The Thermal Decomposition of Quaternary Ammonium Hydroxides. Part 5.† The Importance of Conformational Factors in β-Eliminations from Quaternary Hydroxides derived from Piperidines, Morpholines, and Decahydroquinolines

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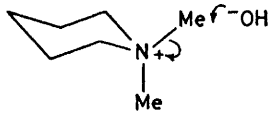
Classical work on the thermal decomposition of the 1-methylmethohydroxides of piperidine and *C*-methylpiperidines has been confirmed, although the elimination products from 2- and 3-methylpiperidines contain small proportions of isomeric alkenes. The products of thermal decomposition of 3-oxa-6-azoniaspiro[5,5]undecane hydroxide show that β-elimination occurs several times faster in a morpholine ring than in a piperidine ring. The requirement for easy elimination in six-membered rings is the *anti*-coplanarity of the four centres H_β, C_β, C_α, and N^+. Strikingly, molecules which lack this requirement, such as the 1-methylmethohydroxide of *cis*-2,6-dimethylmorpholine gave no elimination whatever on thermal decomposition. On the other hand, thermal decomposition of the 1-methylmethohydroxide of *trans*-3,5-dimethylpiperidine gave *ca.* 50% β-elimination. Elimination of the β-hydrogens of an α-attached methyl group are strongly preferred to elimination of ring β-hydrogens, as in the degradation of *cis*-2,6-dimethylpiperidine, but a β-attached oxygen atom allows the corresponding morpholine compound to undergo 16% elimination of a ring hydrogen. The 1-methylmethohydroxides of substituted *trans*- and *cis*-decahydroquinolines (type 1) undergo elimination of a β-hydrogen in a 2-alkyl group, as expected from conformational considerations. However, a *cis*-molecule in which the type 2 conformation is dominant such as the 1-methylmethohydroxide of *cis*(4H,4aH),*cis*(4aH,8aH)-decahydro-2,2,4-trimethylquinoline, undergoes an appreciable proportion of elimination of the correctly oriented 8ax-H in the cyclohexane ring. In all cases reported, the direction of elimination is readily explained by reference to stereochemical considerations and to the steric and inductive effects of β-attached substituents.

In a historic paper in 1950, Barton [1] suggested that certain 1,2-elimination reactions from the cyclohexane rings in steroidal molecules required the *trans*-coplanarity of the four atomic centres involved. McKenna [2] extended the concept to include the β-elimination reaction occurring during the thermal decomposition (Hofmann degradation) of the quaternary hydroxides of reduced heterocyclic bases. It now seems likely that concerted ionic 1,2-elimination reactions only occur with ease when the four participating centres are coplanar.[3,4] The majority of substituted cyclohexanes probably undergo elimination reactions from a transition state with a chair-like conformation in which coplanarity necessarily involves anti-coplanarity. The consequence for cyclohexylammonium hydroxides is the preferential elimination of an axial β-hydrogen.[4] The consequence for the quaternary hydroxides of heterocyclic bases with six-membered rings is the preferential elimination of an equatorial β-hydrogen.

The decompositions described in this paper were performed, as earlier (*cf.* ref. 5), by the thermal decomposition of syrupy quaternary hydroxides without added base. The reactions have been studied solely by product analysis: no attempt was made to investigate the mechanism of elimination, a subject which has become blurred during the past ten years.[6] Nevertheless, the observations herein are consistent with the occurrence of a concerted β-elimination of the *E*2 type, as shown in (1). The substitution reaction (2), which is in competition with elimination,[7] involves attack of hydroxide ion on an *N*-methyl carbon, producing methanol and the cyclic tertiary base; in the present work no cases were encountered in which the nucleophile attacks a ring α-carbon to produce ring scission.[8]

(1)



(2)

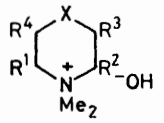
The thermal decomposition of 1,1-dimethylpiperidinium hydroxide (3) gave a mixture of 5-dimethylaminopent-1-ene (11) (96%) and 1-methylpiperidine (24) (4%) (analysis by g.l.c.). Wittig and Burger [9] had recorded yields of 77 and 10% respectively, whilst earlier workers,[10] without the benefit of g.l.c. and n.m.r. spectroscopy, had noted (11) as the sole product. Archer [7] has reported 100% elimination under decomposition conditions of 60° and 0.005 mmHg pressure. The thermal decomposition of 1,1,4-trimethylpiperidinium hydroxide (4) gave a comparable result, the

† Part 4, D. A. Archer, H. Booth, and R. D. Stangroom, *J. Chem. Soc.* (*C*), 1970, 2276.

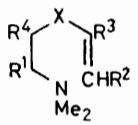
[1] D. H. R. Barton, *Experientia*, 1950, **6**, 316.
[2] J. M. McKenna, *Chem. and Ind.*, 1954, 406.
[3] C. H. Depuy, R. D. Thurn, and G. F. Morris, *J. Amer. Chem. Soc.*, 1962, **84**, 1314; J. L. Coke and M. P. Cooke, jun., *ibid.*, 1967, **89**, 6701; J. Sicher, *Angew. Chem. Internat. Edn.*, 1972, **11**, 200.
[4] M. P. Cooke, jun., and J. L. Coke, *J. Amer. Chem. Soc.*, 1968, **90**, 5556; J. L. Coke, G. D. Smith, and G. H. Britton, *ibid.*, 1975, **97**, 4323.
[5] H. Booth, N. C. Franklin, and G. C. Gidley, *J. Chem. Soc.*, 1968, 1891.
[6] *Cf.* D. J. McLennan, *Quart. Rev.*, 1967, **21**, 490; F. G. Bordwell, *Accounts Chem. Res.*, 1970, **3**, 281; 1972, **5**, 374; W. H. Saunders, jun., *ibid.*, 1976, **9**, 19.
[7] *Cf.* D. A. Archer, *J. Chem. Soc.* (*C*), 1971, 1327.
[8] H. Booth and F. E. King, *J. Chem. Soc.*, 1958, 2688.
[9] G. Wittig and T. F. Burger, *Annalen*, 1960, **632**, 85.
[10] A. W. Hofmann, *Ber.*, 1881, **14**, 659; A. Ladenburg, *ibid.*, 1883, **16**, 2057; A. Ladenburg, M. Mugdan, and O. Brzostovicz, *Annalen*, 1894, **279**, 344; J. V. von Braun, W. Teuffert, and K. Weissbach, *ibid.*, 1929, **472**, 121; J. V. von Braun and E. Anton, *Ber.*, 1931, **64**, 2865.

product being a mixture of the unsaturated open-chain base (12) (98%, by g.l.c.) and the saturated cyclic base (25) (2%). Making the reasonable assumption that the rates of substitution at α-carbon are similar in (3) and (4), it is clear that elimination of a 3-hydrogen in (4) is not hindered by the 4-methyl substituent.

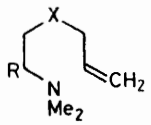
The decomposition of (5) gave a mixture consisting of



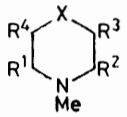
	X	R^1	R^2	R^3	R^4
(3)	CH_2	H	H	H	H
(4)	CHMe	H	H	H	H
(5)	CH_2	H	Me	H	H
(6)	CH_2	H	H	Me	H
(7)	CH_2	Me	Me	H	H
(8)	CH_2	H	H	Me	Me
(9)	O	H	H	H	H
(10)	O	Me	Me	H	H



	X	R^1	R^2	R^3	R^4
(11)	CH_2	H	H	H	H
(12)	CHMe	H	H	H	H
(13)	CH_2	H	Me	H	H
(14)	CH_2	Me	H	H	H
(15)	CH_2	Me	Me	H	H
(16)	CH_2	H	H	H	Me
(17)	CH_2	H	H	Me	H
(18)	CH_2	H	H	Me	Me
(19)	O	H	H	H	H
(20)	O	Me	Me	H	H



	X	R
(21)	CH_2	H
(22)	CH_2	Me
(23)	O	Me



	X	R^1	R^2	R^3	R^4
(24)	CH_2	H	H	H	H
(25)	CHMe	H	H	H	H
(26)	CH_2	H	Me	H	H
(27)	CH_2	Me	Me	H	H
(28)	CH_2	H	H	Me	H
(29)	CH_2	H	H	Me	Me
(30)	O	H	H	H	H
(31)	O	Me	Me	H	H

the terminal olefin (21) (86%), reported by Merling [11] as the sole product, the saturated amine (26) (1%), δ 1.02 (d, J 6 Hz, CMe), together with (13) (9%), δ 1.63 (CMe) and 5.38 (=CH), and (14) (4%), δ 0.87 (d, J 6.6 Hz, CMe) and 2.45 (5-H).

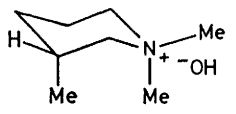
Merling and Jacobi [12] degraded (6) to an unsaturated amine thought to be (16), although (17) was also considered. Classical work using open-chain compounds [13,14] has demonstrated that β-alkyl groups reduce the ease of elimination of a β-hydrogen, a situation which is reflected in the 'Hofmann Rule' and which has been rationalised either by invoking steric effects [15] or by postulating a reduced acidity of the β-hydrogen due to the inductive effect of the alkyl substituent.[16]

In our hands the decomposition of (6) gave (16) (92%, by g.l.c.), (17) (2%), together with the saturated amine (28) (6%).[17] The formation of (17) by *anti*-elimination would require elimination of 3eq-H from a transition state similar to (32), which possesses a severe *syn*-axial methyl–methyl repulsion. Interestingly, thermal decomposition of the apparently equivalent open-chair hydroxide (33) gives an olefin which contains as much as 27% 2-methylpropene.[14] Both the formation of (17) from (6) and of 2-methylpropene from (33) are likely to take place by *syn*-elimination, but it is not clear why the yields are markedly different.

The thermal decomposition of 4,4-dimethylmorpholinium hydroxide (9) was reported by Knorr and Matthes [18] to yield the vinyl ether (19) as the sole product. Repetition of this decomposition gave a mixture consisting of β-dimethylaminoethyl vinyl ether (19) (97 ± 2%) and 4-methylmorpholine (30) (3 ± 2%). β-Elimination in the morpholine ring is expected to be easier than in the piperidine ring, as the inductive effect of the oxygen atom causes an increased acidity of

[11] G. Merling, *Annalen*, 1891, **264**, 310.
[12] G. Merling and W. Jacobi, *Annalen*, 1894, **278**, 7.
[13] A. W. Hofmann, *Annalen*, 1851, **78**, 253; 1852, **79**, 11; C. F. Ingold and C. C. N. Vass, *J. Chem. Soc.*, 1928, 3128; P. A. S. Smith and S. Frank, *J. Amer. Chem. Soc.*, 1952, **74**, 509.
[14] A. C. Cope, N. A. LeBel, H.-H. Lee, and W. R. Moore, *J. Amer. Chem. Soc.*, 1957, **79**, 4720.
[15] H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, 1966, **88**, 1425, 1430.
[16] C. K. Ingold, *Proc. Chem. Soc.*, 1962, 265; C. K. Ingold, E. D. Hughes, and D. V. Banthorpe, *J. Chem. Soc.*, 1960, 4045.
[17] H. Booth, *Progr. N.M.R. Spectroscopy*, 1969, **5**, 343.
[18] L. Knorr and H. Matthes, *Ber.*, 1899, **32**, 736.

the β-hydrogen atoms. This was confirmed by thermal decomposition of 3-oxa-6-azoniaspiro[5,5]undecane



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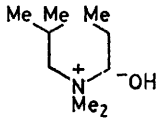

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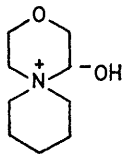

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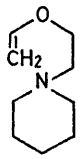

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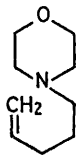


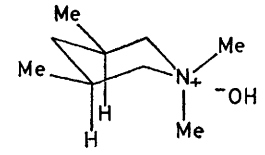
(36)

hydroxide (34), which gave a mixture consisting of 1-(2-vinyloxyethyl)piperidine (35) (86%) and 4-(pent-4-enyl)morpholine (36) (14%). Thus ring opening of the morpholine ring is appreciably easier than that of the piperidine ring by the Hofmann degradation reaction.

Next some simple disubstituted piperidines and morpholines were examined to test the degree of specificity of the elimination reaction. As expected, thermal decomposition of *cis*-1,1,2,6-tetramethylpiperidinium hydroxide *cis*-(7) proceeded with ease, the product consisting of 6-dimethylaminohept-1-ene (22) (99%) and *cis*-1,2,6-trimethylpiperidine *cis*-(27) (1%). Since no less than six β-hydrogen atoms are available for elimination to give (22), the absence of the isomeric alkene (15) is understandable. At the same time the result demonstrates that equilibration of simple alkenes does not occur during the thermal decomposition of quaternary ammonium hydroxides.

The thermal decomposition of *cis*-1,1,3,5-tetramethylpiperidinium hydroxide *cis*-(8) produced *cis*-1,3,5-trimethylpiperidine and methanol. The complete absence of (18) provides a good demonstration of the importance, for easy elimination in six-membered rings, of the stereochemical requirement of *anti*-coplanarity. The major conformation (37) lacks a suitably oriented β-hydrogen. Evidently the minor conformation (38), which possesses correctly oriented β-hydrogen atoms but which has two *syn*-axial methyl–methyl repulsions, yields a transition state for β-elimination which is considerably higher in energy than that leading to substitution at the *N*-methyl carbon.

The most stable conformation of *trans*-1,1,3,5-tetramethylpiperidinium hydroxide *trans*-(8) is (39), which is rapidly equilibrated, by ring inversion, with an identical conformation. Conformation (39) was confidently expected to undergo relatively easy β-elimination, as it



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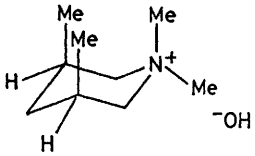

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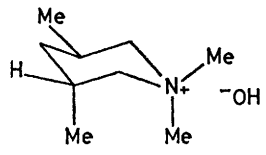

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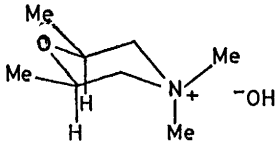

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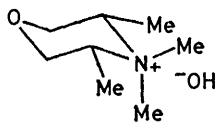

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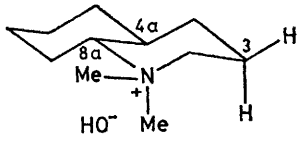

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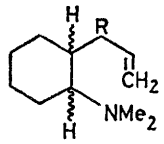
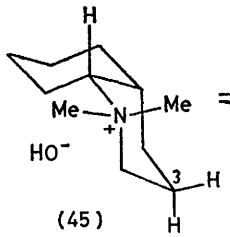


(43) R = H
(44) R = Me



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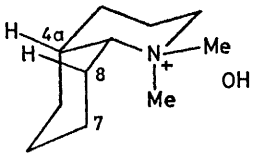


(46)

contains an equatorial β-hydrogen atom at C-3. In practice the alkene (18) was accompanied by an almost equal quantity of the substitution product, *trans*-1,3,5-trimethylpiperidine, *trans*-(29) (46%). In this case the β-methyl substituent hinders β-elimination and allows substitution at the *N*-methyl carbon atom to be effective as a competing reaction.

Despite the ease of β-elimination from 4,4-dimethylmorpholinium hydroxide (9), steric requirements may become overriding in particular cases. Thus the thermal decomposition of *cis*-2,4,4,6-tetramethylmorpholinium hydroxide, of which (40) is the dominant conformation, yielded *cis*-2,4,6-trimethylmorpholine and methanol. On the other hand, thermal decomposition of *cis*-

3,4,4,5-tetramethylmorpholinium hydroxide *cis*-(10), of which (41) is the dominant conformation, gave a mixture of (23) (83%), (20) (16%), and the saturated amine *cis*-(31). It is interesting to compare this result with that from *cis*-1,1,2,6-tetramethylpiperidinium hydroxide (7). The elimination of a ring β-hydrogen in the morpholine (but not the piperidine) case is no doubt due to the inductive effect of the ether oxygen atom. The fact that the minor elimination product (20) is the more thermodynamically stable of the two alkenes (20) and (23) demonstrates that the elimination reaction is kinetically controlled.

cis- and *trans*-Decahydroquinoline are valuable in allowing a detailed examination of the stereochemical requirement of the Hofmann degradation. Thermal decomposition of *trans*-decahydro-1-methylquinoline methohydroxide (42) gave solely the alkene *trans*-(43),[19] for the only correctly oriented β-hydrogen is the equatorial hydrogen at C-3. *cis*-Decahydro-1-methylquinoline methohydroxide is a mixture of the type 1 conformation (45) and the type 2 conformation (46) (*cf.* ref. 20), which are interconvertible by a double ring inversion. Conformation (45) is clearly favoured because it lacks the severe repulsive interaction between 7-CH_2 and NCH_3 present in (46). The ^1H n.m.r. spectrum of the iodide corresponding to (45) ⇌ (46) (chemical shifts in Table 2) shows that the lowfield signal assigned to the 8a-H is a doublet (separations 12 Hz), each component being a triplet (separations 2.5 Hz), in agreement with a preponderance of (45). It was therefore expected that the transition state for elimination of the correctly oriented 8ax- or 4a-H from (46) would be so high in energy that elimination would occur from (45), by loss of 3eq-H, giving solely *cis*-(43), as reported.[19]

The 1-methyl methohydroxide (47) of *trans*(2H,4aH),-*trans*(4aH,8aH)-decahydro-2-methylquinoline was synthesised from the secondary base of known stereochemistry[21] by standard reactions. Thermal decom-

[19] S. Fujise, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, **8**, 185; B. Bailey, R. D. Haworth, and J. McKenna, *J. Chem. Soc.*, 1954, 967.

[20] H. Booth and D. V. Griffiths, *J.C.S. Perkin II*, 1973, 842.

[21] H. Booth, D. V. Griffiths, and M. L. Jozefowicz, *J.C.S. Perkin II*, 1976, 751.

TABLE 1

Chemical shifts (δ) for protons in decahydro-2,2,4-trimethylquinoline and decahydro-1,2,2,4-tetramethylquinoline ($CDCl_3$; 220 MHz)

		Chemical shifts					
Stereochemistry	Formula	8a-H	8eq-H	5eq-H	2-Me	4-Me	Others
trans(4H,4aH)*trans*(4aH,8aH)	(68)	2.42		1.97	1.11, 1.15	0.87	1.51,[a] 1.06,[b] 0.54[c]
trans(4H,4aH)*trans*(4aH,8aH)	(69)	2.07		1.48	1.16, 0.95	0.86	2.24[d]
cis(4H,4aH)*cis*(4aH,8aH)	(75)	3.08	1.73		1.14, 1.12	0.84	1.90[e]
cis(4H,4aH)*cis*(4aH,8aH)	(77)	2.46	1.97		1.10, 0.88	0.79	2.06[d]

[a] 3eq-H. [b] 3ax-H. [c] 4a-H. [d] N-Me. [e] 4ax-H, by decoupling.

TABLE 2

Chemical shifts (δ) for protons in salts of decahydroquinolines and substituted decahydroquinolines (100 and 220 MHz)

Substituent	Salt	Stereochemistry	Formula	Solvent	2eq-H	2ax-H	8a-H	8eq-H	NMe	NH^+	Others
None	HCl	*trans*(4aH,8aH)		D_2O	3.39	2.98	2.77				
None	HCl	*trans*(4aH,8aH)		$CDCl_3$	3.45	2.84	2.65	2.27		9.27, 9.63	
None	HCl	*cis*(4aH,8aH)		D_2O	← 3.03, 3.25, 3.40 →						
None	HCl	*cis*(4aH,8aH)		$CDCl_3$	← 3.02—3.40 →					9.11, 9.66	
1-Me	HCl	*trans*(4aH,8aH)		D_2O	3.48	3.07	2.80	2.28	2.83		
1-Me	HCl	*trans*(4aH,8aH)		$CDCl_3$	3.47	2.96	2.61	2.19	2.80		
1-Me	MeI	*trans*(4aH,8aH)	(42) *	$CDCl_3$	3.95	3.80	3.60	2.25	3.45, 3.16		
1-Me	MeI	*cis*(4aH,8aH)	(45) ⇌ (46) *	$CDCl_3$	3.63	3.38	3.85	2.54	3.51, 3.37		
2,2,4-Me_3	HCl	*trans*(4H,4aH),*trans*(4aH,8aH)	(68), HCl	$CDCl_3$	1.65[a]	1.46[a]	2.88	2.35		9.25, 9.45	2.09,[b] 0.95,[c] 0.86[d]
2,2,4-Me_3	HCl	*cis*(4H,4aH),*cis*(4aH,8aH)	(75), HCl	D_2O	1.45[a]	1.42[a]	3.73				2.15,[e] 0.93[c]
2,2,4-Me_3	HCl	*cis*(4H,4aH),*cis*(4aH,8aH)	(75), HCl	$CDCl_3$	1.82[a]	1.53[a]	3.61			8.2[f] 9.8	0.94[c]
1,2,2,4-Me_4	MeI	*trans*(4H,4aH),*trans*(4aH,8aH)	(53)	$CDCl_3$	1.56[a]	1.71[a]	3.78	2.32	3.21, 3.11		2.20,[b] 0.98[c] 1.22[d]
1,2,2,4-Me_4	MeI	*cis*(4H,4aH),*cis*(4aH,8aH)	(61)	$CDCl_3$	1.55[a]	1.71[a]	4.29		3.27, 3.19		0.95[c]
1,2,2,4-Me_4	MeI	*trans*(4H,4aH),*cis*(4aH,8aH)	(56)	$CDCl_3$	1.52[a]	1.66[a]	4.23		3.46, 3.27		1.00[c]

[a] 2-Me. [b] 5eq-H. [c] 4-Me. [d] 4a-H. [e] 4ax-H. [f] NH-ax (by decoupling).
* I^- instead of HO^-.

position of (47) occurred by elimination of β-hydrogen atoms from the methyl substituent, giving the alkene (49). That the *trans*-stereochemistry of the ring junction in (47) was retained in the degradation product was confirmed by hydrogenation of (49) to the known saturated amine (50).[22] The formation of (49) was anticipated, in view of the direction of elimination which occurred in the Hofmann degradation of 1,2-dimethylpiperidine (see earlier). Also unexceptional was the thermal decomposition of the 1-methyl methohydroxide (48) of *trans*(4H,4aH),*trans*(4aH,8aH)-decahydro-4-methylquinoline. The sole decomposition product was the unsaturated amine *trans*-(44), which was converted by hydrogenation into the known saturated amine (51).[22]

TABLE 3

^{13}C chemical shifts (p.p.m. downfield from Me_4Si) for the unsaturated amines (64)—(66) in $CDCl_3$ (multiplicities, from off-resonance spectra, in parentheses)

Carbon atom	(64)	(65)	(66)
1	66.1 (d)	64.5 (d)	130.7 (d)
2	41.7 (d)	44.3 (d)	128.1 (d)
3	26.7 [a] (t)	27.0 [a] (t)	43.0 (d)
4	25.7 [a] (t)	25.5 [a] (t)	25.9 [a] (t)
5	25.1 [a] (t)	24.6 [a] (t)	25.5 [a] (t)
6	44.9 (t)	44.1 (t)	22.6 [a] (t)
1′	29.7 (d)	30.6 (d)	32.4 (d)
2′	23.4 [a] (t)	24.0 [a] (t)	42.4 (t)
3′	145.7 (s)	145.5 (s)	56.4 (s)
4′	111.2 (t)	111.3 (t)	23.0 (q)
Me_2N	44.4 (q)	44.6 (q)	38.6 (q)
1′-CH_3	18.3 (q)	18.0 (q)	19.0 (q)
3′-CH_3	22.1 (q)	22.1 (q)	23.3 (q)

[a] Assignments may need to be exchanged.

A sample of decahydro-2,2,4-trimethylquinoline, supplied by Monsanto and prepared by catalytic hydrogenation of 1,2-dihydro-2,2,4-trimethylquinoline (*cf.* ref. 23) contained three of the four theoretically possible diastereoisomers. As described later, all three amines were obtained as their 1-methyl methohydroxide derivatives (52), (54) ⇌ (55), and (58) ⇌ (59), which were then subjected to thermal decomposition. As anticipated from conformation (52), and by analogy with (5), the decomposition of (52) gave entirely the unsaturated amine (62). The *trans*-geometry of the 1,2-disubstituted cyclohexane (62) was confirmed by further degradative studies. Earlier work [23] had demonstrated that decomposition of *trans*-2-alkylcyclohexyl-*NNN*-trimethylammonium hydroxides *trans*-(63) gave almost exclusively a 3-alkylcyclohexene, whereas the isomeric *cis*-(63) gave a preponderance of 1-alkylcyclohexene. In the present study, hydrogenation of the unsaturated amine (62) was followed by treatment with methyl iodide; decomposition of the derived methohydroxide then gave a 3-alkylcyclohexene.

Methohydroxides (54) ⇌ (55) and (58) ⇌ (59) both possess a *cis*-ring fusion and differ only in the stereochemistry at C-4. Conformation (55) has more *syn*-axial interactions (Me–Me) than (54) and the type 1 conformation (54) is therefore expected to be dominant in the equilibrium mixture; this was confirmed by the ^{1}H n.m.r. spectrum of the methiodide (56) ⇌ (57) (Table 2), which revealed the 8a-H at δ 4.23 as a doublet (*J* 13 Hz), each line showing further small couplings, in agreement with conformation (56). In conformation (54), none of the β-hydrogen atoms in the cyclohexane ring, *i.e.* at C-4a or -8, has the correct orientation for easy elimination. Consequently, the fact that thermal decomposition gave (64) as the only elimination product was understandable; g.l.c. analysis indicated the presence of *ca.* 3% of the substitution product (72) ⇌ (73). The methohydroxide (58) ⇌ (59), prepared from the tertiary base of known stereochemistry (see below), was expected to exist largely in the type 2 conformation (59). The preponderance of (59) was conclusively established from the ^{1}H n.m.r. spectrum of the methiodide (60) ⇌ (61), which showed 8a-H as a broad singlet ($W_{\frac{1}{2}}$ 13.5 Hz), corresponding to three relatively small vicinal couplings with 4a-, 8ax-, and 8eq-H. The fact that (58) ⇌ (59) may undergo β-elimination from a transition state similar in geometry to (59) raises the possibility of elimination of 4a- and/or 8ax-H, both of which have the correct orientation for easy elimination. These pathways compete with that involving elimination of β-hydrogen from the methyl groups at C-2. In the event, the thermal decomposition of (58) ⇌ (59) gave a mixture of (65) (73%), (66) (20%), and (76) ⇌ (77) (7%). The elimination products (65) and (66), separated by preparative g.l.c., were identified by their ^{1}H and ^{13}C n.m.r. spectra. The complete absence of the alkene (67) is a good illustration of the general applicability of the so-called Hofmann rule. At the same time, the fact that only (59) out of (59) and (54), undergoes elimination of the 8ax-H demonstrates the importance of stereochemical considerations. It is of interest that the diastereoisomers (64) and (65) give ^{13}C n.m.r. spectra in which the chemical shifts of *most* of the structurally identical carbon atoms show differences (Table 3).

Crude decahydro-2,2,4-trimethylquinoline was obtained by hydrogenation of 1,2-dihydro-2,2,4-trimethylquinoline over Raney nickel.[23] A pure sample of *trans*(4H,4aH),*trans*(4aH,8aH)-decahydro-2,2,4-trimethylquinoline (68) was prepared from the isomeric mixture by crystallisation of the salt with 3,5-dinitrobenzoic acid. The *trans*-ring junction in (68) was established from the ^{1}H n.m.r. spectrum which included at δ 2.42 a triplet (separations 10.5 Hz) each part a doublet (separations 4 Hz), assigned to 8a-H. Further, the presence at abnormally low field (δ 1.97) of a doublet (separation 13 Hz), assigned to 5eq-H, proves that the 4-methyl group is equatorial, where it can exert on the 5eq-H the normal *syn*-axial deshielding.[24] Finally, the equatorial nature of the 4-methyl group is confirmed by the shielding effect exerted on the adjacent ring proton 4a-H,[24] which is seen at abnormally high field, δ 0.54

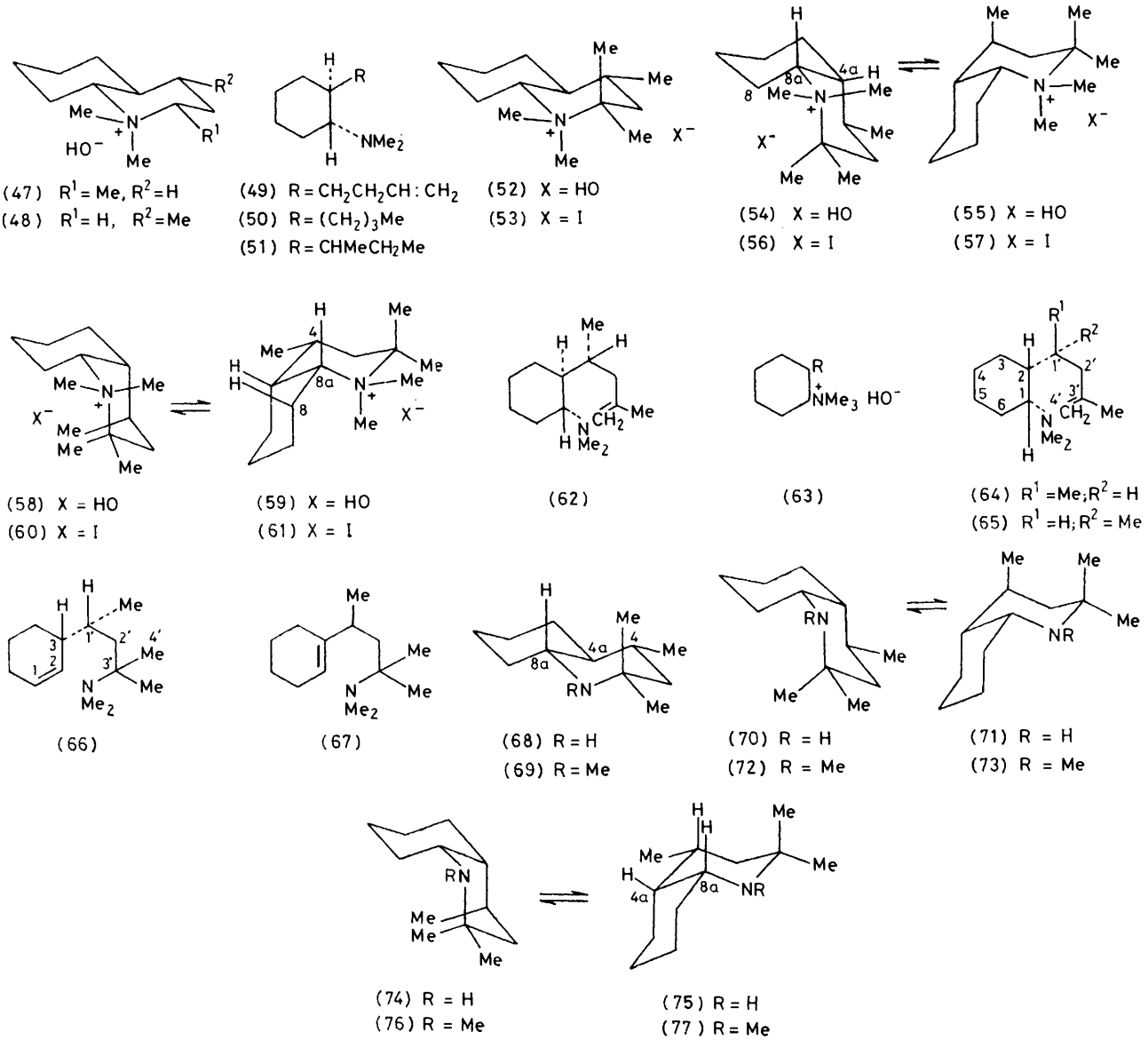
[22] H. Booth, G. C. Gidley, and N. C. Franklin, *Tetrahedron*, 1967, **23**, 2421.

[23] B. E. Wilde (Monsanto Chemicals Ltd.), B.P. 764,957 (*Chem. Abs.*, 1957, **51**, 12986).

[24] H. Booth, *Tetrahedron*, 1966, **22**, 615.

[*cf.* the position of 4a-H at δ 0.70, in the ^{1}H n.m.r. spectrum of *trans*(4H,4aH),*trans*(4aH,8aH)-4-methyldecahydroquinoline [21]].

cis(4H,4aH),*cis*(4aH,8aH)-Decahydro-2,2,4-trimethylquinoline (74) ⇌ (75) was obtained through its hydrochloride (see Experimental section). The ^{1}H n.m.r. spectrum of (74) ⇌ (75) gave parameters (Table 1) which indicate a preponderance of conformation (75). In the first place, the lowest field signal, at δ 3.08, was a poorly resolved quartet (separations 2.7 Hz), indicative of 8a-H in (75), where all the vicinal couplings for 8a-H are expected to be small, corresponding to dihedral angles of *ca.* 60°. In the second place, the equatorial orientation of the 4-methyl substituent in (74) ⇌ (75) was established from the multiplet at δ 1.90, which was assigned to 4-H because (in a double irradiation experiment) irradiation of this signal caused the 4-methyl doublet (*J* 6.8 Hz) to collapse to a singlet. The band width of the multiplet for 4-H, measured at 220 MHz, was 38 Hz. Now the band width is approximately $(3J_{Me,CH} + J_{4\text{-}H,3eq\text{-}H} + J_{4\text{-}H,3ax\text{-}H} + J_{4\text{-}H,4a\text{-}H})$. Thus $(J_{4\text{-}H,3eq\text{-}H} + J_{4\text{-}H,3ax\text{-}H} + J_{4\text{-}H,4a\text{-}H})$ is *ca.* 17.6 Hz. Furthermore, $(J_{4\text{-}H,3eq\text{-}H} + J_{4\text{-}H,4a\text{-}H})$ is ⩽8 Hz, *whether the orientation of* 4-H *is axial or equatorial.* Consequently $J_{4\text{-}H,3ax\text{-}H}$ is ⩾9.6 Hz, proving that 4-H is *axial.*



A third isomer (70) ⇌ (71) was only obtained as its 1-methyl methiodide (56) ⇌ (57). Methylation with formaldehyde and formic acid of the original crude decahydro-2,2,4-trimethylquinoline gave a mixture of the three 1-methyl derivatives (69), (72) ⇌ (73), and (76) ⇌ (77). When this mixture, in ether, was treated with an excess of methyl iodide, the isomer (76) ⇌ (77) remained unchanged, whilst (69) and (72) ⇌ (73) [dominant conformation (72)] were converted into the corresponding methiodides (53) and (56). Isomer (76) ⇌ (77) should exist entirely in conformation (77),

which is expected to react very slowly with methyl iodide on account of steric hindrance. However, the methiodide (61) was readily obtained when (77) was treated with methyl iodide in boiling acetonitrile. The separation of methiodides (53) and (56) was achieved by steady state distribution between a solvent system of water and chloroform.

EXPERIMENTAL

General details for the measurement of ^1H and ^{13}C n.m.r. spectra, and for analytical and preparative g.l.c. were given earlier.[21,25] Unless otherwise stated, thermal decompositions of quaternary hydroxides were carried out as described previously.[5]

Thermal Decomposition of 1,1-*Dimethylpiperidinium Hydroxide* (3).—The methohydroxide gave a liquid, b.p. 116—118° at 761 mmHg, consisting of 1-methylpiperidine (24) (4%, g.l.c.) and 5-dimethylaminopent-1-ene (11) (96%), identified by ^1H n.m.r. signals (CCl_4) at δ 5.75 (1 H, m, CH=), 4.90 (2 H, m, CH_2=), and 2.10 (6 H, s, Me_2N). Conversion of the mixture into the picrate, and recrystallisation, gave pure 5-*dimethylaminopent-1-ene picrate*, m.p. 75° (Found: C, 46.0; H, 5.2; N, 16.0. $C_{13}H_{18}N_{14}O_7$ requires C, 45.6; H, 5.3; N, 16.4%). Decomposition of the picrate with lithium hydroxide gave 5-dimethylaminopent-1-ene, b.p. 116° at 760 mmHg (100% pure by g.l.c.).

Thermal Decomposition of 1,1,4-*Trimethylpiperidinium Hydroxide* (4).—The methohydroxide (from the methiodide, m.p. 298°) gave, on thermal decomposition, a liquid, b.p. 126—128° at 760 mmHg consisting of 1,4-dimethylpiperidine (25) [2%, g.l.c. retention time and ^1H n.m.r. signals at δ 0.91 (d, *J* 6.3 Hz, *Me*CH) and 2.67 (d, *J* 12 Hz, 2-, 6eq-H)] and 5-dimethylamino-3-methylpent-1-ene (12) [98%, ^1H n.m.r. signals at δ 5.63 (1 H, m, 2-H), 4.90 (2 H, m, 1-H), 2.16 (2 H, m, 5-H), 2.10 (6 H, s, Me_2N), 1.38 (2 H, m, 4-H), and 0.98 (3 H, d, *J* 6.1 Hz, MeC)]. Conversion of the mixture to the picrate gave pure 5-*dimethylamino*-3-*methylpent*-1-*ene picrate*, m.p. 104° (Found: C, 47.2; H, 5.4; N, 15.9. $C_{14}H_{20}N_4O_7$ requires C, 47.2; H, 5.6; N, 15.7%).

Thermal Decomposition of 1,1,2-*Trimethylpiperidinium Hydroxide* (5).—The methohydroxide [from the methiodide (10 g), m.p. 320°] gave on decomposition an oil (2.9 g), b.p. 125—131° at 761 mmHg, containing mostly 6-dimethylaminohex-1-ene (21) (86%, by g.l.c.). The ^1H n.m.r. spectrum included signals at δ 5.75 (1 H, m, 2-H), 4.93 (2 H, m, 1-H), 2.15 (2 H, m, 6-H), 2.10 (6 H, s, Me_2N), 2.05 (2 H, m, 3-H), and 1.40 (4 H, m, 4-, 5-H). The minor components, identified from the ^1H n.m.r. spectrum (see Discussion) were 6-dimethylaminohex-2-ene (13) (9%), 5-dimethylaminohex-1-ene (14) (4%), and 1,2-dimethylpiperidine (26) (1%).

Thermal Decomposition of 1,1,3-*Trimethylpiperidinium Hydroxide* (6).—The methohydroxide [from the methiodide (10 g), m.p. 193—194°] gave an oil (3.4 g), b.p. 127—131° at 760 mmHg. The major component (92% by g.l.c.) was 5-dimethylamino-4-methylpent-1-ene (16), δ 5.70 (1 H, m, 2-H), 4.94 (2 H, m, 1-H), 2.12 (6 H, s, Me_2N), and 0.87 (3 H, d, *J* 6.7 Hz, MeC). Weak signals at δ 4.62 (m) and 2.62 (d, *J* 10 Hz) were assigned, respectively, to the olefinic protons of 5-dimethylamino-2-methylpent-1-ene (17) (2%) and the 6-equatorial protons of 1,3-dimethylpiperidine (28) (6%) (*cf.* ref. 17).

Thermal Decomposition of 4,4-*Dimethylmorpholinium Hydroxide* (9).—The methohydroxide [from the methiodide (10 g), m.p. 245—247°] gave an oil (4.2 g), b.p. 114—118° at 760 mmHg, consisting of β-dimethylaminoethyl vinyl ether (19) (97%), δ 6.40 (1 H, q, CH=), 3.95 (2 H, m, CH_2=), 3.70 (2 H, t, CH_2O), 2.51 (2 H, t, CH_2N), and 2.20 (6 H, s, Me_2N), and 4-methylmorpholine (30) (3%, g.l.c. retention time). Conversion of the mixture to the picrate, gave β-dimethylaminoethyl vinyl ether picrate, m.p. 105—107° (lit.,[18] 85°).

3-*Oxa*-6-*azoniaspiro*[5,5]*undecane Bromide*.—A mixture of 1,5-dibromopentane (20 g), water (250 cm³), and sodium hydroxide (10 g) was stirred at 100° whilst morpholine (12 g) was added during 1 h. The mixture was heated at 100° for a further 12 h, cooled in ice and saturated with sodium hydroxide. The upper layer was separated and dried over solid potassium hydroxide. The filtered solution was dissolved in dry ethanol (20 cm³) and treated with dry ether (100 cm³). Filtration of the precipitated solid, followed by crystallisation from ethanol–ether gave needles of 3-oxa-6-azoniaspiro[5,5]undecane bromide (6.1 g), m.p. 280—282° (lit.,[26] 235—238°) (Found: C, 46.0; H, 7.8; N, 5.8. Calc. for $C_9H_{18}BrNO$: C, 45.8; H, 7.6; N, 5.9%).

Thermal Decomposition of 3-*Oxa*-6-*azoniaspiro*[5,5]*undecane Hydroxide* (34).—The oily hydroxide derived from the above bromide, was degraded to give an oil, containing (g.l.c.) 1-(2-vinyloxyethyl)piperidine (35) (86%), δ 6.34 (1 H, q, CH=), 3.90 (2 H, octet, CH_2=), 3.70 (2 H, t, CH_2O), 2.50 (2 H, t, CH_2N), and 2.40 (4 H, m, 2-, 6-H of piperidine) and 4-pent-4-enylmorpholine (36) (14%), δ 5.75 (1 H, m, CH=) and 4.95 (2 H, m, CH_2=).

Thermal Decomposition of cis-1,1,2,6-*Tetramethylpiperidinium Hydroxide* cis-(7).—The methohydroxide, from the corresponding methiodide [27] (8 g), m.p. 290—292°, was degraded to give an oil (2.6 g), b.p. 142—148° at 758 mmHg, containing 6-dimethylaminohept-1-ene (22) (99%; g.l.c.), δ 5.70 (1 H, m, CH=), 4.90 (2 H, m, CH_2=), 2.45 (1 H, m, *CH*NMe_2), 2.10 (6 H, s, Me_2N), and 0.85 (3 H, d, *Me*CH), and *cis*-1,2,6-trimethylpiperidine *cis*-(27) (1%), δ 2.10 (s, MeN) and 1.04 (d, *Me*CH). Conversion of the mixture into the picrate gave 6-*dimethylaminohept*-1-*ene picrate*, m.p. 157° (Found: C, 48.3; H, 6.0; N, 15.2. $C_{15}H_{22}N_4O_7$ requires C, 48.6; H, 6.0; N, 15.1%).

Thermal Decomposition of cis-1,1,3,5-*Tetramethylpiperidinium Hydroxide* cis-(8).—The methohydroxide prepared from the tertiary base [28] through the methiodide (8.0 g), m.p. 272° (lit.,[29] 272—276°), gave on thermal decomposition an oil (3.1 g), containing methanol (g.l.c.) and *cis*-1,3,5-trimethylpiperidine (g.l.c. retention time, ^1H n.m.r. spectrum, and picrate, m.p. and mixed m.p. 141—142°).

Thermal Decomposition of trans-1,1,3,5-*Tetramethylpiperidinium Hydroxide* trans-(8).—The methohydroxide, from the methiodide [28] (1.6 g), m.p. 233—235°, gave on thermal treatment an oil (0.5 g) containing methanol (g.l.c.) and a mixture of *trans*-1,3,5-trimethylpiperidine (45%; g.l.c. retention time) and 5-dimethylamino-2,4-dimethylpent-1-ene (18) (54%), δ 4.62br (CH_2=), 2.10 (s, MeN and Me_2N), 1.70br (s, MeC=), 0.93 (d, *Me*CH in saturated base), and 0.85 (d, *Me*CH in unsaturated base).

Thermal Decomposition of cis-2,4,4,6-*Tetramethy*

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[26] F. F. Blicke and E. B. Hotelling, *J. Amer. Chem. Soc.*, 1954, **76**, 5099.
[27] H. Booth, J. H. Little, and J. Feeney, *Tetrahedron*, 1968, **24**, 279.
[28] H. Booth and J. H. Little, *J.C.S. Perkin II*, 1972, 1846.
[29] Y. Kawazoe, M. Tsuda, and M. Ohnisi, *Chem. and Pharm. Bull. Japan*, 1967, **15**, 51.

morpholinium Hydroxide (40).—The methohydroxide prepared from the tertiary base [28] through the methiodide (10 g), m.p. 234°, was decomposed to give an oil (3.9 g) containing methanol (g.l.c.) and *cis*-2,4,6-trimethylmorpholine (g.l.c. retention time, ^{1}H n.m.r. spectrum, and picrate, m.p. and mixed m.p. 156—158°).

Thermal Decomposition of cis-3,4,4,5-*Tetramethylmorpholinium Hydroxide* cis-(10).—*cis*-3,4,5-Trimethylmorpholine [28] was converted by an excess of methyl iodide in acetonitrile into cis-3,4,4,5-*tetramethylmorpholinium iodide*, plates (EtOH), m.p. 295° (Found: C, 35.6; H, 6.8; N, 5.1. $C_8H_{18}INO$ requires C, 35.4; H, 6.7; N, 5.1%). The methohydroxide from this methiodide (6.5 g) was decomposed to give an oil, b.p. 140—152° (bath temp.) at 757 mmHg, containing *cis*-3,4,5-trimethylmorpholine (1%; g.l.c. retention time), allyl 2-dimethylaminopropyl ether (23) (83%) and propenyl 2-dimethylaminopropyl ether (20) (16%). The ^{1}H n.m.r. spectrum of the mixture included signals at δ 5.85 (12 lines, CH= of allyl), 5.15 (m, CH_2= of allyl), 3.88 (m, OCH_2CH=), 2.18 (s, Me_2N), 1.52 (q, *J* 6 and 0.5 Hz, *Me*CH=), and 0.98 (d, *Me*CH).

Thermal Decomposition of trans(2H,4aH),trans(4aH,8aH)-*Decahydro*-1,2-*dimethylquinoline Methohydroxide* (47).—*trans*(2H,4aH),*trans*(4aH,8aH)-Decahydro-2-methylquinoline, purified through the salt with 3,5-dinitrobenzoic acid,[21] was converted into the *N*-methyl derivative, b.p. 104—107° at 14 mmHg, by the normal Eschweiler–Clarke procedure.[30] The tertiary base was dissolved in dry ether and treated with an excess of methyl iodide. After 24 h the methiodide was filtered off and crystallised from ethanol, m.p. 188°. *trans*(2H,4aH),*trans*(4aH,8aH)-Decahydro-1,2-dimethylquinoline methohydroxide, prepared in the usual way from the above methiodide, was heated to 150° under reflux. Ether extraction of the mixture, followed by distillation of the dried extracts, gave trans-2-(*but*-3-*enyl*)*cyclohexyldimethylamine*, b.p. 99—101° at 15 mmHg. The derived *picrate* had m.p. 115—115.5° (Found: C, 52.8; H, 6.5; N, 13.7. $C_{18}H_{26}N_4O_7$ requires C, 52.7; H, 6.3; N, 13.7%). The ^{1}H n.m.r. spectrum of the base included signals at δ 5.70 (m, CH=), 4.90 (m, CH_2=), and 2.20 (s, Me_2N).

The unsaturated base, in methanol, absorbed 1.05 mol. equiv. H_2 when hydrogenated over palladised charcoal at room temperature and atmospheric pressure. Filtration of the mixture, followed by distillation, gave *trans*-2-butylcyclohexyldimethylamine, the derived picrate having m.p., and mixed m.p. with an authentic sample,[22] 117—117.5° (Found: C, 52.0; H, 6.8; N, 13.6. Calc. for $C_{18}H_{28}N_4O_7$: C, 52.4; H, 6.8; N, 13.6%).

Thermal Decomposition of trans(4H,4aH),trans(4aH,8aH)-*Decahydro*-1,4-*dimethylquinoline Methohydroxide* (48).—*trans*(4H,4aH),*trans*(4aH,8aH)-Decahydro-4-methylquinoline,[21] purified through the salt with 3,5-dinitrobenzoic acid, was converted by the Eschweiler–Clarke method into *trans*(4H,4aH),*trans*(4aH,8aH)-decahydro-1,4-dimethylquinoline, b.p. 102—106° at 15 mmHg. The tertiary base, without further purification, was converted by an excess of methyl iodide in ether into trans(4H,4aH),-trans(4aH,8aH)-*decahydro*-1,4-*dimethylquinoline methiodide*, needles (EtOH), m.p. 285—186° (Found: C, 46.5; H, 7.7; N, 4.1. $C_{12}H_{24}NI$ requires C, 46.6; H, 7.8; N, 4.5%). The corresponding methohydroxide was degraded at 160° under reflux, and ether extraction followed by distillation yielded trans-2-(1-*methylprop*-2-*enyl*)*cyclohexyldimethylamine*, b.p. 90—93° at 13 mmHg. The *picrate* had m.p. 126—127° (Found: C, 52.6; H, 6.4; N, 13.5. $C_{17}H_{26}N_4O_7$ requires C, 52.7; H, 6.4; N, 13.7%). The ^{1}H n.m.r. spectrum of the base included signals at δ 5.90 (octet, $CHCH$=CH_2), 4.90 (m, CH_2=), 2.20 (s, Me_2N), and 0.87 (d, *J* 7 Hz, *Me*–CH).

Hydrogenation of the unsaturated base in methanol over palladised charcoal, followed by the usual method of working up, gave *trans*-2-(1-methylpropyl)cyclohexyldimethylamine, picrate, m.p. 162—163°, mixed m.p. with an authentic sample [22] 159—161°.

trans(4H,4aH),trans(4aH,8aH)-*Decahydro*-2,2,4-*trimethylquinoline* (68).—A distilled commercial sample [23] of decahydro-2,2,4-trimethylquinoline (90 g) was dissolved in hot ethyl acetate (500 ml) and treated with 3,5-dinitrobenzoic acid (106 g). The crystalline salt (186 g) which appeared on cooling the mixture was filtered and recrystallised several times from methanol. The 3,5-*dinitrobenzoic acid salt* of trans(4H,4aH),trans(4aH,8aH)-*decahydro*-2,2,4-*trimethylquinoline* (53.5 g, 27%) had m.p. 266—268° (Found: C, 58.3; H, 7.0; N, 10.6. $C_{19}H_{27}N_3O_6$ requires C, 58.0; H, 6.9; N, 10.7%). The pure base was liberated from the salt with aqueous sodium hydroxide. trans(4H,4aH),trans(4aH,8aH)-*Decahydro*-2,2,4-*trimethylquinoline* had b.p. 230.5° at 760 mmHg (Found: C, 79.6; H, 12.8. $C_{12}H_{23}N$ requires C, 79.5; H, 12.8%). The derived *hydrochloride*, needles from ether–ethanol, had m.p. 283—285° (Found: N, 6.2. $C_{12}H_{12}ClN$ requires N, 6.5%). The *picrolonate*, orange needles from aqueous ethanol, had m.p. 288—290° (Found: C, 59.2; H, 6.9; N, 15.4. $C_{22}H_{31}N_5O_5$ requires C, 59.3; H, 7.0; N, 15.7%).

trans(4H,4aH),trans(4aH,8aH)-*Decahydro*-1,2,2,4-*tetramethylquinoline* (69).—The foregoing base (20 g) was converted by the Eschweiler–Clarke method into trans-(4H,4aH),trans(4aH,8aH)-*decahydro*-1,2,2,4-*tetramethylquinoline* (18.6 g, 86%), b.p. 117—119° at 14 mmHg (Found: C, 80.2; H, 12.7. $C_{13}H_{25}N$ requires C, 79.9; H, 12.9%). The derived *picrate*, needles from ethanol, had m.p. 174.5—175.5° (Found: C, 53.9; H, 6.5. $C_{19}H_{28}N_4O_7$ requires C, 53.8; H, 6.7%). The *picrolonate*, plates from ethanol, had m.p. 185—186° (Found: C, 60.2; H, 6.8; N, 15.3. $C_{22}H_{33}N_5O_5$ requires C, 60.1; H, 7.2; N, 15.2%). The *methiodide*, prepared in 92% yield from the base and methyl iodide in ether during three days, formed needles from ethanol, m.p. 259—260° (Found: C, 50.2; H, 7.9; N, 4.1. $C_{14}H_{28}NI$ requires C, 49.9; H, 8.3; N, 4.2%).

Thermal Decomposition of trans(4H,4aH),trans(4aH,8aH)-*Decahydro*-1,2,2,4-*tetramethylquinoline Methohydroxide* (52).—The methohydroxide, prepared from the foregoing methiodide (9.6 g), was degraded at 160—180° and 20 mmHg. Extraction of the distillate with ether, followed by distillation of the dried extracts, gave trans-2-(1,3-*dimethylbut*-3-*enyl*)*cyclohexyldimethylamine* (3.58 g, 61%), b.p. 112—113° at 14 mmHg (Found: N, 7.0. $C_{14}H_{27}N$ requires N, 6.7%). The derived *picrolonate*, yellow needles from ethanol, had m.p. 150—151° (Found: C, 60.7; H, 7.7. $C_{24}H_{35}N_5O_5$ requires C, 60.9; H, 7.5%).

The ^{1}H n.m.r. spectrum of the unsaturated base (in benzene) included a broad 2 H singlet at δ 4.73 (CH_2=) and additional signals at δ 2.17 (s, Me_2N), 1.72br (s, MeC=), and 0.74 (d, *J* 5.6 Hz, *Me*CH). The i.r. spectrum (liquid film) showed strong absorption at 880 cm^{-1} (C–H out of plane deformation of R_2C=CH_2). Absorption at 790—850 cm^{-1} (C–H out of plane deformation of R_2C=CHR) was negligible.

[30] *Cf.* M. L. Moore, *Org. Reactions*, 1949, **5**, 301.

trans-2-(1,3-*Dimethylbutyl*)*cyclohexyldimethylamine*.—The foregoing unsaturated base (2.75 g) was dissolved in ethanol (20 ml) and hydrochloric acid (0.1 ml, 30%) and hydrogenated over palladised charcoal (0.4 g, 10%) during 12 h, when 1.02 mol. equiv. of H_2 was absorbed. The usual work up gave trans-2-(1,3-*dimethylbutyl*)*cyclohexyldimethylamine* (2.30 g, 88%), b.p. 109—110° at 12 mmHg. The derived *picrolonate*, needles from ethanol, had m.p. 135—137° (Found: C, 60.6; H, 7.3; N, 14.6. $C_{24}H_{37}N_5O_5$ requires C, 60.6; H, 7.8; N, 14.7%). The *methiodide*, prepared in 95% yield from the saturated base and methyl iodide in boiling ether during 4 h, had m.p. 99—101° (Found: C, 50.7; H, 8.7; N, 3.6. $C_{15}H_{32}IN$ requires C, 51.1; H, 9.1; N, 4.0%).

The ^1H n.m.r. spectrum of the saturated base in benzene included signals at δ 2.20 (s, Me_2N), 1.01 (d, *J* 5.0 Hz, *Me*CH), and 0.83 (d, *J* 5.3 Hz, Me_2CH). After acidification of this solution with CF_3CO_2H, the ^1H spectrum included signals at δ 2.39 (d, *J* 4.3 Hz, MeN of $Me_2\overset{+}{N}H$) and 2.18 (d, *J* 5.3 Hz, MeN of $Me_2\overset{+}{N}H$), a pattern which is typical [22] of *trans*-2-substituted cyclohexyldimethylamines.

Thermal Decomposition of trans-2-(1,3-*Dimethylbutyl*)-NN-*dimethylcyclohexylamine Methohydroxide*.—The above methiodide (1.8 g) was converted into the corresponding methohydroxide, which was decomposed at 160—170° and 15 mmHg. The distillate was extracted with ether and the extracts were washed successively with hydrochloric acid (10%) and water. Distillation of the dried ether gave 3-(1,3-*dimethylbutyl*)*cyclohexene* (0.4 g, 31%), b.p. 90—95° (bath temp.) at 10 mmHg (Found: C, 87.2; H, 12.8. $C_{12}H_{22}$ requires C, 87.2; H, 12.8%). The ^1H n.m.r. spectrum in benzene included an AB-type quartet at δ 5.68 (2 H, CH=CH) and three overlapping doublets at 0.92, 0.86, and 0.78 (CH_3CH). The i.r. spectrum (liquid film) included a strong absorption at 715 cm^{-1} (C–H out of plane deformation of $R^1CH{=}CHR^2$). Absorption at 790—850 cm^{-1} (C–H out of plane deformation of $R^1_2C{=}CHR^2$) was negligible.

cis(4H,4aH),cis(4aH,8aH)-*Decahydro*-2,2,4-*trimethylquinoline* (75).—The mother liquors remaining from the preparation and crystallisation of the 3,5-dinitrobenzoic acid salt of *trans*(4H,4aH),*trans*(4aH,8aH)-decahydro-2,2,4-trimethylquinoline were evaporated to dryness and the residue was treated with aqueous sodium hydroxide (10%). The liberated bases were recovered by extraction into ether and evaporation of the dried (KOH) extracts. The crude bases (10 g) were dissolved in dry ether (20 ml) and treated with anhydrous hydrogen chloride. The salt (11.4 g) was filtered, crystallised from dry ether–ethanol, and finally sublimed at 150° and 0.03 mmHg. cis(4H,4aH),cis(4aH,8aH)-*Decahydro*-2,2,4-*trimethylquinoline hydrochloride* had m.p. 216—217° (Found: C, 66.3; H, 11.1; N, 6.5. $C_{12}H_{24}ClN$ requires C, 66.6; H, 11.1; N, 6.5%).

cis(4H,4aH),cis(4aH,8aH)-*Decahydro*-1,2,2,4-*tetramethylquinoline* (77).—A crude commercial sample of decahydro-2,2,4-trimethylquinoline (58 g), formic acid (200 ml; 98%), and aqueous formaldehyde (150 ml; 36%) were mixed, with cooling, and the mixture was heated under reflux for 24 h. The solution was cooled, treated with concentrated hydrochloric acid (50 ml), and evaporated under reduced pressure to a small volume. The aqueous residue was washed with ether, basified with an excess of sodium hydroxide solution (30%), and extracted with ether. The dried ethereal extracts were evaporated to remove ether, leaving a residue of crude *N*-methylated bases (54 g). The product (50 g) was dissolved in ether (300 ml) and treated with methyl iodide (25 ml) at room temperature and in the dark, during two weeks. The solid produced (A) was filtered and treated in the subsequent preparation (see below). The ethereal filtrate, on evaporation, gave cis(4H,4aH),cis(4aH,8aH)-*decahydro*-1,2,2,4-*tetramethylquinoline*, b.p. 255.5° at 760 mmHg. The *picrate*, from ethanol, had m.p. 162—163.5° (Found: C, 53.5; H, 6.9; N, 13.3. $C_{19}H_{28}N_4O_7$ requires C, 53.8; H, 6.6; N, 13.2%).

Thermal Decomposition of trans(4H,4aH),cis(4aH,8aH)-*Decahydro*-1,2,2,4-*tetramethylquinoline Methohydroxide* (54).—The crude methiodide (A), obtained in the preceding preparation, was shown by ^1H n.m.r. spectroscopy (Table 2 and Discussion section) to be a mixture of *trans*(4H,4aH),-*trans*(4aH,8aH)-decahydro-1,2,2,4-tetramethylquinoline methiodide (53) (75%) and *trans*(4H,4aH),*cis*(4aH,8aH)-decahydro-1,2,2,4-tetramethylquinoline methiodide (56) (25%). The mixture was separated using a Quickfit steady state distribution machine equipped with 100 cells each of 25 ml. The crude methiodides were partitioned between $CHCl_3$ and water. A transfer ratio of 32 upper phase transfers to 4 lower phase transfers was maintained during the separation procedure, and the upper phase eluant was monitored periodically by ^1H n.m.r. spectroscopy. The fraction after 424—441 upper phase transfers was found to contain pure *trans*(4H,4aH),*cis*-(4aH,8aH)-decahydro-1,2,2,4-tetramethylquinoline methiodide (56). The corresponding methohydroxide (54), prepared in the usual way from the methiodide, was decomposed as a syrup at 160° and 12 mmHg. Extraction of the distillate with ether, followed by evaporation of the dried extracts, gave *cis*-2-(1,3-dimethylbut-3-enyl)cyclohexyldimethylamine (64), identified by ^{13}C (Table 3) and ^1H n.m.r. spectral data. The ^1H n.m.r. spectrum included signals at δ 4.67 (m, $CH_2{=}$), 2.59 (q, *J* 3.5 and 12.5 Hz, $CHNMe_2$), 2.26 (s, Me_2N), 1.71br (s, MeC=), and 0.89 (d, *J* 6.9 Hz, *Me*CH).

Thermal Decomposition of cis(4H,4aH),cis(4aH,8aH)-*Decahydro*-1,2,2,4-*tetramethylquinoline Methohydroxide* (59).—*cis*(4H,4aH),*cis*(4aH,8aH)-Decahydro-1,2,2,4-tetramethylquinoline was heated with an excess of methyl iodide in dry, redistilled acetonitrile for one week. Addition of dry ether precipitated the methiodide, m.p. 256—257°. The ^1H n.m.r. spectrum in $CDCl_3$ included a broad singlet ($W_{\frac{1}{2}}$ 13.5 Hz) at δ 3.71 for 8a-H. The syrupy methohydroxide prepared from the above methiodide (6.4 g), was decomposed at 160° and 12 mmHg. The product, isolated by ether extraction of the distillate, was separated by preparative g.l.c. into two unsaturated amines. The *major* product, of longer retention time, was *cis*-2-(1,3-dimethylbut-3-enyl)cyclohexyldimethylamine (65), identified by ^{13}C (Table 3) and ^1H n.m.r. spectral data. The ^1H n.m.r. spectrum included signals at δ 4.69 (m, $CH_2{=}$), 2.27 (s, Me_2N), 1.70br (s, MeC=), and 0.95 (d, *J* 6.5 Hz, *Me*CH). The *minor* product was identified by ^{13}C (Table 3) and ^1H n.m.r. spectral data as 3-(1,3-dimethyl-3-dimethylaminobutyl)cyclohexene (66). The ^1H n.m.r. spectrum included signals at δ 5.72 (d, J_{AB} 10.5 Hz, $CH_A{=}$), 5.53 (d, J_{AB} 10.5 Hz, $CH_B{=}$), 2.21 (s, Me_2N), 1.00 (s, Me_2C), and 0.93 (d, *J* 6.6 Hz, *Me*CH).

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