rification by flash column chromatography (silica, hexane) yielded the adduct as a white crystalline solid (570 mg) >90% erythro (remaining, threo isomer).

Fluorination of Anhydrous Potassium Perfluorooctanoate. Anhydrous potassium perfluorooctanoate (7 g) was suspended in FC-75 (450 mL) and the mixture cooled to −78 °C under N_2. Fluorine (1% in nitrogen, partial pressure, 50 mmol) was passed into the solution through a vibrating mixer shaft over 12 h. The cold reaction mixture was filtered through glass wool into an ice-cold Pyrex erlenmeyer flask, and the solution was stored at −20 °C. Analysis by titration indicated a concentration of 2.95 mmol/L of oxidant after 10 mmol of fluorine have been added, 7.7 mmol/L after 20 mmol, 11.1 after 30, 14.25 after 40, 28.05 after 50, and 25.0 mmol/L after filtration. This represents approximately a 25% utilization of available fluorine and a 81% conversion of the acid salt based on total oxidant produced.

Analysis for perfluorooctanoyl hypofluorite was carried out as described previously on a portion of the solution (150 mL, 3.6 mmol of oxidant) and the percentage of **20** relative to total oxidant determined to be 28.5%.

Fluorination of Enol Acetates. A cold CH_2Cl_2 solution (−20 °C) of the enol acetates **23**–**25** (4.5 mmol) was added in one portion to 5 mmol of oxidizing solution originating either from the anhydrous or the hydrated potassium perfluorooctanoate. The mixture was well stirred for 1 to 2 min with the aid of the vibromixer, poured into thiosulfate solution, and washed with water until neutral. Flash chromatography and crystallization yielded the corresponding fluoro ketones **26**–**28** in 85%, 60%, and 85% yield, respectively, identical in all respects with the same fluoro ketones prepared with CF_3COOF.[10]

Initiation of Tetrafluoroethylene. A 500-mL polymer kettle was loaded with 200 mL of water and 1 g of perfluorooctanoic acid as surfactant. Oxygen was flushed from the system by pressuring to 90 psi with argon and evacuating to 100 mm, 3 times. A 1-L cylinder containing 33 g of tetrafluoroethylene was connected to the kettle and the system pressurized to atmospheric with tetrafluoroethylene. Then 15 mL of the initiator solution (4.5 mequiv/L) composed mainly of a perfluoroacyl hypofluorite as **20** was injected with stirring, and the kettle pressurized to 70 psi with tetrafluoroethylene. Once tetrafluoroethylene absorption ceased, the system was evacuated, and a second cylinder containing 33 g of tetrafluoroethylene was attached. After another 2 tetrafluoroethylene cylinders were emptied, the system was allowed to stand overnight. The following morning, a fifth tetrafluoroethylene cylinder was attached and it too was emptied below atmospheric pressure by the still living radical polymerization. The product was filtered, washed with 1:1 methanol–water, and dried to give 147 g (89%) of white poly(tetrafluoroethylene). The polymer was molded to a white plug at 372 °C. (The polymer, prepared similarly by using standard persulfate initiation, undergoes significant discoloration with gas evolution at this temperature.)

Initiation of Tetrafluoroethylene/Perfluoropropyl Vinyl Ether. A 500-mL polymer kettle was loaded with 200 mL of perfluoro-2-butyltetrahydrofuran and sealed. Three times the kettle was pressurized to 90 psi with argon; the contents of the kettle were stirred for 1 min, and then the pressure in the kettle was reduced to 100 mm, by evacuation to remove traces of oxygen. A 1-L cylinder containing 33 g of tetrafluoroethylene was attached to the kettle so as to permit introduction of tetrafluoroethylene as desired. Pressure in the kettle was brought to 14.7 psi by addition of tetrafluoroethylene from the cylinder. Next, 1 mL of perfluoropropylvinyl ether and then 5 mL of the hypofluorite solution **20** (as initiator) were injected into the kettle. When the tetrafluoroethylene cylinder was fully opened to the kettle, internal pressure was brought to 44 psi. After 92 min, pressure in the system had dropped to 10 psi. The resulting product was filtered, washed with CCl_2FCF_2Cl, and dried to give 31.13 g of solid white polymer. When extruded at 372 °C, the polymer gave a white, translucent product. (Again, copolymer prepared similarly by using standard persulfate initiation undergoes significant discoloration with gas evolution at this temperature.)

Long-Lived Trialkylamine Radical Cations Containing C_α–H Bonds in Acyclic Alkyl Groups

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Chemical reversibility is observed in the cyclic voltammogram of 9-neopentyl-9-azabicyclo[3.3.1]nonane (**3**), allowing measurement of its $E^{\circ\prime}$ value, 0.83 V vs. SCE in acetonitrile. Replacement of the *tert*-butyl group of **3** by isopropyl or phenyl leads to a much shorter radical cation lifetime, and $E^{\circ\prime}$ could not be reliably measured for the 9-isobutyl or 9-benzyl compounds **6** or **7**. The barrier for nitrogen inversion of **3**, which must be accompanied by NCH_2 rotation, is 12.0 kcal/mol at −10 °C, 5 kcal/mol higher than the barrier for its 9-ethyl analogue **9**. The dihedral angle between C_α–H and the nitrogen p orbital axis in the cation radical is argued to be important in determining cation radical lifetime. Observation of chemical reversiblity in the CV of 9-(2-adamantyl)-9-azabicyclo[3.3.1]nonane, **5**, required in situ drying of the solvent with alumina, as well as fast scan rates or low temperatures.

Trialkylamine radical cations are typically long-lived in strong acids but are very rapidly deprotonated at the α-carbon by the neutral amine.[1] This proton transfer is rapid enough that most trialkylamine cation radicals do not survive the milliseconds required to observe any cation reduction wave at 20 V/s scan rate in a cyclic voltammetry (CV) experiment[2] and give totally irreversible CV curves. The weakening of C_α–H bonds of amine cation radicals proves to be strongly dependent on the overlap with the half-filled p orbital at nitrogen, and the 9-azabicyclo-

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(1) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

(2) Kochi and co-workers give a lifetime of 10^{-2}/(scan rate, V/s)s as the lifetime for first seeing a reduction wave in a CV curve (ref 6c, footnote 9), but this assumes perfect electrochemical reversibility and no distortion. It seems to us to be an overly optimistic lower limit in practice.

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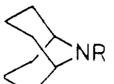
Table I. CV Data for 2 and 3 in Butyronitrile[a]

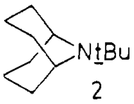
compd	temp, °C	scan rate, V/s	E_p^{ox}, V	$E°'$, V	ΔE_p, V	i^{ox}/i^{red}
3[b]	+20	0.2	0.93_5	0.88_5	0.10_0	3.1
	20	1.0	0.96_3	0.91_3	0.10_0	1.8
	20	1.0[d]	0.92	0.88	0.08	1.6
	20	2.0[d]	0.92	0.89	0.06	1.4
	20	5.0[d]	0.93	0.90	0.07	1.2
	−18	0.2	0.90_5	0.87_0	0.07_0	1.1
	−34	0.2	0.90_0	0.85_8	0.08_5	1.1
	−35	1.0	0.96_7	0.87_0	0.19_5	0.9_5
2[c]	+24	0.2	0.74_5	0.71_2	0.06_5	1.0
	−20	0.2	0.71_5	0.67_5	0.08_0	1.0
	−38	0.2	0.72_0	0.66_5	0.11_0	1.0
	−58	0.2	0.72_0	0.65_0	0.14_0	1.0

[a] Containing 0.15 M TBAP, Pt disk electrode, vs. SCE. [b] Substrate concentration 5.4 mM. [c] Substrate concentration 2.9 mM. [d] Measured off a photograph of an oscilloscope trace.

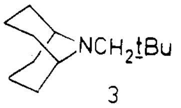
[3.3.1]nonyl R_2N group **1**, which holds its α-hydrogens in the nodal plane of this orbital, leads to far longer cation radical lifetimes. The 9-*tert*-butylamine **2**, which lacks an



1(R)



2



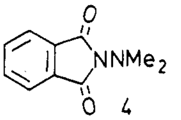
3

"unprotected" α-hydrogen and has a completely chemically reversible CV curve (cation reduction wave as large as neutral oxidation wave) in acetonitrile even at slow scan rate, showing that 2^+ lasts seconds in the presence of neutral **2**,[3] but its ethyl, *n*-propyl, isopropyl, and 2-adamantyl analogues all gave completely irreversible CV curves, even at fast scan rates.[4] Lewis and Ho[5] have reported that photochemically generated singlet *trans*-stilbene is highly selective at removing a methyl hydrogen compared to an isopropyl hydrogen from diisopropylmethylamine, as expected for preferential loss of an α-proton which is lined up with the p orbital of the amine radical cation.

Steric crowding of alkyl groups which have α-hydrogens is known to lead to long lifetimes for polyalkylated hydrocarbon cation radicals. For example, the ESR work of Berndt and Eierdanz has shown that tetraneopentyl ethylene radical cation is far more kinetically stable than is tetramethylethylene cation radical,[6a] and both ESR and CV studies show a much greater kinetic stability for hexaethylbenzene cation radical than for its hexamethyl analogue.[6b–d] In this work we have examined the effect of alkyl group shape in **1(R)** on radical cation lifetime using CV.

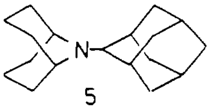
Results: Reversibility CV Curves of 1(R)

Butyronitrile was used in place of the acetonitrile of our earlier work[3,4] so that lower temperatures could be obtained. Table I compares the behavior of the *tert*-butyl compound **2** with the neopentyl compound **3**. At room temperature 3^+ is shortlived, as indicated by the large oxidation to reduction peak current ratio, i_p^a/i_p^c, found at slow scan rates, but at fast scan rates (5 V/s) or lower temperatures (−18 °C) a nearly chemically reversible CV ($i_p^a/i_p^c = 1.0$) is obtained. There is definite evidence that the decomposition of 3^+ is affected by neutral **3** because i_p^a/i_p^c decreases from 3.1 to 1.9 at 0.2 V/s scan rates when the concentration of **3** is reduced from 5.4 to 2.2 mM. We tried adding another base to observe an increase in i_p^a/i_p^c, but not many are available because an acceptable base needs to oxidize at a much higher potential than 0.9 V to avoid obscuring the $2,2^+$ oxidation wave. We used diacyl hydrazide **4**, which has a conveniently high $E°'$ of 1.44 V vs. SCE in acetonitrile.[7] It appears to be not quite basic



enough to show a large effect on the peak–current ratio of **3**, but we did observe a slight increase. At −8 °C, 0.5 V/s scan rate, and 2.2 mM **2**, i_p^a/i_p^c increased from 1.2 without added **4** to 1.7 with 24 mM of **4**. Table I also shows the low-temperature CV of **2**, which was examined to see how the CV of a trialkylamine which does not have the complication of cation radical deprotonation is affected at low temperature. We observed a 0.06_2-V decrease in $(E_p^a + E_p^c)/2$ as the temperature was lowered 82 °C, or a -0.7_6 mV/deg temperature coefficient. Part of the change may well be caused by drift of $(E_p^a + E_p^c)/2$ from $E°'$ as the temperature is lowered, because these quantities are only required to be very close[8] when the wave shape is theoretical, and $\Delta E_p = E_p^a - E_p^c$ is 57([273 + T(°C)]/298) mV. For our −58 °C data, the ΔE_p observed is 0.10 V greater than the 0.04 V theoretical value, presumably indicating rather slow heterogeneous electron-transfer rates at low temperature. Nevertheless, negative temperature coefficients in the range −0.32 to −0.45 mV/deg have been observed for several electrochemically reversible reductions,[9] and the temperature coefficients for nine *o*-phenylenediamines were found to range from −0.35 to −0.80 mV/deg,[10] suggesting that use of the average of the peak potentials as $E°'$ does not lead to huge errors for amines. To allow comparison with earlier work, we also measured $E°'$ for **3** in acetonitrile containing 0.1 M tetrabutylammonium perchlorate to be 0.83 V. It is 0.66 V for **2** under the same conditions,[3,4] so in both solvents it is thermodynamically 4.0 ± 0.2 kcal/mol more difficult to oxidize **3** than **2**. An ill-resolved ESR spectrum of 3^+ was obtained at −95 °C using intra muros electrolysis in butyronitrile, and a g factor of 2.0043 was obtained, to be compared with g = 2.0041 for 2^+.[4] No splittings were determined from this very broad spectrum.

We reported previously[4] that the 2-adamantyl substituted **1(R)** case, **5**, gave only irreversible oxidation by CV,



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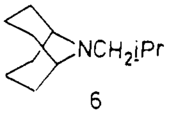

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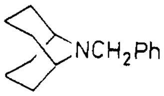

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even at low temperature. Restudy of this system has shown that when the "alumina suspension" technique introduced by Hammerich and Parker[11] for obtaining es-

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(3) Nelsen, S. F.; Kessel, C. R. *J. Chem. Soc., Chem. Commun.* **1977**, 490.

(4) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

(5) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1980**, *102*, 1752.

(6) (a) Berndt, A.; Eierdanz, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 690. (b) Parker, V. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *21*, App 1. (c) Fritz, H. P.; Artes, R. O. *Electrochim. Acta* **1981**, *26*, 417. (d) Howell, J. O.; Covabs, J. M.; Amatore, C.; Klasinc, L.; Wrightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(7) Nelsen, S. F.; Blackstock, S. C.; Rumack, D. T. *J. Am. Chem. Soc.* **1983**, *105*, 3115. In response to a referee's question, in our experience **4** appears to be a more effective kinetic base than pyridine or 2,6-lutidine for alkylamine cation radicals.

(8) For a discussion, see footnote 6 of ref 6d.

(9) Van Duyne, R. P.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 142.

(10) Nelsen, S. F.; Clennan, E. L.; Echegoyan, L.; Grezzo, L. A. *J. Org. Chem.* **1978**, *43*, 2621.

(11) Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537.

Table II. CV Data for 5–7 in Butyronitrile[a]

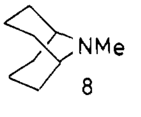
compd	temp, °C	scan rate, V/s	E_p^{ox}, V	$E°'$, V	ΔE_p, V	i^{ox}/i^{red}
5[b]	+23	0.2	0.89_0	irev		
	+23	1.0[c]	0.92	irrev		
	+23	2.0[c]	0.91	irrev		
	+23	20.0[c]	0.98	0.90	0.17	ca. 1
	−43	0.2	0.90	irrev		
	−43	0.5	0.93	irrev		
	−43	2.0[c]	0.99	0.86	0.22	ca. 3
	−43	20.0[c]	1.08	0.88	0.20	ca. 1
	−66	0.2	0.86_5	irrev		
	−66	0.5	0.90_0	0.83	0.14_5	2.3
	−66	2.0[c]	0.95	0.85	0.20	1.4
	−66	20.0[c]	1.08	0.92	0.17	1.0
6[d]	+25	0.2	0.91_5	irrev		
	+25	5.0[c]	1.06	irrev		
	−25[e]	5.0[c]	0.91	0.86	0.10	1.3
	−25[e]	20.0[c]	0.95	0.86	0.17	1.0
7[d]	+25	0.2	0.94	irrev		
	+25	5.0[c]	1.06	irrev		
	−40	0.2	0.98	irrev		
	−40	5.0[c]	1.08	irrev		
	−40	20.0[c]	1.15	irrev		

[a] Containing 0.15 M TBAP, at a platinum disk electrode, reported vs. SCE. All three examples used the "alumina suspension" technique.[8] [b] 1.7 mM substrate concentration. [c] Measured off a photograph of an oscilloscope trace. [d] 1.9 mM substrate concentration. [e] See text for discussion of these results, which were not repeatable.

pecially dry solvent for CV is employed, 5^+ reduction waves can be observed at fast scan rates and/or low temperature. Their "alumina suspension" technique involves adding activated alumina to the CV cell, agitating vigorously to suspend the alumina, and recording the CV scan immediately after the particles of alumina settle. Our data are summarized in Table II. The large ΔE_p values and drift in $(E_p^a + E_p^c)/2$ observed with the scan rate at −66 °C do not instill confidence that $E°'$ has been measured with great accuracy, but **5** appears to have an $E°'$ value quite close to that of **3**. Also included in Table II are measurements on **6** and **7**. Even using the suspended alumina drying technique,[11] 6^+ and 7^+ are clearly far less kinetically stable than 5^+, and in most experiments no chemical reversibility at all was observed. We do quote two −25 °C scans for **6** in which we did observe cation reduction waves but were unable to repeat this result on another day, so these data may well not be significant.

Results: Nitrogen Inversion/Alkyl Group Rotation in 3 and Related Compounds

Understanding why 3^+ is so much longer lived than 5^+–7^+ under CV conditions requires some knowledge of steric effects in these systems, and the ^{13}C NMR of **3** provided an entry to considering the conformation of the neopentyl group in this compound. We were initially surprised to discover that the $C_{2,4,6,8}$ ^{13}C NMR peak of **3** is broad at room temperature, because these signals are averaged rapidly on the NMR time scale at much lower temperatures when smaller alkyl groups are present. The methyl analogue **8** shows a coalescence temperature, T_c, for $C_{2,4,6,8}$ of −90 °C, where $\Delta G^\ddagger = 8.11$ (4) kcal/mol,[12] and the ethyl analogue **9** has a T_c of −118 °C, $\Delta G^\ddagger = 7.13$ (2) kcal/mol.[13] Averaging of $C_{2,4}$ with $C_{6,8}$ for **3** is obviously far slower than when a smaller N_9-alkyl group is present, and quantitative variable-temperature line-shape analysis (see Figure 1) gave T_c of −10 °C, where $\Delta G^\ddagger$ is 12.05 (4) kcal/mol, while an Eyring plot gave activation parameters $\Delta H^\ddagger$ 12.4 (3) kcal/mol, $\Delta S^\ddagger$ 1.3 (11) eu. The large increase in $\Delta G^\ddagger$ to $C_{2,4}$ and $C_{6,8}$ exchange upon replacing the methyl group of **9** by the *tert*-butyl group of **3** is clearly caused by the fact that NCH_2 rotation must accompany nitrogen inversion. The stablest conformation of **3** is expected to resemble **3a**, with a C_1,N_9,C_{10},C_{11} dihedral angle ϕ of about 90°, which keeps the *tert*-butyl group as far as possible from the bicyclic ring. Nitrogen inversion without NCH_2 rotation would give the ridiculously strained conformation **3b**. One expects NCH_2 rotation to become easier as the nitrogen is flattened, and the transition state for $C_{2,4}$,$C_{6,8}$ interconversion ought to have both a flat nitrogen and the *tert*-butyl group being forced past the bulky bicyclononyl group. We considered this question more quantitatively using Allinger MM2[14] force field calculations. The amine force field in MM2 cannot handle nitrogen inversion or compounds with very flat nitrogens properly because the lone pair is treated as a very soft heteroatom with a short bond, so the transition state for nitrogen inversion (planar at nitrogen) cannot be calculated. For **1(R)**, however, we already know that the transition state for nitrogen inversion lies about 7–8 kcal/mol above the ground state



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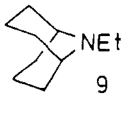

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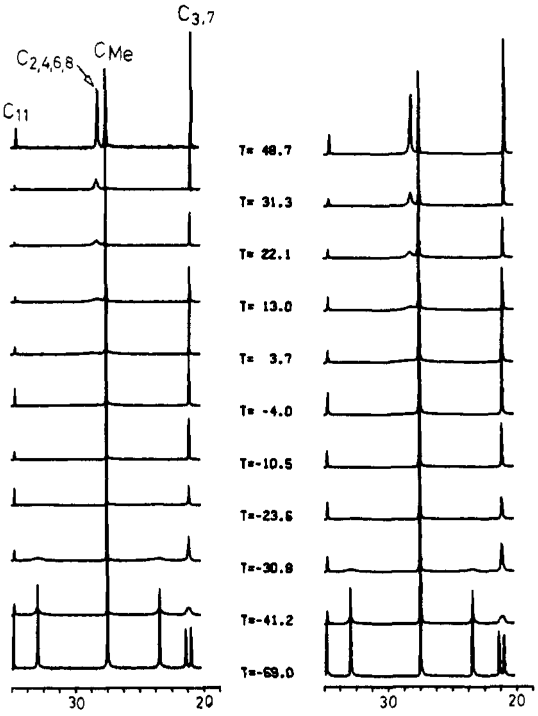
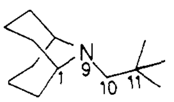
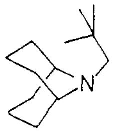


Figure 1. Left column, partial ^{13}C NMR of **3** at temperatures between $+48._7$ and −69 °C; right column, simulations with the rate constants for exchange of pairs of carbons shown (units, s^{-1}).



3a



3b

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[12] Nelsen, S. F.; Weisman, G. R.; Clennan, E. L.; Peacock, V. *J. Am. Chem. Soc.* **1976**, *98*, 6893.

[13] Nelsen, S. F.; Steffek, D. J.; Cunkle, G. T.; Gannett, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 6641.

[14] Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127; Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, Program No. 395.

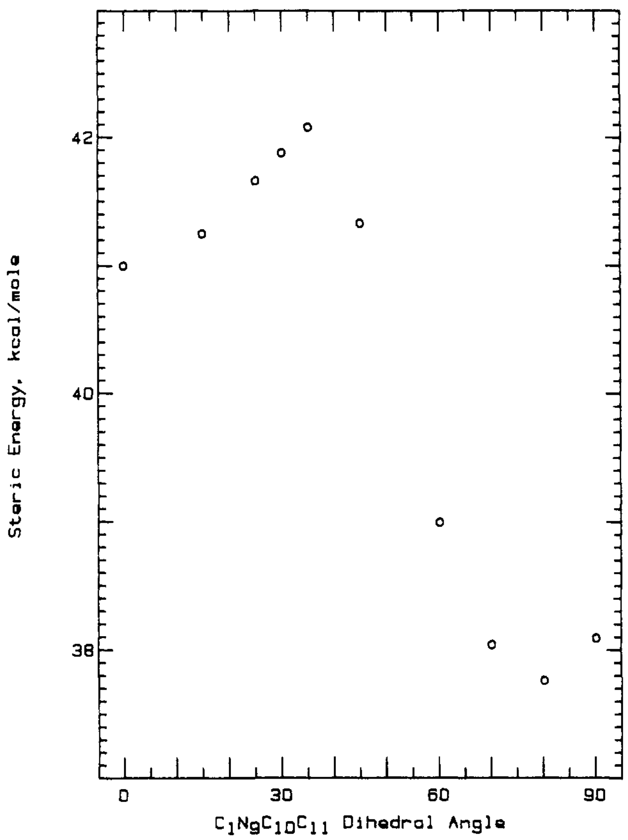

Figure 2. MM2 steric energies for **3** with the nitrogen atom artificially constrained to be flat to simulate the transition state for nitrogen inversion as a function of the $C_1N_9C_{10}C_{11}$ dihedral angle for N-CH_2 twist.

from the measured barriers for **8** and **9**, and the nitrogen flattening energy ought to be very similar for **3a**, since the *tert*-butyl group is tucked out of the way of the bicyclic system. We therefore simply left out the lone pair, restricted the nitrogen to be flat, and calculated the energy of this artificial geometry for **3** as a function of ϕ, the dihedral angle of the $C_{10}H_2$–$C_{11}Me_3$ bond with the $C_1N_9C_5$ plane. The results are shown in Figure 2. According to molecular mechanics, the stablest flat nitrogen form of **3** has $\phi = 80°$, near the 90° we expected on qualitative grounds, and the maximum energy occurs at $\phi = 35°$. The 0° conformation has the *tert*-butyl group rotated to give perfect staggering about the C_{10}–C_{11} bond, but significant eclipsing interaction occurs when ϕ is increased, which causes forced rotation about this bond to decrease the C_1H methyl interaction. The 4.2 kcal/mol energy increase in going from $\phi = 80°$ to the $\phi = 35°$ maximum energy conformation agrees well with the experimentally observed 4–5 kcal/mol increase in $\Delta G^{\ddagger}$ for $C_{2,4}$,$C_{6,8}$ interconversion in **3** compared to **8** or **9**.

Discussion: Thermodynamic and Kinetic Stabilities of 1(R)$^+$

Differences in $E^{\circ\prime}$ values represent differences in the thermodynamic ease of electron removal in solution. Only the vertical ionization potential, vIP, is easily determined for amines in the gas phase by photoelectron spectroscopy, because the lone pair ionization band is nearly Gaussian in shape due to the flattening at N which occurs upon electron loss. Aue, Webb, and Bowers[15] have determined that the adiabatic ionization potential, aIP, which is the exact gas-phase analogue of $E^{\circ\prime}$, is about 0.77 eV less than vIP for unstrained trialkylamines. The large axial *tert*-butyl group of **2** leads to flattening at nitrogen in **2** relative to CH_2R'-substituted **1(R)**, which lowers vIP of **2** relative to **3**. Literature data[4,16] allows estimation of the vIP of **3** to be 0.33 eV higher than that of **2**. Experimentally, $E^{\circ\prime}$ is 0.17–0.18 V (4 kcal/mol) higher for **3** than for **2** in acetonitrile and butyronitrile, significantly less than the vIP difference. Extensive correlations of $E^{\circ\prime}$ and vIP for tetraalkylhydrazines when rehybridization does not accompany alkyl group size enlargement have shown that $E^{\circ\prime}$ changes are significantly smaller than vIP changes,[17] and recent measurements of aIP for a few tetraalkylhydrazines have indicated that a decrease in the energy of solvent stabilization for the cation is important in causing the smaller $E^{\circ\prime}$ than vIP change.[18] The measured 4 kcal/mol increase in $E^{\circ\prime}$ for **3** over **2** is therefore reasonable, although we would not have been able to predict the size of the change accurately. We do not know $E^{\circ\prime}$ for the 2-adamantyl derivative **5** as accurately, but it appears to be close to that for **3**, despite the fact the alkyl group size considerations[16] predict a lower vIP for **5** than for **3** by about 0.15 eV. Decreased radical cation solvent stabilization for **5**$^+$ relative to **3**$^+$ easily rationalizes the similarity in their $E^{\circ\prime}$ values.

The order of cation lifetimes in the presence of neutral observed in the CV studies is **2**$^+$ (no decomposition on the CV time scale) $\gg$ **3**$^+$ $\gg$ **5**$^+$ ("alumina suspension" technique required to observe reduction at fast scan rate) $\gg$ **6**$^+$,**7**$^+$ (irreversible by CV). This lifetime order is rather clearly not that of simple steric hindrance to the approach of base to the α-proton. The most hindered compound for α-deprotonation, **5**$^+$, has an intermediate lifetime, while there is a large lifetime difference for **3**$^+$ and **6**$^+$, although approach of base along the C_α–H axis ought to be similar in steric hindrance. A large kinetic stabilization obviously accompanies holding a C_α–H in the nodal plane of the p orbital at nitrogen in the cation radical, as in the bicyclic portion of the molecule. Kochi and co-workers[6c] have attributed the increase in lifetime for hexaethylbenzene cation over hexamethylene cation principally to forcing the CH_2–CH_3 bond to lie perpendicular to the plane of the benzene ring, making the C_α–H bonds have a unfavorable angle with the spin/charge bearing p orbital axis for weakening the C_α–H bonds. We attribute the obseved stability order for **1(*R*)**$^+$ to similar considerations. If a $\cos^2 \theta$ relationship of C_α–H bond weakening to a lone pair, C_α–H dihedral angle θ, is assumed, the minimum energy of $\phi = 80°$ MM2 structure for **3** with a planar nitrogen (used here as a model for **3**$^+$) has $\theta \sim 50°$ for the smallest θ C_α–H bond, which would lead to only 41% as much bond weakening as for a $\theta = 0°$ conformation. The barrier for twisting **3**$^+$ to $\theta = 0°$ is estimated to be 4.2 kcal/mol by the MM2 calculations, making the population of **3**$^+$ with a greatly weakened C_α–H bond very low. Similar MM2 calculations on the isobutyl compound **6** with a flat nitrogen to mimic **6**$^+$ give a minimum energy θ value of about 30°, predicting 75% as much bond weakening as the maximum amount at $\theta = 0°$ (still assuming, for argument, a $\cos^2 \theta$ relationship) and only a 1.8 kcal/mol barrier for twisting θ to 0°. The MM2 calculation on flat nitrogen models for **3**$^+$ and **6**$^+$ successfully predict, then, far less effective kinetic stabilization for the isobutyl-substituted cation **6**$^+$ than for the neopentyl-substituted cation **3**$^+$, in

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agreement with our hypothesis that bond weakening imposed by θ changes are important in determining the lifetimes of amine cation radicals.

Similar MM2 calculations on **5** with a flat nitrogen to mimic $\mathbf{5}^+$ give a minimum energy of θ of about 30° and a 2.3 kcal/mol barrier for rotating θ to 0°. Steric factors involving the ease of base approach to the C_α–H bond are doubtless also involved in determining the deprotonation rate. We suggest that the reason for the "alumina suspension" technique being effective at increasing the lifetime of $\mathbf{5}^+$ is that **5** is such a hindered base that residual water is the principal base deprotonating $\mathbf{5}^+$, in the absence of alumina to decrease the concentration of residual water.

Experimental Section

Preparations of **6** and **7** were entirely analogous to those of **2**, **3**, and **5**, which have been reported previously.[4]

9-Isobutyl-9-azabicyclo[3.3.1]nonan-3-one was prepared by adding 1.21 g (16.4 mmol) of isobutylamine to 2.00 g (16.4 mmol) of cycloocta-2,6-dienone[9] in 15 mL of methanol. After being stirred at room temperature for 3 days, the solution was concentrated to afford 3.23 g (100%) of the virtually pure ketone as a pale yellow oil: ^{1}H NMR V 3.3 (br s, 2 H), 2.70 (dd, J = 17, 13 Hz, 2 H), 2.43 (d, J = 13 Hz, 2 H), 2.22 (d, J = 17 Hz, 2 H), 2.0–1.4 (m, 7 H), 0.98 (d, J = 12.5 Hz, 6 H); IR 1710, C = 0; ^{13}C NMR δ 211.7 (CO), 61.3 (CH_2), 54.9 (CH), 42.8 (CH_2), 30.0 (CH_2), 27.4 (CH), 20.6 (CH_3), 16.7 (CH_2).

9-Isobutyl-9-azabicyclo[3.3.1]nonane (6) was prepared by the Wolff–Kishner reduction of the keto compound. A mixture of 2.04 g (10.5 mmol) of the keto derivative, 3.8 g of 85% KOH, and 2.5 g of hydrazine hydrate in 30 mL of ethylene glycol was heated to 130–140 °C for 2 h in a 50-mL flask equipped with a 3-in. Vigreaux column and a distillation head. The temperature was raised to 210 °C over 1.5 h during which time some liquid distilled over a 100 °C. The mixture was held at 210 °C for 6 h. After cooling, the combined pot and distillate were poured into 75 mL of H_2O and extracted with 5 × 70 mL of pentane. The combined organic layers were dried ($MgSO_4$) and concentrated to afford 1.61 g (85%) of **6** as a pale yellow oil: ^{1}H NMR δ 2.55 (br s, 2 H), 2.24 (d, J = 11 Hz, 2 H), 2.0–1.2 (m, 13 H), 0.75 (d, J = 10 Hz, 6 H); IR, no NH or CO; ^{13}C NMR δ 61.2 (CH_2), 51.7 (CH), 27.3 (CH_2), 27.3 (CH), 21.2 (CH_2), 20.8 (CH_3); exact mass for $C_{12}H_{23}N$, calcd 181.1825, found 181.1830, error 2.8 ppm.

9-Benzyl-9-azabicyclo[3.3.1]nonan-3-one was prepared by adding 0.59 g (5.5 mmol) of benzylamine to 0.66 g (5.5 mmol) of cycloocta-2,6-dienone[19] in 6 mL of methanol. After being stirred at room temperature for 3 days, the solution was concentrated to give 1.24 g (98%) of the ketone as a white solid, mp 65–68 °C: ^{1}H NMR δ 7.5–7.2 (m, 5 H), 3.90 (s, 2 H), 3.30 (br s, 2 H), 2.75 (dd, J = 16, 7.5 Hz, 2 H), 2.25 (d, J = 16 Hz, 2 H), 2.0–1.8 (m, 2 H), 1.6–1.4 (m, 4 H); IR 1710 (CO).

9-Benzyl-9-azabicyclo[3.3.1]nonane (7) was prepared by the Wolff–Kishner reduction of the corresponding keto compound by using the same procedure as described for **6**. 1.0 g (4.4 mmol) of the ketone afforded 0.45 g (48%) of **6** as a pale yellow oil after column chromatography (alumina, hexane/12% methanol) of the crude reaction product: ^{1}H NMR δ 7.5–7.2 (m, 5 H), 3.92 (s, 2 H), 2.78 (br s, 2 H), 2.2–1.3 (m, 12 H); ^{13}C NMR δ 140.7 (C), 128.3 (CH), 128.0 (CH), 126.5 (CH), 56.7 (CH_2), 50.5 (CH), 27.1 (CH_2), 21.0 (CH_2); IR, no Co; exact mass for $C_{15}H_{21}N$, 215.1669, found 215.1673, error 0.1 ppm.

Dynamic NMR of 9-Neopentyl-9-azabicyclo[3.3.1]nonane (3). Data were taken in a Varian XL-100 spectrometer operating in the FT mode and analyzed on a Harris Slash 7 computer using the software previously described.[20] The sample used was 1.0 M in CD_2Cl_2: at 48.7 °C, the chemical shifts were δ 66.2 (C_{10}), 54.3 ($C_{1,5}$), 34.1 (C_{11}), 28.1 ($C_{2,4,6,8}$), 27.5 (C_{Me}), 21.1 ($C_{3,7}$); at −69.0 °C, 65.3 (C_{10}), 53.6 ($C_{1,5}$), 34.1 (C_{11}), 32.3 ($C_{6,8}$), 27.1 (C_{Me}), 23.2 ($C_{2,4}$), and 21.3, 20.9 (C_3, C_7).

Cyclic Voltammetry Measurements. The apparatus used was a Princeton Applied Research (PAR) 173 Potentiostat, a PAR 179 Digital Coulometer, and a PAR 175 Universal Program. Scans less than 1 V/s were recorded on a Houston Instrument Omnigraphic 2000 X/Y recorder, and those at faster scan rates were photographed from a Tektronix 5000 storage oscilloscope. The low-temperature cell and electrode were that described previously.[21] The butyronitrile (Eastman Reagent Grade) was purified by stirring over 11 g of $KMnO_4$ and 7.7 g of Na_2CO_3 per liter for 16 h, followed by distillation through a 24-in. Vigreaux column at 15 mmHz pressure of nitrogen. This was repeated 3 times. The last time the first and last quarter of the distillate was discarded, and the middle portion was stored in a brown bottle over alumina which had been activated at 350 °C for 24 h. Burdich and Jackson "distilled in glass" acetonitrile was used as received. Eastman tetra-*n*-butylammonium perchlorate was recrystallized from 1:1 H_2O/EtOH and dried in vacuo prior to use as supporting electrolyte. The "alumina suspension" employed 1–2 g of activated alumina (Woehlm activity grade 1) added to the CV cell and vigorously stirred with a nitrogen stream for at least 5 min prior to allowing it to settle and acquiring data. IR compensation was employed for all CV experiments.

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Registry No. **2**, 64776-36-9; **3**, 73321-19-4; **5**, 73321-02-5; **6**, 97877-71-9; **6** 3-oxo derivative, 97877-72-0; **7**, 57659-50-4; **7** 3-oxo derivative, 2291-58-9; cycloocta-2,6-dienone, 1460-21-5.

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