MIXED ELECTROLYTIC REDUCTION OF 1,4-DIMETHYLPYRIDINIUM METHYL SULFATE WITH ACETONE AND OF 1-METHYLPYRIDINIUMMETHYL SULFATE WITH CYCLOPENTANONE*

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Mixed electrolytic reduction of the mentioned quaternary salts with acetone or cyclopentanone, respectively, on lead electrodes affords in addition to the products of reduction of the quaternary salts mainly amino alcohols *Ii*, *IIIi*, or *Id*, *Ig*, *IId*, *IIId* as well as further by-products.

Some time ago we described[1] mixed electrolytic reduction of some pyridine bases with ketones and mixed electrolytic reduction of 1,4-dimethylpyridinium methyl sulfate with acetone and methyl ethyl ketone. In this paper we discuss mixed electrolytic reduction of 1,4-dimethylpyridinium methyl sulfate with acetone in greater detail and, further, the similar reduction of 1-methylpyridinium methyl sulfate with cyclopentanone.

In the first case we obtained after electrolytic reduction on lead electrodes in dilute sulfuric acid a mixture of products from which we isolated by distillation and preparative gas chromatography 1,4-dimethylpiperidine (*Ia*), 1,4-dimethyl-3-piperideine (*IIa*), 2-isopropenyl-1,4-dimethyl-3-piperideine (*IIh*), 2-(2-hydroxy-2-propyl)-1,4-dimethyl-3-piperideine (*IIi*), 1,4-dimethyl-6-(2-hydroxy-2-propyl)-3-piperideine (*IIIi*), 1-methyl-4-tert-butyl-3-piperideine (*IIj*), ← 2,5,7,7-tetramethyl-2-aza-6-oxabicyclo-[3,2,1]-octane (*IV*), and eventually a mixture of tricyclic compounds, most probably 1,1′ : 4,4′-tetramethyl-2,2′ : 4,4′-bipiperidylene (*V*) and 1,1′ : 4,4′-tetramethyl-2,4′ : : 4,2′-bipiperidylene (*VI*). Substance *IIj* is formed probably by a Wagner–Meerwein rearrangement of 4-(2-hydroxy-2-propyl)-1,4-dimethylpiperidine (*IXa*), which we could not detect in the reaction mixture in this case; however, in the case of a similar mixed electrolytic reduction of 1-ethyl-4-methylpyridiniumethyl sulfate alcohol *IXb* was isolated[2]. The structure of the bicyclic compound *IV* followed from its elemental analysis and the analysis of IR and NMR spectra. In the case of a mixture of compounds formed by dimerization of 1,4-dimethyl-3-piperideine or of some of its precursor we cannot exclude the structure formed by connection of the positions,

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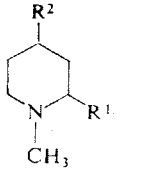
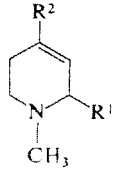
3,4 : 3′,4′ or 3,4 : 4′,3′, *i.e.* *VII* and *VIII*. In view of the fact that under the given conditions reactions on carbon atoms 2 or 4 took always place we consider it more probable that it is a mixture of compounds *V* and *VI*.

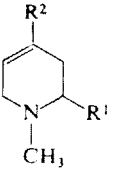
Mixed electrolytic reduction of 1-methylpyridinium methyl sulfate with cyclopentanone again afforded under similar conditions a mixture of products of which only some were analogous to the compounds isolated after the first electrolytic reduction. This was in the first place 1-methyl-3-piperideine; further 2-(1-hydroxy-1-cyclopentyl)-1-methyl-3-piperidine (*IId*) and 6-(1-hydroxy-1-cyclopentyl)-1-methyl-3-piperideine (*IIId*). In addition to this we also demonstrated in the reaction mixture the presence of 4-(1-hydroxy-1-cyclopentyl)-1-methylpiperidine (*Ig*), 2-(1-hydroxy--1-cyclopentyl)-1-methylpiperideine (*Id*), 2-cyclopentyl-1-methylpiperidine (*Ic*), 2--cyclopentyl-1-methyl-3-piperideine (*IIc*), 6-cyclopentyl-1-methyl-3-piperideine (*IIIc*) and eventually 4-(1-cyclopentenyl)-1-methylpiperidine (*If*), and 4-(1-cyclopentenyl)--1-methyl-3-piperideine (*IIf*).



I



II



III

a; $R^1 = H$, $R^2 = CH_3$

b; $R^1 = H$, $R^2 =$ 

c; $R^1 =$  , $R^2 = H$

d; $R^1 =$  , $R^2 = H$

e; $R^1 = H$, $R^2 =$ 

f; $R^1 = H$, $R^2 =$ 

g; $R^1 = H$, $R^2 =$ 

h; $R^1 = CH_2{=}C(CH_3)-$, $R^2 = CH_3$

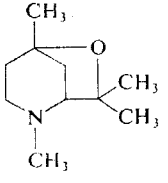
i; $R^1 = (CH_3)_2C(OH)-$, $R^2 = CH_3$

j; $R^1 = H$, $R^2 = (CH_3)_3C$

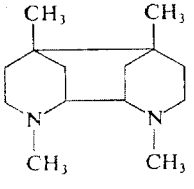
From the results it is evident that the mentioned electrolytic reductions have only limited similarity. In both cases the products of electrolytic reductions of quaternary salts were detected, *i.e.* 1,4-dimethylpiperidine (*Ia*), 1,4-dimethyl-3-piperideine (*IIa*) or 1-methylpiperidine[3] and 1-methyl-3-piperideine. The main difference of both mixed electrolytic reductions consists in the fact that in the second in addition to amino alcohols *Id*, *Ig*, *IId*, *IIId* the products of further reduction, *Ic*, *Ie*, *IIc*, *IIIc* are also formed; their analogues could not be detected after mixed electrolytic reduction of 1-methylpyridinium methyl sulfate with acetone. In contrast to this, during the

last mentioned reduction the bicyclic compound *IV* and the dimeric products *V* and *VI* are also formed.

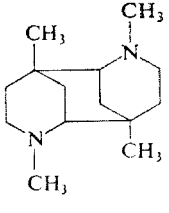
The formation of 1-methyl-4-tert-butyl-3-piperideine (*IIj*) is also interesting. The compounds with two double bonds, *IIh* and *IIf*, are formed probably during distillation, by dehydration of corresponding alcohols *IIi* or *IIf*, resp. Some of the products of mixed electrolytic reduction of 1-methylpyridinium methyl sulfate with cyclopentanone were prepared synthetically. On reduction of the methiodide of 2-(1-hydroxy-1-cyclopentyl) pyridine with sodium borohydride we obtained a mixture from which we isolated piperideine derivatives *IId* and *IIId*, and the piperidine derivative *Id*. The latter was obtained in pure state by hydrogenation of the mentioned reduction mixture. Similarly we prepared by reduction of 2-cyclopentylpyridine methiodide the mixture *IIc* and *IIIc* from which *Ic* is formed by hydrogenation. Amino alcohol *Ig* was obtained by an analogous reduction of 4-(1-hydroxy-1-cyclopentyl)pyridine methiodide and subsequent hydrogenation of the unsaturated amino alcohol *IIg* thus formed. In a similar manner we prepared 4-(1-cyclopentenyl)-1-methyl-3-piperideine (*IIf*) and 4-cyclopentyl-1-methylpiperidine (*Ie*).



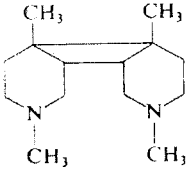
IV



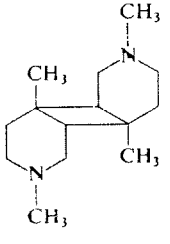
V



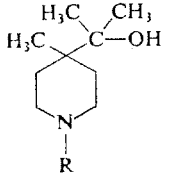
VI



VII



VIII



IXa, R = CH_3
IXb, R = C_2H_5

EXPERIMENTAL

Gas chromatography was carried out on Chrom II apparatus (column length 170 cm, diameter 0·6 cm, 20% Tridox on porovina, nitrogen as carrier gas). Preparative gas chromatography was carried out on an apparatus of non-commercial origin[4]. The NMR spectra were measured on a Varian XL-100-15 instrument at 100·1 MHz in deuteriochloroform; working temperature was

37°C. The IR spectra were recorded with a Perkin-Elmer, Model 325, spectrograph. The mass spectra were measured on a Gas Chromatograph-Mass Spectrometer LKB 9000, Produkter AB Stockholm. Temperature data are not corrected.

1,4-Dimethylpyridinium Methyl Sulfate

Distilled dimethyl sulfate (63·2 g; 0·51 mol) dissolved in 50 ml of methanol was added to a solution of 47·8 g (0·51 mol) of 4-methylpyridine in 200 ml methanol and the mixture refluxed for 26 hours. After distillation off of methanol a quaternary salt was obtained: yield 109·8 g (97%), m.p. 32–33°C.

Mixed Electroreduction of 1,4-Dimethylpyridinium Methyl Sulfate with Acetone

A solution of the above quaternary salt (109·8g; 0·5 mol), 20% sulfuric acid (530 ml), and acetone (210 ml) was electrolysed with a 160 Ahours current (intensity 13A/hour) (204%). The catholyte was freed from acetone in a vacuum, the solution was alkalized and extracted with chloroform. The dried chloroform solution was submitted to fractional distillation and gave a mixture of 12 substances in 5 fractions (the polymeric distillation residue weighed 1·25 g): 1st fraction up to 85°C/9 Torr (9·07 g), 2nd fraction 85–105/12 Torr (10·2 g), 3rd fraction 105–115°C/12 Torr (10·6 g), 4th fraction 125–140°C/9 Torr (11·27 g), and 5th fraction up to 100°C/0·7 Torr (3·1 g).

From the first fraction 1,4-dimethylpiperidine[5] (*Ia*) (2%) and 1,4-dimethyl-3-piperideine[6] (*IIa*) (5·7%) were isolated by GLC.

From the second fraction the following compounds were isolated: 2-Isopropenyl-1,4-dimethyl-3-piperideine (*IIh*) (7·4%), b.p. 62·5–63·5°C 10 Torr; for $C_{10}H_{17}N$ (152·2) calculated: 79·44% C, 11·30% H, 9·26% N; found: 79·63% C, 11·59% H, 9·46% N; NMR spectrum (p.p.m.): $\underline{CH}_3$—C=CH_2 1·67 (bs), $\underline{CH}_3$—C=CH 1·73 (bs), CH_2—CH_2 1·80–2·56 (m), CH_3—N 2·23 (s) CH—N 2·77–3·10 (m), CH_2 = 4·47–4·97 (m), CH = 5·09 (m); (M^+) = 151. 1-Methyl-4-tert-butyl-3-piperideine (*IIj*) (11·6%), b.p. 74–76·5°C/10 Torr; for $C_{10}H_{19}N$ (153·3) calculated: 78·36% C, 12·50% H, 9·13% N, found: 78·22% C, 12·50% H, 9·39% N; NMR spectrum (p.p.m.): CH_3—C 1·04 (s), C—CH_2—C 2·13–2·40 (m), CH_3—N 2·34 (s), CH_2—N 2·51 (t; 5·5 Hz), N—CH_2—C = 2·93 (m), CH = 5·42 (m); (M^+) = 153. Hydrogenation of an aqueous solution of the hydrochloride of the mentioned base on Adams catalyst gave 1-methyl-4-tert-butylpiperidine hydrochloride (*Ij*) the NMR spectrum of which was in agreement with literature data[7]. 1,4,6,6-Tetramethyl-4-aza-7-oxabicyclo[3,2,1]octane (*IV*) (11·6%), b.p. 77·5–79°C/10 Torr; for $C_{10}H_{19}NO$ (169·3) calculated: 70·96% C, 11·31% H, 8·28% N; found: 70·96% C, 11·31% H, 8·55% N; IR spectrum (in cm^{-1}): ν(C—O—C) 1100 (s), 1114 (s), 1130 (s), 1139 (s), and 1152 (s); NMR spectrum (p.p.m.): CH_3—C 1·18 (s), CH_3—C—CH_3 1·31 (s) and 1·43 (s), CH_2—C—CH_2 1·45–2·10 (m), $CH_e\underline{H}_a$—N 2·54–2·77 (m), CH_3—N 2·57 (s), CH—N 2·87 (m), $C\underline{H}_eH_a$—N 3·03–3·36 (m); (M^+) = 169.

The third fraction contained a small amount of two substances which could not be separated and identified (totally 2·3%), and further the following amino alcohols: 2-(2-Hydroxy-2-propyl)-1,4-dimethyl-3-piperideine (*IIi*) (28·7%), b.p. 96·5–99°C/10 Torr; for $C_{10}H_{19}NO$ (169·3) calculated: 70·96% C, 11·31% H, 8·28% N; found: 70·88% C, 11·40% H, 8·19% N; NMR spectrum (p.p.m.): CH_3—C 1·08 (s) and 1·23(s), CH_2—C = 1·40–2·25 (m), CH_3—C = 1·76 (bs), CH_3—N = 2·45 (s), CH_2—N—CH 2·54–3·16 (m), CH = 5·42 (m); (M^+) = 169. 6-(2-Hydroxy-2-propyl)-1,4-dimethyl-3-piperideine (*IIIi*) (3·9%), b.p. 102°C/10 Torr; for $C_{10}H_{19}NO$ (169·3) calculated: 70·96% C, 11·31% H, 8·28% N; found: 71·06% C, 11·49% H, 8·15% N; NMR spectrum (p.p.m.): CH_3—C 1·16 (s) and 1·23 (s), CH_3—C = 1·71 (bs), $C\underline{H}_2$—CH 1·88–2·12 (m), CH_3—N 2·43 (s), CH 2·63 (t; 6 Hz), CH_2—N 2·96–3·48 (m), CH = 5·45 (m); (M^+) = 169.

The fourth fraction contained in addition to a small amount of an unidentified substance (2·1%) a mixture of substances (24·4%); for $C_{14}H_{26}N_2$ (222·4) calculated: 75·62% C, 11·79% H, 12·60% N; found: 75·80% C, 11·66% H, 12·65% N; (M^+) = 222, further fragments: 220, 219, 218, 111, 110; NMR spectrum: CH_3—C 0·77 (s) and 1·00 (s), CH_3—N 2·15 (s) and 2·23 (s), other 0·90—3·35; on analysing the NMR spectra we found that it was a mixture of 1,1′,4,4′-tetramethyl-2,2′:4,4′-bipiperidylene (*V*) and 1,1′,4,4′-tetramethyl-2,4′:4,2′-bipiperidylene (*VI*) in a 4·5 : 1 ratio. The last fraction polymerized on standing in a refrigerator.

Mixed Electrolytic Reduction of 1-Methylpyridinium Methyl Sulfate with Cyclopentanone

A mixture of 41·7 g (0·2 mol) of a quaternary salt prepared similarly to the preceding one, 123 g of cyclopentanone, 150 ml of methanol and 150 ml of 20% sulfuric acid was reduced electrolytically on lead electrodes for 65 A hours. (200% of the theory, at 12 A/hour). The catholyte, containing two layers, was freed from neutral material by steam distillation and the residual solution was alkalized and extracted with chloroform. From the chloroform solution 9·6 g of product of b.p. 65—98°C/10 Torr, and 18 g of a polymeric residue were obtained. Chromatography on alumina (activity II) gave two products which were identified as 2-(1-hydroxy-1-cyclopentyl)-1-methyl-3-piperideine (*IId*), 41·2%, and 4-(1-hydroxy-1-cyclopentyl-1-methylpiperidine (*Ig*), 7·8%. In the remaining mixture the following components were identified by gas chromatography (comparison with standards): 1-methyl-3-piperideine (1·6%), 2-cyclopentyl-1-methylpiperidine (*Ic*) (3·8%), 4-cyclopentyl-1-methylpiperidine (*Ib*) (4·8%), 6-cyclopentyl-1-methyl-3-piperideine (*IIIc*) (13·9%), 4-(1-cyclopentenyl)-1-methylpiperidine (*If*) (1·5%), 2-cyclopentyl-1-methyl-3-piperideine (*IIc*) (1·9%), 4-(1-cyclopentenyl)-1-methyl-3-piperideine (*IIf*) (traces), 2-(1-hydroxy-1-cyclopentyl)-1-methylpiperidine (*Id*) (5·8%), 6-(1-hydroxy-1-cyclopentyl)-1-methyl-3-piperideine (*IIId*) (17·4%).

Hydrogenation: A solution of 0·15 g of the mentioned mixture in 2 ml of acetic acid was hydrogenated on 8 mg of Adams catalyst (consumption 20 ml of hydrogen). 0·12 g of a mixture were obtained in the conventional manner. According to gas chromatography it contained: 1-methylpiperidine (1·5%), 2-cyclopentyl-1-methylpiperidine (*Ic*) (20%), 4-cyclopentyl-1-methylpiperidine (*Ib*) (6%), 2-(1-hydroxy-1-cyclopentyl)-1-methylpiperidine (*Id*) (64·5%) and 4-(1-hydroxy-1-cyclopentyl)-1-methylpiperidine (*Ig*) (8%).

Reduction of 2-(1-Hydroxy-1-cyclopentyl)-1-methylpyridinium Iodide

Sodium borohydride (8·5 g) in 70 ml of water was added to a solution of 61 g (0·2 mol) of the mentioned quaternary salt (prepared from 2-(1-hydroxy-1-cyclopentyl)pyridine[8] and methyl iodide) in 140 ml of water and 8·5 g of sodium hydroxide in 140 ml of water and the mixture stirred for 2 hours (spontaneous heating). It was extracted with chloroform and distillation gave 32 g (89%) of a yellow-orange product, b.p. 111—117°C/12 Torr. According to gas chromatography it was a mixture of 2-(1-hydroxy-1-cyclopentyl)-1-methyl-3-piperideine (*IId*) (25%), 6-(1-hydroxy-1-cyclopentyl)-1-methyl-3-piperideine (*IIId*) (38%), 2-(1-hydroxy-1-cyclopentyl)-1-methylpiperidine (*Id*) (3%), and 2-(1-hydroxy-1-cyclopentyl)pyridine (34%). The first two substances were isolated from the mixture chromatographically on alumina (act. II).

2-(1-*Hydroxy*-1-*cyclopentyl*)-1-*methyl*-3-*piperideine* (IId), b.p. 115°C/12 Torr. For $C_{11}H_{19}NO$ (181·3) calculated: 72·88% C, 10·56% H, 7·73% N; found: 72·96% C, 10·48% H, 7·89% N. IR spectrum (in cm^{-1}): γ(C—H) in CH=CH 666 (m), ν(C=C) 1 640 (s), $\nu(CH_3)$ 2 800 (s), ν(=CH— 3 023 (m), ν(OH) 3 400 (diffuse band). NMR spectrum (p.p.m.): CH_3—N 2·48 (s), CH_2—N 2·0—3·1, CH—N 2·8—2·9 (m), CH = 5·55—5·75 (m), and 5·85—6·10 (m), other at 1·3—3·1.

6-(1-*Hydroxy*-1-*cyclopentyl*)-1-*methyl*-3-*piperideine* (IIId), b.p. 111°C/12 Torr. For $C_{11}H_{19}NO$ (181·3) calculated: 72·88% C, 10·56% H, 7·73% N; found: 72·83% C, 10·69% H, 7·87% N. IR spectrum (in cm^{-1}): γ(C—H) in CH=CH 647 (s), ν(C=C) 1 644 (m), $\nu(CH_3)$ 2 779 (m), ν(=CH— 3 023 (s), ν(OH) 3 370 (diffuse band). NMR spectrum (p.p.m.): CH_3—N 2·46 (s), CH – N 2·86 (t; 6 Hz), CH_2—N 3·17—3·30 (m), CH = 5·52—5·94 (m), others between 1·40—2·20.

Hydrogenation. A solution of 7·1 g of the mixture in 45 ml of acetic acid was hydrogenated on 220 mg of Adams catalyst (consumption 680 ml of hydrogen). Working up gave 5·2 g of yellow-green liquid from which crystals separated melting at 78—79°C (cyclohexane), corresponding to 2-(1-hydroxy-1-cyclopentyl)piperidine. For $C_{10}H_{19}NO$ (169·26) calculated: 70·95% C, 11·31% H, 8·28% N; found: 71·06% C, 11·35% H, 8·16% N. IR spectrum (in cm^{-1}): ν(NH), (OH) 3 100—3 650, after dilution 3 380 and 3 500. NMR spectrum (p.p.m.): CH—N—CH_2 2·35—2·80 (m) and 2·98—3·23 (m), other 1·20—1·90. Mother liquor, b.p. 112°C/13 Torr (individual according to GLC), corresponds to 2-(1-hydroxy-1-cyclopentyl)-1-methylpiperidine (*Id*). For $C_{11}H_{21}NO$ (183·3) calculated: 72·08% C, 11·55% H, 7·64% N; found: 72·06% C, 11·70% H, 7·66% N. IR spectrum (in cm^{-1}): $\nu(CH_3)$ 2 790 (s), ν(OH) 3 100—3 640, 3 430 (max.). NMR spectrum: (p.p.m.): CH_3—N 2·39 (s), other 1·10—1·90.

2-*Cyclopentylpyridine methiodide*, m.p. 90—93°C, prepared from 2-cyclopentylpyridine[9] and methyl iodide. For $C_{11}H_{16}IN$ (289·2) calculated: 45·69% C, 5·58% H, 43·89% I, 4·84% N; found: 45·87% C, 5·83% H, 43·81% I, 5·10% N.

Reduction of 2-Cyclopentylpyridine Methiodide with Sodium Borohydride

A solution of 7 g of the quaternary salt in 15 ml of water was mixed with 15 ml of 15% sodium hydroxide and 1 g of sodium borohydride in 7 ml of water and the mixture was steam distilled. Using the conventional procedure a product of b.p. 95°C/10 Torr (2·7 g) was isolated from the distillate. Gas-liquid chromatography gave the following fractions:

a) b.p. 82°C/10 Torr, 31% (according to gas–liquid chromatography). For $C_{11}H_{19}N$ (165·3) calculated: 79·94% C, 11·59% H, 8·47% N; found: 79·97% C, 11·85% H, 8·32% N. IR spectrum (in cm^{-1}): γ(C—H) in CH=CH 650 (s), ν(C=C) 1 690 (m), $\nu(CH_3)$ 2 783 (s), ν(=CH—) 3 038 (m). NMR spectrum (p.p.m.): CH_2—C= 1·95—2·20 (m), CH_3—N 2·40 (s), CH_2—N 2·58—2·74 (m), CH—N 2·8—3·0 (m), CH = 5·50—5·70 (m) and 5·75—5·95 (m), other 1·15—1·85. These data correspond to structure *IIc*.

b) b.p. 87°C/10 Torr, 60% (according to gas–liquid chromatography). For $C_{11}H_{19}N$ (165·3) calculated: 79·94% C, 11·59% H, 8·47% N; found: 80·11% C, 11·82% H, 8·50% N. IR spectrum (in cm^{-1}): γ(C—H) in CH=CH 653 (s), ν(C=C) 1 648 (m), $\nu(CH_3)$ 2 780 (s), ν(=CH—) 3 020 (s). NMR spectrum (p.p.m.): CH—N 1·90—2·60, CH_3—N 2·36 (s), CH_2—N 3·12—3·25 (m), CH= 5·50—5·90 (m), other 1·10—2·68. These data correspond to structure *IIIc*. According to gas–liquid chromatography the mixture further contains 2-cyclopentylpyridine (9%).

2-Cyclopentyl-1-methylpiperidine (*Ic*)

A solution of 0·8 g of the above mentioned reduction mixture in 13 ml of acetic acid was hydrogenated on 32 mg of Adams catalyst (consumption 200 ml of hydrogen). After the conventional working up 0·62 g of product were obtained, b.p. 95—97°C/12 Torr, which according to gas–liquid chromatography represents a mixture of *Ic* and 2-cyclopentylpiperidine. We further heated 0·6 g of the reduction mixture with 2 ml of formic acid and 1 ml of 40% formaldehyde solution for 7 hours. Chromatographically pure *Ic* (0·41 g) was obtained, b.p. 102°C/18 Torr. For $C_{11}H_{21}N$ (167·3) calculated: 79·02% C, 12·66% H, 8·32% N; found: 79·09% C, 12·73% H, 8·30% N. IR

spectrum (in cm^{-1}): $\nu(CH_3)$ 2775 (s). NMR spectrum (p.p.m.): CH_3—N 2·31 (s), CH_2—N 2·80—3·03 (m), others 1·15—2·37.

The methiodide of 4-(1-hydroxy-1-cyclopentyl)pyridine was prepared by boiling a methanolic solution of the corresponding pyridine base[9] with methyl iodide, m.p. 139°C (ethanol). For $C_{11}H_{16}INO$ (305·2) calculated: 43·29% C, 5·29% H, 4·59% N; found: 43·56% C, 5·26% H 4·49% N.

4-(1-Hydroxy-1-cyclopentyl)-1-methyl-3-piperideine (*IIg*)

Reduction of 4-(1-hydroxy-1-cyclopentyl)pyridine methiodide with sodium borohydride was carried out analogously to the reduction of 2-(1-hydroxy-1-cyclopentyl)pyridine. A product of m.p. 61—65°C (after vacuum sublimation) was obtained. For $C_{11}H_{19}NO$ (181·3) calculated: 72·88% C, 10·56% H, 7·73% N; found: 72·73% C, 10·80% H, 7·54% N. IR spectrum (in cm^{-1}): γ(C—H) in C=CH 823 (m), ν(C=C) 1670 (m), $\nu(CH_3)$ 2790 (s), ν(=CH—) 3024 (m), ν(OH) 3200 and 3360 (diffuse bands), 3608 (m). NMR spectrum (p.p.m.): CH_3—N 2·34 (s), CH_2—C= 2·17—2·35 (m), N—CH_2—CH_2 2·45—2·62 (m), N—CH_2—C= 2·90—3·00 (m), CH= 5·60 to 5·72 (m), other 1·2—1·9.

4-(1-Hydroxy-1-cyclopentyl)-1-methylpiperidine (*Ig*)

Hydrogenation of *IIg* was carried out in a similar manner as the hydrogenation of the products after reduction of 2-(1-hydroxy-1-cyclopentyl)pyridine methiodide; m.p. 76°C (after vacuum sublimation), yield 94%. For $C_{11}H_{21}NO$ (183·3) calculated: 72·08% C, 11·55% H, 7·64% N; found: 72·19% C, 11·73% H, 7·87% N. IR spectrum (in cm^{-1}): $\nu(CH_3)$ 2780 (s), ν(OH) 3100 to 3550 (3340 max.), 3620 (free OH). NMR spectrum (p.p.m.): CH_3—N 2·25 (s), CH_2—N 2·80 to 3·03 (m), other 1·20—2·05.

4-Cyclopentyl-1-methyl-3-piperideine (*IIe*)

4-Cyclopentylpyridine methiodide was reduced with sodium borohydride in a similar manner as 2-cyclopentylpyridine methiodide, giving a product of b.p. 91°C/10 Torr in 49% yield. The yellow-green product turns red in the light. For $C_{11}H_{19}N$ (165·3) calculated: 79·94% C, 11·59% H, 8·47% N; found: 79·95% C, 11·61% H, 7·87% N. IR spectrum (in cm^{-1}): γ(C—H) in C=CH 820 (s), ν(C=C) 1675 (m), $\nu(CH_3)$ 2780 (s), ν(=CH—) 3028 (m). NMR spectrum (p.p.m.): CH_2—C= 2·00—2·26 (m), CH_3—N 2·34 (s), N—CH_2—CH_2 2·52 (t; 6 Hz), N—CH_2—C= 2·83—2·97 (m), CH= 5·33—5·46 (m), other 1·2—1·9.

4-Cyclopentyl-1-methylpiperidine (*Ie*)

This was prepared by hydrogenation of *IIe* (Adams catalyst), b.p. 96°C/10 Torr. For $C_{11}H_{21}N$ (167·3) calculated: 79·02% C, 12·66% H, 8·32% N; found: 79·15% C, 12·68% H, 8·36% N. IR spectrum (in cm^{-1}): $\nu(CH_3)$ 2780 (s). NMR spectrum (p.p.m.): CH_3—N 2·29 (s), CH_2—N 2·72—2·94 (m), other 0·90—2·05.

Elemental analyses were carried out in the analytical laboratory of our Department (head Dr L. Helešic). The measurements of the infrared spectra (head Dr P. Adámek) and the mass spectra (head Dr V. Kubelka) were carried out in the service departments of our Institute.

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