72. *Synthetical and Stereochemical Investigations of Reduced Cyclic Bases. Part I. Hydrogenation Products of Indole and the Exhaustive Methylation of an* N-*Methyloctahydroindole.*

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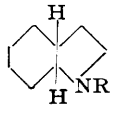
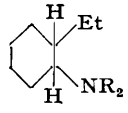
Raney nickel reduction of indole in methanol solution gives N-*methyloctahydroindole* (I, R = Me), probably the *cis*-isomer. Unlike *cis*-2-methyloctahydroindole, which affords a dimethyl-2-*n*-propyl*cyclo*hexylamine (Fujise, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, **9**, 91), exhaustive methylation of the base (I, R = Me) unexpectedly severs the nitrogen atom from the *cyclo*hexane ring with the formation of *dimethyl-β*-cyclo*hexylethylamine*, which was synthesised for comparison. In order to determine the configuration of " perhydroindole " (Willstätter, Seitz, and v. Braun, *Ber.*, 1925, **58**, 385), cis- and trans-2-*ethyl*cyclo*hexylamine* (II, R = H) have been synthesised and appear to demonstrate the identity of this base with the *cis*-isomeride.

THE preparation of *cis-trans*-forms of decalin, hydrindane, and bi*cyclo*octane, chiefly by Hückel and Linstead, and the physical and chemical properties of the isomerides, have very largely confirmed the predictions of the tetrahedral theory of stereochemistry in its application to *ortho*-carbodicyclic systems. The existence of stereoisomerides has also been recorded when the dicyclic nucleus includes a hetero-atom, as in decahydroquinoline (Hückel and Stepf, *Annalen*, 1927, **453**, 163) and decahydro*iso*quinoline (Helfer, *Helv. Chim. Acta*, 1923, **6**, 785; 1926, **9**, 814), but a review of the literature reveals that less is known of other types of condensed heterocyclic structures, and in the octahydroindole series, for example, *cis-trans*-isomerism has apparently never been observed.

The absence of stereoisomerism among the octahydroindoles is not likely to be due, *a priori*, to the excessive instability of one of the two theoretically possible structures on account of valency distortion. The normal angle of the carbon–nitrogen–carbon valencies is known to be virtually identical with that of the carbon bonds in the unstrained *cyclo*pentane ring, so the stereochemistry of octahydroindole may be likened to that of hydrindane. Accordingly, on this analogy it is to be expected that the *cis*-structure would be strainless and readily formed, and that the *trans*-form, while theoretically capable of synthesis from the appropriate monocyclic intermediates, would, on account of its strained configuration, be produced in relatively small amounts during the complete hydrogenation of indole.

The reduction of indole to an octahydro-derivative has been carried out by Willstätter and Jacquet (*Ber.*, 1918, **51**, 777) at room temperature in acetic acid over platinum, and by Adkins and Coonradt (*J. Amer. Chem. Soc.*, 1941, **63**, 1563) at high temperature and pressure with a Raney nickel catalyst. The m. p.'s of the derived benzenesulphonamides indicate that despite these widely different conditions the reduction products were essentially identical. According to the tetrahedral theory this hydroindole is probably the *cis*-isomer, but its exact structure has never been ascertained. On the other hand, the octahydro-derivative obtained by the platinum-catalysed reduction of 2-methylindole in acetic acid has definitely been shown to possess the *cis*-configuration by applying the process of exhaustive methylation (Fujise, *loc. cit.*). Hydrogenation of the resulting methine gave a dimethyl-2-*n*-propyl*cyclo*hexylamine, at once recognised as the *cis*-isomeride since it had previously been derived from that decahydroquinoline already known from the work of Hückel and Stepf (*loc. cit.*) to possess the *cis*-configuration. In view of its formation under identical conditions, it is evident that the known octahydroindole (I, R = H) is also a *cis*-compound, but in order to obtain conclusive evidence on this point, we proposed to submit the base to exhaustive methylation and to compare the degradation product with the appropriate synthetical *cis-trans*-isomers of definitely established constitution.

(I.) 



(II.)

By analogy with the 2-methyl derivative, the exhaustive methylation of octahydroindole was expected to lead to a vinylamine and on subsequent reduction to yield one of the stereoisomeric N-*dimethyl*-2-*ethyl*-cyclo*hexylamines* (II, R = Me). These compounds have not hitherto been described, but in the course of experiments on the nickel-catalysed reduction of indoles, v. Braun, Bayer, and Blessing (*Ber.*, 1924, **57**, 392) isolated a " perhydroindole," which was eventually formulated as 2-ethyl*cyclo*hexylamine (II, R = H) (Willstätter, Seitz, and v. Braun, *loc. cit.*). No opinion has been expressed as to its stereochemical structure, and syntheses of the *cis-trans*-isomerides of ethyl*cyclo*hexylamine were therefore undertaken, both to provide intermediates for the preparation of the isomeric tertiary amines (II, R = Me) and to throw light on the constitution of perhydroindole.

The synthetical work originated from 2-ethyl*cyclo*hexanone (Vavon and Mitchovitch, *Bull. Soc. chim.*, 1929, **45**, 961), prepared by acid hydrolysis of ethyl 2-ethyl*cyclo*hexanonecarboxylate. The ketone afforded a 2 : 4-*dinitrophenylhydrazone*, and reduction of the ketoxime under suitable conditions gave the desired isomeric ethyl*cyclo*hexylamines. The configurations assigned to the products are based on Skita's observation (*Ber.*, 1920, **53**, 1792) that reduction in acid media leads predominantly to the formation of *cis*-, whereas reduction in neutral or alkaline conditions affords the *trans*-isomerides. As certain physical properties, *e.g.*, b. p., density, and refractive index, are generally slightly higher for the *cis*- than for the *trans*-forms (Auwers, *Annalen*, 1919, **419**, 92; 1920, **420**, 84), the validity of Skita's generalisation is readily established, and this has already been done with the closely analogous 2-methyl*cyclo*hexylamines (Skita, *Ber.*, 1923, **56**, 1014). The base obtained by reduction of 2-ethyl*cyclo*hexanone oxime with sodium and ethyl alcohol, or by the superior method of catalytic reduction with Raney nickel in saturated alcoholic ammonia, the latter to reduce secondary amine formation (cf. *Org. Synth.*, 1943, **23**, 72), we therefore regard as *trans*-ethyl*cyclo*hexylamine (II, R = H). It is a colourless liquid rapidly converted in air into a white mass of carbonate, but it was characterised by three crystalline derivatives, the *picrate* (m. p. 198—199°), *benzenesulphonamide* (m. p. 131°), and *trimethylammonium iodide* (m. p. 182°), all of which differ from the corresponding derivatives of perhydroindole (v. Braun *et al.*, *loc. cit.*). Methylation to the tertiary amine was effected by the convenient method of Sommelet and Farrand (*Bull. Soc. chim.*, 1924, **35**, 446; see also Clarke, Gillespie, and Weisshaus, *J. Amer. Chem. Soc.*, 1933, **55**, 4571), *viz.*, heating with formaldehyde and formic acid. The resulting *trans*-*N*-dimethyl-2-ethyl*cyclo*hexylamine (II, R = Me), a colourless liquid unaffected by exposure to air, gave with methyl iodide the salt, m. p. 182°, already prepared from the *trans*-primary base.

For the preparation of the *cis*-series, 2-ethyl*cyclo*hexanone oxime was heated under pressure with ammonium formate (Leuckardt reaction). The crude *N*-formyl compound was hydrolysed, and the amine purified through its *benzenesulphonamide*. Hydrolysis of this derivative with concentrated hydrochloric acid in a sealed tube afforded *cis*-2-ethyl*cyclo*hexylamine (II, R = H), like the *trans*-isomer, a colourless oil rapidly forming in the air a solid carbonate. The *cis*-amine was also obtained by catalytic reduction of the oxime in acid solution and characterised by the *benzenesulphonamide* (m. p. 161°) and *picrate* (m. p. 189°). Methylation with formaldehyde and formic acid gave in good yield, *cis*-*N*-dimethyl-2-ethyl*cyclo*hexylamine, which afforded a crystalline *methiodide* (m. p. 231°). The m. p.'s recorded by v. Braun for the derivatives of perhydroindole are : benzenesulphonamide 120°, picrate 189—190°, and trimethylammonium iodide 231°. No definite reason for the divergence in the sulphonamide m. p.'s can be offered, but the correspondence between the other two pairs of derivatives may be taken to indicate that perhydroindole is *cis*-2-ethyl*cyclo*hexylamine. This apparently exceptional formation of a *cis-cyclo*hexylamine under *neutral* conditions can, however, be reconciled with the Skita rule if it is allowed that the perhydroindole is produced through the octahydro-compound, which, for reasons already indicated, very probably has the *cis*-structure.

Because they are unaffected by exposure to the air, the *cis*- and *trans*-dimethyl*cyclo*hexylamines are more

suitable than the corresponding primary amines for physical measurements, and the refractive index and density determinations (made by Dr. Strauss of this Laboratory) are recorded in the experimental section. The relationship between the two series is in accord with the stereochemical structures assigned on the basis of Skita's conclusions.

Owing to lack of suitable high-pressure apparatus, when this work was begun we had great difficulty in the preparation of octahydroindole by Raney nickel hydrogenation in *cyclo*hexane or dioxan. By using ethanol as a solvent, dihydroindole was readily obtained, but on raising the temperature to effect further reduction, *N*-alkylation also occurred (cf. Winans and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 306) and a quantitative yield of N-*ethyloctahydroindole* resulted. Reduction in methanol likewise afforded N-*methyloctahydroindole*, and the crystalline *methiodide* of this base was used for the Hofmann degradation.

Somewhat surprisingly, in view of the results with decahydroquinoline and 2-methyloctahydroindole (Fujise, *loc. cit.*), decomposition of the quaternary hydroxide ruptured the bond by which the nitrogen atom is attached to the *cyclo*hexane ring, and a methine base was obtained, subsequently identified as a β-*dimethylaminoethyl*cyclo*hexene*, $C_6H_9 \cdot CH_2 \cdot CH_2 \cdot NMe_2$, from its reduction to β-*dimethylaminoethyl*cyclo*hexane* (III). By methylating β-phenylethylamine to the *N*-dimethyl derivative, which was then completely hydrogenated over Raney nickel, the amine (III) was synthesised, and a comparison of the *picrate*, *picrolonate*, and *methiodide* with the corresponding salts of the hydroindole exhaustive methylation product definitely established the identity of the latter.

Experimental.

Ethyl cyclo*Hexanone*-2-*carboxylate* (Kötz, *Annalen*, 1907, **358**, 198).—The yield of this ester, b. p. 106°/11 mm., obtained by Kötz (50%) is raised to 61% by heating the *cyclo*hexanoneglyoxylic ester at 140° under reduced pressure in a flask packed with glass wool (Found: C, 63·4; H, 8·2. Calc. for $C_9H_{14}O_3$: C, 63·5; H, 8·2%).

2-*Ethyl*cyclo*hexanone* (cf. Vavon and Mitchovitch, *loc. cit.*).—The *cyclo*hexanonecarboxylate (93 g.) was heated with powdered sodium (12·6 g.) in refluxing benzene (500 c.c.) for 3 hours. After the addition of ethyl iodide (79 g.) and a further 8 hours' heating, the benzene layer was washed, dried, and distilled, giving ethyl 2-ethyl*cyclo*hexanone-2-carboxylate (93 g., 86%), b. p. 122—124°/14 mm. By refluxing with hydrochloric acid (500 c.c. of 20%) and occasionally distilling the alcohol produced, the ester (87 g.) was largely hydrolysed in 16 hours. Ether extraction of the diluted solution gave the colourless ketone (41 g.), b. p. 73·5—74·5°/35 mm., of which the 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol in red needles, m. p. 162° (Found: C, 54·6; H, 6·0. $C_{14}H_{18}O_4N_4$ requires C, 54·9; H, 5·9%).

trans-2-*Ethyl*cyclo*hexylamine*.—(i) From the ethyl*cyclo*hexanone (10 g.), hydroxylamine hydrochloride (9 g.), and sodium acetate in hot aqueous alcohol, an oxime (10 g.) was prepared, b. p. 111°/11 mm., m. p. *ca.* 35—40° (Vavon and Mitchovitch, *loc. cit.*, give m. p. 60°). It was dissolved in refluxing absolute alcohol (100 c.c.) to which sodium (8 g.) was added in portions. At the end of the reaction the cold solution was acidified with hydrochloric acid, and the alcohol removed under reduced pressure. The residue was strongly basified with potassium hydroxide, and the amine (6·7 g.) isolated by ether as a colourless oil, b. p. 65°/17 mm., which rapidly became covered by a white film of carbonate. Alcoholic picric acid gave a *picrate* (yield 80%), m. p. 195—198°, which on recrystallisation from alcohol formed yellow, flat prisms, m. p. 198—199° (decomp.) (Found: C, 47·4; H, 5·7. $C_8H_{17}N,C_6H_3O_7N_3$ requires C, 47·2; H, 5·6%).

With benzenesulphonyl chloride, a pyridine solution of the base afforded a *benzenesulphonamide*, crystallising in masses of minute needles, m. p. 131° (Found: C, 62·8; H, 7·7. $C_{14}H_{21}O_2NS$ requires C, 62·9; H, 7·8%). *trans*-2-Ethyl*cyclo*hexylamine reacted vigorously with methyl iodide, and the resulting N-*dimethyl*-2-*ethyl*cyclo*hexylamine methiodide* separated from ethyl acetate in colourless, short prisms, m. p. 182° (Found: I, 42·9. $C_{11}H_{24}NI$ requires I, 42·9%).

(ii) The oxime (11 g.), dissolved in alcohol saturated with ammonia, was hydrogenated over Raney nickel for 3 hours at 130° at an initial pressure of 83 atm. The filtered solution was acidified with hydrochloric acid, the alcohol evaporated, and the base liberated by alkali was extracted with ether and distilled. The product (7·8 g., 79%) had b. p. 149—151°/745 mm., and was identified as *trans*-2-ethyl*cyclo*hexylamine by the benzenesulphonamide of m. p. and mixed m. p. 131°.

trans-N-*Dimethyl*-2-*ethyl*cyclo*hexylamine*.—The primary amine (5·8 g.), dissolved in formic acid (4·2 g. of 100%) and aqueous formaldehyde (7·9 c.c. of 35%), was heated on a steam-bath, carbon dioxide being rapidly evolved. After 1 hour the solution was boiled for 2—3 minutes, and the base liberated by addition of potassium hydroxide was extracted with ether. Traces of primary and secondary amines were eliminated by nitrous acid, leaving the purified N-*dimethyl*-2-*ethyl*cyclo*hexylamine* (5·5 g.), b. p. 187·5—188·5°/745 mm., $d_{26°}$ 0·8464; $n_{20°}$ 1·4573 (Found: N, 8·8. $C_{10}H_{21}N$ requires N, 9·0%). With methyl iodide the metho-salt already prepared from the primary base was obtained, m. p. and mixed m. p., 182°.

cis-2-*Ethyl*cyclo*hexylamine*.—(i) 2-Ethyl*cyclo*hexanone (11 g.) was heated with ammonium formate (16·5 g.) in a sealed tube at 210° for 12 hours. Water was then added, and by ether extraction the ethyl*cyclo*hexylformamide (10 g.), b. p. 145—155°/12 mm., was isolated, and was hydrolysed by refluxing with alcoholic potassium hydroxide (15 g. in 110 c.c.). Evaporation of the acidified solution and ether extraction of the basified residue gave the crude amine, and this was heated at 100° for 10 minutes with pyridine (21 c.c.) and benzenesulphonyl chloride (12·5 g.). After 3 crystallisations from alcohol, the *benzenesulphonamide* formed colourless, square tablets, m. p. 161° (Found: C, 62·7; H, 7·7. $C_{14}H_{21}O_2NS$ requires C, 62·9; H, 7·8%).

The amide (5·5 g.) was heated with concentrated hydrochloric acid (15 c.c.) in a sealed tube at 175° for 12 hours. The tarry ether-soluble layer was removed and the aqueous solution basified, thus liberating *cis*-2-ethyl*cyclo*hexylamine, a colourless mobile oil, b. p. 64°/16 mm., rapidly covered by a white crust of carbonate on exposure to the air. The *picrate*, m. p. 189°, separated from water in long yellow needles (Found: C, 47·3; H, 5·9. $C_8H_{17}N,C_6H_3O_7N_3$ requires C, 47·2; H, 5·6%).

(ii) 2-Ethyl*cyclo*hexanone oxime (8·5 g.) in alcoholic solution (50 c.c.) containing concentrated hydrochloric acid (8 c.c.) was hydrogenated over palladised charcoal catalyst at atmospheric pressure for 3 days. Water was added, unchanged oxime recovered by ether extraction after removal of alcohol under reduced pressure, and the base liberated by alkali. The *cyclo*hexylamine (1 g.) distilled at 69—73°/20 mm., leaving a large residue, and was identified by the benzenesulphonamide, m. p. and mixed m. p. 161°.

cis-N-*Dimethyl*-2-*ethyl*cyclo*hexylamine*.—A solution of the primary amine (0·8 g.) in aqueous formaldehyde (1·3 c.c. of 35%) and formic acid (0·62 g.) was heated at 100° until effervescence ceased (1 hour), and then refluxed for a further 5 minutes. The *cis*-amine (0·7 g.) obtained by ether extraction of the cooled and basified solution had b. p. 82—83°/20 mm., $d_{23°}$ 0·8657, $n_{20°}$ 1·4585. The action of methyl iodide in dry ether precipitated the base *methiodide*, which crystal-

lised from acetone–ether in colourless needles, m. p. 231° (decomp.) (Found: C, 44·7; H, 8·2; N, 4·8. $C_{11}H_{24}NI$ requires C, 44·4; H, 8·1; N, 4·7%).

1-*Ethyloctahydroindole*.—Indole (1 mol.) was hydrogenated in *cyclo*hexane or dioxan (15 mols.) at 100—110 atm. in presence of Raney nickel. With increasing temperature, *i.e.*, up to 150—160°, 1 mol. of hydrogen was absorbed, corresponding to the formation of dihydroindole, but thereafter no observable reduction occurred until, at 200°, further very slow absorption took place. Fractionation of the product and purification through a picrate (m. p. *ca.* 130—135°) gave a small quantity of a base which after distillation yielded *octahydroindole picrolonate*, crystallising from ethanol in yellow rhombic tablets, m. p. 220° with subsequent darkening (Found: C, 55·7; H, 5·4. $C_8H_{15}N,C_{10}H_8O_5N_4$ requires C, 55·5; H, 5·9%).

The reduction of indole in ethanol solution at 100—110° and a maximum pressure of 90—100 atm. gave the theoretical amount of 2 : 3-dihydroindole, b. p. 89—94°/10 mm. (Found: C, 80·4; H, 8·0; N, 11·8. Calc. for C_8H_9N: C, 80·6; H, 7·6; N, 11·8%), identified by the picrate, m. p. 174°. Further reduction, which was accompanied by *N*-ethylation, required a temperature of 150—160°, and the yield of 1-*ethyloctahydroindole*, a colourless oil of b. p. 68°/11 mm., was quantitative (Found: C, 78·1; H, 12·4; N, 9·8. $C_{10}H_{19}N$ requires C, 78·4; H, 12·4; N, 9·1%). The amine *picrate* crystallised from alcohol in fine, bright yellow prisms, m. p. 147—150° (Found: N, 15·0. $C_{10}H_{19}N,C_6H_3O_7N_3$ requires N, 14·7%).

1-*Methyloctahydroindole*.—A solution of indole (10 g.) in methyl alcohol (100 c.c.) was hydrogenated at 170° and an initial pressure of 80 atm. with a Raney nickel catalyst. The filtered and acidified solution was evaporated, and extraction of the basified product gave 1-*methyloctahydroindole* (9 g.) as a colourless oil, b. p. 178—179°/757 mm. (Found: C, 77·2; H, 12·2. $C_9H_{17}N$ requires C, 77·7; H, 12·2%). The base *methiodide*, which was precipitated at room temperature from a solution of 1-methyloctahydroindole in ether containing methyl iodide, crystallised from acetone–ether in long, colourless needles, m. p. 201° (Found: I, 45·0. $C_{10}H_{20}NI$ requires I, 45·2%). On warming the iodide with saturated alcoholic picric acid, a *methopicrate* was obtained, which crystallised from alcohol in long, yellow needles, m. p. 194° (Found: C, 49·6; H, 5·8. $C_{16}H_{22}O_7N_4$ requires C, 50·2; H, 5·8%).

β-*Dimethylaminoethyl*cyclo*hexene*.—Dimethyloctahydroindolinium iodide (12·5 g.) was dissolved in water (60 c.c.) and shaken for 1 hour with silver oxide, freshly prepared from silver nitrate (10 g.) and sodium hydroxide (2·4 g.). The filtered solution was evaporated at 50°, and the syrupy residue of quaternary hydroxide decomposed by heating under reduced pressure at 90—100°. The base distilling was taken up in ether, and the solution dried and evaporated, β-*dimethylaminoethyl*cyclo*hexene* being isolated from the residue (3·6 g.) as a colourless oil, b. p. 84°/14 mm., which decolourised bromine water and aqueous potassium permanganate (Found: C, 77·8; H, 12·7. $C_{10}H_{19}N$ requires C, 78·5; H, 12·4%). The amine *picrolonate* crystallised from ethanol in yellow needles, m. p. 184—185° (Found: C, 57·4; H, 6·5. $C_{10}H_{19}N,C_{10}H_8O_5N_4$ requires C, 57·6; H, 6·5%). Addition of excess methyl iodide to the base dissolved in ether precipitated the *methiodide*, which separated from acetone–ether in microscopic rhombs, m. p. 226—227° (Found: C, 44·7; H, 7·7. $C_{11}H_{22}NI$ requires C, 44·7; H, 7·5%).

β-*Dimethylaminoethyl*cyclo*hexane*.—The dimethylaminoethyl*cyclo*hexene (2·6 g.) was hydrogenated in the form of its hydrochloride in ethanol solution (50 c.c.) over palladised charcoal at atmospheric pressure. After filtration, the solution was evaporated, and the residue basified and extracted in ether. β-Dimethylaminoethyl*cyclo*hexane (2·3 g.) was thus isolated as an oil, b. p. 83°/15 mm., characterised by its *picrolonate*, which crystallised in yellow needles from ethanol, m. p. 191° (Found: C, 57·2; H, 7·0. $C_{10}H_{21}N,C_{10}H_8O_5N_4$ requires C, 57·3; H, 6·9%). The picrate, yellow needles, m. p. 150°, from ethanol, and methiodide, colourless prisms, m. p. 224°, from acetone–ether, were also prepared.

Dimethyl-β-phenylethylamine.—Benzyl cyanide (50 g.), dissolved in saturated alcoholic ammonia (500 c.c.), was hydrogenated, initially at 90 atm., over Raney nickel for 7 hours at 110°. After acidification of the filtered solution with hydrogen chloride, water was added to dissolve the crystalline precipitate, and the alcohol distilled under reduced pressure. The aqueous residue was then extracted with ether and basified, whereupon β-phenylethylamine was liberated, and when isolated with ether the pure base distilled as a colourless liquid, b. p. 89·5—91°/91 mm., characterised by the picrate, m. p. 169°, in agreement with the recorded values.

To a solution of the β-phenylethylamine (24·2 g.) in formic acid (18·5 g.), formaldehyde (35 c.c. of 35%) was added, and the mixture warmed on a steam-bath for 1 hour. When the reaction had been completed by brief refluxing, the tertiary amine was isolated by addition of alkali and ether extraction. The product (21 g.) was a colourless oil, b. p. 203—205°, and the picrate had m. p. 135° (Decker and Becker, *Ber.*, 1912, **45**, 2407, record m. p. 133—134°) (Found: C, 50·7; H, 4·7. Calc. for $C_{16}H_{18}O_7N_4$: C, 50·8; H, 4·8%).

Reduction of the tertiary amine (10 g.), dissolved in methanol (100 c.c.), over Raney nickel for 16 hours at 200° with an initial hydrogen pressure of 83 atm. was accompanied by extensive hydrogenolysis. However, after filtration and evaporation of the acidified solution, which was then basified and extracted with ether, β-dimethylaminoethyl*cyclo*hexane (1 g.) was obtained as a colourless liquid distilling at 87—88°/21 mm. Alcoholic picric acid afforded the *picrate*, crystallising from ethanol in long, yellow needles, m. p., alone or mixed with the salt obtained from *N*-methyloctahydroindole by the Hofmann degradation, 150° (Found: C, 50·3; H, 6·1. $C_{10}H_{21}N,C_6H_3O_7N_3$ requires C, 50·5; H, 6·2%). Similarly, the *methiodide*, which separated from acetone–ether in fine, colourless needles, was identified with the corresponding salt from the same source by its m. p. and mixed m. p. of 219—220° (Found: C, 44·6; H, 8·1; N, 4·9. $C_{11}H_{24}NI$ requires C, 44·4; H, 8·1; N, 4·7%).

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