

Reactions of Bis(N,N'-bicyclic) Diazenium Dications

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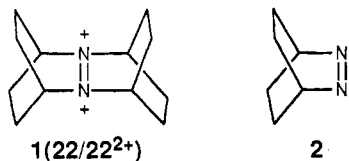
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Received February 1, 1994*

Eleven bis(N,N'-bicyclic) diazenium dications were generated from the corresponding hydrazines by NOPF₆ oxidation. Their reactivity depends greatly upon the sizes of the bicyclic rings. (We designate bicyclic ring size using the number of atoms in the two bridges in addition to the dinitrogen bridge all the compounds share.) Compounds with 21 rings alkylate acetonitrile at 240 K by opening a C_α-N⁺ bond to produce a trialkyldiazenium cation, with ΔG[‡] for the reaction increasing by at least 5.5 kcal/mol as the second bicyclic ring size increases. Compounds with an unsaturated bridge also alkylate acetonitrile; 22/u22²⁺ only cleaves the u22 bridge and reacts faster than 21/22²⁺, which only cleaves the 21 bridge. C_α-N⁺ cleavage of 22 and larger rings by acetonitrile has not been observed. 21/22²⁺ is significantly more acidic than 22/22²⁺, but both are β-deprotonated by pyridine to produce aminoaziridinium cations at 240 K. At least mostly the *exo* 21 ring proton is lost from 21/22²⁺. Dications with 23 and 24 bridges deprotonate at the α-carbon instead of the β-carbon, and 22/23²⁺ is slightly more kinetically acidic than 21/22²⁺. 22/24²⁺ is deprotonated rapidly by ether at 235 K.

Introduction

Most tetraalkylhydrazines give radical cations which are long-lived in solution, but their dications have sub-millisecond life times in cyclic voltammetry (CV) experiments.¹ Incorporating the alkyl substituents into bicyclic rings which hold the bridgehead C_α-H bonds near the nodal plane of the p orbitals of the planar nitrogens of the dication oxidation state ("Bredt's rule protection")² greatly increases dication life time, so the fastest decomposition reaction is loss of a proton from C_α. Bis(N,N'-bicyclic) ["sesquibicyclic"] hydrazines give the longest-lived dications,³ and the dication from 2,7-diazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradecane is isolable from water as 1²⁺(PF₆)₂.⁴ We shall use the sizes of the bicyclic bridges present in addition to the dinitrogen bridges common to all to designate these compounds: 1 is 22/22²⁺, and has two 22 rings. The X-ray structure of 1²⁺(PF₆)₂ shows planar nitrogens and an N=N bond length of 1.270(5) Å, only slightly larger than the electron diffraction N=N bond length of 1.243(3) Å of the neutral 22 azo compound 2.⁵ Changing bicyclic ring size in 22/22²⁺ by the removal

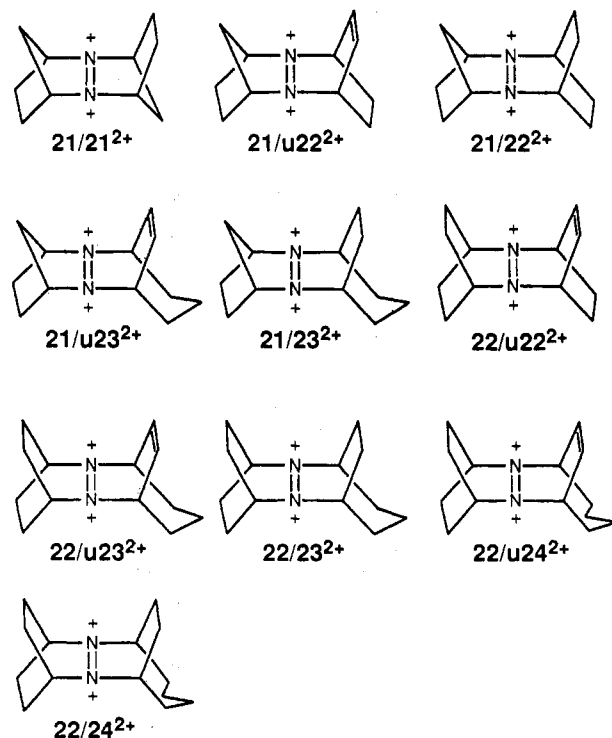


or introduction of methylene groups, or by introducing an

unsaturation in a two-atom bridge leads to very large changes in reactivity, as will be discussed here.⁶

Results

Dications from 10 sesquibicyclic hydrazines in addition to 22/22²⁺ (1) were studied in this work, and their structures are shown below. The hydrazine precursors were prepared by the proton-driven Diels-Alder addition of cyclic dienes to protonated bicyclic azo compounds.³ These compounds show CV curves with chemically reversible first and second oxidation waves at 0.2 V/s scan



* Abstract published in *Advance ACS Abstracts*, May 1, 1994.

(1) For reviews of hydrazine electron transfer chemistry see (a) Nelsen, S. F. *Acc. Chem. Res.* 1981, 14, 131. (b) Nelsen, S. F. in *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 3, Chapter 1, p 1.

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

(3) (a) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *J. Am. Chem. Soc.* 1984, 106, 3366. (b) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *Tetrahedron* 1986, 42, 1769. (c) Nelsen, S. F.; Frigo, T. B.; Kim, Y. *J. Am. Chem. Soc.* 1989, 111, 5387.

(4) Nelsen, S. F.; Blackstock, S. C.; Haller, K. J. *Tetrahedron* 1986, 42, 6101.

(5) (a) Chiang, J. F.; Chiang, R. L.; Kratus, J. *J. Mol. Struct.* 1975, 26, 125. (b) For a less-refined microwave structure, see Harmony, M. D.; Talkington, T. L.; Nardi, R. N. *Ibid.* 1984, 175, 175.

(6) For preliminary communications see: (a) Nelsen, S. F.; Wang, Y. *J. Am. Chem. Soc.* 1991, 113, 5905. (b) Nelsen, S. F.; Wang, Y. *J. Am. Chem. Soc.* 1992, 114, 7924.

Table 1. NMR Data for Bridgehead Positions of Sesquibicyclic Hydrazines and Their Dications at 240 K in CD₃CN^a

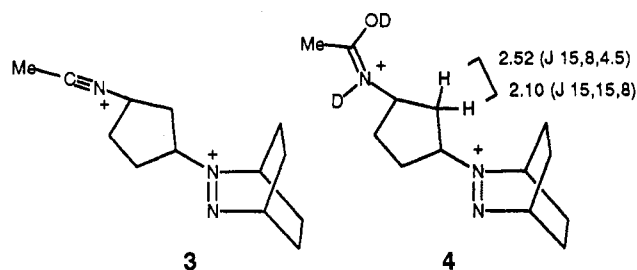
system	diazenium dications			neutral hydrazines			shift upon removing 2e ⁻	
	$\delta_{H^{2+}}$	$\delta_{C^{2+}}$	$\Delta\delta_{C^{2+}}$	δ_{H^0}	δ_{C^0}	$\Delta\delta_{C^0}$	$\delta_{H^{2+}} - \delta_{H^0}$	$\delta_{C^{2+}} - \delta_{C^0}$
21/21	unobsd	unobsd	-	3.40, 3.56	61.6, 56.5	5.1	-	-
21/u22	unobsd	unobsd	-	3.45, 3.59	63.3, 54.5	8.8	-	-
21/22	6.19, 6.44	89.8, 76.8	13.0	2.72, 3.30	61.4, 49.8	11.6	3.47, 3.14	28.4, 27.0
21/u23	6.27, 6.39	91.1, 76.7	14.4	3.45, 3.51	65.8, 53.1	7.7	2.82, 2.88	25.3, 18.1
21/23	5.87, 6.31	91.7, 75.6	16.1	2.98, 3.35	64.0, 54.3	9.7	2.89, 2.96	27.1, 21.3
22/u22 ^b	6.16, 6.91	82.1, 80.2	1.9	2.60, 3.35	54.2, 50.8	3.4	3.56, 2.56	27.9, 24.0 ^c
22/22 ^c	6.25	81.3	[=0]	2.71	51.0	[=0]	3.54	30.3
22/u23 ^b	6.20, 6.39	82.7, 82.3	0.4	2.70, 3.28	58.3, 54.2	4.1	3.50, 3.11	24.4, 28.1 ^c
22/23 ^{b,c}	5.90, 6.17	84.1, 81.8	2.6	2.77, 2.92	54.6, 53.5	1.1	3.13, 3.25	29.5, 28.3 ^c
22/u24 ^b	unobsd	unobsd	-	2.62, 3.30	57.9, 56.2	1.7	-	-
22/24 ^b	5.91, 6.09	82.5, 81.3	1.5	2.51, 3.06	59.2, 55.5	3.7	3.40, 3.23	23.3, 25.8 ^c

^a Order of shifts reported same as order of rings in the designation, where known (see b). ^b Bridgehead carbons not assigned. ^c Isolated and studied at room temperature.

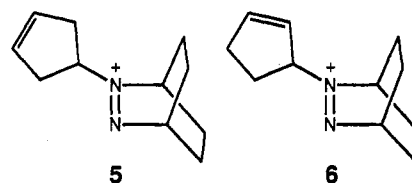
rates in acetonitrile containing 0.1 M tetraethylammonium perchlorate except 21/21, for which the dication reduction wave is vanishingly small. As might be expected, CV data for 22/u32 are very similar to those for the previously studied 32/u22.⁷ 22/u24 shows a broad first CV wave with $(E_{p1ox} - E_{p1red})/2$ of -0.47 V vs SCE ($E_{p1ox} - E_{p1red} = 0.24$ V), and a chemically irreversible second oxidation wave, $E_{p2ox} = 0.94$ V. The corresponding numbers for 22/24 are -0.56 (0.09); +0.81 (irrev) V.

Both 22/22²⁺ 3a,4 and 22/23²⁺ 6b have been isolated as acetonitrile-solvated PF₆⁻ salts by precipitation with ether, but the dications from the other hydrazines are too unstable to isolate in this manner. They were generated by NOPF₆ oxidation of the hydrazine near 240 K in CD₃CN and characterized by NMR. Dications 21/21²⁺, 21/u22²⁺, and 22/u24²⁺ were not detected under these conditions, but essentially only dication signals were initially observed for the other eight compounds. The most characteristic dication signals are their strongly downfield-shifted bridgehead protons and carbons (Table 1). The bridgehead protons move downfield 3.1–3.5 δ and the carbons 18–30 δ upon removal of two electrons from the hydrazine precursors. The bridgehead carbons for 21/u22 and 21/22 have been assigned by deuteration,⁸ and the differences are large enough to allow those of 21/u23 and 21/23 to be confidently assigned by analogy. Only small chemical shift differences are present for the other compounds, and bridgehead carbon assignments have not been attempted.

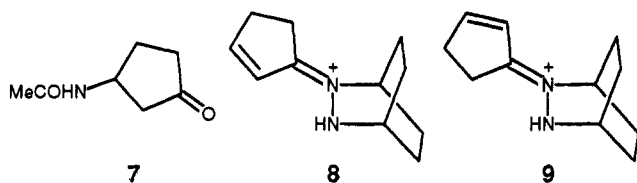
We shall first discuss the decomposition of 21/22²⁺, which has been the most thoroughly studied dication and provided the most information about decomposition pathways for dications with 21 and 22 bicyclic rings. 21/22²⁺ has a half-life of about 5 min at room temperature in CD₃CN and gives several products. The major initial product is assigned as the 21 ring-cleavage nitrilium adduct 3, but is accompanied by its hydrolysis product, protonated acetamide adduct 4, produced from 3 by residual D₂O in the CD₃CN. 3 shows broad 22 ring bridgehead proton signals at 5.35 and 5.80 δ and complex multiplets at 4.88 and 5.39 δ . We assign the latter two signals to the five-membered ring tertiary hydrogens α to the nitrilium and diazenium functionality, respectively, because hydrolysis to 4 shifts the bridgehead signals under 0.03 δ , while the latter two signals move to 4.41 and 5.42 δ , upfield shifts of 0.47 and 0.17 δ , respectively. Neither



the CD₃ nor the nitrile ¹³C-NMR signals are observed for 3, but the amide carbonyl of 4 is observed at 177.0 δ . Olefinic trialkyldiazenium cations 5 and 6 are also formed in



significant amounts. Basic hydrolysis of the decomposition products from 21/22²⁺ in unlabeled acetonitrile gave an 85% yield of 22 azo compound 2 (isolated by distillation) but no 21 azo compound was detected, verifying that cleavage in the smaller ring predominates. Hydrolysis of 3–6 should produce dihydro-2, which is rapidly oxidized to 2 by air. A 17% yield of the unstable 3-acetamidocyclopentanone (7) was also obtained. 7 was independently



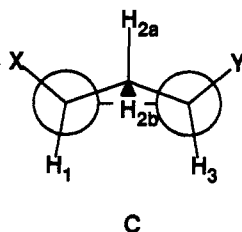
prepared (in similarly low yield) by acetic anhydride acetylation of the adduct of ammonia and 2-cyclopenten-1-one and is an expected hydrolysis product of 3 and 4. Reaction of 2 and silver tetrafluoroborate with 3-bromocyclopentene followed by precipitation, solvent removal, and redissolution produced a mixture of 6 and its iminium 1,3 hydrogen shift isomers 8 and 9 (which appear to be more stable than 6), while reaction with 4-bromocyclopentene produced an even worse mixture, containing 5, 6, 8, and 9. Although 5 and 6 are too unstable to isolate conveniently, these experiments demonstrate that they can be independently generated by alkylation of 2. The half life for 21/22²⁺ decomposition at 240 K is about 35 h, it is converted to a mixture of 3 and 4 with the fraction of 4 increasing with time, and significant amounts of olefins

(7) For 22/u23 (this work) -0.30(0.07), +1.00(0.17) V; and for 23/u22 -0.27(0.07), +1.00 (0.08) V.^{3c}

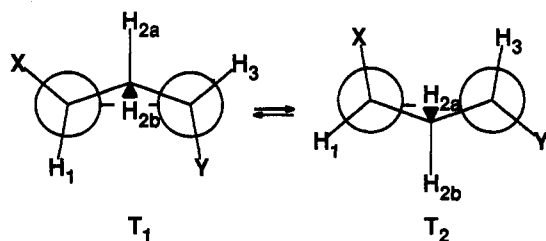
(8) (a) William, D. R.; Harigaya, T.; Moore, J. L. *J. Am. Chem. Soc.* 1984, 106, 7641. (b) Mihelich, E. D.; Hite, G. A. *Ibid.* 1992, 114, 7318. (c) Semmelhack, M. F.; Zhang, N. *J. Org. Chem.* 1989, 54, 4483.

5 and 6 are not detected. It appears from experiments in which varying amounts of hydrolysis of 3 to 4 are allowed before warming that both 5 and 6 arise principally from decomposition of 3 at higher temperatures.

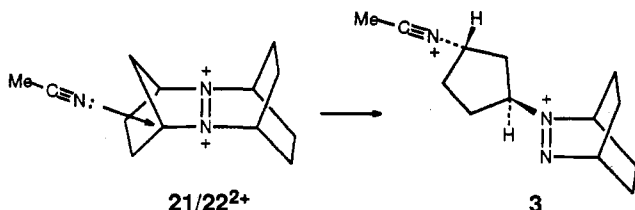
21/22²⁺ is therefore unstable in acetonitrile because it alkylates the very weakly nucleophilic nitrile nitrogen, even at 240 K. Strain relief is obviously important in this reaction, both because only the 21 ring is cleaved and because 22/22²⁺ does not undergo an analogous reaction even at room temperature.^{6a} We shall now consider whether this unusual alkylation reaction involves principally S_N1 or S_N2 character. Only one diastereomer of 4 is produced, and the proton NMR shifts and splitting constants for the CH₂ group between the substituted carbons are shown on the structure above. Significant differences in both chemical shift difference and coupling constants are observed for the protons at C₂ of *cis* and *trans* 1,3-disubstituted five-membered rings.⁸ These differences may be rationalized using the idealized Newman projections of envelope conformations shown below. The *cis* isomer strongly prefers conformation C, with the



substituents pseudoequatorial, which leads to large chemical shift differences for the hydrogens at C₂, and nearly equal $J_{1,2}$ and $J_{1,3}$ values, with $J_{1,2a}$ approaching a diaxial value, and $J_{1,2b}$ a diequatorial value. The *trans* isomer has a significantly smaller chemical shift difference because each C₂ hydrogen is *syn* to a substituent, and the unequally populated T₁ and T₂ conformations lead to J

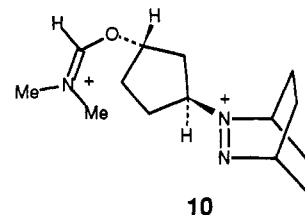


values which depend upon the conformational mixture, so the $J_{1,2}$ and $J_{2,3}$ values are typically significantly different. The difference in chemical shifts at C₂ for *cis*-1,3-diaminocyclopentane is 1.05 δ .⁹ Both the $\Delta\delta$ and J values at C₂ for 4 show 3 to be the *trans* diastereomer shown below, which is the geometry expected if S_N2 cleavage occurs. If S_N1 cleavage occurs, it appears to us



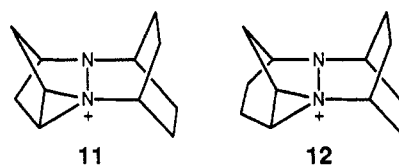
either that reaction with solvent has to be so fast that the *cis* face of the cyclopentane ring is still effectively blocked

by the departing group, or that internal return, i.e. capture of the incipient carbocation by the divalent nitrogen of the trialkyldiazonium cation formed, must be fast enough to win out over capture by acetonitrile from the *cis* face. We believe that rate-limiting C_α-N⁺ cleavage can be excluded by the following experiment. When 2 equiv of dimethylformamide are included in the solvent used for the reaction (initial concentrations: 21/22, 0.12; DMF, 0.24; CD₃CN, ~19.7 M), decomposition of 21/22²⁺ becomes significantly faster than in pure acetonitrile, and the principal product becomes 10, which was independently



generated in deuterated form by running the oxidation in DMF-*d*₇. We formulate 10 as the O-alkylated alkylation product because MeOSO₂F is known to give almost exclusively O-alkylation of DMF,¹⁰ and we expect even more O-selectivity with a branched alkyl group. The ratio of 10:(3 + 4) produced is about 10:1, which appears to require that at least the reaction with DMF is proceeding with nucleophilic solvent assistance. If both the MeCN and DMF reactions are assumed to be first order in solvent, the ~10:1 product ratio for ~1:82 reactant ratio requires DMF attack to be about 820 times faster than acetonitrile attack, corresponding to about a 4 kcal/mol lower ΔG^\ddagger at 240 K.

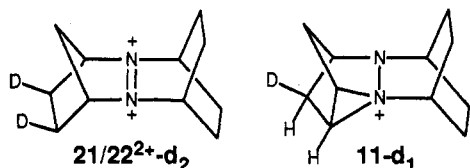
Addition of pyridine to a solution of 21/22²⁺ in CD₃CN at 240 K does not produce C_α-N⁺ cleavage products analogous to 3 or 10, but instead the C_β deprotonation product of the 21 ring, 11, is formed. Despite the much greater nucleophilicity of pyridine than acetonitrile or DMF, its S_N2 attack at the rather hindered C_α position



should be slowed sterically, and pyridine is far more basic than either; only deprotonation was observed. 11 shows the 7 carbon signals expected for rapid inversion of the trisubstituted nitrogen on the NMR time scale. In its ¹H-NMR, tertiary hydrogen signals at 3.42 and 3.88 δ show the ill-resolved couplings characteristic of 22 ring bridgehead signals, and narrower signals with no resolved coupling occur at 3.96 and 4.02 δ with 2:1 integration ratio and are attributed to the tertiary hydrogens in the tricyclic ring. Formation of 11 is analogous to deprotonation of 22/22²⁺ under these conditions to give 12,^{6a} but only 21 ring deprotonation is observed for 21/22²⁺. The precursor to the 21 ring *exo-d*₂ labeled dication 21/22²⁺-*d*₂ was available from previous work¹¹ and produced 11 which also had a 2:1 ratio in the downfield CH region, establishing that the deuterium loss product 11-*d*₁ is the major product. There must be enough preference for *exo*

(10) Alder, R. W. *Chem. Ind.* 1973, 983.

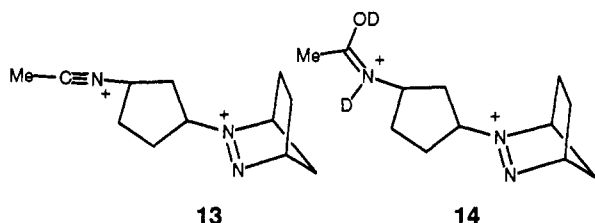
(11) Nelsen, S. F.; Petillo P. A.; De Felippis, J.; Wang, Y.; Chen, L.-J.; Yunta, M. J. R.; Neugebauer, F. A. *J. Am. Chem. Soc.* 1993, 115, 5608.



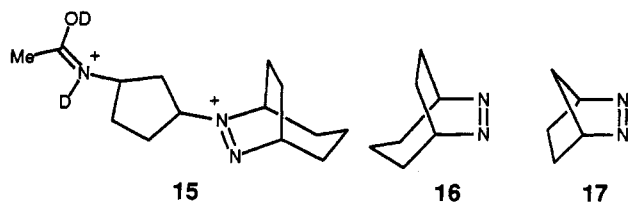
relative to *endo* C_β deprotonation to overcome the primary isotope effect for reaction of **21/22²⁺-d₂** with pyridine. The rate constant for reaction of pyridine with **21/22²⁺** in acetonitrile, k_{pyr} , was measured using double potential chronoamperometry experiments,¹² generating the dication from **21/22²⁺**-PF₆⁻ so the strongly basic neutral compound is not present. Four separate runs at ([pyridine], mM, [21/22²⁺-PF₆⁻], mM) gave k_{pyr} , M⁻¹ s⁻¹ values of (24.7, 3.47) 11.6; (24.7, 1.67) 12.1; (49.5, 1.57) 11.6; and (71.2, 1.67) 11.7, average $k_{\text{pyr}} = 11.7 \text{ M}^{-1} \text{ s}^{-1}$. Experiments using **21/22-d₂²⁺**-PF₆⁻ gave (24.7, 1.72) 4.3; (49.6, 2.20) 3.7, average $k_{\text{pyr}} = 4.0 \text{ M}^{-1} \text{ s}^{-1}$. These results are completely consistent with the conclusion from NMR spectra that **21/22²⁺** is deprotonated selectively at the *exo* position of the **2** bridge of the **21** bicyclic ring, and evaluates $k_{\text{H}}/k_{\text{D}}$ for this reaction as 2.9.

As for **12**,^{6a} warming **11** results in aziridinium ring cleavage, producing **5** cleanly. Experiments at 293 K gave ratios of **11**:**5** of 1.00:0.33 after 5 min, 1.00:0.70 after 25, 1.00:1.32 after 40, and 1.00:2.70 after 60 min, which produces a linear first-order plot with $k_{\text{dec}}(293 \text{ K}) = 3.5_8 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} = 32.2 \text{ min}$, $\Delta G^\ddagger(293 \text{ K}) = 21.8 \text{ kcal/mol}$. The previously reported^{6a} half-life for **12** at 273 K is 24_6 min, corresponding to $k_{\text{dec}}(273 \text{ K}) = 4.7 \times 10^{-5} \text{ s}^{-1}$, $\Delta G^\ddagger(273 \text{ K})$ of 21.3 kcal/mol. Despite larger expected strain relief upon aziridinium ring cleavage, **11** is slightly more thermally stable than **12**.

The more strained **21/21²⁺** is significantly more reactive than **21/22²⁺** and was not detected by NMR at 240 K. Analogous **21** C_α-N⁺ ring cleavage products were observed by NMR and are assigned as **13** and **14**. When the NOPF₆ oxidation was conducted at room temperature,



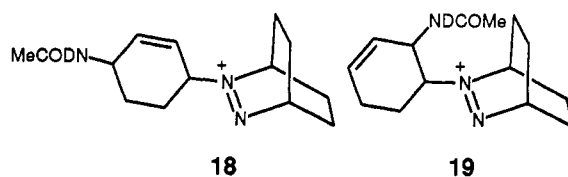
approximately 10–20% of the product consisted of cyclopentenyl-substituted diazenium cations, presumably the **21** ring analogues of **5** and **6**. The less-strained **21/23²⁺** is slightly more stable at room temperature than is **21/22²⁺**, having a half-life of about 20 min. The four characteristic downfield signals for a product assigned as **15**, the **23** analogue of **4**, were observed by NMR. Basic



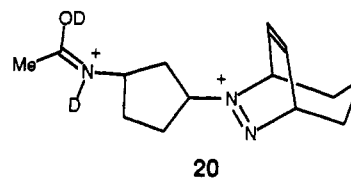
(12) (a) Childs, W. V.; Maloy, J. T.; Keszthelyi, C. P.; Bard, A. J. *J. Electrochem. Soc. Electrochem. Sci.* 1977, 874. (b) Schwartz, W. M.; Shain, I. *J. Phys. Chem.* 1965, 69, 30; 1966, 70, 845.

hydrolysis of the reaction products gave a nearly quantitative yield of the **23** azo compound **16**, and the **21** azo compound **17** was not detected, showing that only cleavage of the **21** ring is detectable. We presume that both of these **21**-ring-containing dications decompose by alkylating acetonitrile.

The unsaturated dications are even more reactive than their saturated analogues. We were unable to observe **21/u22²⁺** by NMR at 240 K before its decomposition, and the product mixture observed was very complex; we suspect that competitive cleavage of both rings is occurring. **22/u22²⁺** has a half-life of about 8 h at 240 K, but its lifetime is less than 1 min at room temperature. Its basic hydrolysis product gave a high yield (about 90%) of **22** azo compound **2**, showing that at least the majority of the cleavage takes place in the unsaturated ring, which has allylic C_α-N⁺ bonds. The proton NMR of the low temperature product mixture is very complex, but the ¹³C-NMR shows that two acetamide adducts are produced in similar amounts. The NMR is consistent with allylic isomers produced by formal S_N2 and S_N2' attack, **18** and **19**, but we do not have information on either stereochemistry or



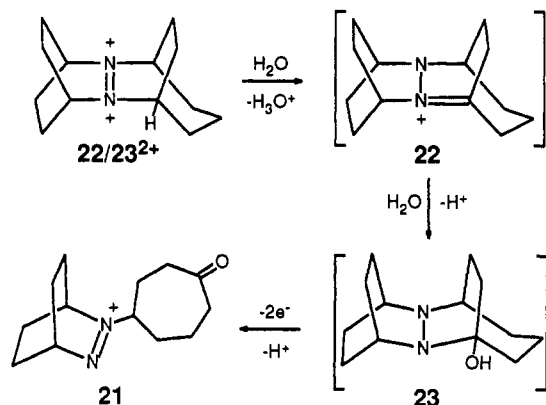
regiochemistry of these products. The dication from **21/u23** has a lifetime of about 80 s at room temperature, which is longer than that of **22/u22²⁺**. A single acetamide adduct was observed by proton and carbon NMR after decomposition of **21/u23²⁺**, and basic hydrolysis of the product mixture gave no **21** azo compound **17** but did give 1,3-cycloheptadiene, the expected product from the **u32** azo compound. We conclude that **21/u23²⁺** undergoes acetonitrile-assisted cleavage of its **21** ring faster than any reactions of its **u23** ring, and that the acetamide adduct observed is **20**. The less strained **22/u23²⁺** has a half-life at room temperature of 18.3 min, relatively



accurately determined by observing the decrease of its UV absorption spectrum, which followed first-order kinetics. An NMR study showed that a complex mixture of products is produced.

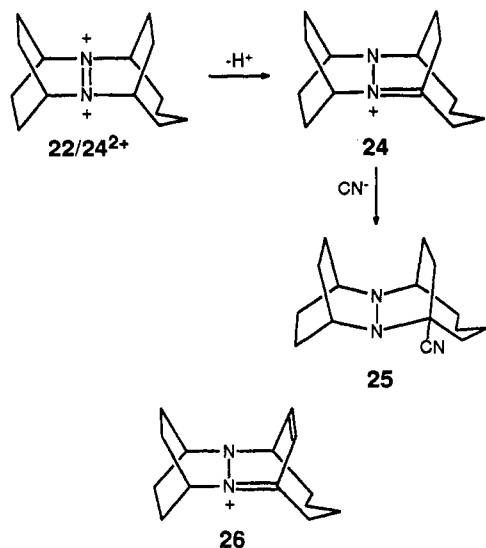
Although **22/23²⁺** does not react with acetonitrile, it is considerably harder to handle than **22/22²⁺** because it is extremely sensitive to water (and more basic compounds). When water is added to a CD₃CN solution of **22/23²⁺** (traces of D₂O are always present), the dication signals disappear rapidly, and the radical cation **22/23^{•+}** is produced, as shown both by its ESR spectrum and the fact that dication is regenerated when additional NOPF₆ is added. A broadened NMR spectrum showing singlets at 5.46 and 5.80 and a triplet at 5.01 δ in 1:1:1 ratio is also produced, which we suggest is the keto diazenium cation **21**. Basic hydrolysis produces low yields (about 18%) of the **22** azo compound **2** and 1,4-cycloheptanedione, the expected hydrolysis products of **21**. We suggest that bases

such as water deprotonate **22/23²⁺** at C_α of the 23 ring, producing the very strained and unobserved **22**, which adds water to give the also unobserved α-hydroxyhydrazine **23**, which should be both quite basic and easily oxidized. Ring opening and loss of electrons and a proton would give the observed **22/23⁺** and **21**. We have been unable to find conditions where **22** builds up enough to observe spectroscopically, but believe that observing cleavage of

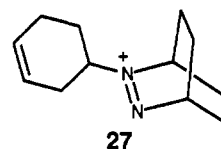


the larger ring (**23**), obtaining 1,4-cycloheptadione as a hydrolysis product, and generating a reducing agent by adding water are best explained by the C_α proton loss postulated. The rate constant for reaction of **22/23²⁺** with pyridine in acetonitrile at room temperature was evaluated by analysis of the effect of scan rate on the CV of **22/23²⁺**PF₆⁻ as $k_{\text{pyr}} = 80 \text{ M}^{-1} \text{ s}^{-1}$.¹³

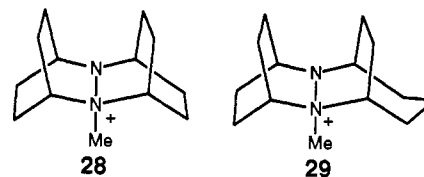
Dication **22/24²⁺** was generated either from the radical cation with 1 equiv of NOPF₆ or from the neutral compound with **2** and was characterized at 235 K. It is especially unstable and decomposes slowly (apparent half-life about 7–8 h) to give the **24** ring C_α deprotonation product **24** even without intentionally adding base. The dication is exceedingly acidic and is rapidly quenched to produce **24** by addition of ether at 235 K. In contrast to **22**, which we have not even succeeded in detecting spectroscopically, **24** was isolated as the hexafluorophosphate salt and crystallized to analytical purity and was further characterized by addition of cyanide to produce α-cyanohydrazine **25**. The unsaturated dication **22/u24²⁺** shows exactly analogous behavior and was quenched with ether to produce the twisted azadiene **26** hexafluorophosphate, which was characterized by NMR.



The most stable diazenium dication available, **22/22²⁺**, was examined for reactions with various bases. Addition of pyridine to CD₃CN solutions at 248 K deprotonates it over a period of a few hours to aminoaziridinium cation **12**, which is stable at this temperature and can be generated in good yield.^{6a} Sodium hydroxide in D₂O deprotonates it to **12** rapidly at 273 K, where the half-life for aziridinium ring cleavage of **12**, which cleanly gives the cyclohexenyl diazenium cation **27**, is 4.1 h. Other hard bases which



deprotonate **22/22²⁺** slowly at 273 K in acetonitrile to initially give mixtures of **12** and **27** are benzyltrimethylammonium fluoride, potassium carbonate in D₂O, sodium acetate, and tetramethylammonium chloride (which is almost insoluble in CD₃CN). We note that although **22/22²⁺** is the least acidic diazenium dication available, it is effectively a carbon acid which is stronger than HCl in acetonitrile, because its deprotonation product **12** is produced by chloride. Proton loss from **22/22²⁺** is not detectably reversible under any conditions we have found, and it seems likely to us that the large geometry reorganization which occurs upon proton loss, and generation of a relatively basic amino nitrogen atom, precludes protonation of **12** to **22/22²⁺** by a low activation energy pathway. This dication is also a powerful oxidant, reducing to the radical cation at $E^\circ = +0.86 \text{ V vs SCE}$.³ Tetramethylammonium bromide and sodium iodide both reduce **22/22²⁺** to the radical cation at 273 K with generation of the dihalogen, while sodium thiophenoxide reduces it all the way to the neutral compound, with generation of diphenyl disulfide. Reaction of **22/22²⁺** with sodium borohydride produces the protonated hydrazine in 90% yield, while reaction with methyl lithium gives a 55% yield of the methylated diazenium cation **28**. These reactions presumably involve electron transfer and proceed by



mechanisms resembling those postulated for far less easily reduced substrates, such as alkyl halides (for borohydride reduction) and ketones (for alkyllithium reduction).¹⁴ Cation **28** is efficiently produced in another unusual electron transfer reaction when the neutral hydrazine is reacted with dimethyldioxirane,¹⁵ which we have postulated is another case where **22/22²⁺** reacts efficiently with a methyl radical source to give N-methylation. Even the considerably stronger acid **22/23²⁺** gives the corresponding N-methylated diazenium cation **29** upon treatment with methyl lithium, although only in 26% yield. An undetermined amount of **22/23²⁺** was also produced, but no

(13) Work in collaboration with D. H. Evans, University of Delaware. Details to be published separately.

(14) See for example (a) Ashby, E. C. *Acc. Chem. Res.* 1988, 21, 414. (b) Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* 1987, 109, 1195.

(15) Nelsen, S. F.; Scamehorn, R. G.; Felippis, Wang, Y. *J. Org. Chem.* 1993, 58, 1657.

products containing an α methyl group were detected, which we envisioned would arise if **22** were formed.

Discussion

C $_{\alpha}$ -N $^{+}$ Bond Cleavages. The data available on half-lives for compounds undergoing C $_{\alpha}$ -N $^{+}$ cleavage in CD $_3$ CN are summarized in Table 2, along with differences in

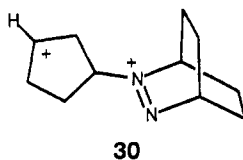
Table 2. Comparison of Room Temperature Lifetimes in CD $_3$ CN, Relative Cleavage Barriers for R $_2$ NNR $_2^{2+}$, and AM1-Calculated Enthalpies for Cleavage

system	$t_{1/2}$, S ^a	$\Delta\Delta G^{\ddagger}$	cleaved ^c	AM1 calcd cleavage ^d
21/21	<0.1 (CV)	<-4.7	only <u>21</u> present	-4.4[-5.6](21)
21/u22	>2 (CV)	>-3.0	both?	+0.1[-2.4](21) ^e +8.4[+14.1](u22) ^e
22/u22	<60 (NMR)	<-1.0	only u22	+9.7[+18.7](u22) ^e
21/u23	~80 (NMR)	-0.8	only <u>21</u>	+0.1[+0.4](21) ^e +15.3[+27.8](u23) ^e
21/22	300 (NMR)	=0	only <u>21</u>	=0.0[=0.0](21)
22/u23	1100 (UV)	+0.8	unknown	+17.3[+31.3](u23) ^e
21/23	1200 (NMR)	+0.8	only <u>21</u>	+1.9[+1.5](21)
22/22	>1.7 $\times 10^6$	>+3.8	only <u>22</u> present	+21.4[+28.9](22)

^a Method used to determine the half-life is shown in parentheses. ^b ΔG^{\ddagger} , kcal/mol, relative to 21/22 $^{2+}$, assuming all decompositions are the same order. ^c Difference in calculated $\Delta\Delta H_f$ for compound and for 21/22 $^{2+}$. First number: $\Delta\Delta H_f$ calculated as $\Delta H_f(\text{C}_{\alpha}\text{-N S}_{\text{N}1}$ cleavage product) - $\Delta H_f(\text{diazenium dication})$, kcal/mol. This difference is -35.2 kcal/mol for 21/22 $^{2+}$. [Second number, in brackets: $\Delta\Delta H_f$ calculated as $\Delta H_f(\text{C}_{\alpha}\text{-N S}_{\text{N}2}$ hydride cleavage product) - $\Delta H_f(\text{diazenium dication})$. This difference is -327.077 for 21/22 $^{2+}$.] ^e The calculations obviously are not close to correct for the unsaturated compounds (see text).

ΔG^{\ddagger} relative to 21/22 $^{2+}$ assuming the reactions are all the same order. 22 ring cleavage has not been detected, and ΔG^{\ddagger} for reaction of 22/22 $^{2+}$ is at least 3 kcal/mol higher than that for the compounds which do cleave. 21 ring cleavage is very sensitive to the size of the other bicyclic ring, 21/21 $^{2+}$ having a barrier at least 4.7 kcal/mol lower than that for 21/22 $^{2+}$. The increase in ΔG^{\ddagger} for expanding the second bicyclic ring one more methylene group is much smaller, $\Delta\Delta G^{\ddagger}$ being +0.8 kcal/mol for 21/23 $^{2+}$. C $_{\alpha}$ -N cleavage is significantly faster for allylic bonds, and for u22 than for u23 rings. At 240 K 22/u22 $^{2+}$ has a 0.7 kcal/mol lower u22 cleavage barrier than does 21 cleavage of 21/22 $^{2+}$.

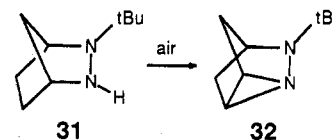
Also included in Table 2 are AM1-calculated relative exothermicities for C $_{\alpha}$ -N $^{+}$ cleavage. Two numbers are shown relative to 21/22 $^{2+}$ for each compound. The first is differences in $\Delta H_f(\text{C}_{\alpha}\text{-N S}_{\text{N}1}$ cleavage product) - $\Delta H_f(\text{diazenium dication})$, which are listed relative to that for $\Delta H_f(\mathbf{30}, \text{the } \underline{21} \text{ ring } \text{S}_{\text{N}1} \text{ cleavage product}) - \Delta H_f(21/22^{2+})$, which is -35.2 kcal/mol. The second, shown in



brackets, is the difference in ΔH_f for the C $_{\alpha}$ -N hydride-cleavage product and the dication, which is also listed relative to the value for 21/22 $^{2+}$, which is -327.1 kcal/mol. These calculated relative cleavage enthalpy differences are rather close to the observed $\Delta\Delta G^{\ddagger}$ values for 21/21 $^{2+}$, 21/22 $^{2+}$, and 21/23 $^{2+}$; AM1 calculations appear to handle the effect of second bicyclic ring size on 21 ring strain adequately. The calculations also predict much greater

stability for 22/22 $^{2+}$, suggesting that we are far from being able to observe acetonitrile-assisted 22 ring cleavage for this compound. Calculations on the unsaturated compounds rather clearly do not come as close to the experimental data as do those on the saturated compounds. Neither the much greater reactivity for 21 cleavage of 21/u22 $^{2+}$ versus 21/u23 $^{2+}$ nor the greater u22 cleavage reactivity of 22/u22 $^{2+}$ than the 21 cleavage reactivity of 21/22 $^{2+}$ is predicted. The effect of introducing an unsaturated 2 bridge in these compounds on C $_{\alpha}$ -N reactivity is not calculated well.

Deprotonation Reactions. Although 22/22 $^{2+}$ is β -deprotonated by pyridine in acetonitrile at room temperature, this reaction is too slow to be studied electrochemically and the rate constant has not been measured. The rate constant for deprotonation of 21/22 $^{2+}$ under these conditions is 11.7 M $^{-1}$ s $^{-1}$, there is a strong preference for β -*exo* 21 ring hydrogen loss, and k_H/k_D for the reaction is 2.9. These β -deprotonations are similar to deprotonation of norbornyl cation to nortricyclene¹⁶ and that occurring in the homoenolization of camphenilone studied by Nikon and co-workers.¹⁷ A significant difference between diazenium dication β -deprotonation and the above reactions is that conditions have not been found where the aminoaziridinium product reprotonates to produce diazenium dication. The hydrogen removed is clearly determined by kinetics, not thermodynamics. The observed 21/22 $^{2+}$ deprotonation product **11** is unlikely to be the thermodynamically most stable one, as the two 22 ring β -deprotonation products are calculated to be 5.3 and 6.0 kcal/mol more stable than **11**. Weakening of the C $_{\beta}$ -H bonds in the dication should be principally determined by the "W-plan" overlap between these bonds and the p orbitals at nitrogen. This interaction is significantly larger for a 21 bicyclic ring than for a 22 bicyclic ring and is presumably the source of the greater reactivity for the 21 ring. AM1 calculations appear to make the correct prediction here, obtaining a slightly larger positive charge for the 21 ring β -*exo* hydrogens ($q = 0.191$) than for the 22 ring ($q = 0.184$ *syn* to the 1 bridge, 0.185 *anti* to the 1 bridge). The most easily experimentally accessible measure of N π -rich orbital, C $_{\beta}$ -H $_{\text{exo}}$ electronic interaction is the ESR splitting constant, $a(\text{H}_x)$, which is directly proportional to spin density at the hydrogen nucleus and provides a quantitative measure of the relative amount of spin which reaches the hydrogen atom by all mechanisms. Although $a(\text{H}_x)$ is a property of a radical instead of a closed shell species, the greater C $_{\beta}$ -H bond weakening for 21 than for 22 rings occurs in radicals as well as closed shell species. In an example closely structurally related to the cases under consideration, the 21 ring trialkylhydrazine **31** is oxidized by air to give aminoaziridine **32** as the major

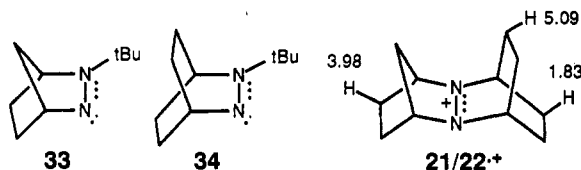


product,¹⁸ while its 22 ring analogue is less sensitive to air

(16) Sargent, G. D. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds., Wiley: New York, 1972; p 1099.

(17) (a) Nikon, A.; Lambert, J. L. *J. Am. Chem. Soc.* **1964**, *84*, 4604. (b) Nikon, A.; Hammons, J. H.; Lambert, J. L.; Williams, R. O. *Ibid.* **1965**, *85*, 3713. (c) Nikon, A.; Lambert, J. L. *Ibid.* **1966**, *88*, 1905. (d) Nikon, A.; Lambert, J. L.; Oliver, J. E. *Ibid.* **1966**, *88*, 2787.

and does not give an analogous product. The hydrazyl radical **33** has a lifetime of about 10 h, producing mostly



32 and starting hydrazine as decomposition products, under conditions where **34** lasts for months. Deuterium labeling has shown that only the *exo* hydrogen is removed in producing **32**, making the analogy with **21/22⁺** deprotonation close. The radical cation **21/22⁺** has the $\alpha(H_x)$ values shown above.¹¹ $\alpha(H_x)$ is very sensitive to W-plan overlap, and the non-W **21** splitting is over twice as large as the corresponding **22** splitting. Examples of sp^2 hybridized carbons as the spin-bearing orbitals for interaction with H_x are provided by bicyclic semidiones, where $\alpha(H_x)$ for the **21** and **22** compounds are 2.43 and 2.13, respectively.¹⁹

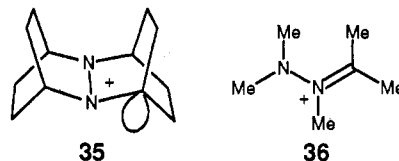
The β -deprotonation product from **21/22⁺**, **11**, is comparable in thermal stability to that from **22/22⁺**, **12**. The AM1 $\Delta\Delta H_f$ values are very different for **11** \rightarrow **5** (-50 kcal/mol) and **12** \rightarrow **27** (-26 kcal/mol), but as pointed out previously,^{6a} concerted chelotropic elimination for this conversion is a forbidden reaction, and the N^+-C bonds presumably cleave one at a time. Single N^+-C bond cleavages to give the hydrazine radical cation β -yl radicals are calculated to have similar $\Delta\Delta H_f$ values, -11.8 and -11.0 kcal/mol, respectively, in qualitative agreement with the similar activation barriers for the decomposition reactions.

Neither **22** nor **21** ring diazenium dications show any tendency for $C_\alpha-H$ deprotonation, as expected from their Bredt's rule protection. It is clear from the above experiments that this protection from α -deprotonation breaks down for **23** rings. This was a surprise to us, because the $C_\alpha-H$ bond is rather close to the nodal plane of the nitrogen p orbital of the dication. If the $C_\alpha-H$ bond, p orbital axis twist angle is θ , hyperconjugative bond weakening is expected to be proportional to $\cos^2 \theta$. As estimated by AM1 calculations, θ for diazenium dications are nearly independent of second ring size, and θ [$\cos^2 \theta$] values are **22**: 90.0° [0]; **21**: 71.1 \pm 0.2° [0.10]; **32**: 77.1 \pm 0.1° [0.05]. Despite small hyperconjugative bond weakening of $C_\alpha-H$, and $C_\beta-H$ bond deprotonation products closely analogous to that produced from **22/22⁺**,²⁰ **22/23⁺** is considerably more acidic and deprotonates at C_α of the **23** ring. k_{pyr} for **22/23⁺** is 6.8 times that for **21/22⁺**, which deprotonates exclusively β in its **21** ring. Table 3 compares AM1 calculations on the deprotonation products from **22/22⁺**, **35**; **22/23⁺**, **22**; and **22/24⁺**, **24**, with the pentamethyl compound **36** as an acyclic model of similar substitution pattern. AM1 predicts that the β -deprotonation product of **22/23⁺** is about 5 kcal/mol more stable than the α -deprotonation product, but kinetics, not thermodynamics, are expected to determine the products formed; only products derived from the

Table 3. AM1 Calculations on α -Deprotonated Diazenium Dications

dication	22/22	22/23	22/24	iPrMe ₃ N ₂
α -deprot species	35	22	24	36
$d(^+N=C_\alpha)$, Å	1.435	1.343	1.335	1.334
fractional change ^a	\approx 0	0.92	0.99	\approx 1
$^+N=C_\alpha$ twist, deg	79.0	38.2	26.5	2.9
$\Delta\alpha_{av}$ ^b at N^+ , C_α	4.6, 4.9	0.7, 2.1	0.1, 0.7	0.0, 0.0
$\Delta\Delta H_f(B-\alpha)$ ^c	-28.9	-4.7	+15.9	-

^a Fractional change in $d(^+N=C_\alpha)$ between **35** and **36**. ^b $120^\circ - \alpha_{av}$, the average of the bond angles at ^+N and C_α . ^c Difference in heats of formation calculated by AM1 for the most-stable β - and α -deprotonation products.



α -deprotonation product were observed. Although the α deprotonation product **22** is predicted to have 38° of twist at its $^+N=C$ bond, it has substantial calculated double bond character, with a bond length 92% of the way from that of **35** (essentially no double bond character) to that of the unconstrained **36**. The isolable iminium cation derived from **22/24⁺**, **24**, is calculated to have the same bond length as **36** and 26° of twist about its $^+N=C$ bond.

Summary

The adjacent formally positive nitrogens of diazenium dications make them exceptionally reactive. They are among the strongest carbon acids studied in solution, and powerful Bredt's rule protection is necessary to slow down $C_\alpha-H$ deprotonation enough for significant dication lifetime. **22/24⁺** is rapidly deprotonated at C_α of its **24** ring by ether at 235 K to give the isolable bridgehead iminium cation **24**, and water rapidly deprotonates **22/23⁺** at C_α of the **23** ring, although the product is so reactive that it has not been spectroscopically detected. The C_β hydrogens of smaller bicyclic ring dications are the positions attacked by bases. Chloride in acetonitrile slowly β -deprotonates **22/22⁺** to aminoaziridinium cation **12**, but methyl lithium methylates it at nitrogen, presumably by an electron-transfer mechanism. Pyridine deprotonates **21/22⁺** exclusively at the β -*exo* position of the **21** ring, a factor of 6.8 slower than it α -deprotonates **22/23⁺**. Diazenium dications having **21** rings decompose in acetonitrile not containing added bases by S_N2 cleavage of the $C_\alpha-N^+$ bond, which occurs at 240 K. While **21/22⁺** is a more powerful alkylating agent for acetonitrile than is $MeOSO_2F$, **21/21⁺** reacts with acetonitrile with an activation barrier at least 4.7 kcal/mol lower. Allylic bond weakening causes the **u22** ring of **22/u22⁺** to cleave with a barrier at least 1 kcal/mol lower than that for the **21** ring of **21/22⁺**, but $C_\alpha-N^+$ cleavage of **22/22⁺** by acetonitrile has not been observed (ΔG^\ddagger is at least 3.8 kcal/mol higher than that of **21/22⁺**).

Experimental Section

General Methods. ¹H NMR spectra were taken on either a Bruker AM500 FT-NMR operating at 500.134 MHz or a Bruker WP270 FT-NMR operating at 270.13 MHz. ¹³C NMR spectra were taken on either a Bruker AM500 FT-NMR operating at 125.56 MHz or a Bruker AM360 operating at 90.556 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane, δ . High-resolution mass spectra (HRMS) were

(18) (a) Nelsen, S. F.; Landis, R. T., II. *J. Am. Chem. Soc.* 1973, 95, 2719. (b) Nelsen, S. F.; Parmelee, W. P. *J. Am. Chem. Soc.* 1980, 102, 2732. (c) A minor product also arises from abstraction of the other *exo* hydrogen, also stereoselectively.

(19) Russell, G. A.; Chang, K. Y. *J. Am. Chem. Soc.* 1965, 87, 4381.

(20) AM1 calculations get the result that the most-stable C_β -deprotonation product of **22/23⁺** is that from removal of a hydrogen from the 3 bridge, and that the three products from 2 bridge deprotonation are 5.3, 6.6, and 6.8 kcal/mol higher in ΔH_f , respectively.

obtained from the Mass Spectroscopy Center at the University of Wisconsin—Madison. CV curves were obtained from EG&G PAR's Model 273 Potentiostat/Galvanostat operated with the Model 270 Electrochemical Analysis System. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. Solvents: All deuterated solvents were used as stored over molecular sieves. CD₃CN was distilled from CaH₂. CH₃CN used for CV was fractionally distilled from B₂O₃ prior to use, and that used for oxidation reactions was fractionally distilled from P₂O₅, deaerated with Ar, and passed through active neutral alumina oxide prior to use. Et₂O and tetrahydrofuran were fractionally distilled from purple sodium benzophenone ketyl under N₂ immediately prior to use. Dimethylformamide was vacuum distilled from P₂O₅ or CaH₂ after predrying over molecular sieves. Methylene chloride was distilled from either CaH₂ or P₂O₅ prior to use. Pentane was distilled from CaH₂. Pyridine and trimethylamine were distilled from CaH₂ and stored over molecular sieves.

NMR Spectra of Diazenium Dications. Dications 22/22²⁺ ^{3a} and 22/23²⁺ ^{6b} were isolated, and their NMR spectra were taken at room temperature. The other hydrazines were oxidized with excess NOPF₆ at about 240 K in CD₃CN, and ¹H and ¹³C NMR spectra were taken at 240 K. ¹H NMR chemical shifts are reported in δ using the solvent peak at 1.93 ppm as internal standard, and ¹³C NMR chemical shifts are reported in δ using the solvent peak at 1.3 ppm.

21/22²⁺: ¹H 1.76–1.78 (m, 2H), 1.92–1.94 (m, 2H), 2.16–2.18 (m, 2H), 2.65 (d, J = 12.5 Hz, 1H), 2.69–2.70 (m, 2H), 2.75–2.77 (m, 2H), 2.86–2.90 (m, 1H), 2.98–3.01 (m, 2H), 6.19 (br s, 2H), 6.43 (br s, 2H); ¹³C 30.01, 30.12, 33.18, 50.49, 76.84, 89.78.

22/22²⁺: ^{3a} ¹H 2.08–2.13 (m, 8H), 2.70–2.76 (m, 8H), 6.23 (br s, 4H); ¹³C 30.31, 81.45.

21/23²⁺: ¹H 1.59 (m, 1H), 1.78 (m, 1H), 2.14–2.26 (m, 6H), 2.56–2.59 (m, 3H), 2.79–2.81 (m, 3H), 3.10–3.13 (m, 2H), 5.87 (br s, 2H), 6.31 (br s, 2H); ¹³C 20.02, 25.29, 26.88, 30.66, 51.01, 75.59, 91.70.

22/23²⁺: ¹H 1.88–1.93 (m, 1H), 1.94–2.01 (m, 2H), 2.14–2.20 (m, 4H), 2.29–2.35 (m, 3H), 2.56–2.58 (m, 2H), 2.72–2.74 (m, 2H), 2.81–2.86 (m, 4H), 5.90 (br s, 2H), 6.17 (br s, 2H); ¹³C 20.61, 25.53, 25.93, 30.55, 31.70, 81.85, 84.11.

22/24²⁺: NMR data were recorded from mixture of 22/24²⁺ and 24. ¹H: 1.8–2.9 (complex, signals were obscured by hydrogens of 24), 5.91 (br s, 2H), 6.09 (br s, 2H); ¹³C 24.22 (br), 24.89, 29.33, 30.52, 45.23 (br), 81.63, 82.46. Broadened signals at 45.23 and 24.22 probably correspond to carbons of the tetramethylene bridge, undergoing conformational change at an intermediate rate at 240 K.

21/u23²⁺: ¹H 1.53 (ddd, J = 16.0, 13.0, 5.0 Hz, 2H), 1.65–1.68 (m, 1H), 1.84–1.92 (m, 1H), 2.12, 2.19 (br dtd, J = 16.0, 4.5, 2.0 Hz, 2H), 2.20–2.22 (m, 2H), 2.59, (d, J = 12.0 Hz, 1H), 2.68 (br d, J = 12.0 Hz, 1H), 3.13–3.15 (m, 2H), 6.27 (br s, 2H), 6.40 (br dt, J = 5.50, 3.0 Hz, 2H), 6.76 (t, J = 7.0 Hz, 2H); ¹³C 20.00, 20.15, 30.65, 52.91, 76.69, 91.07, 125.62.

22/u22²⁺: ¹H 1.5–2.8 (m), 6.10 (br s, 2H), 6.16 (br s, 2H), 6.91 (t, J = 3.4 Hz, 2H); ¹³C 29.56, 30.05, 30.21, 80.19, 82.09, 129.49.

22/u23²⁺: ¹H 1.78–1.79 (m, 1H), 1.83 (dd, J = 16.0, 4.3 Hz, 1H), 1.94–1.98 (m, 4H), 2.18–2.24 (m, 4H), 2.67–2.69 (m, 2H), 2.86–2.88 (m, 2H), 6.20 (br s, 2H), 6.39 (br dt, J = 6.2, 3.5 Hz, 2H), 6.78 (t, J = 3.5 Hz, 2H); ¹³C 20.13, 20.63, 30.37, 32.15, 82.18, 82.68, 125.67.

Decomposition of 21/22²⁺. To a solution of 21/22²⁺ (25.2 mg, 0.142 mmol) in 0.1 mL of CD₃CN in an NMR tube was added a solution of NOPF₆ (84.0 mg, 96%, 0.460 mmol) in 0.3 mL CD₃CN at 0 °C under Ar. NMR spectra showed an approximately 1:1 mixture of diazenium cation derivatives 3 and 4. ¹H NMR for 3: 1.5–2.8 (m), 4.8 (m, 1H), 5.3 (br, 1H), 5.6 (m, 1H), 5.8 (br, 1H); for 4: 1.5–2.8 (m), 4.4 (q, J = 9.2 Hz, 1H), 5.3 (br, 1H), 5.4 (m, 1H), 5.8 (br, 1H); ¹³C NMR δ_c for 3: 23.73, 23.95, 25.83, 26.20, 29.81, 30.85, 35.89, 58.42, 69.88, 70.61, 78.96; for 4: 21.86, 22.02, 24.07, 24.31, 28.09, 28.74, 34.03, 50.49, 67.67, 68.26, 77.81. The ratio of 3 to 4 is dependent upon the dryness of solvent, and 3 was completely hydrolyzed to 4 by addition of a few drops of D₂O. ¹H NMR for 4: 1.40–1.49 (m, 2H), 1.51–1.58 (m, 2H), 1.65–1.69 (m, 1H), 1.88–1.95 (m, 1H), 1.98–2.03 (m, 1H), 2.10 (ddd, J = 14.8, 14.8, 8.0 Hz, 1H), 2.19 (m, 1H), 2.52 (ddd, J = 15.0, 8.0, 4.5 Hz, 1H), 4.44 (sextet, J = 6.5 Hz, 1H), 5.34 (br, m, 1H), 5.47, (septet, J = 3.5 Hz, 1H), 5.81 (br, s, 1H).

Decomposition of 21/22²⁺. A solution of NOPF₆ (750.0 mg, 96%, 4.11 mmol) in 10 mL of CH₃CN was added to a solution of 21/22²⁺ (350.0 mg, 1.97 mmol) in 10 mL CH₃CN at –30 °C *via* cannula. The resulting solution was stirred at room temperature for 30 min and solvent removed in a stream of Ar. The residue was stirred with 20 mL of 10% NaOH for 30 min. The aqueous solution was extracted with CH₂Cl₂ (5 × 20 mL), and the organic layer was dried over MgSO₄, filtered, and concentrated. Kugelrohr distillation gave 2 at 35 °C/0.3 mmHg (184.2 mg, 85.0%) and 7 at 130 °C/0.3 mmHg (47.2 mg, 17.0%), NMR as reported below.

3-(Acetylamino)cyclopentanone (7). A solution of 2-cyclopentanone (50 mL, d = 0.980, 0.597 mmol) in liquid ammonia (20 mL) was refluxed for 5 h under N₂ and was further stirred at room temperature for 3 h. The excess NH₃ was evaporated and the residue dissolved in acetic anhydride (5 mL) at 0 °C under N₂. After stirring for 1 h at 0 °C, the unreacted cyclopentanone and solvent were pumped away, and product was isolated by Kugelrohr distillation at 130 °C/0.2–0.3 mmHg: 15.3 mg (18.2%) of a white solid, mp 101–102 °C; IR (cm⁻¹) 1745, 1673; ¹H NMR (CDCl₃) δ 1.87 (m, 1H), 1.99 (s, 3H), 2.10 (dd, J = 18.5, 7.6 Hz, 1H), 2.26 (m, 1H), 2.39 (m, 2H), 2.66 (dd, J = 18.5, 6.9 Hz, 1H), 4.55 (m, 1H), 6.08 (br, 1H); ¹³C NMR (CDCl₃) δ_c 23.26, 29.75, 37.13, 44.95, 47.88, 142.96, 169.96; HRMS calcd for C₇H₁₁NO₂ 141.0789, found 141.0774.

2-(3'-Cyclopentenyl)-2,3-diazabicyclo[2.2.2]oct-2-ene Cation (6) Tetrafluoroborate and Iminium Ions 8 and 9. To a mixture of of 22 azo compound 2^{3a} (43.1 mg, 0.391 mmol) and AgBF₄ (79.1 mg of 98%, 0.398 mmol) in 5 mL of CH₂Cl₂ was added freshly prepared 3-bromocyclopentene²¹ (60 mg, 0.408 mmol) at –30 °C under Ar, immediately producing a yellowish solid (AgBr). After stirring at –30 °C for 30 min, AgBr was filtered off and ether (~20 mL) added slowly to precipitate the product. After washing with ether (3 × 10 mL) and drying *in vacuo* for 3 h, 45.1 mg (43.6%) of a white solid was obtained, which became orange upon exposure to air. NMR data in CD₃CN showed that 6 is not stable, slowly isomerizing to iminium ions 8 and 9 in a ratio of 2.2:1 (or 1:2.2). ¹H NMR δ (CD₃CN) δ : 1.43–1.62 (m, 4H), 2.10–2.29 (m, 4H), 2.50–2.62 (m, 4H), 5.32 (br, s, 1H), 5.73 (m, 1H), 5.81–5.97 (br, m, 2H), 6.50 (br, m, 1H); ¹³C NMR (a mixture of 6 and 8/9 in CD₃CN, 125.56 MHz) δ_c : 23.53, 23.74, 26.08, 26.22, 28.51, 32.68, 67.13, 69.24, 87.40, 125.18, 145.06; D₂O was added to ensure the complete isomerization of 6 to 8/9. ¹H NMR: δ (mixture of 8/9) major isomer 1.85–2.19 (complex, the signals for the two species are badly overlapped), 2.83–2.86 (br, m, 2H), 2.91–2.93 (br, m, 2H), 3.50–3.53 (br, m, 1H), 4.58 (sept, J = 1.76 Hz, 1H), 6.70 (dt, J = 5.8, 2.0 Hz, 1H), 7.46 (dt, J = 5.8, 2.7 Hz, 1H); minor 1.85–2.19 (complex, the signals for the two species are badly overlapped), 2.86–2.87 (br, m, 2H), 2.92–2.97 (br, m, 2H), 3.44–3.46 (br, m, 1H), 4.26 (sept, J = 1.8 Hz, 1H), 6.76 (dt, J = 5.7, 2.0 Hz, 1H), 7.58 (dt, J = 5.7, 2.4 Hz, 1H); ¹³C NMR δ_c major isomer 25.01, 25.43, 30.92, 33.15, 49.20, 57.14, 125.09, 164.50, 172.95; minor 24.56, 24.90, 30.14, 33.39, 49.03, 56.92, 125.87, 167.13, 173.44.

2-(4'-Cyclopentyl)-2,3-diazabicyclo[2.2.2]oct-2-ene Cation (5) Tetrafluoroborate. Freshly prepared 4-bromocyclopentene²¹ (60 mg, ~0.408 mmol) was added to a mixture of 22 azo compound 2 (33.6 mg, 0.305 mmol) and AgBF₄ (~65 mg, 98%, 0.327 mmol) in 5 mL of CH₂Cl₂ at –78 °C under Ar by syringe. The solution became cloudy, and after stirring for 2.5 h at –78 °C the yellow precipitate was filtered through Celite under Ar and the filtrate concentrated. The residue was dried *in vacuo* 1 h, and NMR showed that a mixture of 5 and 6 with ~20% of iminium ions 8/9 in a ratio 5:6:8/9 of ~1:1.5:0.6 was produced. ¹H NMR δ (of the mixture, CD₃CN) for 5: 1.2–3.0 (complex, all signals for the four cations are badly overlapped), 5.24, (br, s, 1H), 5.74–5.75 (br, m, 1H), 5.86–5.88 (m, 1H), 5.91–5.92 (m, 1H), 6.48–6.51 (m, 1H); data for 6 and 8/9 are consistent with those reported in the previous experiment. ¹³C NMR for 5, δ_c : 22.01, 26.23, 37.69, 62.68, 69.18, 79.51, 128.71; data for 6 and 8/9 are consistent with those reported in previous experiment.

Reaction of 21/22²⁺ with DMF-*d*₇. A solution of 21/22 (14.0 mg) in 0.4 mL DMF-*d*₇ was added with a solution of NOPF₆

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(excess) in 0.2 mL of DMF-*d*₇ at 240 K. NMR showed that a very clean product we assign as 10-*d*₇⁺ was generated: ¹H NMR (DMF-*d*₇) δ 1.62–1.68 (m, 2H), 1.81–1.86 (m, 2H), 2.22–2.35 (m, 6H), 2.45–2.52 (m, 1H), 2.65–2.73 (m, 1H), 2.84–2.95 (m, 2H), 5.45 (br, quintet, *J* = 2.0 Hz, 1H), 5.72 (br, t, *J* = 4.0 Hz), 5.92–5.94 (m, 2H); ¹³C NMR (DMF-*d*₇) δ, 23.27, 23.36, 25.34, 25.52, 28.02, 31.36, 37.08, 68.71, 69.52, 78.63, 90.54. Upon addition of K₂CO₃ of D₂O solution, the 10-*d*₇⁺ spectrum disappeared, and a mixture of a new species showing four methine protons at 5.85 (br, s, 1H), 5.72 (m, 1H), 5.65 (br, 1H), and 5.40 (m, 1H) δ, which we think is an isomer, and about 40% of rearranged elimination products 8 and 9 were observed.

Decomposition of 21/22²⁺ with DMF in CD₃CN. Dication 21/22²⁺ (0.056 mmol) was generated in CD₃CN at 240 K by NOPF₆. DMF was added into the solution at 240 K and NMR spectra were taken after 4, 16, 40, and 50 h. NMR spectra showed the principal product was 10, in at least 10:1 excess over 3 + 4.

2-Azonias-7-azapentacyclo[6.2.2.1^{3,4}.0^{2,7}.0^{2,4}]tridecane (11⁺) Hexafluorophosphate. Dication 21/22²⁺ (0.112 mmol) was generated in an NMR tube in CD₃CN by excess NOPF₆ at 240 K. Pyridine was then added at 240 K and NMR showed 11⁺ was produced: ¹H NMR (CD₃CN) 1.65–1.70 (m, 2H), 1.75–2.00 (m, 8H), 2.10–2.30 (m, 2H), 3.42 (br m, 1H), 3.88 (br m, 1H), 3.96 (s, 2H), 4.03 (s, 1H); ¹³C NMR (CD₃CN) δ, 24.18, 26.32, 33.54, 45.08, 51.05(1 C), 55.44(1 C), 56.35(1 C). 11⁺ rearranges to the iminium tautomer of 5 upon warming. ¹³C NMR (CD₃CN, 125.56 MHz) δ: 23.43, 26.08, 37.51, 68.94, 79.29, 128.55.

Decomposition of 21/21²⁺. A solution of 21/21²⁺ was generated from 21/21^{3b} in CD₃CN at 240 K by excess NOPF₆ under Ar. NMR was immediately taken at 240 K which showed no dication, but instead its decomposition products 13 and 14. ¹H NMR (CD₃CN) δ for 13: 1.3–2.8 (complex, signals were badly overlapped with those of 14⁺), 4.85 (br, s, 1H), 5.4 (br, m, 1H), 5.60 (br, s, 1H), 5.81 (br, s, 1H). For 14: 1.3–2.8 (complex, signals badly overlapped), 4.40 (sextet, *J* = 6.8 Hz, 1H), 5.28 (br, m, 1H), 5.57 (br, s, 1H), 5.79 (br, s, 1H). ¹³C NMR of these mixtures was not taken. For 14 (after D₂O addition): ¹³C NMR (CD₃CN) δ, 23.67, 24.76, 30.37, 30.47, 35.77, 46.32, 72.88, 81.52, 82.18.

Decomposition of 21/23²⁺. Dication 21/23²⁺ generated from 21/23^{3b} at 240 K by reaction with excess NOPF₆ in CD₃CN and slowly decomposed to 15 through the acetonitrile adduct. 15 showed the characteristic ¹H-NMR signals for bridgehead and other two methine protons: 4.4 (m, 1H), 5.0 (br, s, 1H), 5.35 (br, m, 1H), 5.6 (br, s, 1H).

Decomposition of 22/u22²⁺. A solution of dication was generated by oxidation of 22/22^{3a} with excess NOPF₆ in CD₃CN at 240 K, and D₂O was added after dication decomposition was complete. NMR showed that two major diazenium cation isomers, tentatively assigned as 18 and 19, were produced. ¹³C NMR (CD₃CN) δ, 23.61, 23.67, 24.71, 25.93, 25.95, 26.30, 47.37, 68.24, 69.83, 75.44, 124.23, 135.52, 176.0 (and 23.51, 23.70, 24.14, 25.90, 26.05, 26.09, 46.76, 68.69, 69.83, 74.07, 124.36, 135.22, 175.86); ¹H NMR (CD₃CN) δ 1.5–2.5 (complex), 4.52 (m, 1H), 4.60 (m, 1H), 5.3–6.2 (complex). The solution was concentrated and the residue was stirred with 10% NaOH for 5 min. Extraction with CH₂Cl₂, drying, and concentration gave 22 azo compound 2.

Decomposition of 21/u23²⁺. Dication 21/u23²⁺ generated from 21/u23^{3b} in CD₃CN was allowed to decompose at room temperature. D₂O was added to hydrolyze the remaining nitrilium adduct, and the product observed by NMR was assigned as 20 from its NMR spectra: ¹H NMR (CD₃CN) δ 1.4–2.5 (complex), 4.3 (m, 1H), 5.2–5.8 (m, complex), 6.5 (s, 2H); ¹³C NMR (CD₃CN) δ, 17.42, 20.40, 20.81, 29.79, 30.56, 36.84, 52.06, 72.17, 74.79, 79.51, 124.76, 127.33, 174.34. The solution was concentrated, stirred with 10% NaOH for 5 min, and extracted with CH₂Cl₂, and the organic layer was dried, filtered, and concentrated; the NMR spectrum showed 1,3-cycloheptadiene.

Decomposition of 22/23²⁺. A solution of 22/23²⁺ (41.6 mg, 0.084 mmol) in 0.4 mL of CD₃CN was added with saturated K₂CO₃/D₂O solution. NMR indicated that a trialkyldiazenium cation with three methine hydrogens we assign as 21⁺ was produced: ¹H NMR δ 1.50–2.50 (complex) 4.9 (br, t, 1H), 5.4 (br, s, 1H), 5.8 (br, s, 1H). The solution was concentrated and the residue was stirred with 10% NaOH (5 mL) for 5 min. The resulting solution was extracted with CH₂Cl₂ (3 × 10 mL), and the organic layer was dried, filtered, and concentrated. NMR of crude material showed 22 azo compound 2 and 1,4-cycloheptanedione in a ratio of 1:1. 1,4-cycloheptanedione was isolated by kugelrohr distillation as 1.9 mg (18%) of a colorless oil, ¹H NMR²² (CDCl₃) δ 1.96–2.00 (m, 2H), 2.64 (s, 4H), 2.67–2.70 (m, 4H); ¹³C NMR (CDCl₃) δ, 20.13, 37.92, 43.57, 210.26.

2-Methyl-2-azonia-7-azatetracyclo[6.2.2.2.3^{0,2,7}]-tetradecane (28) Hexafluorophosphate. A mixture of 22/22²⁺ (60.8 mg, 0.126 mmol) and 5 mL of THF was treated 1.4 M MeLi in ether (0.25 mL, 0.35 mmol) at –78 °C under N₂. The solution became yellow, and undissolved dication gradually disappeared. After stirring 2 h at –78 °C under N₂, the solution temperature was raised to 0 °C and stirred for another 4 h. After quenching with H₂O, the organic phase was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The organic layers were combined, dried over Na₂SO₄, and concentrated to give 28 as a yellow solid, 24.2 mg, 54.6%, having the same ¹H NMR as an authentic sample prepared by methylation of 22/22.²³

3-Cyano-2,9-diazabicyclo[8.2.2.2^{3,8}.0^{2,9}]hexadecane (25). A mixture of 24PF₆^{6b} (11.6 mg, 0.306 mmol) and KCN (~100 mg) in 10 mL of CH₃CN/H₂O (5:1) was stirred at 0 °C under N₂ for 5 h. Excess KCN was filtered, the yellow filtrate was extracted with 3 × 10 mL portions of pentane, and the organic layer was dried over MgSO₄, filtered, and concentrated. Kugelrohr distillation at 70 °C/0.25 mmHg gave 43.6 mg (58.1%) of slightly yellow oil: ¹H NMR (CDCl₃) 1.36–1.47 (m, 2H), 1.50–1.60 (m, 4H), 1.78–1.97 (m, 4H), 2.00–2.12 (m, 6H), 2.24–2.32 (m, 3H), 2.5–2.62 (m, 1H), 2.63 (br, s, 1H), 3.09 (dd, *J* = 10.1, 3.2 Hz, 1H), 3.19 (br, s, 1H); ¹³C NMR (CDCl₃, 125.56 MHz) δ, 24.61 (br), 25.69, (br), 26.40 (br), 26.49 (br, 2CH₂), 26.56, 27.43, 30.98, 34.90, 41.23, 52.31, 55.13, 58.66, 59.80, 123.35; HRMS calcd for C₁₅H₂₃N₃ 245.1892, found 245.1891.

2,9-Diazabicyclo[8.2.2.2^{3,8}.0^{2,9}]hexadeca-2,15-diene Hexafluorophosphate Cation (26). A solution of 22/u24^{6b} in CH₃CN was oxidized with 2 equiv of NOPF₆ at –35 °C under Ar, and ether was added to deprotonate the dication and precipitate the product, which was washed with ether several times: ¹H NMR (CD₃CN) δ 1.3–2.3 (complex), 2.7 (ddd, 1H), 3.0 (m, 1H), 3.8 (br, s, 1H), 4.2 (br, s, 1H), 4.7 (br, s, 1H), 6.5 (m, 2H); ¹³C NMR (CD₃CN, 125.56 MHz) δ, 24.00, 26.03, 26.11, 26.49, 28.13, 28.73, 33.14, 33.33, 35.68, 53.96, 56.60, 59.78, 125.74, 134.30, 171.23.

Calculations. AM1 calculations²⁴ were carried out using the VAMP programs.²⁵

Acknowledgment. We thank the National Institutes of Health for partial financial support under GM 29549, and the major instrument programs of both NIH and NSF for providing the instrumentation. We thank Dennis Evans for providing help with analysis of electrochemical data.

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