Reagent grade KI and $NaNO_3$ were dried at 110 °C and used without further purification. Reagent grade sublimed iodine was resublimed before use. Perchloric acid stock solution prepared from reagent grade $HClO_4$ (70%) was standardized against potassium acid phthalate.

Kinetic Runs.[12] All kinetic runs were carried out in aqueous solution, adjusted to a constant ionic strength of 1.00 M with 2.5 M $NaNO_3$. Since **3** and **4** are weak bases, the substrates were buffers in the kinetic runs; aqueous $HClO_4$ was used to set the buffer ratios ([conjugate acid]/[base]) to preselected values. In all runs, the ratios of substrate concentration to $[I_3^-]$ and of $[I^-]$ to $[I_3^-]$ were greater than 20. Pseudo-first-order rates were followed spectrophotometrically at 400 nm[2] by using a Bausch and Lomb Spectronic 20 fitted with an Arthur H. Thomas rotocell and a Bausch and Lomb Spectronic 600 fitted with water-jacketed cuvettes. In a few instances, rates were determined by titration.[4] A Beckman Zeromatic pH meter was used to determine pH values. Except in runs designed to determine the order in I^-, $[I^-]$ was set at 0.24 M for both substrates. The temperature was held at 30.0 ± 0.2 °C.

Product Analysis. The products of the iodination of **3** were studied by Pauly and Arauner.[14] Both mono- and diiodo products were found. At 30 °C under conditions similar to those of the kinetics runs, the product was found to be 2-iodo-4-methylimidazole by comparing the NMR spectra of the iodination product and **3**; the proton peak corresponding to C2 in **3** was absent in the product.[15] The product was prepared by refluxing a solution containing 0.1 M **3** and 0.5 M I_3^- for 45 min. Excess iodine was removed with sodium bisulfite, and the product was separated from the aqueous solution by extraction with ether.

If I_3^- is in excess, **4** is diiodinated. A solution of **4** together with K_2HPO_4 catalyst was titrated with aqueous I_2 to the starch end point. The indicated stoichiometric equation is given by eq 12.

$$C_4H_6N_2 + 2I_3^- \rightarrow C_4H_4N_2I_2 + 2H^+ + 4I^- \quad (12)$$

The diiodo product was prepared for elemental analysis by refluxing a solution 0.05 M in **4**, 0.01 M in $HClO_4$, 0.10 M in I_2, and 1.0 M in KI for 30 min. The white crystals that separated from the cooled solution were recrystallized from water; mp 204–206 °C uncor (melting attended by loss of I_2). The purified product was analyzed by Bernhardt Microanalytical Laboratory. Anal. Calcd for $C_4H_4N_2I_2$: C, 14.4; H, 8.4; N, 1.2; I, 76.0. Found: C, 14.4; H, 8.4; N, 1.1; I, 76.2. The NMR spectrum of **4** exhibited a singlet at δ 7.1 relative to Me_4Si attributed to protons in the equivalent 4 and 5 positions. The NMR spectrum of the purified diiodo product revealed peaks for the methyl protons but none for the protons at the 4 and 5 positions, indicating the compound to be 4,5-diiodo-2-methylimidazole. In kinetic runs, the ratio of the initial concentrations of **4** and I_3^- was never less than 20. For the investigation of the iodinated product of the kinetic runs, a solution with a ratio of [**4**] to $[I_3^-]$ of 20 was prepared. This solution, essentially the same as those of actual kinetic runs, was allowed 48 h to react, after which all I_3^- had disappeared. The solution was then extracted with ether. The solid extract (mainly **4**) was dissolved in acetone and analyzed by ascending paper chromatography. Whatman No. 1 paper was used together with BuA solvent and iodine vapor location agent.[16] Two spots with R_f values of 61 and 75 were located. In separate chromatographic runs, R_f values for **4** and 4,5-diiodo-2-methylimidazole of 61 and 93 were observed. In view of the absence of a spot for 4,5-diiodo-2-methylimidazole in the chromatogram for the kinetic run, we conclude that the spot with the R_f value of 75 is the monoiodinated product 4(5)-iodo-2-methylimidazole.

Registry No. **3**, 822-36-6; **4**, 693-98-1; 2-iodo-4-methylimidazole, 73746-43-7; 4,5-diiodo-2-methylimidazole, 73746-44-8; 4-iodo-2-methylimidazole, 73746-45-9.

(12) Adapted from the kinetic techniques reported by Berliner.[13]
(13) E. Berliner, *J. Am. Chem. Soc.*, **72**, 4003 (1950).
(14) H. Pauly and E. Arauner, *J. Prakt. Chem.*, 118, 33 (1928).
(15) G. S. Reddy, R. T. Hobgood, and J. H. Goldstein, *J. Am. Chem. Soc.*, **84**, 336 (1962).
(16) I. Smith, Ed., "Chromatographic and Electrophoretic Techniques", Vol. I, Interscience, New York, 1960.

N-Nitrosodecahydroquinolines. Conformational Analysis by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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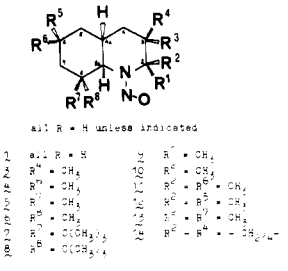
NMR spectra (^{13}C and ^1H) of *N*-nitroso-*trans*-decahydroquinoline (**1**), *N*-nitroso-*cis*-decahydroquinoline (**2**), 17-methyl- or 17-*tert*-butyl-substituted *N*-nitrosodecahydroquinolines, and *N*-nitroso-*trans-syn-trans*-perhydroacridine were recorded, and the conformational properties of the compounds were determined by comparison with the spectra of the parent amines and with the aid of substituent parameters. Molecular strain in 2β- and 8β-substituted trans compounds is minimized by partial escape of the piperidine moiety into nonchair conformations.

N-Nitrosamines have drawn considerable interest as synthetic intermediates since it was found that the α carbanions obtained by lithiation will react in good yields with various electrophiles.[1,2] It was also found that the methyl groups in *N*-nitroso-2,6-*cis*-dimethylpiperidines prefer the sterically constrained syn-axial conformation to relieve the still more severe strain of the alternate form[2-4] and that equilibration between *cis*- and *trans*-2,6-dimethyl compounds could be achieved by catalysis

Chart I



all R = H unless indicated

1 all R = H
2 R4 = CH3
3 R7 = CH3
4 R2 = CH3
5 R5 = CH3
6 R7 = C(CH3)3
R8 = C(CH3)3
7 R7 = CH3
8 R6 = CH3
9 R5 = R8 = CH3
10 R5 = R7 = CH3
11 R6 = R4 = -CH2CH2-

(1) D. Seebach and D. Enders, *Angew. Chem., Int. Ed. Engl.*, **14**, 15 (1975); D. Seebach, D. Enders, and B. Renger, *Chem. Ber.*, **110**, 1852 (1977); B. Renger, H.-O. Kalinowski, and D. Seebach, *ibid.*, **110**, 1866 (1977).
(2) R. R. Fraser and T. B. Grindley, *Can. J. Chem.*, **53**, 2465 (1975); R. R. Fraser, T. B. Grindley, and S. Passannanti, *ibid.*, **53**, 2473 (1975).

0022-3263/80/1945-3111$01.00/0

Chart II

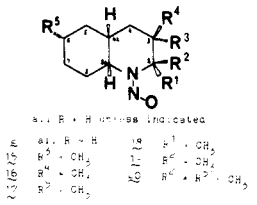


Chart III

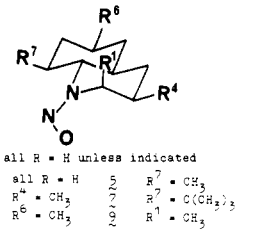
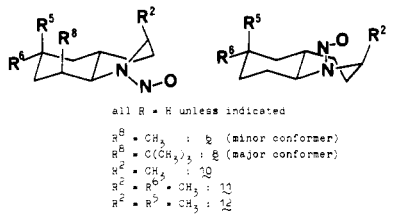


Chart IV



with base.[2] Application of these reactions to *N*-nitroso-*trans*-decahydroquinolines might provide an easy access to 2α-substituted[5] *trans*-decahydroquinolines needed for another investigation,[6] and it seemed useful to establish the conformational situation in the *N*-nitrosodecahydroquinolines prior to synthetic work.

The nitrosamines shown in Charts I and II were prepared from the parent amines,[7] the configuration and preferred conformation of which had been previously investigated by ^{13}C and ^{1}H NMR spectroscopy.[7] The ^{13}C NMR shift data and the 100-MHz ^{1}H NMR data of **1–20** are collected in Tables I and II. Compounds **1** and **2** had been previously synthesized, and their ^{1}H NMR spectra were recorded.[4,8] Part of the results reported in the sequel to this paper have been presented as a short communication.[9]

Results and Discussion

The noise-decoupled ^{13}C spectrum of **1** shows eight well-resolved signals, which can be assigned to the respective carbon atoms by off-resonance decoupling and by comparison with the 3α- and 6α-methyl derivatives **3** and **4**.[5] Compared to the parent amines, C-8a in these compounds is shifted substantially downfield (+4.8 ppm), C-2 is very much upfield (−7 to −8.5 ppm), and C-8 is also upfield shifted (−4 to −5 ppm). A comparison with shift effects established for *N*-nitroso-2-methylpiperidines[2] shows that the N–O bond must be orientated anti to the N(1)–C(8a) bond. This is in agreement with an earlier analysis of the ^{1}H NMR spectrum.[4,8] Carbon atom 3 is shifted upfield by −1.7 to −2.4 ppm; shift effects on the remaining carbon atoms are small (≤0.9 ppm) with the largest for C-6 (−0.8 ± 0.1 ppm), which is orientated "doubly δ" to the ring nitrogen. Carbon atoms 6 and 7, already very close in the parent amine, are not resolved. There is no indication that either the cyclohexane or the piperidine ring is in other than a chair conformation (with N-1 close to being trigonally hybridized to allow maximum electronic overlap in the N–N–O group) because of the ~2.1 kcal/mol additional strain[2] between C-8 and the nitroso nitrogen ($A_{1,3}^{anti}$ strain; cf. Chart III).

Comparison of the spectrum of **4** with that of **1** shows only the well-known shift effects of an equatorial methyl group on a cyclohexane ring.[7,10] In **3**, on the other hand, C-8 is shifted considerably (+0.85 ppm) in addition to C-3 and C-4. This may be caused by some slight deformation of the piperidine ring by the 3-methyl group and a resulting change in strain between C-8 and the nitroso nitrogen.

The equatorial methyl group at C-8 in **5** apparently has no pronounced effect on the geometry of the *N*-nitroso-*trans*-decahydroquinoline system, as indicated by the chemical shifts of the carbon atoms not being directly influenced by the methyl substituent and by the similarity of the downfield region of the proton spectra of **5** and **1**. Surprisingly, the same seems to be true for *N*-nitroso-8α-*tert*-butyl-*trans*-decahydroquinoline (**7**), where the strain between the equatorial *tert*-butyl group and the nitroso substituent must be considerable. Experiments with Dreiding models show that an inversion of the piperidine ring into a boat or twist form produces no palpable relief of strain.

The situation is different in the isomeric, axially 8-substituted compounds **6** and **8**. *N*-Nitroso-8β-methyl-*trans*-decahydroquinoline exists in two conformations (ratio of ~9:1). The major conformer, by comparison of the NMR spectra with that of **1** and with that of the parent amine, seems to be still in the double-chair form. In the minor conformation one of the two rings apparently is no longer a chair. The resulting shift changes are so substantial that it is difficult to determine which ring has assumed that boat or twist shape. Only carbon atoms 8a (probably by a compensation of effects), 5, and 6 and CH_3 are shifted less than 1 ppm compared to the shifts in the amine. This, and the couplings of the proton at C-8a (H-9) which are very similar to those of the major conformer and the parent amine, points to a deformation of the piperidine part of the molecule. In the *tert*-butyl analogue **8**, again two sets of signals are observed; assignment in this case was aided by comparison with the spectrum of the 2,3,3,4,4a,8a-hexadeuterio analogue, where the signals due to the deuterated carbons either disappear or are split into triplets (C-2, C-4). Comparison with **6** and **1** shows that **8** exists predominantly in the conformation corresponding to the minor form of **6**, with only one ring in the chair form. Model considerations show that the strain due to both the C-8/N–O interaction and the interaction between the *tert*-butyl and the nitroso group is relieved if the piperidine ring assumes a twist or boat form with the hydrogens at C-3 and C-4 in the eclipsed position (Chart IV, left conformation).

(3) R. K. Harris and R. A. Spragg, *J. Mol. Spectrosc.*, **23**, 158 (1967).
(4) Y. L. Chow, *Can. J. Chem.*, **45**, 53 (1967); Y. L. Chow, C. J. Colon, and J. N. S. Tam, *ibid.*, **46**, 2821 (1968); Y. L. Chow and C. J. Colon, *ibid.*, **46**, 2827 (1968).
(5) Nomenclature: α means that the substituent is on the opposite side of the ring from the hydrogen at C-4a and β means that it is on the same side of the ring as the hydrogen at C-4a. In the *cis*-decahydroquinoline series, conformation A means C-5 is axial and C-8 is equatorial on the piperidine ring; conformation B means C-5 is equatorial and C-8 is axial.
(6) (a) F. W. Vierhapper, E. L. Eliel, and G. Zuñiga, to be submitted for publication; (b) E. L. Eliel, V. S. Rao, F. W. Vierhapper, and G. Z. Juaristi, *Tetrahedron Lett.*, 4339 (1975).
(7) F. W. Vierhapper and E. L. Eliel, *J. Org. Chem.*, **40**, 2734 (1975); **42**, 51 (1977); **44**, 1081 (1979); E. L. Eliel and F. W. Vierhapper, *ibid.*, **41**, 199 (1976).
(8) H. Booth and A. H. Bostock, *J. Chem. Soc., Perkin Trans. 2*, 615 (1972).
(9) F. W. Vierhapper, *Monatsh. Chem.*, 111, 551 (1980).
(10) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **94**, 5318 (1972).

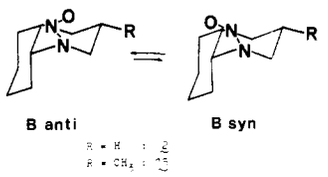
N-Nitroso-2α-methyl-*trans*-decahydroquinoline (**9**), as do **1**, **3**, and **4**, exists in only one conformation. The shift effects compared to the shifts of the parent amine are very similar to those for **1**, except for C-8a and C-2. This points to a relief of the CH_3/C-8a gauche interaction upon nitrosation of the amine due to the flattening of the C-8a/N-1/C-2 region and confirms the results[2] with *N*-nitroso-2-methylpiperidines that the additional strain due to a syn-orientated, axial 2-methyl group is quite small. The 2β-methyl-substituted *N*-nitroso-*trans*-decahydroquinolines, in contrast, are very badly strained. The analogously substituted *N*-nitroso-2,6-dimethylpiperidines exist in the chair form with syn-axial methyl groups.[2,3] Because of the trans fusion of the two rings, the strain in **10** can only be relieved by the N–N–O group being twisted from the planar arrangement with maximum electronic overlap (a process for which $\Delta G^{\ddagger} > 20$ kcal/mol has been determined[2,3]), or the piperidine portion of the molecule must assume a conformation other than the chair conformation. The ^{13}C spectrum shows that **10** at room temperature exists in two conformations in a ratio of ~3:1, with the piperidine ring in a boat or twist shape. Assignment of signals was possible by comparison with those of the deuterated analogue and with the signals for **11** and **12**. Comparison of the latter with the parent amine shows that the carbocyclic portion of the molecule is not palpably distorted even when an additional 1.8 kcal/mol of strain is introduced by the axial methyl group at C-6. The signals of corresponding carbon atoms in the two conformers with very different chemical shifts (e.g., C-2) are already slightly broadened at 60 °C. At 130 °C (in Me_2SO-d_6) conformational inversion is fast enough to show single resonances for all C atoms except C-2 and CH_3. This is in contrast to the situation in **2** (see below) and is best explained by conformations with rather high ground-state energy. The two conformations in Chart IV are suggested. In the left form the hydrogens at C-3 and C-4 are eclipsed (as in 8), with C-4a additionally compressed by the methyl group but with the C-8/NO interaction relieved. The right conformation (with hydrogens at C-4 and 4a eclipsed) avoids the CH_3/C-4a interaction but reintroduces the C-8/NO strain. Both forms, however, allow the nitroso group to retain its partial double bond character.

In contrast to the *N*-nitroso-2β-methyl-*trans*-decahydroquinolines **10**–**12**, *N*-nitroso-*trans-syn-trans*-perhydroacridine (**14**), because of its very rigid structure, exists

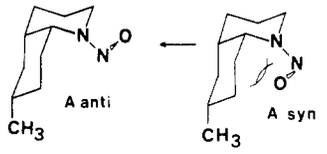
with all three rings in the chair form. In the ^{13}C room-temperature spectrum the signals for C-4a,10a and for C-8a,9a are very broad and are still broad at 60 °C, indicating slow rotation or oscillation around the N–N bond. At −30 °C 13 sharp signals are observed. The $\Delta G^{\ddagger}$ of inversion is thus very much reduced compared to that for the *N*-nitrosopiperidines and *trans*-decahydroquinolines as a result of the strained ground state in **14**. The 13 signals in the frozen spectrum show that the N–N–O plane is not bisecting but is only twisted from the favorable planar arrangement. Comparison of the chemical shifts and shift effects of **14** with those of **10** confirms that the piperidine rings in the two molecules must have different conformations.

N-Nitroso-2β,8α-dimethyl-*trans*-decahydroquinoline (**13**) exists in two conformations at room temperature. The signals of C-8a, C-2, C-8, and 2-CH_3 of the major form are

Scheme I



Scheme II



rather broad. At 100 °C (in Me_2SO-d_6) conformational coalescence has not yet taken place; the signals of the minor conformation are slightly broadened, but the originally broad signals of the major form are sharper. At 130 °C coalescence has been reached, and only single resonances for all carbons (except C-2, which is still too broad to be detected) are observed. It appears that the major of the two conformations present at room temperature corresponds to the perhydroacridine derivative, with both rings in the chair form and the nitroso group forced from the planar arrangement; apparently the deformation of the piperidine ring is insufficient to relieve the additional strain between the 8-methyl and the NO. Raising the temperature slightly accelerates rotation (or oscillation) around the N–N bond in the major form, as for **14**. At 130 °C inversion between this two-chair conformer and the minor form with a deformed piperidine ring is fast enough so that only one average set of signals is visible.

The room-temperature ^{13}C spectrum of *N*-nitroso-*cis*-decahydroquinoline (**2**) shows 18 sharp resonances, corresponding to two conformations in a ratio of 45:55. Comparison with the low-temperature spectrum of the parent amine[7,11] and with the spectrum of **15**, which also shows two conformers in an identical proportion, allows assignment of signals and confirms the results of an earlier 220-MHz ^1H NMR investigation:[8] the two forms are the conformations shown in Scheme I, with the "anti" form slightly preferred. While $\Delta G°$ between the two forms is small (120 cal/mol), $\Delta G^{\ddagger}$ must be very large,[2,3] since raising the probe temperature to 130 °C did not result in any noticeable broadening of the individual signals.

Introduction of an α-methyl group at C-6 in **17** excludes the conformations B (Scheme I), where the methyl substituent would be forced into a position syn-axial to C-4 ($\Delta G° \approx 5.5$ kcal/mol). As a consequence, only 10 resonances corresponding to the conformation A-anti in Scheme II are observed. Since 5% of an additional conformer is easily detected by ^{13}C NMR (corresponding to a difference in free energy of 1.8 kcal/mol), the results for **2** and **17** allow an estimation of $\Delta G°$ for **2** as <3.7 and >1.8 kcal/mol in favor of conformations B.

N-Nitrosamine **16**, derived from 3β-methyl-*cis*-decahydroquinoline, exists in two conformations, in a ratio of ~7:3. Comparison with the spectra of **2**, **15**, and **17**, corrected for the effects of methyl substitution, shows that a double-chair conformation with an equatorial methyl group (A-anti) must be excluded. The shifts of the minor conformer agree well with the B-syn form in Scheme I corrected for a axial 3-methyl. The major conformer,

(11) H. Booth, D. V. Griffiths, and M. L. Jozefowicz, *J. Chem. Soc., Perkin Trans. 2*, 751 (1976).

Table I. ^{13}C NMR Chemical Shifts of *N*-Nitrosodecahydroquinolines[a,b]

compd[c]	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-8a	C-4a	CH_3	C-q
1	40.4_3 (-7.1)	24.8_8 (-2.4)	31.8_4 (-0.6)	32.4_6 (-0.2)	25.4_2 (-0.9)	25.4_2 (-0.2)	28.9_3 (-5.2)	66.8_6 ($+4.8$)	43.9_5 ($+0.6$)		
3	46.6_2 (-8.2)	31.0_7 (-1.7)	40.8_5 (-0.5)	32.3_7 (-0.2)	25.4_1 (-0.8)	25.4_1 (0.0)	29.7_8 (-3.9)	66.3_1 ($+4.8$)	43.5_4 ($+0.3$)	19.0_9 (-0.5)	
4	40.4_9 (-6.9)	24.8_4 (-2.3)	31.8_6 (-0.6)	41.0_9 (-0.3)	31.8_6 (-0.7)	33.9_8 (-0.2)	28.7_3 (-5.1)	66.8_2 ($+4.9$)	43.5_2 ($+0.6$)	22.11 (-0.3)	
5	42.5_3 (-5.0)	25.1_4 (-1.8)	32.4_6 (-0.2)	32.7_5 (-0.3)	25.4_8 (-0.4)	34.9_2 (0.0)	32.4_6 (-5.1)	74.0_3 ($+6.1$)	44.9_2 ($+2.7$)	19.5_8 ($+1.0$)	
6 (89)	40.3_5 (-7.3)	23.3_1 (-4.2)	31.4_5 (-1.6)	33.2_9 (0.0)	19.7_3 (-0.5)	32.5_3 (-0.3)	29.3_2 (-3.8)	69.1_6 ($+4.6$)	34.7_3 (-0.9)	12.9_8 ($+0.4$)	
(11)	45.8_6 (-1.8)	22.6_1 (-4.9)	25.7_3 (-7.3)	33.1_6 (-0.1)	20.2_7 (0.0)	30.3_6 (-2.5)	28.8_2 (-4.3)	64.5_9 (0.0)	30.7_5 (-4.9)	12.2_7 (-0.4)	
7	43.4_8 (-3.8)	24.4_4 (-3.2)	32.6_1 (-0.9)	32.9_4 (-0.7)	25.0_4 (-1.4)	27.4_8 (-0.9)	44.6_7 (-6.3)	70.1_5 ($+4.7$)	46.9_0 ($+3.1$)	29.4_6 (-0.4)	35.9_8 ($+0.9$)
8 (86)	45.8_1 (-2.9)	22.7_1 (-4.6)	27.2_3 (-7.4)	33.7_5 (-0.1)	22.2_6 ($+0.2$)	27.4_3 (-2.5)	42.7_9 (-3.8)	65.5_9 (-2.6)	32.2_4 (-3.9)	31.6_0 (-1.1)	34.98 ($+0.6$)
(14)	38.9_0 (-9.8)	*d*	*d*	*d*	21.4_0 (-0.6)	*d*	46.2_6 (-0.3)	70.2_6 ($+2.0$)	*d*	32.2_4 (-0.5)	*d*
9	42.7_0 (-4.8)	29.3_5 (-2.0)	26.9_3 ($+0.1$)	32.5_2 ($+0.1$)	25.4_7 (-0.8)	25.4_7 (-0.3)	29.2_4 (-5.1)	61.9_8 ($+8.0$)	43.5_8 (-0.3)	15.3_6 (-3.3)	
10 (76)	47.7_0 (-4.7)	25.1_8 (-9.8)	24.1_0 (-8.3)	33.7_0 ($+1.5$)	25.4_6 (-0.8)	24.7_8 (-0.7)	31.7_6 (-2.0)	61.5_2 (-0.3)	37.0_5 (-5.3)	17.8_8 (-5.1)	
(24)	53.3_1 ($+0.4$)	29.4_5 (-5.5)	26.0_8 (-6.3)	33.1_4 ($+0.9$)	26.0_8 (-0.1)	*d*	30.3_3 (-3.5)	61.7_4 (-0.1)	37.6_3 (-4.7)	*d*	
	e	*d*	26.9	25.0	33.2_8	25.5_3	24.8_8	31.7	61.8_9	37.6_0	*d*
11 (73)	47.7_6 (-4.8)	25.2_3 (-9.7)	24.0_5 (-8.4)	42.2_8 ($+1.2$)	31.8_3 (-0.7)	33.3_3 (-0.8)	31.5_5 (-2.1)	61.4_0 (-0.4)	36.8_2 (-5.1)	$17.9_4{}^f$ (-5.0)	$22.0_5{}^g$ (-0.4)
(27)	53.4_2 ($+0.9$)	29.4_5 (-5.5)	26.0_4 (-6.4)	41.6_0 ($+0.5$)	32.7_5 ($+0.2$)	33.8_7 (-0.2)	29.8_6 (-3.8)	61.7_0 (-0.1)	37.1_6 (-4.8)	*d*	$22.0_5{}^g$ (-0.4)
12 (78)	48.1_4 (-4.4)	25.1_0 (-9.9)	24.0_7 (-8.6)	39.2_9 ($+1.3$)	26.8_3 (-0.9)	29.9_4 (-0.9)	25.6_9 (-2.4)	62.2_4 (-0.5)	30.6_6 (-5.4)	$17.6_8{}^f$ (-5.3)	$17.8_0{}^g$ (-0.5)
(22)	53.5_7 ($+1.0$)	29.3_8 (-5.6)	26.1_5 (-6.5)	38.8_7 ($+0.9$)	27.1_8 (-0.5)	*d*	*d*	62.4_4 (-0.3)	*d*	*d*	18.7_2 ($+0.4$)
13 (70)	57.1 ($+4.4$)	29.0_1 (-5.5)	[33.5_0] ($+0.9$)	33.5_0 ($+0.8$)	25.8_3 (0.0)	35.3_6 ($+0.6$)	38.8 ($+1.6$)	69.7 ($+1.8$)	39.1_4 (-2.1)	$22.7_8{}^f$ (-0.3)	$19.5_4{}^h$ ($+1.1$)
(30)	52.6_2 (-0.1)	29.7_3 (-4.8)	*d*	33.3_2 ($+0.6$)	25.6_5 (-0.2)	35.3_6 ($+0.6$)	36.5_0 (-0.7)	73.5_4 ($+5.6$)	42.0_1 ($+0.7$)	$20.3_8{}^f$ (-2.7)	$19.9_0{}^h$ ($+1.4$)
e	*d*	28.7_5	33.2_4	33.2_4	25.5_9	35.3_2	37.7	71.2	40.3	21.3^f	$19.4_5{}^h$
14[i]	26.2_3 (0.0)	25.3_9 (-0.2)	33.3_5 (-0.3)	33.3_5 (-0.3)	25.3_9 (-0.2)	26.2_3 (0.0)	30.1_6 (-2.2)	43.8 ($+0.6$)	70.6 ($+8.5$)		
j	[26.5_3] ($+0.3$)	[25.1_3] (-0.4)	33.5_0 (-0.3)	32.5_0 (-1.1)	[24.9_0] (-0.7)	[25.4_4] (-0.8)	[29.5_7] (-2.8)	44.1_2 ($+0.9$)	[69.4_6] ($+7.4$)		
2 (55)	35.4_9 (-4.3)	24.9_1 (-2.3)	24.3_4 ($+0.4$)	30.4_3 (-1.2)	20.5_9 (-0.1)	25.0_1 (-1.1)	26.2_1 ($+1.0$)	60.9_2 ($+7.1$)	36.3_4 ($+0.7$)		
(45)	46.6_9 ($+6.6$)	26.3_6 (-0.9)	24.6_2 ($+0.7$)	30.8_3 (-0.5)	20.2_5 (-0.4)	25.2_6 (-0.8)	23.0_3 (-2.1)	49.4_1 (-4.5)	34.5_9 (-1.0)		
15 (55)	41.6_0 (-6.2)	31.2_3 (-2.2)	33.5_0 (0.0)	30.6_3 (-1.1)	20.2_0 (-0.5)	25.2_9 (-0.8)	26.0_9 ($+0.2$)	60.4_7 ($+6.9$)	35.9_0 (-0.6)	19.1_8 (-0.6)	
(45)	53.2_8 ($+5.5$)	32.5_4 (-0.8)	33.6_8 ($+0.1$)	30.6_3 (-1.1)	20.0_8 (-0.6)	25.2_9 (-0.8)	23.0_9 (-2.9)	48.8_5 (-5.0)	34.2_2 (-2.2)	18.8_8 (-0.9)	

16 (74)	42.8_5	27.2_1	34.2_2	28.5_9	22.6_0	26.6_7	23.3_7	60.7_1	33.3_2	18.1_0
	(−12.7)[f]	(+0.6)	(−5.9)	(+2.4)	(−4.0)	(+6.0)	(−9.3)	(+6.0)	(−2.7)	(−1.6)
(26)	51.6_6	27.7_5	30.3_3	30.3_3	19.9_6	25.1_1	22.7_8	49.3_3	28.5_9	16.6_6
	(−3.9)[f]	(+1.2)	(−9.7)	(+4.2)	(−6.6)	(+4.5)	(−9.9)	(−5.4)	(−7.5)	(−3.0)
17	40.1_0	19.9_6	[29.7_3]	34.2_5	32.4_8	[29.5_5]	27.8_1	60.0_6	37.4_6	22.4_8
	(−8.0)	(−1.7)	(−1.1)	(+0.2)	(−0.7)	(+0.3)	(−5.4)	(+5.4)	(+1.7)	(−0.3)
18 (91)	53.8_1	35.3_4	[24.2_0]	30.7_0	20.2_4	[25.3_7]	[23.5_0]	50.1_4	34.7_0	19.1_2
	(−5.2)	(−0.2)	(−1.0)	(−1.1)	(−1.3)	(−1.1)	(−4.2)	(−5.2)	(−1.3)	(−4.5)
(9)	43.8_7	[24.5_5]	[24.7_1]	25.8_5	25.8_5	20.8_2	27.8_1	56.0_6	36.9_8	15.6_6
	(−1.4)[f]	(−11.0)	(−0.5)	(−6.0)	(+4.4)	(−5.7)	(+0.1)	(+0.8)	(+1.0)	(−7.9)
19 (57)	43.0_3	[30.3_1]	[20.5_7]	[31.1_4]	[20.4_2]	25.7_9	29.6_7	61.4_1	36.0_3	18.8_8
	(−10.6)[f]	(+0.3)	(−10.8)	(+5.5)	(−7.0)	(+5.0)	(−4.1)	(+5.8)	(+0.3)	(−4.4)
(43)	50.6_7	[30.4_6]	[20.5_7]	[31.0_7]	[20.7_7]	25.5_4	26.2_4	53.9_6	34.9_3	22.4_1
	(−2.9)[f]	(+0.5)	(−10.8)	(+5.5)	(−6.6)	(+4.7)	(−7.6)	(−1.6)	(−0.8)	(−0.9)
20 (65)	45.4_0	[30.2_2]	[23.6_0]	37.6_0	27.6_2	[26.0_2]	[28.7_2]	59.9_6	35.3_7	17.7_3[f]
	(−7.9)[f]	(+0.5)	(−7.3)	(+3.4)	(−5.6)	(−3.3)	(−4.4)	(+5.5)	(+0.3)	(−5.5)
(35)	50.8_6	[30.6_1]	[21.0_7]	36.3_8	30.8_0	[23.8_9]	[25.6_9]	54.2_5	34.4_2	[21.1_9][f]
	(−2.5)[f]	(+0.9)	(−9.8)	(−2.1)	(−2.4)	(−5.5)	(−7.4)	(−0.3)	(−0.6)	(−2.0)	[21.9_6][g] (−0.8)

[a] In parts per million; recorded as 1 M solutions in $CDCl_3$ plus 2–5% Me_4Si at 30 °C unless indicated. Ambiguous assignments are in brackets. Signals broadened due to slow conformational inversion are reported to only one decimal place. [b] The numbers in parentheses are the shift differences relative to the parent amine (see Experimental Section and ref 7, 8, and 11): $\delta_{nitrosamine} - \delta_{amine}$. [c] For formulas and numbering see the structures in the text. Parenthesized values indicate amounts of conformers (percent) if two conformations were observed. [d] Not seen because overlaid by a signal of the major conformation. [e] In Me_2SO-d_6 at 130 °C. [f] 2-CH_3. [g] 6-CH_3. [h] 8-CH_3. [i] C-1, 30.1; ppm (−2.2); C-9, 40.8$_6$ (+1.0); C-9a, 43.8 (+0.6); C-10a, 70.6 (+8.5). [j] At −30 °C: C-1, [29.9$_9$] ppm (−2.4); C-9, 40.6$_5$ (+0.7); C-9a, 39.4$_0$ (−3.9); C-10a, [72.0$_5$] (+10.0). [k] Shift difference to corresponding conformation of parent amine at −80 °C (see ref 7). [l] Parent amine is in ring-inverted conformation.

Scheme III

however, does not fit with either of the double-chair forms; it seems that the strain imposed by the axial methyl group in the anti-B conformation causes the piperidine ring to adopt a form other than the chair form and that such a conformation not only is more stable than the ring-inverted, CH_3-equatorial one but also (by 0.5 kcal/mol) is more stable than the B-syn conformation. This surprising fact can only be explained by a much higher interaction between CH_3 and C-4a, with a much reduced stability of the piperidine chair conformation compared to the parent amine and with a substantial strain between the nitroso oxygen and the axial methyl in the (not observed) β-anti, double-chair form. Elevation of the probe temperature to 130 °C has no effect; as in the case of **2** not even a broadening of individual lines is observed.

In *N*-nitroso-2β-methyl-*cis*-decahydroquinoline (**18**) the B-anti conformation is excluded because of the very severe strain between the nitroso oxygen and CH_3. In the B-syn form, only the 2.1-kcal/mol $\Delta G°$ between CH_3 and the nitroso nitrogen is encountered. A corresponding interaction with C-8, plus the strain due to the axial methyl at C-2, arises in conformation A. In the spectrum of **18**, two

sets of signals in a ratio of 91:9 are observed, corresponding to B-syn and A-anti. In the low-temperature spectrum of the parent amine[11] no trace of conformation A was seen. As in case of **9**, the axial 2-methyl group in the nitroso derivative causes less strain since it bends outward from the ring due to the planar configuration of N-1.

The conformations of *N*-nitroso-2α-methyl-*cis*-decahydroquinoline with an equatorial methyl group are subject to the very severe strain which in the analogous trans compounds **10–12** caused the piperidine ring to adopt nonchair conformations. Similar to the *N*-nitroso-*cis*-2,6-dimethylpiperidine, **19** exists in the conformation with the 2-methyl group syn-axial to C-8 (Scheme III), the "anti" form with the oxygen orientated toward the methyl group predominating slightly (ratio of 57:43). Neither the ^{13}C NMR spectrum (which cannot be compared with the parent amine) nor the 100-MHz ^1H NMR spectrum (in which the protons at C-2 and C-8a are overlaid) allow one to say to which extent the piperidine ring deviates from the chair form.

An attempt to shift the conformational equilibrium of **19** toward the conformation with an equatorial 2-methyl group by the introduction of a 6α-methyl group, which, as in **17**, upon inversion to B would be syn-axial to C-4, was unsuccessful. Comparison of the ^1H and ^{13}C spectra of **19** and **20** shows that **20** still occupies the conformations with 2-CH_3 syn-axial to C-8. The narrow resonance of the proton at C-8a (due to the three small gauche couplings with the neighboring hydrogens) of **17** is not seen, and both the downfield region and the 2-CH_3 methyl shifts in the proton spectra of **19** and **20** are very similar. The complexity of the ^{13}C spectrum, the lack of comparison with

Table II. Melting Points and ^{1}H NMR Data of *N*-Nitrosodecahydroquinolines

compd	mp, °C	^{1}H NMR[a] H-2e	H-9	H-8e	H-2a	CH_3
1	32–33[b]	5.25 (d, 13 of m)	3.37 (m, w = 22)		2.40	
3	55–56	5.23 (d, 12 of dd, 4)	3.28 (dd, 11 of d, 4)	2.52 (d, 13 of m)		0.93 (d, 6)
4	64	5.22 (d, 13 of m)	3.31 (m, w = 26)		2.43	0.94 (d, 6)
5	22–24	5.21 (d, 14 of m)	3.15 (dd, 10)		2.40[c]	1.07 (d, 6)
6	49–50[d]	4.91 (d, 15 of m)	3.44 (d, 10.4 of d, 3)	2.98 (m, w = 16)	2.44 (dd, 12)	1.15 (d, 7)
6	*e*	4.65 (d, 14 of m)	3.86 (d, 14 of d, 4)		~3.8 (overlaid by H_9)	0.86 (d, 7)
7	78–79	4.95 (d, 12 of m)	3.49 (d, 10 of d, 9)		2.65[c]	0.94 (s)
8	30–31[d]	4.76 (d, 14 of m)	4.04 (d, 12 of d, 4)		4.06 (overlaid by H_9)	0.98 (s)
8	*e*	5.03 (d, 14 of m)				1.02 (s)
9	85–86	5.46 (q, 7 of m)	3.48 (m, w = 24)	2.49 (d, 12 of m)		1.10 (d, 7)
10	29–30[d]	4.58[g] (m, w = 18)	3.74 (m, w = 24)	2.84 (m, w = 18)		1.18 (d, 7)
10	*e*	5.03[g] (m, w = 22)	~3.7[m]	2.84[m]		
11	55–56[d]	4.46[g] (m, w = 18)	3.74 (dd, 11 of d, 4)	2.85 (d, 14 of m)		0.95[h] (d, 6), 1.19[i] (d, 7)
11	*e*	5.04[g] (m, w = 20)	~3.7[m]	2.85[m]		0.95[h] (d, 6)
12	25–26[d]	4.63[g] (m, w = 16)	3.72 (m, w = 24)	2.62 (m, w = 16)		1.04[h] (d, 7), 1.22[i] (d, 7)
12	*e*	5.03[g] (m, w = 22)	~3.7[m]	2.62[m]		1.04[h] (d, 7)
13	*f, d*	4.68[g] (q, 7 of m)	3.40 (dd, 10)			0.77[j] (d, 6), 1.59[i] (d, 7)
13	*e*	4.31[g] (d, 14 of q, 7)	3.40 (dd, 10)			1.06[j] (d, 6), 1.42[i] (d, 7)
14	86–87		3.08[k] (m, w = 32)	2.32[l] (m, w = 20)		
2	7–9[d]	~4.6[n]	5.03 (m, w = 18)		2.70 (dd, 12 of d, 4)	
2	*e*	~4.6, overlaid with H-2e of major conformer			3.66 (dd, 13 of d, 4)	
15	41–43[d]	4.91 (d, 14 of d, 4)	4.69 (d, 12 of m)		2.14 (d, 14 of d, 11)	1.00 (d, 6)
15	*e*	4.50 (d, 14 of d, 4)	5.05 (d, 12 of m)		3.28 (d, 14 of d, 11)	1.09 (d, 6)
16	*f, d*		3 protons between 4.5 and 3.4 ppm, not resolved			0.89 (d, 7)
	e	5.12 (m, w = 22)	2 protons between 4.5 and 3.4 ppm, not resolved			1.03 (d, 7)
17	62–64	5.07 (d, 14 of dd, 5 of d, 2)	4.01 (m, w = 8)	2.79 (d, 14 of dd, 7)	2.46 (d, 14 of dd, 7)	0.92 (d, 6)
18	*f, d*		5.22 (m, w = 17)	3.98 (m, w = 22)		1.64 (d, 6)
19	19–20[d]		5.2–4.6, not resolved			1.13 (d, 7)
19	*e*		5.2–4.6, not resolved			1.47 (d, 7)
20	*f, d*		5.15–4.50, not resolved			1.15[i] (d, 7), 1.04[h] (d, 7)
20	*e*		5.15–4.50, not resolved			1.45[i] (d, 7), 1.06[h] (d, 7)

[a] In parts per million; as 1 M solutions in $CDCl_3$ plus 2–5% Me_4Si. Reported values are centers of signals in the spectra. Parenthesized information is as follows: multiplicity, coupling constant (in hertz); w is the width at half-height (in hertz). Only clearly recognizable signals are reported. [b] Lit.[4] mp 32–33 °C. [c] Overlaid with another proton. [d] Major conformer. [e] Minor conformer. [f] Did not crystallize. [g] Piperidine ring not in chair form. [h] 6-CH_3. [i] 2-CH_3. [j] 8-CH_3. [k] Proton at C-4a,10a. [l] Equatorial proton at C-4,5. [m] Overlaid by major conformer. [n] Overlaid by minor conformer.

the parent amine (in which both 2-CH_3 and 6-CH_3 are in equatorial positions), and the lack of shift parameters makes it impossible to decide if the methyl group at C-6 is indeed syn-axial to C-4 on a chair-shaped cyclohexane ring. Both a syn-axial, CH_3/C-4 interaction and a deformation of the cyclohexane chair into a twist or boat form mean an additional ≥5.5 kcal/mol in favor of conformation A in Scheme III. The fact that no conformation A is detected means that the combined $A_{1,3}^{syn}$ and $A_{1,3}^{anti}$ strain of the nitroso group (to 2-CH_3 and C-8 in **19**) must exceed the value reported as a lower limit for the *N*-nitroso-2,6-*cis*-dimethylpiperidine $\Delta G° \geq 6.2$ kcal/mol)[2] by at least another 1 kcal/mol.

In summary, the NMR spectral data of the 20 *N*-nitroso compounds confirm the substantial (~2.1 kcal/mol)[2] interaction between a nitroso and an anti-equatorial substituent on a piperidine ring (seen in the preference of **2** for the conformations in Scheme I) and the very large $A_{1,3}^{syn}$ strain between the nitroso oxygen and a syn-equatorial carbon atom (>7 kcal/mol). In the 2β-methyl trans compounds this strain is reduced by the piperidine portion of the molecule escaping into nonchair forms; in the 2α-methyl cis compounds conformations with syn-axial, CH_3/C-8 interactions are adopted. Only in the rigid perhydroacridine derivative, and possibly in one conformation of **13**, is the N–N–O group twisted from the preferred arrangement with C-2, C-8a, N-1, and N–O in a plane. The steric congestion caused by an equatorial substituent (CH_3 or $(CH_3)_3C$) at C-8 does not cause any pronounced deformations of the *N*-nitroso-*trans*-decahydroquinoline skeleton, whereas the corresponding axial substituents lead to a deformation of the piperidine ring in part of the compounds.

Experimental Section

NMR spectra were recorded on a Varian XL-100-15 pulsed Fourier transform nuclear magnetic resonance spectrometer. ^1H NMR spectra were recorded in the CW mode in 5-mm o.d. tubes. ^{13}C NMR spectra were measured at 25.16 MHz, in the pulsed mode, as 1 M solutions in 12-mm o.d. tubes. The solvent in both cases was $CDCl_3$ with 2–5% Me_4Si admixed as internal reference; the deuterium of the solvent provided the lock signal. High-temperature ^{13}C NMR spectra were recorded in Me_2SO-d_6. Integration of ^{13}C spectra to determine conformational ratios was effected by multiplying signal height with half-width and comparing the areas of matching pairs of signals.

Melting points were determined on a Kofler micro hot stage equipped for low-temperature melting point determination. Microanalysis was performed at the Institute of Physical Chemistry, Universität Wien.

Starting Amines. The parent amines for **1–10** and **14–17** were synthesized as described previously.[7] In addition, an improved yield of 3α-methyl-*cis*-decahydroquinoline could be obtained by the hydrogenation of 3-methyl-$\Delta^{1,8a}$-octahydroquinoline. 2-Methyl-*cis*-decahydroquinolines and 2α-methyl-*trans*-decahydroquinoline were obtained as minor products besides large amounts of 2β-methyl-*trans*-decahydroquinoline upon high-pressure hydrogenation of 2-methylquinoline.[11] 2β,6α-Dimethyl-*trans*-decahydroquinoline, 2β,6β-dimethyl-*trans*-decahydroquinoline, and 2α,6α-dimethyl-*cis*-decahydroquinoline (the parent amines for **11**, **12**, and **20**) were obtained by high-pressure hydrogenation of 2,6-dimethylquinoline. 2β,8α-Dimethyl-*trans*-decahydroquinoline, the parent amine of **13**, previously prepared by a different procedure,[6] was obtained by high-pressure hydrogenation of 2,8-dimethylquinoline.

When the trans-ring-fused decahydroquinolines were crystalline (*trans*-decahydroquinoline and 3α-methyl-, 6α-methyl-, and 2β,6α-dimethyl-*trans*-decahydroquinoline) they were separated from the reaction mixtures by crystallization and recrystallized from petroleum ether. The mother liquors, or the liquid reaction mixtures, were converted into a mixture of benzamides which was heated to reflux with 9 M HCl for 3 h. Amines isolated afterward were found to be very largely trans ring fused, independent of methyl substitution, with only small amounts of cis impurities. The recovered bezamides were heated to reflux with a large excess of 9 M HCl for ~100 h. Isolation of amines after that period gave practically pure cis-fused decahydroquinolines. Experimental details are given below for the 3-methyldecahydroquinolines. The remaining mixtures of isomers were separated by preparative GC on a column packed with 20% Carbowax 20-M plus 10% KOH on Chromosorb W.[7]

3-Methyl-2,3,4,4a,5,6,7,8-octahydroquinoline was prepared in a manner analogous to the synthesis of 2,3,4,4a,5,6,7,8-octahydroquinoline.[7,12]

1-[2-(2-Methyl-2-cyanoethyl)cyclohexen-1-yl]pyrrolidine (21) was prepared from 60 g of cyclohexen-1-ylpyrrolidine and 29 g of methacrylonitrile in anhydrous DMF after heating for 30 h and distillation: bp 102–106 °C (0.5 torr); yield 53%.

1-[2-(2-Methyl-3-aminopropyl)cyclohexen-1-yl]pyrrolidine (22) was prepared from 46 g of **21** with 9 g of $LiAlH_4$ in ether (yield of crude material 95%); the product was used without further purification.

3-Methyl-2,3,4,4a,5,6,7,8-octahydroquinoline (23) was prepared from **22** in 62% yield after distillation: bp 90–92 °C (7 torr); mp (for the picrate) 129 °C. Anal. Calcd for $C_{16}H_{20}N_4O_7$: C, 50.53; H, 5.30. Found C, 50.45; H, 5.50.

3-Methyldecahydroquinolines. A mixture of 9.06 g of **23** in ethanol was hydrogenated at room temperature in a Parr shaker-type apparatus over Raney nickel from 10 g of alloy.[13] When no further uptake was observed, the catalyst was filtered off, and the material after distillation of the solvent was distilled in a Kugelrohr apparatus to give a mixture of 7.5 g of decahydro compounds, which were converted into the benzamides (12 g). These were heated to reflux in 25 mL of 9 M HCl for 3 h. The unhydrolyzed amides (6.1 g) were separated from a mixture of (mainly) 3α-methyl-*trans*-decahydroquinoline (which crystallized; mp 81 °C[7]), 3β-methyl-*trans*-decahydroquinoline, and traces of 3α-methyl-*cis*-decahydroquinoline (3.6 g). The recovered amides were heated to reflux in 125 mL of 9 M HCl for 100 h. The resulting amines (3 g) were 55% 3β-methyl-*cis*-decahydroquinoline and 45% 3α-methyl-*cis*-decahydroquinoline, which were separated by preparative gas chromatography and identified by comparison with authentic materials.[7]

2-Methyldecahydroquinolines. 2-Methylquinoline (40 g) in cyclohexane was hydrogenated over Raney nickel from 30 g of alloy[13] at 165 °C and 260 atm of H_2 for 3 days to give a mixture of 57% 2β-methyl-*trans*-decahydroquinoline, 32% 2α-methyl-*cis*-decahydroquinoline, and 11% of the two other isomers. Reaction of 36 g of this mixture with benzoyl chloride gave the benzamides, which were heated to reflux with 120 mL of 9 M HCl for 2 h. This gave 17.5 g (48%) of 2β-methyl-*trans*-decahydroquinoline, ~90% pure by GC. Repeated hydrolysis of the recovered benzamides for 4 h gave 7.2 g (20%) of a mixture of 65% 2β-methyl-*trans*-, 24% 2α-methyl-*cis*-, and 11% 2β-methyl-*cis*-decahydroquinoline, which was separated by preparative GC;[7] identification of the compounds was made by comparison with authentic materials.[7,11] The recovered benzamide (17.4 g) crystallized (melting point after recrystallization from petroleum ether 84 °C); after 14.6 g of the benzamide in 120 mL of 9 M HCl was heated for 100 h, 6 g of 2α-methyl-*cis*-decahydroquinoline was obtained, >95% pure by GC.

2,6-Dimethyldecahydroquinolines. 2,6-Dimethylquinoline[14] (15.7 g) was hydrogenated in cyclohexane over Raney nickel from 8 g of alloy[13] at 180 °C and 120 atm of H_2 for 3 days. After distillation in a Kugelrohr apparatus the mixture of products crystallized partly. The liquid (3.5 g) was taken off with a Pasteur pipet, and the solid was recrystallized from petroleum ether and was identified as 2β,6α-dimethyl-*trans*-decahydroquinoline. The liquid was found (by GC) to consist of 22% 2α,6α-dimethyl-*cis*-decahydroquinoline, 31% 2β,6α-dimethyl-*trans*-decahydroquinoline, 31% 2β,6β-dimethyl-*trans*-decahydroquinoline, and 16% of other isomers with higher retention times which were not

(12) L. A. Cohen and B. Witkop, *J. Am. Chem. Soc.*, **77**, 6595 (1955).
(13) Prepared according to "Organicum", Addison-Wesley, Reading, MA, 1973, p 686.
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identified. This mixture was separated by preparative GC. Identification of the isomers was unambiguous by comparison of their ^{13}C NMR spectra with the known spectra[7,11] of the C-2 and C-6 monomethylated compounds.

2β,6α-Dimethyl-*trans*-decahydroquinoline: mp 38–39 °C; mp (for the picrate) 151–153 °C; ^{13}C NMR ($CDCl_3$) δ 61.77 (C-8a), 52.54 (C-2), 41.94 (C-4a), 41.06 (C-5), 34.90 (C-3), 34.09 (C-7), 33.66 (C-8), 32.57 (C-6), 32.41 (C-4), 22.97 (2-CH_3), 22.42 (6-CH_3). Anal. Calcd for $C_{11}H_{21}N$: C, 78.97; H, 12.65. Found: C, 79.05; H, 12.57.

2α,6α-Dimethyl-*cis*-decahydroquinoline: mp (for the picrate) 174–175 °C; ^{13}C NMR ($CDCl_3$) δ 54.50 (C-8a), 53.32 (C-2), 35.03 (C-4a), 34.25 (C-5), 33.23 (C-6), 33.07 (C-8), 30.90 (C-4), 29.76 (C-3), 29.36 (C-7), 23.20 (2-CH_3), 22.77 (6-CH_3). Anal. Calcd for $C_{17}H_{24}N_4O_7$: C, 51.51; H, 6.10. Found: C, 51.45; H, 6.23.

2β,6β-Dimethyl-*trans*-decahydroquinoline: mp (for the picrate) 171–173 °C; ^{13}C NMR ($CDCl_3$) δ 62.69 (C-8a), 52.58 (C-2), 38.00 (C-5), 36.05 (C-4a), 35.01 (C-3), 32.63 (C-4), 30.79 (C-7), 28.11 (C-8), 27.72 (C-6), 22.99 (2-CH_3), 18.32 (6-CH_3). Anal. Calcd for $C_{17}H_{24}N_4O_7$: C, 51.51; H, 6.10. Found: C, 51.50; H, 5.93.

2β,8α-Dimethyl-*trans*-decahydroquinoline. 2,8-Dimethylquinoline[14] (15.7 g) was hydrogenated as reported above for 2,6-dimethylquinoline. The mixture of products was found by GC to consist of 50% 2β,8α-dimethyl-*trans*-decahydroquinoline besides five other isomers in smaller amounts. The compound was isolated by preparative GC and identified by comparison with authentic material.[6]

2,3,3,4,4a,8a-Hexadeuteriodecahydroquinolines. The deuterated analogues of 2α- and 2β-methyl-*trans*-decahydroquinoline and 2α-methyl-*cis*-decahydroquinoline (with the methyl protons also largely exchanged against deuterium) were obtained by reduction of 2-methyl-5,6,7,8-tetrahydroquinoline with sodium and ethan-*d*-ol followed by preparative GC as previously described.[7] In an analogous manner 2,3,3,4,4a,8a-hexadeuterio-8β-*tert*-butyl-*trans*-decahydroquinoline was prepared from 8-*tert*-butyl-5,6,7,8-tetrahydroquinoline.[15]

Synthesis of *N*-Nitrosodecahydroquinolines and *N*-Nitrosoperhydroacridine (1–20). In the same manner as in a literature procedure,[1] a solution of the parent amine in anhydrous THF was stirred in a stoppered flask at room temperature with a 5–10 molar excess of ethyl nitrite[16] until the starting amine had disappeared (TLC; Al_2O_3 on $CHCl_3$; detection by treatment with iodine vapor). The necessary reaction times varied, depending on the steric hindrance in the amine, between 1 (e.g., *trans*- or *cis*-decahydroquinoline) and 8 (for 8α-*tert*-butyl-*trans*-decahydroquinoline) days. The recognition of the end of the reaction was facilitated by the disappearence of a precipitate originally formed in the reaction mixture. In the case of sterically less hindered amines the precipitate did not form. When the reaction was complete, solvent and excess ethyl nitrite were distilled off, and the residue was dissolved in petroleum ether and filtered. The petroleum ether was distilled off, and the residue was distilled in a Kugelrohr apparatus (bp 80–110 °C, air-bath temperature, 0.05 torr). If the compounds crystallized they were recrystallized from petroleum ether at low temperature; the melting points are included in Table II. All compounds gave satisfactory elemental (C, H) analysis. Care was taken in all handling of the compounds, bearing in mind their potential carcinogenic character.[1]

Registry No. 1, 15104-09-3; 2, 36041-75-5; 3, 73698-09-6; 4, 73698-10-9; 5, 73698-11-0; 6, 73698-12-1; 7, 73698-13-2; 8, 73698-14-3; 9, 73698-15-4; 10, 73698-16-5; 11, 73698-17-6; 12, 73698-18-7; 13, 7698-19-8; 14, 24506-23-8; 15, 73698-20-1; 16, 73698-21-2; 17, 73698-22-3; 18, 73698-23-4; 19, 73698-24-5; 20, 73698-25-6; 21, 73698-26-7; 22, 73698-27-8; 23, 73698-28-9; 2α,6α-dimethyl-*cis*-decahydroquinoline, 73698-33-6; cyclohexen-1-ylpyrrolidine, 1125-99-1; methacrylonitrile, 126-98-7; 3β-methyl-*trans*-decahydroquinoline, 52679-13-7; 2-methylquinoline, 91-63-4; 2,6-dimethylquinoline, 877-43-0; 2β,6α-dimethyl-*trans*-decahydroquinoline picrate, 73698-34-7; 2α,6α-dimethyl-*cis*-decahydroquinoline picrate, 73698-35-8; 2β,6β-dimethyl-*trans*-decahydroquinoline picrate, 73698-36-9; 2,8-dimethylquinoline, 1463-17-8.

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Notes

New Synthesis of Perfluorocyclooctatetraene

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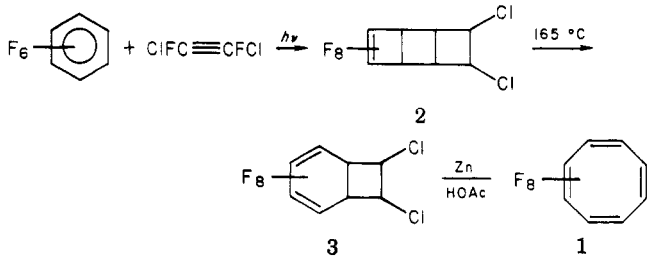
Cyclooctatetraene serves as a precursor for a wide range of organic and organometallic compounds.[3] Eventually its perfluorinated counterpart (1) may assume a parallel role in the field of fluorocarbon chemistry.

Gerace, Lemal, and Ertl have reported a synthesis of this volatile white solid in four steps from perfluorobenzene (overall yield ~20%).[4] Photoisomerization of the benzene to its Dewar isomer[5] followed by ozonolysis yielded perfluorocyclobutene-3,4-dicarboxylic acid, which was converted to its anhydride and irradiated to give 1. Vapor-phase photolyses are not easy to scale up to the tens-of-grams level, and there are two such steps in this synthesis. Hence a new approach is needed if 1 is to become conveniently available in quantity.

Scheme I



We now wish to describe a rather different three-step synthesis of 1 from the same progenitor, perfluorobenzene

(1) Goodyear Fellow, 1976–1977.
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