p. 134—134·5°; *styphnate*, m.p. 145°), whilst over 30% Pd–C, 1-$C_{10}H_7Me$ is formed; from 4 : 9-dimethyldecahydronaphthalene with 30% Pd–C, 1-$C_{10}H_7Me$ and 1 : 5-$C_{10}H_6Me_2$ are formed. Methyloctahydronaphthalene (II), made by the dehydration of 1-methyl-2-butenyl*cyclo*hexanol, with 30% Pd–C affords $C_{10}H_8$ and 1-$C_{10}H_7Me$ and with Pt–asbestos, only 1-$C_{10}H_7Me$, proving (II) to be essentially the 9-Me compound, whilst the methyloctahydronaphthalene from 2-methyl-1-butenyl*cyclo*hexanol with 30% Pd–C gave $C_{10}H_8$ and a trace of 1-$C_{10}H_7Me$, and with Pt–asbestos, only 1-$C_{10}H_7Me$, showing it to be a mixture of the 1- and 9-Me compounds. *γ*-*o*-Tolylvaleryl chloride with CS_2 and $AlCl_3$ affords 1-*keto*-4 : 5-*dimethyltetrahydronaphthalene*, b.p. 154—156°/18 mm., m.p. 56°, reduced (Na–EtOH) to the corresponding alcohol, which is dehydrogenated (Se) to 1 : 8-*dimethylnaphthalene*, b.p. 140/18 mm., m.p. 63°. (I) is not identical with 1 : 2-, 1 : 4-, 1 : 5-, or 1 : 8-$C_{10}H_6Me_2$. J. D. R.

Structure of naphthalene, hydrindene, and tetralin derivatives. (Miss) N. McLeish and N. Campbell (J.C.S., 1937, 1103—1108).—Existing evidence in favour of a static 1 : 2 ethylenic linking in $C_{10}H_8$ is reviewed and supported by the facts that the Br in 1 : 2-, 2 : 1-, and 4 : 1-$C_{10}H_6Br$·NO_2 is reactive towards piperidine, and non-reactive in other bromonitronaphthalenes; the same applies to the chloronitronaphthalenes. Similarly the reactivity of the Br in 6-bromo- and non-reactivity in 4-bromo-5-nitrohydrindene confirms the structure of hydrindene, but although the Br in 6-bromo-7-nitro- is reactive, and in 6-bromo-5-nitro-tetrahydronaphthalene is unreactive, the evidence is too conflicting to decide the positions of the double linkings. 6 : 2-$C_{10}H_6Br$·NH_2, by diazotisation and treatment with $CuSO_4$–SO_2, affords 6-*bromo*-2-*nitronaphthalene*, m.p. 190°. 6-Bromo-5-aminohydrindene in C_5H_5N with *p*-C_6H_4Me·SO_2Cl and Br affords 4 : 6-*dibromo*-5-*p*-*toluenesulphonamidohydrindene*, m.p. 199—200°, hydrolysed (H_2SO_4) to 4 : 6-dibromo-5-aminohydrindene, m.p. 71° (lit. 70°), reduced by Sn–HCl–EtOH to 4-bromo-5-aminohydrindene, m.p. 50—51°, converted by diazotisation and $CuSO_4$–SO_2 into 4-*bromo*-5-*nitrohydrindene* (an oil). 6-Bromo-5-aminohydrindene was similarly converted into 6-*bromo*-5-*nitrohydrind*-

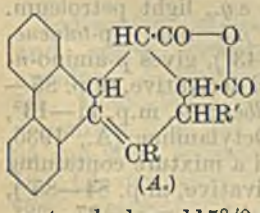
ene, m.p. 44—45°. 6-*Bromo*-7-, m.p. 53—54°, and 6-*bromo*-5-*nitro*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 101—102°, are formed by the usual methods from the 6-NHAc-compounds. J. D. R.

Tautomerisation reactions in the anthracene series. E. Bergmann and O. Blum-Bergmann (J. Amer. Chem. Soc., 1937, **59**, 1439—1441).—9 : 10-Dichloro-9 : 10-diphenyl-9 : 10-dihydroanthracene in boiling AcCl gives HCl and 2-chloro-9 : 10-dihydroanthracene, synthesised by treating 1-chloroanthraquinone with MgPhBr and dehydrating the product by boiling HCO_2H. The decomp. is assumed to involve formation of the quinolid product (*A*) and thence of 2 : 9-dichloro-9 : 10-diphenyl-9 : 10-dihydroanthracene. The 9 : 10-dichloro-9 : 10-dinaphthyl compound is so unstable that HCl in boiling C_6H_6 converts 9 : 10-dihydroxy-9 : 10-di-α-naphthyl-9 : 10-dihydroanthracene directly into 2-chloro-9 : 10-di-α-naphthylanthracene (synthesised from the chloroquinone and 1-$C_{10}H_7$·MgBr). Several known reactions, which are best explained by quinolid tautomerisation, are discussed. R. S. C.


(*A*.)

Synthesis of triphenylene. E. Bergmann and O. Blum-Bergmann (J. Amer. Chem. Soc., 1937, **59**, 1441—1442).—Mg 9-phenanthryl bromide and $(\cdot CH_2 \cdot CO)_2O$ in Et_2O give *γ-keto-γ-9-phenanthrylbutyric acid*, m.p. 176° (*Me* ester, m.p. 88°), the *semicarbazone*, m.p. 237° (decomp.), of which with NaOEt in H_2 at 200° gives *γ-9-phenanthrylbutyric acid*, m.p. 173°; this is cyclised by P_2O_5 in PhMe at 100° to 4-*keto*-1 : 2 : 3 : 4-*tetrahydrotriphenylene*, m.p. 101°, which affords (Clemmensen) 1 : 2 : 3 : 4-tetrahydrotriphenylene, m.p. 120—121° (obtained in small yield by dehydrogenation of dodecahydrotriphenylene), and a little (?) *di*-1 : 2 : 3 : 4-*tetrahydro*-4-*triphenylenyl*, m.p. 300°. The former hydrocarbon and Se at 320° give triphenylene (9 : 10-benzphenanthrene). R. S. C.

Diene reactions involving aromatic nuclei. Phenanthrene system. E. Bergmann and F. Bergmann (J. Amer. Chem. Soc., 1937, **59**, 1443—1450).—Maleic anhydride (I) adds to 9-vinylphenanthrene and to some, but not to all, *α*- and β-substituted derivatives thereof, occurrence or absence of addition depending on both the nature and position of the substituent. The greater reactivity of the phenanthrene as compared with the $C_{10}H_8$ derivatives is ascribed to the more olefinic nature of the phenanthryl radical. Phenanthrene derivatives which form adducts give orange-red or red picrates; similar saturated or unreactive derivatives form yellow picrates. The reactions described below are for synthesis or proof of structure. The following are prepared by the Grignard reaction, the adducts mentioned being of type (*A*), no addition occurring if no adduct is mentioned: 1-cyclo*pentenyl*-, b.p. 115°/0·04 mm. (*picrate*, m.p. 82°), and 6-*methoxy*-1-cyclo*pentenyl*-*naphthalene*, m.p. 148°, 9-*allyl*- (II), b.p. 161—163°/1·25 mm. (*picrate*, m.p. 115°), 9-iso*propenyl*-, m.p. 38°, b.p. 163°/20 mm. (purified by $H_2C_2O_4$ at 150°; *picrate*, m.p. 108°; *adduct*, m.p. 262°), 9-1′-Δ¹-cyclo*pentenyl*-, b.p. 185°/0·85 mm. [purified by $H_2C_2O_4$; some 9 : 9′-*diphenanthryl* (III), b.p. 220—250°/3 mm. (*picrate*, m.p. 163°), also formed; *picrate*, m.p. 120°; *adduct* (IV), m.p. 275—276°], and 9-1′-Δ¹-cyclo*hexenyl*-*phenanthrene* (V), m.p. 132°, b.p. 190—200°/1·25 mm. (*picrate*, m.p. 141—142°), *benzyl*-9-*phenanthrylcarbinol* (VI), m.p. 120°, the *acetate* of which at the b.p., 220—240°/0·4 mm., gives 9-*styrylphenanthrene* (VII), m.p. 118° (*dipicrate*, m.p. 164°, unstable; *adduct*, m.p. 249—250°), α-9-*phenanthrylstyrene* (VIII), b.p. 180—190°/1 mm., m.p. 142°, 3-9′-*phenanthrylindene*, b.p. 230°/0·7 mm., m.p. 121·5° (*picrate*, m.p. 132°), and 4-9′-*phenanthryl*-1 : 2-*dihydronaphthalene*, b.p. 220—300°/1·25 mm., m.p. 184·5°. The reversible nature of the diene reaction is proved by the observation that formation of (IV), which is completely insol. in the solvent, ceases short of completion, but can be thereafter continued if the adduct formed is removed and heating of the mother-liquor is continued. 1-Vinylnaphthalene and (I) in boiling xylene give *tetrahydrophenanthrene*-1 : 2-*dicarboxylic anhydride*, m.p. 169—170°, and *acid*, m.p. 244° (decomp.). α-9-Phenanthrylethyl alcohol with Ac_2O gives the *acetate*, m.p. 107°, and with $KHSO_4$ affords a *polymeride* (? *dimeride*), b.p. 280°/0·2 mm. (*picrate*, m.p. 173°), of 9-*vinylphenanthrene*, the monomeric *form* of which was once obtained, b.p. 150—160°/1 mm. [with (I) gives *tetrahydrotriphenylene*-1 : 2-*dicarboxylic acid*, m.p. 218—220°], autoxidisable, from the Me xanthogenate; this derivative, however, usually gave 9-ethylphenanthrene. The Tschugaev reaction with (VI) leads to a similar reduced product, 9-β-*phenylethylphenanthrene* (IX), b.p. 220—230°/0·8 mm., m.p. 81·5° (*picrate*, m.p. 133°). KOH–EtOH isomerises (II) to 9-*propenylphenanthrene*, b.p. 179°/2·5 mm. (*picrate*, m.p. 108°), which with (I) gives the *adduct*, m.p. 264°. The structure of (V), which is unchanged by $AlCl_3$, is proved by reaction with Br, formation of a violet colour with hot conc. H_2SO_4, and oxidation (CrO_3) to phenathrenequinone; its failure to react with (I) is ascribed to fixation of the 9 : 10- and Δ¹-ethylenic linkings in the *trans*-position to each other. By reaction with Na (VIII) affords αδ-*diphenyl*-αδ-*di*-9-*phenanthrylbutane*, m.p. 243·5°, and (III) gives 10 : 10′-*dihydro*-9 : 9′-*diphenanthrylidene*, m.p. 303° [*perbromide* (Br_3), cryst.]. A Na_2 derivative is obtained from (VII) and thence by isomerisation in alkali (IX); that isomerisation occurs at this stage is evidenced by the fact that the Na_2 salt and dry CO_2 give a *dicarboxylic acid*, m.p. 279°, which does not form an anhydride. 9-Phenylphenanthrene, b.p. 170—190°/1·25 mm., m.p. 110° [obtained from (V) by Se at 340°], does not react with Na, but with Li rapidly gives a violet solution and thence 9-phenyl-9 : 10-dihydrophenanthrene, m.p. 84°, previously obtained by PCl_5 from α-2-diphenylstyrene, the latter reaction being thus proved to have involved ring-closure. CH:CNa and *cyclo*hexanone give 2-hydroxy-*cyclo*hexylacetylene (X), b.p. 86°/17 mm., and the glycol, b.p. 160—164°/3 mm., m.p. 102—103°.

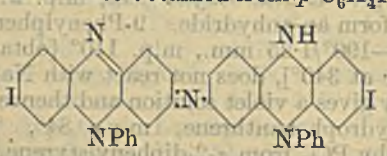

(*A*.)

Hydrogenation of (X) under all conditions tried gives mainly ethyl*cyclo*hexanol, b.p. 70—75°/18 mm., but the crude product contained some 1-vinyl*cyclo*hexan-1-ol, since dehydration with $H_2C_2O_4$ gives polymeric 1-*vinyl*-Δ^1-cyclo*hexene*, b.p. 160°, as well as ethyl*cyclo*hexene, b.p. 49°/30 mm. With $H_2C_2O_4$ at 150° (30 min.) (X) gives *cyclo*hexanone and, by rearrangement to *cyclo*hexenylacetaldehyde, followed by oxidation, also some *cyclo*hexenylacetic acid. $CH_2Bz{\cdot}CH_2{\cdot}CO_2Et$ and CH:CNa give *γ-hydroxy-γ-phenyl-*Δ^δ*-n-hexinenoic acid*, m.p. 242·5°, and, by condensation of 2 mols. of the ester, 2 : 5-*dibenzoyl*-cyclo*hexane*-1 : 4-*dione*, m.p. 200° (*bisphenylhydrazone*, m.p. 274°; *Me*$_2$ *ether*, m.p. 204°), which probably exists as the dienol since it dissolves in alkali to give dark solutions. R. S. C.

Tar hydrocarbons. I. Reduction products of pyrene. E. A. Coulson (J.C.S., 1937, 1298—1305).—Pyrene (I) hydrogenated (H_2–MoO_3–S–C) at 400°/100 atm. in 4 hr. yields 3 : 4 : 5 : 8 : 9 : 10- (II) and 1 : 2 : 3 : 4 : 5 : 12-hexahydropyrene (III), and 1 : 2-*dihydropyrene* (IV), m.p. 132° (*picrate*, m.p. 147°); in 6 hr., 1 : 2 : 6 : 7-*tetrahydropyrene* (V), m.p. 138°, is also formed. With Na in boiling $C_5H_{11}{\cdot}OH$, (I) yields (II) and (III), and some decahydropyrene; (III) yields (IV), (IV) yields 1 : 2 : 3 : 4 : 5 : 6 : 7 : 12 : 13 : 16-*decahydropyrene* (VI), m.p. 68°, (II) yields 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*decahydropyrene* (VII), m.p. 68°, whilst (III) gives a mixture of (VI) and (VII). (IV) when oxidised (H_2O_2 in AcOH) gives 9 : 10-*dihydrophenanthrene*-4 : 5-*dicarboxylic acid*, m.p. 256°, and with aq. $KMnO_4$, diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid (VIII), also obtained by oxidation (aq. $KMnO_4$) of (V). 2-Bromo-*m*-xylene, oxidised ($KMnO_4$) and esterified, affords *Me* 2-*bromoisophthalate*, b.p. 190—191°/22 mm., hydrolysed (HCl) to 2-bromo*iso*phthalic acid, m.p. 218°, converted by Cu at 180° into (VIII). J. D. R.

Decomposition of aniline nitrite. J. C. Earl (J.C.S., 1937, 1129—1131).—NH_2Ph nitrite (A., 1933, 498) (of which the Et_2O solution is now evaporated under reduced pressure of dry N_2) decomposes in N_2 at −6° to −8°/60 mm., giving diazoaminobenzene, and a $CHCl_3$-insol. liquid consisting mainly of benzenediazonium nitrite. E. W. W.

Reaction between aniline and iodine. H. H. Hodgson and E. Marsden (J.S.C., 1937, 1365—1366).—At 20—150° I iodinates NH_2Ph, the products being *p*-$C_6H_4I{\cdot}NH_2$ and NH_2Ph,HI if 1 mol. of I is used, but including 2 : 4-$C_6H_3I_2{\cdot}NH_2$ if >1 mol. of I is used. At >150° a vat *dye*, $C_{36}H_{23}N_3I_2$, probably (I), is formed, which is also obtained from *p*-$C_6H_4I{\cdot}NH_2$ and



(I.)

NH_2Ph at 220—230°. Pure *p*-$C_6H_4I{\cdot}NH_2$ at 220° gives only 2 : 4-$C_6H_3I_2{\cdot}NH_2$ and I. Distillation of (I) with Zn dust gives NH_3, PhNC, NH_2Ph, and phenazine. R. S. C.

Diphenylcarbazone. P. Krumholz and E. Krumholz (Monatsh., 1937, **70**, 431—436).—The material, m.p. 157°, previously considered to be *diphenylcarbazone* (I), NPh:N·CO·NH·NHPh, is a 1 : 1 mol. compound thereof with $CO(NH{\cdot}NHPh)_2$, from which it is separated by its solubility in alkali. Pure (I) (*Na* salt) has m.p. 127° and k_s about 10^{-8}, and gives the reactions previously held to be characteristic of (I), except the CrO_4'' reaction. R. S. C.

Auto-oxidation of diphenylcarbazone. P. Krumholz and H. Watzek (Monatsh., 1937, **70**, 437—446).—Diphenylcarbazone (I) absorbs one mol. of O_2 in the presence of NH_3 to form the betaine (II), $\begin{matrix}NPh{\cdot}N\\NPh{:}N\end{matrix}\!\!>\!C{\cdot}O^-$. Oxidation is slower in the presence of Na_2CO_3 or NH_4Cl; in the latter case about 0·5 mol. of O_2 is utilised, doubtless owing to partial disproportionation of (I) to (II) and $CO(NH{\cdot}NHPh)_2$. In the absence of O_2 1 mol. of (I) is oxidised by 2CuO–NH_3; even traces of Cu catalyse the aërial oxidation enormously and the oxidation occurring when it is not added is believed to be due to unavoidable traces; 0·5—1 × 10^{-7} mol. of Cu per litre as impurity would suffice to give the observed rate of oxidation. This hypothesis is supported by the fact that 3 × 10^{-7} mol. of KCN per litre prevents oxidation, presumably by formation of CuCN which cannot be oxidised by air to Cu^{II}. The rate of oxidation is independent of the (I) concn., but depends on the [Cu] and [NH_3]; with 3·75 × 10^{-7} mol. of Cu per litre, this rate is a max. in 0·1N-NH_3. Other bases and catalytically active metals may be used, but are less effective, especially the metals. R. S. C.

Rearrangement of the alkylanilines. VIII. Migration of large groups. W. J. Hickinbottom (J.C.S., 1937, 1119—1125; cf. A., 1932, 1124).—*n*-Amylaniline heated with $CoCl_2$ or $CoBr_2$ yields p-*amino*-n-*amylbenzene*, b.p. 130°/16 mm. (*hydrochloride*; *sulphate*; *Ac*, m.p. 101°, and p-*toluenesulphonyl*, m.p. 68—69°, derivatives), with *amylaminoamylbenzene* (?), b.p. 180—185°/16 mm. n-*Hexylaniline*, b.p. 158°/28 mm. (*hydrobromide*; p-*toluene*-, m.p. 67—68°, and m-*nitrobenzene-sulphonyl* derivative, m.p. 79—80°) (from NH_2Ph and *n*-$C_6H_{13}I$), gives p-*amino*-n-*hexylbenzene*, b.p. 146—148°/17 mm. (*hydrochloride*; *sulphate*; *Ac* derivative, m.p. 91°), with p-n-*hexylamino*-n-*hexylbenzene*, b.p. 203—204°/18 mm. [*hydrochloride* (I)]. n-*Heptylaniline*, b.p. 160—161°/21 mm. (*hydrobromide*; p-*toluene*-, m.p. 76°, and m-*nitrobenzene-sulphonyl* derivative, m.p. 96°), yields p-*amino*-n-*heptylbenzene* (II), b.p. 159°/18 mm. (*hydrochloride*; *Ac* derivative, m.p. 91—92°), with p-n-*heptylamino*-n-*heptylbenzene*, b.p. 220—223°/18 mm. [*hydrochloride* (III), m.p 83—85°], also prepared from (II) and *n*-$C_7H_{15}Br$. The hydrochlorides (I) and (III) are sol. in org. solvents, *e.g.*, light petroleum. n-*Octylaniline*, b.p. 177—178°/25 mm. (p-*toluenesulphonyl* derivative, m.p. 42—43°), gives *p*-amino-*n*-octylbenzene (p-*toluenesulphonyl* derivative, m.p. 85—86°), with p-n-*octylamino*-n-*octylbenzene*, m.p. 11—13°, b.p. 232—235°/14 mm. *sec.*-Octylaniline (A., 1935, 1489) gives octene, NH_2Ph, and a mixture containing amino*sec.*-octylbenzene (*Ac* derivative, m.p. 84—85°), and an isomeride. *Dodecylaniline*, m.p. 27—28°,

b.p. 212—214°/13 mm. (*hydrochloride*, m.p. 88—91°; p-*toluenesulphonyl* derivative, m.p. 53—54°) [obtained with *didodecylaniline* (?), b.p. 280—295°/12 mm., from $C_{12}H_{25}I$ (IV) and NH_2Ph], gives p-*aminododecylbenzene* (V), m.p. 41—42° (*Ac* derivative, m.p. 101—101·5°), with p-*dodecylaminododecylbenzene*, m.p. 48—49° (*hydrochloride*, m.p. 84—85°; *nitrosoamine*, m.p. 40—41°), also obtained from (IV) and (V). Cetylaniline (*nitrosoamine*, m.p. 40—41°; *p-toluenesulphonyl* derivative, m.p. 64—65°) yields p-*aminocetylbenzene*, m.p. 51—52° (*Ac*, m.p. 102·5—103·5°, and p-*nitrobenzylidene*, m.p. 71°, derivatives), with p-*cetylaminocetylbenzene*, m.p. 62—63° (*nitrosoamine*, m.p. 55°). *cyclo*Hexylaniline with $CoCl_2$ at 247° gives cyclohexene, NH_2Ph, and *p*- and *o*-aminophenyl-*cyclo*hexane (A., 1932, 1242). $NH_2Ph{\cdot}CH_2Ph$ gives NH_2Ph, *p*-aminodiphenylmethane [p-*nitrobenzylidene* derivative, m.p. 101—102°; condensation *product* with 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$, m.p. 128—128°; p-*benzyl*-αβ-*diphenylthiocarbamide*, m.p. 148—149°], and *o*-aminodiphenylmethane (?), with 2 : 4-*dibenzylaniline*, m.p. 49—50° (*Ac* derivative, m.p. 145—146°), and a *tert.*-amine (*mercurichloride*, m.p. 190—193°).

E. W. W.

The solid carbon–oxygen complex. I. Oxidative action of graphitic oxide and active carbon plus oxygen on some aromatic amines. A. H. Carter, L. de V. Moulds, and H. L. Riley (J.C.S., 1937, 1305—1312).—The amine was heated for several hr. on the water-bath with graphitic oxide (I), the prep. of which is described. (*a*) Pure NH_2Ph afforded azophenine (II) and a mauveine-type dye (III). Commercial NH_2Ph containing *o*- and *p*-$C_6H_4Me{\cdot}NH_2$ gave (II) and (III) and a rosaniline dye (IV), (*b*) NHPhMe yielded a complex resinous substance and *NN'N''*-trimethylpararosaniline (V), (*c*) $NPhMe_2$ afforded Me-violet (VI) (as sulphate), leuco-crystal-violet (VII), and 4 : 4'-dimethyldiaminodiphenylmethane (VIII). The $CHPh_3$ dyes were present as sulphates, the SO_4'' being derived from H_2SO_4 occluded in (I). The mechanism of the reactions is discussed, and the results show that (I) is similar in its oxidising action to PbO_2 and H_2O_2. By bubbling air through a mixture of the amine and "active" charcoal at 100°, the following results were obtained: (*a*) NH_2Ph yielded tarry products and only small quantities of unidentified iminoquinone derivatives, but with H_2SO_4-treated charcoal a little (II) and a substance probably allied to induline-3B were obtained; commercial NH_2Ph also gave (IV); (*b*) NHPhMe gave a complex resin, but with H_2SO_4-treated charcoal some (V) was also obtained; (*c*) $NPhMe_2$ gave (VII) and (VIII), but with H_2SO_4-treated C or when H_2SO_4 was added, (VI) was also obtained. The parallelism between the results of the two methods of oxidation indicates a fundamental similarity between (I) and the active C–O complex.

J. G. A. G.

Iodination of *p*-aminobenzenesulphonamide and some symmetrical azobenzenesulphonamides. J. V. Scudi (J. Amer. Chem. Soc., 1937, 59, 1480—1483).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (I) (Ac derivative, m.p. 214°) and ICl in H_2O or AcOH give 94 and 90%, respectively, of 3-*iodo*- (II), m.p. 179—180° (*Ac* derivative, m.p. 216°), and 96—99 and 73—77%, respectively, of 3 : 5-*di-iodo*-4-*aminobenzenesulphonamide* (III), m.p. 265° (decomp.). Hot 10% HCl and (II) give (III) and (I), and (III) and hot 20% HCl give (I) and (II). I in $NaHCO_3$ or NaOH or $KMnO_4$ converts (I) into *azobenzene*-4 : 4'-*disulphonamide*, m.p. >270°. Similarly (II) gives 2 : 2'-*di-iodoazobenzene*-4 : 4'-*disulphonamide*, m.p. >270°, but (III) and $KMnO_4$ give 3 : 5-*di-iodo*-4-*nitrosobenzenesulphonamide*, m.p. >270°.

R. S. C.

Preparation of [sulphonamide] compounds of therapeutic value.—See B., 1937, 842.

Associating effect of the hydrogen atom.—See A., I, 513.

Benzenesulphonyl derivatives of *o*-nitroaniline and *o*-phenylenediamine. L. H. Amundsen (J. Amer. Chem. Soc., 1937, 59, 1466—1467).—Benzenesulphon-*o*-nitroanilide (I), m.p. 102·2—102·5°, is best obtained from *o*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ and $PhSO_2Cl$ (0·5 mol.) in dioxan. *Dibenzenesulphon*-o-*nitroanilide*, m.p. 189·8—190·5°, is best obtained from $PhSO_2Cl$ and the Na salt, m.p. 239—240°, of (I) in dioxan, and on reduction (H_2–Pt or Fe–AcOH) gives *dibenzenesulphon*-o-*aminoanilide*, m.p. 149·5—149·9°. *o*-$PhSO_2{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$, m.p. 169·3—170°, gives a *benzenesulphonate*, m.p. 204·9—205·4°. *o*-$(PhSO_2{\cdot}NH)_2C_6H_4$, m.p. 190·3—190·8°, is best prepared in hot PhMe, and its Na_2 salt, m.p. >275°, affords *tribenzenesulphon*-o-*phenylenediamide*, m.p. 157·1—157·3°, previously held to be the $(PhSO_2)_4$ derivative. M.p. are corr.

R. S. C.

Reaction of α-oxides with arylamines. J. O. Gabel (Trav. Inst. Chim. Charkov, 1935, 1, 53—67).—The author's published papers (1925—1935) are reviewed.

R. T.

Stereochemistry of deuterium compounds. II. α-Methylbenzylamine. L. E. Young and C. W. Porter (J. Amer. Chem. Soc., 1937, 59, 1437—1438; cf. this vol., 132).—By several treatments with D_2O *d*- (I) (obtained as *l*-malate from the *dl*-base), $[\alpha]^{20}_{5461}$ +44·66°, and *l*-$CHPhMe{\cdot}NH_2$ [obtained as *dl*-malate from the mother-liquors from (I)], $[\alpha]^{20}_{5461}$ −45·39°, b.p. of both 187·4° (corr.), d^{24} 0·9458, give d- and l-NN-*dideutero*-α-*methylbenzylamine*, b.p. 188·4°, with reduced optical rotation, $[\alpha]^{20}_{5461}$ +42·88°, −43·77°, d^{24} 0·9615, recoverted by H_2O into $CHPhMe{\cdot}NH_2$ of unchanged [α] and *d*.

R. S. C.

Stereochemistry of dicyclic ring systems. III. Stereoisomerism of hydrindane and its derivatives. IV. Hydrindanes substituted in the six-membered ring. W. Hückel, R. Schlüter, W. Doll, and F. Reimer (Annalen, 1937, 530, 166—183; cf. A., 1935, 971).—The following preps. were carried out for comparative purposes to be discussed later. *cis*-Hexahydrohydrindanes substituted in the 6-membered ring behave similarly to the corresponding decahydronaphthalene derivatives. The catalytic hydrogenation of hydrindenes is much more rapid than that of the corresponding tetrahydronaphthalene derivatives. Hydrogenation of 4-acetamidoindane, m.p. 126° (100 g.), in decahydronaphthalene in the presence of Ni at 200°/80 atm. gives *forms*, m.p. 131° (55 g.) and 93° (16 g.), of 4-*acetamido*-cis-*hexahydrohydrindane*, a difficultly separable mixture being obtained by the use of Pt in

AcOH at 60°/4 atm.; with 20% HCl at 150—160° these give *forms*, b.p. 85°/11 mm., m.p. −14° (*Bz* derivative, m.p. 177°), and b.p. 85°/11 mm. (*Bz* derivative, m.p. 163°), of 4-*amino*-cis-*hexahydrohydrindane*, the former being obtained from *cis*-hydrindane-4-oxime by hydrogenation and the latter by Na–EtOH. The former base with HNO_2–AcOH gives mainly a cis-*hexahydrohydrindan*-4-*ol* (I), forms, m.p. 16° and 31°, b.p. 104°/11 mm. (*H phthalate*, m.p. 134°; *phenylurethane*, m.p. 81°; p-*nitrobenzoate*, m.p. 86°; *H succinate*, m.p. 47°), with a small amount of an oily *isomeride* (II) (*H phthalate*, m.p. 146°; p-*nitrobenzoate*, m.p. 56°; p-*benzamidobenzoate*, m.p. 180—181°), and Δ^4-*hexahydroindene* (III), b.p. 53°/11 mm.; the second base reacts more slowly with HNO_2 and gives 20% of hydrocarbon. The alcoholate of (I) in boiling decahydronaphthalene gives (II) quantitatively, and (II) is best prepared by treating the mixed bases with HNO_2 and isomerising the alcoholate of the crude product. Oxidation of (II) affords 2-carboxy-*cis*-*cyclo*pentanepropionic acid, m.p. 99—100°. Ni-hydrogenation at 180—200° of 5-hydroxyindane, m.p. 54°, gives mainly the form (IV), b.p. 112—115°/13 mm., m.p. 20° (*H phthalate*, m.p. 144—145°; *H*, m.p. 146—147°, and *Me phthalate*, m.p. 54—58°, of the *Me ether*; *phenylurethane*, m.p. 74°; p-*nitrobenzoate*, m.p. 75°; *H succinate*, m.p. 47—48°), of 5-hydroxyhexahydrohydrindane with a little hydrocarbon and isomeric 5-OH-compound (V), new m.p. 43°, b.p. 106°/13 mm. (*H phthalate*, m.p. 106—107°; *oxalate*, m.p. 84°; p-*nitrobenzoate*, m.p. 61°). Ni-hydrogenation at 180° of 5-acetamidoindane, m.p. 180°, gives the *Ac* derivative, m.p. (+$2H_2O$) 53°, (anhyd.) 63°, of 5-aminohexahydrohydrindane (VI), b.p. 90°/12 mm., m.p. < −20° (Bz derivative, m.p. 145°; *Me carbamate*, m.p. 83°), and the Ac derivative, m.p. 108°, of the isomeride (VII) (Bz derivative, m.p. 165—166°; *Me carbamate*, m.p. 88°); the latter base with (?) 20% of the former is obtained by reduction of the mixed *cis*-hydrindane-5-oximes by Na–EtOH; the Bz derivative of this oxime undergoes spontaneous resolution in Et_2O or C_6H_6, giving the active *Bz* derivative, m.p. 140°, and thence an *oxime*, m.p. 59—60°; the *cis*-structure of this ketone is thus proved. With HNO_2 (VI) gives pure (V) and a little of a *hydrocarbon*, oxidised to *cis*-*cyclo*pentane-1 : 3-diacetic acid (VIII); HNO_2 converts (VII) mainly into (IV), but some (V) and a hydrocarbon, oxidised to (VIII), are also formed.

R. S. C.

Intramolecular rearrangement. M. Sommelet (Compt. rend., 1937, **205**, 56—58; cf. A., 1923, i, 202).—$CHPh_2$·NMe_3Br with Ag_2O in H_2O gives an aq. solution of $CHPh_2$·NMe_3·OH (I) from which H_2O is removed by distillation. (I) decomposes at 130—150° to give $CHPh_2$·OH, $(CHPh_2)_2O$, $CHPh_2$·OMe, NMe_3, NMe_2·$CHPh_2$ (cf. A., 1933, 262), and a small amount of (II) (below), formed by loss of 1 H_2O from (I). Concn. of an aq. solution of (I) over P_2O_5 finally leaves o-*benzylbenzyldimethylamine* (II) [formed by dehydration of (I) followed by rearrangement], b.p. 189—190°/16 mm. (*methiodide*, m.p. 224—225°; *ethiodide*, m.p. 167°; *allyliodide*, m.p. 135°), converted by Ac_2O with formation of NMe_2Ac into the *acetate*, b.p. 205°/22 mm., of o-*benzylbenzyl alcohol*, b.p. 197—199°/19 mm. (*Ph carbamate*, m.p. 77°), which is oxidised (CrO_3) to o-*benzylbenzoic acid*, m.p. 116—117° (*amide*, m.p. 164—165·5°).

J. L. D.

Derivatives of 4-*cyclo*hexyldiphenyl. III. F. R. Basford (J.C.S., 1937, 1440—1443).—4-*cyclo*Hexyldiphenyl (I) when nitrated (HNO_3–AcOH) affords 2- (II), m.p. 164·5°, and 4′-*nitro*-4-*cyclohexyldiphenyl* (III), m.p. 124°. (II) is oxidised (CrO_3–AcOH) to 2-nitrodiphenyl-4-carboxylic acid, and reduced ($SnCl_2$) to 2-*amino*-4-*cyclohexyldiphenyl*, m.p. 102° (*Ac*, m.p. 116°, and *Bz*, m.p. 158°, derivatives), whilst on dehydrogenation (Br) 2-*nitro*-1 : 4-*diphenylbenzene*, m.p. 125°, is formed, reduced ($SnCl_2$) to 2-*amino*-1 : 4-*diphenylbenzene*, m.p. 169° (*Bz* derivative, m.p. 144°). (III) is oxidised (Na_2CrO_7–aq. AcOH) to 4-nitrodiphenyl-4′-carboxylic acid, and reduced ($SnCl_2$) to 4′-*amino*-4-*cyclohexyldiphenyl* (IV) (*hydrochloride*, m.p. 90°; *Ac*, m.p. 225°, and *Bz*, m.p. 240°, derivatives), and on dehydrogenation (Br) yields 4′-*nitro*-1 : 4-*diphenylbenzene*, m.p. 211°. (IV) when diazotised and treated with KI affords 4-*cyclohexyl*-4′-*diazonium perbromide*, m.p. 105°, converted (hot EtOH) into 4′-bromo-4-*cyclo*hexyldiphenyl. (I) with HNO_3 alone affords *trinitro*-4-*cyclohexyldiphenyl*, m.p. 235°, and with *p*-NO_2·C_6H_4·COCl in CS_2 with $AlCl_3$ yields 4′-p-*nitrobenzoyl*-4-*cyclohexyldiphenyl*, m.p. 175°, also formed by nitration of 4′-benzoyl-4-*cyclo*hexyldiphenyl. 4-*cyclo*Hexyldiphenyl-4′-carboxylic acid with $SOCl_2$ affords the *chloride*, m.p. 109°. 4 : 4′-Di*cyclo*hexyldiphenyl is nitrated to a $(NO_2)_2$-compound, m.p. 182°, reduced (Fe–HCl–EtOH) to a *diamine*, m.p. 225°.

J. D. R.

Nitration and halogenation of *NN′*-diphenylethylenediamine and its derivatives. II. A. E. Schouten (Rec. trav. chim., 1937, **56**, 863—872; cf. this vol., 335).—Halogenation and nitration of $(CH_2$·$NHPh)_2$ (I) and its derivatives proceeds until all *o*- and *p*-positions are substituted, but only one NO_2 can be introduced into each Ph of the diacetylated *sec.*-amines. *NN′*-Diphenylpiperazine (II) and its derivatives are converted into [2 : 4 : 6-$(NO_2)_3C_6H_2$·$N(NO_2)$·CH_2·]$_2$ etc. by abs. HNO_3. 1 : 3 : 4-$C_6H_3Cl(NO_2)_2$ and $(CH_2$·$NH_2)_2$ in EtOH give *NN′-di*-5-*chloro*-2-*nitrophenylethylenediamine*, m.p. 249°, the Ac_2 derivative, m.p. 229°, of which with abs. HNO_3 at 0° gives *NN′-di*-5-*chloro*-2 : 4 : 6-*trinitrophenylethylenedinitroamine*, m.p. 170°, explosive. Similarly are obtained *NN′-di*-5-*bromo*-2-*nitrophenylethylenediamine*, m.p. 260° (Ac_2 derivative, m.p. 209°), and *NN′-di*-5-*bromo*-2 : 4 : 6-*trinitrophenylethylenedinitroamine*, m.p. 187°, explosive. *NN′-Di*-2 : 4-*dibromophenylethylenediamine*, m.p. 138° (Ac_2 derivative, m.p. 227°), is obtained from (I) or its 2 : 2′- or 4 : 4′-Br_2-derivative by Br in AcOH and in $CHCl_3$ with Br gives *NN′-di*-2 : 4 : 6-*tribromophenylethylenediamine*, m.p. 129° (Ac_2 derivative, m.p. 234°). *NN′*-Di-2- and -4-nitrophenylethylenediamine and Br–AcOH give the known 4 : 4′-dibromo-2 : 2′- and 2 : 2′-dibromo-4 : 4′-dinitro-compounds, respectively. Cl_2 in AcOH without cooling degrades (I) to $(CH_2$·$NH_2)_2$, but at 0° in AcOH or $CHCl_3$ gives *NN′-di*-2 : 4 : 6-*trichlorphenylethylenediamine*, m.p. 104° (Ac_2 derivative, m.p. 243°). $(CH_2$·$NPhAc)_2$ and abs. HNO_3 at −10° give the 4 : 4′-$(NO_2)_2$-compound, which

resists further nitration, as also does the 2 : 2′-$(NO_2)_2$-compound. Diacet-*NN′*-di-*o*-bromophenylethylenediamide gives *diacet*-NN′-*di*-2-*bromo*-6-*nitrophenylenediamide*, m.p. 228°, the orientation of which is decided by deacetylation and further bromination to the 2 : 2′ : 4 : 4′-tetrabromo-6 : 6′-dinitro-compound, which is also obtained by nitration and deacetylation of diacet-*NN′*-di-2 : 4-dibromophenylethylenediamide. Diacet-*NN′*-di-*p*-chloro- and -bromo-phenylethylenediamide give the known 2 : 2′-$(NO_2)_2$-compounds, and the 2 : 2′ : 4 : 4′-tetrabromo-diacetamide gives *diacet*-NN′-*di*-2 : 4-*dibromo*-6-*nitrophenylethylenediamide*, m.p. 243°. (II), m.p. 164°, is prepared from (I) and $(CH_2Br)_2$ at 150°. *p*-$C_6H_4Cl{\cdot}NH_2$, $(CH_2Br)_2$, and NaOAc at 140° give NN′-*di*-p-*chlorophenylpiperazine*, m.p. 239°. NN′-*Di*-p-*bromophenylpiperazine*, m.p. 227°, is obtained as a by-product in the prep. of $(CH_2{\cdot}NH{\cdot}C_6H_4Br\text{-}p)_2$. R. S. C.

Azo-dyes. III. A. Rollett [with R. Birkner, K. R. Posselt, J. Hochstrasser, and J. Stern] (Monatsh., 1937, **70**, 425—430; cf. this vol., 97).—The absorption spectra of a no. of azo-dyes are determined in buffered solutions. Changes of colour are noted for dyes from NH_2Ph and many derivatives thereof with 1 : 4- and 1 : 5-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ at p_H 3—5, with 1 : 6- and 1 : 7-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ at p_H 4—5, with 1 : 4- and 1 : 7-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ at p_H 9—10, with 1 : 5-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ at p_H 8—9, and with 1 : 6-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ at p_H 10. The p_H at which colour change occurs appears to be determined mainly by the $C_{10}H_8$ component of the dye. The ultra-violet adsorption spectra of α-$C_{10}H_7{\cdot}NH_2$, 1-$C_{10}H_7{\cdot}SO_3H$, 1 : 7-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$, 1 : 4-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ and -$NMe_2{\cdot}C_{10}H_6{\cdot}SO_3H$ in buffered solutions are recorded. R. S. C.

Hydrazones and semicarbazides from *p*-thiocyanophenylhydrazine. Z. Horii (J. Pharm. Soc. Japan, 1935, **55**, 880—887).—*p*-$NH_2{\cdot}C_6H_4{\cdot}CNS$ is diazotised and reduced ($SnCl_2$) to p-*thiocyanophenylhydrazine*, m.p. 95—96°, isolated as the *hydrochloride*, decomp. 188°, which condenses with carbonyl compounds in 95% EtOH to give p-*thiocyanophenylhydrazones* of the following: $COMe_2$, m.p. 128·5—129°; $AcCO_2H$, m.p. 191—191·5°; COPhMe, m.p. 109—110°; PhCHO, m.p. 135—136°; *o*-, m.p. 172—173°, *m*-, m.p. 167°, and *p*-$OH{\cdot}C_6H_4{\cdot}CHO$, m.p. 154°; *o*-, m.p. 147—148°, and *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, m.p. 129—129·6°; heliotropin, m.p. 153—154°; veratraldehyde, m.p. 117°; *iso*vanillin, m.p. 148—149°; 4-methoxy-3-ethoxybenzaldehyde, m.p. 113—114°; resorcylaldehyde, m.p. 191—192°; 2 : 4-$(OMe)_2C_6H_3{\cdot}CHO$, m.p. 129—129·5°; *p*-tolualdehyde, m.p. 118—119°; cuminaldehyde, m.p. 140°; *o*-, m.p. 171°, *m*-, m.p. 161—162°, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, m.p. 185—186°; *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$, m.p. 158—159°; *m*-$C_6H_4Cl{\cdot}CHO$, m.p. 125—125·5°; 2 : 5-$OH{\cdot}C_6H_3Cl{\cdot}CHO$, m.p. 217—218°; 2 : 3 : 5-$OH{\cdot}C_6H_2Cl_2{\cdot}CHO$, m.p. 223—224°; cinnamaldehyde, m.p. 138—140°; furfuraldehyde, m.p. 124°; β-$C_{10}H_7{\cdot}CHO$, m.p. 207—208°; *d*-galactose, m.p. 181·5°; *d*-mannose, m.p. 185—186°; *l*-arabinose, m.p. 160—160·5°. The following are also described: *acetonyl*-p-*thiocyanophenylhydrazine*, m.p. 217°; 1-p-*thiocyanophenylsemicarbazide*, m.p. 217°, and its 4-*Ph*, m.p. 239—239·5°, 4-o-, m.p. 188—189°, -m-, m.p. 230°, and -p-*tolyl*, m.p. 238—239° derivatives, and the *thio*-derivatives of these, m.p. 187°, 190—191°, 163—164°, 177—178°, 170—171°.

Ch. Abs. (*r*)

Reactions of thiocarbonyl chloride. V. With compounds containing the NH·NH_2 group. T. Beckett and G. M. Dyson (J.C.S., 1937, 1358—1362; cf. this vol., 274).—$CSCl_2$ and arylhydrazines react thus: $3CSCl_2 + 2NH_2{\cdot}NH{\cdot}C_6H_4R \rightarrow CS[N(NCS){\cdot}C_6H_4R]_2$ (*A*) + 6HCl; (*A*) → $C_6H_4R{\cdot}NCS + C_6H_4R{\cdot}N(NCS)_2$ (*B*); (*B*) → $NH_2{\cdot}C_6H_2R(NCS)_2$ (*C*); (*C*) + $CSCl_2$ → $C_6H_2R(NCS)_3$ (*D*) + 2HCl. Compounds (*D*) are the products isolated, unless R = *p*-NO_2 or -Br; in the latter cases compounds (*B*) are obtained, but as sole products only if 10% of HCl is present. In 10% HCl NHPh·NH_2 and $CSCl_2$ give PhNCS and 1 : 2 : 4-*trithiocarbimidobenzene*, m.p. 156°, which with NH_2Ph or $C_6H_4Br{\cdot}NH_2$ in C_6H_6 gives 1 : 2 : 4-*tris*(*phenyl*-, m.p. 120°, or -4-*bromophenyl*-*thiocarbamido*)*benzene*, m.p. 183°, respectively, with dry EtOH gives 3 : 4-*dithiocarbamidophenylthiourethane*, m.p. 74°, and with dry NH_3–C_6H_6 gives 1 : 2 : 4-*trithiocarbamidobenzene*, m.p. 170°, converted by HCl–C_6H_6 into H_2S and 2 : 5-*dithiocarbamidoaniline*, m.p. 149·5°. *s*-$C_6H_3(NH_2)_3$ and $CSCl_2$ in 7% HCl give 1 : 3 : 5-*trithiocarbimidobenzene*, m.p. 143°. $CSCl_2$ and $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ in aq. Et_2O give s-*dicarbamidothiocarbamide*, m.p. 215° (decomp.), which gives colours or coloured ppts. with many metals; it detects $0{\cdot}25 \times 10^{-6}$ g. of Cu or 1×10^{-6} g. of Co in 50 ml. of H_2O. $CSCl_2$ and aq. $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl afford 3 : 5-*dithiocarbimidothiocarbonyldicarbamide* (I), $CS[N(NCS){\cdot}CO{\cdot}NH_2]_2$, m.p. 186—194° (decomp.), decomposed by Zn dust and dil. HCl to $(CH_2O)_3$ and by dil. alkali to H_2S, N_2H_4, CO_2, and NH_3, and converted by NH_2Ph, $C_6H_4Me{\cdot}NH_2$, or $C_6H_4Br{\cdot}NH_2$ into 2-*thion*-1-*phenyl*-(II), m.p. 198°, -p-*tolyl*-, m.p. 208°, and -p-*bromophenyl*-*dicarbamide*, $NHAr{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, m.p. 202°, respectively, the two first-mentioned of these products being also obtained from $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ and ArNCS. $CSCl_2$ and $NH_2{\cdot}CO{\cdot}NH{\cdot}NHPh$ in aq. Et_2O give s-*diphenyldicarbamidothiocarbamide*, $CS(NH{\cdot}NH{\cdot}CO{\cdot}NHPh)_2$, m.p. 223°, which gives a ppt. with Hg^{II} salts in concns. of $>1 \times 10^{-6}$; $NH_2{\cdot}CO{\cdot}NH{\cdot}NPh_2$ in dil. HCl, however, gives 3 : 5-*dithiocarbamido*-1 : 1 : 7 : 7-*tetraphenylthiocarbonyldicarbamide*, $CS[N(CNS){\cdot}CO{\cdot}NPh_2]$, m.p. 133°, which with NH_2Ph in ligroin gives 3 : 5-*bis*(*phenylthiocarbamido*)-1 : 1 : 7 : 7-*tetraphenylthiocarbonyldicarbamide*, $CS[N(CO{\cdot}NPh_2){\cdot}NH{\cdot}CS{\cdot}NHPh]_2$, decomposed by hot 10% HCl into CO_2, H_2S, PhNCS, and NHPh·CO·NH·NHPh. (I) in hot abs. EtOH affords 3 : 5-*dithiourethanocarbonyldicarbamide*, $CS[N(CO{\cdot}NH_2){\cdot}NH{\cdot}CS{\cdot}OEt]_2$, m.p. 30—32°, which with NH_2Ph–EtOH yields (II) and $CS(NHPh)_2$. $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH_2$,HCl and $CSCl_2$ in H_2O give NN′-*dithiocarbimido*-NN′-*dioxamylthiocarbamide*, m.p. 223°, reduced by Zn dust and dil. acid to $(CH_2O)_3$, CO_2, H_2S, and NH_3, and converted by NH_2Ph into 1-*oxamyl*-4-*phenylthiosemicarbazide*, NHPh·CS·NH·NH·CO·CO·NH_2, m.p. 185·5°, which is also obtained from $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH_2$ and PhNCS in EtOH and is hydrolysed thereto by hot H_2O.

NH_2·NHMe,H_2SO_4 gives NN′-*dithiocarbimidodimethylthiocarbamide*, m.p. 139°, decomposed by 20% NaOH and converted by NH_2Ph into $CS(NHPh)_2$ and NHPh·CS·NH·NHMe, m.p. 153° (also obtained from NH_2·NHMe and PhNCS). *Dithiocarbimidothiocarbamide*, decomp. 196—200°, is obtained from $CSCl_2$ and aq. N_2H_4 or $CS(NH{\cdot}NH_2)_2$ in 10% HCl, and with NH_2Ph or $C_6H_4Me{\cdot}NH_2$ gives $CS(NHAr)_2$ and dithio-*p*-urazine, $CS<^{NH\cdot NH}_{NH\cdot NH}>CS$, m.p. 202—203°, also obtained from K ethylxanthate and $CS(NH{\cdot}NH_2)_2$ in EtOH. NH_2·NPh_2,HCl and $CSCl_2$ give N-*thiocarbimidodiphenylamine*, m.p. 63°. NH_2·NPhMe in 5% HCl gives N-*thiocarbimidophenylmethylamine*, an oil, which with NH_2Ph yields NHMe·CO·NH·NPh_2, $CO(NHPh)_2$, and PhNCS. *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ in 10% HCl gives NN′-*dithiocarbimidobis*-p-*nitrophenylthiocarbamide* (*A*; R = NO_2), cryst., sol. in 2N-NaOH, reacting with benzidine, reduced by Sn–HCl to NH_4Cl, H_2S, $(CH_2O)_3$, and *p*-$C_6H_4(NH_2)_2$, and converted by NH_2Ph into NN′-*diphenylthiocarbamidobis*-p-*nitrophenylthiocarbamide*, m.p. 143°, which is hydrolysed by HCl.
$NH_2{\cdot}CS{\cdot}NH{\cdot}NH_2$ and $CSCl_2$ give 3 : 5-*dithiocarbimidothiocarbonyldithiocarbamide*, $CS[N(NCS){\cdot}CS{\cdot}NH_2]_2$, m.p. 240—250° (decomp.), which with NH_2Ph gives $CS(NHPh)_2$ and dithiourazole. R. S. C.

Influence of substituents on the coupling of phenols with diazonium salts. D. H. Richardson (J.C.S., 1937, 1363—1365).—By coupling 1 mol. of *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}HSO_4$ with 1 mol. each of two phenols and determining the halogen in the dye, it is shown that relative rates of coupling for $C_6H_4R{\cdot}OH$ are R = *o*-Cl 0·51, *m*-Cl 0·36, *o*-Br 0·84, *m*-Br 0·63, H 1, *o*-I 1·13, *m*-I 1·24, *o*-Me 6·6, and *o*-OMe 28·4. Thus, Br has a greater inductive effect than Cl, and I has an activating effect; the *m*- (coupling) position is more powerfully activated by meso- and electro-meric (OMe) than by inductive (Me) effects; from results with $C_6H_3Cl_2{\cdot}OH$ and $C_6H_3Br_2{\cdot}OH$ it is deduced that the deactivating effect reaches the coupling position by one side of the C_6H_6 ring at one time. R. S. C.

Preparation of *m*-tolyl *iso*propyl ether from *m*-cresol and *iso*propyl chloride. T. Boyd and E. F. Degering (J. Amer. Chem. Soc., 1937, **59**, 1399).—*m*-$C_6H_4Me{\cdot}OPr^{\beta}$ (23—27 g.) is prepared by slowly heating *m*-cresol (25 g.), $Pr^{\beta}Cl$ (30 c.c.), and NaOH (9·2 g.) to 150° in an autoclave, maintaining at 150—160° for 3 hr., and extracting with C_6H_6. A. Li.

Cleavage of diphenyl ethers by sodium in liquid ammonia. II. *meta*-Substituted diphenyl ethers. A. L. Kranzfelder, J. J. Verbanc, and F. J. Sowa (J. Amer. Chem. Soc., 1937, **59**, 1488—1490; cf. this vol., 239).—Cleavage of the following ethers, ROR′, by Na in liquid ammonia gives the stated % of ROH, the residue being R′OH: R = Ph, R′ = 3-$NH_2{\cdot}C_6H_4$, 28, 3-OMe·C_6H_4, 53, 3-C_6H_4Me, 38, or 3-$CO_2H{\cdot}C_6H_4$, 64; R = 2-OMe·C_6H_4, R′ = 3-OMe·C_6H_4, 24; R = 3-OMe·C_6H_4, R′ = 4-C_6H_4Me, 8; R = 2-C_6H_4Me, R′ = 3-C_6H_4Me, 47; R = 3-C_6H_4Me, R′ = 4-C_6H_4Me, 23%. These and previous results are interpreted on the basis of electromeric and inductive effects, Na or the electron concerned being considered as a nucleophyllic reagent; the explanation is not entirely satisfactory for *o*-substituents. The following substituents strengthen the link between O and substituted Ph: *o*- > *m*-Me > *m*-NH_2 > *p*-Me > *p*-OMe > *o*- > *p*-NH_2; the following weaken this linking: *m*- > *o*-OMe > *m*- > *o*- > *p*-CO_2Na. The following are described: *Ph* 3-*nitro*-, b.p. 174°/8 mm., 3-*amino*-, b.p. 194°/10 mm., 3-*methoxy*-, b.p. 127°/2 mm., 3-*carboxy*- (I), m.p. 139°, 2 : 3-, b.p. 152°/2 mm., and 3 : 4-*dimethoxy-phenyl*, b.p. 163°/22 mm., and vic-, b.p. 152°/2 mm., m.p. 48·5°, and as-*o*-*xylyl ether*, b.p. 174°/4 mm. All these require 2 Na for cleavage, except (I), which requires 3. R. S. C.

Derivatives of *o*-hydroxybenzylsulphonic acid. E. A. Shearing and S. Smiles (J.C.S., 1937, 1348—1351).—The reaction (*A*), $CH_2(C_{10}H_6{\cdot}OH)_2 + Na_2SO_3 \rightleftharpoons OH{\cdot}C_{10}H_6{\cdot}CH_2{\cdot}SO_3Na$ (I) + $C_{10}H_7{\cdot}ONa$, is shown to be reversible and may be used to prepare *as*-di-2-hydroxynaphthyl-1-methanes, but not all dihydroxynaphthylmethanes are thus cleaved. When β-$C_{10}H_7{\cdot}OH$, CH_2O, and Na_2SO_3 react to form (I), reaction occurs partly by (*A*) and partly by way of $OH{\cdot}C_{10}H_6{\cdot}CH_2{\cdot}OH$, which then reacts with Na_2SO_3. Compounds, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}SO_3H$, are prepared, usually in small yield, from *o*-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ (not $CH_2Ph{\cdot}OH$) and $NaHSO_3$ or from the phenols, CH_2O, and Na_2SO_3; they are characterised by conversion into benzylsultones, *o*-$Ar<^{CH_2}_{O}>SO_2$. R in 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}CH_2R$ is unusually mobile, which is paralleled by fission of di-2-hydroxynaphthyl 1-sulphide (II) by Na_2SO_3 to β-$C_{10}H_7{\cdot}OH$ and *Na* 2-*hydroxynaphthyl*-1-*thiolsulphonate*, +0·5H_2O [which reform (II) in hot alkali], and by alkaline reduction of (II) to β-$C_{10}H_7{\cdot}OH$ and 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}SH$. The following are described: *di*-6-*bromo*-2-*hydroxynaphthyl*-1-*methane*, m.p. 240°, stable to Na_2SO_3; 3-, m.p. 200° (decomp.), and 6-*bromodi*-2-*hydroxynaphthyl*-1-*methane*, m.p. 210° (decomp.); *Na* and *Pb* 6-*bromo*-2-*hydroxynaphthyl*-1-*methanesulphonate*; *Na* 2-*hydroxyphenyl*-, 4-*hydroxy*-p-*tolyl*-3-, 4-*hydroxy*-m-*xylyl*-5-, and 2-*hydroxy*-p-*xylyl*-5-*methanesulphonate* (*Ba* salt); 5-*methyl*-, m.p. 91·5°, and 5 : 7-*dimethylbenzylsultone*, m.p. 92·5°; *phenyl*-, m.p. 87°, p-*tolyl*-, m.p. 103°, and 2-*hydroxy*-2′-*nitrophenyl*-3 : 5-*dimethylbenzylsulphone*, m.p. 168°, unstable to alkali. β-$C_{10}H_7{\cdot}OH$ with 4 : 1 : 3 : 5-$OH{\cdot}C_6H_2Me_2{\cdot}CH_2Cl$ in C_6H_6 or 4 : 1 : 3 : 5-$OH{\cdot}C_6H_2Me_2{\cdot}CH_2{\cdot}OH$ in AcOH gives 1-2′-*hydroxy*-3′ : 5′-*dimethylbenzyl*-2-*naphthol*, m.p. 175° (*Ac*$_2$ derivative, m.p. 99°). R. S. C.

Fused carbon rings. XII. A simple synthesis of derivatives of decahydronaphthalene from *cyclo*hexanone, and observations on *cyclo*hexane*spiro*butyrolactone and allied compounds. XIII. Synthesis of derivatives of decahydronaphthalene containing an angular methyl group. R. P. Linstead, A. B.-L. Wang, J. H. Williams, and (in part) K. D. Errington. XII. R. P. Linstead, A. F. Millidge, and A. L. Walpole (J.C.S., 1937, 1136—1140, 1140—1145).—XII. 1-Δ$^{\gamma}$-*Butenyl*cyclo*hexanol* (I), b.p. 95—96°/10 mm. [obtained from *cyclo*hexanone and $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}MgBr$ (II)], is dehydrated by $H_2C_2O_4$ at 125—135° to 1-Δ$^{\gamma}$-*butenyl*-

Δ^1-cyclo*hexene* (III), b.p. 60—62°/10 mm., and by P_2O_5–H_3PO_4 at 160° to a mixture of (III) and $\Delta^{9:10}$-octahydronaphthalene (A., 1929, 76), also obtained from *trans*-decahydro-β-naphthol and P_2O_5–H_3PO_4, or from *trans*-Δ^2-decahydronaphthalene and P_2O_5. With AcOH–Ac_2O–H_2SO_4, (I) gives *cis*-decahydro-β-naphthol, also obtained from (III) and AcOH–H_2SO_4. That (I) has a Δ^γ-structure is shown by oxidation ($KMnO_4$) to *γ-cyclo*hexane*spiro*butyrolactone (IV), new m.p. 20—20·5°, new b.p. 130—133°/12 mm. (cf. A., 1928, 289). This is also prepared (H_2SO_4) from β-*cyclo*hexylidenepropionic acid (V), new m.p. 47—48°, obtained from *cyclo*hexanealdehyde (VI), $CH_2(CO_2H)_2$, and $N(CH_2{\cdot}CH_2{\cdot}OH)_3$. Sircar's (IV) and (V) (*loc. cit.*) are contaminated with one another, and, contrary to his statement, β-*cyclo*hexylacrylic acid (VII) [from (VI), $CH_2(CO_2H)_2$, and C_5H_5N] when boiled with 40% aq. KOH gives a mixture of (V) (54%) and (VII). Boiling H_2O hydrolyses (IV) only very slightly.

XIII. 2-Methyl-1-Δ^γ-butenyl*cyclo*hexanol (A., 1936, 846) and AcOH–Ac_2O–H_2SO_4 give a mixture containing cis-9-*methyldecahydro*-β-*naphthol* (VIII), m.p. 72°, oxidised by HNO_3 to cis-1-*methyl*cyclo*hexane*-1 : 2-*diacetic acid* (IX), m.p. 190°. The last when distilled with $Ba(OH)_2$ yields cis-8-*methyl*-2-*hydrindanone* (X), m.p. 39—40°, b.p. 105°/14 mm. (*semicarbazone*, m.p. 220°), which is oxidised to 1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid. Oxidation of (VIII) by CrO_3 yields cis-2-*keto*-9-*methyldecahydronaphthalene* (XI), m.p. 17—18°, b.p. 122—123°/14 mm. (*semicarbazone*, m.p. 210—212°). The structure of (XI) and of the *cis*-3-keto-9-methyl (*i.e.*, 2-keto-10-methyl) isomeride (XII) (this vol., 197) is established by their common oxidation to (IX). Both (XI) and (XII) similarly belong to the same stereochemical series, regarded as *cis*. The mixture from which (VIII) is removed is oxidised to (XI). Oxidation of the impure alcohol with HNO_3 gives (IX), with a C_{11}-acid, m.p. 164° (cf. A., 1936, 846), probably trans-1-*methyl*cyclo*hexane*-1 : 2-*diacetic acid*. Clemmensen reduction of (XI) gives cis-9-*methyldecahydronaphthalene* (XIII), m.p. −22°, b.p. 79°/11 mm., and dehydration of (VIII) cis-9-*methyloctahydronaphthalene* (XIV), b.p. 78—80°/12 mm. which on oxidation gives (IX), and thus contains the Δ^2-form. The evidence for the *cis*-configuration of the above series lies in the physical properties of (XIII), (XI), cis-8-*methylhydrindanone*, m.p. 10—14°, b.p. 56°/10·5 mm. [obtained by Clemmensen reduction of (X)], and (XIV), which all have high *d* and *n*, and normal [*R*], and in the parallel formation of a *cis*-compound from (I). The methyloctahydronaphthalenes obtained (A., 1936, 846) by direct cyclisation of methylbutenyl*cyclo*hexanols are mixtures of isomerides, perhaps containing trans-9-*methyl*-$\Delta^{4:10}$-*octahydronaphthalene*. 2 : 6-*Dimethyl*-Δ^γ-*butenyl*cyclo*hexanol*, b.p. 100—105°/10 mm. [obtained from 2 : 6-dimethyl*cyclo*hexanone (A., 1931, 1303) and (II)], is dehydrated (P_2O_5–H_3PO_4) to Δ^1-1 : 10(= 4 : 9)-*dimethyloctahydronaphthalene*, b.p. 86—90°/10 mm., which is hydrogenated to 1 : 10(= 4 : 9)-*dimethyldecahydronaphthalene*, b.p. 84—85°/10 mm. (of which the physical properties show that it is mainly *cis*), which with $AlCl_3$ is converted into the trans-*form*, b.p. 76—78°/10 mm. E. W. W.

Reaction between formaldehyde and naphthols. A. Castiglioni (Gazzetta, 1937, **67**, 324—326).—The product from CH_2O and α-$C_{10}H_7{\cdot}OH$ in conc. HCl is regarded as *di*-(α-*hydroxynaphthyl*)*carbinol*, and that from β-$C_{10}H_7{\cdot}OH$ (cf. A., 1935, 877) as *iso*-1 : 2 : 7 : 8-dibenzoxanthen (cf. A., 1934, 779). E. W. W.

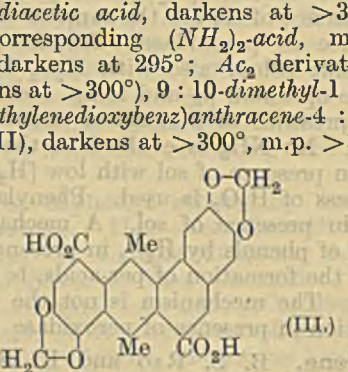
Synthesis of ethers of eugenol and *iso*eugenol. S. Ishikawa and M. Matsuhashi (Sci. Rep. Tokyo Bunrika Daigaku, 1937, **3**, **A**, 165—172).—Eugenol β-phenylethyl ether, b.p. 192—196°/5 mm., m.p. 29°, obtained in 37% yield from eugenol (I) and $CH_2Ph{\cdot}CH_2Cl$ with KOH in EtOH or K_2CO_3 in $COMe_2$, is converted by KOH–EtOH at 100° into styrene and *iso*eugenol (II). iso*Eugenol* β-*phenylethyl ether*, b.p. 210—212°/6 mm., is obtained from (II), $CH_2Ph{\cdot}CH_2Cl$, and KOH–EtOH. *Eugenol γ-phenylpropyl ether*, b.p. 200—205°/4 mm., from (I), $CH_2Ph{\cdot}CH_2{\cdot}CH_2Cl$, and KOH–EtOH, is isomerised by alkali to iso*eugenol γ-phenylpropyl ether*, b.p. 200—204°/3 mm., which gives MeCHO when ozonised. (I), $CHPh{:}CH{\cdot}CH_2Cl$, and KOH–EtOH give o-*cinnamyl*iso*eugenol*, b.p. 200—207°/3 mm. (*phenylurethane*, m.p. 149°), ozonised to PhCHO and MeCHO. H. W.

Oxidation of phenols by means of hydrogen peroxide in presence of inorganic catalysts. B. C. Kar (J. Indian Chem. Soc., 1937, **14**, 291—319).—The kinetics of the oxidation by means of H_2O_2 in presence of tungstic acid sol (I) of quinol, pyrogallol, guaiacol, and a mixture of *p*-$C_6H_4(NH_2)_2$ and α-$C_{10}H_7{\cdot}OH$ have been studied, the temp., p_H, and concns. of H_2O_2, sol, and substrate being varied. In some cases molybdic and vanadic acid sols have also been studied. The oxidation of pyrocatechol, *p*-cresol, tyrosine, and tryptophan by H_2O_2 in presence of (I) has also been studied. The results are compared with those obtained with H_2O_2 in presence of peroxidases (cf. lit.). All phenolic substances can be oxidised by H_2O_2 in presence of one of the above-mentioned sols, CO_2 being produced when high concns. of H_2O_2 and sol are used. KCN and $HgCl_2$ (strong poisons for peroxidases), heat, and ultra-violet light have little effect on the activity of the sols. At low $[H_2O_2]$ the products obtained in the presence of sol are the same as those obtained in presence of peroxidase. Tincture of guaiacum gives a blue colour also with H_2O_2 in presence of sols. The optimum p_H and temp. coeff. of the oxidation in presence of peroxidase and of sol are not the same. No NH_3 is evolved in the oxidation of tyrosine in presence of sol with low $[H_2O_2]$, but only when excess of H_2O_2 is used. Phenylalanine is not oxidised in presence of sol. A mechanism for the oxidation of phenols by H_2O_2 in presence of the sols, involving the formation of per-acids, is proposed and discussed. The mechanism is not the same as that for oxidation in presence of peroxidase. H. G. M.

β-Asarone. B. S. Rao and K. Subramaniam (J.C.S., 1937, 1338—1340).—β- (I), b.p. 162—163°/12 mm., and α-asarone (II), m.p. 62—63°, b.p. 167—168°/12 mm., are *cis–trans* isomerides. Both are polymerised by HCl with development of a blue colour. KOH at 200—220° converts (I) into (II). Short treatment of (I) with SeO_2 in hot EtOH gives (II), but longer treatment gives a complex mixture

including 2 : 5-dimethoxypropenylbenzene (*picrate*, m.p. 87°; *nitrosite*, m.p. 118°). Reduction of (I) by Na–EtOH gives 1 : 2 : 4 : 5-$C_6H_2Pr^a(OMe)_3$. Br and (I) in CS_2–Et_2O at −20° give mainly a liquid *dibromide* with a little asarone dibromide, m.p. 82—83°, both converted by Cu in C_6H_6 into diasarone monobromide, m.p. 122°. HNO_2 converts (I) and (II) into asarone *ψ*-nitrosite. $Hg(OAc)_2$ and (I) give α-2 : 4 : 5-*trimethoxyphenylpropane*-αβ-*diol*, an oil, whereas (II) gives an oily *isomeride*; both glycols are converted into a *substance*, $C_{24}H_{32}O_8$, m.p. 204—205°, by distillation at 4 mm. or by treatment with Ac_2O at <40°. R. S. C.

Synthesis of 6 : 7-methylenedioxy-1 : 4-dimethylphenanthrene and of certain substituted 9 : 10-dimethyl-1 : 2 : 5 : 6-dibenzanthracenes. R. B. Akin and M. T. Bogert (J. Amer. Chem. Soc., 1937, **59**, 1564—1567).—1 : 4 : 2-$C_6H_3Me_2$·CH_2·CO_2K and 6-nitropiperonal (I) in Ac_2O at 105—110° give 2-*nitro*-4 : 5-*methylenedioxy*-α-p-*xylylcinnamic acid*, m.p. 209·4—209·9° (*Me* ester, m.p. 157·5—158°), reduced ($FeSO_4$–NH_3) to the *NH*$_2$-*acid*, m.p. 216—217°, which yields (Pschorr) 6 : 7-*methylenedioxy*-1 : 4-*dimethylphenanthrene*-10-*carboxylic acid*, m.p. 221—222°, converted by basic Cu carbonate (less well by Cu) in quinaldine into 6 : 7-*methylenedioxy*-1 : 4-*dimethylphenanthrene*, m.p. 166·5—167° (*picrate*, m.p. 155—158°, dissociates in solvents). Attempts to open the CH_2O_2 ring of this ether failed. 2 : 5-*Di*(*cyanomethyl*)-p-*xylene* (prep. from the dichloride by NaCN in aq. EtOH), m.p. 157·8—158·3°, affords p-*xylylene*-2 : 5-*diacetic acid* (II), m.p. 254—255° (*Me*$_2$ ester, m.p. 61°), and thence (condensation with *o*-NO_2·C_6H_4·CHO, reduction, and Pschorr reaction) *di*-o-*nitrobenzylidene*-p-*xylylene*-2 : 5-*diacetic acid*, m.p. 330° (decomp. from 290°), the corresponding (*NH*$_2$)$_2$-*acid*, decomp. 293—296° (softens at 285°), and 9 : 10-*dimethyl*-1 : 2 : 5 : 6-*dibenzanthracene*-4 : 8-*dicarboxylic acid*, m.p. >350° (sinters at 335°), decarboxylated by Cu in quinaldine to 9 : 10-dimethyl-1 : 2 : 5 : 6-dibenzanthracene, m.p. 203—204°. Similar reactions, starting from (I) and (II), lead to *di*-(2′-*nitro*-4′ : 5′-*methylenedioxybenzylidene*)-p-*xylylene*-2 : 5-*diacetic acid*, darkens at >300° (*Na*$_2$ salt), the corresponding (*NH*$_2$)$_2$-*acid*, m.p. 350° (sinters and darkens at 295°; *Ac*$_2$ derivative, m.p. >350°, darkens at >300°), 9 : 10-*dimethyl*-1 : 2 : 5 : 6-*di*-(3′ : 4′-*methylenedioxybenz*)*anthracene*-4 : 8-*dicarboxylic acid* (III), darkens at >300°, m.p. >350°, and



(III.)

9 : 10-*dimethyl*-1 : 2 : 5 : 6-*di*-(3′ : 4′-*methylenedioxybenz*)-*anthracene*, m.p. 279—281° (sinters at 261—266°), the CH_2O_2 rings of which could not be opened by $AlBr_3$. M.p. are corr. R. S. C.

Reactions of sodium mono- and di-sulphides with 1-chloro-2-nitro-, 2-chloro-1-nitro-, and 1-chloro-4-nitro-naphthalene. H. H. Hodgson and E. Leigh (J.C.S., 1937, 1352—1353).—1 : 2-, m.p. 80·5—81°, 2 : 1-, m.p. 99—100°, and 1 : 4-$C_{10}H_6Cl$·NO_2, m.p. 87—87·5° (2 mols.), and Na_2S_2 (1 mol.) in hot EtOH give 1 : 13, 1 : 12, and 1 : 12 mixtures, respectively, of dinitrodinaphthyl mono- and di-sulphides; in C_6H_6 the latter are almost the sole products; with Na_2S in EtOH the proportions are 1 : 1·2, 1 : 0·8, and 1 : 1·5, respectively, the disulphide being formed from the thiol which is the initial product. The Na salts of the thiols and $C_{10}H_6Cl$·NO_2 give 1 : 1′-*dinitro*-2 : 2′-, m.p. 203—204°, 2 : 2′-, m.p. 204—205°, and 4 : 4′-*dinitro*-1 : 1′-*dinaphthyl sulphide*, m.p. 239—240°. 4 : 4′- and 2 : 2′-*Dinitro*-1 : 1′- and 1 : 1′-*dinitro*-2 : 2′-*dinaphthyl disulphide* melt at 188—189°, 176—177°, and 188—190°, respectively. R. S. C.

Isomerisation of methylene*cyclo*hexane oxide to hexahydrobenzaldehyde and deamination of the corresponding amino-alcohol to *cyclo*heptanone. M. Tiffeneau, P. Weill, and B. Tchoubar (Compt. rend., 1937, **205**, 54—56).—Methylene*cyclo*hexane (cf. A., 1906, i, 563) with BzO_2H affords *epoxymethylcyclohexane* (I), b.p. 103—104°, which is isomerised by $ZnCl_2$ at 100° to hexahydrobenzaldehyde. When (I) is heated with excess of conc. aq. NH_3 in a sealed tube it affords 1-*hydroxy*-1-cyclo*hexylmethylamine*, b.p. 106°/16 mm. (*hydrochloride*, m.p. 205°), which with $NaNO_2$ in dil. AcOH at room temp. gives *cyclo*heptanone after a semipinacolin change and a rupture of the ring (cf. this vol., 241; A., 1935, 1240; 1920, i, 2; 1913, i, 181). J. L. D.

Addition of hydracids to the epoxides, and hypohalogenous acids to the ethylenic derivatives, methylene*cyclo*hexane, and methyl*cyclo*hexene and their epoxides. M. Tiffeneau, P. Weill, and B. Tchoubar (Compt. rend., 1937, **205**, 144—146; cf. A., 1932, 394; 1923, i, 8; 1906, i, 228).—Methylene*cyclo*hexane adds HOCl to give 1-*chloro*-1-*hydroxymethylcyclohexane* (I), m.p. 75° (in which Cl is linked to the more substituted C), which is converted by aq. KOH into the *epoxide* (II), b.p. 42°/15 mm., and by MgEtBr into C_6H_{11}·CHO. (II) reacts with dry HCl in cold Et_2O to give (I). 1-Methyl-1 : 2-epoxy*cyclo*hexane with dry HCl in cold Et_2O and 1-methyl-Δ^1-*cyclo*hexene with HOCl afford *cis*- and *trans*-2-chloro-1-methyl*cyclo*hexanol (III) (in which Cl is linked to the less substituted C) respectively. Removal of Cl with Mg from the *cis*-form gives rise mainly to 2-methyl*cyclo*hexanone and a little acetyl*cyclo*pentane, which is the sole product obtained in a similar reaction with the *trans*-form (cf. A., 1934, 1098). J. L. D.

Preparation of 5-bromo-2-methoxybenzyl alcohol and 5-bromo-2-methoxybenzaldehyde. R. Quelet and M. Paty (Compt. rend., 1937, **205**, 146—148; cf. this vol., 146).—*p*-C_6H_4Br·OMe with CH_2O, dry HCl, and $ZnCl_2$ affords 5-bromo-2-methoxybenzyl chloride (I), converted by boiling aq. K_2CO_3 into 5-*bromo*-2-*methoxybenzyl alcohol* (II), m.p. 72° (*phenylurethane*, m.p. 121·5°). (I) with boiling NaOAc affords 5-*bromo*-2-*methoxybenzyl acetate*, m.p. 64°, converted by boiling aq. EtOH–KOH into (II). (I)

when boiled with $Cu(NO_3)_2$ and AcOH [or when boiled with aq. EtOH–$(CH_2)_6N_4$] affords 5-bromo-2-methoxybenzaldehyde, m.p. 114·5° (*semicarbazone*, m.p. 244—245°), and a little 5-bromo-2-methoxybenzoic acid. J. L. D.

Hydrocarbons, halogen derivatives, ethers, and esters derived from tetrahydroionol. J. Kandel (Compt. rend., 1937, **205**, 63—65; cf. this vol., 108).—β-Ionone (1 mol.) absorbs 2 H (Ni) under pressure at room temp.; at 50° 4—6 H is absorbed and at 230—240° reduction is complete to tetrahydroionol (I), also obtained from α-ionone. At 290° (I) loses H_2O and is then further hydrogenated to 1 : 3 : 3-*trimethyl*-2-*butyl*cyclo*hexane* (*tetrahydroionane*), b.p. 95—96°/14 mm. (I) with $NaHSO_4$ affords *dihydroionane*, b.p. 98·5°/16·5 mm., and with dry HCl at 100°, or with HBr, or with I–red P it affords the corresponding *Cl*-, b.p. 128—128·5°/17 mm., *Br*-, b.p. 138·5—139°/16 mm., and *I*-, b.p. 151·5—152°/14 mm., -derivatives, respectively. The Na derivative of (I) with the appropriate alkyl iodide affords the *Me*, b.p. 118°/13·5 mm., *Et*, b.p. 123·5°/13 mm., and Pr^{β}, b.p. 131—132°/15 mm., *ethers*, respectively. (I) with trioxymethylene and dry HCl gives the *chloromethyl* derivative, b.p. 150—151°/15 mm., converted by MgEtBr and $MgPr^{\beta}Br$ into the Pr^{α}, b.p. 133—134°/14 mm. and Bu^{β}, b.p. 142—143°/15 mm., *ethers*, respectively. (I) with HCO_2H–Ac_2O gives the *formate*, b.p. 134—134·5°/15 mm., with o-$C_6H_4(CO)_2O$-C_5H_5N the *H phthalate*, m.p. 79° (*allophanate*, m.p. 164°), with AcCl, PrCl, and BzCl, the acetate, b.p. 141·5—142°/15·5 mm. (cf. A., 1916, i, 16), *propionate*, b.p. 151·5—152°/15·5 mm., and *benzoate*, b.p. 210·5—211°/13 mm., respectively. J. L. D.

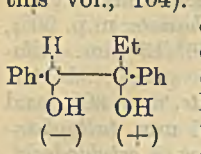
Reducing and condensing action of alkali benzyloxides on ketones, aldehydes, and αβ-unsaturated alcohols. P. Mastagli (Compt. rend., 1937, **204**, 1656—1658; cf. this vol., 102).—Michler's ketone with N-CH_2Ph·OK at 210° affords the hydrol, CH_2Ph·OH being oxidised to BzOH. COPhMe under similar conditions affords *αγ-diphenylpropanol* (80%), b.p. 194°/15 mm. (*allophanate*, m.p. 99°), and *αγ-diphenyl*-β-*benzyl*-n-*propyl alcohol* (20%), b.p. 254—255°/15 mm., oxidised (CrO_3) to the corresponding ketones. Similarly, p-C_6H_4Me·COMe affords *γ-phenyl*-α-p-*tolylpropyl alcohol*, b.p. 200°/13 mm. (*allophanate*, m.p. 111°). β-$C_{10}H_7$·COMe similarly affords *γ-phenyl*-α-2-*naphthylpropyl alcohol*, m.p. 63°, oxidised by CrO_3 to the corresponding *ketone*, m.p. 93° and by HNO_3 to β-$C_{10}H_7$·CO_2H. Cinnamyl alcohol similarly affords *γ-phenyl*-β-*benzyl*-n-*propyl alcohol*, b.p. 202°/15 mm. (*allophanate*, m.p. 140°), oxidised to β-*phenyl*-α-*benzylpropionic acid*, m.p. 89°. α-Butyl-, -amyl-, and -hexyl-cinnamaldehydes with N-CH_2Ph·ONa (the K derivative causes reduction) at 100° afford α-butyl-, -*amyl*-, b.p. 162°/12 mm. (*allophanate*, m.p. 160°), and -hexyl-cinnamyl alcohol, respectively. Many straight-chain aldehydes similarly afford two products, one obtained as a result of an aldol condensation and the other by the introduction of CH_2Ph into the aldehyde. Thus $Pr^{\alpha}CHO$ gives β-*ethylhexanol*, b.p. 85°/16 mm. (*allophanate*, m.p. 125°), and β-*benzyl*-n-*butyl alcohol*, b.p. 134°/15 mm. (*allophanate*, m.p. 134°); hexaldehyde gives β-*butyloctanol*, b.p. 132°/15 mm. (*allophanate*, m.p. 119°), and β-*benzyl*-n-*hexyl alcohol*, b.p. 155°/15 mm. (*allophanate*, m.p. 144°); octaldehyde gives β-*hexyldecyl*, b.p. 177°/15 mm. (*allophanate*, m.p. 90°), and β-*benzyl*-n-*octyl alcohol*, b.p. 176°/15 mm. (*allophanate*, m.p. 124°); nonaldehyde gives β-*heptylundecyl*, b.p. 198°/15 mm. (*allophanate*, m.p. 80°), and β-*benzyl*-n-*nonyl alcohol*, b.p. 186°/15 mm. (*allophanate*, m.p. 115°); decaldehyde gives β-*octyldodecyl*, b.p. 215°/15 mm. (*allophanate*, m.p. 69°), and β-*benzyl*-n-*decyl alcohol*, b.p. 200°/15 mm. (*allophanate*, m.p. 117°); undecaldehyde gives β-*nonyltridecyl*, b.p. 235°/15 mm. (*allophanate*, m.p. 80°), and β-*benzyl*-n-*undecyl alcohol*, b.p. 207°/14 mm. (*allophanate*, m.p. 97°); dodecaldehyde gives β-*decyltetradecyl*, b.p. 250°/15 mm. (*allophanate*, m.p. 72°), and β-*benzyl*-n-*dodecyl alcohol*, b.p. 221°/15 mm. (*allophanate*, m.p. 109°); Δ$^{\alpha}$-undecenaldehyde gives β-*nonenetridecenyl*, b.p. 235°/15 mm. (*allophanate*, m.p. 75°), and β-*benzyl*-n-*undecenyl alcohol*, b.p. 211°/15 mm. (*allophanate*, m.p. 109°). J. L. D.

Addition of hypochlorous acid to phenylbutadiene and isomerisation of the corresponding epoxide to phenylcrotonaldehyde. D. Abragam and Y. Deux (Compt. rend., 1937, **205**, 285—286; cf. this vol., 225).—Phenylbutadiene (I), obtained from CHPh:CH·CHO and MgMeBr or CHMe:CH·CHO and MgPhBr, with cold aq. HOCl affords the chlorohydrin of phenylvinyl glycol, converted by KOH in Et_2O into the epoxide (II) (cf. A., 1930, 769), the structure of which is indicated by its reduction (H_2–Raney Ni) to α-phenyl-*n*-butyl alcohol, dehydrogenated (Cu at 280—300°) to $COPhPr^{\alpha}$. (II) at 250° and 16 mm. affords CHMe:CPh·CHO (cf. this vol., 246). J. L. D.

Action of magnesium ethyl bromide and of magnesium bromide on ββ-dimethylstyrene oxide. M. Poctivas and (Mlle.) B. Tchoubar (Compt. rend., 1937, **205**, 287—288; cf. A., 1932, 392; 1921, i, 788).—ββ-Dimethylstyrene oxide (I) with $MgBr_2$,Et_2O at <100° affords mainly (90%) $CPhMe_2$·CHO (II) and a little (10%) β-phenylbutan-γ-one (III). Interaction of (I) with MgEtBr affords a mixture of approx. equal amounts of α-phenyl-ββ-dimethyl-*n*-butyl alcohol and γ-phenyl-β-methyl-*n*-pentan-β-ol, oxidised (CrO_3) to PhCHO, BzOH, and COPhEt but no COPhMe, which is obtained by oxidising a mixture of the alcohols obtained synthetically from (II) and (III) with MgEtBr. Thus, the rate of isomerisation of (I) by $MgBr_2$ is much slower than its rate of reaction with MgEtBr. J. L. D.

Stereochemical structure. VIII. Stereochemical relationship of the α- and the β-forms of substituted hydrobenzoins. (a) Ethylhydrobenzoin (α-form). R. Roger (J.C.S., 1937, 1048—1051).—Attempted reduction of the stereoisomeric compounds of formula OH·CHPh·CPhEt·OH to CH_2Ph·CPhEt·OH was not successful; mild agents were without action, and HI caused dehydration, as did HNO_3 in the attempt to obtain COPh·CPhEt·OH. Other oxidising agents are unsatisfactory, but when the glycol is dissolved in MgEtI and PhCHO in C_6H_6 is added, the *r*-ethylhydrobenzoin (α-form) gives *r*-ethylbenzoin, and *D*(+)-ethylhydrobenzoin (α-form)

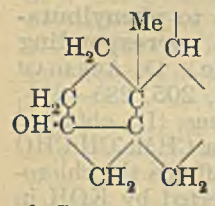
(I) gives (+)-*ethylbenzoin* (II), m.p. 71°, $[\alpha]_{5461}^{20}$ +252·7° in EtOH, −182·4° in CS_2, $[\alpha]_{5791}^{20}$ −155·5° in CS_2 (cf. this vol., 104). If no inversion of the mandelyl complex occurs during the conversion of *D*(−)-mandelic acid (III) into (I), or during the dissolution of (I) in MgEtI, (I) has the annexed structure. Although (II) is the optical antipode of the (−)-ethylbenzoin from (+)-α-hydroxy-α-phenyl-*n*-butyric acid (IV) (*loc. cit.*), it is not possible to connect the configurations of (III) and (IV).



E. W. W.

Manufacture of *tert.*-alkylaryloxyalkanols.—See B., 1937, 760.

Sterol group. XXXIII. Constitution of the isomeric ethers of cholesterol. J. H. Benyon, I. M. Heilbron, and F. S. Spring (J.C.S., 1937, 1459—1461; cf. this vol., 190, 344).—Cholesteryl *p*-toluenesulphonate and KOAc in 50% $COMe_2$ give *i*-cholesteryl acetate and thence *i*-cholesterol (I) in good yield; this with HCl–AcOH gives cholesteryl chloride, with Br–Et_2O gives tribromocholestane, and with K and MeI in C_6H_6 gives cholesterol Me "*iso*"-ether. The relation of the *d*-ethers to (I) is thus proved. *X*-Ray examination proves the OH of (I) to be in position 3 and (I) is considered to contain the grouping shown.



R. S. C.

Molecular rearrangements in the sterols. II. Constitution of the isomeric ethers of cholesterol. E. G. Ford and E. S. Wallis (J. Amer. Chem. Soc., 1937, **59**, 1415—1416; cf. this vol., 99).—The so-called *cis*-cholesteryl ethers are *i*-cholesteryl ethers, probably formed by mol. rearrangement, since the K salt of *i*-cholesterol with MeI in C_6H_6 gives a Me ether, m.p. 78—78·5°, $[\alpha]_D^{22}$ +54° in $CHCl_3$, identical with "*cis*-cholesteryl Me ether." *epi*Cholesterol gives a *Me ether*, m.p. 88—89°, $[\alpha]_D^{20}$ −46·3° in $CHCl_3$.

R. S. C.

Cholesterol derivatives. Y. Urushibara, T. Ando, H. Araki, and A. Ozawa (Bull. Chem. Soc. Japan, 1937, **12**, 353—355).—Cholestenone with MgPhBr and α-$C_{10}H_7$·MgBr yields respectively 3-*phenyl*-, m.p. 174—175°, $[\alpha]_D^{29}$ −133° in $CHCl_3$, and 3-α-*naphthyl-cholestadiene*, m.p. 131—133°, $[\alpha]_D^{29}$ −49·7° in $CHCl_3$ (*picrate*, m.p. 161—163°). The intermediate OH-compound, unlike 7-hydroxy-7-phenylcholesterol (cf. Weinhouse and Kharasch, this vol., 192), could not be isolated. All m.p. are corr.

F. R. G.

***X*-Ray investigations of additive compounds of cholesterol.** F. Klötzer (Z. Krist., 1937, **95**, 338—367).—Unlike ergosterol, cholesterol (I) forms loose additive compounds with EtOH, MeOH, C_5H_5N, C_6H_6, and H_2O, which give distinctive powder diagrams. The monohydrate of (I) could be obtained in three forms when recryst. from EtOH–Et_2O solution. The normal form had *a* 12·82, *c* 12·25 A., 16 mols. in unit cell. The structure of the other forms is discussed. From MeOH–Et_2O solution the *compound*, $C_{27}H_{45}$·OH,0·5MeOH, was obtained as triclinic crystals (*a* 6·24, *c* 12·27 A., 4 mols. in unit cell; space-group C_1 or C_i). Single crystals of (I) obtained from a melt had *a* 10·5, *c* 14·2 A.; 8 mols. in unit cell; space-group C_1 or C_i. Contrary to the results of Bernal, who may have examined an additive compound (cf. A., 1932, 327, 658), the lattice of (I) is similar to that of ergosterol.

H. J. E.

Activation of cholesterol and cholesterilene.—See A., III, 364.

Sterols. XVI. Lanasterol and agnosterol. R. E. Marker, E. L. Wittle, and L. W. Mixon (J. Amer. Chem. Soc., 1937, **59**, 1368—1373; cf. this vol., 424).—Lanosteryl acetate is reduced (PtO_2) to *α-dihydro*-, m.p. 119°, isomerised by HCl in $CHCl_3$ to *β-dihydro-lanosteryl acetate*, m.p. 149°. These two when hydrolysed give the *dihydrolanosterols* (α-, m.p. 148°, β-, m.p. 162°), oxidised by Cu (250° and 2 mm. pressure) to the *-stenones* (α-, m.p. 122°, β-, m.p. 149°; 2 : 4-*dinitrophenylhydrazones*, α-, m.p. 213°, β-, m.p. 230°); the ketones when reduced (Na + $Pr^{\beta}OH$) yield the original sterols, which are therefore not epimeric. Lanosterol (I) and α-dihydrolanosterol (II) are dehydrogenated by Pt-black to the corresponding ketones (with no naphthol or PhOH), indicating the presence of an angular Me group. The acetates of (I) and (II) on vigorous oxidation (CrO_3) yield the same *acid*, $C_{25}H_{46}O_2$, m.p. 81° (*Me* ester, m.p. 67°), whilst that of (II) on mild oxidation (CrO_3) affords a mixture of α-, m.p. 150°, and β- (also produced on boiling α- with Ac_2O) *-ketodihydrolanosteryl acetate*, m.p. 152°, both hydrolysed to the same *ketodihydrolanosterol*, m.p. 134°, which with Ac_2O yields the β-acetate, and is reduced by Na + $Pr^{\beta}OH$ to a *hydroxydihydrolanosterol*, m.p. 165°. Ac_2O converts this into a mixture of its *acetate*, m.p. 130°, and (removing one OH group) *dihydroagnosteryl acetate*, m.p. 169°, identical with that prepared from natural agnosterol.

A. Li.

Subsidiary sterols from yeast. V. Zymosterol and ascosterol. H. Wieland and Y. Kanaoka [with, in part, W. E. Bachmann] (Annalen, 1937, **530**, 146—151; cf. this vol., 243).—Zymosterol (improved isolation), m.p. 126° (cloudy), 138° (clear) [*formate*, m.p. 75—76°; acetate, m.p. 105—106°; *benzoate dibromide*, m.p. 156—162° (decomp.); acetate dibromide, m.p. 176° (decomp.)], is shown to be $C_{27}H_{43}$·OH; the H_2-derivative, m.p. 120—121°, $[\alpha]_D^{21}$ +28·7° in $CHCl_3$, with BzO_2H gives an *oxide*, m.p. 120° (decomp.). Ascosterol, m.p. 146—147°, $[\alpha]_D^{23}$ +45·1° in $CHCl_3$ (benzoate, m.p. 135—136°, $[\alpha]_D^{21}$ +41·1°; *acetate*, m.p. 152—153°, $[\alpha]_D^{22}$ +21·5° in $CHCl_3$), is shown to be $C_{27}H_{43}$·OH; it gives a H_2-derivative, m.p. 130—131° (*acetate*, m.p. 106—107°), which gives Liebermann's reaction and is yellow in $C(NO_2)_4$. Both these sterols thus contain two ethylenic linkings.

R. S. C.

Preparation of a homologue of *epi*coprosterol in the ergosterol series. F. Wetter and K. Dimroth (Ber., 1937, **70**, [*B*], 1665—1672).—Ergosteryl acetate–maleic anhydride is converted by gentle hydrolysis with NaOEt–EtOH at 50—60° into *ergosterol–maleic acid*, m.p. 120° (decomp.), $[\alpha]_D^{20}$ −46·3° in MeOH (*Me_2* ester, m.p. 72°), which when

heated rapidly to 120° and then slowly to 180° gives ergosterol–maleic anhydride, m.p. 202° (yield 80%), oxidised to *ergosterone–maleic acid*, m.p. 188°, which passes into ergoster-5-one–maleic anhydride. This at 220°/0·0005 mm. affords ergosterone (I), m.p. 132°, $[\alpha]_D^{20}$ −0·52° in $CHCl_3$ (cf. Oppenauer, this vol., 250) (*semicarbazone*, m.p. 251°), and an αβ-unsaturated *ketone*, m.p. 183°. The mother-liquors from (I) yield iso*ergosterone* (II), $C_{28}H_{42}O$, m.p. 110° (*semicarbazone*, m.p. 236°), which has a very marked tendency towards enolisation. (I) is isomerised to (II) by boiling HCl–MeOH. Hydrogenation of (I) proceeds similarly to that of cholestenone. In presence of Pd-black and EtOAc it absorbs 2 H_2 with formation of a non-cryst. product (II) (*semicarbazone*, $C_{29}H_{49}ON_3$, m.p. 238—239°), further hydrogenated (Pt-black in EtOAc) to a *compound*, $C_{28}H_{48}O$, m.p. 162° (*acetate*, m.p. 80°). Hydrogenation (PtO_2 in AcOH) of (II) followed by hydrolysis of the product and treatment of it with digitonin gives a ppt. from which *trans*-ergostanol is isolated, leaving a non-precipitable *substance*, $C_{28}H_{50}O$, m.p. 139—140°, $[\alpha]_D^{21}$ +24·8° in $CHCl_3$ (*acetate*, m.p. 99°), believed to be a homologue of *epi*coprosterol. H. W.

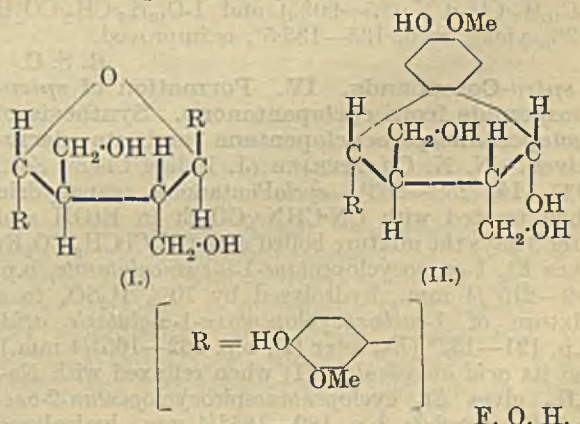
Introduction of double linkings into bile acids and sterols. II. Production of cholestadienol. E. Dane and Y. Wang (Z. physiol. Chem., 1937, **248**, I—III; cf. this vol., 61).—The dibromide (I) of cholesterol (II) when boiled with C_5H_5N yields chiefly (II), but when $AgNO_3$ is added at room temp. to (I) in C_5H_5N impure *cholestadienol* (probably $\Delta^{4:6}$), m.p. 115—121° (*digitonide*, m.p. 207—224°; *dinitrobenzoate*, m.p. 194°), is obtained. W. McC.

α- and β-Œstradiol. A. Butenandt and C. Goergens (Z. physiol. Chem., 1937, **248**, 129—141; cf. Whitman *et al.*, this vol., 289).—Fractional crystallisation from EtOH of the 95 : 5 mixture of œstradiols obtained by reduction of œstrone with Ni–H_2 yields α-œstradiol (I), m.p. 175—176°, $[\alpha]_D^{18}$ +78° in EtOH [3-*Me ether*, m.p. 97—98°; 3-*benzoate* (II), m.p. 192—193°; 3 : 17-*dibenzoate*, m.p. 168—169°; 3 : 17-*diacetate*, m.p. 125—126°], and β-œstradiol (III), m.p. 216—218°, $[\alpha]_D^{18}$ +56·7° in EtOH [3-*Me ether*, m.p. 109—110°, 3-*benzoate* (IV), m.p. 150—151°, 3 : 17-diacetate, m.p. 139—140°]. (II) and (IV) in AcOH with CrO_3 at approx. 20° give œstrone benzoate. (I) is pptd. by digitonin, but (III) is not. 1 g. of (I) contains 20 × 10^6, 1 g. of (III) 0·6—0·8 × 10^6, and 1 g. of (II) 13—15 × 10^6 mouse units. (I), which probably has the same configuration as has natural testosterone, differs from (III) only in the configuration of the groups attached to $C_{(17)}$. W. McC.

Steroids and related compounds. I. Isomeric cholestenediols. V. A. Petrow (J.C.S., 1937, 1077—1081).—Attempts to prepare $\Delta^{4:6}$-cholestadien-3-ol (I) from Δ^4-cholestene-3 : 6-diol, or by dehalogenation of cholesteryl ester dibromides, are unsuccessful. Cholestane-3 : 5 : 6-triol diacetate (improved prep.) with H_2SO_4 in Ac_2O, followed by BzCl in C_5H_5N, gives 3 : 6-*dibenzoyloxy*-Δ^4-*cholestene*, m.p. 163·5—164·5—182°, which is stable up to about 290°/5 mm., and then resinifies. The diacetate distils unchanged. Cholesteryl benzoate with H_2O_2–AcOH gives 5-*hydroxy*-3-*benzoyloxy*-6-*acetoxycholestane*, m.p. 162·5—163·5°, $[\alpha]_D$ −23·8° (all rotations in $CHCl_3$), which with H_2SO_4 in AcOH yields 3-*benzoyloxy*-6-*acetoxy*-Δ^4-*cholestene*, m.p. 138·5°; this decomposes above 280°/5 mm., but evolves BzOH, and does not give (I). Cholesteryl Me ether with H_2O_2–AcOH forms a product hydrolysed to 5 : 6-*dihydroxy*-3-*methoxycholestane*, m.p. 154°, $[\alpha]_D$ −4·8° (6-*benzoyloxy*-compound, m.p. 96·5—97·5°, $[\alpha]_D$ −33·1°), of which the 6-*OAc*-compound, m.p. 118·5—119·5°, $[\alpha]_D$ −30·1°, is dehydrated by H_2SO_4 in Ac_2O to 6-*acetoxy*-3-*methoxy*-Δ^4-*cholestene*, m.p. 121·5—122·5°, $[\alpha]_D$ +166·6°; this again distils unchanged. Cholesteryl acetate dibromide is dehalogenated by KOAc in abs. EtOH to cholesteryl acetate and cis-4-*hydroxy*-3-*acetoxy*-Δ^5-*cholestene*, m.p. 176—177°, $[\alpha]_D$ −84·4° [acetylated to *cis*-3 : 4-diacetoxy-Δ^5-cholestene (II), and hydrolysed to *cis*-Δ^5-cholestene-3 : 4-diol (III)], and by $AgNO_3$–C_5H_5N to a product acetylated to (II). "Monobromocholesteryl bromide" is 5 : 5′-*dibromo*-3 : 3′-*dibenzoyloxy*-6 : 6′-*dicholestanyl*, which is dehalogenated ($AgNO_3$–C_5H_5N) to (III). Cholesteryl benzoate dibromide with KOAc–EtOH or $AgNO_3$–C_5H_5N gives (II). E. W. W.

Sterol ("sapogenol") from Shoyu oil. I. T. Kazuno (J. Biochem. Japan, 1937, **25**, 251—259).—The unsaponifiable fraction of the oil yields *sapogenol*, $C_{30}H_{50}O_3$, m.p. 258°, $[\alpha]_D^{21}$ +93·06° in $CHCl_3$ [*triacetate* (I), m.p. 178—179°; *tribenzoate*, m.p. 184—186°; *bromotriacetate* (II), decomp. 194°, which with AcOH–Zn gives an *isomeride* (III), m.p. 204°; *Br*-derivative, decomp. 310°, which on acetylation gives only (III) and is produced by hydrolysis of (II) or (III)]. Oxidation (CrO_3) of (I) under varying conditions yields a *product*, $C_{30}H_{45}O_4Ac_3$, m.p. 265—266°, a *diketone*, $C_{29}H_{44}O_2$, m.p. 250—251° (*dioxime*, m.p. 265—267°) [reduced (Clemmensen) to $C_{29}H_{48}$, m.p. 160°], and a monocarboxylic *acid*, $C_{30}H_{44}O_4$, m.p. 213° (*Me* ester, m.p. 174°). F. O. H.

Configuration of olivil and *iso*olivil. B. L. Vanzetti and P. Dreyfuss (Atti R. Accad. Lincei, 1937, [vi], **25**, 133—136).—Synthesis and properties of olivil (I) and *iso*olivil (II) (cf. A., 1934, 1099; 1936, 842) and analogy with similar compounds indicate the spatial configurations shown.



F. O. H.

Preparation and properties of *N*-chloro-derivatives of *p*-sulphonamidobenzoic acid. I. Zilberg

(Prom. Org. Chim., 1937, **3**, 26—29).—Chlorination of aq. *p*-$CO_2Na{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (I) at 55—60° yields the *N*-Cl- (II) and -Cl_2-derivative (III) of (I), the proportion of (III) increasing with time. The (III) content of the ppt. obtained by adding HCl or AcOH to the reaction mixture is inversely $\propto$ [H·], and the same effect is obtained by adding acid to a solution of (II) in aq. Na_2CO_3. The reaction 2(II) $\rightarrow$ (III) + (I) is postulated. R. T.

Some benzoylthiobenzamides. L. Musajo and V. Amoruso (Gazzetta, 1937, **67**, 301—306).—Arguments in favour of the *N*-Bz structure for these compounds are reviewed. Thiobenzamide suspended in aq. $NaHCO_3$ gives with BzCl a red product, which on attempted purification gives Bz_2S_2 (?), and may contain an unstable *S*-benzoyl*iso*thiobenzamide. Slightly modified methods for the prep. of *N*-methylthiobenzanilide, and of *S*-methyl- and *S*-benzyl-*iso*thiobenzanilide, are described; SS′-*ethylenebis*iso-*thiobenzanilide* has m.p. 75—76°. E. W. W.

Thio-acids. (Mlle.) F. Bloch (Compt. rend., 1937, **204**, 1342—1344; cf. A., 1903, i, 42).—MgPhBr with CS_2 in Et_2O containing I affords phenylcarbithionic acid, converted ($SOCl_2$) into the chloride (cf. A., 1921, i, 25), which is hydrolysed to thiobenzoic acid (I), an indistillable oil, the *Na* salt, m.p. 130°, of which with I gives Bz_2S_2 [also obtained from BzSH and I (cf. A., 1903, i, 418)], which indicates that a tautomeric form of (I) suffers oxidation. J. L. D.

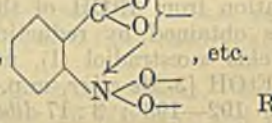
Manufacture of di- and tri-iodo-derivatives of acylamino-acids and their salts.—See B., 1937, 841.

Effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride. Y. Urushibara and M. Takebayashi (Bull. Chem. Soc. Japan, 1937, **12**, 356—358).—The lowering by O_2 of the rate of reaction of Br with CHPh:CH·CO_2H in the dark (cf. Bauer and Daniels, A., 1934, 1216) has been studied quantitatively. No peroxide formation could be detected. F. R. G.

1-Naphthylacetic acid. S. C. J. Olivier and J. Wit (Rec. trav. chim., 1937, **56**, 853—857).—The prep. of 1-$C_{10}H_7{\cdot}CH_2Br$ (32%) and thence of 1-$C_{10}H_7{\cdot}CH_2{\cdot}CN$ (85—90%) and 1-$C_{10}H_7{\cdot}CH_2{\cdot}CO_2H$ (92% yield), m.p. 135—135·5°, is improved. R. S. C.

***spiro*-Compounds. IV. Formation of *spiro*-compounds from *cyclo*pentanone. Synthesis of *cyclo*pentane*spirocyclo*pentane and its derivatives.** N. N. Chatterjee (J. Indian Chem. Soc., 1937, **14**, 259—263).—*cyclo*Pentanone cyanohydrin when treated with CN·CHNa·CO_2Et in EtOH and after 3 days the mixture boiled with $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ gives *Et*$_2$ 1-*cyano*cyclo*pentane*-1-α-*cyanoglutarate*, b.p. 208—215°/4 mm., hydrolysed by 70% H_2SO_4 to a mixture of 1-*carboxy*cyclo*pentane*-1-α-*glutaric acid*, m.p. 131—132° [*Et*$_3$ ester (I), b.p. 162—165°/4 mm.], and its *acid anhydride*. (I) when refluxed with Na–C_6H_6 gives *Et*$_2$ cyclo*pentane*spirocyclo*pentan*-2-*one*-3 : 5-*dicarboxylate*, b.p. 180—185°/4 mm., hydrolysed by 20% H_2SO_4 to cyclo*pentane*spirocyclo*pentan*-2-*one*-5-*carboxylic acid* (II), m.p. 67° (*semicarbazone*, m.p. 232°; *Et* ester, b.p. 131—132°/4 mm.), reduced (Clemmensen) to an uncrystallisable acid, the Ca salt of which when heated with CaO gives cyclo-*pentane*spirocyclo*pentane*, b.p. 60°/12 mm., in poor yield. This slowly decolorises $KMnO_4$ and is slightly less stable than the *cyclo*hexane analogue. (II) when oxidised with conc. HNO_3 and then distilled gives *cyclo*pentanecarboxylic acid. H. G. M.

Bromoalkyl derivatives of salicylic acid. E. Moness and W. G. Christiansen (J. Amer. Pharm. Assoc., 1937, **26**, 618—620).—Attempts to prepare α-bromoacrylyl chloride from K α-bromoacrylate and SO_2Cl_2 or $POCl_3$, and αβ-dibromopropionylsalicylic acid from salicylic acid and αβ-dibromopropionyl chloride, yielded only resinous polymerisation products. Na salicylate with dibromopropene in $COMe_2$ gave *bromoallyl salicylate* (I), b.p. 125—130°/1—2 mm. [impure *Ac* derivative (II) prepared]. (I) and (II) are superior to aspirin in antipyretic activity, but approx. 3 times as toxic. F. O. H.

***Ortho*-effect. I. Influence of substituents in the *o*-position on the chemical characters of carboxylic acids and their derivatives.** J. F. J. Dippy, D. P. Evans, J. J. Gordon, R. H. Lewis, and H. B. Watson (J.C.S., 1937, 1421—1425).—The regularities and irregularities of the effect of *o*-substituents are discussed. The effect is held to be due partly to steric hindrance, partly to H bond formation or chelation between *o*-substituents if one is polar, and partly to other causes. Structures are postulated such as $C_6H_4\langle^{C(\cdot O)\ldots O}_{OH}$, intermediate between *o*-OH·$C_6H_4{\cdot}C(\cdot O)^-_2$ and *o*-O:$C_6H_4{:}\overset{-}{C}(\cdot O){\cdot}OH$, or $C_6H_4\langle^{C(\cdot O)-}_{CH_2\cdot H}\rangle O$,  , etc. R. S. C.

Benzylidenepyruvic acids. III. L. Musajo (Gazzetta, 1937, **67**, 307—312).—Amorphous benzylidenepyruvic acid (II), from PhCHO (II) and $AcCO_2H$ (III) (cf. A., 1933, 64), is a polymeride, $(C_{10}H_8O_3)_n$; from b.p. in AcOH, $n = 1$, and from f.p., $n = 2$ in AcOH or in PhOH, 3 in $PhNO_2$. The Br-free acid, m.p. 279° (IV), obtained as a by-product from Br and (I) (cf. A., 1931, 221), best prepared in Et_2O, is converted by Br in AcOH or EtOH into a red or a yellow *substance*, respectively, both m.p. 210°, and both reconverted into (IV) when dissolved in alkali and acidified. (I) and (II) with NH_3 in EtOH yield 2-*phenyl*-4 : 5-*diketotetrahydropyrrole* (?), m.p. 215° (decomp.), and a *substance*, m.p. 230° (decomp.). E. W. W.

Syntheses in the carane group. I. Synthesis of 2 : 2-dimethyl*cyclo*heptane-1 : 3-dicarboxylic acid. P. C. Guha and D. K. Sankaran (Ber., 1937, **70**, [*B*], 1683—1688).—Condensation of Br·$[CH_2]_4{\cdot}$Br with αα′-dicyano-ββ-dimethylglutarimide and NaOMe in boiling MeOH gives a poor yield of 1 : 3-*dicyano*-2 : 2-*dimethyl*cyclo*heptane*-1 : 3-*dicarboxylimide* (I), m.p. 298°, the constitution of which

follows from the formation of an *Ag* salt and hydrolysis by H_2SO_4 to suberic acid. Boiling dil. alkali transforms (I) into 1 : 3-*dicarbamyl*-2 : 2-*dimethyl*cyclo*heptane*-1 : 3-*dicarboxylic acid* (II), m.p. 256°, and 1 : 3-*dicyano*-2 : 2-*dimethyl*cyclo*heptane*-1 : 3-*dicarboxylic acid* (III), m.p. 165—166°. Further treatment with alkali of (II) or (III) leads to 2 : 2-*dimethyl*cyclo*heptane*-1 : 1 : 3 : 3-*tetracarboxylic acid*, m.p. 173—174° (*Et*$_4$ ester, b.p. 110—115°/3 mm.), decarboxylated at 200—210° to 2 : 2-*dimethyl*cyclo*heptane*-1 : 3-*dicarboxylic acid*, m.p. 127—128° after softening at 112° (*Et*$_2$ ester, b.p. 138—140°/7 mm.). H. W.

Syntheses in the carane group. II. New synthesis of caronic and homocaronic acid. P. C. Guha and D. K. Sankaran (Ber., 1937, **70**, [*B*], 1688—1691).—CMe_2N_2 (improved prep. from $CMe_2{:}N{\cdot}NH_2$) condenses with Et_2 fumarate or maleate at −18° to the pyrazoline derivative, $N{\cdot}CH(CO_2Et)>N{-}CMe_2>CH{\cdot}CO_2Et$, which loses N_2 at 200—240° with production of *Et*$_2$ trans-*caronate*, b.p. 240—241°, hydrolysed by KOH–H_2O to *trans*-caronic (1 : 1-dimethyl*cyclo*propane-2 : 3-dicarboxylic) acid (I), m.p. 213°. (I) is isomerised by Ac_2O at 220° to *cis*-caronic acid, m.p. 176°. Similarly CMe_2N_2 and Et_2 glutaconate give the *pyrazoline* compound, $N{\cdot}CH(CO_2Et)>N{-}CMe_2>CH{\cdot}CH_2{\cdot}CO_2Et$, m.p. 152—153°, which gives successively *Et*$_2$ *homocaronate*, b.p. 253°, and trans-*homocaronic* [2 : 2-*dimethyl*cyclo*propane*-1-*carboxylic*-3-*acetic*] *acid*, m.p. 191—192°, isomerised to the *cis*-acid, m.p. 135—136°. H. W.

αα′-Dicyclohexylsuccinic acids. (Miss) A. R. Murray and T. W. J. Taylor (J.C.S., 1937, 1450—1453).—Many attempts to prepare αα′-di*cyclo*hexylsuccinic and αβ-di*cyclo*hexylpropionic acids by standard methods failed. Et H *cyclo*hexylmalonate, m.p. 44—45°, best prepared from the Et_2 ester by KOH, boils at 163°/15 mm. with partial decomp. to $C_6H_{11}{\cdot}CH_2{\cdot}CO_2Et$; electrolysis of the K salt gives *Et*$_2$ (?) meso-, m.p. 120°, and (?) dl-αα′-*dicyclohexylsuccinate*, m.p. 60°. Hydrolysis of the former gives the (?) dl-, m.p. 147° (*anhydride*, m.p. 62·5°, gives the *semianilide*, m.p. 225°), and (?) meso-*acid*, m.p. 225°, +2H_2O; hydrolysis of the second ester gives the anhydride and the second acid. R. S. C.

Analogues of damascenine. I. Synthesis of methyl esters of dimethoxy-*N*-methylanthranilic acids. V. M. Rodionov and A. M. Fedorova (Bull. Acad. Sci. U.R.S.S., 1937, 501—509).—Hemipinimide is converted by the Hoffmann reaction into 3 : 4- (I) and 5 : 6-dimethoxyanthranilic acid (II). The *Me* ester, m.p. 68—70°, of (I) with MeI in MeOH (110°; 5 hr.), or with *p*-$C_6H_4Me{\cdot}SO_3Me$ (III) (100°; 90 min.), affords *Me* 3 : 4-*dimethoxy*-N-*methylanthranilate*, m.p. 110—112°. The N-*benzylidene* derivative, m.p. 148—150°, of (II) with MeOH in H_2SO_4 yields the *Me* ester, m.p. 49—51° (*hydrochloride*, m.p. 185—186°), of (II), which with (III) affords *Me* 5 : 6-*dimethoxy*-N-*methylanthranilate*, m.p. 61—62° (*hydrochloride*, m.p. 171—172°). R. T.

β-Arylglutaconic acids. III. Condensations with phenolic ethers. G. R. Gogte (Proc. Indian Acad. Sci., 1937, **5**, A, 535—542; cf. A., 1935, 1366).—Acetonedicarboxylic acid, from citric acid and conc. H_2SO_4, diluted with H_2O reacts with PhOH at <0° to give coumarin-4-acetic acid (I), m.p. 184° [Limaye's product (cf. A., 1927, 974) when recrystallised has m.p. 184°], and ββ-4 : 4′-*dihydroxydiphenylglutaric acid* (II), m.p. 235° (decomp.) [*Et*$_2$ ester, m.p. 158—159°; *Me*$_2$ ester, m.p. 189°; *Ac*$_2$ derivative, m.p. 188—189° (decomp.) (*Et*$_2$ ester, m.p. 135°); *Me*$_2$ *ether* (III), m.p. 158°, which when heated affords the *anhydride*, m.p. 104—105°, converted by heating with NH_2Ph into the *semianilide*, m.p. 187°; *anhydride*, m.p. 204—205°], different from that obtained by Dixit and Gokhale (A., 1935, 353), as it gives no (I) with conc. H_2SO_4 and when heated gives no anhydride but loses CO_2. β-*p*-Tolylglutaconic acid with PhOH and H_2SO_4 gives no analogue of (II), as the glutaconic acid is decomposed by H_2SO_4. β-*p*-Anisylglutaconic acid (IV) with PhOMe and 75% aq. H_2SO_4 at room temp. affords (III), which with warm 80% H_2SO_4 is converted into (IV). β-*o*-Anisylglutaconic acid does not condense with PhOMe. Hot dil. acids have no effect on (III), but when heated with CaO it affords *as*-di-*p*-anisylethylene, which establishes the structure of (II). A $CO(CH_2{\cdot}CO_2H)_2$–H_2SO_4 mixture with PhOMe at 0° affords (III). $CO(CH_2{\cdot}CO_2H)_2$ and PhOEt yield β-p-*phenetylglutaconic acid*, m.p. 170° (decomp.) [*hydroxyanhydride*, m.p. 178°; *semianilide*, m.p. 180° (decomp.)], which with PhOEt, or by ethylating (II), gives ββ-*di*-p-*phenetylglutaric acid*, m.p. 157—158° (*anhydride*, m.p. 119—120°), which when heated with CaO gives *as*-di-*p*-phenetylethylene. β-6-Methoxy-*m*-tolylglutaconic acid (V) or $CO(CH_2{\cdot}CO_2H)_2$ with *o*-$C_6H_4Me{\cdot}OMe$ in 80% H_2SO_4 at 0° affords ββ-*di*-(6-*methoxy*-m-*tolyl*)*glutaric acid*, m.p. 187° (*Ba* salt; *anhydride*, m.p. 156°; *semianilide*, m.p. 189°), converted by warm 80% H_2SO_4 into (V) (cf. A., 1932, 512) and by heating with CaO into as-*di*-(6-*methoxy*-m-*tolyl*)*ethylene*, m.p. 106°. β-6-*Ethoxy*-m-*tolylglutaconic acid*, m.p. 174° (decomp.) (*hydroxyanhydride*, m.p. 188°; *semianilide*, m.p. 173°), or $CO(CH_2{\cdot}CO_2H)_2$ with *o*-$C_6H_4Me{\cdot}OEt$ gives ββ-*di*-(6-*ethoxy*-m-*tolyl*)*glutaric acid*, m.p. 204° (decomp.) (*Ba* salt; *anhydride*, m.p. 104—105°; *semianilide*, m.p. 155—156°), converted when heated with CaO into as-*di*-(6-*ethoxy*-m-*tolyl*)*ethylene*, m.p. 95—96°. J. L. D.

Formation of dopa [*l*-3 : 4-dihydroxyphenylalanine] by exposure of tyrosine solutions to ultra-violet radiation. L. E. Arnow (J. Biol. Chem., 1937, **120**, 151—153).—Ultra-violet irradiation of tyrosine (I) solutions results in destruction of (I) and formation of *l*-3 : 4-dihydroxyphenylalanine, which is also destroyed by ultra-violet irradiation. J. L. C.

Thyroxine from quinol monomethyl ether and 3 : 4 : 5-tri-iodonitrobenzene. A. J. Savitzkĭ (Med. exp., Ukraine, 1934, No. 1, 39—49).—A modified synthesis is described. It is possible to avoid etherification and obtain α-amino-β-(3 : 5-di-iodo-4-4′-hydroxyphenoxyphenyl)propionic acid directly; this is then iodinated to thyroxine in good yield. Ch. Abs. (*r*)

Synthesis of compounds related to the sterols, bile acids, and œstrus-producing hormones.

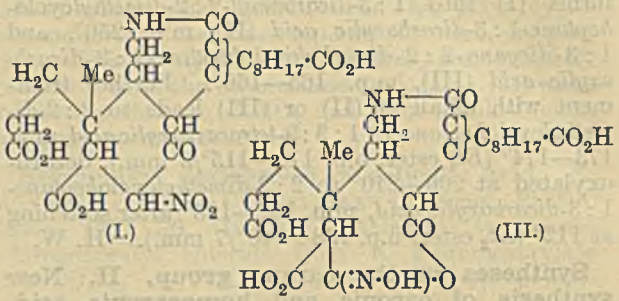
XI. A " diene-synthesis " of phenanthrene and hydrophenanthrene derivatives. A. COHEN and (in part) F. L. WARREN (J.C.S., 1937, 1315—1320).—An extension and correction of previous work (cf. A., 1936, 71). 1-Vinylnaphthalene and maleic anhydride in xylene give, not dihydro- (*loc. cit.*), but homogeneous 1 : 2 : 3 : 11-*tetrahydro-phenanthrene*-1 : 2-*dicarboxylic anhydride* (I), m.p. 186—189°, unsaturated to $KMnO_4$ or to BzO_2H, which is converted by boiling AcOH–HCl into saturated 1 : 2 : 3 : 4-*tetrahydrophenanthrene*-1 : 2-*dicarboxylic anhydride* (II), m.p. 220°. Either (I) with NaOH–Me_2SO_4 or (II) with MeOH–HCl gives the Me_2 ester (III), m.p. 105—106°, of the acid from (II). Dehydrogenation of (I) or (II) gives phenanthrene-1 : 2-dicarboxylic anhydride (IV). With MeMgI, (II) forms (III) and the *dimethyl-lactone* (V), m.p. 213·5—214·5° (*K* salt of the OH-acid), with a *keto-ester* (?), b.p. 185—190°/0·2 mm. With Na in EtOAc, followed by 5N-HCl at 100°, (II) gives only 1′ : 3′-diketo*cyclo*pentenophenanthrene. Hydrogenation of (I) gives a mixture containing (II). 6-Methoxy-1-vinylnaphthalene gives (cf. *loc. cit.*) 7-*methoxy*-1 : 2 : 3 : 11-*tetrahydrophenanthrene*-1 : 2-*dicarboxylic anhydride*, m.p. 171—175°, unsaturated to $KMnO_4$, dehydrogenated (Pt at 280°) to 7-methoxyphenanthrene-1 : 2-dicarboxylic anhydride (VI). 2-Vinylnaphthalene gives 2 : 3 : 4 : 12-*tetrahydrophenanthrene*-3 : 4-*dicarboxylic anhydride*, m.p. 170—180°, dehydrogenated to phenanthrene-3 : 4-dicarboxylic anhydride.

No œstrogenic activity is detected in (I), (II), (IV), (V), or (VI), or in the 3 : 4-H_2-derivatives of (VI) or of the corresponding 7-OH-compound. E. W. W.

3-Hydroxy-6-keto*allo*cholanic acid and synthesis of α-3 : 6-dihydroxy*allo*cholanic acid. G. SUGIYAMA (J. Biochem. Japan, 1937, **25**, 157—165).—3-Hydroxy-6-keto*allo*cholanic acid (Fernholz, A., 1935, 773), isolated from bile as the *Ac* derivative, m.p. 210—212°, is hydrogenated to α-3 : 6-*dihydroxy*-allo*cholanic acid* (I), m.p. 247°, $[\alpha]_D^{20}$ +9·36° in EtOH. The differentiation of (I) from Wieland's $(OH)_2$-acid (A., 1926, 723) is discussed. F. O. H.

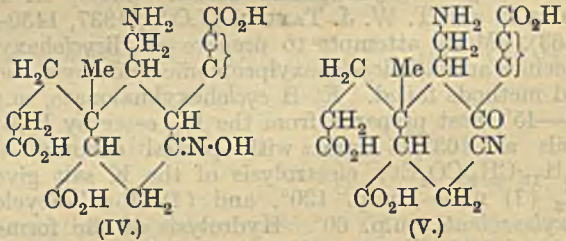
Toad bile. VI. Constitution of trihydroxy-*iso*sterocholenic acid. T. SHIMIZU and T. KAZUNO (J. Biochem. Japan, 1937, **25**, 245—249; cf. A., 1936, 469).—Me *iso*sterocholenate, converted into ozonide and treated successively with H_2O, N-NaOH, and dil. HCl, yields a bisnorcholanic acid, m.p. 208—210°; similar treatment of Me trihydroxy*iso*sterocholenate (I) affords bisnorcholic acid. Hence (I) has the double linking between $C_{(22)}$ and $C_{(23)}$ and the three OH at $C_{(3)}$, $C_{(7)}$, and $C_{(12)}$. F. O. H.

Bile acids. LII. (A) Constitution of the " β-acid " $C_{24}H_{34}O_{10}N_2$ and the compound $C_{24}H_{36}O_{11}N_2$ obtained from the " α-acid " by addition of water. (B) Determination of nitrogen according to Van Slyke. (C) Constitution of the " oxidation product," $C_{24}H_{36}O_9N_2$. M. SCHENK (Z. physiol. Chem., 1937, **248**, 174—182; cf. this vol., 246).—(A) The α-acid (I) is converted by short treatment with boiling 10% HCl into the " nitroamino-acid " (II), $C_{24}H_{36}O_{11}N_2$, and by 90% H_2SO_4 at 100° into the " β-acid " (III), which does not afford a product analogous to (II). (I) and (III) behave as tetrabasic acids. (I) in EtOH gives with $FeCl_3$ a reddish-yellow liquid from which a pale ppt. separates, whereas (III) under similar conditions gives an intense



brownish-red colour or ppt. The possibility that the change represents a simple tautomerisation is discounted by the apparent impossibility of transforming (III) into (I). (III) when boiled with acid and then rendered alkaline gives a solution which reduces cold Fehling's solution and Ag_2O–NH_3 probably owing to elimination of NH_2OH. (II) gives a pale brown colour with Fehling's solution. In (II) the NO_2–CO grouping appears more stable than in (I). (I), (II), and (III) give NH_3 when boiled with acids and evolve N_2 by Van Slyke's method.

(B) Results of Van Slyke determinations can be used only with great caution if at all in elucidating the constitution of the bile acids. (I) gives 92% and the analogously-constituted nitrobilianic acid only 55% of the calc. amount of N_2. Bilianic acid does not yield N_2, but its oxime-lactam and dioxime evolve large amounts of gas which may not be exclusively N_2. The acid (IV) gives very high N vals.; it appears



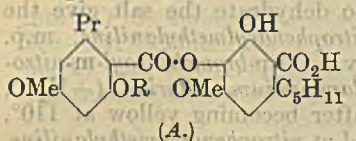
probable that the " by-product B " obtained by the action of 90% H_2SO_4 on (IV) (*loc. cit.*) is unchanged (IV).

(C) The " oxidation product," obtained from (IV) and alkaline $KMnO_4$, after prolonged boiling with HCl does not reduce Fehling's solution or Ag_2O–NH_3 after addition of alkali. NH_3 is formed; it is probably (V), although the presence of CO could not be established by oximation. H. W.

β-Hyodeoxycholic acid from pig's bile.—See A., III, 377.

Lichen substances. LXXXIII. New depside, bonic acid; synthesis of bonic acid and of homosekikaic acid. Y. ASAHINA and T. KUSAKA (Ber., 1937, **70**, [*B*], 1815—1821).—Percolation of the thalli of *Ramalina boninensis*, Y. Asahina, with Et_2O and treatment of the dried extract with C_6H_6 gives *d*-usnic acid and *bonic acid* (I), $C_{25}H_{32}O_8$, m.p. 134·5° [*Me* ester (II), m.p. 86°], converted by excess of CH_2N_2 in $COMe_2$ into Me ramalinolate Me_3 ether, m.p. 74—

75°. Hydrolysis of (I) by conc. H_2SO_4 at 0° affords 2 : 3-*dihydroxy*-4-*methoxy*-6-n-*amylbenzoic acid* (III), m.p. 143—144°, and divaricatic acid Me ether, m.p. 64°, whilst the latter substance and *Me* 2 : 3-*dihydroxy*-4-*methoxy*-6-n-*amylbenzoate* (IV), m.p. 74°, are obtained similarly from (II). 3-Hydroxy-2 : 4-dimethoxy-6-*n*-amylbenzaldehyde is converted into the corresponding *anil*, which is demethylated by NH_2Ph,HI to 2 : 3-*dihydroxy*-4-*methoxy*-6-n-*amylbenzylideneaniline*, m.p. 101°; this is hydrolysed to 2 : 3-*dihydroxy*-4-*methoxy*-6-n-*amylbenzaldehyde* ($+1H_2O$) (V), m.p. 68—69°, which is treated with $ClCO_2Et$ in C_5H_5N and then oxidised by $KMnO_4$ in $COMe_2$ to 4-*methoxy*-2 : 3-*dicarbethoxy*-6-n-*amylbenzoic acid*, m.p. 101°; this is transformed by 2N-NH_3 at 20° into (III), whereas the corresponding *Me* ester, m.p. 43—44°, is converted by cautious treatment with KOH at 18° into (IV). (V) and divaricatyl chloride Me ether in C_5H_5N at room temp. give *bonaldehyde*, m.p. 105—106°, converted by successive action of $ClCO_2Et$ in C_5H_5N and $KMnO_4$ in $COMe_2$ at 40—50° into *carbethoxybonic acid*, m.p. 126°, hydrolysed to (I), which is therefore *A* (R = Me).

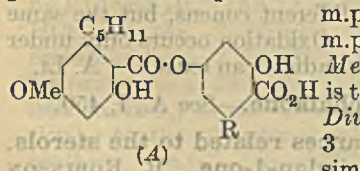


(*A*.)

Carbethoxydivaricatyl chloride and (V) in Et_2O–C_5H_5N give non-cryst. *carbethoxyhomosekikaldehyde* (*hydrazone*, m.p. 186—187°), transformed by $ClCO_2Et$ followed by oxidation into *dicarbethoxyhomosekikaic acid*, m.p. 101°, whence homosekikaic acid, m.p. 133—134° (Me ester, m.p. 106°), which is therefore *A* (R = H). H. W.

Lichen substances. LXXXIV. Occurrence of homosekikaic acid in *Cladoniæa*. Y. Asahina and T. Kusaka [with, in part, T. Sasaki] (Ber., 1937, 70, [*B*], 1821—1823).—Homosekikaic acid (I) is obtained from Japanese *C. subpityrea*, Sandst., but not from the European lichen. With fumarprotocetraric acid (I) is isolated from *C. pityrea*, Flk., *f. phyllophora*, Mudd. H. W.

Lichen substances. LXXXV. Synthesis of perlatolic and imbricaric acid. Y. Asahina and I. Yosioka (Ber., 1937, 70, [*B*], 1823—1826).—4-*Methoxy*-2-*carbethoxy*-6-n-*amylbenzoyl chloride* (I), from the corresponding *acid*, m.p. 72—73°, and $SOCl_2$, condenses with 2 : 4-dihydroxy-6-*n*-amylbenzaldehyde in Et_2O to the non-cryst. *carbethoxyperlatolaldehyde* (p-*nitrophenylhydrazone*, m.p. 176—178°), which is converted by $ClCO_2Et$ in C_5H_5N at −15° followed by $KMnO_4$ in $COMe_2$ into *dicarbethoxyperlatolic acid*, m.p. 83—84°, whence perlatolic acid, m.p. 107—108° (*Me* ester, m.p. 48—49°, and its *Me*$_2$ *ether*, m.p. 57°), which is therefore *A* (R = C_5H_{11}).



(*A*)

Divarinaldehyde, b.p. 170°/3 mm., m.p. 71—73°, similarly condenses with (I) to the non-cryst. *carbethoxyimbricaraldehyde* (p-*nitrophenylhydrazone*, m.p. 163°), whence *dicarbethoxyimbricaric acid*, m.p. 102—103°, and imbricaric acid, m.p. 122° (*Me* ester *Me*$_2$ *ether*, m.p. 86—87·5°), which hence is *A* (R = Pr). H. W.

Lichen substances. LXXXVI. Synthesis of divaricatic and anziaic acid. Y. Asahina and M. Hiraiwa (Ber., 1937, 70, [*B*], 1826—1828).—Dicarbethoxydivarinaldehyde is oxidised by $KMnO_4$ in H_2O–$COMe_2$ at 40° to *dicarbethoxydivaric acid*, m.p. 81°, transformed successively into divaric acid, its Me ester, and divaricatinic acid. Carbethoxydivaricatinic acid is converted into the corresponding chloride, which condenses with divarinaldehyde in C_5H_5N at −15° to dicarbethoxydivaricataldehyde, which is further carbethoxylated and then oxidised to *dicarbethoxydivaricatic acid*, m.p. 101°, whence divaricatic acid identical with the natural substance. *Dicarbethoxyolivetolcarboxylic acid*, m.p. 62—63°, is converted into the chloride, which when treated successively with olivetolaldehyde in C_5H_5N and $ClCO_2Et$ in Et_2O gives *tricarbethoxyanzia-aldehyde*, an oil, which is oxidised by $KMnO_4$ and $MgSO_4$ at 40° to *tricarbethoxyanziaic acid*, m.p. 108°; this is hydrolysed to anziaic acid, identical with the product from natural sources. H. W.

Cannizzaro reaction. Y. Urushibara and M. Takebayashi (Bull. Chem. Soc. Japan, 1937, **12**, 328—329).—Evidence is given showing that the Cannizzaro reaction may be regarded as a chain reaction, in which the peroxide of the aldehyde is actively concerned. The reaction is not catalysed by ferro-magnetic metals. F. N. W.

Hydrolysis of *N*-substituted benzaldoximes. P. Grammaticakis (Compt. rend., 1937, **205**, 60—62).—*N*-Benzylbenzaldoxime with MgEtBr gives *benzyl*-α-*phenylpropylhydroxylamine*, m.p. 99° (*hydrochloride*, m.p. 180°; *Ph carbamate*, m.p. 155°), oxidised to *benzylidene*-α-*phenylpropylamine oxide*, m.p. 116°, hydrolysed (HCl) to α-*phenylpropylhydroxylamine*, m.p. 75° (*hydrochloride*, m.p. 135°), and PhCHO. Similarly prepared, *benzylidene*-α-p-*tolylpropylamine oxide* and α-p-*tolylpropylhydroxylamine* have m.p. 112° and 82° (*hydrochloride*, m.p. 132°), respectively; *N-benzyl*-N-α-p-*anisylpropylhydroxylamine*, m.p. 78°, is oxidised to *benzylidene*-α-p-*anisylpropylamine oxide*, m.p. 88° and 97°, hydrolysed to PhCHO, NH_2OH, and α-*p*-anisylpropyl alcohol, which loses H_2O to give α-p-anisyl-Δ^{α}-propene. *N*-Benzyl-*p*-anisaldoxime with MgPhBr or *N*-benzylbenzaldoxime with *p*-OMe·C_6H_4·MgBr affords *N-benzyl*-N-α-p-*anisylbenzylhydroxylamine*, m.p. 108° (*hydrochloride*, m.p. 190°), oxidised to *benzylidene*-α-p-*anisylbenzylamine oxide*, m.p. 160°, identical with the product obtained from the Na derivative of *p*-methoxybenzophenoneoxime and CH_2PhCl, and from which N is eliminated by hydrolysis. J. L. D.

Catalytic hydrogenation of cinnamaldehyde and citronellal. M. Delépine and C. Hanegraaff (Compt. rend., 1937, **205**, 185—188).—CHPh:CH·CHO (I) and citronellal (II) in EtOH (sometimes containing NaOH) with H_2–Raney Ni afford products, the extent of reduction being assessed from the I val. and the amount of ·CHO present. Ni–Pt is a better catalyst in the reduction of (I) and if, in addition, 10N-NaOH is added after 1 hr. (when most of the reduction is accomplished), the reaction is completed in 1 hr. more as against a total of 4 hr. without NaOH and 8 hr. without Pt or NaOH.

The product is $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. In the total reduction of (II), neither NaOH nor Pt has much accelerating influence. Reductions carried out for shorter periods show that in (I) the double linking is reduced more readily than ·CHO, whereas in (II) ·CHO is rapidly reduced and the double linking but slowly. In the reaction with (II), NaOH plays a part in the reduction. J. L. D.

Chloromethylation of anisaldehyde. Conversion into 4-methoxy-3-hydroxymethylbenzaldehyde. R. Quelet and J. Allard (Compt. rend., 1937, **205**, 238—240; cf. A., 1901, i, 726).—*p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ (2 mol.), 40% CH_2O, and $ZnCl_2$ with HCl (gas) at 90° afford 4-*methoxy*-3-*chloromethylbenzaldehyde* (I), m.p. 60° (*semicarbazone*, m.p. 192—193°), oxidised (warm 5% $KMnO_4$) to 4-*methoxy*isophthalic *acid*, m.p. 273—275°. When crude (I) is boiled with aq. K_2CO_3 it affords 4-*methoxy*-3-*hydroxymethylbenzaldehyde*, m.p. 50° (*phenylurethane*, m.p. 103°). (I) with NaOMe and NaOEt affords, respectively, 4-*methoxy*-3-*methoxymethyl*-, m.p. 35° (*semicarbazone*, m.p. 150°), and -3-*ethoxymethyl*-*benzaldehyde*, b.p. 173—175°/15 mm. (*semicarbazone*, m.p. 141°). J. L. D.

Manufacture of benzaldehydes containing trifluoromethyl groups.—See B., 1937, 761.

Action of magnesium methyl bromide on 2 : 4 : 6-trichlorobenzoyl chloride. W. E. Ross and R. C. Fuson (J. Amer. Chem. Soc., 1937, **59**, 1508—1510).—Addition of 2 : 4 : 6-$C_6H_2Cl_3{\cdot}COCl$ (I) to 10 mols. of MgMeI gives 2 : 4 : 6-trichloroacetophenone (II), m.p. 51° (*benzylidene* derivative, m.p. 100—101°); use of 1—2 mols. of MgMeI leads, however, to *di*-2 : 4 : 6-*trichlorobenzoylmethane* (II), m.p. 160—161° (red $FeCl_3$ colour; *Cu* derivative; gives $2CH_4$ with MgMeI, only 1 mol. being liberated rapidly), also obtained by heating (II) with MgMeI and then adding (I), and previously (A., 1933, 66) considered to be (I). NaOBr converts (I) into 2 : 4 : 6-*trichloro*-ααα-*tribromoacetophenone*, m.p. 77—78°, stable to hot 40% aq. NaOH, but decomposed by hot 20% NaOH–EtOH (no $C_6H_2Cl_3{\cdot}CO_2H$ was obtained). NaOCl gives ααα-2 : 4 : 6-*hexachloroacetophenone*, b.p. 127—128°/1·5 mm., cleaved by NaOH (20 g.) in 10% aq. EtOH (100 c.c.) to $C_6H_2Cl_3{\cdot}CO_2H$. Cl_2–AcOH or aq. NaOCl converts (II) into *dichlorodi*-2 : 4 : 6-*trichlorobenzoylmethane*, m.p. 106—108°; *dibromodi*-2 : 4 : 6-*trichlorobenzoylmethane*, m.p. 135—136°, is obtained by analogous methods. R. S. C.

Enol betaines. VI. Enol betaines without pyridine ring. F. Krohnke and W. Heffe (Ber., 1937, **70**, [*B*], 1720—1727).—*m*-Nitrophenacyl bromide and $NPhMe_2$ give m-*nitrophenacylphenyldimethylammonium bromide*, m.p. 154° (decomp.) (corresponding *perchlorate*, m.p. 192°, *sulphate*, m.p. 227°, and *chloride*, m.p. 132—133°), converted by N-NaOH in presence of Et_2O into the orange-coloured *betaine* (I), $NO_2{\cdot}C_6H_4{\cdot}CO^-{\cdot}{:}CH{\cdot}N^+PhMe_2$ (+0·33H_2O), m.p. 74—75°. The action of alkali on p-*bromophenacylphenyldimethylammonium bromide*, m.p. 153° (corresponding *sulphate*, m.p. 183°), or 3 : 4-*dichlorophenacylphenyldimethylammonium bromide*, m.p. 141·5°, gives colourless hydrates of bases which lose $1H_2O$ when dried, giving the colourless *enol betaines* (II), m.p. 119° (decomp.), and (III), m.p. 115—116° (slight decomp.), re-convertible into the salts. Their reactions resemble those of (I) so closely that the structures must be identical. Since (II) and (III) give orange solutions in $PhNO_2$, doubtless owing to the formation of an additive compound, it appears that in (I) there is a subsidiary valency relationship between the two N atoms. The new bases do not give a colour with chloranil and only a somewhat subdued colour with picryl chloride. Generally CH in them is much less reactive than in the pyridinium-methine enol betaines. Thus *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and (II) give the expected keto-nitrone slowly at 50° whereas in the C_5H_5N series the change is instantaneous at 0°. The diminished reactivity of CH is also shown by the formation of *O*-derivatives with acyl chlorides. Thus (I) and BzCl in $CHCl_3$ afford O-*benzoyl*-m-*nitrophenacylphenyldimethylammonium chloride* (+1H_2O), m.p. 128° after becoming yellow at 90° (greatly dependent on the mode of heating) (corresponding *sulphate*, m.p. 178—179° after softening and becoming green at 155°). Attempts to dehydrate the salt give the orange O-*benzoyl*-m-*nitrophenacylmethylaniline*, m.p. 114—115°. Similarly, O-p-*bromobenzoyl*-m-*nitrophenacylphenyldimethylammonium chloride* (+H_2O), m.p. 112° (decomp.) after becoming yellow at 110°, yields O-p-*bromobenzoyl*-m-*nitrophenacylmethylaniline*, m.p. 119°. Analogously, O-*benzoyl*-p-*bromophenacylphenyldimethylammonium chloride*, m.p. 117° [corresponding *sulphate* (+H_2O), m.p. (anhyd.) 171°, and *bromide*, m.p. 115°], affords O-*benzoyl*-p-*bromophenacylmethylaniline*, m.p. 131°. O-m-*Nitrobenzoyl*-p-*bromophenacylphenyldimethylammonium chloride*, m.p. 135° (decomp.), gives an orange resin when heated. The possible activity of the enol O in pyridinium enol betaines is established by the conversion of dibenzoylmethylpyridinium enol betaine by BzCl in $CHCl_3$ into O-*benzoyldibenzoylmethylpyridinium chloride* (+3H_2O), m.p. 105° (corresponding *picrate*, *perchlorate*, *iodide*, *bromide*, *sulphate*, *chromate*, *nitrate*, and *oxalate*). 3-*Nitro*-4-*methylphenacylphenyldimethylammonium bromide*, m.p. 131°, gives the corresponding *enol betaine*, *trihydrate*, m.p. 86°, *semihydrate*, m.p. 116°.

Reply is made to Gustafsson (this vol., 386). H. W.

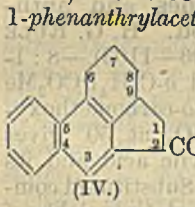
Two-step oxidation of benzoin to benzil. L. Michaelis and E. S. Fetcher (J. Amer. Chem. Soc., 1937, **59**, 1246—1249).—The purple colour in the oxidation of benzoin is due to a unimol. radical, $COPh{\cdot}\dot{C}Ph{\cdot}OH$ (and not a bimol. compound), since the total colour is (very nearly) the same in columns of solution (benzoin and benzil in NaOH–EtOH, in absence of O_2) having different concns. but the same total amount of solute. Oxidation occurs only under conditions in which this radical can exist. A. Li.

Polymorphism of chalkone.—See A., I, 450.

Synthesis of substances related to the sterols. XVII. 8-Methylhydrindan-1-one. R. Robinson and J. Walker (J.C.S., 1937, 1160—1161).—The impure hydrogenation product of the unsaturated compound from Et 2-methyl-1-γ-methoxypropylcyclohexan-1-ol-2-carboxylate (this vol., 197) is purified by heating with $KHSO_4$ and renewed hydrogenation

(Pd–$SrCO_3$) to *Et* 2-*methyl*-1-*γ*-*methoxypropyl*cyclo*hexane*-2-*carboxylate*, b.p. 138—140°/12 mm., which with HBr–Ac_2O followed by KOAc–AcOH and 2·5% KOH–MeOH gives *Et* 2-*methyl*-1-*γ*-*hydroxypropyl*-cyclo*hexane*-2-*carboxylate*, b.p. 160—165°/13 mm. This is converted after hydrolysis [$Ba(OH)_2$–MeOH and KOH–EtOH] by oxidation with $KMnO_4$ into 2-methyl*cyclo*hexane-2-carboxylic-1-β-propionic acid, cyclised to 8-methylhydrindan-1-one (cf. this vol., 343). E. W. W.

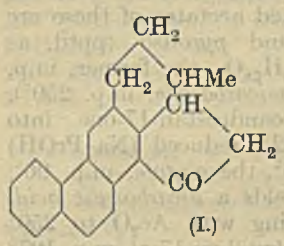
Substances with a female hormone effect. Synthesis of 4 : 5-benzo-6 : 7 : 8 : 9-tetrahydroacenaphthen-2-one. J. Hoch (Compt. rend., 1937, **205**, 65—67).—$CHNa(CO_2Et)_2$ with β-1-naphthylethyl bromide affords *Et*$_2$ β-1-*naphthylethylmalonate*, b.p. 200—202°/2 mm., hydrolysed (EtOH–KOH) to β-1-*naphthylethylmalonic acid*, m.p. 159°, which by loss of CO_2 gives *γ*-1-*naphthylbutyric acid* (I), m.p. 107—108°. (I) is cyclised by $SnCl_4$ to 1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 98°, converted by $CH_2Br{\cdot}CO_2Et$ in presence of Zn in C_6H_6 into *Et* 3 : 4-*dihydro*-1-*phenanthrylacetate* (II), b.p. 238—241°/12 mm., the H_2-derivative of which (H_2–Pt-black) with EtOH–KOH gives 1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylacetic acid* (III), m.p. 134°, the chloride of which is cyclised ($AlCl_3$ in C_6H_6 at 0°) to 4 : 5-*benzo*-6 : 7 : 8 : 9-*tetrahydroacenaphthen*-2-*one* (IV), m.p. 112° (*semicarbazone*, m.p. 240—242°). 3 : 4-*Dihydro*-1-*phenanthrylacetic acid*, m.p. 147°, obtained by hydrolysing (II), when heated with S at 180—200° affords 1-*phenanthrylacetic acid*, m.p. 189—190°, and some 1-*methylphenanthrene*, m.p. 119° (*picrate*, m.p. 135°). J. L. D.


(IV.)

Phenanthrene series. XV. Substitution in 9 : 10-dihydrophenanthrene : tetracyclic compounds derived from it. A. Burger and E. Mosettig (J. Amer. Chem. Soc., 1937, **59**, 1302—1307).—The oxime of 2-acetyl-9 : 10-dihydrophenanthrene is converted by HCl and Ac_2O in glacial AcOH into 2-*acetamido*-, m.p. 173—174°, hydrolysed to 2-*amino*-9 : 10-*dihydrophenanthrene* (oily) [*hydrochloride*, m.p. 323—325° (decomp.) in vac.; *picrate*, m.p. 203° (decomp.)]; the 2-*propionamido*-derivative, m.p. 109—110°, is obtained similarly. Methylation (Me_2SO_4) of the amine gives a methiodide which when heated yields 2-*dimethylamino*-, m.p. 65—66° (*hydrochloride*, m.p. 186—188°), and diazotisation followed by boiling yields 2-*hydroxy*-9 : 10-*dihydrophenanthrene*, m.p. 111·5—113° (2-*OMe*- and -*OAc*-derivatives, oily). 9 : 10-Dihydrophenanthrene (I) is converted by HCl and HCN ($AlCl_3$) followed by decomp. with dil. HCl into the -2-*aldehyde*, b.p. 185°/2 mm. [*semicarbazone*, m.p. 235—236° (decomp.); p-*nitrophenylhydrazone*, m.p. 242—244° (decomp.)], which is oxidised ($KMnO_4$) to the -2-carboxylic acid, and reduced (PtO_2) to the -2-*carbinol*, m.p. 77—78° (*α*-*naphthylurethane*, m.p. 145—146°). 1 : 2-Benzanthracene (characterised by its picrate and quinone) is prepared from (I) by condensation ($AlCl_3$ in $PhNO_2$) with $(\cdot CH_2{\cdot}CO)_2O$ giving β-2-(9 : 10-*dihydrophenanthroyl*)-*propionic acid*, m.p. 157·5—158·5° [also obtained by condensing (Na) the 2-bromoacetyl compound with $CH_2(CO_2Et)_2$]; this is reduced (Zn–Hg) to *γ*-2-(9 : 10-*dihydrophenanthryl*)*butyric acid*, m.p. 92°, cyclised with 85% H_2SO_4 to 8-*keto*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene*, m.p. 97—98° (*oxime*, m.p. 197—198°); the *semicarbazone*, m.p. 277—279° (decomp., in vac.), of this is reduced (Na, EtOH) and the product dehydrogenated with Se at 300°. *cyclo*Pentenophenanthrenes are prepared from the -2-aldehyde of (I) by condensation with $CH_2(CO_2H)_2$ (in C_5H_5N) to β-2-(9 : 10-*dihydrophenanthroyl*)*acrylic acid*, m.p. 153—154°; cyclisation (PCl_6 in C_6H_6, then $AlCl_3$) gives a mixture of 1′- (20%), m.p. 143—144° [*semicarbazone*, m.p. 263—268° (decomp., in vac.)], and 3′-*keto*-9 : 10-*dihydro*-2 : 3-cyclo*pentenophenanthrene* (80%), m.p. 131—132° [*semicarbazone*, m.p. 261—263° (decomp., in vac.); *oxime*, m.p. 243—245° (decomp.)]; reduction (Zn–Hg) followed by dehydrogenation of these two gives 1 : 2- and 2 : 3-cyclo*pentenophenanthrene*, m.p. 84—84·5° (*picrate*, m.p. 156—157°; *styphnate*, m.p. 158—159°). A. Li.

Synthesis of 2 : 3-*cyclo*pentenophenanthrene. E. Bergmann and O. Blum-Bergmann (J. Amer. Chem. Soc., 1937, **59**, 1572—1573).—*cyclo*Pentane-1 : 2-dicarboxylic anhydride and 1-$C_{10}H_7{\cdot}MgBr$ in Et_2O give 2-1′-*naphthoyl*cyclo*pentanecarboxylic acid*, $+1{\cdot}5H_2O$, converted by crystallisation from MeOH into the hydroxy-lactone *form*, anhyd., m.p. 169—170° after sintering, and reduced (Clemmensen) to 2-1′-*naphthylmethyl*cyclo*pentanecarboxylic acid*, m.p. 99—101°, which with $SnCl_4$ in PhMe or, better, P_2O_5 in C_6H_6 (H_2SO_4 gives variable results) affords 1-*keto*-2 : 3-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 163—164°. Clemmensen reduction converts this ketone into 2 : 3-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 119—121°, which with Se at 320—340° gives 2 : 3-cyclo*pentenophenanthrene*, m.p. 85—85·5°. R. S. C.

Synthesis of methylcholanthrene. E. Bergmann and O. Blum-Bergmann (J. Amer. Chem. Soc., 1937, **59**, 1573—1575).—5-Keto-6-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene (Cook and Haslewood, A., 1934, 657) with $CH_2Br{\cdot}CO_2Me$ and Zn gives 6-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthrylidene*-5-*acetic acid*, m.p. 231—233° (decomp.), and its *Me* ester, b.p. 240—245°/1·5—2 mm., which with H_2–Pd–$BaSO_4$ in hot AcOH gives, after hydrolysis, 6-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthryl*-5-*acetic acid*, m.p. 192—194·5° (also obtained from the unsaturated acid by H_2–Pd-black in EtOAc). Ring-closure by P_2O_5 in hot C_6H_6 gives the *ketone* (I), m.p. 168—170°, reduced (Clemmensen) to *tetrahydromethylcholanthrene*, m.p. 97—99°, which with Se at 330° affords methylcholanthrene. R. S. C.


(I.)

Transformation reactions of brominated derivatives of cholesterol. IV. Experiments with dibromocholestanone. H. H. Inhoffen (Ber., 1937, **70**, [*B*], 1695—1701).—Treatment of dibromocholestanone with KOBz in PhMe–BuOH at 135° gives mainly the isomeric, singly unsaturated *monobenzoates*,

$C_{27}H_{43}O{\cdot}COBz$, (I), m.p. 177°, $[\alpha]_D^{20}$ +25·9° in $CHCl_3$, and (II), m.p. 137—138°, $[\alpha]_D^{20}$ +58·0° in $CHCl_3$. Alkaline hydrolysis of (I) leads smoothly to cholestane-3 : 4-dione (III), m.p. 147—148° (Butenandt *et al.*, this vol., 63), whereas under similar conditions (II) affords (III) and *cholestane*-2 : 3-*dione* (IV), m.p. (usually) 161—162° or 162—163°, $[\alpha]_D$ +56·9° in $CHCl_3$ (*quinoxaline* derivative, $C_{33}H_{48}N_2$, m.p. 180°; *enol acetate*, m.p. 142°; *enol benzoate*, m.p. 124—124·5°). The constitution of (IV) is established by its oxidation to the dicarboxylic acid $C_{27}H_{46}O_4$, m.p. 196° (Me_2 ester, m.p. 61—61·5°), obtained by Windaus (A., 1914, i, 1066) from cholestanol. H. W.

***epi*Ætiocholane-3 : 17-diol from male urine.** A. Butenandt, K. Tscherning, and H. Dannenberg (Z. physiol. Chem., 1937, **248**, 205—212).—Testosterone is hydrogenated (Pd–$CaCO_3$ in MeOH) to androstan-17-ol-3-one, m.p. 177—178°, and *ætiocholan*-17-*ol*-3-*one* (I), m.p. 139—140°, $[\alpha]_D^{20}$ +32·7° in EtOH (*acetate*, m.p. 143—144°, $[\alpha]_D^{20}$ +27·1° in EtOH; *oxime*, m.p. 211—212°). (I) is reduced by Na and boiling $Pr^{\beta}OH$ to *epi*ætiocholane-3 : 17-diol (II), m.p. 232°, $[\alpha]_D^{20}$ +26·5° in EtOH (*diacetate*, m.p. 121—122°), identical with the product obtained from male urine (which may not exist as such in the urine but be formed during subsequent treatment). Oxidation of (II) affords *ætiocholane*-3 : 17-*dione*, m.p. 128°, $[\alpha]_D^{21}$ +115·2° in abs. EtOH. H. W.

Sterols. XIV. Pyroandrosterone and derivatives. R. E. Marker, O. Kamm, D. M. Jones, and L. W. Mixon. **XV. Synthetic preparation of *epiallo*-pregnanolone, the androgenic principle of human pregnancy urine.** R. E. Marker, O. Kamm, D. A. McGinty, D. M. Jones, E. L. Wittle, T. S. Oakwood, and H. M. Crooks. **XVII. Isolation of pregnanolone from human pregnancy urine.** R. E. Marker and O. Kamm (J. Amer. Chem. Soc., 1937, **59**, 1363—1366, 1367—1368, 1373—1374; cf. this vol., 416).—XIV. Oxidation of neocholestene (O_3) or of β-cholestanol (CrO_3) yields a *dicarboxylic acid*, $C_{27}H_{46}O_4$, m.p. 193°, which when heated with Ac_2O to 250° gives *pyro*-β-*cholestanone*, m.p. 98° (pptd. by digitonin), reduced by $Al(OPr^{\beta})_3$ to *pyro*-β- (separated as digitonide), m.p. 130° (*acetate*, m.p. 77°), and *pyro*-epi-*cholestanol*, m.p. 155° (*acetate*, m.p. 96°), in the ratio 1 : 2; Na + EtOH gives a ratio 3 : 1. The mixed acetates of these are oxidised (CrO_3) to *pyro*- and *pyro*-iso- (pptd. as digitonide) -*androsterone*, $C_{18}H_{28}O_2$, the former, m.p. 124° (*acetate*, m.p. 102°; *semicarbazone*, m.p. 250°). Quinoline converts 3-chloroandrostan-17-one into Δ^2-*androsten*-17-*one*, m.p. 102°, reduced (Na–PrOH) to the *androstenol*, m.p. 165°, the *acetate*, m.p. 96°, of which on ozonisation yields a *dicarboxylic acid*, $C_{19}H_{30}O_5$, m.p. 273°. Heating with Ac_2O to 250° converts this into *pyroandrostan*-2-*on*-17-*ol*, m.p. 197° (*semicarbazone*, m.p. 238°). It is concluded that the double linking in neocholestene and in androstenone is in the 2 : 3-position.

XV. See this vol., 251.

XVII. epi-*Pregnan*-20-*one*-3-*ol*, m.p. 136° (*acetate*, m.p. 99°), the *semicarbazone*, m.p. 248°, of which is isolated from the mother-liquors after the extraction of the *epi-allo*-compound, is oxidised (CrO_3) to pregnanedione, m.p. 120°, and reduced (PtO_2) to a *pregnane*-3 : 20-*diol*, m.p. 230°, not pptd. by digitonin. A. Lr.

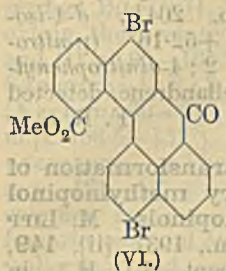
Manufacture of ketones of polycyclic hydroaromatic compounds [progesterone etc.].—See B., 1937, 842.

Manufacture of unsaturated ketones containing a sterol nucleus.—See B., 1937, 842.

Action of organo-magnesium compounds on benzilanils. (Mlles.) M. Montagne and M. Garry (Compt. rend., 1937, **204**, 1659—1661).—Benzilmonoanil (I) with MgMeI affords *methylbenzoinanil*, m.p. 104·5°, easily hydrolysed to methylbenzoin and NH_2Ph. MgEtBr, MgEtI, and MgPhBr with (I) lead to decomp. Benzildianil with MgMeI and MgEtI affords, respectively, the *anils*, m.p. 154° (II) and 181° (III), of *Ph methyl-* and *ethyl-anilinobenzyl ketone* (cf. A., 1905, i, 519). The latter reaction is accompanied by the formation of (I) and NHPhBz. (II) with boiling HCl gives NH_2Ph and a *hydrochloride*, m.p. 145°, easily converted into 2 : 3-diphenyl-1-methylindole (cf. A., 1893, i, 519), whereas (III) affords NH_2Ph and an unidentified oil. J. L. D.

Synthesis of *meso*benzanthrones and anthanthrones by the Ullmann method. H. G. Rule and F. R. Smith (J.C.S., 1937, 1096—1103).—8 : 1-$C_{10}H_6Br{\cdot}CO_2Me$ (A., 1934, 406) and *o*-$C_6H_4I{\cdot}CO_2Me$ with Cu-bronze at 180° give crude Me 8-*o*-carbomethoxyphenyl-1-naphthoate, which in H_2SO_4 at 50° gives 75% of *meso*benzanthrone-8-carboxylic acid and its Me ester, and 11% of anthanthrone. Substituted compounds are obtained similarly; the relative yields of benzanthrones and of anthanthrones are tabulated, and the effect of conditions and of reactivities is discussed. Benzanthronecarboxylic acids are decarboxylated by Cu-bronze in quinoline at 240°, and converted quantitatively into 8 : 3′-keto*meso*benzanthrones by P_2O_5 in *o*-$C_6H_4(CO)_2O$. 1′-*Bromomesobenzanthrone*-8-*carboxylic acid* (I), m.p. 315—316° (*Me* ester, m.p. 194°), is decarboxylated to 1′-bromo*meso*benzanthrone (II), identical with the product (III) from *meso*benzanthrone (IV) and Br; the 1′-structure of (III) is thus confirmed. The product of further bromination of (IV) (G.P. 193,959) must be 6 : 1′-*dibromo*mesobenzanthrone, since the product from (II) and Br is identical with that from decarboxylation of 6 : 1′-*dibromo*mesobenzanthrone-8-*carboxylic acid*, m.p. 354—356° (decomp.). Nitration of (IV) in $PhNO_2$ at 40—50° gives the 1′-NO_2-compound (V) (B., 1928, 598) [now obtained from the 8-*carboxylic acid*, m.p. 310° (decomp.)], but in boiling AcOH the main product is the 2′-NO_2-compound (B.P. 224,522; B., 1925, 583), of which the m.p. is depressed by 6-*nitro*mesobenzanthrone, m.p. 291—292°, from the corresponding 8-*carboxylic acid*, m.p. 286—287° (decomp.). Oxidation (CrO_3) of (I) gives 1′-*bromo*-3′-*hydroxy*mesobenzanthrone-8-*carboxylic acid lactone*, m.p. 321—323°. Reduction ($Na_2S_2O_4$) of (V) gives a blue vat *dye* which deposits a pink *NH*$_2$-*compound* on atm. oxidation. *Me* 6 : 1′-*dibromo*-7 : 8-*benzo*mesobenzanthrone-4″-*carboxylate* (VI), m.p. 233°, also forms an orange vat dye. It is obtained by brief H_2SO_4 treatment of Me_2 4 : 4′-dibromo-1 : 1′-dinaphthyl-8 : 8′-dicarboxylate, which

on prolonged treatment yields 4 : 9-dibromoanthanthrone (orange-red vat *dye*). A similar result is obtained with the unbrominated ester, indicating that the Me ester of type (VI) is stable whilst the acid gives an anthanthrone. Thus benzo*meso*benzanthronecarboxylic acid is converted by H_2SO_4 into anthanthrone very much more rapidly than the Me ester (where steric hindrance intervenes).



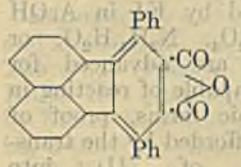
(VI.)

The intermediate product from Et_2 1 : 1′-dinaphthyl-8 : 8′-dicarboxylate is thus not benzo*meso*benzanthronecarboxylic acid (cf. A., 1914, i, 849) but the *Et* ester. 1 : 6-Dibromo-β-naphthylamine is converted (Sandmeyer) into the *nitrile* of 1 : 6-*dibromo*-2-*naphthoic acid*, m.p. 249—250°, of which the *Me* ester, m.p. 99—100°, yields *Me*$_2$ 6 : 6′-*dibromo*-1 : 1′-*dinaphthyl*-2 : 2′-*dicarboxylate*, m.p. 220°, hydrolysed to the 2 : 2′-*dicarboxylic acid*, m.p. 342—344° (decomp.). This is converted (best by $ClSO_3H$) into 2 : 7-*dibromoanthanthrone*, m.p. >360° (violet vat, dyeing cotton a deep orange). The following are also described. 5 : 8 : 1-$C_{10}H_5Br_2$·CO_2H (improved prep.); *Me* 5-*bromo*-2-*iodobenzoate*, m.p. 45—46°; and 2-*iodo*-6-*nitrobenzoic acid*, m.p. 188—189° [from 6-nitroanthranilic acid, new m.p. 189° (decomp.) (improved prep.)] (*Me* ester, m.p. 94°, from the *Ag* salt). Me 5-*bromo*-8-(o-*carbomethoxyphenyl*)-1-*naphthoate*, m.p. 155°. 1′-*Bromo*-8 : 3′-*keto*meso*benzanthrone*, m.p. 326—328° sintering at 200°, except when resolidified and remelted), converted very slowly by alkali into a mixture (*meso*benzanthrone-3′- and -8-carboxylic acids ?). *Me* 7 : 8-*benzo*meso*benzanthrone*-4′-*carboxylate*, m.p. 154°. 6-*Bromo*meso*benzanthrone*, m.p. 182—183°, and its -8-*carboxylic acid*, m.p. 315—316°. 6-*Bromo*-, m.p. 239—240° (sintering 230°), and 6 : 1′-*dibromo*-8 : 3′-*keto*meso*benzanthrone*, m.p. 299—300°. *Me* 5-*nitro*-8-o-*carboxyphenyl*-1-*naphthoate*, m.p. 154—155°. 6-*Nitro*-8 : 3′-*keto*meso*benzanthrone*, m.p. 316—317°.

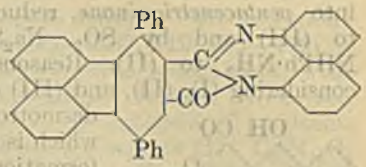
E. W. W.

Colouring of artificial silk [with new alkoxy-*meso*benzanthrones].—See B., 1937, 774.

Heteropolarity. XXIX. Adducts from maleic acid and acecyclone. W. Dilthey and S. Henkels (J. pr. Chem., 1937, [ii], **149**, 85—97).—The behaviour of the three deeply coloured ketones, tetraphenyl*cyclo*pentadienone (tetracyclone) (I), diphenyldiphenylene*cyclo*pentadienone (phencyclone) (II), and 2 : 5-diphenyl-3 : 4-(1 : 8-naphthylene)-$\Delta^{2:4}$-*cyclo*pentadiene (acecyclone) (III) (cf. A., 1935, 1241), is fundamentally similar. The *endo*carbonyldihydrophthalic anhydride is first formed, and loses CO when heated, giving the dihydrophthalic anhydride, which is then dehydrogenated to the highly arylated phthalic anhydride. All three products can be isolated from (I) since the temp. of the respective transformations are sufficiently removed from one another. With (II) the primary addition occurs at 80° but the temp. of evolution of CO is so close to that of dehydrogenation that the H_2-compound can be isolated only with difficulty. With (III) the temp. of addition nearly coincides with that of decarboxylation so that the primary product is not isolable, whereas the H_2- and dehydro-compounds are readily obtained. (III) and maleic anhydride at >150° give 2 : 5-*diphenyl*-3 : 4-(1′ : 8′-*naphthylene*)*phthalic anhydride* (*acephthalide*) (IV), m.p. 322°, in 95% yield, whereas in boiling PhCl the H_2-derivative, m.p. 356°, converted when heated above its m.p. into (IV) and also produced more slowly if fumaric acid is used, is obtained. (IV) is transformed into 2 : 5-*diphenyl*-3 : 4-(1′ : 8′-*naphthylene*)*phthalic acid* (V), m.p. 320°, when

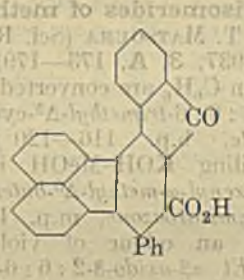


(IV.)



(VI.)

treated successively with NaOH–EtOH and HCl or when boiled with HCl–MeOH. The *Me*$_2$ ester of (V), m.p. 242—243°, is produced from the acid and CH_2N_2 in EtOH or from (III) and (:C·CO_2Me)$_2$ at about 240°. Passage of NH_3 into molten (IV) affords the *imide*, m.p. 330—331°, whilst (IV) and molten NH_2Ph yield the *anilide*, m.p. 334—335°. 2 : 5-*Diphenyl*-3 : 4-(1′ : 8′-*naphthylene*)*phthaloperinone* (VI), m.p. 362°, is derived from (IV) and 1 : 8-$C_{10}H_6(NH_2)_2$ in CO_2 at 250—300°. (IV) is converted by $AlCl_3$ in boiling C_6H_6 into 7-*phenyl*-5 : 6-(1′ : 8′-*naphthylene*)-



(VII.)

(VIII.)

fluorenone-8-*carboxylic acid* (VII), m.p. 341° (*oxime*, m.p. >400°), decarboxylated at 330—360° to 7-*phenyl*-5 : 6-(1′ : 8′-*naphthylene*)*fluorenone*, m.p. 239—240°. (IV) is transformed by molten NaCl–$AlCl_3$ into 5 : 6-(1′ : 8′-*naphthylene*)*difluorenone* (VIII), m.p. 351° (*dioxime*, m.p. >400°) reduced by Zn and AcOH in C_5H_5N to 5 : 6-(1′ : 8′-*naphthylene*)*difluorenol*, m.p. 245—246°, which when distilled with Zn dust gives 5 : 6-(1′ : 8′-*naphthylene*)*difluorene*, m.p. 299°.

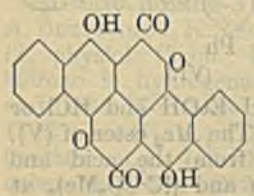
H. W.

Preparation of 4-methoxy-2 : 5-toluquinone. J. N. Ashley (J.C.S., 1937, 1471—1472).—The quinone is prepared from toluquinone and MeOH refluxed with $ZnCl_2$.

R. S. C.

Linear pentacene series. C. Marschalk (Rev. Gen. Mal. Col., 1937, **41**, 353—357; cf. A., 1936, 1513).—6 : 13-Dihydroxy-7 : 12 : 14-triketo-5 : 7 : 12 : 14-tetrahydropentacene (I) (Marschalk *et al.*, A., 1936, 1256) and the compound (II) obtained (G.P. 298,345) by condensing leucoquinizarin with o-$C_6H_4(CO)_2O$ in presence of $AlCl_3$ are oxidised to 6 : 13-*dihydroxypentacene*-5 : 14-7 : 12-*diquinone* (III)

(Ac_2 derivative), also obtained by acetylation of (I) followed by oxidation with PbO_2 and hydrolysis. (III) has been obtained synthetically by condensing 1 : 4-dihydroxyanthraquinone-2 : 3-dicarboxylic anhydride with C_6H_6 to 1 : 4-*dihydroxy*-2-*benzoylanthraquinone*-3-*carboxylic acid*, which is then cyclised. (III) is very readily reduced to (II), which is thus 6 : 7 : 12 : 13-*tetrahydroxypentacene*-5 : 14-*quinone*; this view is confirmed by the isolation of a *tetra-acetate*. (II) and (III) are converted by $Pb(OAc)_4$ into *pentacenetriquinone*, reduced by KI in AcOH to (III) and by SO_2, $Na_2S_2O_4$, N_2H_4,H_2O, or $NHPh{\cdot}NH_2$ to (II). Reasons are advanced for considering (I), (II), and (III) capable of reacting in desmotropic forms, proof of which is afforded by the transformation of (II) into 2 : 3 : 6 : 7-dibenzanthra-9 : 10-quinone and into 2 : 3 : 6 : 7-dibenz-9 : 10-anthrone. (II) is converted by distillation with Zn dust into 9 : 10-dihydropentacene in 50% yield. The product obtained by Russig by the action of air on 1 : 4-dihydroxy-2-naphthoic acid in alkaline solution or in org. media (considered to be a dihydroxypentacenediquinone) is (IV) since it is transformed by fusion with alkali into 1 : 4 : 1′ : 4′-tetrahydroxy-2 : 2′-dinaphthyl. H. W.



(IV.)

Synthesis of aldehydic isomerides of methylionone. S. Ishikawa and T. Matsoura (Sci. Rep. Tokyo Bunrika Daigaku, 1937, **3**, **A**, 173—179).—α-Ionone and $CH_2Cl{\cdot}CO_2Et$ in C_6H_6 are converted by NaOMe into *Et* αβ-*oxido*-δ-2 : 6 : 6-*trimethyl*-Δ^2-cyclo*hexenyl*-β-*methyl*-Δ^γ-*pentenoate*, b.p. 116—120°/2·5 mm., transformed by boiling KOH–MeOH into γ-2 : 6 : 6-*trimethyl*-Δ^2-cyclo*hexenyl*-α-*methyl*-Δ^β-*butenal*, b.p. 85—87°/3 mm. [*thiosemicarbazone*, m.p. 152° (corr.; Berl)], which has an odour of violets. Similarly, β-ionone gives *Et* αβ-*oxido*-δ-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-β-*methyl*-Δ^γ-*pentenoate*, b.p. 146—149°/2 mm., whence γ-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-α-*methyl*-Δ^β-*butenal*, b.p. 131—133°/3 mm. [*thiosemicarbazone*, m.p. 160° (corr.; Berl)]. H. W.

Carbonyl constituents of eucalyptus oils. II. Seasonal variation of *E. cneorifolia* oil. P. A. Berry, A. K. Macbeth, and T. B. Swanson (J.C.S., 1937, 1443—1447).—The oils obtained by monthly distillations of young leaf of *E. cneorifolia* show increase during the period of active growth, and side by side with this a fall in *d*- and a rise in *l*-rotation owing to increase in the terpene content of the oil. No marked similar change is found in the oils from old leaf. The terpenes contain considerable quantities of *l*-β-phellandrene during the flush period, and the biogenetic relationship *l*-β-phellandrene, *l*-phellandral, *l*-4-*iso*propyl-Δ^2-*cyclo*hexan-1-one is suggested. *l*-α-Phellandrene and cymene are also present, the amount of the latter decreasing in the winter months. No cryptal was detected. F. R. S.

***d*-Phellandral and *d*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one.** P. A. Berry, A. K. Macbeth, and T. B. Swanson (J.C.S., 1937, 1448—1450).—The oil of water-fennel contains *d*-phellandral, α_D +116·22° (2 : 4-*dinitrophenylhydrazone*, m.p. 204°), *d*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one, α_D +52·16° (p-*nitrophenylhydrazone*, m.p. 167·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 136°), and *d*-β-phellandrene, detected through the nitrosite. F. R. S.

Stability and capability of transformation of the pinane system in tertiary methylnopinol and in homologous tertiary nopinols. M. Lipp and H. Steinbrink (J. pr. Chem., 1937, [ii], **149**, 107—152).—A substituent (except 1-$C_{10}H_7$) in addition to OH at 4 in *apo*pinane diminishes the stability of the ring system during reactions, particularly during elimination of H_2O. As OH is removed with formation of a double linking, the 7 : 3-union is ruptured and a dicyclic system is not further formed but the bridge remains broken. Mixtures of monocyclic hydrocarbons result, a portion of which containing the double linkings in the α-terpinene position can be removed as maleic anhydride (I) adducts. The production of the same adducts from *tert.*-nopinols and (I) depends on the dehydrating power of (I) which causes loss of H_2O in the initial stages of the change. The formation of hydrochlorides is explained similarly; during replacement of OH by Cl the bridge is broken with production of a double linking. This remains intact during reactions with PCl_5 but becomes saturated when HCl is used. Interaction of nopinone with the appropriate Grignard reagent gives the following compounds: methylnopinol (II), b.p. 88—89°/12 mm., m.p. 58—59°, $[\alpha]_D^{17}$ −2·30° in abs. Et_2O; ethylnopinol, m.p. 44—45°, $[\alpha]_D^{17}$ +3·87° in abs. Et_2O; n-*propylnopinol*, m.p. 41—42°, $[\alpha]_D^{17}$ +10·57° in abs. Et_2O; *benzylnopinol* (III), b.p. 131—132°/0·8 mm., $[\alpha]_D^{20}$ +10·41° in *cyclo*hexane; *phenylnopinol* (IV), m.p. 116—117°, $[\alpha]_D^{16}$ +7·91° in abs. Et_2O, and m.p. 59—60°, $[\alpha]_D^{16}$ +24·5° in abs. Et_2O, respectively; 2-*naphthylnopinol* (VI), m.p. 120—121°, $[\alpha]_D^{20}$ +43·90° in C_6H_6; 1-*naphthylnopinol* (VII), m.p. 163—164°, $[\alpha]_D^{20}$ +84·30° in C_6H_6. (II) is converted by C at 220° into *p*-cymene. $ZnCl_2$ dehydrates (V) in boiling C_6H_6 to a *hydrocarbon*, $C_{15}H_{18}$, b.p. 107—108°/0·25 mm. $H_2C_2O_4$ transforms (IV) and (V) into closely similar *products*, $C_{15}H_{18}$, b.p. 118—119°/1 mm. and 119—120°/1·2 mm., $[\alpha]_D^{20}$ −13·61° and −40·73° in C_6H_6, respectively, which afford the same *dihydrochloride*, $C_{15}H_{20}Cl_2$ (VIII), m.p. 86°, and are hydrogenated to the *hydrocarbon*, $C_{15}H_{22}$, b.p. 105—106°/1·4 mm. The main component is probably $\Delta^{1:7(8)}$-*cyclo*hexadiene. $H_2C_2O_4$ and (III) at 130° give the strongly unsaturated *substance* $C_{16}H_{20}$, b.p. 125—129°/1·5 mm. With HCl in dry Et_2O (II) gives mainly dipentene dihydrochloride. (III), (IV) or (V), and (VI) similarly yield *dihydrochlorides*, $C_{16}H_{22}Cl_2$, m.p. 110·5—111°, $C_{15}H_{20}Cl_2$, m.p. 85—86°, and $C_{19}H_{22}Cl_2$ (IX), m.p. 107—107·5°, respectively; to these a monocyclic structure is ascribed since they are derived also from the corresponding hydrocarbons. (IV) or (V) with PCl_5 in ligroin gives a non-cryst. *monohydrochloride*, transformed by HCl into (VIII); under similar conditions (V) gives an unsaturated *monohydrochloride*, m.p. 99—100°, $[\alpha]_D^{18}$ −101·15° in C_6H_6, transformed by HCl into (IX). (II) is unaffected by borophosphoric acid in C_6H_6. (IV) is converted by Et_3BO_3 at 100°

and then at 160° into a hydrocarbon mixture and a *product* $B(O{\cdot}C_{15}H_{19})_3$, m.p. 204—206°. Attempts to obtain the acetate of (IV) were unsuccessful. (II) and (I) at 90—100° give 3 : 6-*endo*ethylene-3-methyl-6-*iso*propyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride (X), m.p. 60—61°, $[\alpha]_D$ ±0° (corresponding *imide*, m.p. 156·5—157°), identical with that derived from α-terpinene. α-Phellandrene and (I) give an adduct, m.p. 127—127·5°, whereas β-phellandrene yields a complex product. Borneol and (I) at 160° afford fumaric acid and *bornyl H maleate*, m.p. 118—118·5°. *iso*Borneol and camphene hydrate appear to give mainly the corresponding normal esters. (III), (IV) or (V), and (VI) with (I) give *products*, $C_{20}H_{22}O_3$, m.p. 134—135°, $[\alpha]_D$ ±0° (corresponding *imide*, m.p. 183—183·5°), $C_{19}H_{20}O_3$, m.p. 170·5—171°, and $C_{23}H_{22}O_3$, m.p. 201—201·5°, respectively, analogously constituted to (X). Nopinol and (I) give the *adduct*, $C_{13}H_{16}O_3$, m.p. 107—108°, derived from *apo*-α-terpinene.

The optically active hydrocarbon obtained from (VII) and $H_2C_2O_4$ is obviously a mixture with strongly unsaturated components; a maleic anhydride adduct cannot be obtained from it or from (VII). It appears to consist mainly of the limonene analogue $CH_2{:}CMe{\cdot}CH{<}\begin{matrix}CH_2{-}CH\\CH_2{\cdot}CH_2\end{matrix}{>}C{\cdot}C_{10}H_7$-α. HCl and (VII) give an optically inactive *monohydrochloride* (XI), $C_{19}H_{21}Cl$, m.p. 99·5°, which is indifferent towards CaO, and is converted by AgOAc into a mixture of hydrocarbons and by Mg into a somewhat unsaturated hydrocarbon, m.p. 40—42°, of ill-defined composition. Cautious treatment of it with NaOEt gives the homogeneous, optically inactive *hydrocarbon*, $C_{19}H_{20}$, m.p. 55—56°, re-convertible into (XI). With Na and EtOH (XI) gives an optically inactive saturated *hydrocarbon*, $C_{29}H_{24}$, b.p. 128—130°/1·5 mm., which is therefore monocyclic. (VII) and PCl_5 give the *monohydrochloride*, $C_{19}H_{21}Cl$, m.p. 90—90·5°, $[\alpha]_D^{18}$ −132·5° in C_6H_6, which appears saturated towards Br and is converted by 0·2N-NaOEt into the feebly unsaturated *hydrocarbon*, $C_{19}H_{20}$, m.p. 50·5—51°, $[\alpha]_D^{22}$ −88·9° in C_6H_6. H. W.

Resolution of *cis*- and *trans*-norcaryophyllenic acid. H. N. Rydon (J.C.S., 1937, 1340—1342).—*Et cyanonorcaryophyllenate*, b.p. 133—136°/1·5 mm., obtained from Et αα′-dibromo-ββ-dimethyladipate and NaCN, is hydrolysed (KOH) to 3 : 3-*dimethyl*-cyclo*butane*-1 : 2 : 2(1 : 1 : 2)-*tricarboxylic acid*, m.p. 176° (decomp.), decarboxylated to a mixture of *cis*- and *trans*-norcaryophyllenic acid. Resolution of the *dl-cis*-acid through the cinchonidine salt [salt of *d*-acid, m.p. 215° (decomp.), $[\alpha]_{5461}^{20}$ −138·0° in EtOH] gives d-, m.p. 163—165°, $[\alpha]_{5461}^{20}$ +4·9° in $CHCl_3$, and l-*cis*-*norcaryophyllenic acid*, m.p. 165°, $[\alpha]_{5461}^{20}$ −5·9° in $CHCl_3$. The *dl-trans*-acid is resolved through the brucine salt (salt of *l*-acid, $[\alpha]_{5461}^{16\cdot5}$ −81·46° in $COMe_2$) into l-, m.p. 126°, $[\alpha]_{5461}^{18}$ −129·0° in $CHCl_3$, and d-trans-*norcaryophyllenic acid*, m.p. 123—125°, $[\alpha]_{5461}^{18}$ +122·3° in $CHCl_3$, which is identical with the *d*-acid obtained by oxidising caryophyllene. The bearing of this identity on the stereochemistry of caryophyllene is discussed, and it is pointed out that the assumption that natural products possess the most stable configuration is unjustifiable. F. R. S.

Elemic acid from manila elemi resin. IX. Dihydroelemolic acid. M. Mladenović (Monatsh., 1937, 30, 405—408; cf. A., 1936, 340).—Hydrogenation (Pd–C or PtO_2; EtOAc; room temp. or 60°) of elemolic acid (I), purified by way of derivatives, gives only dihydroelemolic acid, m.p. 238°. When purified only by crystallisation, (I), m.p. 220°, gives also a small amount of tetrahydroelemonic acid. Ruzicka's results (A., 1933, 69) were due to the use of impure (I). R. S. C.

Sapogenins of *Polygala senega*. W. A. Jacobs and O. Isler (J. Biol. Chem., 1937, 119, 155—170).—The crude saponin, senegin, from senega root, with EtOH–HCl gives a *prosapogenin*, further hydrolysed by EtOH–H_2O–HCl to a mixed sapogenin (I) containing a dihydroxydibasic acid, *senegenin* (II), $C_{30}H_{44}O_8$ or $C_{30}H_{46}O_8$, m.p. 290—292°, $[\alpha]_D^{23}$ +19° in EtOH (Me_2 ester). In alkali (II) opens a lactone ring and becomes tribasic, but is not regenerated on acidification. It is converted by AcOH–NaOAc into the Ac_2 derivative, m.p. 270° (decomp.), and a *substance*, m.p. 313°. The mixture (I), after removal of (II), gives a second *product*, which when heated with aq. NaOH yields a *dihydroxydicarboxylic acid* Et_1 *ester* (III), $C_{31}H_{50}O_6$ or $C_{31}H_{48}O_6$, m.p. 257° (rapid heating) (*Na* salt; *di*-p-*bromobenzoyl* derivative, m.p. 213°), in which no lactone group can be detected, but which gives the *Et ester diacetate*, with a less sol. *by-product*, no m.p. <340°. With CH_2N_2, (III) gives the *Me Et* ester; with KOH–$C_5H_{11}{\cdot}OH$, the *dihydroxydicarboxylic acid*, m.p. 230°, is obtained. Dehydrogenation (Se) of (II) gives products including a chrysene homologue, $C_{23}H_{22}$, m.p. 246·5°, apparently identical with Ruzicka's product from hederagenin (A., 1932, 517), with a substance, m.p. 198°, apparently trimethylpicene. Dehydrogenation of (III) gives similar products. E. W. W.

Sapogenin of *Gypsophila*. M. S. Taggart and G. H. Richter (Biochem. Z., 1937, 291, 349—353; cf. Karrer and Lier, A., 1926, 401).—The sapogenin, (I), probably $OH{\cdot}C_{24}H_{38}{\cdot}CO{\cdot}CO_2H$ (OH alcoholic) (*hydrazone*), is a pentacyclic α-keto-acid containing no aromatic ring. The semicarbazone of (I) with Na in EtOH at 180° for 8 hr. gives an *acid*, m.p. 302°, containing no active H. (I) treated successively at 150—160° for 10 hr. with HI and for 10 hr. with HI + red P yields the corresponding *hydrocarbon*, $C_{26}H_{44}$, d_4^{28} 0·9354, n_D^{28} 1·5029. W. McC.

Dracorubin. II. H. Brockmann and R. Haase (Ber., 1937, 70, [*B*], 1733—1738; cf. A., 1936, 1260).—Fresh analyses and determinations of mol. wt. of dracorubin (I), m.p. 314—315° when placed in bath preheated to 304°, $[\alpha]_{Cd}^{27}$ −35° in $CHCl_3$, its hydrochloride, *perchlorate*, and *picrate* establish the composition $C_{32}H_{24}O_5$ (instead of $C_{19}H_{14}O_3$) for (I) and its "obvious identity" with the dracocarmin of Hesse (A., 1936, 1435). Treatment of (I) with molten KOH affords COPhMe and BzOH; the latter is also obtained by the oxidation of (I) with CrO_3 or H_2O_2. (I) is rapidly decolorised by Zn dust in AcOH–C_5H_5N but not in AcOH alone; the colour is restored by air. (I) is converted by Br in $CHCl_3$ into *dibromodracorubin*, decomp. about 300° (*hydrobromide*). Hydrogenation (Pt in AcOH) of (I) give the sparingly sol. α-*hydro*-

dracorubin (II), $C_{32}H_{38}O_5$ (possibly $C_{32}H_{40}O_5$), m.p. 248° (decomp.), $[\alpha]_D^{20}$ +74° in C_5H_5N, which appears to contain at least one OH. Since (I) does not contain active H this OH must be formed by reduction of CO, hence fixing the function of a second O in (I). With NH_2OH (I) yields a cryst. product. COPhMe is not formed by the action of molten KOH on (II). (II) is readily oxidised by air and is converted by chloranil in C_6H_6 into β-*dracorubin*, $C_{32}H_{30}O_5$ (? $C_{32}H_{28}O_5$), m.p. 280° (corr.), which resembles (I) very closely and may be present in the crude drug. The mechanism of dehydrogenation is not elucidated but the process occurs in two stages. Oxidation of (I) with H_2O_2 gives a yellow, cryst., optically active *substance*, probably $C_{24}H_{20}O_6$, m.p. 248°, which can be hydrogenated and acetylated and is capable of thermal degradation. H. W.

Butyryl derivative of Congo copal. E. Mertens, L. Hellinckx, and C. de Hoffmann (Bull. Soc. chim. Belg., 1937, **46**, 253—255).—The copal is refluxed with technical abs. $PrCO_2H$ for 4 hr., and the excess of acid then distilled off at 150°. The *product*, m.p. 117—118°, consists of butyric esters of the OH-acid together with the other constituents of the copal. The *d*, acid, sap., ester., and I vals. are recorded. H. G. M.

Preparation of tetrahydrofuran. I. T. Strukov (Chim. Farm. Prom., 1935, No. 1, 35).—Tetramethylene glycol is treated with $SOCl_2$ and the product treated with NaOH and redistilled. Ch. Abs. (*r*)

Preparation of ditetrahydrofurfurylamines.—See B., 1937, 880.

Catalyst for oxidation of furfuraldehyde. V. J. Serdiukov (Maslob. Shir. Delo, 1934, No. 4, 43).—V_2O_5 may be replaced by V–Fe or V–Al alloys (8% V); these alloys are useful for other oxidations. Ch. Abs. (*r*)

Pharmaceutical application of furfuraldehyde. II. A. Mangini (Riv. Biol., 1937, **22**, 482—488).—Furfuraldehyde with *p*- or *o*-anisidine or *p*-phenetidine in EtOH–$AcCO_2H$ affords 6-*methoxy*-, m.p. 242—243° (decomp.) (*Na* salt), 8-*methoxy*-, m.p. 230—231° (decomp.) (*Na* salt), and 6-*ethoxy*-2-(2′-*furyl*)*cinchonic acid*, m.p. 218—219° (decomp.) (*Na* salt), respectively. The pharmacological properties of the above acids are compared with those of other atophan derivatives. F. O. H.

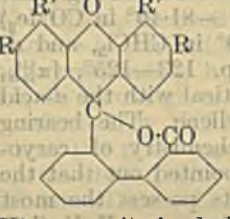
Condensation of methyl pyruvate with methyl malonate in presence of anhydrous zinc chloride. J. W. Baker and (Miss) A. S. Laufer (J.C.S., 1937, 1342—1348).—$AcCO_2Me$ and $CH_2(CO_2Me)_2$ (2 : 1 mol.) condense ($ZnCl_2$) to give *Me* 2-*keto*-3-*methyl*-2 : 5-*dihydrofuran*-5-*malonate*-5-*carboxylate* (I), m.p. 119°, and an unsaturated *ester*, $C_{14}H_{20}O_9$, b.p. 101°/0·6 mm. Hydrolysis of (I) with KOH yields the *Me* H_2 ester, m.p. 145° (decomp.), decarboxylated to 5-*carbomethoxy*-2-*keto*-3-*methyl*-2 : 5-*dihydrofuran*-5-*acetic acid*, m.p. 144°, with $Ba(OH)_2$ affords the *Ba* salt (+$4H_2O$), hydrolysed to 2-*keto*-3-*methyl*-2 : 5-*dihydrofuran*-5-*malonic acid*, m.p. 136° (decomp.), and with HCl forms the -5-*acetic acid* (II), m.p. 124° (*Me* ester, b.p. 126°/1 mm.), and α-methyl-lævulic acid (*p-nitrophenylhydrazone*, m.p. 170°; *p-nitrophenylhydrazone* of Me ester, m.p. 142°). α-Methyl-lævulic acid is obtained by hydrolysis of *Me* δ-*keto*-n-*pentane*-β*γ*-*dicarboxylate*, b.p. 128·5°/12 mm., from $CH_2Ac{\cdot}COMe$ and $CHMeBr{\cdot}CO_2Me$, whilst the β-acid is similarly prepared through *Me* *γ*-*keto*-β-*methyl*-n-*butane*-α*β*-*dicarboxylate*, b.p. 125—126°/11 mm. (*semicarbazone*, m.p. 151°). Hydrolysis of (II) with $Ba(OH)_2$ gives α-*methylmuconic acid*, m.p. 171° [synthesised in a form of high m.p., 276° (decomp.), from α-methyladipic acid], and catalytic reduction yields the H_2-acid, m.p. 96°. Reduction of (I) affords *Me* β-*hydroxy*-δ-*carbethoxy*-n-*pentane*-α*α*β-*tricarboxylate*, m.p. 107·5°, hydrolysed to 2-*keto*-3-*methyltetrahydrofuran*-5-*acetic*-5-*carboxylic acid*, m.p. 186°. Ozonolysis of (I) gives CH_2O and $H_2C_2O_4$ and of (II) yields CH_2O, HCO_2H, and some *dl*-malic acid. The inter relationships of the derivatives are summarised. F. R. S.

Synthesis of 6-methylcoumarin. A. M. Buluigina (Maslob. Shir. Delo, 1934, No. 4, 43—44).—On a semi-technical scale *p*-cresol and fumaric acid with 72% H_2SO_4 give a 40% yield of 6-methylcoumarin, m.p. 73—74°. Ch. Abs. (*r*)

Natural coumarins. XXXII. Partial synthesis of fraxidin and *iso*fraxidin and synthesis of a further derivative of 6 : 7 : 8-trihydroxycoumarin. E. Späth and Z. Jerzmanowska-Sienkiewiczowa (Ber., 1937, **70**, [*B*], 1672—1677).—Partial methylation of fraxetin (7 : 8-dihydroxy-6-methoxycoumarin) (I) with CH_2N_2 gives 8-hydroxy-6 : 7-dimethoxycoumarin and 7-hydroxy-6 : 8-dimethoxycoumarin, identical with fraxidin and *iso*fraxidin respectively. In an attempted synthesis of (I), 6 : 7 : 8-trihydroxycoumarin [prep. from 1 : 2 : 3 : 4-$C_6H_2(OH)_4$ described] is partly methylated but the *product* (II), m.p. 223—224° (vac.), is not identical with (I) and is either 6 : 8-dihydroxy-7-methoxy- or 6 : 7-dihydroxy-8-methoxy-coumarin. Further, pyrogallol carbonate is converted by conc. H_2SO_4 and HNO_3 at −10° into 4-*nitropyrogallol carbonate*, m.p. 151—153° (vac.), which with CH_2N_2 in Et_2O affords 4-*nitropyrogallol carbonate* 3-*Me ether*, b.p. 120—130° (bath)/0·005 mm., m.p. 125—127° (vac.); this is reduced ($ZnCl_2$–conc. HCl) to 3-*aminopyrogallol carbonate* 3-*Me ether*, the *hydrochloride* of which is transformed by H_2O at 140—150° into 1 : 3 : 4-*trihydroxy*-2-*methoxybenzene*, m.p. 101—102·5°, and thence by malic acid and conc. H_2SO_4 at 110—115° into (II). H. W.

Natural coumarins. XXXIII. Constitution of ammoresinol. E. Späth and F. Kesztler (Ber., 1937, **70**, [*B*], 1679—1680).—A reply to Raudnitz (this vol., 383). H. W.

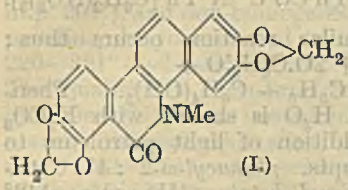
Utilisation of phenanthrene for synthesis of dyes of the type of fluorescein and rhodamine.



B. Bogoslovski (Prom. Org. Chim., 1937, **3**, 299—300).—Diphenic anhydride (I) and *m*-$C_6H_4(OH)_2$ (II), heated with $ZnCl_2$ (210°; 2 hr.), yield an *analogue* of fluorescein (R = OH, R′ = H). *Dyes* of the type of gallein (R = R′ = OH) or rhodamine (R = NEt_2, R′ = H) are obtained by substituting gallic acid or

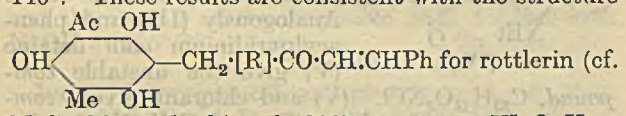
m-OH·C_6H_4·NEt_2 for (II) in the above reaction. The dyes are of no practical importance, both because of their poor dyeing qualities, and because of the low yields of (I) obtained by oxidation of phenanthrene. R. T.

New nitrogenous component of *Sanguinaria canadensis*, L. E. Späth, F. Schlemmer, G. Schenck, and A. Gempp (Ber., 1937, **70**, [*B*], 1677—1679).—Chromatographic analysis of the alkaloids in $CHCl_3$ by Al_2O_3 leads to the isolation of *hydroxysanguinarine* (I), m.p. 360—361° (vac.; corr.), $[\alpha]_D$ ±0°, also obtained by oxidation of sanguinarine nitrate by $K_3Fe(CN)_6$ in alkaline solution. H. W.



(I.)

Rottlerin. H. Brockmann and K. Maier (Naturwiss., 1937, **25**, 460).—Determination as the *p*-nitrophenylhydrazone shows that 1 mol. of PhCHO is formed from 1 mol. of rottlerin (I) when the latter is ozonised. Oxidation of (I) under various conditions yields neither *o*- nor *p*-$C_6H_4(CO_2H)_2$. The action of diazoaminobenzene on (I) yields a cryst. red *dye*, m.p. 206—206·5°, identified as 3-*benzeneazo*-2 : 4 : 6-*trihydroxy*-5-*acetyltoluene*. When (I) is boiled with EtOH, PhMe, or AcOH, it yields a yellow cryst. *product*, $C_{23}H_{22}O_6$ or $C_{27}H_{26}O_7$, m.p. 139—140°. These results are consistent with the structure



for rottlerin (cf. McGookin *et al.*, this vol., 300). W. O. K.

Difurylmethane derivatives. D. Dinelli [with G. B. Marini] (Gazzetta, 1937, **67**, 312—317).—Et furan-2-carboxylate (I) with $(CH_2O)_3$ in H_2SO_4 yields the *Et*$_2$ ester, b.p. 204°/4 mm., of 2 : 2′-*difurylmethane*-5 : 5′-*dicarboxylic acid*, m.p. 238° (also obtained by way of the Me and Me_2 esters). When distilled with Cu, this gives 2 : 2′-difurylmethane, and its 5-*carboxylic acid*, m.p. 118°. With $(MeCHO)_3$ in H_2SO_4, (I) gives the *Et*$_2$ ester, b.p. 210°/5 mm., of αα-2 : 2′-*difurylethane*-5 : 5′-*dicarboxylic acid*, m.p. 216°, decarboxylated (Cu) to the 5-*carboxylic acid*, m.p. 105°, and to αα-2 : 2′-*difurylethane*, b.p. 80°/10 mm. With PhCHO, (I) yields *Et*$_2$ 2 : 2′-*difurylphenylmethane*-5 : 5′-*dicarboxylate*, m.p. 212°. E. W. W.

Amino-acids containing sulphur. I. Synthesis of 2-thienylalanine. H. C. Yuan and H. C. Li (J. Chinese Chem. Soc., 1937, **5**, 214—218).—Thiophen-2-aldehyde Et_2 acetal, b.p. 223° [prep. from Mg 2-thienyl iodide and $CH(OEt)_3$ described], is converted by hippuric acid, fused NaOAc, and Ac_2O at 100° into 2-*phenyl*-4-2′-*thienylideneoxazolone*, m.p. 173—174°, which is transformed by boiling aq. Na_2CO_3 into α-*benzamido*-β-2-*thienylacrylic acid*, m.p. 227—228° (decomp.). This is reduced by Na–Hg to α-*benzamido*-β-2-*thienylpropionic acid*, m.p. 177—178·5°, hydrolysed by 6N-HCl to 2-*thienylalanine*, m.p. 246—246·5° (decomp.) (*picrolonate*, decomp. above 200°). H. W.

Manufacture of indigoid vat dyes [oxythionaphthens].—See B., 1937, 888.

Carbon compounds of the 1 : 9-anthrathiophen series.—See B., 1937, 880.

Structure of the sulphur black dye nigrosulphine K. V. Ufimtzev (Prom. Org. Chim., 1937, **3**, 354—359).—The results and conclusions of Chmelnitzkaja *et al.* (A., 1935, 1384) are questioned. Hydrolysis data suggest the presence of S·SO_3H, but not of SO_3H or S·SO_2H groups. R. T.

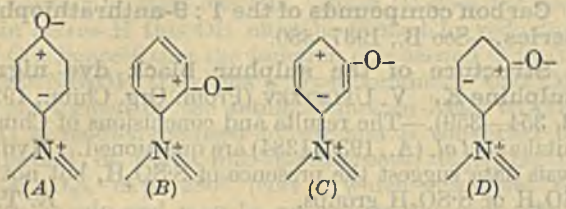
[Derivatives of *cyclo*tetramethylenepyrrole and their molecular compounds with substituted barbituric acids.] H. Ruhkopf (Ber., 1937, **70**, [*B*], 1835; cf. this vol., 307).—An acknowledgment of the publication of Lee and Christiansen (A., 1936, 1268). H. W.

Pyridine-2-acetic acid. M. P. Oparina (Chim. Farm. Prom., 1936, No. 2, 98—101).—Pyridine-2-acetic acid loses CO_2 in H_2O at 50—60°. The Me ester is more stable and may be hydrogenated (Pt) to piperidine-2-acetic acid; it yields CH_4 with Grignard reagents. Ch. Abs. (*r*)

2 : 3 : 6-Triaminopyridine. A. Tschitschibabin and C. Hoffmann (Compt. rend., 1937, **205**, 153—154; cf. A., 1916, i, 163).—2 : 6-Diamino-3-benzeneazopyridine with H_2–Ni in Ac_2O affords 2 : 3 : 6-*triacetamidopyridine*, m.p. 253°, hydrolysed (HCl in sealed tube) to the base (unstable in air), which is isolated as its *dihydrochloride*, m.p. 230° (decomp.) (block). J. L. D.

Mesomerism of 1-hydroxyphenylpyridinium bases. W. Schneider, W. Döbling, and R. Cordua (Ber., 1937, **70**, [*B*], 1645—1665; cf. A., 1924, i, 1107).—The differing colours of solutions of phenol betaines of the type of the 1-hydroxyphenylpyridinium bases are not related to a change of mol. wt. in solution. The simple mol. wt. of the substances in EtOH is not in harmony with the existence of a bimol. red base. Substituents *ortho* to the phenolic OH influence the character and colour of the bases according to the auxochromic or antiauxochromic nature. The lightly coloured NO_2-bases are well marked betaines since the NO_2 groups increase the anionic character of the mol. and so increase the polar contrast to the cationic character dependent on the pyridinium complex. These substituents therefore displace the condition of the mol. towards the betaine structure and also stabilise it so that solvatochromism almost disappears. NH_2 and NHAc groups act in the opposite direction, diminishing the polar contrast within the mol. The condition of the mol. is therefore displaced from the true betaine form. Solvation displaces this condition stepwise in accordance with the nature of the solvent more or less in the sense of an approximation to the betaine structure since the dipoles of the solvent are attracted to the polar centres of the mol. and stabilise the zwitterions as such and saturate the system from without. In the blue and green solutions and particularly in the solid anhydrides the mol. is farthest removed from the betaine condition; therefore the colour is deepest here and the chemical character is most unsaturated. This second, unsaturated limiting

condition, initially interpreted by a quinonoid constitution, is best expressed by the " polar quinonoid " structures *A* and *B*, whilst for *m*-derivatives, which show analogous behaviour, the " polar *m*-quinonoid " constitutions *C* and *D* are available.

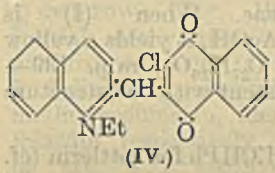


2 : 4 : 6-Triphenylpyrylium iodide, anhyd. NaOAc, and *p*-$NH_2 \cdot C_6H_4 \cdot OH$ in boiling AcOH yield 2 : 4 : 6-*triphenyl*-1-p-*hydroxyphenylpyridinium betaine*, red *hexahydrate* (I), m.p. 199°, and blue-black *anhydride* (II). (I) becomes orange-yellow when cooled in liquid air whereas (II) remains unchanged. The colours of the solutions of (II) in various media are recorded, together with their changes with alterations of temp. (II) and MeI afford 2 : 4 : 6-*triphenyl*-1-p-*anisylpyridinium iodide*, m.p. 305—306°. 2 : 4 : 6-*Triphenyl*-1-o-*hydroxyphenylpyridinium iodide* (+1AcOH), m.p. 188°, gives the corresponding *betaine*. 2 : 4 : 6-*Triphenyl*-1-m-*hydroxyphenylpyridinium iodide*, m.p. 299—300°, is converted by alkali into *compounds* $(C_{29}H_{21}ON)_3$,HI and $(C_{29}H_{21}ON)_{14}$,HI, m.p. 135° and 153° respectively; the corresponding betaine base is non-cryst. (I) in AcOH is converted by conc. HNO_3 at room temp. into 2 : 4 : 6-*triphenyl*-1′-*nitro*-4′-*hydroxyphenylpyridinium nitrate*, decomp. about 175° after softening at about 145°, transformed by alkali into 2 : 4 : 6-*triphenyl*-1-*nitro*-4′-*hydroxyphenylpyridinium betaine*, m.p. 290°. 2 : 4 : 6-*Triphenyl*-1-*nitro*-3′-*hydroxyphenylpyridinium betaine* (+0·5H_2O), m.p. 345° [corresponding *nitrate* (+1H_2O), decomp. about 150° after softening at 130°], and 2 : 4 : 6-*triphenyl*-1-*dinitro*-2′-*hydroxyphenylpyridinium betaine*, m.p. about 335° on block preheated to 330° (corresponding *nitrate*, m.p. about 340°), are described. Reduction of the NO_2-compounds gives the corresponding amines. The readily oxidised 2 : 4 : 6-*triphenyl*-1-*amino*-4′-*hydroxyphenylpyridinium betaine* is isolated as the *benzoate*, $C_{29}H_{22}ON_2$,2BzOH, m.p. 219—220°, transformed by hot Ac_2O into 2 : 4 : 6-*triphenyl*-1-*acetamido*-4′-*hydroxyphenylpyridinium betaine* (+6H_2O), m.p. 198—200°. 2 : 4 : 6-*Triphenyl*-1-*amino*-3′-*hydroxyphenylpyridinium betaine* gives a *chloride* (+1H_2O), m.p. 207—208°, converted by Ac_2O + NaOAc into 2 : 4 : 6-*triphenyl*-1′-*acetamido*-3′-*hydroxyphenylpyridinium betaine* (+4H_2O), m.p. 163—164°. 2 : 4 : 6-*Triphenyl*-1-*diamino*-2′-*hydroxyphenylpyridinium betaine* is transformed by NaOAc and Ac_2O into the Ac_2 derivative, the *chloride* of which has m.p. 225—226° after softening at 210°. 2 : 4 : 6-*Triphenyl*-1-m-*methoxyphenylpyridinium iodide*, m.p. 232°, is converted by conc. HNO_3 in AcOH at 100° into the *substance* $C_{30}H_{23}O_3N_2I$, m.p. (indef.) 140°, reduced to a non-cryst. amine, which gives a pure yellow solution in $CHCl_3$. H. W.

Enol betaines. VII. Explanation of the colour reactions with picryl chloride and chloranil. F. Kröhnke and H. Schmeiss (Ber., 1937, **70**, [*B*], 1728—1732).—The formation of coloured compounds in the reaction between picryl chloride (I) and phenacylcyclammonium salts is attributed to mesomerism as shown by the scheme.

$(NO_2)_3C_6H_2Cl + R \cdot C(O^-){:}CH \cdot N^+\{ \rightarrow HCl + Ph \cdot C(O^-){:}C(N^+Ph) \cdot C_6H_2(NO_2)_3 \rightleftharpoons Ph \cdot CO \cdot C^- \cdot N^+Ph \cdot [C_6H_2(NO_2)_3]$.

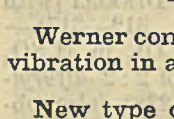
With quinones a similar reaction occurs thus: $Ph \cdot C(O^-){:}CH \cdot N^+C_5H_5 + 2O{:}C_6H_4{:}O \rightarrow Ph \cdot C(O^-){:}C(C_6H_3O_2) \cdot N^+C_5H_5 + C_6H_4(OH)_2$. Phenacylpyridinium salt in H_2O is shaken with K_2CO_3 and (I) in $CHCl_3$; addition of light petroleum to the $CHCl_3$ solution ppts. *phenacyl*-ω-2′ : 4′ : 6′-*trinitrophenylpyridinium enol betaine* (II), m.p. 142° (decomp.) (*perchlorate*, m.p. about 75°). When heated with 5N-HCl (II) yields BzOH. *Phenacyl*-ω-2′ : 4′-*dinitrophenylpyridinium enol betaine*, m.p. 187° (decomp.) (*perchlorate*, m.p. 157°), yields BzOH when warmed with N-NaOH at 50°. *Phenacyl*-ω-5′-*chloro*-2′ : 4′-*dinitrophenylpyridinium enol betaine* has m.p. 167° (decomp.). p-*Methylphenacyl*-ω-2′ : 4′ : 6′-*trinitrophenylpyridinium enol betaine*, m.p. 168—169°, is described. *Phenacyl*-ω-2′ : 4′ : 6′-*trinitrophenyliso*-*quinolinium enol betaine*, m.p. 119—120° (decomp.), gives a *mono-* and *di-hydrate*. 2-Methylquinoline ethiodide and 2 : 3-dichloro-α-naphthaquinone (III) afford the *compound* (IV), which becomes grey at 170—177°. Analogously (III) and phenacylpyridinium enol betaine (V) give the unstable *compound*, $C_{23}H_{14}O_3NCl$. (V) and chloranil give a *compound*, m.p. 185°, whilst (V) and $C_6H_3(NO_2)_3$ give the *adduct*, m.p. 152° (decomp.). H. W.



(IV.)

Werner complexes. Dissimulation of the N–H vibration in ammine complexes.—See A., I, 443.

New type of indole base. J. von Braun and J. Nelles [with A. May] (Ber., 1937, **70**, [*B*], 1767—1776).—4-Benzylpyridine is almost unchanged when passed over reduced Cu turnings at 580—590° whereas the 2-benzyl compound is transformed into the indole *base* (I), m.p. 175—176° (*hydrochloride*, m.p. 132°; *picrate*, m.p. 138°; *methiodide*, m.p. 231°). Alkali and most acids have little action on (I) but AcOH causes a profound change. The green *NO*-compound, m.p. 221—223°, gives colourless solutions in acids; it gives a *methiodide*, m.p. 190°. Reduction of (I) with Na and EtOH or, preferably, amyl alcohol gives the H_4-derivative, b.p. 152—154°/0·3 mm., m.p. 56° (*methiodide*, m.p. 127°; *methochloride*, m.p. 211°; *platinichloride*, m.p. 197°; 3 : 5-*dinitroso*-1 : 2-*tetramethyleneindole hydrochloride*). Reduction of (I) with Sn and HCl gives the H_6-compound, b.p. 118—122°/0·25 mm., m.p. 26° (*hydrochloride*, m.p. 150°; *picrate*, m.p. 132°; *NO*-derivative, m.p. 227°; *methiodide*, m.p. 140°; *methochloride*, m.p. 95°, and the corresponding *platinichloride*, m.p. 194°). 2-Methylpyridine and CH_2PhCl give a quaternary *chloride*, m.p. 95°, converted by heating with Cu into a mixture of



(I.)

4-*benzyl*-2-*methylpyridine*, b.p. 154°/13 mm. (*picrate*, m.p. 117°), which is unchanged at 580°, and 6-*benzyl*-2-*methylpyridine*, b.p. 150°/14 mm. (*picrate*, m.p. 147°), which passes with loss of Me into the base (I). The hygroscopic quaternary *chloride*, m.p. 162°, from 2-$C_{10}H_7$·CH_2Cl and C_5H_5N gives 4-2′-*naphthylmethylpyridine*, m.p. 78° (*picrate*, m.p. 175°; *hydrochloride*, m.p. 201°), and non-homogeneous 2-2′-*naphthylmethylpyridine*, dehydrogenated to the *base*, $C_{16}H_{13}N$, m.p. 220—221° (*hydrochloride*, m.p. 85°; *picrate*, m.p. 128°). The quaternary compound from CH_2PhCl and *iso*quinoline (II) when heated in presence of Cu yields mainly 1-*benzylisoquinoline*, m.p. 50—52° (*picrate*, m.p. 182—184°; *hydrochloride*, m.p. 179—181°; *platinichloride*, decomp. 216—218°). This is dehydrogenated to the *compound* (III), $C_{16}H_{11}N$, m.p. 238°, which has only feebly basic character. It is reduced by Sn and HCl to the H_4-compound, b.p. 170—175°/0·6 mm. (*hydrochloride*, m.p. 155—157°; *picrate*, m.p. 139—140°; *platinichloride*, m.p. 180°; *methiodide*, m.p. 217°), which could not be acetylated and is oxidised by HNO_3 mainly to *o*-$C_6H_4(CO_2H)_2$. The quaternary *compound*, m.p. 210—212°, from (II) and *o*-C_6H_4Me·CH_2Cl yields the *substance*, $C_{17}H_{15}N$, m.p. 60—62° (*picrate*, m.p. 180—181°), which is dehydrogenated to (III). H. W.

Preparation of 8-hydroxyquinoline. O. J. Magidson (Chim. Farm. Prom., 1935, No. 1, 20—23).—Quinoline is sulphonated at 160° with 20% oleum and the Ca salt of the sulphonic acid treated with NaOH at 225°/17—18 atm. Ch. Abs. (*r*)

Iodohydroxyquinolinesulphonic acid. S. Vinaver (Chim. Farm. Prom., 1935, No. 2, 109—110).—Hydroxyquinolinesulphonic acid is best iodinated by addition of I to the Na salt. Ch. Abs. (*r*)

2 : 6- and 2 : 8-dimethyl-4-chloroquinolines. General properties. Reaction with amines. A. Meyer and H. Drutel (Compt. rend., 1937, **205**, 148—151; cf. this vol., 389).—The Na derivatives of 4-hydroxy-2 : 6- and -2 : 8-dimethylquinoline with PCl_5, $POCl_3$, or $SOCl_2$ afford 4-*chloro*-2 : 6- (I), m.p. 63·5°, and -2 : 8-*dimethylquinoline* (II), m.p. 72°, respectively. With NH_2Ph, *p*-C_6H_4Me·NH_2, and α-$C_{10}H_7$·NH_2 (I) and (II) in boiling AcOH give 4-*anilino*-2 : 6-, m.p. 172°, and -2 : 8-, m.p. 121°, 4-p-*toluidino*-2 : 8-, m.p. 127—128°, and 4-α-*naphthylamino*-2 : 8-*dimethylquinoline*, m.p. 155—156°, respectively, which afford cryst. salts and quaternary NH_4 compounds. *o*-C_6H_4Me·NH_2 and β-$C_{10}H_7$·NH_2 do not react. *p*-$C_6H_4(NH_2)_2$ and benzidine each react with 2 mols. of (I) and (II) to give bases isolated as their acetates, viz.: p-*phenylenedi*-4-(2 : 6-, m.p. 325—327° (decomp.), and -(2 : 8-*dimethylquinolinyl*)*amine* + 2*AcOH*, m.p. 309—310° (decomp.); pp′-*diphenyldi*-4 : 4′-(2 : 6-, m.p. 320—322° (decomp.), and -(2 : 8-*dimethylquinolinyl*)*amine* + 2*AcOH* (III), m.p. 305—307° (decomp.). With dil. NaOH (III) gives the free *base*, m.p. 233—234°. With piperazine (I) and (II) give similarly NN-*di*-4-(2 : 6-, m.p. 322—324°, and -(2 : 8-*dimethylquinolyl*)*piperazine*, m.p. 319—320°, respectively. When boiled with NH_2Me, NH_2Et, $NHEt_2$, and $NHPh_2$ (I) and (II) lose Cl to give the acetates of the corresponding OH-compounds. J. L. D.

Carboxylic acid amides derived from aza-compounds.—See B., 1937, 880.

Claisen-type condensations with quinaldine and related ammono-ketone ethers. F. W. Bergstrom and A. Moffat (J. Amer. Chem. Soc., 1937, **59**, 1494—1497).—Quinaldine, EtOBz, and KNH_2 (2·5 mols.) in Et_2O give 2-phenacylquinoline (I), m.p. 116·4—117·1°. Similarly are prepared 2-p-*bromo*-, m.p. 165·7—167·2°, 2-*o*-*chloro*-, m.p. 115·9—117°, 2-p-*methoxy*-, m.p. 154·5—155°, and 2-p-*methyl*-*phenacylquinoline*, m.p. 170—171°, ω-*furoylquinaldine*, m.p. 102·9—103·4°, 2-*phenacyl*-, m.p. 207·8—208·8°, and 2-p-*methoxyphenacyl*-5 : 6-*benzoquinoline* (II), m.p. 158—158·5°, 3-*phenacyl*-2-*methyl*-, m.p. 125·6—126·5°, and 2 : 3-*diphenacylquinoxaline*, m.p. 204·5—205·2°. The alternative structure, 1-benzoyl-2-methylene-1 : 2-dihydroquinoline etc., is not excluded, but is less probable. The substances are weak bases, giving hydrochlorides which dissociate in H_2O, and ketonic derivatives could not be obtained. Aliphatic esters do not undergo the condensation, nor can AcCl, BzCl, *p*-NH_2·C_6H_4·CO_2Et, or *p*-OH·C_6H_4·CO_2Et be used; 2-*n*-propyl-, 4-methyl-, and 2 : 4-dimethyl-quinoline could not be used owing to the insolubility of the K salts. Reduction of (I) could not be effected; $KMnO_4$ gave only BzOH; Br (4 equivs.) gives tribromoquinaldine (II), but 6 equivs. gives also BzBr. Bromination of (II) gives (III) (30), *p*-OMe·C_6H_4·COBr (22), and *p*-OMe·C_6H_4·CO_2H (17%). R. S. C.

Heterocyclic compounds. II. Synthesis of 5-keto-2 : 3 : 5 : 6-tetrahydro-α-quinindene derivatives. S. Z. Ahmad and R. S. Desai (Proc. Indian Acad. Sci., 1937, **5**, A, 543—550).—Equimol. amounts of Et *cyclo*pentanone-2-carboxylate (I) and NH_2Ph at 155—160° afford *cyclo*pentanone-2-carboxyanilide and the cyclised form 5-keto-2 : 3 : 5 : 6-tetrahydro-α-quinindene (cf. A., 1929, 1312). Similarly (I) and *p*-C_6H_4Me·NH_2 afford cyclo*pentanone*-2-*carboxy*-p-*toluidide*, m.p. 130°, and 1-p-*tolylamino*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxy*-p-*toluidide*, m.p. 143°; the former alone is cyclised (conc. H_2SO_4 at 100°) to 5-*keto*-10-*methyl*-2 : 3 : 5 : 6-*tetrahydro*-α-*quinindene*, m.p. 295°. Similarly (I) and *m*-4-xylidine afford cyclo*pentanone*-2-*carboxyxylidide*, m.p. 107—108°, cyclised to 5-*keto*-9 : 10-(or ? 10 : 11-)*dimethyl*-2 : 3 : 5 : 6-*tetrahydro*-α-*quinindene*, m.p. 280°, and 1-*xylidino*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxyxylidide*, m.p. 184°. Similarly (I) with the appropriate amine affords: 1-p-*chloroanilino*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxy*-p-*chloroanilide*, m.p. 173—174°, 1-p-*bromoanilino*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxy*-p-*bromoanilide*, m.p. 179°, 1-*o*-*anisidino*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxy*-*o*-*anisidide*, m.p. 130—131°, 1-α-*naphthylamino*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxy*-α-*naphthalide*, m.p. 164°, and 1-β-*naphthylamino*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxy*-β-*naphthalide*, m.p. 184°. None of these compounds is cyclised with conc. H_2SO_4. 4-Methyl*cyclo*pentanone-2-carboxylate (II) with NH_2Ph and *p*-C_6H_4Me·NH_2 affords products which cannot be obtained cryst., but are cyclised (warm conc. H_2SO_4) to 5-*keto*-, m.p. 249°, and 5-*keto*-2 : 10-*dimethyl*-, m.p. 230—231°, -2 : 3 : 5 : 6-*tetrahydro*-α-*quinindene*,

respectively. Similarly treated (II) and *m*-4-xylidine afford 4-*methyl*cyclo*pentanone*-2-*carboxy-xylidide*, m.p. 114°, cyclised to 5-*keto*-2 : 9 : 10-(or ? 2 : 10 : 11-)*trimethyl*-2 : 3 : 5 : 6-*tetrahydro*-α-*quinindene*, m.p. 215°, and 1-*xylidino*-4-*methyl*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxyxylidide*, m.p. 180°. Similarly (II) with *p*-$C_6H_4Cl{\cdot}NH_2$ and *p*-$C_6H_4Br{\cdot}NH_2$ affords 1-p-*chloroanilino*-4-*methyl*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxy*-p-*chloroanilide*, m.p. 167—168° and 1-p-*bromoanilino*-4-*methyl*-$\Delta^{1:2}$-cyclo*pentene*-2-*carboxy*-p-*bromoanilide*, m.p. 185°, respectively. When (II) is boiled with an arylamine for a few min. a *s*-diarylcarbamide is formed. J. L. D.

Friedel–Crafts reaction. I. Synthesis of new pharmaceutical compounds. P. Kränzlein (Ber., 1937, **70**, [*B*], 1776—1787).—4-Amino-*o*-xylene is converted by AcCl and C_5H_5N into 4-*acetamido*-*o*-*xylene*, m.p. 96·5°, which gives 4-*acetamido*-5-*chloro-acetyl*-*o*-*xylene*, m.p. 167°; this, in MeOH–H_2O, is treated successively with NaOH and air whereby 5 : 6-5′ : 6′-*tetramethylindigotin* is obtained, which is oxidised by HNO_3–CrO_3 to 5 : 6-*dimethylisatin* (I), m.p. 214—215°. Attempts to obtain (I) directly from 5 : 6-dimethylindoxyl were unsuccessful. COPhMe, (I), and 33% KOH at 100° yield 2-*phenyl*-6 : 7-*dimethylquinoline*-4-*carboxylic acid* (*dimethyl-atophan*) (II), m.p. 251·5°. 2-*Acetamido*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 106°, is converted by $CH_2Cl{\cdot}COCl$ and $AlCl_3$ in CS_2 into 2-*acetamido*-3-*chloroacetyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 148°, and thence into 5 : 6 : 5′ : 6′-*di*cyclo*tetramethyl-eneindigotin*, which is oxidised to 5 : 6-cyclo*tetra-methyleneisatin*, m.p. 194°. This is converted by COPhMe and 33% KOH into 2-*phenyl*-6 : 7-cyclo-*tetramethylenequinoline*-4-*carboxylic acid* (III), m.p. 237°. 5-*Acetamidohydrindene*, m.p. 104°, affords successively 5-*acetamido*-6-*chloroacetylhydrindene*, m.p. 167°, 5 : 6 : 5′ : 6′-*di*cyclo*trimethyleneindigotin*, 5 : 6-cyclo*trimethyleneisatin*, m.p. 206°, and 2-*phenyl*-6 : 7-cyclo*trimethylenequinoline*-4-*carboxylic acid* (IV), m.p. 261°. (II), (III), and (IV) are probably slightly more toxic than atophan; they have no vitamin-B_2 action and have no advantage over other atophan preps. with respect to uric acid metabolism.

o-$C_6H_4Cl{\cdot}COCl$, 1 : 2 : 4-$C_6H_3Me_2{\cdot}NHAc$, and $AlCl_3$ in CS_2 afford 2′-*chloro*-2-*acetamido*-4 : 5-*dimethyl-benzophenone*, m.p. 173°, hydrolysed by cold, dil. NaOH to 2′-*chloro*-2-*amino*-4 : 5-*dimethylbenzophen-one*, m.p. 120°. *o*-$C_6H_4Cl{\cdot}CO_2H$, *o*-4-xylidine, K_2CO_3, and Cu powder give 3′ : 4′-*dimethyldiphenylamine*-2-*carboxylic acid*, m.p. 188—189°, converted by conc. H_2SO_4 at 80° or, less advantageously, by P_2O_5 in $PhNO_2$ into 2 : 3-*dimethylacridone*, m.p. 297°. This is reduced by Na and boiling amyl alcohol to 2 : 3-*dimethyl*-5 : 10-*dihydroacridine*, m.p. 215°, oxidised by $FeCl_3$ to 2 : 3-*dimethylacridine* (V), m.p. 162°. 3′ : 4′-cyclo-*Tetramethylenediphenylamine*-2-*carboxylic acid*, m.p. 173°, is cyclised by conc. H_2SO_4 at 80° to 2 : 3-cyclo-*tetramethyleneacridone*, m.p. 309°; this is reduced by Na and boiling amyl alcohol to 2 : 3-cyclo*tetramethyl-ene*-5 : 10-*dihydroacridine*, m.p. 169—170°, oxidised ($FeCl_3$) to 2 : 3-cyclo*tetramethyleneacridine* (VI), m.p. 117°. 3′ : 4′-cyclo*Trimethylenediphenylamine*-2-*carboxylic acid*, m.p. 176°, yields successively 2 : 3-cyclo*trimethyleneacridone*, m.p. 338°, 2 : 3-cyclo-*trimethylene*-5 : 10-*dihydroacridine*, m.p. 209°, and 2 : 3-cyclo*trimethyleneacridine* (VII), m.p. 152°. Physiologically, substitution in the 2 : 3-position by alkyl or *cyclo*alkyl groups appears to diminish the toxicity of acridine and also weakens its disinfecting action. The effect is similar to that observed by Kuhn in the flavin series. H. W.

6 : 9-Diamino-2-ethoxyacridine. M. Bazuirin (Chim. Farm. Prom., 1935, No. 2, 108—109).—6-Nitro-9-amino-2-ethoxyacridine is best reduced with Fe filings in slightly acid or neutral solution.

Ch. Abs. (*r*)

Synthesis of anthrapyridines [azanthracenes]. J. von Braun and J. Nelles (Ber., 1937, **70**, [*B*], 1760—1766).—The synthesis of β-azanthracenes is described: *o*-$C_6H_4Me{\cdot}CH_2Cl$ and C_5H_5N give the quaternary *chloride*, m.p. 183°, converted by Cu powder at 250° into *dixylylpyridine*, b.p. 190—195°/0·4 mm., and a mixture (I) of monoxylylpyridines from which *picrates*, m.p. 156—158° (derived from the 2-) and m.p. 136—138° (derived from the 4-compound), respectively, are isolated. Ring-closure of (I) is caused with difficulty by pumice, pumice–PbO_2, or S and is best effected by Cu turnings at 580—590°, whereby α-azanthracene (II), m.p. 114°, and β-azanthracene (III) (*hydrochloride*, m.p. 235°; *methiodide*, m.p. 255°; *picrate*, m.p. 248—250°), are obtained. Treatment of (III) with CrO_3 in AcOH gives the corresponding quinone, m.p. 189—190°, whereas Sn and HCl transform it into the H_4-base, m.p. 147°. The quaternary *chloride*, m.p. 154—156°, from 2-methylpyridine and *o*-$C_6H_4Me{\cdot}CH_2Cl$ gives a mixture (from which *picrates*, m.p. 145°, and m.p. 148—149°, respectively, are prepared), which is dehydrogenated at 580° to a *methyl*-β-*azanthracene*, m.p. 175—183°. C_5H_5N and 2 : 4-$C_6H_3Me_2{\cdot}CH_2Cl$ rapidly afford a non-cryst. quaternary *compound*, converted by Cu into a mixture of bases (*picrates*, m.p. 170—174° after softening at 150°) which at 580° gives the homogeneous *base*, $C_{14}H_{11}N$, m.p. 170—180° (*hydrochloride*, m.p. 244—245°). The hygroscopic quaternary *compound* from C_6H_8N and 1 : 3-dimethyl-4 : 6-dichloromethylbenzene yields a mixture of bases from which a *product*, $C_{26}H_{20}N_2$, m.p. 142°, is isolated. The amount of material is inadequate for further work but the two-sided condensation with the base is established. H. W.

Manufacture of 4-hydroxynaphthostyril and its substitution products.—See B., 1937, 880.

Preparation of anthraquinone derivatives.—See B., 1937, 880.

Barbituric acid derivatives. II. Comparison of 2-thiol compounds of 4-imino-5-methylthio-barbituric acid and 5-methylbarbituric acid. T. Nishikawa (J. Chem. Soc. Japan, 1935, **56**, 1487—1494).—The prep. and properties of the 2-Me, -Et, -Pr$^{\alpha}$, -Bu$^{\alpha}$, and -Bu$^{\beta}$ derivatives of 4-imino-5-methylthio- and 5-methylthiobarbituric acids are described. Theoretical explanations are advanced for the observed differences in properties. Ch. Abs. (*r*)

Carbylamines. XXI. Reaction with 1-phenyl-3-methyl-5-pyrazolone. M. PASSERINI and V. CASINI (Gazzetta, 1937, **67**, 332—336).—When boiled with PhNC in C_6H_6, this pyrazolone yields the *anil*, m.p. 153—155°, of 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*aldehyde*, m.p. 173—175° (*phenylhydrazone*, m.p. 158—159°), converted by boiling H_2O into methenyl-bis-(1-phenyl-3-methyl-5-pyrazolone). E. W. W.

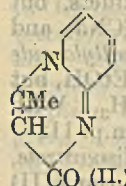
Catalytic fission of the glyoxaline ring. S. EDLBACHER and A. VON SEGESSER (Naturwiss., 1937, 25, 556—557; cf. this vol., 307).—Elimination of 2 mols. of NH_3 is accompanied by loss of 2 mols. of CO_2 during the catalytic fission of histidine by ascorbic acid (I) and traces of Fe. Identical results are obtained with *l*-, *d*-, or *dl*-histidine monohydrochloride; this may be due to the high concn. of (I). The formation of histamine could not be observed. H. W.

[Derivatives of *cyclo*tetramethylenepyrazole and their molecular compounds with substituted barbituric acids.] J. LEE (Ber., 1937, 70, [*B*], 1835).—A claim for priority against Ruhkopf (this vol., 307). H. W.

Piperazine. S. VINAVER (Chim. Farm. Prom., 1934, No. 6, 11—14).—*p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ and $(CH_2Br)_2$ are condensed and the resulting ditoluenesulphonylpiperazine is decomposed with H_2SO_4. Medicinally the H tartrate is preferable to the free base. CH. ABS. (*r*)

Hydrogen cyanide. X. The tetrapolymeride. L. E. HINKEL, G. O. RICHARDS, and O. THOMAS (J.C.S., 1937, 1432—1437).—The previous evidence for the structure of the polymerised form of HCN is critically reviewed, and in support of the quadrimol. structure the following evidence is adduced indicating it to be aminoiminosuccinonitrile (I). With $(CHO)_2$, (I), m.p. 181° (decomp.) (*hydrochloride*, decomp. 134°), affords a *substance*, $C_6H_4ON_4$, decomp. 240°, converted by boiling aq. $H_2C_2O_4$ into 6-*hydroxy*-2 : 3-*dicyanodihydropyrazine*, m.p. 132°, hydrolysed (Na_2O_2) to pyrazinedicarboxylic acid. With the appropriate aldehyde, (I) yields *benzylidene*- (II), m.p. 191° (decomp.), *salicylidene*-, m.p. 234° (decomp.), *m-bromosalicylidene*-, m.p. 250°, *anisylidene*-, m.p. 227° (decomp.), and iso*butylidene-aminoiminosuccinonitrile*, m.p. 91° (decomp.). With Ac_2O, (I) affords successively *acetamidoiminosuccinonitrile* (III), m.p. 164° (decomp.), and *acetamidoacetimidosuccinonitrile*, m.p. 224° (decomp.); (II) with Ac_2O yields *benzylidene-aminoacetimidosuccinonitrile*, m.p. 227° (decomp.). With Ac_2, (I) affords 2 : 3-*dicyano*-5 : 6-*dimethylpyrazine*, m.p. 171°, hydrolysed (Na_2O_2) to 2 : 3-dimethylpyrazinedicarboxylic acid, and with Bz_2, 2 : 3-*dicyano*-5 : 6-*diphenylpyrazine*, m.p. 246°. With HNO_2 (I) yields 4 : 5-dicyano-1 : 2 : 3-triazole, hydrolysed to 1 : 2 : 3-triazole-4 : 5-dicarboxylic acid, whilst (III) with HNO_2 gives 4(or 5)-*cyano*-1 : 2 : 3-*triazole*-5(or 4)-*carboxylamide*, m.p. 219° (decomp.). Oxidation (nitrous fumes) of (II) gives 4 : 5-*dicyano*-2-*phenylglyoxaline*, m.p. 261° (decomp.), hydrolysed (NaOH–EtOH) to 2-phenylglyoxaline-4 : 5-dicarboxylic acid. J. D. R.

[Condensation of] 2-aminopyridine [with ethyl acetoacetate]. G. B. CRIPPA and E. SCEVOLA (Gazzetta, 1937, **67**, 327—332).—2-$C_5H_4N{\cdot}NH_2$ (I) and $CEt_2(COCl)_2$ in C_5H_5N form *diethylmalonbis*-(2-*amidopyridine*), m.p. 115°. With $CH_2Ac{\cdot}CO_2Et$ and conc. HCl at 150—180°, (I) gives first 2-acetoacetamidopyridine, new m.p. 84° (cf. A., 1911, i, 327), which readily loses H_2O to give 4-*keto*-6-*methyl*-1 : 4-*dihydropyridino*-1′ : 2′ : 1 : 2-*pyrimidine* (II), m.p. 123° (*hydrochloride*). E. W. W.



(II.)

Relation between taste and chemical constitution. Naphthoisotriazine group. I. A. NERI and G. GRIMALDI. **II. III.** A. NERI (Gazzetta, 1937, **67**, 273—282, 282—288, 289—293).—I. 1-*p*-Sulphobenzeneazo-β-naphthylamine (I) (as Na salt) and PhCHO in AcOH yield 3-*phenyl*-2-p-*sulphophenyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*, no m.p., sweet (*Na* salt). 2 : 6-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ and PhN_2Cl give 1-*benzeneazo*-β-*naphthylamine*-6-*sulphonic acid* (II) (*Na* salt), which with NaOAc–AcOH–PhCHO yields 2 : 3-*diphenyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic acid*, bitter (*Na* salt, $+6H_2O$). Similarly 1-p-*sulphobenzeneazo*-β-*naphthylamine*-6-*sulphonic acid* (III) gives 3-*phenyl*-2-p-*sulphophenyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic acid*, very sweet. 2-Benzeneazo-α-naphthylamine-4-sulphonic acid (IV) yields 2 : 3-*diphenyl*-2 : 3-*dihydro*-1 : 3 : 4-*naphthoisotriazine*-6-*sulphonic acid*, tasteless; the 2-*p*-sulphobenzeneazo-acid (V) gives the 2-*phenyl*-3-p-*sulphophenyl*-*sulphonic acid*, sweet (Na_2 salt, $+7H_2O$). Sweetness thus apparently depends on *p*-SO_3H being attached to *N*-Ph.

II. With *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ in AcOH, (IV) yields 3-*phenyl*-2-o-*hydroxyphenyl*-2 : 3-*dihydro*-1 : 3 : 4-*naphthoisotriazine*-6-*sulphonic acid*, tasteless (*Na* salt, $+2{\cdot}5$ H_2O); the corresponding 3-p-*sulphophenyl*-*sulphonic acid*, from (II), is sweet. Similarly (I) gives 2-p-*sulphophenyl*-3-o-*hydroxyphenyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*, tasteless (Na_2 salt, $+2{\cdot}5$ H_2O), and (II) yields 2-*phenyl*-3-o-*hydroxyphenyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic acid*, bitter, whilst (III) gives the corresponding 2-p-*sulphophenyl*-*sulphonic acid*, tasteless. In this group *p*-SO_3H attached to *N*-Ph is not sufficient to cause sweetness.

III. With 35% CH_2O in AcOH, (IV) gives 3-*phenyl*-2 : 3-*dihydro*-1 : 3 : 4-*naphthoisotriazine*-6-*sulphonic acid*, bitter (*Na* salt, $+4{\cdot}5H_2O$), and (V) the corresponding 3-p-*sulphophenyl*-*sulphonic acid*, tasteless. From (I), 2-p-*sulphophenyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*, tasteless, is obtained, whilst from (II), 2-*phenyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphthoisotriazine*-8-*sulphonic acid*, bitter, and from (III), the corresponding 2-p-*sulphophenyl*-*sulphonic acid*, of salt taste, are prepared. E. W. W.

Manufacture of vat dyes of the anthraquinone series.—See B., 1937, 887.

Optical absorption of porphyrins. XI.—See A., I, 442.

Acetylenic thioamides. D. E. WORRALL (J. Amer. Chem. Soc., 1937, 59, 1486—1487).—CPh:CNa

and MeNCS give *γ-phenylpropiolthiomethylamide* (I), m.p. 78—80° (decomp.), giving with alcoholic alkali NH_2Me and COPhMe amongst other products, but not polymerising even in alkali. CPh:CNa and CH_2:CH·CH_2·NCS give *γ-phenylpropiolthioallylamide* (II), m.p. 60—61°, unstable when solid or in EtOH, but stable in Et_2O, and not polymerised by NH_3. With NH_2OH–EtOH (I) and (II) give 3-*methyl*-, m.p. 112—113° (*dibromide*), and 3-*allyl-amino*-5-*phenyl*isooxazole, m.p. 102—103°, respectively; in conc. solutions (II) gives also 2-*phenacylthiazole*, m.p. 168—169° (decomp.) after sintering, which is the main product if only 1 mol. of NH_2OH is used. With N_2H_4 (I) and (II) give (?) 3-(5′-*thio*-3′-*phenylpyrazolyl*-2′-)5-*phenylpyrazole*, m.p. 169—170° (converted by conc. H_2SO_4 into CO_2 and COPhMe), but (II) gives also some 3-*allylamino*-5-*phenylpyrazole*, m.p. 98°. R. S. C.

Physical constants of morpholine. V. H. Dermer and O. C. Dermer (J. Amer. Chem. Soc., 1937, **59**, 1148—1149).—Physical consts. of morpholine, b.p. 128·9°, f.p. −4·9 ± 0·1°, purified, if necessary *via* the H oxalate, are recorded. R. S. C.

Phenolic morpholines etc.—See B., 1937, 981.

Benzthiazyl disulphides.—See B., 1937, 880.

Intermediates for dyes [benzthi- and benzselen-azolines].—See B., 1937, 880.

Anthraquinone derivatives (anthraselenazoles).—See B., 1937, 881.

Iodo-derivatives of thiodiazolines of formaldehyde. H. Wuyts and W. Deshommes (Bull. Soc. chim. Belg., 1937, **46**, 231—240).—β-Thio-*p*-toluoyl-α-phenylhydrazine with CH_2O in EtOH–HCl gives 3-*phenyl*-5-p-*tolyl*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m.p. 111—112°, which with 6 I in $CHCl_3$ gives a I_5-derivative (I), m.p. 109°, with the formation of 1 mol. of HI; with excess of I a I_7-derivative, m.p. 116°, is also obtained. When dissolved in $COMe_2$ and pptd. with Et_2O (I) readily loses 2 I to give a I_3-derivative, m.p. 106°. By similar methods 3-phenyl-5-α-naphthyl-2 : 3-dihydro-1 : 3 : 4-thiodiazole yields a I_5- (II), m.p. 118°, and a I_3- (III), m.p. 145·5°, -derivative; 3 : 5-diphenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazole gives I_5-, m.p. 98°, and I_3-, m.p. 151·5°, -derivatives; and 3-phenyl-5-benzyl-2 : 3-dihydro-1 : 3 : 4-thiodiazole gives a I_5-, m.p. about 55—57°, and a I_3-, m.p. about 85°, -derivative. The I_3-derivatives with I–$CHCl_3$ yield the I_5-derivatives. The fusion diagram of mixtures of (II) and (III) is given and confirms the individuality of the unstable I_5-derivatives. Conversion of (II) into (III) is particularly facile, being achieved by washing (II) with CS_2, or by repeatedly shaking an Et_2O suspension with a starch solution until no further blue colour is formed. H. G. M.

(A) **Cyanine dyes from amino-derivatives of benzthiazole.** (B) **Cyanine dyes from isomeric dimethylbenzthiazoles.** A. I. Kiprianov and E. D. Sitsch (Trav. Inst. Chim. Charkov, 1936, **2**, 15—24, 25—32).—(A) 5-*Dimethylamino*-1-*methylbenzthiazole*, m.p. 71°, prepared from 5-amino-1-methylbenzthiazole and *p*-$C_6H_4Me·SO_3Me$, or by a Bernthsen synthesis from $NPhMe_2$, yields a coloured 2-N- (I) and a colourless 5-N-*methiodide*, both m.p. 250° (decomp.), and a 2-N- (II), m.p. 242°, and 5-N-*ethiodide*, m.p. 149°; the yield of 2-*N*-derivative rises with increasing duration and temp. of reaction with the alkyl iodides. 5-*Diethylamino*-1-*methylbenzthiazole*, b.p. 185—195°/15 mm. [2-N-*ethiodide* (III), m.p. 76°], was prepared analogously. In picoline (at the b.p.) $CH(OEt)_3$ and (I) or (II) yield 5 : 5′-*bis*(*dimethylamino*)-2 : 2′-*dimethyl*- (IV), m.p. 244°, or -2 : 2′-*diethyl-thiocarbocyanine iodide* (V), and 5 : 5′-*bis*(*diethylamino*)-2 : 2′-*diethylthiocarbocyanine iodide* (VI) is prepared similarly from (III). The 8-*Me* derivative of (IV) is obtained when NMe_3 is added to the reaction mixture. The 8-*Me* derivatives of (V) and (VI) are prepared similarly to them, using $CMe(OEt)_3$ in place of $CH(OEt)_3$. 2-Iodoquinoline ethiodide and (I) in EtOH–KOH (1 hr. at the b.p.) yield 5-*dimethylamino*-1-*methyl*-2′-*ethylthio*-ψ-*cyanine iodide*, m.p. 171°, whilst with quinoline methiodide 5-*dimethylamino*-1′ : 2-*dimethylthio*isocyanine *iodide*, m.p. 176°, is obtained. Max. light absorption data are recorded for the above dyes. The dyes are valuable sensitisers of photographic emulsions.

(B) Thiolacet-toluidide in aq. NaOH and aq. $K_3Fe(CN)_6$ at 7° yield 1 : 3-*dimethylbenzthiazole*, b.p. 161—163°/55 mm., the *ethiodide*, m.p. 150°, of which gives 3 : 3′-*dimethyl*- or 3 : 3′ : 8-*trimethyl*-2 : 2′-*diethylthiocarbocyanine iodide* when heated with $CH(OEt)_3$ or $CMe(OEt)_3$, respectively. 2-Amino-4-methylthiolphenol and Ac_2O in C_6H_6 (at the b.p.; 2 hr.) yield 1 : 4-*dimethylbenzthiazole*, b.p. 153—156°/25 mm., m.p. 34°, from the *ethiodide*, m.p. 195—196°, of which are prepared 4 : 4′-*dimethyl*- and 4 : 4′ : 8-*trimethyl*-2 : 2′-*diethylthiocarbocyanine iodide*. The sensitising action of the isomeric dyes is unaffected by position of the Me, but the greatest bathochromic effect is given by the 4 : 4′-Me_2 derivatives. R. T.

Isolation of erythroidine, an alkaloid of curare action, from *Erythrina americana*, Mill. K. Folkers and R. T. Major (J. Amer. Chem. Soc., 1937, **59**, 1580—1581).—The seeds of *E. americana* contain 0·7—0·9% of *erythroidine*, $C_{16}H_{19}O_3N$, m.p. 94–96° [*hydrochloride*, m.p. 228—229° (decomp.), $[\alpha]_D^{25}$ +109·7° in H_2O], which has curare action when administered orally or by injection. R. S. C.

Lupin studies. XII. Alkaloids of *Lupinus laxus*, Rydb. J. F. Couch (J. Amer. Chem. Soc., 1937, **59**, 1469—1471; cf. A., 1936, 1131).—*L. laxus* contains sparteine, *d*-lupanine [*di*-d-*camphorsulphonate*, m.p. 245—246·5° (corr.)], trilupine, and a small amount of a *substance*, $C_{15}H_{24}O_2N_2$, m.p. 176—177°, $[\alpha]_D^{31}$ +133·2° in H_2O. R. S. C.

Ergot alkaloids. XII. Synthesis of substances related to lysergic acid. W. A. Jacobs and R. G. Gould, jun. (J. Biol. Chem., 1937, **120**, 141—150).—A more detailed account of matter previously abstracted (this vol., 219). 3 : 4-*Trimethyleneindole*, m.p. 58·5—59° (*picrate*, m.p. 164—166°), and 8-*amino*-1-*hydroxymethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 111—112° (*hydrochloride*, *picrate*, m.p. 206—207°; N-*Bz* derivative, m.p. 195·5—197°), were also prepared by reduction (Na–BuOH) of Me 8-amino-1 : 2 : 3 : 4-tetrahydro-1-naphthoate (m.p. 75—76°). 3 : 1-$NH_2·C_{10}H_6·CO_2H$

was converted into 5 : 6-*benzoquinoline*-7-*carboxylic acid*, m.p. 298—300° [*hydrochloride*; 3'-NO_2-derivative, m.p. 310°; 3'-*amino-lactam* (formula, *loc. cit.*), m.p. 280° (*hydrochloride*; 1 : 2 : 3 : 4-H_4-derivative, m.p. 248—249°). This lactam was reduced (Na–BuOH) to the corresponding indole, named *ergoline*, m.p. 175—183° (*hydrochloride*), and 3'-*amino*-7-*hydroxymethyl*-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydro*-5 : 6-*benzoquinoline*, m.p. 80—85° (*dihydrochloride*).

F. R. G.

***Strychnos* alkaloids. XCIV. Oxidation of strychnine to monohydroxystrychnine, the so-called ψ-strychnine.** H. LEUCHS (Ber., 1937, **70**, [*B*], 1543—1547).—Examination of a series of strychnine (I) residues discloses the presence of monohydroxystrychnine (ψ-strychnine) (II). Since (II) is not present in technical (I) its origin lies in atm. oxidation. Preparatively (I) in $CHCl_3$ is exposed to air in the presence of N-NH_3 and $Cu(OH)_2$ and the product is treated with MeOH. After hydrolysis with 0·25N-HCl and addition of NaOAc a homogeneous *material*, m.p. 233°, $[\alpha]_D^{20}$ +104°/*d* in $CHCl_3$, is obtained which is more or less rapidly (?) isomerised to (II), m.p. 263°, $[\alpha]_D^{20}$ −129°/*d* in $CHCl_3$, by dissolution in N-HCl and repptn. from the hot solution by NH_3. Strychnine oxide appears to be formed also. H. W.

***Strychnos* alkaloids. XCV. Transformations of ψ-strychnine.** H. LEUCHS, H. GRUNOW, and K. TESSMAR (Ber., 1937, **70**, [*B*], 1701—1707; cf. this vol., 394).—ψ-Strychnine hydrochloride, whether crystallised from cold or hot solution, is $C_{21}H_{22}O_5N_2$,HCl,2H_2O, whereas the perchlorate is anhyd. if obtained from hot solution, whilst when crystallised from cold solution and then heated at 100° and 125°/15 mm. it is $C_{21}H_{20}O_2N_2$,$HClO_4$ (cf. Robinson and Blount, A., 1932, 1147). ψ-Strychnine Me ether with MeI affords the methiodide, m.p. 216°, of Robinson and Blount but the product does not contain OMe and hence is $C_{21}H_{22}O_3N_2$,MeI; it is accompanied by a (?) *hydriodide*, m.p. (indef.) 244°, which yields the base, $C_{22}H_{24}O_3N_2$ (I), when treated with NH_3. (I) is transformed by PhCHO and aq. KOH under relatively mild conditions into the *monobenzylidene* derivative, $C_{29}H_{28}O_3N_2$, m.p. 246—248° (vac.), and under more drastic conditions into the dibenzylidene compound, m.p. 284—286°, of Robinson and Blount. Hydrogenation (PtO_2) of $C_{22}H_{24}O_3N_2$ gives rapidly the base, $C_{22}H_{26}O_3N_2$, m.p. 293° (vac.) [*perchlorate*; :CHPh derivative, m.p. 255—261° (vac.)]. Ring-fission of ψ-strychnine methiodide gives the *tert.* base, $C_{23}H_{26}O_3N_2$, m.p. 188—190° (vac.), which contains OMe and is hydrogenated to the *base*, $C_{23}H_{30}O_3N_2$ (II), m.p. 123—125° [:CHPh derivative, m.p. 198—200° (vac.)]. Hydrolysis of (II) with 2N-HCl affords (I). ψ-Strychnine (III) gives a *benzylidene* derivative, isolated as the *Et ether*, $C_{30}H_{30}O_3N_2$, m.p. 202° or m.p. (vac.) 208—209°. Hydrogenation of (III) affords *dihydro-ψ-strychnine*, m.p. 130—135° (decomp.), $[\alpha]_D^{20}$ +34·5°/*d* in $CHCl_3$ [*Me ether*, m.p. about 209° (decomp.), $[\alpha]_D^{20}$ +75·7°/*d* in $CHCl_3$; *NO*-derivative, m.p. 228° (decomp.), $[\alpha]_D^{20}$ +443°/*d* in $CHCl_3$]. H. W.

Berbine derivatives. V. Constitution of 8 : 9 : 16 : 17-tetradehydrocorydalinium salts. W. AWE [with H. ETZRODT and H. UNGER] (Arch. Pharm., 1937, **275**, 405—410; cf. this vol., 219).—Contrary to Gadamer (cf. A., 1911, i, 153), 8 : 9 : 16 : 17-tetrahydrocorydalinium iodide, decomp. from 225—230°, obtained from corydaline by I or $Hg(OAc)_2$ (identity of the product being confirmed by the absorption spectrum), with CH_2Ph·MgBr or MgPhBr gives 2 : 3 : 11 : 12-*tetramethoxy*-9-*benzyl*-16-*methyl*-16 : 17-*didehydroberbine hydriodide*, m.p. 186°, and 2 : 3 : 11 : 12-*tetramethoxy*-9-*phenyl*-16-*methylberbine*, m.p. 209°, respectively, the latter product being reduced by Zn–Cd–Hg in aq. HCO_2H to 9-phenylcorydaline. R. S. C.

Solanine-*s*. L. H. BRIGGS (J. Amer. Chem. Soc., 1937, **59**, 1404—1405).—Solanine-*s* [*nitrate*, m.p. 296° (decomp.); *hydriodide*, m.p. 283—284° (decomp.); *oxalate*, m.p. 238° (decomp.); *tartrate*, m.p. 222° (decomp.)] has been isolated from *Solanum auriculatum* (cf. Oddo *et al.*, A., 1905, i, 455). The formula indicated by analysis, $C_{44}H_{75}O_{18}N$ (solanidine-*s*, $C_{26}H_{43}O_3N$), is confirmed by the work of Rochelmeyer (this vol., 80), and differs only by H_2O from that of solancarpine (Saiyed and Kanga, *ibid.*, 39), with which it appears to be identical. A. LI.

***Senecio* alkaloids. IV. Alkaloids of *S. vulgaris*. Degradation of senecionine.** L. KONOVALOVA and A. ORÉKHOV (Bull. Soc. chim., 1937, [v], **4**, 1285—1290; cf. A., 1935, 1387; 1936, 1277).—$C_2H_4Cl_2$ extracts senecionine (cf. A., 1936, 617, 1002) which with boiling N-NaOH gives senecic acid and retronecine (I), m.p. 120—121° (hydrochloride, m.p. 164—165°) (cf. A., 1935, 365). In N-HCl with H_2–Adams' catalyst (I) gives *retronecanol*, m.p. 98—99° [picrate, m.p. 210—211° (*lit.*, 208°); *picrolonate*, m.p. 184—185°] (cf. A., 1935, 365), which with conc. H_2SO_4 at 145—150° affords heliotridene, reduced (H_2–Adams' catalyst) to heliotridane. The chemical relationships of the *Senecio* and heliotrope alkaloids are discussed. J. L. D.

Sinomenine. XLV. Synthesis of *N*-methyltuduranine methyl ether. K. GOTO, R. INABA, and H. NOZAKI (Annalen, 1937, **530**, 142—146; cf. A., 1936, 88).—2 : 4-NO_2·C_6H_3(OMe)·CH_2·CO_2H affords 2-*nitro*-4-*methoxyphenylacethomoveratrylamide*, m.p. 132°, converted by P_2O_5 in PhMe into 6 : 7-*dimethoxy*-1-2'-*nitro*-4'-*methoxybenzyl*-3 : 4-*dihydroisoquinoline*, m.p. 156° (84% yield), the methiodide of which with Zn dust and conc. HCl gives 6 : 7-*dimethoxy*-1-2'-*amino*-4'-*methoxybenzyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 102° (*dihydrochloride*, +0·5H_2O, m.p. 226°). With HNO_2, followed by Zn–HCl, this affords 3 : 5 : 6-*trimethoxyaporphine hydrochloride*, m.p. 245° (decomp.) (24% yield); resolution by tartaric acid gives the active *bases*, m.p. 108° after sintering at 100°, $[\alpha]_D^{12}$ −136·94°, +138·16° in MeOH (l-*base* d-, m.p. 203—205°, and d-*base* l-*tartrate*, m.p. 204° after sintering at 200°); the *l*-base is identical with *N*-methyltuduranine Me ether, now obtained cryst. from tuduranine. Identity is confirmed by degradation of the *dl*-base to the same de-*N*-Me compound as is obtained from the natural *l*-compound. R. S. C.

Organo-arsenic compounds. IV. Heterocyclic ring containing arsenic. H. N. DAS-GUPTA

(J. Indian Chem. Soc., 1937, **14**, 231—236).—$CHCl{:}CH{\cdot}AsCl_2$ (I) heated with C_6H_6 with or without anhyd. $AlCl_3$ affords a mixture containing phenyl-β-chlorovinylchloroarsine (II), b.p. 138—142°/3 mm., and *diphenyl-β-chlorovinylarsine* (III), b.p. 190—198°/3 mm. ($HgCl_2$ *derivative*, m.p. 238°). MgPhBr converts (I) and (II) into (III). With $AlCl_3$ in CS_2 (II) affords 1-chloroarsindole, converted by MgMeI into 1-*methylarsindole*, b.p. 142—145°/6 mm. (*methiodide*, decomp. 216—218°; $HgCl_2$ *derivative*, m.p. 150—151°. The Cl-compounds are vesicants. P. G. C.

Composition of Grignard reagents as determined by precipitation with dioxan. C. R. Noller and W. R. White (J. Amer. Chem. Soc., 1937, **59**, 1354—1356).—Treatment of the Grignard solution 2MgRX (or $Mg_2R_2X_2$) $\rightleftharpoons MgR_2 + MgX_2$ with dioxan ppts. all but MgR_2. If the mixture is shaken before separating the ppt., the proportion of MgR_2 left in solution rises rapidly to a const. val.; hence the method is useless for determining the composition of the original solution. Addition of MgR_2 or MgX_2 to such a solution has little effect on the composition of the ppt. A. Li.

4 : 4′-Organo-magnesium derivatives of diphenyl. Catalytic action of magnesium iodide. R. Gibert (Compt. rend., 1937, **205**, 443—445; cf. A., 1934, 880).—4 : 4′-Di-iodo- and -bromodiphenyl and Mg afford the Mg_2 derivative (no Mg_1 derivative was formed), reacting normally with H_2O and with PhCN, and with $COPh_2$ to give 4 : 4′-di(hydroxydiphenylmethyl)diphenyl (cf. A., 1907, i, 503) and a *substance*, m.p. 216°. The yield of Mg_2 compounds is increased by adding Mg halide (cf. A., 1934, 397). J. L. D.

Action of bromine on proteins. F. Lieben and R. Tandler [with P. Weiss] (Biochem. Z., 1937, **292**, 82—91; cf. A., 1928, 1388).—In brominated caseinogen Br is much more firmly bound than in brominated collagen and gelatin. In brominated proteins Br is very probably not attached to the rings of cyclic NH_2-acid residues. W. McC.

Structure of protein monolayers.—See A., I, 511.

Protein films.—See A., I, 511.

Cryolysis of casein.—See A., I, 515.

Chondroitinsulphuric acid.—See A., III, 340.

Free amino- and carboxyl groups in proteins.—See A., III, 340.

Photosynthetic melanins.—See A., III, 374.

Determination of [amino-acid] coefficient *D*.—See A., III, 374.

Crystalline protein with high lactogenic activity.—See A., III, 375.

Manometric determination of volatile substances soluble in water with special reference to ether. M. Jowett (Biochem. J., 1937, **31**, 1097—1100).—The application of a const.-vol. manometer to the determination of volatile gases and liquids sol. in H_2O, the partition of which between aq. and gaseous phases varies considerably with temp., is described. F. O. H.

Volumetric micro-determination of oxygen (ter Meulen procedure). (Mlle.) A. Lacourt (Compt. rend., 1937, **205**, 280—282).—The O is converted into H_2O and this acts on cinnamoyl chloride, liberating HCl which is titrated. A precision of ±0·3% on quantities of 3—5 mg. can be obtained. F. J. G.

Determination of organic halogen compounds in presence of free sulphur. C. B. Medinski and I. V. Kostrov (Zavod. Lab., 1937, **6**, 696—698).—A modified Dennstedt apparatus is described. R. T.

Analysis of nitrogenous organic compounds. II. General method of detection of nitrogen. Z. E. Golbraich (J. Appl. Chem. Russ., 1937, **10**, 1135—1139).—The substance is heated with MnO_2, and the combustion gases are absorbed in H_2O, to which Griess–Ilosvay reagent is then added; a red coloration indicates N. In the case of inorg. compounds addition of sugar is recommended. R. T.

Analytical uses of Nessler's reagent. III. Determination of formaldehyde, pyrogallol, tannic and gallic acids; their absolute oxygen values. M. Goswami and A. Shaha (J. Indian Chem. Soc., 1937, **14**, 208—231).—CH_2O, pyrogallol (in absence of O_2), tannic and gallic acids can be micro-determined by treating with Nessler's reagent, dissolving the pptd. Hg in standard I solution, and titrating with $Na_2S_2O_3$. P. G. C.

Electrotitration of acids in benzene solution.—See A., I, 529.

3 : 5-Dinitro-*p*-toluic acid as a reagent for the identification of amines. P. P. T. Sah and K. H. Yuin (J. Chinese Chem. Soc., 1937, **5**, 129—133).—The 3 : 5-*dinitro*-p-*toluates* of the following amines are suitable for identification purposes: NH_2Ph, m.p. 159—160°, *o*-, m.p. 146—147°, *m*-, m.p. 128—129°, and *p*-$C_6H_4Me{\cdot}NH_2$, m.p. 157—159°, α-, m.p. 137—138°, and β-$C_{10}H_7{\cdot}NH_2$, m.p. 112—113°, *o*-, m.p. 188—189°, and *p*-$OH{\cdot}C_6H_4{\cdot}NH_2$, m.p. 207—208°, *p*-aminodiphenyl, m.p. 178—179°, benzidine, m.p. 231—232°, C_5H_5N, m.p. 150—151°, quinoline, m.p. 149—151°, *o*-, m.p. 142—143°, and *p*-toluquinoline, m.p. 155—156°, quinaldine, m.p. 121—122°, *p*-toluquinaldine, m.p. 122—123°, NH_3, m.p. 226—228°, NH_2Me, m.p. 206—207°, $CO(NH_2)_2$, m.p. 137—138°, *p*-xylidine, m.p. 162—163°, *p*-$C_6H_4Cl{\cdot}NH_2$, m.p. 164—165°, *p*-$C_6H_4Br{\cdot}NH_2$, m.p. 119—120°, and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$, m.p. 214—216°. F. R. S.

Determination of proline in protein hydrolysates.—See A., III, 374.

Leuco-bases as analytical reagents. A. Ionesco-Matiu and C. Popesco (Bull. Soc. chim., 1937, [v], **4**, 1230—1235).—Methylene-blue and $Na_2S_2O_4$ in the presence of HCl give a leuco-base (I), stable in air for 12 hr. Nascent H, NaHS, Na_2SO_3, $NaHSO_3$, and $Na_2S_2O_5$ do not stabilise (I). Neutral salts, except $Hg^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, etc. salts, do not, and only aldehydes amongst many org. substances, affect (I). Oxidation to the coloured form is facilitated by light. Stabilisation of (I) by $Na_2S_2O_4$ may be due to the formation of an $\cdot S{\cdot}SO_3H$ derivative (cf. A., 1911, i, 1006). J. L. D.