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PROTON MAGNETIC RESONANCE STUDIES OF CYCLIC COMPOUNDS—VI*

CIS- AND *TRANS*-2,6-DIMETHYLPIPERIDINE AND *CIS* (2,4), *CIS* (4,6), *CIS* (2,6)-2,4,6-TRIMETHYLPIPERIDINE

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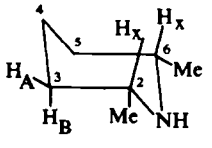
Abstract—*cis*- and *trans*-2,6-Dimethylpiperidine have been purified by preparative VPC. The configurations of the bases have been confirmed by analysis of their PMR spectra, and of the spectra simplified by spin decoupling. One of the three isomeric 2,4,6-trimethylpiperidines has been purified by preparative VPC and shown by PMR spectroscopy to have the *cis* (2,4), *cis* (4,6), *cis* (2,6)-stereochemistry.

THE two isomers of 2,6-dimethylpiperidine were first prepared by Marcuse and Wolffenstein[1] in 1899, but their configurations were not established until 1954, when an optical resolution of the N-methyl *trans*-base was carried out by Lukes and Jizba.[2] More recently, after our investigation had begun, the two isomers were distinguished simply and effectively by examination of the PMR spectra of their N-benzyl derivatives;[3] the benzylic protons of *trans*-N-benzyl-2,6-dimethylpiperidine are magnetically non-equivalent, whereas the corresponding protons of the *cis*-base are equivalent.

In our work, three samples, A, B and C, of 2,6-dimethylpiperidine were obtained. Sample A was prepared by catalytic hydrogenation of 2,6-dimethylpyridine over Raney nickel. Reduction of 2,6-dimethylpyridine by sodium in boiling ethanol gave sample B, whilst sample C was a commercial preparation (Aldrich Chemical Company). An excellent separation of the *cis*- and *trans*-isomers was obtained by analytical VPC (see Experimental). Thus sample A was shown to contain 90% *cis*- base, 10% *trans*-base; sample B contained 74% *cis*-base and 26% *trans*-base; sample C proved to be pure *cis*-2,6-dimethylpiperidine. Pure *trans*-2,6-dimethylpiperidine was isolated from sample B by preparative VPC (see Experimental). Earlier workers separated the bases by fractional distillation,[4,5] or by fractional crystallization of the derived hydrochlorides.[5]



I

* Part V, H. Booth and J. H. Little, *Tetrahedron* **23**, 291 (1967).

The spectrum at 60 Mc/s (CCl_4) of *cis*-2,6-dimethylpiperidine, which is largely a single conformation (I), showed clearly the following features: (i) an almost symmetrical eleven-line multiplet at $\tau = 7{\cdot}44$, due to the 2,6-protons; (ii) a doublet ($J \sim 6$ c/s), at $\tau = 9{\cdot}03$, due to the methyl protons. The remainder of the spectrum was complicated, so that it was impossible to determine directly the chemical shifts of the protons at positions 3, 4 and 5. The spectrum was hardly affected by change of solvent to $CDCl_3$ or C_6H_6, and no additional information was directly available from the 100 Mc/s spectrum (Fig. 1). The low-field multiplet in the latter spectrum (Fig. 2, lower

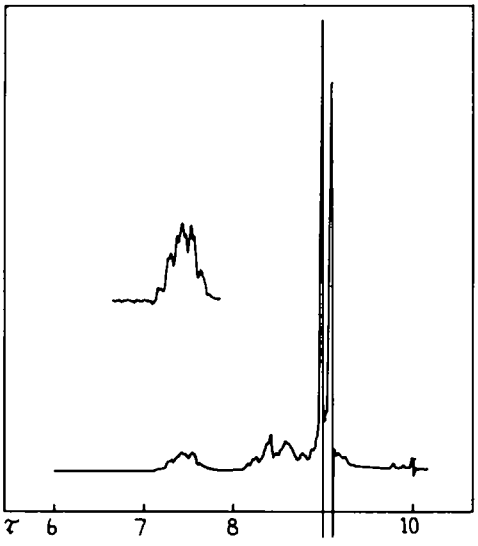


FIG. 1 Spectrum of *cis*-2,6-dimethylpiperidine ($CDCl_3$; 100 Mc)

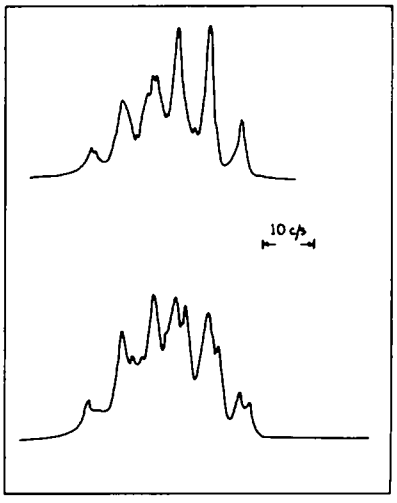


FIG. 2 Resonance of H_X in *cis*-2,6-dimethylpiperidine ($CDCl_3$; 100 Mc). *Lower curve*: normal spectrum; *Upper curve*: decoupled by irradiation of H_A ($\tau = 8{\cdot}45$).

curve) was analyzed in the following way. The 2,6-protons can be regarded, approximately, as the X portion of an ABC_3X spin system. Since $J_{AC} = J_{BC} = 0$, it was anticipated that the X resonance would consist of 4 lines (X part of ABX), each further split into a 1,3,3,1-quartet by coupling with the methyl protons (C_3). The separation of the *outer* lines of the X-multiplet is therefore given by the expression.

$$J_{AX} + J_{BX} + 3J_{XC} \ (J_{AX} \text{ and } J_{BX} \text{ assumed to have the same sign})$$

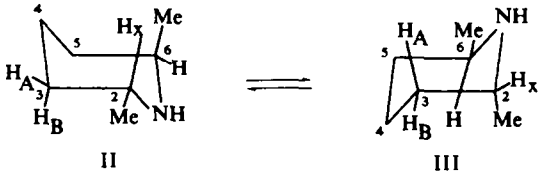
and this was measured as 31·0 c/s. From the methyl doublet, J_{XC} was measured as 6·2 c/s, giving $(J_{AX} + J_{BX})$ as 12·4 c/s. This confirms the *cis*-configuration, since in conformation (I), J_{AX} and J_{BX} are expected to be ~ 3 c/s and ~ 10 c/s respectively.

Spin decoupling experiments, using frequency sweep at 100 Mc/s, corroborated the interpretation just outlined. First, the region of the methyl doublet ($\tau = 9{\cdot}0$) was irradiated, whilst the signal at $\tau = 7{\cdot}45$ was observed. However, it was not possible to eliminate J_{CX} without simultaneously eliminating J_{BX}, since H_X collapsed to a narrow signal, half-intensity width ~ 5 c/s. It was deduced that ν_B and ν_C were not greatly different. Secondly, irradiation was applied in the region $\tau = 8{\cdot}0$ to $\tau = 8{\cdot}6$, where the resonance of H_A was expected to be found. Irradiation at $\tau = 8{\cdot}45$ caused the 11-line multiplet of H_X to collapse to two overlapping 1,3,3,1-quartets (Fig. 2). The coupling constant J_{BX} was given, approximately, by the separation of these quartets, and this was measured as 10·8 c/s. This value is characteristic of a vicinal axial:axial coupling, thus proving conformation (I) and confirming the *cis*-configuration for this particular isomer.

The treatment outlined above gives an accurate value ($\pm 0{\cdot}2$ c/s) for $(J_{AX} + J_{BX})$, but not for the separate coupling constants. However, the decoupling experiments indicated that $\nu_A - \nu_B$ is $\geqslant 0{\cdot}45$ ppm (45 c/s at 100 Mc/s). Thus, from the 100 Mc. spectrum the appropriate separations within the 11-line multiplet for H_X may be taken as being *approximately* equal to J_{AX} and J_{BX}. This method gives J_{AX} as $2{\cdot}1 \pm 0{\cdot}2$ c/s and J_{BX} as $10{\cdot}4 \pm 0{\cdot}2$ c/s. Now the first order treatment of an ABX system gives *high* values for the smaller coupling constant J_{AX} and *low* values for the larger coupling constant J_{BX}. Consequently, the results are realistically quoted as:

$$J_{AX} = 1{\cdot}9 \pm 0{\cdot}2 \text{ c/s} \qquad \text{and} \qquad J_{BX} = 10{\cdot}6 \pm 0{\cdot}2 \text{ c/s},$$

since the separations of the X lines of an ABX spectrum in which $\nu_A - \nu_B = 45$ c/s, $J_{AB} = -12$ c/s, $J_{AX} = 2$ c/s and $J_{BX} = 10{\cdot}6$ c/s, are calculated to be 2·15 c/s and 10·45 c/s. The 'discrepancy' due to a first order treatment is thus about 0·2 c/s. It is worth noting that whilst the magnitude of such discrepancies is, as expected, proportional to the reciprocal of $(\nu_A - \nu_B)$, it is also proportional to the coupling constant difference $(J_{BX} - J_{AX})$.



II III

trans-2,6-Dimethylpiperidine will exist at room temperature as a mixture of rapidly interconverting and energetically equivalent conformations (II) and (III). The spectrum

of the *trans*-base at 60 Mc/s (CCl_4) showed general features which were similar to those in the *cis*-isomer. The 2,6-protons appeared at $\tau = 6{\cdot}92$ as a symmetrical 10-line multiplet, whilst the resonance of the methyl protons was a doublet ($J \sim 6{\cdot}5$ c/s) at $\tau = 8{\cdot}95$. The spectrum showed no simplification in $CDCl_3$, or when examined at 100 Mc/s (Fig. 3). The low-field multiplet was therefore analyzed as for the *cis*-isomer. Measurements gave

$$J_{AX} + J_{BX} + 3J_{XC} \text{ as } 29{\cdot}2 \text{ c/s} \qquad \text{and} \qquad J_{XC} \text{ as } 6{\cdot}5 \text{ c/s}.$$

Thus ($J_{AX} + J_{BX}$) is 9·7 c/s, confirming the *trans*-configuration, since

$$J_{AX} = \tfrac{1}{2}(J_{e_3a_2} + J_{a_3e_2})$$

and is expected to be ~ 3 c/s, whilst

$$J_{BX} = \tfrac{1}{2}(J_{a_3a_2} + J_{e_3e_2})$$

and is expected to be ~ 6 c/s.

In spin decoupling experiments (100 Mc/s), irradiation in the region of the methyl doublet eliminated both J_{CX} and J_{BX}, leaving H_X as a narrow singlet, half-intensity width $\sim 4{\cdot}5$ c/s. Irradiation at $\tau = 8{\cdot}45$ (H_A) caused the low field multiplet to collapse to a clean 1,4,6,4,1-quintet (Fig. 4), separations 6·1 c/s. It is not possible to say that H_X is *equally* coupled to H_C and H_B, since the spectrum may be a deceptively simple one, if $\nu_B = \nu_C$. We can only conclude, from the decoupled spectrum, that

$$\tfrac{1}{2}(J_{BX} + J_{CX}) \sim 6{\cdot}1 \text{ c/s}.$$

Since J_{CX} is 6·5 c/s, then J_{BX} is $\sim 5{\cdot}7$ c/s. This value of J_{BX} is only approximate, since it is obtained using a decoupled spectrum, but it is characteristic of an averaged (aa $\rightleftharpoons$ ee) vicinal coupling and it is sufficient to prove that the base being examined has the *trans*-configuration (II $\rightleftharpoons$ III). As with the *cis*-isomer, accurate values of

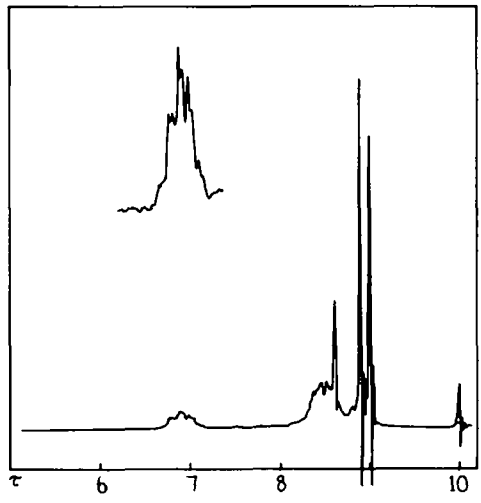


FIG. 3 Spectrum of *trans*-2,6-dimethylpiperidine ($CDCl_3$; 100 Mc/s).

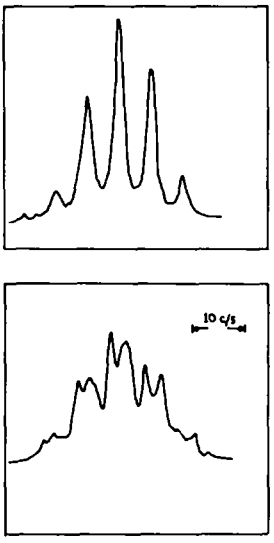


FIG. 4 Resonance of H_X in *trans*-2,6-dimethylpiperidine ($CDCl_3$; 100 Mc/s). *Lower curve*: normal spectrum. *Upper curve*: decoupled by irradiation at H_A (τ = 8·45).

J_{AX} and J_{BX} may be obtained by a modified first order analysis of the 10-line multiplet for H_X in the undecoupled spectrum at 100 Mc. In this case the spin decoupling experiments showed that $\nu_A - \nu_B$ is $\geqslant$0·35 ppm (35 c/s at 100 Mc). First order analysis gave J_{AX} as 3·3 $\pm$ 0·2 c/s and J_{BX} as 6·5 $\pm$ 0·2 c/s. Calculations similar to those carried out for the *cis*-isomer (see above) show that the discrepancy due to the first order treatment is here only about 0·1 c/s. Hence the results are best quoted as

$$J_{AX} = 3{\cdot}2 \pm 0{\cdot}2 \quad \text{c/s} \qquad \text{and} \qquad J_{BX} = 6{\cdot}6 \pm 0{\cdot}2 \text{ c/s}.$$

Consequently, from (II) and (III),

$$3{\cdot}2 \pm 0{\cdot}2 = \tfrac{1}{2}(J_{e_3a_2} + J_{a_3e_2})$$
$$6{\cdot}6 \pm 0{\cdot}2 = \tfrac{1}{2}(J_{a_3a_2} + J_{e_3e_2})$$

If $J_{e_3a_2}$ in II = $J_{e_3a_2}$ in I, and if $J_{a_3a_2}$ in II = $J_{a_3a_2}$ in I, then

$J_{a_3e_2}$ and $J_{e_3e_2}$ are calculated to be 4·5 $\pm$ 0·6 c/s and 2·6 $\pm$ 0·6 c/s respectively. The

TABLE 1. SPECTRAL DATA FOR *cis*-2,6-DIMETHYLPIPERIDINE (I) AT 100 Mc/s ($CDCl_3$)

(Chemical shifts in τ values, J in c/s)

Methyl protons (doublet, J = 6·3)	9·04
H_A (equatorial), from spin decoupling	~8·45
H_B (axial), from spin decoupling	~9·00
H_X (axial)	7·45
J_{AX} ($J_{e_3a_2}$)	1·9 $\pm$ 0·2
J_{BX} ($J_{a_3a_2}$)	10·6 $\pm$ 0·2

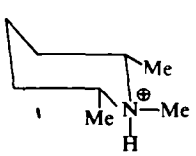
values of 4·5 and 1·9 c/s for $J_{a_3e_2}$ and $J_{e_3a_2}$ respectively, support the earlier suggestion[6] that the maximum effect of an electronegative group R on the vicinal coupling constant $J_{H_1H_2}$ coincides with coplanarity of the system $R—C_1—C_2—H_2$ or $R—C_2—C_1—H_1$. The spectral data for *cis*- and *trans*-2,6-dimethylpiperidine are summarized in Tables 1 and 2.

TABLE 2. SPECTRAL DATA FOR *trans*-2,6-DIMETHYLPIPERIDINE (II ⇌ III) AT 100 Mc/s ($CDCl_3$)

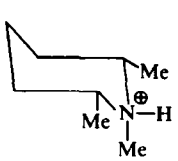
(Chemical shifts in τ values, J in c/s)

Methyl protons (doublet, J = 6·5)	8·98
H_A (equatorial ⇌ axial), from spin decoupling	~8·45
H_B (equatorial ⇌ axial), from spin decoupling	~8·9
H_X (equatorial ⇌ axial)	6·93
J_{AX} $[\frac{1}{2}(J_{e_3a_2} + J_{a_3e_2})]$	3·2 ± 0·2
J_{BX} $[\frac{1}{2}(J_{a_3a_2} + J_{e_3e_2})]$	6·6 ± 0·2

The PMR spectra of the N-methyl derivatives of *cis*- and *trans*-2,6-dimethylpiperidines were also recorded (Table 3). The replacement of NH by N-methyl causes a shielding of the 2,6-protons of piperidines, the axial protons being particularly affected.[7] As a result, the resonance of the 2,6-protons (axial), in *cis*-1,2,6-trimethylpiperidine is not seen clearly, as it occurs at higher field than the N-methyl resonance (τ = 7·9) and is continuous with the resonance due to protons at positions 3, 4 and 5. In the case of *trans*-1,2,6-trimethylpiperidine, however, the resonance of the 2,6-protons is clearly seen at τ = 7·35; the shielding of ~0·4 ppm caused by N-methylation is that expected for a proton which is half equatorial and half axial in character.[7] The spectrum of *trans*-1,2,6-trimethylpiperidine is also interesting in that the resonance for protons at 3, 4 and 5 occurs in a fairly narrow band between τ = 8·3 and τ = 8·7. As a result, the 2,6-protons show virtual long-range coupling[8] to the 4-protons; this leads to a signal for the 2,6-protons containing many more lines than expected. The spectrum of *cis*-1,2,6-trimethylpiperidine in CF_3CO_2H has been reported previously.[9] The rate of proton exchange between the nitrogen atom and the solvent is sufficiently slow to allow observation of signals due to both conformations IV and V (Table 3). Integration gives the proportions of IV and V



IV



V

as 63% and 37% respectively. In view of the high rate of protonation, compared with nitrogen inversion, in N,N-dibenzyl-N-methylamine,[10] it is tempting to take these figures as expressing the relative preferences of methyl and lone pair for the equatorial situation in piperidines. This argument is not acceptable, however, since it is likely

that the rate of nitrogen inversion in piperidines is quite different from that in the dibenzylmethylamine.

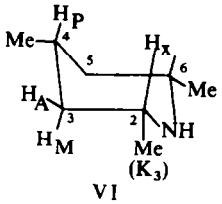
TABLE 3. SPECTRA DATA FOR *cis*- AND *trans*-1,2,6-TRIMETHYLPIPERIDINE AT 60 Mc/s

(Chemical shifts in τ values, *J* in c/s)

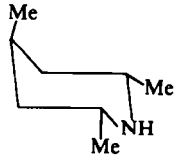
	cis		*trans*
	CCl_4	CF_3CO_2H	CCl_4
C-methyl protons (doublet)	8·96 (*J* 5·5)	8·53 (*J* 6·0) 8·63 (*J* 6·0)	9·07 (*J* 6·5)
N-Methyl protons	7·90[a]	7·03[b] (*J* 5·0) 7·30[b] (*J* 5·5)	7·82[a]
2,6-protons (multiplet)	>8·0	6·35 6·80	7·35

[a] singlet. [b] doublet.

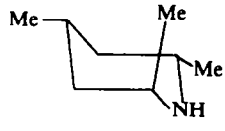
2,4,6-Trimethylpiperidine has three geometrical isomers: *cis* (2,4), *cis* (4,6), *cis* (2,6)-trimethylpiperidine (VI), *trans* (2,4), *trans* (4,6), *cis* (2,6)-trimethylpiperidine (VII), and *trans* (2,4), *cis* (4,6), *trans* (2,6)-trimethylpiperidine (VIII). The *cis*, *cis*,



VI



VII



VIII

cis-isomer is expected to be conformationally homogeneous. Although the *trans*, *trans*, *cis*- and *trans*, *cis*, *trans*-isomers probably exist at room temperature as mixtures of rapidly interconverting chair conformations, the conformations illustrated, each having two equatorial substituents, should constitute at least 90% of the mixture in each case.

Two samples of 2,4,6-trimethylpiperidine were examined. One was a commercial preparation (K. and K. Laboratories Inc.) whilst the other was obtained by reduction of 2,4,6-trimethylpyridine with sodium in boiling ethanol. The samples were examined by analytical VPC, which gave a clean separation into three peaks, presumably due to the three stereoisomers. The commercial preparation was very largely (>95%) a single isomer, isomer A; this isomer also formed the largest proportion (~88%) of the sodium and ethanol reduction product, the remaining isomers, B and C, being present in approximately equal amounts. Preparative VPC has hitherto only allowed us to obtain a pure (~99%) sample of isomer A.

The PMR spectrum of isomer A was measured at both 60 and 100 Mc/s (Fig. 5) in CCl_4, and these measurements showed conclusively that A is *cis*, *cis*, *cis*-trimethyl-

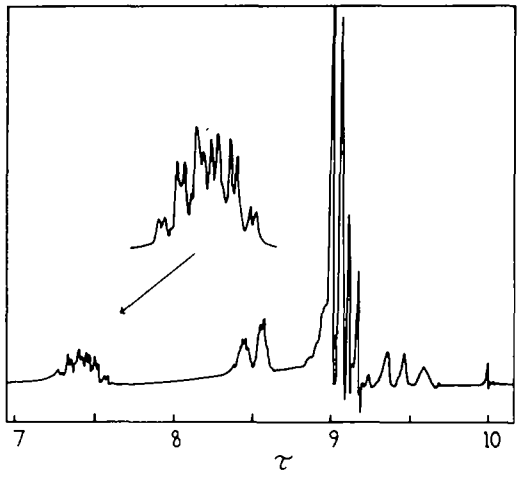


FIG. 5 Spectrum of *cis, cis, cis*-2,4,6-trimethylpiperidine (CCl_4; 100 Mc/s).

piperidine (VI). The evidence is summarized below, and the spectra data are concisely presented in Table 4:

(i) the K_3 protons of the 2,6-methyl groups gave a doublet ($J \sim 6{\cdot}3$ c/s) at $\tau = 9{\cdot}04$;

(ii) the protons of the 4-methyl group gave a doublet ($J \sim 6{\cdot}0$ c/s) at $\tau = 9{\cdot}15$;

(iii) the signal of the equatorial protons (H_A) at 3 and 5 occurred at $\tau = 8{\cdot}50$ as a doublet ($J_{AM} \sim 11{\cdot}0$ c/s), each portion being a multiplet due to further coupling with H_X, H_P and possibly with more distant protons;

(iv) the axial protons (H_M) at 3 and 5 appear at $\tau = 9{\cdot}4$ as a 1,3,3,1-quartet ($J \sim 11$ c/s), due to the approximately equal coupling constants J_{MA} J_{MP} and J_{MX}. The position of H_M at high field, when compared with the position of the corresponding protons in *cis*-2,6-dimethylpiperidine, is entirely consistent with the presence of an *equatorial* methyl group at position 4;[7,11]

(v) the 2,6-protons (H_X) appear at $\tau = 7{\cdot}43$ as a well resolved multiplet (14 lines). The position of the multiplet is almost identical to that due to the 2,6-protons of *cis*-2,6-dimethylpiperidine. Moreover, since protons H_A H_M H_X and H_K are all well shifted from each other, the multiplet for H_X can be analyzed by a first order method.

TABLE 4. SPECTRAL DATA FOR *cis* (2,4), *cis* (4,6) *cis* (2,6)-TRIMETHYLPIPERIDINE (VI) AT 100 Mc/s (CCl_4)

(Chemical shifts in τ values, J in c/s)

2,6-methyl protons (doublet)	9·04 (J 6·3)
4-methyl protons (doublet)	9·15 (J 6·0)
H_A (equatorial)	8·50
H_M (axial)	9·40
H_X (axial)	7·43
J_{AM} (J_{eae_3})	~11·0
J_{AX} (J_{eae_2})	2·0 ± 0·2
J_{MX} (J_{aae_2})	10·75 ± 0·2

H_X is expected to consist of four 1,3,3,1-quartets; in fact, 14 of the 16 lines are visible (Fig. 5). First order analysis gave the following coupling constants:

$$J_{AX} = J_{e3a_2} = 2{\cdot}0 \pm 0{\cdot}2 \text{ c/s}$$
$$J_{MX} = J_{a3a_2} = 10{\cdot}75 \pm 0{\cdot}2 \text{ c/s}.$$

These figures establish the equatorial character of the methyl groups at both positions 2 and 6.

EXPERIMENTAL

PMR spectra: Perkin–Elmer R.10 Spectrometer (60 Mc/s) and Varian HA-100 Spectrometer (100 Mc/s). Spin decoupling was carried out in the frequency sweep mode.

Analytical and preparative VPC. General conditions have been reported previously.[12]

Hydrogenation of 2,6-dimethylpyridine. 2,6-Dimethylpyridine (25 g), dissolved in EtOH (500 ml), was hydrogenated over W6 Raney Ni at 150° and 200 atm. initial press. The mixture was filtered, heated to remove EtOH, and distilled to give a colourless oil (24 g), b.p. 127–130°. Analytical VPC indicated this to be a mixture containing 90% *cis*-2,6-dimethylpiperidine (shorter retention time) and 10% *trans*-2,6-dimethylpiperidine.

Reduction of 2,6-Dimethylpyridine. 2,6-Dimethylpyridine (50 g) was dissolved in hot dry EtOH (800 ml) and Na (85 g) was added in small pieces at a rate sufficient to maintain boiling. The mixture was cooled, acidified (30% HCl) and heated to remove EtOH. The residue was basified (40% NaOH) and the liberated base was collected by steam distillation and extraction into ether. Distillation gave a colourless oil (47 g), b.p. 125–132°, shown by VPC to contain 74% *cis*-2,6-dimethylpiperidine and 20% *trans*-isomer. Preparative VPC (column temp 120°; inject. temp 200°; automatic injection of 0·4 ml mixture) gave *cis*-2,6-dimethylpiperidine (>98% pure) and *trans*-2,6-dimethylpiperidine (>98%). *cis*-2,6-Dimethylpiperidine had b.p. 127–128°, picrate m.p. 163–165°, and hydrochloride m.p. 163–165°, agreeing with lit. values.[1,4,5] *trans*-2,6-Dimethylpiperidine had b.p. 132°, picrate m.p. 125–127°, agreeing with lit. values.[1,4,5] *cis*-1,2,6-Trimethylpiperidine, prepared by the Eschweiler–Clarke method, had b.p. 142–143°, picrate m.p. 225–227° and methiodide m.p. 290°, agreeing with lit.[13] values.

trans-1,2,6-Trimethylpiperidine had b.p. 145–148° and *picrate* (needles, EtOH) m.p. 240–242°. (Found: C, 46·9; H, 5·5; N, 15·8. $C_{14}H_{20}N_4O_7$ requires: C, 47·2; H, 5·7; N, 15·7%.)

Reduction of 2,4,6-trimethylpyridine. 2,4,6-Trimethylpyridine (10 g) was dissolved in hot dry EtOH (200 ml) and Na (15 g) was added during 1 hr. The usual method of working up gave a colourless oil (9·3 g), b.p. 142–148°. Analytical VPC indicated that this was a mixture of three components, with *cis* (2,4), *cis* (4,6), *cis* (2,6)-trimethylpiperidine (shortest retention time) forming about 88% of the total. The *cis, cis, cis*-isomer (99% pure) was isolated by preparative VPC, and had b.p. 142–144°, *picrate* (needles, EtOH) m.p. 161–163°. (Found: C, 47·6; H, 5·9; N, 15·8. $C_{14}H_{20}N_4O_7$ requires: C, 47·2; H, 5·7; N, 15·7%.)

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