The Constitution of Conessine. Part VII. Degradation of Some Reduced Quinoline and Indole Bases.*

By B. Bailey, R. D. Haworth, and J. McKenna.

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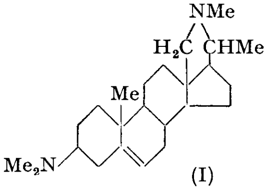
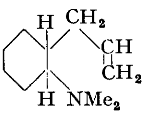
cis- and *trans*-Decahydroquinoline, *cis*-octahydro-1-methylindole, *cis*(?)-octahydro-2-methyl*iso*indole, and homologues thereof have been degraded by the Hofmann and the Emde procedure; in general the reactions take the expected course. The acetic acid cyclisation of methine bases derived from the heterocyclic amines is described.

Recent investigations by Haworth, McKenna, and their collaborators (*J.*, 1953, 1102, 1110, 1115) on the constitution of the steroidal alkaloid conessine have led to the proposal of formula (I); the positions of the double bond and the dimethylamino-group are now well established, and the heterocyclic ring arrangement is probably correct. The Hofmann and the Emde degradation reactions of quaternary ammonium salts have been of considerable utility in elucidating the chemistry of conessine, and, in view of the characteristic behaviour of the alkaloid, it was decided at an early stage of the investigation to carry out parallel degradations with simpler heterocyclic amines. Moreover, it has been found (Haworth, McKenna, Powell, and Woodward, *J.*, 1951, 1736; Favre, Haworth, McKenna, Powell, and Whitfield, *loc. cit.*, p. 1115) that unsaturated methine bases of the type $\underline{\mathrm{CH{=}CH_2\ NMe_2}}$ derived from conessine are readily cyclised on treatment with glacial acetic acid or hot hydroxylic solvents with the production of related quaternary salts $\underline{\mathrm{CH_2{-}CH_2{-}NMe_2^+}}\}\ X^-$ (X = OAc or OH), and it was therefore planned to examine simpler unsaturated methines from the same standpoint.

The Hofmann degradation of *cis*- and *trans*-decahydroquinolines has been described by Fujise (*Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1928, **8**, 185) who found that each base yielded an unsaturated methine, the dihydro-derivatives from which were not identical; formulæ (II) and (III) were therefore suggested for these methines. Confirmation in the



(I)



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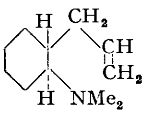

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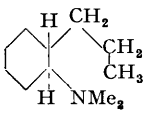

(IV)

case of the methine base (III) derived from *trans*-decahydroquinoline was subsequently (*ibid.*, 1929, **10**, 83) obtained by identification of its dihydro-derivative as *trans*-*NN*-dimethyl-2-propyl*cyclo*hexylamine (IV). We have confirmed Fujise's results and find that each methine base on Emde reduction yields allyl*cyclo*hexane, the constitution of which

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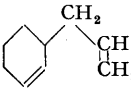
* Part VI, *J.*, 1953, 1115.

follows from its oxidation to *cyclo*hexylacetic acid. Hofmann decomposition of the methine bases (II) and (III) yields doubly unsaturated hydrocarbons [probably identical, and probably 3-allyl*cyclo*hexene (V)] in which the double bonds are not in conjugation. Hofmann decomposition of *trans*-*NN*-dimethyl-2-propyl*cyclo*hexylamine (IV) yields 3-propyl*cyclo*hexene (VI), the constitution of which was proved by oxidation with permanganate to heptane-1 : 4-dicarboxylic acid. Hofmann decomposition of the base (IV) had previously been investigated by Fujise (*loc. cit.*) who showed that the product was not the known 1-propyl*cyclo*hexene; this isomer would not in any case be expected on general considerations (not the least substituted ethylene) and it would probably have yielded a monobasic keto-acid on oxidation.

When the methine base (III) derived from *trans*-decahydroquinoline was boiled with acetic acid it yielded a mixture of quaternary acetates containing a little *trans*-decahydro-1-methylquinoline methoacetate (VII), isolated as iodide by chromatography. The remainder of the cyclised acetates probably consisted of a mixture of the epimeric forms of *trans*-octahydro-1 : 2-dimethylindole methoacetate (VIII; epimeric at $C_{(2)}$) since selenium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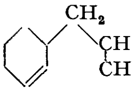
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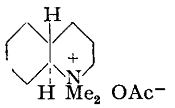
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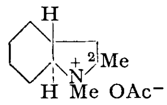
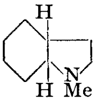

(VIII)

dehydrogenation gave 2-methylindole in addition to some quinoline. Hofmann degradation of the quaternary mixture gave back the parent methine (III). No cyclisation of (III) resulted from boiling in alcohol or aqueous glycol, but with aqueous potassium hydroxide a little quaternary product was obtained and isolated as methiodide.

The methine base (II) derived from *cis*-decahydroquinoline was also found to cyclise readily in acetic acid, but the products were not investigated.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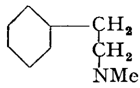
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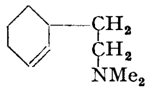
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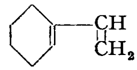
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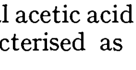
Barltrop, King, and Walley (*J.*, 1945, 277) submitted *cis*-octahydro-1-methylindole (IX) to Hofmann degradation and obtained a β-dimethylaminoethyl*cyclo*hexene which yielded 2′-dimethylaminoethyl*cyclo*hexane (X) on catalytic hydrogenation. We have confirmed the structure of the dihydromethine (X) by Hofmann degradation to vinyl*cyclo*hexane, which gave hexahydrobenzoic acid on permanganate oxidation. Baltrop, King, and Walley did not identify the position of unsaturation in their unsaturated methine, but formula (XI), which appears likely on general grounds (least substituted ethylene), has been confirmed by Emde reduction of the base followed by oxidation of the resulting 3-ethyl*cyclo*hexene to 2-ethyladipic acid. Further Hofmann degradation of the methine (XI) gave an unsaturated hydrocarbon C_8H_{12} with two double bonds in conjugation; the ultra-violet absorptions of this hydrocarbon (at 2295 and 2340 Å) excludes a *cyclo*hexadiene structure and indicate formulæ (XII) or (XIII) or a mixture. Treatment of the methine (XI) with glacial acetic acid gave a mixture of *cis*- and *trans*-octahydro-1-methylindole methoacetates, characterised as the corresponding picrates. In hot alkaline ethylene glycol, (XI) was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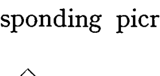
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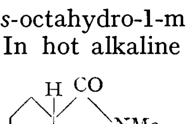
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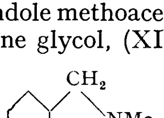
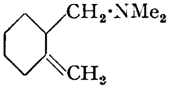

(XVI)

transformed into an unsaturated isomer [possibly 1-2′-dimethylaminoethyl*cyclo*hexene (XIV)] which did not cyclise in acetic acid and which gave 2′-dimethylaminoethyl*cyclo*hexane (X) on catalytic hydrogenation; this interesting reaction will be discussed more fully in a later communication.

Treatment of either *cis*- or *trans*-hexahydrophthalic anhydride with aqueous methylamine gave *cis*-hexahydro-*N*-methylphthalimide (XV). The stereochemical configuration of this imide was shown by (*a*) its formation by distillation of the methylamine salt of *cis*-hexahydrophthalic acid, (*b*) its stability to distillation *in vacuo* at 230°, and (*c*) its hydrolysis by dilute alkali in the cold to *cis*-hexahydrophthalic acid. Analogous reactions of *cis*-hexahydrophthalimide are described by Hückel and Müller (*Ber.*, 1931, **64**, 1981). Reduction of the imide with lithium aluminium hydride gave an octahydro-2-methyl*iso*indole (XVI) which is tentatively formulated as the *cis*-isomer, although further evidence on its stereochemistry is required. Hofmann degradation of the *iso*indole (XVI) gave a low yield of the methine, 1-dimethylaminomethyl-2-methylene*cyclo*hexane (XVII), together with a diamino-ether $C_{20}H_{40}ON_2$. The structure of the methine base (XVII) was proved by (*a*) Emde reduction followed by permanganate oxidation of the 1-methyl-2-methylene*cyclo*hexane to 2-methyl*cyclo*hexanone, (*b*) further Hofmann degradation followed by ozonisation of the 1 : 2-dimethylene*cyclo*hexane, to formaldehyde and *cyclo*hexane-1 : 2-dione, and (*c*) acetic acid cyclisation to the methoacetate of the original *iso*indole (XVI).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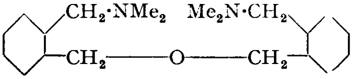
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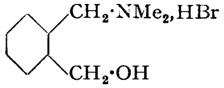
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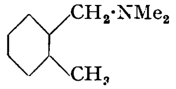
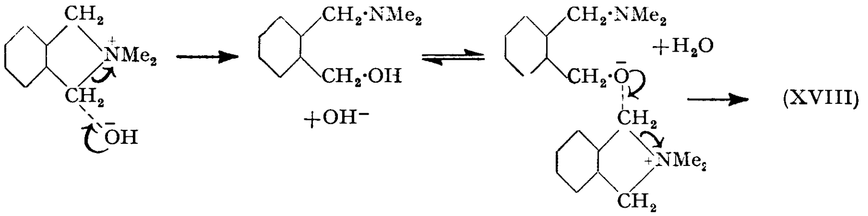

(XX)

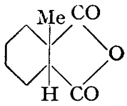
The diamino-ether $C_{20}H_{40}ON_2$ (cf. King, Bovey, Mason, and Whitehead, *J.*, 1953, 250) is tentatively formulated as bis-(2-dimethylaminomethyl*cyclo*hexyl)methyl ether (XVIII), a structure which could readily arise from the *iso*indole methohydroxide by the following series of reactions :



The properties of the diamino-ether are in agreement with the formulation (XVIII). Thus the compound could be neither hydrogenated nor acetylated, but underwent fission with 60% hydrobromic acid to a hydrobromide $C_{10}H_{22}ONBr$, probably 1-dimethylaminomethyl-2-hydroxymethyl*cyclo*hexane hydrobromide (XIX). Hofmann degradation followed by permanganate oxidation also resulted in fission of the ether linkage. The lack of stability of the probable intermediate β-ketonic ether [(XVIII) with :O for each $CH_2{\cdot}NMe_2$ and H] to alkali (derived from the oxidising agent) is understandable (cf. Corbett and Kenner, *J.*, 1953, 2245); the ketone isolated was identified as 2-hydroxymethyl*cyclo*hexanone through the 2 : 4-dinitrophenylhydrazone.

Emde reduction of the above *iso*indole (XVI) gave a 1-dimethylaminomethyl-2-methyl*cyclo*hexane (XX), the constitution of which was shown by Hofmann decomposition followed by oxidation to 2-methyl*cyclo*hexanone.

Reaction of citraconic anhydride and butadiene at 200° gave *cis*-1 : 2 : 3 : 6-tetrahydro-1-methylphthalic anhydride, from which *cis*-hexahydro-1-methylphthalic anhydride (XXI) was obtained by catalytic hydrogenation. Treatment of (XXI) with concentrated hydrochloric acid gave the *trans*-acid which was cyclised to the *trans*-anhydride by refluxing acetyl chloride. These configurations are assigned by analogy with those of the corre-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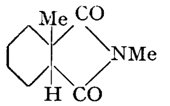
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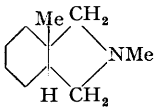
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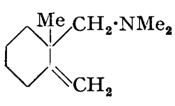
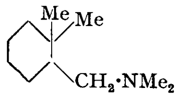

(XXIV)

sponding series of compounds lacking the angular methyl group (Diels and Alder, *loc. cit.*). After the completion of this work our attention was drawn to an abstract of a paper by Nazarov and Kucherov (*Chem. Abs.*, 1953, **47**, 5363) who have also prepared the anhydride (XXI) and its *trans*-isomer. Both hexahydromethylphthalic anhydrides gave the same *N*-methylimide, m. p. 52—53°, on treatment with aqueous methylamine; this imide is assigned a *cis*-structure (XXII) by analogy with the structure of the simpler imide described above. Reduction of (XXII) with lithium aluminium hydride gave *cis*(?)-octahydro-2 : 8-dimethyl*iso*indole (XXIII). Hofmann degradation of the *iso*indole (XXIII) gave a methine base $C_{11}H_{21}N$ in low yield, together with a higher-boiling diamino-ether $C_{22}H_{44}ON_2$ which has not been investigated further. The methine may be formulated as 1-dimethylaminomethyl-1-methyl-2-methylene*cyclo*hexane (XXIV) although direct proof of this structure has not been obtained owing to shortage of material. The methine did not undergo further Hofmann decomposition, as would be expected since there is no hydrogen atom available at the β(angular)-position, and treatment with glacial acetic acid gave the original *iso*indole as methoacetate.



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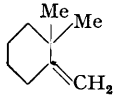

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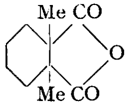

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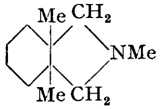

(XXVIII)

Emde degradation of the dimethyl*iso*indole (XXIII) resulted in fission of the heterocyclic ring in a different manner from that just described; the product, 2-dimethylaminomethyl-1 : 1-dimethyl*cyclo*hexane (XXV), gave 1 : 1-dimethyl-2-methylene*cyclo*hexane (XXVI) on Hofmann degradation, and this hydrocarbon was oxidised to 2 : 2-dimethyl*cyclo*hexanone with potassium permanganate.

cis-1 : 2 : 3 : 6-Tetrahydro-1 : 2-dimethylphthalic anhydride (Woodward and Loftfield, *J. Amer. Chem. Soc.*, 1941, **63**, 3167) was hydrogenated to the hexahydro-compound (XXVII), and the latter with methylamine gave the *cis*-hexahydrophthalimide which on reduction with lithium aluminium hydride gave *cis*-2 : 8 : 9-trimethyloctahydro*iso*indole (XXVIII). In this series of compounds the *cis*-configuration may confidently be assigned to both the methyl-imide and the *iso*indole, since neither asymmetric carbon atom carries a hydrogen atom. As would be expected the *iso*indole (XXVIII) gave no methine on attempted Hofmann decomposition of its methohydroxide, but instead the original base was recovered in high yield.

EXPERIMENTAL

trans-2-*Allyl*-NN-*dimethyl*cyclo*hexylamine* (III).—*trans*-Decahydroquinoline (Bailey and McElvain, *J. Amer. Chem. Soc.*, 1930, **52**, 4015) was converted into the 1-methyl derivative (Bamberger and Williamson, *Ber.*, 1894, **27**, 1467) by treatment with formaldehyde and formic acid (Clark, Gillespie, and Weisshauss, *ibid.*, 1933, **55**, 4571); the tertiary base yielded a *picrate*, which separated from ethanol in yellow needles, m. p. 171—173° (Found : C, 50·5; H, 5·6; N, 14·6. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·7; N, 14·7%), and a *methopicrate*, yellow needles (from ethanol), m. p. 141—142° (Found : C, 51·6; H, 6·2; N, 14·4. $C_{17}H_{24}O_7N_4$ requires C, 51·5; H, 6·1; N, 14·1%). Pyrolysis of *trans*-decahydro-1-methylquinoline methohydroxide by Fujise's method (*loc. cit.*) yielded (65%) *trans*-2-allyl-*NN*-dimethyl*cyclo*hexylamine which was separated from a little *trans*-decahydro-1-methylquinoline by fractional crystallisation of the picrates; the methine base picrate (yellow needles from ethanol) had m. p. 100—101° (Fujise gives m. p. 101·5—102°). The unsaturated base was further characterised by the *picrolonate*, which separated from ethanol in yellow needles, m. p. 202—204° (Found: N, 16·2. $C_{21}H_{29}O_5N_5$ requires N, 16·2%), a *methiodide*, prisms (from acetone–ether), m. p. 172—173° (Found: C, 46·8; H, 7·8; I, 41·5. $C_{12}H_{24}NI$ requires C, 46·6; H, 7·8; I, 41·1%), and a *methopicrate*, yellow prisms (from ethanol), m. p. 117—118° (Found : C, 52·8; H, 6·3; N, 13·9. $C_{18}H_{26}O_7N_4$ requires C, 52·7; H, 6·3; N, 13·7%).

Emde Reduction of trans-2-*Allyl*-NN-*dimethyl*cyclo*hexylamine Methochloride*.—*trans*-2-Allyl-*NN*-dimethyl*cyclo*hexylamine methiodide (2 g.) in water (20 c.c.) was shaken with excess of silver chloride for 30 min., and the methochloride solution concentrated and heated on the water-bath with sodium amalgam (5%; 200 g.) which was added in portions during 6 hr.

The resultant allyl*cyclo*hexane (0·3 g.) was purified by distillation from sodium and had b. p. 152—153° (Found : C, 87·1; H, 13·0. Calc. for C_9H_{16} : C, 87·1; H, 12·9%) (de Resseguier, *Bull. Soc. chim.*, 1898, **7**, 431, gives b. p. 148—149°). The hydrocarbon decolorised acidified permanganate. Oxidation of the hydrocarbon (0·45 g.) in acetone (10 c.c.) with potassium permanganate (1·3 g.) at room temperature yielded *cyclo*hexylacetic acid (0·23 g.), b. p. 128—132°/12 mm. (Found : C, 67·3; H, 9·7. Calc. for $C_8H_{14}O_2$: C, 67·6; H, 9·9%), characterised as its amide, m. p. and mixed m. p. 166—168°.

Hofmann Degradation of trans-*2-Allyl-*NN-*dimethyl*cyclo*hexylamine.*—*trans*-2-Allyl-*NN*-dimethyl*cyclo*hexylamine methiodide (2 g.) in ethanol (25 c.c.) and water (25 c.c.) was converted into the methohydroxide which was decomposed by distillation at 200° (bath-temp.). The resultant *hydrocarbon* (0·9 g.), purified by distillation over sodium, had b. p. 148—150° (Found : C, 88·4; H, 11·5. C_9H_{14} requires C, 88·5; H, 11·5%). The hydrocarbon showed no selective absorption in ethanol above 2150 Å.

trans-NN-*Dimethyl-2-propyl*cyclo*hexylamine* (IV) *and its Hofmann Degradation.*—trans-2-*Allyl*-NN-*dimethyl*cyclo*hexylamine* (1 g.) in acetic acid (10 c.c.) was hydrogenated at atmospheric pressure in the presence of Raney nickel (H_2 uptake at N.T.P., 112 c.c. Calc. for one double bond, 134 c.c.). Separation of the catalyst, concentration, and basification with ammonia yielded *trans-NN*-dimethyl-2-propyl*cyclo*hexylamine (0·6 g.), b. p. 206—208°. The picrate melted at 114° and the methiodide at 185° (Fujise, *loc. cit.*, gives b. p. 206° and m. p. 114° and 185° respectively). The base was further characterised as a *methopicrate*, yellow needles (from ethanol), m. p. 103—104° (Found : C, 52·6; H, 6·6. $C_{18}H_{28}O_7N_4$ requires C, 52·4; H, 6·8%). The alkaline solution left after ether-extraction of the hydrogenated base (above) was treated with picric acid solution and yielded a mixture of methopicrates (0·4 g.) similar to that described below.

Hofmann degradation of *trans-NN*-dimethyl-2-propyl*cyclo*hexylamine methiodide by Fujise's method (*loc. cit.*) gave 3-propyl*cyclo*hexene (VI), b. p. (over Na) 155°. Fujise gives b. p. 154—155°. The hydrocarbon (0·15 g.) in acetone (10 c.c.) was oxidised with potassium permanganate (0·6 g.) at room temperature and yielded heptane-1 : 4-dicarboxylic acid (0·14 g.), b. p. 150° (bath-temp.)/0·2 mm. [Found : C, 57·3; H, 8·45%; equiv., 95·9; *M* (Rast), 186. Calc. for $C_9H_{16}O_4$: C, 57·4; H, 8·5%; equiv., 94·0; *M*, 188]; the acid was not obtained crystalline (Mellor, *J.*, 1901, 130, gives m. p. 55°).

Cyclisation of trans-*2-Allyl-*NN-*dimethyl*cyclo*hexylamine* (III) *in Acetic Acid.*—The unsaturated base (1 g.) in glacial acetic acid (10 c.c.) was refluxed for 3 hr., the solution was evaporated under reduced pressure, and the residue basified with ammonia. Extraction with ether yielded no basic fraction, but treatment with excess of aqueous potassium iodide and extraction with chloroform overnight gave a mixture of isomeric methiodides which separated from acetone-ether in colourless prisms, m. p. 223—225° (Found : C, 44·6; H, 7·8; N, 4·75. Calc. for $C_{11}H_{22}NI$: C, 44·7; H, 7·5; N, 4·75%), and was shown by chromatography in chloroform on alumina to contain a little *trans*-decahydro-1-methylquinoline methiodide (corresponding methopicrate, m. p. and mixed m. p. 141—142°). Hofmann degradation of the mixture of methiodides (0·5 g.) yielded *trans*-2-allyl-*NN*-dimethyl*cyclo*hexylamine (III) (0·28 g.). Dehydrogenation of the mixture (0·3 g.) with selenium (0·7 g.) at 320° for 12 hr. and chromatography of the product in light petroleum (b. p. 40—60°) on alumina yielded (*a*) a colourless oil (0·05 g.) which gave no crystalline derivative with picric acid, (*b*) a colourless oil (0·07 g.) which on treatment with alcoholic picric acid afforded 2-methylindole picrate, m. p. 137—138° (Found : C, 50·3; H, 3·6; N, 15·0. Calc. for $C_{15}H_{12}O_7N_4$: C, 50·0; H, 3·3; N, 15·5%) undepressed on admixture with an authentic specimen of m. p. 139°, and (*c*) a colourless oil (0·04 g.) from which was obtained a little quinoline picrate, m. p. and mixed m. p. 202°.

Treatment of the methiodide mixture with aqueous ammonium picrate yielded a mixture of isomeric methopicrates, which could also be obtained directly after cyclisation; the mixture separated from ethanol in yellow needles, m. p. 127—128° (Found : C, 51·6; H, 6·1. Calc. for $C_{17}H_{24}O_7N_4$: C, 51·5; H, 6·1%).

Reactions of cis-*2-Allyl-*NN-*dimethyl*cyclo*hexylamine* (II).—*cis*-Decahydroquinoline was converted into the 1-methyl derivative with formaldehyde and formic acid, and the product characterised as the *picrate*, m. p. 198—199° (Found : C, 50·5; H, 5·8; N, 14·6. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·7; N, 14·7%), and as the *methopicrate*, m. p. 180—181° (Found : C, 51·6; H, 5·9; N, 13·8. $C_{17}H_{24}O_7N_4$ requires C, 51·5; H, 6·1; N, 14·1%), both yellow needles from ethanol. Hofmann degradation (Fujise, *loc. cit.*) gave *cis*-2-allyl-*NN*-dimethyl*cyclo*hexylamine; the unsaturated base picrate had m. p. 134° (Fujise records m. p. 135—138°). A small proportion of *cis*-decahydro-1-methylquinoline was recovered as picrate. Hofmann and Emde degradations of *cis*-2-allyl-*NN*-dimethyl*cyclo*hexylamine yielded the hydrocarbons, C_9H_{14}, b. p. 147—148° (Found: C, 88·4; H, 11·6%), and C_9H_{16}, b. p. 150—152° (Found: C, 87·0; H, 13·0%) respectively, apparently identical with those obtained in the same way from the corresponding unsaturated *trans*-base (see above); the hydrocarbon C_9H_{14} showed no selective absorption in the ultra-violet region, and the hydrocarbon C_9H_{16} was oxidised by permanganate in acetone to *cyclo*hexylacetic acid (amide, m. p. 167—168°).

Cyclisation of *cis*-2-allyl-*NN*-dimethyl*cyclo*hexylamine in boiling glacial acetic acid was complete in 2 hr.; the quaternary product was isolated as *methopicrate* (probably a mixture of isomers), yellow needles (from ethanol), m. p. 208—210° (Found: C, 51·5; H, 6·2. $C_{17}H_{24}O_7N_4$ requires C, 51·5; H, 6·1%)

Hofmann Degradation of cis-*Octahydro*-1-*methylindole* (IX).—*cis*-Octahydro-1-methylindole was prepared by the method of Baltrop, King, and Walley (*loc. cit.*). The picrate separated from ethanol as yellow needles, m. p. 200—201° (Found: C, 48·7; H, 5·5; N, 15·4. Calc. for $C_{15}H_{20}O_7N_4$: C, 48·9; H, 5·4; N, 15·2%). King, Bovey, Mason, and Whitehead (*loc. cit.*) give m. p. 204°. Hofmann degradation (Barltrop, King, and Walley, *loc. cit.*) gave 3-2′-dimethylaminoethyl*cyclo*hexene (XI) of which a *picrate*, yellow needles (from ethanol), m. p. 125—126° (Found: C, 49·8; H, 5·5; N, 14·8. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·7; N, 14·7%), and a *methopicrate*, yellow needles (from ethanol), m. p. 115° (Found: C, 51·3; H, 6·0. $C_{17}H_{24}O_7N_4$ requires C, 51·5; H, 6·1%), were prepared. The methiodide had m. p. 225° (Baltrop, King, and Walley, *loc. cit.*, give m. p. 226°). Catalytic hydrogenation gave 2′-dimethylaminoethyl*cyclo*hexane (X) (methiodide, m. p. 224°; Baltrop, King, and Walley, *loc. cit.*, give m. p. 224°). The *methopicrate*, yellow needles (from ethanol), of (X) had m. p. 114° (Found: C, 51·2; H, 6·4; N, 14·0. $C_{17}H_{26}O_7N_4$ requires C, 51·3; H, 6·5; N, 14·1%). Decomposition of the 2′-dimethylaminoethyl*cyclo*hexane methohydroxide at 200° (bath-temp.) gave *vinyl*cyclo*hexane*, b. p. 150° (bath-temp.) (Found: C, 87·1; H, 12·7. C_8H_{14} requires C, 87·3; H, 12·7%), the constitution of which was shown by oxidation by permanganate in acetone to hexahydrobenzoic acid (amide, m. p. 185—186°).

Hofmann Degradation of 3-2′-*Dimethylaminoethyl*cyclo*hexene* (XI).—Decomposition of the methohydroxide derived from 3-2′-dimethylaminoethyl*cyclo*hexene methiodide (2 g.) in the usual way yielded a *hydrocarbon* (0·3 g.), b. p. (over Na) 134—136° (Found: C, 88·6; H, 11·1. C_8H_{12} requires C, 88·9; H, 11·1%). Ultra-violet absorption: $\lambda_{max.}$ 2295, 2340 (ε 9000, 8500 respectively). Booker, Evans, and Gillam (*J.*, 1940, 1453) give for 1-vinyl*cyclo*hexene (XII) $\lambda_{max.}$ 2300 (ε 8500).

Emde Reduction of 3-2′-*Dimethylaminoethyl*cyclo*hexene Methochloride*.—A solution of this salt, prepared from the methiodide (1 g.), in water (10 c.c.) was reduced by portion-wise addition of sodium amalgam (5%; 150 g.) during 6 hr. at 100°. The crude 3-*ethyl*cyclo*hexene* (0·15 g.) was purified by distillation from sodium and had b. p. 160° (bath-temp.) (Found: C, 87·3; H, 12·9. C_8H_{14} requires C, 87·3; H, 12·7%). Oxidation of this hydrocarbon (0·15 g.) in acetone (5 c.c.) with potassium permanganate (0·5 g.) at room temperature gave 2-ethyladipic acid (0·15 g.), colourless leaflets, m. p. 47—48°, from water [Found: C, 55·0; H, 8·3%; equiv., 88. Calc. for $C_6H_{12}(CO_2H)_2$: C, 55·4; H, 8·0%; equiv., 87]. Lean and Lees (*J.*, 1897, 1067) give m. p. 48—50°. Oxidation with chromium trioxide in acetic acid gave succinic acid.

Cyclisation of 3-2′-*Dimethylaminoethyl*cyclo*hexene* (XI) *in Acetic Acid*.—The unsaturated amine (0·3 g.) in acetic acid (5 c.c.) was refluxed for 5 hr. After concentration and basification with ammonia, no amines were recovered. Addition of potassium iodide and extraction with chloroform yielded a mixture (0·3 g.) of approx. equal parts of *cis*- and *trans*-octahydro-1-methylindole methiodide which were separated by chromatography of a chloroform solution on alumina. The salts were identified by conversion into methopicrates. The *cis*-methopicrate had m. p. 194°, undepressed on admixture with *cis*-octahydro-1-methylindole methopicrate (m. p. 194°) described above; the *trans*-methopicrate had m. p. 169—171° (Found: C, 50·5; H, 6·0. Calc. for $C_{16}H_{22}O_7N_4$: C, 50·2; H, 5·75%), undepressed on admixture with an authentic specimen, m. p. 172°, kindly supplied by Prof. F. E. King.

Reaction of 3-2′-*Dimethylaminoethyl*cyclo*hexene with Alkaline Ethylene Glycol*.—The unsaturated amine (0·5 g.) and potassium hydroxide (5 g.) were heated in ethylene glycol (25 c.c.) containing sufficient water to maintain the temperature of the boiling solution at 150°. After 6 hours' refluxing very little quaternary salt could be isolated, but an unsaturated *base* (0·3 g.), (possibly XIV), b. p. 191°, was obtained. The *picrate*, yellow needles from ethanol, had m. p. 126° (Found: C, 50·1; H, 5·6; N, 14·9. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·75; N, 14·7%). The *methiodide*, colourless prisms from acetone–ether, had m. p. 234—235° (Found: C, 44·5; H, 7·5; N, 5·0. $C_{11}H_{22}NI$ requires C, 44·7; H, 7·5; N, 4·75%). The base was unaffected by refluxing acetic acid, but catalytic hydrogenation yielded 2′-dimethylaminoethyl*cyclo*hexane (X), characterised as the picrate, m. p. 150°, and as the methiodide, m. p. 220—221°, undepressed on admixture with authentic specimens prepared as described above.

cis(?)-*Octahydro-2-methyl*iso*indole* (XVI).—*cis-* or *trans*-Hexahydrophthalic anhydride (Diels and Alder, *Annalen*, 1928, **460**, 98) (1 g.) was warmed on the water-bath for 15 min. with aqueous methylamine (40%; 1·5 c.c.), the solution evaporated under reduced pressure, and the residue distilled, yielding cis-*hexahydro-*N-*methylphthalimide* (XV), b. p. 140—142°/13 mm.; the imide separated from methanol in colourless prisms, m. p. 47—48° (Found: C, 64·6; H, 7·8. $C_9H_{13}O_2N$ requires C, 64·7; H, 7·8%). Hydrolysis of the imide (0·2 g.) in water (1 c.c.) with sodium hydroxide (0·3 g.) was allowed to proceed for 7 days at room temperature; the resultant *cis*-hexahydrophthalic acid separated from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 192° undepressed on admixture with an authentic specimen (Diels and Alder, *loc. cit.*). The imide (5 g.) in dry ether (500 c.c.) was reduced with lithium aluminium hydride (3·2 g.) (Soxhlet method; Uffer and Schlitter, *Helv. Chim. Acta*, 1948, **31**, 1397). The resultant cis(?)-*octahydro-2-methyl*iso*indole* (XVI) had b. p. 70—72°/14 mm., 183—184°/757 mm. (Found: C, 77·6; H, 11·8; N, 10·15. $C_9H_{17}N$ requires C, 77·7; H, 12·2; N, 10·1%). The *picrate*, yellow needles from ethanol, had m. p. 220—222° (decomp.) (Found: C, 49·5; H, 5·7; N, 15·1. $C_{15}H_{20}O_7N_4$ requires C, 49·0; H, 5·4; N, 15·2%). The *picrolonate*, yellow needles from ethanol, had m. p. 171—172° (Found: C, 56·3; H, 5·9; N, 17·1. $C_{19}H_{25}O_5N_5$ requires C, 56·6; H, 6·1; N, 17·4%). The *methiodide* separated from acetone–ether in colourless prisms, m. p. 229—230° (Found: C, 42·7; H, 7·0; N, 4·6. $C_{10}H_{20}NI$ requires C, 42·7; H, 7·1; N, 4·9%). The *methopicrate*, yellow leaflets from ethanol, had m. p. 160—161° (Found: C, 50·0; H, 5·9; N, 14·3. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·75; N, 14·7%).

Hofmann Decomposition of cis(?)-*Octahydro-2-methyl*iso*indole*.—The *iso*indole methiodide (10 g.) was converted into the quaternary hydroxide which was decomposed by distillation *in vacuo*; the product was then redistilled, yielding fractions: (*a*) a colourless oil (2·1 g.), b. p. 60—65°/11 mm., essentially the original octahydro-2-methyl*iso*indole as shown by conversion into the picrate, m. p. 222°, and by failure to cyclise with glacial acetic acid; (*b*) a colourless oil (1·1 g.), b. p. 80—85°/11 mm., a mixture of the *iso*indole and 1-dimethylaminomethyl-2-methylene*cyclo*hexane (XVII); and (*c*) a viscous yellow oil (0·6 g.), b. p. 190—220°/0·4 mm., essentially the diamino-ether, $C_{20}H_{40}ON_2$ (XVIII), described below. Treatment of fraction (*b*) with alcoholic picric acid yielded a little of the *iso*indole picrate, m. p. 222°. The residual 1-dimethylaminomethyl-2-methylene*cyclo*hexane (XVII), b. p. 200°, yielded a *methiodide*, colourless prisms (from acetone–ether), m. p. 142—143° (Found: C, 44·7; H, 7·6; N, 4·4. $C_{11}H_{22}NI$ requires C, 44·8; H, 7·5; N, 4·75%). When this salt (0·5 g.) was converted into the methohydroxide in the usual way and the latter distilled the products were: (*a*) recovered methine base (0·1 g.), identified as the methiodide, m. p. 142—143°; (*b*) 1 : 2-dimethylene*cyclo*hexane (0·1 g.), b. p. 155° (bath-temp.), $\lambda_{max.}$ (in EtOH), 2300 Å (ε 14,130). Ozonisation of the unsaturated hydrocarbon (0·1 g.) in carbon tetrachloride (5 c.c.) at room temperature, followed by steam-distillation of the solution, gave formaldehyde (25%, estimated colorimetrically) and *cyclo*hexane-1 : 2-dione, identified as the bisphenylhydrazone, m. p. 151° (Found: C, 74·1; H, 6·6; N, 19·0. Calc. for $C_{18}H_{20}N_4$: C, 73·9; H, 6·8; N, 19·3%). Kötz, Blendermann, Rosenbusch, and Sirringhaus (*Annalen*, 1913, **400**, 67) give m. p. 150—151°.

Emde Reduction of 1-*Dimethylaminomethyl-2-methylene*cyclo*hexane*.—(a) *With sodium amalgam.* An aqueous solution of the methochloride of the foregoing base, derived from methiodide (0·5 g.) and silver chloride, was reduced with sodium amalgam (150 g.; 5%) which was added portion-wise during 6 hr. The products were methine base (0·15 g.; methiodide, m. p. 142—143°) and 1-*methyl-2-methylene*cyclo*hexane* (0·1 g.), b. p. 145° (bath-temp.) (Found: C, 87·2; H, 12·5. C_8H_{14} requires C, 87·3; H, 12·7%).

(b) *With sodium in liquid ammonia.* The methine methiodide (0·5 g.) in liquid ammonia (150 c.c.) was treated with sodium, added in small portions until a permanent blue colour remained. The hydrocarbon (0·08 g.) isolated from the reaction mixture was identical with that obtained above.

Oxidation of 1-*Methyl-2-methylene*cyclo*hexane*.—The hydrocarbon (0·1 g.) in acetone (10 c.c.) was oxidised at room temperature with potassium permanganate (0·6 g.) which was added portion-wise during 2 hr. No acidic product was obtained, but a ketone (0·08 g.) was isolated and identified as 2-methyl*cyclo*hexanone through the 2 : 4-dinitrophenylhydrazone, m. p. 133°, and the semicarbazone, m. p. 193°, undepressed on admixture with authentic specimens.

Action of Glacial Acetic Acid on 1-*Dimethylaminomethyl-2-methylene*cyclo*hexane*.—The base (0·3 g.) in acetic acid (10 c.c.) was refluxed for 3 hr. After evaporation and basification with ammonia, no base remained. Addition of ammonium picrate to a portion of the alkaline solution yielded a methopicrate (0·45 g.), m. p. 160—161° (after crystallisation from ethanol) undepressed on admixture with the octahydro-2-methyl*iso*indole methopicrate of the same m. p. (described above). Addition of potassium iodide to the remainder of the above alkaline solution and extraction with chloroform overnight gave a methiodide, m. p. 230°, not depressed on admixture with methiodide, m. p. 229—230°, derived from the *iso*indole.

Reactions of the Diamino-ether (XVIII), $C_{20}H_{40}ON_2$.—The *ether* [fraction (*c*), p. 973] [Found : C, 73·9; H, 12·6; N, 8·6%; *M* (in *cyclo*hexane), 317. $C_{20}H_{40}ON_2$ requires C, 74·0; H, 12·4; N, 8·6%; *M*, 324] was characterised as the *dipicrate*, yellow prisms (from ethanol), m. p. 168° (Found : C, 49·4; H, 5·8; N, 14·4. $C_{32}H_{46}O_{15}N_8$ requires C, 49·1; H, 5·9; N, 14·3%), the *dimethiodide*, colourless prisms (from acetone–ether), m. p. 176—178° (Found : C, 43·1; H, 7·5; N, 4·9. $C_{22}H_{46}ON_2I_2$ requires C, 43·4; H, 7·6; N, 4·6%), and the *dimethopicrate*, yellow prisms (from ethanol), m. p. 116—117° (Found: C, 50·2; H, 6·1; N, 13·6. $C_{34}H_{50}O_{15}N_8$ requires C, 50·4; H, 6·2; N, 13·8%). The ether was not hydrogenated in the presence of Raney nickel at pressures up to 5 atm., and did not react with acetic anhydride. Treatment with boiling concentrated hydrobromic acid for 1 hr. gave 1-dimethylaminomethyl-2-hydroxymethyl*cyclo*hexane hydrobromide (XIX), which separated from acetone in colourless needles, m. p. 233—234° (Found : C, 48·0; H, 8·4. $C_{10}H_{21}ON,HBr$ requires C, 47·7; H, 8·7%). Hofmann degradation of the diamino-ether methiodide (0·8 g.) yielded the diamino-ether (0·1 g.) and an unsaturated nitrogen-free ether (XVIII; with $=$O for H and $CH_2{\cdot}NMe_2$), b. p. 180° (bath-temp.). Oxidation of the unsaturated ether with potassium permanganate in acetone at room temperature gave 2-hydroxymethyl*cyclo*hexanone (Mannich and Brose, *Ber.*, 1923, **56**, 833), characterised as the 2 : 4-*dinitrophenylhydrazone*, red prisms (from ethanol), m. p. and mixed m. p. 125—126° (Found : C, 50·2; H, 5·4. $C_{13}H_{16}O_5N_4$ requires C, 50·6; H, 5·2%).

*Emde Reduction of the Octahydro-2-methyl*isoindole.—Reduction of a refluxing methochloride solution prepared from the *iso*indole methiodide (2 g.) with sodium amalgam (200 g., 5%), added during 6 hr., gave 1-dimethylaminomethyl-2-methyl*cyclo*hexane (XX) (0·15 g.), characterised as the *picrate*, yellow needles (from ethanol), m. p. 200—201·5° (Found : C, 50·6; H, 6·4. $C_{16}H_{24}O_7N_4$ requires C, 50·0; H, 6·3%), the *methiodide*, colourless prisms (from acetone–ether), m. p. 198—201° (Found : C, 44·25; H, 8·0. $C_{11}H_{24}NI$ requires C, 44·4; H, 8·1%), and the *methopicrate*, yellow plates (from ethanol), m. p. 156—158° (Found: C, 51·1; H, 6·1. $C_{17}H_{26}O_7N_4$ requires C, 51·3; H, 6·5%).

Hofmann Degradation of 1-*Dimethylaminomethyl*-2-*methyl*cyclo*hexane* (XX).—The base methiodide (0·8 g.) was converted into an aqueous solution of the methohydroxide in the usual way. Evaporation of the solution and distillation of the residue at 150° gave an unsaturated product (0·15 g.) which was oxidised in acetone (10 c.c.) with potassium permanganate (0·6 g.) added during 2 hr. There was thus obtained 2-methyl*cyclo*hexanone (0·09 g.), characterised as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 132—133°.

Preparation of cis- *and* trans-*Hexahydro*-1-*methylphthalic Anhydride*.—After citraconic anhydride (10 g.) and butadiene (6 g.) had been heated in dry benzene (15 c.c.) at 210° for 72 hr., the cooled mixture was added to sodium hydroxide (10%; 80 c.c.) and freed from benzene on the water-bath. Polymeric materials were separated by filtration and the filtrate acidified with hydrochloric acid and extracted with ether for 48 hr. The residue from the ether was slowly distilled *in vacuo*, yielding *cis*-1 : 2 : 3 : 6-tetrahydro-1-methylphthalic anhydride, b. p. 138—140°/13 mm. (Found : C, 65·2; H, 5·8. Calc. for $C_9H_{10}O_3$: C, 65·1; H, 6·1%). Hydrogenation of this anhydride (0·9 g.) in ethanol (5 c.c.) in the presence of Raney nickel was complete in 20 min. (H_2 uptake at N.T.P., 110 c.c. Calc. for one double bond, 121·5 c.c.). The resulting *cis*-hexahydro-1-methylphthalic anhydride (XXI) (0·8 g.) was distilled at 136°/13 mm., and crystallised from methanol in colourless prisms, m. p. 70—71 (Found : C, 64·1; H, 7·0. Calc. for $C_9H_{12}O_3$: C, 64·3; H, 7·1%) (Nazarov and Kucherov, *loc. cit.*, give m. p. 71—72°). This anhydride (1 g.), when heated with concentrated hydrochloric acid (5 c.c.) at 120° for 3 hr., yielded *trans*-hexahydro-1-methylphthalic acid, colourless prisms (from benzene), m. p. 211—212° (Nazarov and Kucherov, *loc. cit.*, give m. p. 212—213°). The acid (1·5 g.) was refluxed for 24 hr. with acetyl chloride (10 c.c.), and the product distilled at 138—140°/14 mm., giving *trans*-hexahydro-1-methylphthalic anhydride (0·6 g.), colourless prisms, m. p. 86—87°, from light petroleum (b. p. 60—80°) (Found : C, 64·4; H, 7·2. Calc. for $C_9H_{12}O_3$: C, 64·3; H, 7·1%) (Nazarov and Kucherov, *loc. cit.*, give m. p. 87—88°).

cis(?)-*Octahydro*-2 : 8-*dimethyl*isoindole (XXIII).—The above *cis*-anhydride (0·9 g.) was warmed with aqueous methylamine (40%; 3 c.c.) on the water-bath for 20 min., the reaction mixture evaporated, and the residue distilled *in vacuo*, giving the *N*-methylimide (XXII) of *cis*-hexahydro-1-methylphthalic acid, b. p. 137—139°/13 mm., which crystallised from methanol in colourless prisms, m. p. 52—53° (Found : C, 66·0; H, 8·0; N, 7·2. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3; N, 7·7%). Reduction of this imide (1 g.) in ether (250 c.c.) with lithium aluminium hydride (1 g.) gave the iso*indole* (XXIII) (0·8 g.), b. p. 168—170° (Found : C, 78·2; H, 12·3; N, 9·2. $C_{10}H_{19}N$ requires C, 78·4; H, 12·4; N, 9·15%). The base yielded a *picrate*, yellow needles (from ethanol), m. p. 226—227° (Found : C, 50·6; H, 5·7; N, 14·7. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·7; N, 14·7%), a *methiodide*, colourless leaflets (from acetone–ether), m. p. 236—237° (Found : C, 44·5; H, 7·3; N, 4·6. $C_{11}H_{22}NI$ requires C, 44·8; H, 7·5; N, 4·75%), and a *methopicrate*, yellow prisms (from ethanol), m. p. 203—204° (Found : C, 51·6; H, 6·0; N, 13·9. $C_{17}H_{24}O_7N_4$ requires C, 51·5; H, 6·1; N, 14·1%).

Hofmann Degradation of cis(?)*-Octahydro-2 : 8-dimethyl*iso*indole.*—The *iso*indole methiodide (7 g.) was converted into quaternary hydroxide which was decomposed in the usual manner. Redistillation of the oily product gave (*a*) a colourless oil (1·8 g.), b. p. 75—94°/11 mm., and (*b*) a viscous yellow oil (0·3 g.), b. p. 180—200°/11 mm. Fraction (*a*) on treatment with methanolic picric acid gave a good yield of the picrate of the original *iso*indole (XXIII) ; decomposition of the picrate mother-liquors with alkali yielded an unsaturated base, probably 1-dimethylaminomethyl-1-methyl-2-methylene*cyclo*hexane (XXIV) (0·25 g.) from which was obtained a *methiodide*, colourless prisms (from acetone–ether), m. p. 202—203° (Found : C, 46·2; H, 7·4; N, 4·75. $C_{12}H_{24}NI$ requires C, 46·6; H, 7·8; N, 4·5%), and a *methopicrate*, yellow prisms (from ethanol), m. p. 159—160° (Found : C, 52·0; H, 6·4; N, 13·5. $C_{18}H_{26}O_7N_4$ requires C, 52·7; H, 6·3; N, 13·6%). Attempted Hofmann decomposition of the methiodide, m. p. 202—203°, gave no hydrocarbon, but an oily base was obtained which yielded the original methiodide on treatment with methyl iodide.

When the unsaturated base [(XXIV) from fraction (*a*) above] was refluxed with acetic acid, and the cyclised product isolated as methopicrate, yellow prisms of m. p. 204° were obtained, undepressed on admixture with the methopicrate of the above octahydro-2 : 8-dimethyl*iso*indole (XXIII) of the same m. p.

Treatment of fraction (*b*) (above) with methanolic picric acid gave a *picrate* which recrystallised from ethanol in yellow prisms, m. p. 156° (Found : C, 50·2; H, 6·1. $C_{34}H_{50}O_{15}N_8$ requires C, 50·4; H, 6·2%).

Emde Degradation of cis(?)*-Octahydro-2 : 8-dimethyl*iso*indole.*—The *iso*indole methiodide (0·8 g.) in liquid ammonia (200 c.c.) was treated with a slight excess of sodium, and the resulting basic mixture (0·35 g.) separated by fractional crystallisation of the picrates from ethanol. There was thus obtained octahydro-2 : 8-dimethyl*iso*indole picrate, yellow needles, m. p. and mixed m. p. 226—227° (Found : C, 50·3; H, 5·5; N, 14·7. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·75; N, 14·7%), and a larger fraction, yellow prisms, m. p. 136—137° (Found : C, 51·5; H, 6·0; N, 14·1. $C_{17}H_{26}O_7N_4$ requires C, 51·3; H, 6·5; N, 14·1%). The latter *picrate* is that of 2-dimethylaminoethyl-1 : 1-dimethyl*cyclo*hexane (XXV) ; the corresponding *methiodide* separated from acetone–ether in colourless prisms, m. p. 267—268° (Found : C, 46·4; H, 8·0; N, 4·2. $C_{12}H_{26}NI$ requires C, 46·3; H, 8·4; N, 4·5%), and the *methopicrate*, yellow leaflets from ethanol, had m. p. 169—170° (Found : C, 51·8; H, 6·8. $C_{18}H_{28}O_7N_4$ requires C, 52·4; H, 6·8%).

Hofmann Degradation of the Methiodide of the Base (XXV).—The methiodide (0·4 g.) was converted into methohydroxide, distillation of which gave a basic fraction (0·12 g.) and 1 : 1-dimethyl-2-methylene*cyclo*hexane (XXVI) (0·15 g.), b. p. 155°. Oxidation of the hydrocarbon (0·15 g.) in acetone (10 c.c.) with potassium permanganate (0·6 g.) at room temperature gave 2 : 2-dimethyl*cyclo*hexanone (0·09 g.), identified as the semicarbazone, m. p. 200°, undepressed on admixture with an authentic specimen (Auwers and Lange, *Annalen*, 1913, **401**, 320).

cis*-Octahydro-2 : 8 : 9-trimethyl*iso*indole* (XXVIII).—Catalytic hydrogenation of *cis*-1 : 2 : 3 : 6-tetrahydro-1 : 2-dimethylphthalic anhydride (Woodward, *loc. cit.*) over Raney nickel in ethanol at atmospheric pressure yielded *cis*-hexahydro-1 : 2-dimethylphthalic anhydride (XXVII), b. p. 139—140°/12 mm., which recrystallised from benzene in colourless prisms, m. p. 56° (Found : C, 65·7; H, 7·6. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%). This anhydride (0·9 g.), when warmed on the water-bath for 15 min. with aqueous methylamine (40% ; 3 c.c.), yielded the *cis-N*-methylimide (0·8 g.), b. p. 141°/12 mm. Reduction of the imide (0·8 g.) in ether (250 c.c.) with lithium aluminium hydride (1·5 g.) gave *cis*-octahydro-2 : 8 : 9-trimethyl*iso*indole (XXVIII) (0·5 g.), b. p. 186°, characterised as the *picrate*, yellow needles (from ethanol), m. p. 227—230° (Found : C, 51·6; H, 6·0; N, 14·4. $C_{17}H_{24}O_7N_4$ requires C, 51·5; H, 6·1; H, 14·1%), the *picrolonate*, yellow prisms (from ethanol), m. p. 188—189° (Found: N, 16·3. $C_{21}H_{29}O_5N_5$ requires N, 16·2%), the *methopicrate*, yellow prisms (from ethanol), m. p. 240—241° (Found: C, 52·7; H, 6·2; N, 13·5.

$C_{18}H_{26}O_7N_4$ requires C, 52·7; H, 6·3; N, 13·7%), and the *methiodide*, colourless hygroscopic prisms (from acetone–ether), m. p. 231° (Found: C, 46·8; H, 7·8; N, 4·5. $C_{12}H_{24}NI$ requires C, 46·6; H, 7·8; N, 4·5%). The methiodide gave no methine on attempted Hofmann decomposition, the *iso*indole (XXVIII) being recovered.

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