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Extremely Congested Hydrazine Radical Cations

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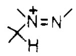
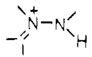
Addition of *tert*-butyllithium to the N_2 *tert*-butylated diazenium cations derived from bicyclic azo compounds gave 2,3-di-*tert*-butyl-2,3-diazabicyclo[2.2.1]heptane (**6**), its 7,7-spirocyclopropyl analogue (**9**), and its bicyclo-[2.2.2]octane analogue (**10**). These very hindered tetraalkylhydrazines are unusually sensitive to both air and heat, and their radical cations decompose thermally at 25 °C with rate constants of approximately 1, 0.1, and 10 s^{-1}, respectively, undergoing de-*tert*-butylation. Despite their kinetic instability, these radical cations are thermodynamically slightly easier to form by one-electron removal from the neutral hydrazine than are analogues with the *tert*-butyl groups replaced by methyl groups. Destabilization of the neutral form by the bulky *tert*-butyl substituents almost exactly balances destabilization of the radical cationic form, leading to very small charges in $E^{\circ\prime}$ as the size of the alkyl groups is increased.

Trialkyldiazenium cations I may be prepared by oxidation of hydrazines and alkylation of azo compounds,[1,2] but they rearrange to the more stable aminoimmonium tautomer II easily. *tert*-Butylation of bicyclic azo compounds gives diazenium salts which have no easily lost α-hydrogens, and 1^+–3^+ are examples of I which are stable to aqueous acid and many bases. Their hydroxides appear to be completely ionic, for no NMR evidence is observed for a hydroxyhydrazine form, even at pH 13.[1] Nucleophiles which are poorer leaving groups do give covalent adduct formation, and Snyder's group has studied the cyanide adduct of 3^+.[2b]


I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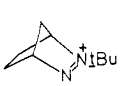
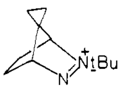

1^+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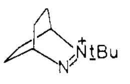
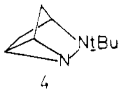

3^+

Results

Hindered Tetraalkylhydrazine Preparation. We first treated 1^+ with *tert*-butyllithium in hopes of generating **4**, the major autoxidation product of trialkylhydrazine **5**.[3] We thought that deprotonation of 1^+ was a possible way of forming **4**, by analogy with homoenolization of 2-norbornanone derivatives,[4] but had failed to see reaction of 1^+ with several weaker bases. Instead of deprotonation, however, a good yield of the *tert*-butyl adduct **6** was obtained.[3] We still find this reaction surprising. 1^+ is easily reduced ($E^{\circ\prime}$ (1^+,1·) is −0.72 V vs. SCE in acetonitrile[1c]), and *tert*-butyllithium is a good reductant, so we would have expected electron transfer to occur. For example, reaction with alkyl iodides, which are harder to reduce than 1^+, results in reactions initiated by electron transfer.[5] Electron transfer should generate a **1·**,*t*-**Bu·** radical pair, and if this occurred, it seems surprising to us that hydrogen atom transfer disproportionation of these radicals to give isobutane and **4** and/or isobutylene and **5** does not predominate. The combination product **6** is quite hindered, and *tert*-butyl radicals do not even combine efficiently with each other—they give about 80% disproportionation.[6] Our interpretation[3] of the autoxidation of **5**, which gives **4** in up to 88% yield, is that oxygen-centered radicals give efficient abstraction of the exo hydrogen at C_5 at **1·**, and even **1·** reacts slowly with **1·** to give mainly **4** and **5**.[3] Easily oxidized bases including aryloxide, alkylthiolate, and methoxide react with $1^+BF_4^-$ solutions to give varying yields of **4** and **5**, presumably because electron-transfer reactons generate **1·**–base-derived radical pairs.[7] The reaction of $1^+BF_4^-$ with *tert*-butyllithium to give **6** is, however, conducted at −78 °C in tetrahydrofuran, where the salt appears completely insoluble, and electron transfer may somehow be inhibited. We have found that **4** is inert to *tert*-butyllithium in THF even at room temperature, so it cannot be an intermediate in the formation of **6**. Whatever the reason for its success, the reaction generating **6** is convenient to run and useful, since it is difficult to think of other viable routes to this interesting hindered hydrazine.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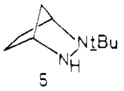
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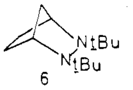
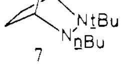

6

Other alkyllithiums add to 1^+, for *n*-butyllithium and methyllithium–tetramethylethylenediamine (TMEDA) give the analogous alkyl adducts **7** and **8**. Oddly, commercial methyllithium did not appear to react with $1^+BF_4^-$ suspended in THF, even at room temperature, but addition of TMEDA to the mixture resulted in formation of **8**. Because it is easier to make **7** and **8** by quenching the *tert*-butyllithium–azo compound adduct with the alkyl iodide, we did not further investigate the above reactions.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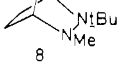
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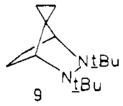
As expected, *tert*-butyllithium reacts with 2^+ and 3^+ to generate **9** and **10**, respectively. These compounds are among the most sterically congested known hydrazines and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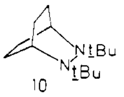
10

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[1] (a) Nelsen, S. F.; Landis, R. T., II *J. Am. Chem. Soc.* **1973**, *95*, 5422. (b) Nelsen, S. F.; Landis, R. T., II *Ibid.* **1973**, *95*, 6454. (c) Nelsen, S. F.; Landis, R. T., II *Ibid.* **1974**, *96*, 1788.

[2] (a) Heyman, M. L.; Snyder, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 4416. (b) Snyder, J. P.; Heyman, A. R.; Gundestrop, M. *J. Org. Chem.* **1978**, *43*, 2224.

[3] Nelsen, S. F.; Parmelee, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 2832.

[4] Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; p 114.

[5] Garst, J. R. *Free Radicals* **1973**, *1*, 539.

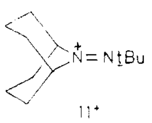
[6] (a) Kraus, J.; Calvert, J. *J. Am. Chem. Soc.* **1957**, *79*, 5921. (b) Nelsen, S. F.; Bartlett, P. D. *Ibid.* **1966**, *88*, 137.

[7] See ref 4 and the Ph.D. Thesis of W. P. Parmelee, University of Wisconsin—Madison, 1980.

0022-3263/81/1946-3453$01.25/0

are unusually reactive. They decompose slowly in solution at room temperature, regenerating the diazenium salts 1^+–3^+, apparently because of air oxidation. About half of a sealed sample of **6** in Me_2SO decomposed, presumably thermally, to **5** as the major product, upon heating at 150 °C for 2 h. The order of increasing ease of thermal decomposition is **6** < **9** < **10**, which is also the order of increasing steric congestion. The thermal lability of **10** precluded its purification by VPC, and we were forced to use the crude material from the *tert*-butyllithium addition, which appeared to be at least 90% **10** by NMR, in the work discussed below.

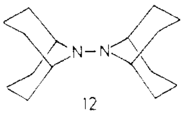
We failed to observe the desired *N*,*N*-di-*tert*-butylhydrazine when *tert*-butyllithium was reacted with $11^+BF_4^-$;[8] the product mixture was complex and not investigated.



11^+

One- and Two-Electron Oxidation of 6, 9, and 10.

In addition to being highly sterically congested, these hydrazines lack easily lost α-hydrogens; they are Bredt's rule protected.[8] Because **12** and related Bredt's rule protected hydrazines are the only ones known to have reversible second oxidation waves (their dications have lifetimes of seconds in acetonitrile, while all hydrazines with removable α-hydrogens show extremely rapid decomposition of their dications) and isolable radical cations, we studied the cyclic voltammetry (CV) of these compounds to see if their oxidized forms would exhibit similar persistence. Not only are the second oxidation waves for **6**, **9**, and **10** completely irreversible, even at fast scan rates (dication lifetimes under about 10 ms) but also the first oxidation waves prove to be irreversible at low scan rates. The lack of reversibility is caused by short radical cation lifetime, because the first oxidation wave becomes more reversible at faster scan rates and lower temperatures. Approximate rate constants for thermal decomposition of these cations were determined by comparing the heights of the oxidation and reduction waves at various scan rates,[9] yielding rate constants for radical cation decomposition at 25 °C of approximately 1 s^{-1} for $6^{+\cdot}$, 0.1 s^{-1} for $9^{+\cdot}$, and 10 s^{-1} for $10^{+\cdot}$. The order of reactivity is certain, although the latter number is less accurate than the former two because of extra current in the CV of the impure sample of **10** we were forced to use because of the thermal instability of this material.



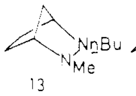
12

In temperature, scan rate combinations where the $6^{+\cdot}$ reduction wave is smaller than the **6** oxidation wave, a new totally irreversible reduction wave appears at −0.7 V vs. SCE when the reduction scan is extended to the negative region. This reduction wave becomes smaller as the scan rate is increased or temperature is lowered, and less $6^{+\cdot}$ decomposes during the scan, so it is clearly caused by a $6^{+\cdot}$ decomposition product. Addition of $1^+BF_4^-$ to the solution causes the reduction wave to grow, and the oxidation wave for $1\cdot$,1^+ oxidation appears, for the 1^+ reduction is completely reversible.[1] We attribute the totally irreversible wave to the 1^+,$1\cdot$ reduction as well, although we initially found its irreversibility to be confusing. We believe that acid is produced when $6^{+\cdot}$ decomposes (presumably from deprotonation of *tert*-butyl cation), so that the $1\cdot$ produced upon reduction of 1^+ is immediately protonated as it is formed and reduced immediately to **5**, resulting in an irreversible reduction wave being observed. Protonated $1\cdot$ is $5^{+\cdot}$, and it is formed at an electrode which is about 0.8 V negative of the potential where **5** is oxidized to $5^{+\cdot}$,[1] so its reduction must be rapid. Since the only proton source in our solution is the *tert*-butyl cation from $6^{+\cdot}$ decomposition, only enough acid is present to protonate the $1\cdot$ formed from the 1^+ arising from $6^{+\cdot}$ decomposition, and added $1^+BF_4^-$ exhibits the expected reversibility of the 1^+,$1\cdot$ couple in the absence of acid. This explanation of the lack of reversibility for the $1\cdot$ produced upon reduction of the 1^+ formed when $6^{+\cdot}$ decomposes was placed on firmer ground by adding $Me_4N^+OH^-$ to the CV solution, which caused the reduction wave at 0.7 V to become reversible, presumably by scavenging protons from *tert*-butyl cation.

The first oxidation wave for **6** is totally reversible at −25 °C, because $6^{+\cdot}$ does not decompose on the CV time scale (several seconds) at this temperature, and no reduction wave is observed for 1^+ near −0.7 V. When the oxidation scan is extended to the second wave for **6**, this wave is totally irreversible, showing that 6^{2+} is very short-lived, and the irreversible 1^+ reduction wave appears as expected if 6^{2+} cleaves to 1^+ and t-Bu^+.

Chemical oxidation of **6** with $NO^+BF_4^-$ gives 1^+, as identified by its NMR spectrum. Coulommetric oxidation at the first wave gave $n = 1.1$, and concentration followed by extraction with D_2O showed only 1^+ as the only observed product by NMR. An n value of 1 would only be expected if **6** protonated and was electro inactive, but we neither observed $6H^+$ nor showed that it would be stable under our reaction conditions.

9 and **10** show completely analogous electrochemistry to **6**, except for their slower and faster radical cation decomposition, respectively. Compounds lacking adjacent *tert*-butyl groups, including **7**, and **8**, and **13**–**16** give long-lived radical cations on the CV time scale and hence reversible first oxidation CV waves, but irreversible second oxidation waves, accompanied by the appearance of irreversible reduction waves in the negative region. More than one reduction wave is sometimes observed (**8**, **13**), and α-deprotonation products are probably formed. The potentials measured in this work are summarized in Table I. The peak potentials for the irreversible waves (second oxidation wave of all compounds, and the reduction waves) are of course influenced by kinetics and not thermodynamically significant. The ESR spectra of $6^{+\cdot}$, $9^{+\cdot}$, and $10^{+\cdot}$ are all very complex because of the many long-range splittings present; even their nitrogen splittings could not be extracted. The spectrum of 5,6-*exo*,*exo*-6-$d_2^{+\cdot}$ (prepared from the dideuterio azo compound employed previously[3]) was narrowed sufficiently to allow determination of a (2N) as 13.5 gauss.



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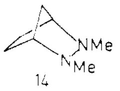

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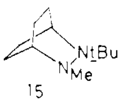

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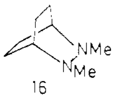

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Discussion

Decomposition of $6^{+\cdot}$ and Its Analogues. A conceivable pathway for $6^{+\cdot}$ decomposition is through the electron-transfer disproportionation shown in eq 1, because the dication is very unstable, as demonstrated by its totally

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[8] Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

[9] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

Table I. CV Results for Bicyclic Tetraalkylhydrazines[a]

compd	first oxidn $E°'$, V	second oxidn E^{ox}_p, V[b]	redn[c] E^{red}_p, V[b]
6	0.16	0.91	−0.70
7	0.19	1.24	−0.66
8	0.21	1.22	−0.54, −1.08
13	0.18	0.97	−0.76, −1.17, −1.35
14	0.20	1.02	−1.20
9	0.12	1.10	−0.70
10	0.03	0.95	−0.82
15	0.11	1.18	−0.64
16	0.07		

[a] Solvent, acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate; reference electrode, SCE; working electrode, gold; temperature, 23 ± 1 °C. [b] Scan rate 200 mV/s unless otherwise noted. [c] These appear when the CV scan includes the second oxidation wave for compounds lacking adjacent *tert*-butyl groups and also upon decomposition of the radical cations of **6**, **9**, and **10**.

irreversible CV, and the product is the same, de-*tert*-butylation to $\mathbf{1}^+$ (eq 2). We argue, however, that electron-transfer disproportionation cannot explain the short lifetime of $\mathbf{6}^+$. All non-Bredt's rule protected hydrazine dications have very short lifetimes (totally irreversible second oxidation waves), and so a rapid decomposition of the dication is always available, although even the benzylated compounds have been shown to decompose by α-hydrogen loss,[10] not alkyl group cleavage. The disproportionation equilibrium (eq 1) is controlled by the energy separation of the first and second electron-transfer equilibria. $\Delta G°$ for eq 1 is 23.06 kcal/mol $(E°'_2 - E°'_1)$ at room temperature. For **12**, which has a long-lived dication so that $E°'_2$ may be measured, $\Delta G°$ is 27.4 kcal/mol endothermic, which is far higher than the observed $\Delta G^{\ddagger}$ for $\mathbf{6}^{+}\cdot$ decomposition; its observed rate of decomposition, 1 s^{-1}, corresponds to $\Delta G^{\ddagger}$ (25 °C) of 17 kcal/mol. A rapid following reaction causes the peak potential to appear less positive than $E°'$, so $E°'_2$ is not directly measurable for non-Bredt's rule protected hydrazines, which show irreversible second oxidation waves. Nevertheless, if the following reactions are all very fast, the peaks will be shifted a comparable amount from $E°'$ for all hydrazines, and in fact the second oxidation waves for all hydrazines studied peak in the range 0.9 to 1.25 V vs. SCE, indicating comparable destabilizations for the dications. Furthermore, over 100 examples of tetraalkylhydrazine radical cations are known which are long-lived on the CV time scale (no decomposition in tens of seconds), and many of these have been shown to last for hours at millimolar concentration.[11] The similarity of their second oxidation peak potentials with those for **6**, **9**, and **10** makes it impossible for us to believe that the latter compounds can be decomposing through eq 1 and 2. Instead, these radical cations decompose by N–*t*-Bu CN bond cleavage because of their great steric destabilization.

$$2\,\mathbf{6}^{+}\cdot \rightleftarrows \mathbf{6}^{2+} + \mathbf{6} \qquad (1)$$

$$\mathbf{6}^{2+} \rightarrow \mathbf{1}^{+} + t\text{-Bu}^{+} \qquad (2)$$

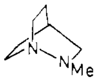
We are unable, however, to distinguish the two modes of bond cleavage illustrated for $\mathbf{6}^{+}\cdot$ in eq 3 and 4. Each would probably be followed by a rapid electron transfer. We unquestionably see $\mathbf{1}^+$ at the electrode after $\mathbf{6}^{+}\cdot$ decomposition, but since $\mathbf{1}\cdot$ oxidizes 0.9 V negative of **6**, it will react faster with any reagent capable of oxidizing **6**, and that does not show the cleavage go through eq 3. We also definitely have an acid at the electrode, or the $\mathbf{1}^+$ reduction wave would be reversible, but *t*-Bu· could well be oxidized to *t*-Bu$^+$ after the cleavage. Unfortunately, $E°'$ (*t*-Bu·, *t*-Bu$^+$) remains unknown, so the relative exothermicities of eq 3 and 4 cannot yet be reasonably estimated.

$$\mathbf{6}^{+}\cdot \rightarrow \mathbf{1}^{+} + t\text{-Bu}\cdot \qquad (3)$$

$$\mathbf{6}^{+}\cdot \rightarrow \mathbf{1}\cdot + t\text{-Bu}^{+} \qquad (4)$$

Electron-Transfer Equilibria. The values of $E°'_1$ for the first electron transfer of tetraalkylhydrazines have received considerable study.[12] Because of the large geometry change when an electron is removed from a hydrazine, the thermodynamics of hydrazine oxidation is principally controlled not by the highest occupied molecular orbital energy effect which dominates most other electron transfers which have been studied,[13] although these are clearly present,[12] but by strain-energy differences between the neutral and cation radical forms.

The most unusual feature of the electrochemistry of **6**, and **9**, and **10** is that their radical cations decompose rather rapidly, in contrast to other tetraalkylhydrazine radical cations. A few unstable tetraalkylhydrazine radical cations have been previously described, but the cause of their kinetic instability is rather different. For example, $\mathbf{17}^{+}\cdot$ is even less persistant than $\mathbf{10}^{+}\cdot$, since the former shows only irreversible oxidation, even at fast scan rates,[14] but it is clearly destabilized thermodynamically by the great twist about the NN bond imposed by its structure, and $E°'$ for **17** is estimated to be >15 kcal/mol higher than that for an untwisted model.[14] Another unstable hydrazine radical cation is that from **18**. Here the radical cation cannot relax toward its olefin-like preferred geometry because of its caged structure, and the nitrogens from strongly bent, as shown by its high a(N) value of 26.8 gauss, and here $E°'$ is 13.8 kcal/mol higher than expected from an unconstrained model.[14]



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18

Substitution of *tert*-butyl for methyl substituents in acyclic hydrazines makes it thermodynamically more difficult to remove an electron: *tert*-butyltrimethylhydrazine has a 0.16 V (3.7 kcal/mol) higher $E°'$ than tetramethylhydrazine, and *N,N'*-di-*tert*-butyldimethylhydrazine has $E°'$ raised by an additional 0.08 V (1.8 kcal/mol). Increased steric interaction between *tert*-butyl and methyl on adjacent nitrogens when the structure charges from that of the neutral hydrazine (preferably almost tetrahedral nitrogens, with a lone pair–lone pair dihedral angle near 90°) to that of the radical cation (preferably planar at nitrogen, with parallel p orbitals), tending to increase $E°'$, dominates over factors tending to lower $E°'$ for the *tert*-butyl substitued compounds (lower ionization potentials and reduced interaction between alkyl substituents on the same nitrogen when the nitrogens flatten). In the bicyclic systems discussed here, substitu-

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[10] Kinlen, P. J.; Evans, D. A.; Nelsen, S. F. *J. Electroanal. Chem.* **1979**, *97*, 265.

[11] Nelsen, S. F.; Weisman, G. R.; Hintz, P. J.; Olp, D.; Fahey, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 2916.

[12] (a) Nelsen, S. F.; Hintz, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 7108. (b) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *Ibid.* **1976**, *98*, 3281. (c) Nelsen, S. F.; Peacock, V. E.; Kessel, C. R. *Ibid.* **1978**, *100*, 7017.

[13] Nelsen, S. F. *Isr. J. Chem.* **1979**, *18*, 45.

[14] Nelsen, S. F.; Kessel, C. R.; Brace, H. N. *J. Am. Chem. Soc.* **1979**, *101*, 1874.

tion of two methyls by *tert*-butyl groups actually slightly lowers $E^{\circ\prime}$ (by 0.04 V, 0.9 kcal/mol, for both **6** vs. **14** and **10** vs. **16**), despite the fact that *syn-tert*-butyl groups are present in the radical cations, so steric destabilization of the radical cation must be considerably increased compared to that of the acyclic compounds. This great steric destabilization of the radical cations of **6**, **9**, and **10** shows up in their usual instability; they cleave off *tert*-butyl groups rather rapidly. Because $E^{\circ\prime}$ is almost unaffected, we conclude that steric destabilization of the neutral form (caused by interaction of the *tert*-butyl groups with the methylene groups of the bicyclic ring) almost exactly cancels the strain in the radical cations, leading to the observed $E^{\circ\prime}$ values, despite the destabilization of the radical cations by the adjacent *tert*-butyl groups. This result of rather low $E^{\circ\prime}$ because of ground-state destabilization qualitatively resembles our results for the strained tricyclic tetraalkylhydrazines which are forced to be much more planar at nitrogen in the neutral form than normal.[15] The nitrogen splitting in the ESR spectrum of $\mathbf{6}^{+\cdot}$ is smaller than that for its dimethyl analogue $\mathbf{14}^{+\cdot}$ (13.5 compared to 16.0 gauss[11]). We previously argued[11] that $\mathbf{14}^{+\cdot}$ is in a syn-fused conformation at nitrogen and somewhat bent and that, for a given degree of bend, a syn-fused conformation has a larger nitrogen splitting, but in the absence of knowing how stretching the NC bonds affects the nitrogen splitting, it seems unwise to attempt to describe the geometry of $\mathbf{6}^{+\cdot}$ from a single parameter.

Conclusion

Strain in the neutral and cationic forms of bicyclic hydrazines when methyl is replaced by larger alkyl groups nearly cancels, leading to only small changes in the thermodynamic ease of oxidation. The cations of **6**, **9**, and **10** decompose rather rapidly by N-*t*-Bu bond breakage, because they are extremely strained by their adjacent *tert*-butyl groups, but are long-lived on the CV time scale at low temperature. Despite the Bredt's rule protection of these species, their dications decompose rapidly on the CV time scale even at low temperature, also by N-*t*-Bu cleavage. The steric hindrance introduced and more stable cationic cleavage product available when tertiary alkyl groups are substituted at the nitrogens of a hydrazine indicate that structure **12**, which achieves Bredt's rule stabilization without the introduction of tertiary substituents, may prove to provide maximum lifetimes for tetraalkylhydrazine radical cations and dications.

Experimental Section

2,3-Di-*tert*-butyl-2,3-diazabicyclo[2.2.1]heptane (6) has had its preparation described previously,[3] as have the diazenium salts $\mathbf{1}^+$–$\mathbf{3}^+$.[1]

2-*tert*-Butyl-3-*n*-butyl-2,3-diazabicyclo[2.2.1[heptane (7) was prepared as **6**,[3] using 100 mg of $\mathbf{1}^+BF_4^-$ (0.42 mmol), 25 mL of THF, and 0.47 mL (0.66 mmol) of *n*-butyllithium. The NMR of the crude product showed it to be principally **7**, and purification was by VPC:[16,17] ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7 Hz, 3 H), 1.05 (s, 9 H), 1.11–1.26 (m), 1.26–1.49 (m), 1.87–2.07 (m), 2.35–2.62 (m), 2.67–2.89 (m), 3.41 (br s, 1 H), 3.46 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.22 (q), 20.88 (t), 21.98 (t), 28.24 (q), 40.44 (d), 31.30 (d), 36.23 (d), 54.93 (d), 57.72 (b), 57.85 (q), 58.40 (d).

3-*tert*-Butyl-3-methyl-2,3-diazobicyclo[2.2.1]heptane (8). The preparation of quenching the *tert*-butyllithium–diazabicycloheptene adduct with methyl iodide has been described previously.[3] A mixture of 0.1 g of $\mathbf{1}^+BF_4^-$, 20 mL of dry THF, and 1 mL of TMEDA was stirred at room temperature with 0.2 mL of 2.2 M methyllithium (0.44 mmol) for 12 h, 0.1 g of NH_4Cl was added, and the slurry was stirred for 1 h and filtered. Separation of 8 from TMEDA was accomplished by VPC.

7-Spirocyclopropyl-2,3-di-*tert*-butyl-2,3-diazabicyclo-[2.2.1]heptane (9). A slurry of 265 mg (1 mmol) of $\mathbf{2}^+BF_4^-$ in 30 mL of dry THF at −78 °C was treated with 1.1 mL (1 mmol) of *tert*-butyllithium added dropwise. After 2 min, 0.1 g of ammonium chloride was added and the mixture allowed to warm to room temperature. After filtration and concnetration, **9** was isolated by preparative VPC:[17] ^{1}H NMR ($CDCl_3$) δ 0.34–0.51 (m, 2 H), 0.85–0.98 (m, 2 H), 0.19 (s, 9 H), 1.26 (s, 9 H), 1.47–2.11 (m, 4 H), 2.84 (br s, 1 H), 3.19 (d, J = 4.2, 1 H); ^{13}C NMR ($CDCl_3$) δ 4.7 and 10.5 (t, cyclopropyl C), 30.4, 31.5 (q, methyl C), 28.7, 33.3 (t, C_4, C_5) 56.2, 57.6 (s, *t*-Bu C), 62.9, 66.7 (d, C_1, C_4); IR 2980, 1470, 1370, 1220 cm^{-1}.

2,3-Di-*tert*-butyl-2,3-diazabicyclo[2.2.2]octane (10) was prepared from 0.1 g (0.39 mmol) of $\mathbf{3}^+BF_4^-$ and 0.2 mL of 1.97 M *tert*-butyllithium (0.39 mmol). Concentration gave an oil which we could not purify by VPC because of decomposition: ^{1}H NMR ($CDCl_3$) δ 1.3 (br, 18 H), 1.0–2.0 (m, 8 H), 3.3 (br, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.89 (t, C_{5-8}, 31.52 (q, *t*-Bu Me), 48.24 (d, $C_{1,4}$), 57.72 (s, *t*-Bu C).

2-*tert*-Butyl-3-methyl-2,3-diazabicyclo[2.2.2]octane (15) was prepared from 0.1 g (0.39 mmol) of $\mathbf{3}^+BF_4^-$, usiing the same method as for **8**, and purified by VPC:[16,17] ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 9 H), 1.3–2.5 (complex, 8 H), 2.56 (s, 3 H), 2.9 (br s, 1 H), 3.2 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.6 (t), 21.20 (t), 27.50 (t), 28.99 (q), 29.70 (t), 46.39 (q), 47.98 (d), 52.30 (d), 57.40 (s); IR (CCl_4) 2980, 2890, 1220 cm^{-1}.

Electrochemical experiments were performed as previously described.[8,18] The solvent was acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). Acetonitrile was distilled through a Vigreux column after purification.[18] The coulometric oxidation of **6** was determined on 17 mg (0.08 mmol) of **6** in preelectrolyzed acetonitrile containing 0.1 M TBAP, at a potential of 0.5 V. When the current diminished to zero (at which point *n* was 1.1), the CV was scanned from 0 to −1 V, and the peak for the diazenium reduction was found to have 75% of the current as that observed for **6** oxidation of the same solution before electrolysis. Solvent was stripped by using rotary evaporation, and the salts were extracted with D_2O. Only $\mathbf{1}^+$ was observed by NMR. Data employed in measuring the decomposition rates of $\mathbf{6}^{+\cdot}$, $\mathbf{9}^{+\cdot}$, and $\mathbf{10}^{+\cdot}$ were recorded with a Biomation 802 transient recorder.[19]

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Registry No. 1^+ BF_4^-, 41322-56-9; 2^+ BF_4^-, 52053-30-2; 3^+ BF_4^-, 43008-10-2; **6**, 74352-74-2; **7**, 77903-37-8; **8**, 42842-99-9; **9**, 77903-38-9; **10**, 77903-39-0; **13**, 77903-40-3; **14**, 14287-89-9; **15**, 77903-41-4; **16**, 14287-92-4.

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[15] Nelsen, S. F.; Hollinsed, W. C.; Grezzo, L. A.; Parmelee, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 7347.

[16] Varian Aerograph 90-P instrument, 6 ft × $^3/_8$ in. 15% XF-1150 on Chromosorb W column.

[17] Empirical formula established by high-resolution mass spectrometry (AEI MS-902).

[18] Nelsen, S. F.; Clennan, E. L.; Evans, D. H. *J. Am. Chem. Soc.* **1978**, *100*, 4012.

[19] For a complete description of the methods used to estimate the lifetimes of $\mathbf{6}^{+\cdot}$, $\mathbf{9}^{+\cdot}$, and $\mathbf{10}^{+\cdot}$, see: Parmelee, W. P. Ph.D. Thesis, University of Wisconsin, 1980, p 142.