dihydroquinolines (16a, 16b, and 16c). To a solution of 1,3-dimethyl-2-ethyl- (**18a**, 1.422 g, 6.44 mmol), 1-methyl-2-propyl-3-ethyl- (**18b**, 1.607 g, 6.44 mmol), or 1-methyl-2-isobutyl-3-isopropylquinolinium chloride (**18c**, 1.787 g, 6.44 mmol) in 10 ml of water was added 10 ml of 20% potassium hydroxide at 0–5°. Alkylidenequinoline (**16a, 16b,** or **16c**) was liberated immediately as a yellow oil, which was extracted with 40 ml of ligroin (bp 110–120°). To the boiling ligroin solution was added dropwise 1.496 g (13.0 mmol) of ethyl azidoformate. The mixture was refluxed for 1 hr. All procedures were carried out under a nitrogen atmosphere. Distillation of the reaction mixture gave 1.655 g (94.5%) of **2a**, 1.748 g (90.5%) of **2b**, or 2.083 g (98.5%) of **2c**, respectively.

Registry No.—**1a**, 51904-95-1; **1b**, 57091-58-4; **1c**, 57091-59-5; **1d**, 16021-59-3; **2a**, 57091-60-8; **2b**, 57091-61-9; **2c**, 57091-62-0; **3a**, 57091-63-1; **3d**, 57091-64-2; **4**, 57091-65-3; **6**, 57091-66-4; **7**, 57091-67-5; **8**, 57139-17-0; **9**, 57091-68-6; **10**, 57091-69-7; **11**, 57091-70-0; **12**, 57091-71-1; **16a**, 57091-72-2; **16b**, 57091-73-3; **16c**, 57091-74-4; **18a**, 55539-76-9; **18b**, 55539-77-0; **18c**, 55539-78-1; ethyl azidoformate, 817-87-8; methyl bromide, 74-83-9; ethyl bromide, 75-00-3; 2-(*N*-methylamino)benzaldehyde, 7755-70-6.

References and Notes

(1) H. Plieninger and D. Wild, *Chem. Ber.*, **99**, 3070 (1966).
(2) T. Sakan, S. Matsubara, H. Takagi, Y. Tokunaga, and T. Miwa, *Tetrahedron Lett.*, 4925 (1968).
(3) G. Schroeter, A. Gluschke, S. Geotzky, J. Huang, G. Irmisch, E. Laves, O. Schrader, and G. Stier, *Ber.*, **63**, 1308 (1930).
(4) L. H. Briggs and G. C. De Ath, *J. Chem. Soc.*, 456 (1937); R. W. Richard and R. M. Smith, *Tetrahedron Lett.*, 2361 (1966).
(5) A. Cromarty and G. R. Proctor, *Chem. Commun.*, 842 (1968); A. Cromarty, K. E. Hque, and G. R. Proctor, *J. Chem. Soc. C*, 3536 (1971).
(6) Various types of ring expansion reactions using azides are reviewed in the following books: (a) S. Patai, Ed., "The Chemistry of the Azide Group", Interscience, New York, N.Y., 1971; (b) W. Lwowski, Ed., "Nitrenes", Interscience, New York, N.Y., 1970, and references cited therein.
(7) Y. Sato, H. Kojima, and H. Shirai, *Tetrahedron*, **30**, 2695 (1974).
(8) R. Levine, J. A. Conroy, J. T. Adams, and C. R. Houser, *J. Am. Chem. Soc.*, **67**, 1510 (1945).
(9) P. Friedländer, *Ber.*, **15**, 2574 (1882); A. Steinforff, *ibid.*, **37**, 979 (1904).
(10) W. H. Mills and R. S. Wishart, *J. Chem. Soc.*, **117**, 585 (1920).

Carbon-13 Nuclear Magnetic Resonance Spectra of Saturated Heterocycles. IV. *trans*-Decahydroquinolines

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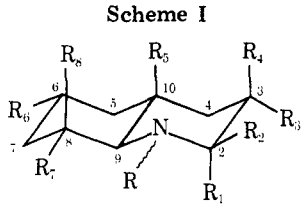
^{13}C NMR spectra of a number of methyl-substituted *trans*-decahydroquinolines and perhydrobenzo[*h*]quinolines are reported. Assignment of signals was accomplished by a combination of off-resonance decoupling, parametrization of substituent effects, and comparison with the spectra of a number of specifically deuterated analogues. Spectra of the *N*-methyl, *N*-ethyl, and *N*-isopropyl derivatives and of the hydrochlorides and trifluoroacetates of a number of the amines are tabulated. Parameters for methyl substitution, replacement of CH_2 by NH, and protonation have been calculated.

Stereochemical problems are increasingly being investigated by ^{13}C magnetic resonance techniques,[1] the chemical shifts constituting a very sensitive probe for conformational properties. Since the numerous signals of substances with high molecular weight can be assigned only with difficulty, an approach involving the recording of spectra of smaller model compounds which constitute subunits of the large molecules, combined with the tabulating of substituent effects, has been successfully applied[1] in a number of systems.

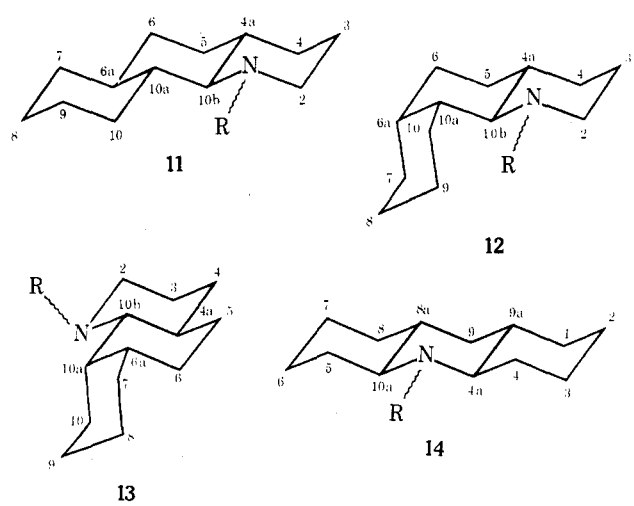
The *trans*-decahydroquinoline framework forms part of a considerable number of natural products. In order to acquire information on the conformational equilibrium of the NCH_3 group (axial–equatorial) in *N*-methylpiperidine and in *N*-methyl-*trans*-decahydroquinoline (**1**),[2] a series of methyl-substituted *trans*-decahydroquinolines[3] (Scheme I, **2–10**, R = H) and perhydrobenzo[*h*]quinolines (Scheme II, **11–13**, R = H), and their *N*-methyl, *N*-ethyl, and *N*-isopropyl derivatives [Schemes I, II, R = CH_3, CH_2CH_3 and $CH(CH_3)_2$] were synthesized[4–6] and their proton[6] and ^{13}C NMR spectra recorded. The conclusions concerning the NCH_3 equilibrium have been reported elsewhere;[2] here the complete ^{13}C NMR data of the compounds are presented and analyzed in terms of substituent parameters.

Scheme I



1. R_1–R_8 = H
2. R_1 = CH_3; R_2–R_8 = H
3. R_2 = CH_3; R_1, R_3–R_8 = H
4. R_4 = CH_3; R_1, R_2, R_4–R_8 = H
5. R_5 = CH_3; R_1–R_4, R_7–R_8 = H
6. R_5 = CH_3; R_1–R_4, R_6–R_8 = H
7. R_6 = CH_3; R_1–R_5, R_7, R_8 = H
8. R_7 = CH_3; R_1–R_6, R_8 = H
9. R_8 = CH_3; R_1–R_7 = H
10. R_5, R_7 = CH_3; R_1–R_4, R_6, R_8 = H

Scheme II



11 **12** **13** **14**

Configuration and Assignment of Signals. The ^{13}C

Table I
^{13}C Chemical Shifts[a] for *trans*-Decahydroquinolines[b]

Compd[c]		C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9[d]	C-10[d]	CH_3
Parent	1	47.33	27.29	32.46	32.64	26.29	25.64	34.00	62.09	43.34	
2α-Methyl	2	47.53	31.33	26.79	32.47	26.29	25.74	34.31	53.96	43.92	18.62
2β-Methyl	3	52.37	34.98	32.41	32.24	26.21	25.47	33.79	61.85	42.37	22.95
3α-Methyl	4	54.85	(32.79)	41.38	(32.59)	26.20	25.67	33.72	61.55	43.22	19.61
3β-Methyl	5	52.25	28.62	38.07	32.81	26.31	25.74	33.73	62.27	37.51	17.68
6α-Methyl	7	47.38	27.16	32.42	41.41	32.59	34.20	33.79	61.90	42.88	22.43
8α-Methyl	8	47.55	26.93	32.62	33.02	25.84	34.90	37.51	67.97	42.22	18.59
8β-Methyl	9	47.67	27.46	(33.02)	(33.29)	20.23	(32.87)	33.16	64.58	35.61	12.63
10-Methyl	6	48.13	22.97	(39.88)	(40.53)	21.48	25.97	28.88	64.31	33.94	15.60
8α-10-Dimethyl	10	48.64	22.87	(40.35)	(40.96)	21.31	35.52	31.72	70.65	33.98	18.95 (8) 16.75 (10)

[a] In $CDCl_3$, parts per million from Me_4Si. Parentheses indicate that assignments are not unambiguous. [b] For characterization of the *trans*-decahydroquinolines see ref 6. [c] *trans*-Decahydroquinoline; "β" means "on the same side of the ring as the hydrogen on C-10"; "α" means "on the side opposite to this hydrogen". [d] 9 and 10 are used in preference to 8a and 4a to allow unambiguous use of "a" for "axial".

spectrum of *trans*-decahydroquinoline has previously been recorded and discussed,[7] and the various signals have been assigned[7] by comparison with the corresponding data for *trans*-decalin and use of parameters derived by comparing piperidines with cyclohexanes. The signals for C-4 and C-5, previously reported[7] to have identical chemical shifts, were resolved by our instrument. To assign these signals, and a number of signals in several methyl-substituted compounds unambiguously, selectively deuterated analogues were synthesized as needed.[6] In the proton noise-decoupled spectrum of *trans*-decahydroquinoline-*2,3,3,4,9,10-d*$_6$ the signals for C-9 and C-10 (previously identified in *trans*-decahydroquinoline as doublets in the off-resonance decoupled spectrum; C-9, next to the nitrogen, resonating at lowest field) and for C-3 are not observed because of the absence of the nuclear Overhauser enhancement and by being dissipated into triplets and a quintet. C-2 and C-4 are seen as triplets, being substituted with one proton and one deuterium; C-2, next to the nitrogen, is also the most downfield triplet in the off-resonance decoupled spectrum of *trans*-decahydroquinoline.[7] The signals of C-5 and C-8 are shifted upfield by ~0.1 ppm in the deuterated compounds by the β effect of the deuterium[8] at C-9 and C-10, the signal of C-8 being diminished somewhat in intensity because of some deuterium substitution on this carbon.[6] Signals for C-6 and C-7 are practically unshifted by the deuteration, but a small additional signal for C-7, due to the small amounts of deuterium at C-8, is visible ~0.1 ppm upfield of the main signal. Thus the ^{13}C NMR spectrum of the hexadeuterated analogue of *trans*-decahydroquinoline corroborates the signal assignments previously made,[7] and, in addition, affords an unequivocal assignment of the now resolved C-4 and C-5 resonances.

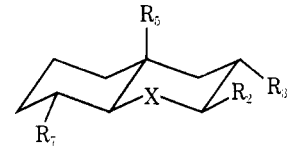
The configuration of compounds **4–10**[9] (trans fusion of the rings, equatorial or axial orientation of the CH_3 groups), which was previously inferred from their ^1H NMR spectra,[6] is now confirmed by the ^{13}C NMR data; while decahydroquinolines with cis ring fusion[3] have at least one ring ^{13}C NMR signal at higher field than 25 ppm because of γ-gauche interactions, among the trans isomers only **6, 9,** and **10** (Table I), the compounds with axial CH_3, show such high-field ring signals (due to γ-gauche interactions involving the methyl group). Moreover, the signals of the axial methyl groups (in **2, 5,** and **9**) are invariably at higher field than the corresponding equatorial signals (in **3, 4,** and **8**).

Ring carbon signals were assigned either by applying the parameters for methyl-substituted cyclohexanes[10a,b] and decalins[10c] to the parent compound **1** or by using parameters for replacement of CH_2 with NH[7] on appropriate decalins.[10c] Additional information was obtained by off-resonance decoupling and, for compounds **2, 3, 6, 8,** and **9**, by comparison with selectively deuterated analogues, as described for **1**. Some signals occurring in very narrow spectral ranges could not be assigned unambiguously; their tabulated values are parenthesized.

Assignment of the signals in the tricyclic compound **14** was accomplished by comparison of signal intensities, off-resonance decoupling, and comparison with **1** and *trans-syn-trans*-perhydroanthracene.[13] Configurational assignment and assignment of signals in the perhydrobenzo[*h*]quinolines (**11–13**) rests on comparison with **8** and **9**, with the corresponding perhydrophenanthrenes,[13] and also on the changes in chemical shifts upon N-methylation (see below).

Comparison with Carbocyclic Analogues. While the similarities of the compounds in Tables I and II with the corresponding methyl-*trans*-decalins and perhydrophenanthrenes, at least in the portion of the molecule remote from the nitrogen, are sufficient to make configurational assignments unambiguous, replacement of CH_2 by NH gives rise to considerable shift differences in the vicinity of the heteroatoms, as shown in Table III.

The C atoms α to the nitrogen are strongly deshielded but to a somewhat different extent; the tertiary carbon (C-9) is influenced less than the secondary (C-2). If C-2 is tertiary as in **3**, the effect is reduced (+19.2 ppm). The β effect is mildly shielding for C-8 and C-10; there is no consistent effect for C-3 and nearly no effect for Me(e)-2 (compare **3** and **15**).



	X	R_2	R_3	R_5	R_7
3	NH	CH_3	H	H	H
15	CH_2	CH_3	H	H	H
4	NH	H	CH_3	H	H
16	CH_2	H	CH_3	H	H
6	NH	H	H	CH_3	H
17	CH_2	H	H	CH_3	H
8	NH	H	H	H	CH_3
18	CH_2	H	H	H	CH_3

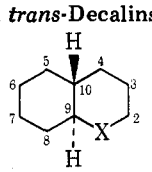
The upfield shift differences for C atoms γ to the site of replacement are in agreement with observations reported elsewhere[14] relating to upfield γ shifts by oxygen and nitrogen atoms. The shielding effect of the nitrogen on anti-per-

Table II
^{13}C Chemical Shifts[a] of Perhydrobenzo[*h*]quinolines[b] (11–13), Perhydroacridine[b] (14), and Their *N*-Methyl Derivatives (11m–14m)

C atom[c]	*trans-anti-trans*-PBQ		*trans-anti-cis*-PBQ		*trans-syn-cis*-PBQ		*trans-syn-trans*-PA	
	11	11m	12	12m	13	13m	14	14m
C-2	47.49	55.99	47.64	56.32	47.74	58.28	26.21	(25.83)
C-3	26.84	19.25	(27.10)	19.62	27.51	25.71	25.57	(26.10)
C-4	32.28	33.21	32.63	33.52	33.04	32.96	33.66	31.03
C-4a	41.81	31.75	(43.47)	31.52	35.99	34.56	62.10	69.28
C-5	32.75	33.56	28.33	28.99	33.15	33.47	33.66	31.03
C-6	34.11	34.45	32.05	32.50	25.45	25.28	25.57	(26.10)
C-6a	45.59	42.77	37.41	37.38	36.95	36.89		
C-7	33.73	33.79	26.72	26.69	32.33	32.56	26.21	(25.83)
C-8	(26.31)	(26.51)	(27.27)	(26.91)	21.60	21.65	32.34[d]	33.46[d]
C-8a							43.25[e]	40.99[e]
C-9	(26.33)	(26.55)	20.58	21.09	26.78	26.90	39.91	40.69
C-10	28.85	29.36	(27.18)	(26.88)	21.07	20.55		
C-10a	47.64	44.62	(41.46)	37.71	42.11	38.44	62.10	69.28
C-10b	66.09	69.11	57.14	60.39	65.40	72.77		
N-CH_3		33.15		33.02		42.34		36.07

[a] In parts per million, from internal Me_4Si in $CDCl_3$. Parentheses indicate that assignments are not unambiguous. [b] For characterization of compounds see ref 6. [c] For nomenclature see Scheme II. [d] Identical with C-1. [e] Identical with C-9a.

Table III
Shift Differences $\Delta\delta$[a] between *trans*-Decahydroquinolines[b] (X = NH) and *trans*-Decalins[c] (X = CH_2)



C atom	Effect	Shift difference[a]
C-2	α	+20.2 ± 0.5[d]
C-3	β	0.0 ± 0.4
C-4	γ	−2.3 ± 0.3
C-5	γ	−1.9 ± 0.3
C-6	δ	−0.9 ± 0.2
C-7	γ	−1.5 ± 0.4
C-8	β	−0.6 ± 0.3
C-9	α	+18.1 ± 0.4
C-10	β	−0.9 ± 0.6
Me(e)-2	β	+0.1[e]
Me(e)-3	γ	−3.2[e]
Me(e)-8	γ	−1.2[e]
Me(a)-10	γ	−0.2[e]
Me(e)-6	ϵ	−0.4[e]

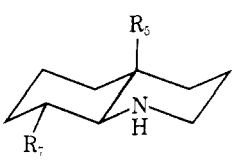
[a] In parts per million. A plus sign indicates that the signal in the NH compound is downfield from the signal in the CH_2 analogue. The differences reported are averages for all the pairs of compounds considered (see footnotes *b*, *c*) with their standard deviations. [b] Compounds 1, 3, 4, 6, 7, 8, 11, 12, 13, and 14, for which ^{13}C NMR spectra of CH_2 analogues are reported,[10c,13] were used in the calculation. [c] *trans*-Decalins,[10c] perhydrophenanthrenes,[13] and perhydroanthracene[13] corresponding to compounds in footnote *b* were used. [d] 3 was excluded. [e] Single occurrence. Data refer to resonance of methyl groups at position and in conformation indicated.

iplanar methyl groups ($\Delta\delta$ between **16**[10c] and **4**, −3.2 ppm) is more pronounced than on equally orientated methylene groups (C-5, −1.9; C-7, −1.5 ppm). Again (cf. ref 14) antiperiplanar methyl groups (−3.2 ppm) are more affected than gauche methyl groups ($\Delta\delta$ CH_3 between **17**[10c] and **6**, −0.2 ppm; between **18**[10c] and **8**, −1.2 ppm). The particularly large γ-gauche effect for C-4 (−2.3 ppm) suggests that at least part of the effect is transmitted through bonds, since C-4 is doubly γ to N-1. A similar explanation may apply to the comparatively large δ effect (−0.9 ppm).

The fact that the ^{13}C NMR spectra of the carbocyclic compounds in Table III were recorded as neat substances[10c,13] but the spectra of the amines were recorded in $CDCl_3$ introduces some uncertainty into the $\Delta\delta$ values because of potential solvent effects; however, comparison of the shift value of cyclohexane in $CDCl_3$ (27.15 ppm) with the literature value[10a] of the neat substance (27.38 ppm) suggests that the effect is not large. Reported[7] $\Delta\delta$ values for piperidine vs. cyclohexane suffer from the same shortcoming.

Shift Effects Produced by Methyl Substitution. Parameters were calculated for the shifts of the ring carbon atoms upon replacement of hydrogen by methyl substituents. The parameters used by Dalling, Grant, and Paul[10c] for the methyldecalins cannot be directly applied to the nitrogen analogues, since the position of the nitrogen relative to the methyl must be taken into account; this leads to a substantial increase in the number of parameters.[11,12] Starting with *trans*-decahydroquinoline, and developing α, β, and γ parameters for replacement of H by CH_3, one arrives at the results (column labeled "found") in Table IV. Comparison with values reported in the literature for the methylcyclohexanes[10b] (Table IV, column labeled "calcd") indicates that the effect of methyl substitution in the carbocycle and the nitrogen heterocycle are nearly the same. With but one exception the Dalling–Grant parameters[10b] predict the chemical shifts in *trans*-decahydroquinolines to within 2 ppm, quite frequently to within 1 ppm, the better agreement occurring, not unexpectedly, for substituents more remote from the nitrogen.

The values for γ_e (−0.4 ± 0.3 ppm), δ_e (−0.1 ± 0.4 ppm), and δ_a (+0.4 ± 0.2 ppm) are not included in Table IV because of their relatively small size. The δ_a value is deshielding and considerably larger than the value reported for the methylcyclohexanes[10b] (−0.06 ± 0.13 ppm). An equally large δ value is obtained by comparing the chemical shifts of the 8α-methyl groups (R_7 = CH_3) in **8** (18.56 ppm) and **10** (18.92 ppm): δ_{ae} = +0.36 ppm. The reverse effect (of the equatorial on the axial methyl group) is even larger (R_5 = CH_3 in **6**, 15.57 ppm; in **10**, 16.72 ppm; δ_{ea} = +1.5 ppm).



6, R_5 = CH_3; R_7 = H
8, R_5 = H; R_7 = CH_3
10, R_5 = R_7 = CH_3

Table IV
Effects of Methyl Substitution on ^{13}C Chemical Shifts in *trans*-Decahydroquinoline

Effect,[a,b] ring atom	Value: Found	Value: Calcd[b]	Compd
α_e, 2	+5.0	+6.0	3
α_e, 3	+5.5	+6.0	4
α_e, 6	+6.3	+6.0	7
$\alpha_e + \alpha_e\beta_e$, 8	+3.5	+3.5	8
$\alpha_e + \alpha_e\beta_e + \gamma_a + G_\gamma + \beta_e\gamma_a$, 8	−2.3	−1.7	10
β_e, 3	+7.7	+9.0	3
β_e, 2	+7.5	+9.0	4
β_e, 4	+8.9	+9.0	4
β_e, 5	+8.8	+9.0	7
β_e, 7	+8.6	+9.0	7
β_e, 7	+9.3	+9.0	8
$\beta_e + \delta_a$, 7	+9.9	+8.9	10
$\beta_e + \alpha_e\beta_e$, 9	+5.9	+6.5	8
$\beta_e + \alpha_e\beta_e + \beta_a + \alpha_e\beta_a + G_\beta$, 9	+8.6	+7.7	10
α_a, 2	+0.2	+1.4	2
α_a, 3	+1.3	+1.4	5
$\alpha_a + \alpha_a\beta_e$, 8	−0.8	−2.0	9
$\alpha + Q - T + 4V_g$,[c] 10	−9.4	−10.2[c]	6
$\alpha + Q - T + 4V_g + \gamma_e$,[c] 10	−9.4	−10.1[c]	10
β_a, 3	+4.0	+5.4	2
β_a, 2	+4.9	+5.4	5
β_a, 4	+5.6	+5.4	5
$\beta_a + \beta_a\gamma_e$, 7	+7.2	+7.0	9
$\beta_a + \alpha_e\beta_a$, 9	+2.5	+2.5	9
$\beta_a + \beta_a\gamma_e + G_\beta$, 4	+7.4	+5.7	6
$\beta_a + \beta_a\gamma_e + G_\beta$, 5	+7.9	+5.7	6
$\beta_a + \beta_a\gamma_e + G_\beta + \delta_e$, 4	+7.9	+5.5	10
$\beta_a + \beta_a\gamma_e + G_\beta + \delta_e$, 5	+8.3	+5.5	10
$\beta_a + \alpha_e\beta_a + G_\beta$, 9	+2.2	+1.2	6
γ_a, 4	−5.7	−6.4	2
γ_a, 9	−8.1	−6.4	2
γ_a, 10	−5.8	−6.4	5
γ_a, 6	−6.1	−6.4	9
$\gamma_a + \beta_e\gamma_a$, 10	−7.7	−7.2	9
$\gamma_a + G_\gamma$, 3	−4.3	−4.4	6
$\gamma_a + G_\gamma$, 6	−4.8	−4.4	6
$\gamma_a + G_\gamma$, 3	−4.4	−4.4	10
$\gamma_a + \gamma_e + G_\gamma$, 6	−5.0	−4.4	10
$\gamma_a + \beta_e\gamma_a + G_\gamma$, 8	−5.1	−5.2	6

[a] In parts per million; plus sign indicates downfield from signal in *trans*-decahydroquinoline. [b] Parameters of Table IV, ref 10b, were used for calculated values, if not otherwise indicated. [c] Since no comparable parameter was given in ref 10b, the values from ref 10c are used for α, Q, T, and V_g

This is of some consequence since methyl substituents are frequently used as holding groups in monocyclic systems and their influence on δ positions is usually disregarded.

***N*-Methyl Derivatives.** ^{13}C NMR spectra of the *N*-methyl derivatives[2] of compounds **1–14** (Schemes I, II, R = CH_3, **1m–14m**) were recorded in $CDCl_3$ and (in some cases) in C_6D_6. The data are collected in Tables II and V.

As in the case of the NH precursors, assignment of signals was accomplished by recording the off-resonance decoupled spectra, by comparison with the carbocyclic analogues[10c,13] and (in the case of **1m, 2m, 3m, 6m, 8m,** and **9m**) through selectively deuterated analogues. The NCH_3 signals were easily detected in the off-resonance decoupled spectra except for **8m, 11m,** and **12m,** in which the NCH_3 resonances occur in a rather crowded spectral region; in the case of **8m** the NCD_3 analogue was therefore synthesized[2] in which the CD_3 signal disappeared because of loss of the NOE and dissipation of the signal through coupling with the deuterium.

While the *N*-methyl group in **1m, 4m,** and **7m** is mobile, it is biased toward the equatorial position by the axial C–CH_3 in **5m, 6m,** and **9m** and by C-10 in **13m,** and toward the axial position by the equatorial C–CH_3 in **8m** and by C-10 in **11m** and **12m.** By means of the equation $\delta = \delta_e n_e + \delta_a n_a$, the mole fractions of the axial and equatorial conformer in the mobile case (and therefore K and $-\Delta G°$) were calculated. These results are reported in detail elsewhere;[2] ≥95% of the NCH_3 are found to be in the equatorial position at room temperature in $CDCl_3$. Compounds **8m, 11m,** and **12m** allow the calculation of the shift influences of an axial *N*-methyl group on the ring C atoms; compounds **5m, 6m, 9m,** and **13m** (and, if the ≤5% axial NCH_3 are neglected in a first approximation, also **1m, 4m,** and **7m**) provide the analogous influence of an equatorial NCH_3. The effects are relatively constant; their averaged values are summarized in Table VI. Shielding and deshielding influences are qualitatively the same as in analogous methylcyclohexanes,[10a,b] but the effects in the *N*-methyldecahydroquinolines are generally larger. Most noticeable is the relatively large (−1.5 ppm) shielding γ_e effect. Since it occurs in the equatorially biased compounds as well as in the mobile ones, it cannot be due to a γ_a contribution. The effect is quenched by an axial methyl substituent at the ring carbon under consideration (C-3 in **5m** and C-10 in **6m**). The shielding of the γ_a effect is unusually large also: −7.5 ppm at C-3, −10.8 ppm at C-10 compared to −7.2 ppm for axial methyl in cyclohexane.[10b] Once again there is a sizable deshielding δ_a effect (0.9 ppm); this effect is negligible in methylcyclohexanes.[10b]

Since only a few ^{13}C NMR spectra of carbocyclic analogues of the *N*-methyl-*trans*-decahydroquinolines are reported,[10c] calculations of the effects resulting from replacement of C by N suffer from being based on insufficient data. The direction of such effects (deshielding for α, otherwise shielding) is, however, identical with that recorded in Table III for the secondary amines. The α effect on the methyl carbon is larger (+22.5 ppm) than on methylene and methine carbon (see above). The β effects on C-3 (−1.5 ppm) and C-10 (−2.0 ppm) are more upfield shifting than for the NH compounds. The chemical shifts in the spectra recorded in deuteriobenzene are 0.25–0.70 ppm more downfield from Me_4Si than the values obtained in $CDCl_3$. The solvent effect is largest at C-3 (average +0.44 ppm) and C-4 (average +0.49 ppm) and smallest at C–CH_3 (average +0.17 ppm) and N–CH_3 (average +0.04 ppm).

Comparison of the signals in *N*-methyl-*trans*-decahydroquinoline with **4m–7m** and **9m** allows calculation of parameters for *C*-methyl substitution; the values so obtained are similar to the ones in Table IV for *trans*-decahydroquinoline.

Because of the additional γ_g interaction to which the *N*-methyl group is subject in **2m, 3m,** and **14m,** compared to the other model compounds, no conclusions on the axial-equatorial equilibrium can be drawn from the NCH_3 chemical shift. However, since the γ_a effects brought about by the NCH_3 group are fairly large (see Table VI), C-3 and C-10 in **2m** and **3m,** and C-8a and C-9a in **14m** should be considerably upfield shifted in comparison to the secondary amines if the axial NCH_3 conformer were present in appreciable amounts at equilibrium. The point is further discussed below.

A very large (−9.6 ppm) shielding effect on the axial CH_3 in **2** is observed upon N-methylation; a similar effect (−9.5 ppm) is seen for the analogously positioned C-8 in 3-α-methyl-*cis*-decahydroquinoline (**19**, R = H → R = CH_3).[3] This effect should be compared to the combination of the upfield shifting "γ_g" and "buttressing" effects seen in analogously substituted methylcyclohexanes[10a,b] (e.g., for the axial group in **20**) and methyldecalins[10c] (e.g., the carbocyclic analogue of **19** minus the 3-methyl group). The effect in the carbocycles is considerably smaller (−5.8 ppm in **20**; −6.33 ppm in 1-α-methyl-*cis*-decalin). There is thus an additional factor due to the nitrogen atom. The effect re-

Table V
^{13}C Chemical Shifts[a] of *N*-Methyl-*trans*-decahydroquinolines (1m–10m)[b]

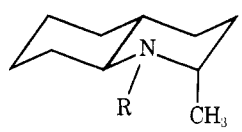
Compd[c]		C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9[d]	C-10[d]	C–CH_3	NCH_3
Parent	1m	57.94	25.80	32.59	33.06	26.01	25.87	30.47	69.25	41.84		42.59
		58.27	26.13	33.13	33.38	26.48	26.30	30.80	69.55	42.08		42.73
2α-Methyl	2m	55.97	31.62	26.92	32.94	26.21	26.03	30.94	60.03	42.51	9.08	39.53
2β-Methyl	3m	59.72	34.65	32.75	33.52	25.77	26.07	30.86	69.19	41.51	21.93	37.14
3α-Methyl	4m	65.56	30.95	41.35	32.96	25.95	25.76	30.29	68.57	41.65	19.68	42.39
		66.10	31.24	(41.94)	33.29	26.50	26.15	30.74	68.96	(41.97)	19.87	42.61
3β-Methyl	5m	63.57	28.51	38.22	33.12	26.05	25.80	30.14	70.11	36.23	18.77	43.01
		63.77	29.29	39.00	33.50	26.55	26.19	30.66	70.40	36.79	18.95	42.97
10-Methyl	6m	59.19	22.15	(40.32)	(40.67)	21.19	26.14	25.08	71.92	34.10	17.35	43.11
		59.36	22.56	(40.33)	(41.39)	21.56	26.45	25.44	71.85	34.48	17.49	42.93
6α-Methyl	7m	58.06	25.92	32.53	41.82	32.28	34.40	30.38	69.06	41.48	22.29	42.84
		58.32	26.36	33.06	42.06	32.59	34.71	30.78	69.28	41.76	22.54	42.92
8α-Methyl	8m	56.06	19.44	33.65	34.12	25.73	35.66	34.47	70.72	31.76	18.94	33.23
		56.34	19.88	34.22	34.38	26.08	35.92	34.77	70.78	31.74	19.02	33.28
8β-Methyl	9m	58.23	25.80	33.01	33.67	20.18	32.64	29.22	71.98	34.25	12.11	42.29
		58.32	26.23	33.42	33.92	20.61	32.63	29.71	71.98	34.53	12.02	42.33
8α,10-Dimethyl	10m	55.44	16.87	41.35	43.78	21.49	36.70	29.88	71.75	34.91	(19.97)	35.26
											(19.73)	

[a] In parts per million, from internal Me_4Si. First line of signals: solvent $CDCl_3$. Second line of signals: solvent C_6D_6. [b] For characterization of compounds see ref 2 and 6. [c] *trans*-Decahydroquinoline. [d] For nomenclature see footnote *d*, Table I.

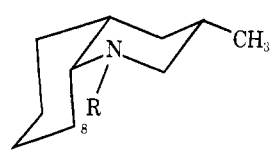
Table VI
Effect[a] of Axial[b] and Equatorial[c] NCH_3 Groups on Ring Shifts in *trans*-Decahydroquinoline

	Axial NCH_3			Equatorial NCH_3		
Ring atom[d]	Effect	Parameter	(Lit.)[e]	Effect	Parameter	(Lit.)[e]
C-2	+8.6 ± 0.1	$\beta_a + \beta_a\gamma_e$	(+7.0)	+10.8 ± 0.2	β_e	(+9.0)
C-3	−7.5 ± 0.1	γ_a	(−6.4)	−1.5 ± 0.4	γ_e	(+0.05)
C-4	+0.9 ± 0.1	δ_a	(−0.06)	+0.1 ± 0.2	δ_e	(−0.2)
C-5	+0.9 ± 0.2	δ_a	(−0.06)	+0.3 ± 0.1	δ_e	(−0.2)
C-6	*f*	ϵ_a		−0.3 ± 0.1	ϵ_e	
C-7	*f*	δ_a		+0.1 ± 0.2	δ_e	(−0.2)
C-8	−3.3 ± 0.3	γ_g	(−2.8)[g]	−3.6 ± 0.2	γ_g	(−2.8)[g]
C-9	+3.0 ± 0.2	$\beta_a + \alpha_e\beta_a$	(+2.5)	+7.4 ± 0.3	$\beta_e + \alpha_e\beta_e$	(+6.6)
C-10	−10.8 ± 0.8	$\gamma_a + \beta_e\gamma_a$	(−7.2)	−1.4 ± 0.1	γ_e	(+0.05)

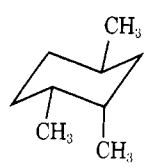
[a] In parts per million. Plus sign indicates downfield shift. The values given are averages of the compounds considered (see footnotes *b*, *c*) with their standard deviations. [b] Compounds 8m, 11m, and 12m were used for the calculation. [c] Compounds 1m, 4m, 5m, 6m, 7m, 9m, and 13m were used for the calculation. [d] For nomenclature see Scheme I. [e] Parameters and their values (in parentheses) are those for methylcyclohexanes, ref 10b. [f] Values were too divergent for averaging. [g] The parameter is reported[10b] for a methyl group.



2, R = H 18.62 ppm
2m, R = CH_3 9.08 ppm



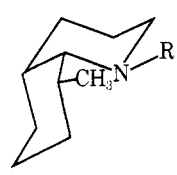
19



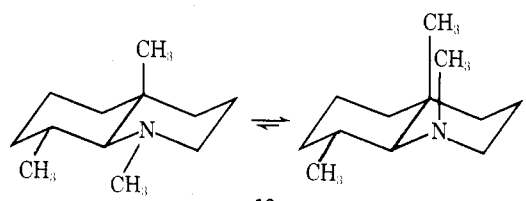
20

quires the presence of both the *N*-methyl group and the axial lone pair; it is absent in the NH analogs (which must exist with predominantly equatorial NH[15]) and it is reduced in the amine hydrochlorides, to a value even smaller than in the carbocyclic analogues ($2H^+Cl^- \rightarrow 2m_eH^+Cl^-$, $\Delta\delta = -3.57$ ppm).

The position of the NCH_3 group in **10m** cannot be estimated from the chemical shift of its signal since this group is compressed in both the axial and the equatorial position by either a syn-axial or a peri methyl group. Results[3] with 8α-methyl-*cis*-decahydroquinoline (**21**) and its *N*-methyl derivative (**21m**), in which the NCH_3 group cannot escape the per interaction, indicate that such an interaction is downfield shifting[16] [CH_3 (8α), **21** → **21m**, $\Delta\delta = +4.6$ ppm]. The NCH_3 signal in **10m** has a chemical shift of 35.26 ppm;



21, R = H
21m, R = CH_3



10m

this points to a substantial contribution of downfield shifted axial NCH_3 rather than to a downfield shifted equatorial NCH_3 which should have a shift of ~45 ppm. Accordingly, the compressed CH_3(10) group is shifted downfield by 3.0–3.2 ppm (the two *C*-methyl groups in **10m** are too close for unambiguous assignment) but the essentially uncompressed $CH_3(8\alpha)$ group is shifted downfield by only 0.8–1.0 ppm. Also the γ effect on C-3 is large and upfield (−6.1

Table VII
^{13}C Chemical Shifts[a] of *N*-Ethyl- and *N*-Isopropyl-*trans*-decahydroquinolines

Compd[b]	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-CH_3	NCH	NCHCH_3	NCHCH_3
1-Et	52.63	25.91	32.80	33.26	26.05	25.91	30.10	65.29	42.07		46.29	9.18	
4-Et	60.33	30.93	41.54	33.14	26.00	25.85	29.99	64.55	41.90	19.78	46.12	9.03	
6-Et	53.55	22.25	(40.39)	(40.99)	21.20	26.24	24.84	67.55	34.23	17.31	46.41	8.58	
8-Et	49.64	18.73	33.80	34.53	25.76	35.80	34.20	72.19	33.37	19.05	36.63	13.92	
9-Et	52.58	25.78	33.21	33.86	20.19	32.64	28.73	67.63	34.52	12.41	45.58	9.20	
1-*i*-Pr	44.21	26.35	33.29	33.52	25.97	26.10	29.46	64.24	42.43		45.96	21.95	11.88
4-*i*-Pr	51.88	31.33	42.04	33.36	25.87	26.00	29.33	63.57	42.17	19.96	45.79	21.93	11.82
6-*i*-Pr	45.40	22.07	(40.32)	(41.70)	21.04	26.36	24.44	67.00	34.51	17.29	45.86	22.58	12.17
8-*i*-Pr	45.56	25.85	33.82	34.68	25.57	36.09	33.88	71.56	37.83	20.18	45.35	24.55	22.76
9-*i*-Pr	44.24	25.97	33.69	34.09	20.16	32.67	28.39	66.35	34.83	12.31	44.90	21.75	11.84

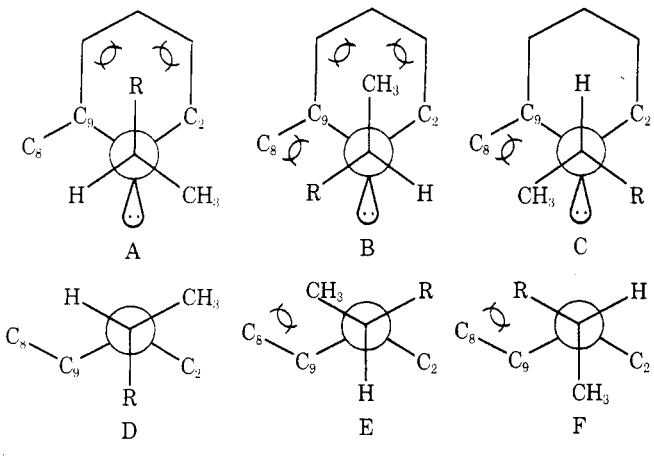
[a] In $CDCl_3$; parts per million from internal Me_4Si. [b] See Scheme I; Et, R = CH_2CH_3; *i*-Pr, R = $CH(CH_3)_2$. For melting points of derivatives and ^1H NMR data see ref 2.

ppm), indicating axial substitution on N. The same indication follows from the rather large downfield shifts of C-4 and C-5 (similarly as in **8m**). The combined force of these arguments indicates that the NCH_3 group in **10m** is largely axial. There is also confirmation, for the case of CH_3–CH_3 interactions, of the downfield shifting effect of syn-axial groups on each other reported elsewhere[16] in similar situations.

***N*-Ethyl and *N*-Isopropyl Derivatives.** The ^{13}C NMR spectra of the *N*-ethyl (Scheme I, R = C_2H_5) and *N*-isopropyl [Scheme I, R = $CH(CH_3)_2$] derivatives of **1, 4, 6, 8,** and **9** were recorded; the chemical shifts are collected in Table VII. Assignment of the methyl signals was done by off-resonance decoupling and, in the case of **4**-*i*-Pr and **8**-*i*-Pr, confirmed by recording the spectra of the $NCD(CD_3)_2$ analogues. Assignment of the signals of the ring C atoms in case of **1**-Et, **8**-Et, and **9**-Et, and **1**-*i*-Pr, **8**-*i*-Pr, and **9**-*i*-Pr, was confirmed by investigating the ring-deuterated compounds.

Comparison with the NCH_3 compounds shows that shift changes on C atoms remote from the nitrogen are relatively minor (an exception is **8**-*i*-Pr, see below). Both C-2 and C-9 are less downfield shifted in **1**-Et, **4**-Et, **6**-Et, and **9**-Et compared to the NCH_3 analogues because of additional gauche interactions; the same is true for C-2 but not for C-9 in **8**-Et, which exists in conformation A (R = H, Scheme III); a gauche interaction of C-9 with the methyl group

Scheme III



1-Et, **4**-Et, **6**-Et, **8**-Et, **9**-Et, R = H
1-*i*-Pr, **4**-*i*-Pr, **6**-*i*-Pr, **8**-*i*-Pr, **9**-*i*-Pr, R = CH_3

would require contributions of the unfavorable rotamers B and C.

In **1**-*i*-Pr, **4**-*i*-Pr, **6**-*i*-Pr, and **9**-*i*-Pr, C-9 is still somewhat downfield shifted compared to the NH analogues by the β effect of the methine carbon, but the effect is nearly compensated by the gauche interactions with the methyl groups; C-2 is already upfield shifted. This suggests predominance of rotamer D in Scheme III (R = CH_3), where C-2 has two gauche interactions and C-9 only one. (Conformers E and F suffer from an *i*-Pr–Me/C-8 syn-axial interaction.)

In **8**-*i*-Pr the methine carbon (45.35 ppm) of the isopropyl group is very much downfield compared to the methyl in **8m** (33.23 ppm) and the methylene in **8**-Et (36.63 ppm); C-3, on the other hand, is much less shielded (relative to the NH compound, $\Delta\delta$ = −1.1 ppm) than **8m** ($\Delta\delta$ = −7.5 ppm) or **8**-Et ($\Delta\delta$ = −8.2 ppm). Since the isopropyl methyl groups are encountering very severe sterical interactions in the isopropyl-axial conformations (see Scheme III) A–C, the possibility exists that the *N*-isopropyl group is partially in the equatorial position in spite of the peri interaction with the methyl group on C-8 that this would cause.

The diastereotopic isopropyl methyl groups in **1**-*i*-Pr, **4**-*i*-Pr, **6**-*i*-Pr, and **9**-*i*-Pr show shift differences of ~10 ppm; this finds its parallel in the proton spectra[2] of these compounds with shift differences of the methyl protons of ~0.3 ppm.

Ring-Deuterated *trans*-Decahydroquinolines. In connection with the earlier mentioned study of ring-deuterated *trans*-decahydroquinolines, the *2,3,3,4,9,10*-d_6 analogues of **1, 2, 3, 8,** and **9**, of their *N*-methyl derivatives, and of the *N*-ethyl and *N*-isopropyl derivatives of **1, 8,** and **9** were prepared. Compounds **1**-d_6 and **9**-d_6 and their *N*-alkyl derivatives contained small amounts of *2,3,3,4,8,9,10*-d_7 products because some exchange of the axial proton at C-8 occurred during synthesis, and **2**-d_6 and **3**-d_6 were admixed with substantial amounts of higher deuterated material owing to extensive exchange in the CH_3 group.[6]

The shift effects of the deuterium on the various carbon atoms are in agreement with results reported in the literature.[8,17,18] C atoms devoid of proton substituents (C-3, C-9, and C-10, and C-2 in **2**-d_6 and **3**-d_6) could not be detected in the proton noise-decoupled spectra, their signals being very small because of loss of the NOE, long relaxation times, and dissipation of the signals into triplets and quintets. C atoms substituted with one deuterium and one proton (C-4 in **1, 2, 3, 8,** and **9**, and C-2 in **1, 8,** and **9**) were split into triplets (J_{CD} ~ 20 Hz). C-2 was shifted upfield by 0.5–0.7 ppm, and C-4 by 0.6–0.8 ppm largely by the deuterium bound to it.

β effects of deuterium were seen on C-5 and C-8; the signals of these carbons were broadened by C–C–D coupling and shifted upfield by ~0.1 ppm relative to those of the protonated analogues. C-7 displayed a small satellite signal, ~0.1 ppm upfield of the main one, resulting from the minor amount of deuteration at C-8 which had occurred

Table VIII
^{13}C Chemical Shifts[a] of *trans*-Decahydroquinolinium Chlorides[b] and Trifluoroacetates[c]

Entry no.	Compd[d]	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_3
1	$1H^+Cl^-$	44.85	22.50	30.09	32.12	24.94	24.84	29.87	61.29	39.11	
		−2.48	−4.79	−2.37	−0.52	−1.35	−0.80	−4.13	−0.80	−4.22	
2	$2H^+Cl^-$	48.43	27.50	24.75	32.01	24.94	24.94	29.72	54.44	39.44	14.61
		+0.90	−3.83	−2.04	−0.46	−1.35	−0.80	−4.59	+0.48	−4.48	−4.01
3	$3H^+Cl^-$	54.26	30.78	30.46	32.00	24.87	24.87	29.59	61.71	38.36	19.31
		+1.89	−4.20	−1.95	−0.24	−1.34	−0.60	−4.20	−0.14	−4.01	−3.64
4	$6H^+Cl^-$	45.04	18.78	38.02	39.50	20.50	25.21	25.21	63.28	33.61	16.06
		−3.09	−4.19	−1.86	−1.03	−0.98	−0.76	−3.67	−1.03	−0.33	+0.46
5	$8H^+Cl^-$	45.85	22.31	30.19	32.44	24.64	34.63	35.18	66.94	38.83	19.20
		−1.70	−4.62	−2.43	−0.58	−1.20	−0.27	−2.33	−1.03	−3.39	+0.61
6	$9H^+Cl^-$	45.56	22.24	30.71	32.85	19.09	31.85	30.19	64.29	32.49	13.24
		−2.11	−5.22	−2.31	−0.44	−1.14	−1.02	−2.97	−0.34	−3.12	+0.61
7	$1H^+TFA^-$	48.44	24.16	30.75	33.24	26.17	25.95	32.06	65.07	41.77	
		+1.11	−3.13	−1.71	+0.60	−0.12	+0.31	−1.94	+2.98	−1.53	
8	$6H^+TFA^-$	49.12	20.28	38.71	40.90	21.55	26.35	27.39	67.42	35.35	15.32
		+0.99	−2.69	−1.17	+0.37	+0.07	+0.38	−1.49	+3.11	+1.41	−0.28
9	$8H^+TFA^-$	48.80	24.01	30.78	33.57	25.78	35.61	37.39	70.82	41.42	17.90
		+1.25	−2.92	−1.84	+0.55	−0.06	+0.71	−0.12	+2.85	−0.80	−0.69
10	$9H^+TFA^-$	48.77	23.98	31.29	33.90	20.09	33.12	32.55	68.00	34.86	12.30
		+1.10	−3.48	−1.73	+0.61	−0.14	+0.25	−0.61	+3.42	−0.75	−0.35

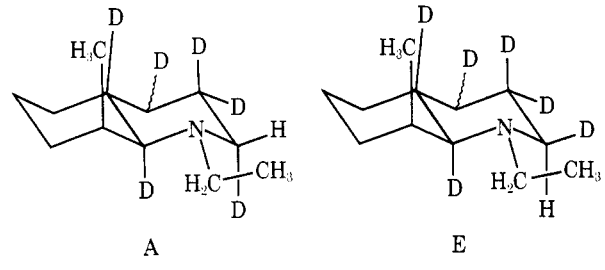
[a] First line of figures for each compound: shift in parts per million from internal Me_4Si. Second line: shift difference from the free amine in $CDCl_3$ (Table I) (salt − amine). A plus sign indicates that the signal in the salt is downfield from the signal in the free amine. [b] In $CDCl_3$. [c] In trifluoroacetic acid. [d] See Scheme I for compound identification. Cl^- indicates chloride; TFA^-, trifluoroacetate.

(vide supra). In compound 8, for the same reason, a deuterium satellite of the methyl resonance was seen.

Increase in line width for C atoms γ to the site of deuterium is generally small. However, broadening may occur,[8] due to a combination of long-range coupling and differential chemical shifting, especially in compounds which are either highly deuterated (coupling effect) or in which hydrogen and deuterium substitution coexist at the γ carbon (differential shift effect). Observation of such broadening allowed unambiguous assignment of the signals due to C-3 and C-6 in **6** and **6m**; the spectra of the *8,8,9-*d_3 analogues containing approximately 40% *8,9-*d_2 because of incomplete deuteration (the amount of d_2 compound could be estimated from the intensities of the two signals for C-7, 0.1 ppm apart) showed a threefold increase in line width for the signal of C-6 compared to the undeuterated compound whereas the signal for C-3 was unchanged.

The methyl group of the ethyl function in 1-Et-d_6 and 9-Et-d_6 (but not in 8-Et-d_6), and the upfield methyl group of the isopropyl function in 1-*i*-Pr-d_6 and 9-*i*-Pr-d_6 (but not in 8-*i*-Pr-d_6) showed two signals (shift difference 2.0 and 2.4 Hz for the ethyl and 0.7 and 0.9 Hz for the isopropyl methyl group). In the case of the ethyl compounds the larger of the two peaks was upfield, in case of the isopropyl, downfield. No doubling was seen for the downfield methyl in the isopropyl groups of 1-*i*-Pr-d_6 and 9-*i*-Pr-d_6, and only one signal could be detected for the corresponding methyl groups in 1-Et-*9*-d_1 and 1-*i*-Pr-*9*-d_1; admixture with undeuterated material still gave an unsplit signal. This finding, combined with the absence of any doubling in 8-Et-d_6 and 8-*i*-Pr-d_6 (or, of course, in any of the undeuterated compounds), forces one to the conclusion that the doubling of the methyl signals is caused by the deuterium at C-2. The hexadeuterated compounds are mixtures of isomers with axial or equatorial deuterium at C-2 and C-4 and since C-4 is quite distant from the *N*-alkyl groups, C-2 must be implicated in the doubling. In the presumably most favored rotational form of 1-Et or 8-Et, the CH_3 of the ethyl group is much closer to equatorial deuterium on C-2 (Scheme IV, E) than to axial deuterium (Scheme IV, A). The deuterium vs. proton shift effect may act through

Scheme IV



bonds (but this seems unlikely, since no effect is observed at the methylene carbon at the ethyl group, which is closer (γ) to the deuterium at C-2) or, more likely, it may act through space; no clear-cut decision can, however, be made on the basis of the available evidence.

Protonated *trans*-Decahydroquinolines.[19] The chemical shifts of a number of protonated *trans*-decahydroquinolines and *N*-methyl-*trans*-decahydroquinolines are collected in Tables VIII–X. Also recorded in these tables are the differences in chemical shift between the salts (protonated amines) and the free amines (in $CDCl_3$).[20]

Comparison of the data for the hydrochlorides and trifluoroacetates in Table VIII shows that for C atoms remote from the nitrogen (C-5, C-6, C-7) the shift differences $\Delta\delta$ (salt − free amine) for the two are quite similar (1.0–0.4 ppm), while close to the nitrogen they vary considerably. For example, for **1**, **6**, **8** (Table VIII, entries 1, 7; 4, 8; 5, 9), **6m**, **8m**, and **9m** (compare entries 18, 19, and 20 in Table IX with 27, 28, and 29 in Table X), the shift for C-2 upon formation of the hydrochloride is upfield, but for the trifluoroacetate it is downfield. The shift difference changes are brought about largely by the change in solvent and only in small part by the change of the gegenion; thus *N*-methyl-*trans*-decahydroquinoline hydrochloride and trifluoroacetate in $CDCl_3$ have very similar chemical shifts (Table IX, entry 11; Table X, entry 23). The same is true for the hydrochloride and trifluoroacetate in trifluoroacetic acid (Table IX, entry 13; Table X, entry 21). In contrast, the shifts for corresponding salts in $CDCl_3$ and CF_3COOH dif-

Table IX
^{13}C Chemical Shifts[a] of *N*-Methyl-*trans*-decahydroquinolinium Chlorides[b]

Entry no.	Compd[b]	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_3	NCH_3
11	$1m_eH^+Cl^-$[c]	56.77	22.87	30.08	32.45	24.58	25.07	27.21	69.31	39.18		40.41
		−1.17	−2.93	−2.51	−0.61	−1.43	−0.80	−3.26	+0.06	−2.66		−2.18
12	$1m_aH^+Cl^-$[d]	54.15	18.19	30.31	32.73	24.88?	24.88?	28.16	65.62	33.38		32.82
13	$1m_eH^+Cl^-$[c,e]	59.71	24.80	31.03	33.69	25.88	26.28	29.41	73.19	42.33		42.14
		+1.77	−1.00	−1.56	+0.63	−0.13	+0.41	−1.06	+3.93	+0.49		−0.45
14	$2m_eH^+Cl^-$[f]	58.81	28.85	24.76	32.38	24.65	25.29	27.21	62.55	39.86	11.04	38.59
		+2.84	−2.77	−2.16	−0.56	−1.56	−0.74	−3.73	+2.52	−2.65	+1.96	−0.94
15	$2m_aH^+Cl^-$[d]	59.30	23.30	g	32.82	25.04?	25.04?	28.07	59.30	33.69	15.52	35.70
16	$3m_eH^+Cl^-$[f]	63.06	32.84	30.77	32.94	24.17	25.41	27.47	70.65	38.90	18.68	35.97
		+3.34	−1.81	−1.98	−0.58	−1.60	−0.66	−3.39	+1.46	−2.61	−3.25	−1.17
17	$3m_aH^+Cl^-$[d]	59.72	25.60	g	g	25.03?	25.03	28.15	67.51	31.60	17.74	25.81
18	$6m_eH^+Cl^-$	57.56	19.65	37.77	39.88	20.10	25.44	22.86	71.66	34.89	16.95	41.77
		−1.63	−2.50	−2.55	−0.79	−1.09	−0.70	−2.22	−0.26	+0.79	−0.40	−1.34
19	$8m_aH^+Cl^-$	55.67	18.13	30.36	33.03	24.52	34.68	33.59	71.22	33.51	18.88	32.71
		−0.39	−1.31	−3.29	−1.09	−1.21	−0.98	−0.88	+0.50	+1.75	−0.06	−0.52
20	$9m_eH^+Cl^-$	57.61	22.61	30.53	33.16	18.85	32.03	28.03	71.91	32.91	12.65	40.11
		−0.62	−3.19	−2.48	−0.51	−1.33	−0.61	−1.19	−0.07	−1.34	+0.54	−2.18

[a] First line of figures: shift in parts per million from Me_4Si. Solvent $CDCl_3$ if not otherwise indicated. Second line: shift difference from the unprotonated amine in $CDCl_3$ (Table V). [b] See Scheme I for compound identification. The symbol m indicates an *N*-methyl compound; the subscripts e or a refer to the equatorial or axial position of the *N*-methyl substituents. 1m, 2m, and 3m gave mixtures of hydrochlorides; the major component with the NCH_3 equatorial, the minor with NCH_3 axial. No second component could be detected in the hydrochlorides of 6m, 8m, and 9m. [c] The ≤5% axial NCH_3 in the amine was neglected for the calculation of Δδ salt-amine. [d] Since the NCH_3 in the amine is predominantly equatorial, no Δδ was calculated. [e] Solvent trifluoroacetic acid. [f] The contribution of axial NCH_3 in the amine was neglected for calculation of Δδ. [g] Overlaid by a signal of the major (NCH_3 eq) component.

Table X
^{13}C Chemical Shifts[a] of *N*-Methyl-*trans*-decahydroquinolinium Trifluoroacetates[b]

Entry no.	Compd[b]	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_3	NCH_3
21	$1m_eH^+TFA^-$[c]	60.06	24.95	31.07	33.74	25.93	26.34	29.59	73.57	42.68		42.39
		+2.12	−0.85	−1.52	+0.68	−0.08	+0.47	−0.88	+4.32	+0.84		−0.20
22	$1m_aH^+TFA^-$[d]	57.54	19.27	31.29	34.11	26.13?	26.13?	30.45	69.99	35.27		34.80
23	$1m_eH^+TFA^-$[c,e]	57.09	23.01	30.11	32.49	24.70	25.14	27.37	69.95	39.54		40.54
		−0.85	−2.79	−2.48	−0.57	−1.31	−0.73	−3.10	+0.70	−2.30		−2.05
24	$1m_aH^+TFA^-$[d,e]	54.19	18.03	30.30	32.76	25.00?	25.00?	28.37	65.84	33.42		33.19
25	$3m_eH^+TFA^-$[f]	66.77	34.12	31.51	34.26	25.73	26.70	30.31	74.43	42.93	19.76	38.26
		+7.05	−0.53	−1.24	+0.74	−0.04	+0.63	−0.55	+5.24	+1.42	−2.17	+1.12
26	$3m_aH^+TFA^-$[d]	64.29	26.87	31.95	g	26.48	26.24	30.65	72.25	34.75	18.65	27.93
27	$6m_eH^+TFA^-$	60.89	(21.03)	38.77	41.44	(21.13)	26.65	24.56	75.70	36.48	16.20	42.60
		+1.70	−1.12	−1.55	+0.77	−0.06	+0.51	−0.52	+3.78	+2.38	−1.15	−0.51
28	$8m_aH^+TFA^-$	57.98	19.25	31.35	34.35	25.61	35.72	34.95	75.69	34.85	17.30	34.18
		+1.92	−0.19	−2.30	+0.23	−0.12	+0.06	+0.48	+4.97	+3.09	−1.64	+0.95
29	$9m_eH^+TFA^-$	60.30	24.67	31.34	34.40	20.03	33.29	29.73	76.12	35.71	11.56	41.93
		+2.07	−1.13	−1.67	+0.73	−0.15	+0.65	+0.51	+4.14	+1.46	−0.55	−0.36

[a] First line of figures: shift in parts per million from Me_4Si. Solvent trifluoroacetic acid if not otherwise indicated. Second line of figures: shift difference from the free amine in $CDCl_3$ (Table V). [b] See Scheme I for compound identification and footnote *b*, Table IX. 1m and 3m gave mixtures of salts; the major component with the NCH_3 group equatorial (m_e), the minor with the NCH_3 axial (m_a). 6m, 8m, and 9m gave only one set of signals in trifluoroacetic acid. [c] The ≤5% axial NCH_3 in the free amine was neglected for the calculation of the shift difference salt — amine. [d] Since the NCH_3 in the amine was predominantly equatorial, no Δδ was calculated. [e] Solvent $CDCl_3$. [f] The contribution of axial NCH_3 in the free amine was neglected for the calculation of δ. [g] Overlaid with a signal of the major (NCH_{3e}) component.

fer considerably (Table IX, entries 11 and 13; Table X, entries 21 and 23) and by about the same amounts. This variation in chemical shift may be due to prevalence of ion pairs in the less polar solvent chloroform, but of solvated ions in the more polar solvent trifluoroacetic acid.

Comparison of hydrochlorides and unprotonated amines in the same solvent ($CDCl_3$) allows the calculation of protonation effects. Values taken from Tables VIII and IX are in agreement with data reported for piperidines,[22] piperidones,[23] and aliphatic amines.[19] Generally, the introduction of a positive charge at the nitrogen leads to shielding of both close-by and distant carbon atoms through polarization of the C–H bond. Exceptions occur for α carbons which bear methyl substituents (compounds **2**, **2m$_e$**, **3**, **3m$_e$**; entries 2 and 3 in Table VIII and 14 and 16 in Table IX); this is in accord with observations made in aliphatic amines.[19] However, C-9, though tertiary, is frequently shifted upfield in the *trans*-decahydroquinolines (Table VIII, entries 1, 3, 4, 5, and 6; Table IX, entries 18 and 20) although in other cases it displays the expected downfield shift (Table VIII, entry 2; Table IX, entries 11, 14, 16, and 19).

The carbon atoms β to the nitrogen become strongly shielded upon protonation, the effect being larger in the secondary (NH) than in the tertiary (NCH_3) amines, again in accord with what is seen in acyclic compounds.[19] The same difference has been observed in piperidines vs. *N*-methylpiperidines[21] and has been attributed to the allegedly preferred equatorial position of the lone pair in the NH (but not in the *N*-methyl) compound; in the light of other

work on the position of lone pair in piperidine[15] and in the light of the analogy with acyclic amines,[19] this explanation is no doubt incorrect.[24]

In agreement with earlier work[21] and with molecular orbital calculations,[25] we find an "alternating and attenuating" shift effect[21] upon protonation as one moves away from the ring nitrogen atom; the upfield shifts are $\alpha < \beta > \gamma < \delta$. In the case of the δ effect at C-6 this may, however, be an artifact resulting from the dual through-bond path (C-9–C-8–C-7–C-6 and C-9–C-10–C-5–C-6); results in the aliphatic series[19] in general show that C_γ is more upfield shifted than C_δ.

Whereas the *N*-methyl-*trans*-decahydroquinolinium chlorides (Table IX) are all conformationally homogeneous, this is not true of all of their amine precursors. In the case of **1m** (and probably also **2m** and **3m**) the *N*-methyl group is largely (≥95% in case of **1m**) equatorial and we felt justified in disregarding the axial component and to indicate $\Delta\delta$ (Table IX, entries 11, 14, and 16) as the difference between the equatorial salt and the mobile amine. Compounds **6m** and **9m**, on the other hand, are conformationally homogeneous and the $\Delta\delta$ values (entries 18 and 20) for these species are accurate for a *N*-methyl-*trans*-decahydroquinoline with equatorial *N*-methyl.

Compound **8m** has the novel feature of a conformationally homogeneous axial NCH_3 and displays slightly different shifts upon protonation (entry 19) than the equatorial analogues (β effect, lesser upfield shift at C-3 and C-8, larger downfield shift at C-10; enhanced γ-effect, larger upfield shift at C-4, C-5, and C-7). Other salts with axial NCH_3 ($\mathbf{1m_aH^+}$, $\mathbf{2m_aH^+}$, and $\mathbf{3m_aH^+}$; entries 12, 15, and 17 in Table IX) display similar absolute chemical shifts in those regions not directly affected by the substituent groups, suggesting little perturbation of the molecule by the methyl group at C-8.

In summary, the study of 14 *trans*-decahydroquinolines has enabled us to establish the effect of methyl substitution on the chemical shifts of various ring carbons and to compare shifts in saturated nitrogen heterocycles with those in analogous carbocycles. Deuteration, easily effected in this series, has proved extraordinarily helpful in signal assignment. A corresponding study of the *N*-methyl homologues has permitted assessment of the effect of conformationally homogeneous equatorial and axial *N*-methyl groups on ring carbon signals; in addition it has corroborated the effect of ring methyl substituents on the shifts of the ring carbon atoms in the parent *N*-methyl-*trans*-decahydroquinoline. A strongly upfield shifting effect of an equatorial *N*-methyl (axial lone pair) on an axial *C*-methyl on the adjacent carbon atom was discovered; this effect is similar to the known[26] effect on an axial proton. Axially and equatorially *N*-ethyl and *N*-isopropyl substituted *trans*-decahydroquinolines were also investigated. Finally, it proved possible to explore the effect of protonation on chemical shifts at α, β, γ, and δ positions in conformationally well-defined amines. While the nature of the acid (HCl, CF_3COOH) has little effect on the shift differences upon protonation, there is a strong effect of solvent, especially on those shifts (α, β) in the vicinity of the nitrogen; it is not permissible to compare shifts in trifluoroacetic acid with those in chloroform.

Experimental Section

Carbon-13 spectra were recorded on a Varian XL-100 pulsed Fourier transform nuclear magnetic resonance spectrometer operating at 25.16 MHz.[27] Samples were observed in 10-mm o.d. tubes, at 20 ± 5% solutions in deuteriochloroform or trifluoroacetic acid with 2–5% Me_4Si added as internal reference substance at 29 ± 1°C. The solvents provided the internal lock signal (deuterium or fluorine). 8-K, 16-K, or 32-K data point spectra were measured depending on the required degree of resolution; digital resolution was 0.6 Hz (0.025 ppm) at 8-K data points and 2500-Hz sweep width. The accuracy of the chemical shifts is estimated to be ± 0.03 to ± 0.05 ppm.[27]

The *trans*-decahydroquinolines and perhydrobenzo[*h*]quinolines were synthesized from 5,6,7,8-tetrahydroquinolines[5] and 5,6,6a,7,8,9,10,10a-octahydrobenzo[*h*]quinolines,[5] or from $\Delta^{1,9}$-octahydroquinolines,[6] through sodium–ethanol reduction.[6] Ring-deuterated analogues were prepared in an analogous way by reduction in ethanol-*O*-*d* with were prepared in an analogous way by reduction in ethanol-*O*-*d* with sodium.[6] *N*-Methyl, *N*-ethyl, and *N*-isopropyl derivatives were synthesized by known methods.[2] Preparative details, melting points of derivatives, and pertinent ^1H NMR data are reported elsewhere.[2,5,6]

The hydrochlorides were precipitated by passing gaseous HCl into the solutions of the amines in anhydrous ether. After evaporation of the solvent the hydrochlorides were dissolved in $CDCl_3$. The trifluoroacetates of the *N*-methyl compounds were prepared by adding the amine slowly into rapidly stirred, chilled excess trifluoroacetic acid.

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Registry No.—1, 767-92-0; 1 Cl^-, 4678-90-4; 1 TFA^-, 57288-91-2; **1m**, 875-63-8; **1m** Cl^-, 875-65-0; **1m** TFA^-, 57288-92-3; 1-Et, 771-30-2; 1-*i*-Pr, 19079-76-6; **2**, 18610-37-2; **2** Cl^-, 18610-38-3; **2m**, 18609-07-9; **2m** Cl^-, 18609-08-0; **3**, 18609-01-3; **3** Cl^-, 18609-02-4; **3m**, 18609-11-5; **3m** Cl^-, 18609-12-6; **3m** TFA^-, 57288-93-4; **4**, 52601-71-5; **4m**, 52008-63-6; 4-Et, 55970-19-9; 4-*i*-Pr, 55970-23-5; **5**, 52679-13-7; **5m**, 55970-11-1; **6**, 45846-79-5; **6** Cl^-, 57288-94-5; **6** TFA^-, 57289-06-2; **6m**, 52008-65-8; **6m** Cl^-, 57288-95-6; **6m** TFA^-, 57288-96-7; 6-Et, 55970-17-7; 6-*i*-Pr, 55970-21-3; **7**, 57288-97-8; **7m**, 55970-13-3; **8**, 52761-68-9; **8** Cl^-, 55905-31-2; **8** TFA^-, 57288-98-9; **8m**, 55970-12-2; **8m** Cl^-, 57288-99-0; **8m** TFA^-, 57289-00-6; 8-Et, 55970-18-8; 8-*i*-Pr, 55970-22-4; **9**, 52730-00-4; **9** Cl^-, 55905-28-7; **9** TFA^-, 57289-01-7; **9m**, 52008-64-7; **9m** Cl^-, 57289-02-8; **9m** TFA^-, 57289-03-9; 9-Et, 55970-16-6; 9-*i*-Pr, 55970-20-2; **10**, 55970-15-5; **10m**, 57289-04-0; **11**, 55925-21-8; **11m**, 57289-05-1; **12**, 55925-23-0; **12m**, 57345-27-4; **13**, 55925-22-9; **13m**, 57345-28-5; **14**, 16726-19-5; **14m**, 16726-26-4.

References and Notes

(1) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972; (c) N. K. Wilson and J. B. Stothers, *Top. Stereochem.*, **8**, 1 (1974).
(2) E. L. Eliel and F. W. Vierhapper, *J. Am. Chem. Soc.*, **96**, 2257 (1974); **97**, 2424 (1975).
(3) The spectral data of a number of *cis*-decahydroquinolines will be reported elsewhere.
(4) F. W. Vierhapper and E. L. Eliel, *J. Am. Chem. Soc.*, **96**, 2256 (1974).
(5) F. W. Vierhapper and E. L. Eliel, *J. Org. Chem.*, **40**, 2729 (1975).
(6) F. W. Vierhapper and E. L. Eliel, *J. Org. Chem.*, **40**, 2734 (1975).
(7) H. Booth and D. V. Griffiths, *J. Chem. Soc., Perkin Trans. 2*, 842 (1973).
(8) A. P. Tulloch and M. Mazurek, *J. Chem. Soc., Chem. Commun.*, 692 (1973).
(9) The configurations of **2** and **3** had been determined previously by ir and ^1H NMR spectroscopy: V. I. Artyukhin, D. V. Sokolov, L. K. Orazbaeva, and G. S. Litvinenko, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, **17**, 57 (1967). The configuration of **6** had been inferred by analogy from its formation by sodium–ethanol reduction of 10-methyl-$\Delta^{1,9}$-octahydroquinoline, without conclusive evidence: T. Henshall and E. W. Parnell, *J. Chem. Soc.*, 661 (1962).
(10) (a) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967); (b) *ibid.*, **94**, 5318 (1972); (c) D. K. Dalling, D. M. Grant, and E. G. Paul, *ibid.*, **95**, 3718 (1973).
(11) Cf. for 1,3-dioxanes: G. M. Kellie and F. G. Riddell, *J. Chem. Soc. B*, 1030 (1971).
(12) Cf. for 1,3-dithianes, Part III: E. L. Eliel, V. S. Rao, and F. G. Riddell, *J. Am. Chem. Soc.*, in press.
(13) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **96**, 1827 (1974).
(14) E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Schell, and D. W. Cochran, *J. Am. Chem. Soc.*, **97**, 322 (1975).
(15) I. D. Blackburne, A. R. Katritzky, and Y. Takeuchi, *Acc. Chem. Res.*, **8**, 300 (1975).

(16) For similar observations see S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973); S. H. Grover and J. B. Stothers, *Can. J. Chem.*, **52**, 870 (1974).
(17) H. N. Colli, V. Gold, and J. E. Pearson, *J. Chem. Soc., Chem. Commun.*, 408 (1973).
(18) W. Kitching, M. Bullpitt, D. Doddrell, and W. Adcock, *Org. Magn. Reson.*, **6**, 289 (1974).
(19) Shifts in ^{13}C resonances in acyclic amines have recently been discussed by J. E. Sarneski, H. L. Suprenant, F. K. Molen, and C. N. Reilley, *Anal. Chem.*, **47**, 2116 (1975).
(20) Comparison with amine data in $CDCl_3$ is appropriate for the hydrochlorides in $CDCl_3$, but may not be so for trifluoroacetates in trifluoroacetic acid, since differential solvent effects on the substance investigated and on the reference compound cannot be excluded. Such effects may be quite sizable.[1b] In view of this difficulty, the significance of results reported[21] for the protonation of neat piperidines with increasing amounts of trifluoroacetic acid is somewhat questionable.
(21) I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **95**, 165 (1973).
(22) M. W. Duch, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1970.
(23) A. J. Jones and M. M. A. Hassan, *J. Org. Chem.*, **37**, 2332 (1972).
(24) It may be noted that, although in compound **8m** the *N*-methyl group is entirely axial and hence the lone pair equatorial, this compound, upon protonation, undergoes a normal upfield shift for C-3, and C-10 is actually shifted downfield (cf. Table IX, entry 19).
(25) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(26) H. P. Hamlow, S. Okuda, and N. Nakagawa, *Tetrahedron Lett.*, 2553 (1964); J. B. Lambert, D. S. Bailey, and B. F. Michel, *J. Am. Chem. Soc.*, **94**, 3812 (1972).
(27) Shift values (parts per million) reported earlier[2-6] were calculated using 25.2 MHz and are corrected in this paper. Standard deviations of the chemical shifts of two samples of **1** prepared and recorded 6 months apart was ± 0.03 ppm; the maximum deviation was 0.05 ppm.

Reaction of Geminal Diesters with the Amine Bases 1,5-Diazabicyclo[4.3.0]non-5-ene, 1,4-Diazabicyclo[2.2.2]octane, and 3-Quinuclidinol

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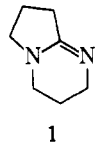
The bicyclic amidine base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 1) transforms relatively hindered geminal diesters to either their corresponding monoesters or monoacids. The composition of the products (monoesters, or monoacids, or a mixture of monoesters and monoacids) can be determined by the reaction time. The bicyclic amine base 1,4-diazabicyclo[2.2.2]octane is useful for the selective decarbalkoxylation of a variety of geminal diesters. The failure to obtain acids as by-products is consistent with previous studies showing that Dabco (2) fails to cleave saturated esters under the same conditions. The bicyclic amine base 3-quinuclidinol (3) is useful for the decarbalkoxylation of a variety of geminal diesters to their corresponding monoesters. Decarbalkoxylation using DBN (1), Dabco (2), and 3-quinuclidinol in *o*-xylene is advantageous in cases where the usual hydrolytic conditions are precluded because of the presence of sensitive moieties, as well as for compounds not soluble in aqueous solvents.

We have reported[1] studies which indicate that the base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 1) is useful for the



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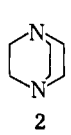

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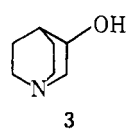

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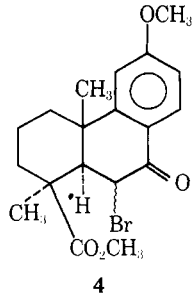
O-alkyl cleavage of hindered methyl esters and for the one-step conversion of bromo ketone **4** to the α,β-unsaturated ketone **5**. Similar results were obtained with 1,5-diazabicyclo[5.4.0]undecene-5.[2] Subsequent studies[3] with the base *N*-phenylbenzamidine indicated that treatment of bromo ketone **4** resulted in only dehydrobromination. Thus *N*-phenylbenzamidine was suggested as a relatively mild and selective dehydrobrominating agent. The base diazabicyclo[2.2.2]octane (Dabco, **2**) has been shown[4,5] to be effective for the decarbalkoxylation of β-keto and vinylogous β-keto esters. Similar results were obtained[6] with 3-quinuclidinol. Although a variety of reagents have been utilized[1,2,4,5,7] for cleaving β-keto and vinylogous β-keto esters, this represented the first report involving the use of a base which contains the bicyclic moiety found in quinine and related Cinchona alkaloids.[8] The suggestion was offered that since the cleavage reactions reported[6] are similar to those found in biological systems,[9] the possibility exists that reactions of this type could be catalyzed by amine bases (alkaloids) in plants.



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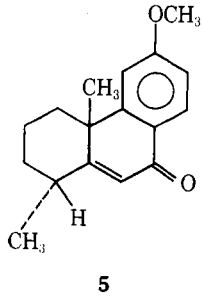

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This paper describes an investigation into the reactivity and the relative selectivity of the amine bases DBN (1), Dabco (2), and 3-quinuclidinol (3) toward geminal diesters.

Results and Discussion

DBN (1). Initial studies with the base DBN involved the investigation of its reactivity with the geminal diester diethyl octadecylmalonate (**6**). Treatment of 1 equiv of **6** with 5 equiv of DBN (1) in 7 equiv of *o*-xylene at reflux for 6 hr gave white, crystalline compound **7** (52% yield) which was identical with an authentic sample of ethyl eicosanoate. The acidified aqueous extract of the reaction mixture yielded crystalline compound **8** (10% yield) which was shown to be eicosanoic acid.[10]

$CH_3(CH_2)_{17}CH(CO_2C_2H_5)_2 \longrightarrow$

6

$CH_3(CH_2)_{18}CO_2C_2H_5 + CH_3(CH_2)_{18}CO_2H$

7 8