Synthesis and Decomposition of Two Cyclic (Four-Ring) Azo Compounds (Δ^1-1,2-Diazetines)

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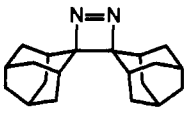
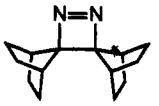
The Δ^1-1,2-diazetines **1** and **2** have been synthesized in three steps from *N*-methyltriazolinedione (MeTAD) and the olefins (adamantylideneadamantane, Ad=Ad, for **1**; 7-norbornylidene-7-norbornane for **2**). Diazetidine **3** (from Ad=Ad + MeTAD) undergoes ring expansion to a pyrazolidine derivative, **5** (subsequently converted to a novel pyrazoline, cyclic (five-ring) azo compound **6**). The structurally-related *N*-methylaminocarbonyl diazetidine **4** undergoes acid-catalyzed ring *contraction* to *N*-aminoaziridine derivative **7a**. Compound **7a** and the corresponding *N*-aminoaziridine derivative **7b** undergo oxidative ring expansion to afford diazetine **1**, accompanied by olefin (Ad=Ad). Efforts to extend this novel synthesis of diazetines to other *N*-aminoaziridines (**8**, **9a**, **9b**, **10**) were unsuccessful, affording only the deazetation product, olefin. Thermal decomposition of diazetine **1** at 137 °C in dodecane ($t_{1/2}$ = 1.5 h) proceeds by two paths: ring-opening to adamantanone azine and deazetation to the olefin Ad=Ad; azine/olefin = 1.9/1. For diazetine **2**, $k_{overall}$ is 60-fold slower than for **1** and azine/olefin = 1/14. Diazetine **1** is rapidly converted to olefin (Ad=Ad) at 25 °C by 10 mol% of $Ar_3N^{\cdot+}$ [$(p\text{-}BrC_6H_4)_3N^{\cdot+}$ SbF_6^-], thought to occur by an electron transfer chain process; diazetine **2** is inert to these conditions. Relative rates of nitrogen loss for **1**, **2**, and tetramethyldiazetine (**15c**) at 137 °C are 1:0.05:3. Some aspects of mechanism of thermal and catalyzed decomposition of diazetines are discussed.

Four-membered cyclic azo compounds (Δ^1-1,2-diazetines)[1] are a little-explored class,[2] raising several questions of mechanistic interest and posing some special problems in synthesis. We describe here the synthesis and decomposition of diazetine **1** ("adamantyl system") and diazetine **2** ("norbornyl system") and several rearrangements involving ring-contraction and ring-expansion in some small-ring heterocycles associated with the synthesis of diazetine **1**.



1

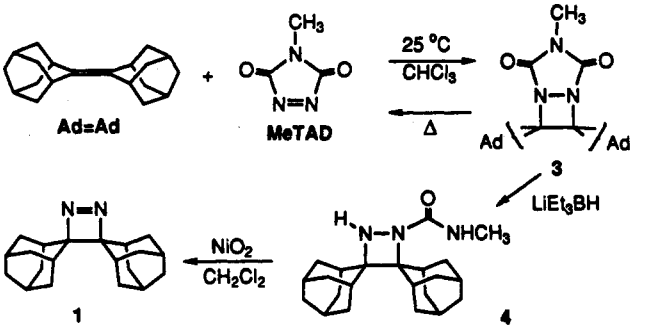


2

Results

Synthesis of Diazetine 1 (Scheme I). Reaction of *N*-methyltriazolinedione (MeTAD) with adamantylideneadamantane (Ad=Ad) affords the diazetidine derivative **3**.[3] Alkaline hydrolysis of **3** to semicarbazide **4** may be effected by carefully-controlled conditions but is complicated by thermal reversion of **3** to MeTAD and olefin (Ad=Ad). A better route to **4** was found in reaction of **3** with triethylborohydride.[4a] Reaction of **4** with nickel peroxide[4b] affords **1**. Diazetine **2** was made by the same sequence of reactions. Scheme I represents a simple three-step route to diazetines. It is, of course, limited to those olefins that do not undergo the ene reaction (the usual reaction of RTAD with olefins possessing allylic hydrogens).[5]

Scheme I



Rearrangements. A. Diazetidine 3 is converted by the action of triethyloxonium tetrafluoroborate to an isomer, assigned structure **5** on the basis of the physical data summarized in the Experimental Section (in particular, 23 lines in the ^{13}C NMR; IR carbonyl absorptions at 1750 and 1700 cm^{-1} (typical for urazoles) vs the absorptions at 1730 and 1675 cm^{-1} in the strained adduct **3**[3]) and the reactions shown in Scheme II (conversion of

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(1) Δ^1-1,2-Diazetines (IUPAC nomenclature) are 1,2-diazacyclobut-1-enes; this particular ring system is indexed by Chemical Abstracts under the name "diazete, 3,4-dihydro".

(2) (a) Rieber, N.; Alberts, J.; Lipsky, J. A.; Lemal, D. M. *J. Am Chem. Soc.* **1969**, *91*, 5668. (b) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409. (c) White, D. K.; Greene, F. D. *J. Am. Chem. Soc.* **1978**, *100*, 6760. (d) Engel, P. S.; Hayes, R. A.; Kiefer, L.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1876. (e) Pincock, J. A.; Druet, L. M. *Tetrahedron Lett.* **1980**, *21*, 3251. (f) Olsen, H. *J. Am. Chem. Soc.* **1982**, *104*, 6836. (g) Cosa, J. J.; Gsponer, H. E.; Staricco, E. H.; Vallana, C. A. *J. Chem. Soc. Faraday Trans. 1*, **1973**, *69*, 1817. (h) Wildi, E. A.; Van Engen, D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 7994. (i) Masamune, S.; Nakamura, N.; Spadaro, J. *J. Am. Chem. Soc.* **1975**, *97*, 918. (j) Timberlake, J. W.; Elder, E. S. In *Comprehensive Heterocyclic Chemistry*; Lwowski, W., Ed.; Pergamon Press: Oxford, 1984; Vol. 7, Part 5, p 449. (k) Richter, R.; Ulrich, H. In *The Chemistry of Heterocyclic Compounds; Small Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1983; Vol. 42, Part 2, p 443. (l) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

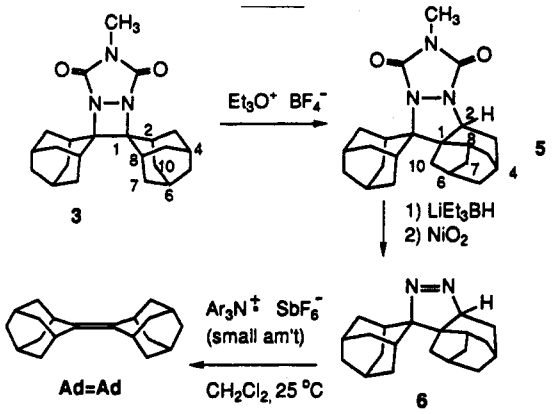
(3) (a) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384. (b) Cheng, C. C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; *J. Org. Chem.* **1984**, *49*, 2910.

(4) (a) Triethylborohydride effects the reduction of an *N,N*-disubstituted amide to alcohol and secondary amine rather than reduction of the carbonyl to methylene. Brown, H. C.; Kim, S. C. *Synthesis* **1977**, 635. (b) Dervan, P. B.; Squillacote, M. E.; Lahti, P. M.; Sylwester, A. P.; Roberts, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 1120. Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774.

(5) See ref 3 and refs cited therein.

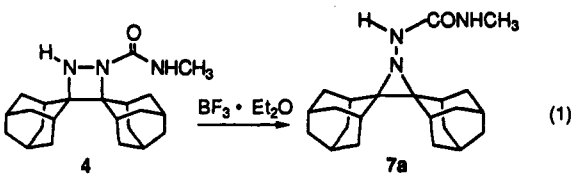
0022-3263/93/1958-5393$04.00/0 © 1993 American Chemical Society

Scheme II



5 to azo compound 6 by the reaction sequence of Scheme I and conversion of 6 to Ad=Ad by the action of (p-$BrC_6H_4)_3N^{\cdot+}$).[6]

B. Semicarbazide 4 is converted by $BF_3{\cdot}Et_2O$ (or more slowly by column chromatography on silica gel) to an isomer assigned structure **7a** (eq 1). This assignment is



(1)

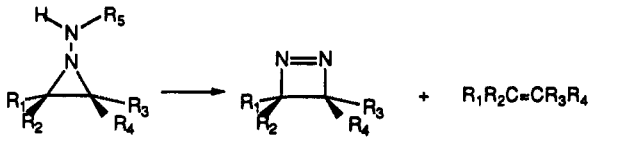
based on spectral data (^1H NMR, 2 exchangeable NH's, and an N-methyl doublet; ^{13}C NMR, 12 lines) and chemical data (see below). The 12-line ^{13}C NMR is consistent with **7a** (i.e. two equivalent 10-line adamantyl moieties) in which the aziridine nitrogen inverts slowly on the NMR time scale. Aziridines substituted at nitrogen with atoms bearing lone pair electrons are known to resist inversion about the nitrogen atom[7] (e.g. phthalimidoaziridines are configurationally stable up to 150 °C).[7b] Hydrolysis of **7a** (80% H_2SO_4, 25 °C, 5 days) led to N-aminoaziridine **7b**.

C. Effect of Oxidants on Aziridine Derivatives 7–11 (Table I). Nickel peroxide converted aziridinyl derivative **7a** to a mixture of diazetine 1 and olefin (Ad=Ad), ratio 1:1.9 (Table I). This constituted a new route to diazetines and warranted further study. N-Aminoaziridine **7b** was subjected to nickel peroxide and to *tert*-butyl hypochlorite at several temperatures. In the best case, a 50% yield of diazetine 1 was obtained by the action of *tert*-butyl hypochlorite on the N-aminoaziridine at −80 °C. We extended the study to three other N-aminoaziridines **8**, **9b**, and **10**. All three cases afforded only olefins and no diazetines (Table I).

Decomposition of Diazetines. A. Thermal (Scheme III). Diazetine 1 decomposes at 150 °C to give adamantanone azine 11 and adamantylideneadamantane (Ad=Ad). Azine is favored over olefin. The azine was shown to be stable to the decomposition conditions. The ratio of azine/olefin shows small sensitivity to solvent polarity or to temperature (solvent, azine/olefin (temp): THF, 2.9 (150 °C), 2.3 (185 °C); benzene, 3.0 (150 °C), 2.4 (185 °C); CH_3CN, 3.8 (150 °C), 4.2 (185 °C); EtOH, 9.5 (150 °C), 6.1 (185 °C)).

(6) This nonobvious transformation is taken up in Discussion.
(7) (a) Felix, D.; Eschenmoser, A. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 224. (b) Carpino, L. A.; Kirkley, R. K. *J. Am. Chem. Soc.* **1970**, *92*, 1784. (c) Brois, S. J. *Trans. N. Y. Acad. Sci.* **1969**, *31*, 931.

Table I. Effect of Oxidants on N-Aminoaziridine Derivatives



	reactant	oxidant conditions	diazetine	olefin (% yield)
7	R_1R_2C = adamantyl R_3R_4C = adamantyl			
	a, R_5 = $CONHCH_3$[a]	NiO_2[b]	1 (35)[c,d]	Ad=Ad (65)[c,d]
	b, R_5 = H	NiO_2[b]	–	Ad=Ad
	b	ROCl[e]	1 (50)[f]	Ad=Ad (30)[f]
	b	ROCl[g]	–	Ad=Ad
8	R_1, R_2, R_3, R_4 = CH_3 R_5 = H	NiO_2[h]	–	$(CH_3)_2C$=$C(CH_3)_2$
		ROCl[e]	–	$(CH_3)_2C$=$C(CH_3)_2$
9	R_1 = R_4 = Ph R_2 = R_3 = H			
	a, R_5 = $CONHCH_3$	NiO_2[h]	–	*trans*-PhCH=CHPh
	b, R_5 = H	NiO_2[h]	–	*trans*-PhCH=CHPh
	b	ROCl[e]	–	*trans*-PhCH=CHPh
10	R_1 = R_3 = Ph R_2 = R_4 = R_5 = H	NiO_2[h]	–	PhCH=CHPh cis/trans = 1/4

[a] Full structure is in eq 1. [b] CH_2Cl_2, 25 °C. [c] Yield from ^1H NMR. [d] Full structure is in Scheme I. [e] *tert*-Butyl hypochlorite, 2,6-di-*tert*-butylpyridine, CH_2Cl_2, −80 °C. [f] Yields of isolated products. [g] Same as *e* but at 25 °C. [h] CH_2Cl_2, −80 °C.

Scheme III

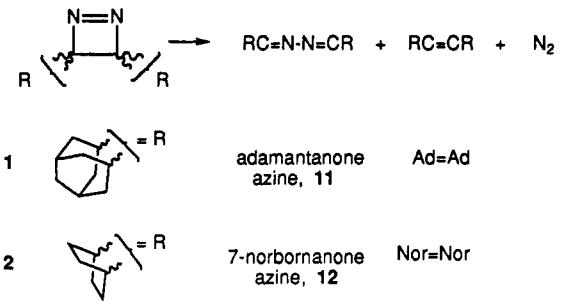


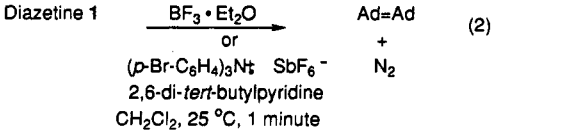
Table II. Rates of Formation of Azine and Alkene from Diazetines 1 and 2 in Dodecane at 137 °C

	rate of formation, $k \times 10^6$ s^{-1}	
diazetine	azine	alkene + N_2
1 ("adamantyl")	83	42
2 ("norbornyl")	0.1	1.3
tetramethyldiazetine[a]	–	125

[a] In diphenyl ether (see ref 2d).

Diazetine 2 ("norbornyl" system) also affords azine (7-norbornanone azine, 12)and olefin (7-norbornylidene-7-norbornane, Nor=Nor). The ratio of azine to olefin is 1:14 (137°°C, dodecane). Decomposition of diazetines 1 and 2 is cleanly first order. The rates of azine and olefin formation are summarized in Table II.

B. Catalyzed Decomposition of Diazetine 1 (eq 2). Boron trifluoride etherate effects conversion of diazetine 1 to adamantylideneadamantane (Ad=Ad) and N_2 at 25 °C. In contrast to the thermal decomposition of 1, no azine is observed.



(2)

The aminium radical cation salt $(p\text{-}BrC_6H_4)_3N^{\cdot+}SbF_6^-$ (10 mol%) also effects conversion of diazetine **1** to olefin (Ad=Ad) and N_2 (and no azine). This reaction was carried out in the presence of 2,6-di-*tert*-butylpyridine, indicating that reaction is proceeding by electron transfer and not by acid catalysis. Diazetine **2** was inert to $(p\text{-}BrC_6H_4)_3N^{\cdot+}SbF_6^-$.

Discussion

Two aspects of this work warrant further discussion: the rearrangements observed and mode of decomposition of four-membered ring azo compounds (diazetines). The former may have some bearing on the latter and is discussed first.

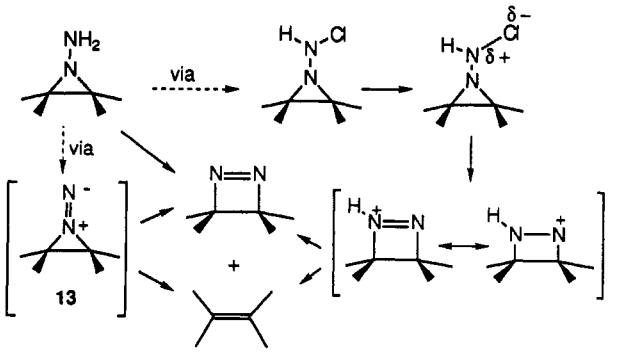
Rearrangements. The study provides some examples of ring contraction and of ring expansion.

Contraction			
four-ring	⟶	three-ring	
4	$BF_3{\cdot}Et_2O$	**7a**	(see eq 1)
Expansion			
(a) four-ring	⟶	five-ring	
3	$Et_3O^+BF_4^-$	**5**	(see Scheme II)
(b) three-ring	⟶	four-ring	
7a	NO_2, 25 °C	1 (35%)	(see Table I)
7a	*tert*-BuOCl, −80 °C	1 (50%)	(see Table I)

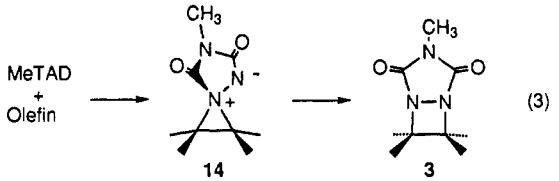
The contraction of **4** to **7a** is an isomerization, i.e., the aziridinyl compound **7a** is more stable than the diazetidinyl compound **4**. This is ascribed to the release of nonbonded interactions between the two adamantyl moieties.[8a] In the case of the closely-related diazetidine **3**, $Et_3O^+BF_6^-$ effects a ring *expansion* isomerization to **5** (Scheme II). Again, the driving force may be release of crowding of the adamantyl moieties. Both reactions involve cleavage, probably heterolysis, of a diazetidinyl C–N bond. The difference between the four-ring → three-ring contraction of **4** → **7a** and the four-ring → five-ring expansion of **3** → **5** lies in the difference and nature of the diazetidine nitrogens in **4** vs **3**; greater basicity and a hydrogen on nitrogen in **4** are the attributes leading to the four-ring to three-ring contraction. The rearrangement within an adamantyl moiety in the reaction **3** → **5** (Scheme II), adamantyl to protoadamantyl, has numerous analogies.[8b]

More surprising, perhaps, is the expansion from three-membered rings to four-membered rings (Table I, **7a** to **1**, **7b** to **1**). These expansion reactions are oxidations, not isomerizations, and are accompanied by a deazetation reaction giving olefin. The rearrangements are reminiscent of cyclopropylcarbinyl → cyclobutyl.[9] Alternatively, the reactions may proceed through a 1,1-diazene, $R_2N^+{=}N^-$,

Scheme IV



e.g. **13** in Scheme IV. It is also pertinent to point out that there is strong evidence for a three-ring → four-ring rearrangement in the formation of diazetidine **3** from MeTAD and olefin (Scheme 1, first step) by way of an aziridinium imide (**14** in eq 3).[3,10]



(3)

Application of the best conditions for the conversion of *N*-aminoaziridine **7b** → diazetine **1** to other *N*-aminoaziridines afforded only olefin (examples **8**, **9a**, **9b**, and **10** in Table I). 3,3,4,4,-Tetramethyldiazetine is a known and stable diazetine.[2b,d] Thus, this seemingly promising and simple route to diazetines has only succeeded in the case of diazetine **1**.

The stereochemistry of the oxidative deazetation of *N*-aminoaziridines has been examined previously.[7b, 11a] *trans*-2,3-Diphenyl-1-aminoaziridine afforded only *trans*-1,2-diphenylethylene (*trans*-stilbene); the cis isomer afforded a mixture of *cis*- and *trans*-stilbene that depended on conditions (97.5% cis/ 2.5% trans from lead tetraacetate, CH_2Cl_2, 0 °C;[11a] 15% cis/85% trans from manganese dioxide, CH_2Cl_2, 0°C).[7b] Under our conditions (Table I) *trans*-reactant **9b** afforded *trans*-stilbene, and *cis*-reactant **10** afforded *cis*-stilbene/*trans*-stilbene = 1/4. The possible involvement of 1,1-diazenes in these (and related) reactions has been discussed.[11,12] Also, of special note in this connection are the stereospecific conversions of *cis*-2,3-dimethylaziridine to *cis*-2-butene and the *trans*-reactant to *trans*-2-butene by difluoramine, possibly via a 1,1-diazene.[13] Rearrangements or ring expansions of 1,1-diazenes are uncommon but have been observed.[12a,14]

(8) (a) Compound **3** (Scheme I) shows severe crowding resulting in a C–C bond length of 1.61 Å for the bond connecting the two adamantyl moieties (see ref 3). This situation is also seen in the dioxetane from Ad=Ad and singlet dioxygen (Hess, J.; Vos, A. *Acta Crystallogr. Sect. B* **1977**, *33B*, 3527. See also Hoehne, G.; Schmidt, A. H.; Lechtken, P. *Tetrahedron Lett.* **1976**, 17, 3587 for thermochemical evidence on the adamantyl–adamantyl strain in the dioxetane. (b) Sinnott, M. L.; Storesund, H. J.; Whiting, M. C. *J. Chem. Soc. Chem. Commun.* **1969**, 1000. Alford, J. R.; McKervey, M. A. *ibid.* **1970**, 615; Lenoir, D.; Schleyer, P. v.R. *Ibid.* **1970**, 941. Fort, R. C., Jr., *Adamantane*, Dekker: New York, 1976; pp 172–181. Two additional patterns of rearrangement in adamantyl systems with positive charge at a C-2 position are described in Gill, G. B.; Hands, D. *Tetrahedron Lett.* **1971**, *12*, 181 and Meijer, E. W.; Kellogg, R. M. ; Wynberg, H. *J. Org. Chem.* **1982**, *47*, 2005.

(9) See Myhre, P. C.; Webb, G. G.; Yannoni, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 8992 and Brittain, W. J.; Squillacote, M. E.; Roberts, J. D. *Ibid.* **1984**, *106*, 7280 and refs cited therein.

(10) Nelson, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 5548.

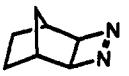
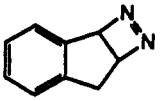
(11) (a) Felix, D.; Müller, R. K.; Horn, U.; Joos, R.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1972**, *55*, 1276. (b) Concerning thermolysis of 1-(acylamino)aziridines, see Carpino, L. A.; Padykula, R. E.; Lee, S.-N.; Han, G. Y.; Kirkley, R. K. *J. Org. Chem.* **1988**, *53*, 6047. (c) Carpino, L. A.; Padykula, R. E. *J. Chem. Soc. Chem. Commun.* **1986**, 747.

(12) (a) Lemal, D. M. In *Nitrenes*; Lwowski, W., Ed.; Interscience: New York, 1970; Chapter 10. (b) Hinsberg, W. D., III; Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 766.

(13) Freeman, J. P.; Graham, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 1761.

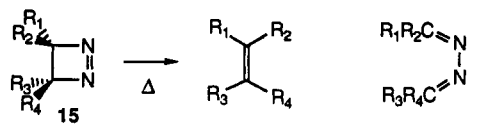
(14) Adams, D. J. C.; Bradbury, S.; Howell, D. C.; Keating, M.; Rees, C. W.; Storr, R. C. *J. Chem. Soc. Chem. Commun.* **1971**, 828. See also Rees, C. W.; Yelland, M. *ibid.* **1969**, 377. (b) Baumgarten, H. E.; Creger, P. L.; Zey, R. L. *J. Am. Chem. Soc.* **1960**, 82, 3977.

Table III. Conversion of 1,2-Diazetines to Olefin and Dinitrogen

compd no.	diazetine structure	rel k (137 °C)	$\Delta G^{\ddagger}$ (137 °C) (kcal/mol)	ref
1 ("adamantyl")		1[a]	32.5	this work[b]
2 ("norbornyl")		0.03[a]	35.2	this work[b]
15c (tetramethyl)		3[c]	31.6[c]	2d
15d (tetrafluoro)		1[d]	32.5[e]	2g
17		1[d]	32.5[f]	2a
		0.8[g]	32.7[h]	2f
18		7[d]	30.9[i]	2a
19		3[j,k]	31.6[l]	2h
20		8×10^5 [m]	21.4[n]	2e

[a] In dodecane; $k_{137\ °C}$ is 4.20×10^{-5} s^{-1} for diazetine 1 (Table II). [b] See Table II. [c] In diphenyl ether, $\Delta H^{\ddagger}$ = 31.7 kcal/mol, $\Delta S^{\ddagger}$ = 0.3 eu. [d] Gas phase. [e] $\Delta H^{\ddagger}$ = 38 kcal/mol, $\Delta S^{\ddagger}$ = 13.5 eu. [f] $\Delta H^{\ddagger}$ = 33.7 kcal/mol, $\Delta S^{\ddagger}$ = 3.0 eu. [g] In isooctane. [h] $\Delta H^{\ddagger}$ = 35.3 kcal/mol, $\Delta S^{\ddagger}$ = 6.4 eu. [i] $\Delta H^{\ddagger}$ = 33.1 kcal/mol, $\Delta S^{\ddagger}$ = 5.4 eu. [j] In cyclooctane. [k] Minor path; major path is k_{C-C} (see text and ref 2h). [l] $\Delta H^{\ddagger}$ = 33.0 kcal/mol, $\Delta S^{\ddagger}$ = 3.5 eu. [m] In benzene. [n] $\Delta H^{\ddagger}$ = 25 kcal/mol, $\Delta S^{\ddagger}$ = 10.8 eu.

Scheme V



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15a $R_1 = R_3 = CH_3$, $R_2 = R_4 = C_2H_5$	√	X
15b $R_1 = R_4 = CH_3$, $R_2 = R_3 = C_2H_5$	√	X

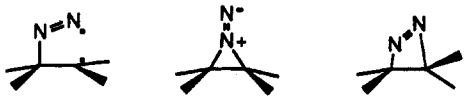
Intramolecular trapping of a 1,1-diazene by a suitably-positioned alkene is also known.[15]

Decomposition of Diazetines. Diazetines 1 and 2 provide three comparisons of interest: (a) C–C vs C–N cleavage (ring-opening to azine vs loss of dinitrogen), (b) relative rates of thermal deazetation, and (c) thermal vs "electron-transfer" decomposition (and acid-catalyzed decomposition) of diazetine 1.

C–C vs C–N Cleavage (ring-opening to azine vs loss of dinitrogen). In general, C–C cleavage (Scheme III and Table II) does not compete with C–N cleavage in decomposition of diazetines. Two special cases are diazetines 19 (shown in Table III) and 1. In compound 19, k_{C-C}/k_{C-N} is approximately 9/1 at 120 °C, ring strain resulting in the cleavage of the central C–C bond in spite of what must be a disrotatory motion. In 1, serious crowding of H's at the adamantyl–adamantyl interface[3,8a] aids in the cleavage of the C–C bond, resulting in azine formation. (The question of concerted (conrotatory) ring-opening vs cleavage to a "diradicaloid" species is not answered by this study. However, the highly-substituted nature of C_3 and C_4 of the 1,2-diazacyclobut-1-ene moiety in 1 points to added difficulty for concerted (conrotatory) ring-opening).[16]

Thermal Deazetation of Diazetines. Three principal observations from previous studies are (a) deazetation occurs with clean cis loss of N_2 (Scheme V),[2c] (b) four-membered cyclic azo compounds (Δ^1-1,2-diazetines) are considerably more resistant to decomposition than expected from analysis of ring strain factors and rates of decomposition of other azo compounds,[2d] and (c) aryl substitution (diazetine 20 in Table III) greatly increases the rate of deazetation.[2e]

The thermal stability of diazetines in all likelihood is associated with the orbital symmetry-forbidden character of a "2s + 2s" retrocycloaddition.[2a] The most probable mode of deazetation of 1,2-diazetines is via rate-determining homolytic cleavage of one C–N bond (16-i) followed by fragmentation to olefin and dinitrogen. Two other mechanistic possibilities are rate-determining isomerization of 1,2-diazetine to the corresponding 1,1-diazene (16-ii) followed by loss of dinitrogen, and "2s + 2a" retrocycloaddition (16-iii).



16-I 16-II 16-III

Diazetines 1, 15c (tetramethyl), 15d (tetrafluoro), 17, 18, and 19 are rather similar in rate of deazetation; 2 is only a factor of 30 slower than 1, and 20 is several powers of 10 faster.[17] The slowness of 2 is probably associated with the unusual nature of the 7-position of the norbornyl system:[17,18] the σ molecular orbital situation at the bridgehead carbons (C_1 and C_4) does not provide the stabilization ("hyperconjugative") to a C-7 radical or cation that *is* provided to the usual alkyl radical or cation (e.g., in dimethylcarbinyl or 2-adamantyl). The similarity in rate of decomposition of 1 and 17 argues strongly against a transition state for deazetation that resembles a 1,1-diazene (16-ii); such a transition state would represent strain decrease for 1 and strain increase for 17 with the resulting expectation of a much greater rate of deazetation for 1 than for 17.

Another diazetine of interest is 2,3-diazabicyclo-[2.2.0]hexa-2,5-diene,[2i] "Dewar Pyridazine", a probable

(15) Hoesch, L.; Egger, N.; Dreiding, A. S. *Helv. Chim. Acta* **1978**, *61*, 795.

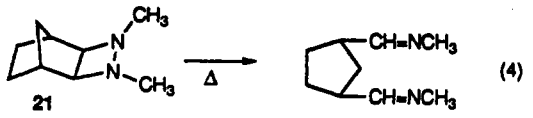
(16) Criegee, R.; Seebach, D.; Winter, R. E.; Börretzen, B.; Brune, H. A. *Chem. Ber.* **1965**, *98*, 2339.

(17) Hoffmann, R.; Mollère, P. D.; Heilbronner, E. *J. Am. Chem. Soc.* **1973**, *95*, 4860.

(18) Nelsen, S. F.; Kapp, D. L. *J. Org. Chem.* **1985**, *50*, 1339.

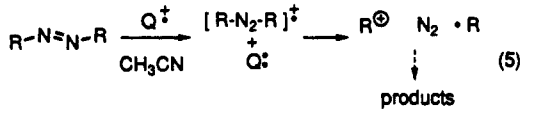
intermediate (not observed) in the oxidation of the corresponding hydrazo compound at −70 °C. It loses dinitrogen at −70 °C affording cyclobutadiene which is rapidly trapped (by self-trapping dimerization or by added dienophiles). Its rate of loss of dinitrogen *at −70 °C* (probably in a concerted 2s + 2s + 2s process) is roughly 10,000 times faster than the rate of loss of dinitrogen from *1 at 137 °C*.[19]

Concerning C–N cleavage, another comparison of interest is **17** vs diazetidine **21**.[20a] The latter decomposes much more slowly than **17** and affords the diimine with no evidence of C–N cleavage (eq 4). From the conditions needed to effect decomposition of **21** one can estimate a $\Delta G^{\ddagger}$ at 400 °C for eq 4 of 40 kcal/mol, i.e. C–N cleavage in **17** is at least 10 kcal/mol easier than a C–N cleavage (unobserved) in **21**.[20b]



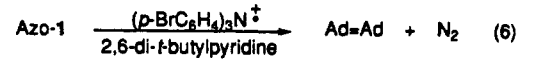
(4)

Catalyzed Decomposition of 1 and 2. Strong oxidizing agents may effect the decomposition of azo compounds (eq 5).[21]

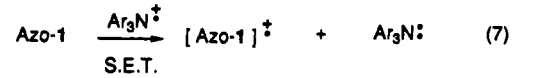


(5)

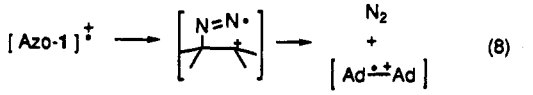
We have briefly examined the effect of these conditions (ratio of triarylaminium radical cation salt to azo compound = 1 to 10) on diazetines **1**, **2**, and azo compound **6**. A huge increase in rate of deazetation of **1** relative to the rate of thermal deazetation is observed; no azine was found (eq 6). The probable mechanism is an electron transfer chain mechanism (eqs 7–9).[22]



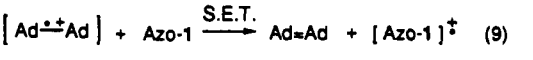
(6)



(7)



(8)



(9)

The unreactivity of **2** under these conditions may be attributed to the difficulty of [azo-**2**]$^{+}$ to undergo C–N cleavage to a 7-norbornyl cation[17] (see earlier discussion in this paper concerning instability of this species) or to undergo fragmentation to dinitrogen and the radical cation of norbornylidenenorbornane (electrochemical data indicate that one-electron oxidation of Nor=Nor is much more costly than oxidation of Ad=Ad ($\Delta\Delta E_o$ = 0.45 V, an energy difference of 10.4 kcal/mol).[19]

Pyrazoline **6** (Scheme II) was also subjected to the conditions of eq 6, resulting in deazetation and formation of Ad=Ad. The radical cation of azo-**6** is well-aligned for C–N cleavage and rearrangement to the radical cation of adamantylideneadamantane with concomitant loss of N_2.

Experimental Section

Semicarbazide 4. To a solution of lithium triethylborohydride (9.25 mL of a 1 M THF solution; 9.25 mmol) was added the diazetidine adduct **3**[3] (1.486 g; 3.395 mmol) in 15 mL of THF over 25 min *via* a syringe pump. A precipitate formed after 30 min and the mixture was stirred a further 4 h. Water was added dropwise until the precipitate redissolved. The reaction mixture was diluted with 300 mL of water, giving 1.204 g (87%) of **4** as a white solid. This material could be carried on in the next step without further purification. Recrystallization from CH_2Cl_2/hexane (25 °C to −78 °C) gave analytically pure semicarbazide **4**: mp 212–215 °C (dec); ^{1}H NMR 6.42 (br m, 1H), 5.02 (s, 1H), 3.62 (br s, 1H), 2.78 (d, 3H), 2.66–1.50 (m, 27H), (when D_2O is added, the resonances at 6.42 and 5.02 ppm disappear and the doublet at 2.78 ppm collapses to a singlet); ^{13}C NMR 163.84, 89.45, 76.18, 38.27, 38.17, 35.35, 34.71, 34.47, 33.73, 33.41, 33.04, 32.78, 31.64, 31.56, 31.03, 30.81, 30.50, 27.45, 27.12, 27.07, 26.86, 26.33. Anal. Calcd for $C_{33}H_{33}N_3O$: C, 74.32; H, 9.36; N, 11.82. Found: C, 74.15; H, 9.34; N, 11.92.

Semicarbazide 4 from Hydrolysis of Diazetidine 3. To a solution of potassium *tert*-butoxide (0.535 g; 4.77 mmol) and water (60 μL;3.33 mmol) in 12.0 mL of DMSO (deoxygenated with a nitrogen stream for 30 min) was added the adduct **3** (61 mg; 0.160 mmol) in one portion. The mixture was stirred for 50 min and then poured into 24 mL of ice-cold water. A white precipitate was collected after 24 h, washed with water and dried at high vacuum. The yield of slightly impure semicarbazide **4**, identified by ^{1}H NMR, was 33 mg (58%), mp 170–180 °C (dec).

Diazetine 1 ("diadamantyl"). The semicarbazide **4** (0.556 g; 1.59 mmol), in 10 mL of freshly distilled CH_2Cl_2, was treated with 10.2 g (27.9 equiv) of nickel peroxide[23] (2.74 mmol active oxygen/g, determined iodometrically). The resulting mixture was stirred for 2.5 h and filtered through Celite. Removal of the solvent gave a white solid which was recrystallized from acetonitrile, affording 0.349 g (74%) of the diazetine **1**, mp 164–167 °C (the solid melts, evolves gas, resolidifies, and then remelts at 250–260 °C). The crude diazetine can be sublimed at 100 °C (0.01–0.005 mmHg) but with considerable loss of material; ^{1}H NMR 2.75 (br d, 4H, J = 12.2 Hz), 2.10, 2.05, 1.99, 1.92, 1.77, 1.72 (all br s, 24H); ^{13}C NMR 90.60 (2C, quaternary), 37.59 (2C, methylene), 34.34 (4C, methylene), 34.28 (4C, methylene), 32.84 (4C, methine), 28.18 (2C, methine), 26.55 (2C, methine); A 2D ^{13}C, ^{1}H heteroCOSY NMR established that the doublet at 2.75 ppm is due to the axial methylene protons on the carbon at 34.34 ppm; IR 2925, 2865, 1471, 1453, 1360, 1100. MS (EI, 100 °C) 296.2 (M^+, 14), 269.2 (33), 268.1 (100), 225.1 (14), 211.1 (18), 175.1 (10), 135.1 (29), 133.1 (23), 132.1 (11), 129.1 (15), 119.1 (12), 117.1 (19), 107.1 (14), 106.1 (11), 105.1 (20), 93 (26), 79.1 (52), 77.1 (22), 67.1 (27), 55.1 (18), 40.7 (37); UV (acetonitrile) λ_{max} 358 nm (e, 95 M^{-1} cm^{-1}). Anal. Calcd for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.45. Found: C, 81.06; H, 9.80: N, 9.33.

1:1 Adduct of MeTAD and 7-Norbornylidene-7-norbornane. To a solution of Nor=Nor[24] (77 mg; 0.41 mmol) in 4.0 mL of dry CH_2Cl_2 was added in one portion 47 mg (0.42 mmol) of

(19) An estimate for $\Delta G^{\ddagger}$ at −70 °C is 12–13 kcal/mole (for a $t_{1/2}$ in the range 1–10 s; see ref 2i).

(20) (a) Landis, M. E.; Bell, L. M.; Madoux, D. C.; Mitchell, J. C.; Schmidt, J. M.; Spencer, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 837. (b) e.g. Some "three-electron stabilization" at N in the transition state of C–N cleavage in **17**; see Greene, F. D.; Burrington, J. D.; Karkowsky, A. M. ACS Symposium Series 69, American Chemical Society: Washington, D. C., 1978, p 122.

(21) Bae, D. H.; Engel, P. S.; Hoque, A. K. M. M.; Keys, D. E.; Lee, W.- K.; Shaw, R. W.; Shine, H. J. *J. Am. Chem. Soc.* **1985**, *107*, 2561. Engel, P. S.; Keys, D. E.; Kitamura, A. *Ibid.* **1985**, *107*, 4964. Engel, P. S.; Robertson, D. M.; Scholz, J. N..; Shine, H. J. *J. Org. Chem.* **1992**, *57*, 6178.

(22) See Todd, W. P.; Dinnocenzo, J. P.; Farid, S.: Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 3601 and ref 4 therein; see also Borhani, D. W.; Greene, F. D. *J. Org. Chem.* **1986**, *51*, 1563.

(23) Preparation and titration of nickel peroxide, Nakagawa, K.; Konaka, R.; Nakata, T. *J. Org. Chem.* **1962**, *27*, 1597.

(24) Bartlett, P. D.; Ho, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 627.

MeTAD (4-methyl-1,2,4-triazoline-3,5-dione).[25] The resulting carmine solution was allowed to stir at room temperature for 16 h. The solution was extracted with a saturated $NaHCO_3$ solution. The organic phase was separated, washed with water and brine, dried with $MgSO_4$, and concentrated *in vacuo*. Recrystallization from methanol gave the diazetidine adduct as a white solid: weight 106 mg (86%); mp softens at 125 °C, melts 144 °C, lit.[26] mp 140–141.5 °C; ^1H NMR ($CDCl_3$) 1.34–1.45 (m, cplx, 8 H), 1.74–1.77 (m, br, 4 H), 2.27–2.31 (m, br, 4 H), 3.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) 159.79 (carbonyl), 90.25 (C adjacent to N), 39.79 methine), 28.37 (methylene), 28.08 (methylene), 26.04 (N-CH_3); mass spectrum 301 (M^+, 1.93), 188 (7.05), 187 (20.0), 186 (20.0).[26] Anal. Calcd for $C_{17}H_{23}N_3O_2$: C, 67.75; H, 7.69; N, 10.62. Found: C, 67.43; H, 8.12; N, 13.93.[26]

Diazetine 2 ("dinorbornyl") was prepared from the 7-norbornylidene-7-norbornane–MeTAD adduct by the procedure for 3 → 4 → 1. Recrystallization of 2 from petroleum ether (reflux to −40 °C) afforded 28 mg (46% yield from the diazetidine) of 2, mp 170–171 °C (melts without decomposition; melt evolves gas at 230 °C). The crude diazetine can be sublimed (80–100 °C; 0.01 mmHg): ^1H NMR 2.44 (m, 4H), 2.19 (m, 4H), 1.81 (m, 4H), 1.45 (d, 4H, J = 7.2 Hz), 1.36 (d, 4H, J = 7.9 Hz); ^{13}C NMR 96.97, 41.34, 28.99, 28.07; MS (EI, 20 °C) 217.0 ($(M + 1)^+$, 0.16), 216.0 (M^+, 0.04), 188.6 (12), 160.2 (39), 159.2 (47), 145.0 (23), 134.1 (25), 133.0 (15), 132.0 (30), 131.0 (64), 129.0 (13), 119.1 (28), 115.1 (21), 107.1 (21), 106.1 (26), 105.1 (39), 93.0 (19), 92.0 (24), 91.0 (100), 79.2 (60), 67.1 (33), 65.0 (24), 40.7 (53); high resolution mass spec calcd for $C_{14}H_{20}$ {[M − N_2]$^+$} 188.1565, found 188.1564 ± 0.0005 amu; UV (dodecane) λ_{max} 355 nm (ϵ = 184 M^{-1} cm^{-1}), 345 nm (ϵ = 205 M^{-1} cm^{-1}).

Thermal Decomposition of Diazetines 1 and 2 Diazetine 1 (51.3 mg, 0.173 mmol) and 5 mL of CH_3CN were sealed in a glass tube and heated at 185 °C for 20 min. Removal of solvent and ^1H NMR analysis showed 2-adamantanone azine and adamantylideneadamantane in a 4:1 ratio. Column chromatography on silica gel (60:40 ether, petroleum ether) afforded 31.2 mg of azine, mp 306–309 °C (dec),[27] and 7.2 mg of adamantylideneadamantane, Ad=Ad, mp 184–186 °C;[28] the azine and the olefin were identical in ^1H NMR with authentic samples. The azine was shown to be stable to the thermal decomposition conditions. Decomposition of diazetine 2 ("dinorbornyl") in dodecane at 137 °C afforded a 14 : 1 mixture of Nor=Nor[24] and the azine of 7-norbornanone,[29] determined by ^1H NMR. These products were identified by comparison with authentic materials.

The effect of solvent on the product ratio for diazetine 1 ("diadamantyl") decomposition was determined by ^1H NMR using the integration of the bridgehead protons of the alkene (singlet at 2.90 ppm) and the azine (singlets at 2.63 and 3.27 ppm). Samples of diazetine 1 and 0.5 mL of the appropriate solvent were degassed (three freeze-pump-thaw cycles), sealed, and heated at 150 °C or 185 °C. The tubes were removed from the bath after the allotted times, opened, concentrated *in vacuo*, dissolved in $CDCl_3$,and analyzed by NMR. The findings are summarized in Results.

Kinetics. The rate of decomposition of each diazetine was determined at 137 °C in dodecane by monitoring the disappearance of the $n \rightarrow \pi^*$ transition in the UV/visible spectrum; at 355 nm for diazetine 2 ("dinorbornyl") and 350 nm for diazetine 1 ("diadamantyl"). Both compounds showed clean first-order behavior. The results are summarized in Table II.

Reaction of Diazetine 1 ("diadamantyl") with BF_3–Et_2O. A solution of the diazetine 1 (6.6 mg; 0.022 mmol) in 1.0 mL of a 0.5 M solution of BF_3–Et_2O in ether (0.5 mmol) was stirred at room temperature. Reaction for 4 h 10 min gave a 1.6:1 mixture of 1 and Ad=Ad by ^1H NMR. When the stirring was continued for a total of 16 h, ^1H NMR showed only Ad=Ad.

Rearrangement of Diazetidine 3 to Pyrazolidine 5. To a solution of triethyloxonium tetrafluoroborate (0.192 g; 1.01 mmol) in 5.0 mL of dry CH_2Cl_2 was added the adduct 3 (0.300 g; 0.786 mmol) in 5.0 mL of CH_2Cl_2 *via* cannula. The resulting solution was stirred for 24 h under argon. A saturated $NaHCO_3$ solution (10 mL) was added and the mixture was extracted with CH_2Cl_2 (30 mL). The combined CH_2Cl_2 extracts were dried over $MgSO_4$ and concentrated. Column chromatography (silica gel; 1:1 ether/petroleum ether) on 100 mg of the crude material gave 56 mg of rearrangement product 5 as a white solid: mp 209–211 °C; ^1H NMR 4.40 (d, 1H), 3.42 (dd, 1H), 3.22 (br d, 1H), 3.02 (s, 3H), 2.84 (dd, 1H), 2.65 (s, 1H), 2.50–1.50 (m, 23H); ^{13}C NMR 153.00, 151.78, 61.54, 61.12, 42.37, 41.29, 38.98, 38.79, 37.60, 36.18, 35.89, 35.70, 34.96, 34.03, 32.91, 32.43, 30.02, 27.08, 26.91, 25:60, 25.30, 25.18, 25.06; IR 2905, 2873, 1750, 1700, 1451, 1391, 1257 cm^{-1}. Anal. Calcd for $C_{23}H_{31}N_3O_2$: C,72.41; H, 8.19; N, 11.01. Found: C, 72.13; H, 8.46; N, 10.74.

Rearrangement of Diazetidine Derivative 4 to Aziridine Derivative 7a. (1) With Boron Trifluoride Etherate. A solution of 4 (1.004 g; 2.82 mmol) and 0.50 mL (4.75 mmol) of BF_3–Et_2O in 30 mL of CH_2Cl_2 was stirred at room temperature for 16 h and quenched at 0 °C with 25 mL of a saturated $NaHCO_3$ solution. The CH_2Cl_2 layer was separated and extracted again with a total of 75 mL of saturated $NaHCO_3$ solution. The organic layer was then dried with $MgSO_4$ and evaporated. Recrystallization from CH_2Cl_2/hexanes gave 0.375 g (37%) of the aziridine derivative 7a: mp 214–215.5 °C (dec); ^1H NMR 6.35 (br d, 1H), 5.50 (s, 1H), 2.91 (d, 3H), 2.00–1.60 (m, 28H) (when D_2O is added, the protons at 6.35 and 5.50 ppm exchange and the resonance at 2.91 ppm becomes a singlet); ^{13}C NMR 160.92, 55.08, 37.36, 36.62, 36.56, 35.72, 34.63, 32.36, 27.32, 27.06, 26.90, 26.20; IR 3425, 3190, 3100, 2940, 2860, 1674, 1540; MS (EI, 80 °C) no M^+ ion is present, 284.3 (2.6), 283.3 (23), 282.3 (100), 268.3 (5), 91.0 (8), 79.1 (7). Anal. Calcd for $C_{22}H_{33}N_3O$: C, 74.32; H, 9.36; N, 11.82. Found: C, 74.13; H, 9.24; N, 11.74.

(2) With Silica Gel. When semicarbazide 4 was subjected to flash column chromatography on silica gel, the material obtained was a mixture of starting material 4 and rearrangement product 5. Longer exposure of 4 to silica gel converted all of 4 to 5 but the mass recovery was poor.

Reaction of Aziridine Semicarbazide 7a with Nickel Peroxide. A mixture of nickel peroxide[23] (111 mg; 2.5 mmol active oxygen/g; 2.78 mmol, added in small portions) and 5.6 mg (0.016 mmol) of the aziridine semicarbazide 7a dissolved in 1.0 mL of CH_2Cl_2 was stirred for 2 h, filtered through Celite to remove excess nickel peroxide, and the filtrate was concentrated under reduced pressure. The ^1H NMR of the crude reaction showed the products to be Ad=Ad and diazetine 1 ("diadamantyl") (ratio 1.9:1). A UV of the products showed the characteristic absorption of the diazetine at 357 nm (CH_2Cl_2).

Aminoaziridine 7b ("diadamantyl"). A solution of aziridine semicarbazide 7a (100 mg; 0.281 mmol) in 2.5 mL of 80% H_2SO_4 (4:1 concd H_2SO_4/water) was stirred at room temperature for 4 days. The reaction was cooled to 0 °C and diluted with 10 mL of ice-cold water. The pH of the solution was brought to 10 with solid KOH, giving a white precipitate. This mixture was extracted (3 x 10 mL) with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, and concentrated, affording 53 mg (63%) of the aminoaziridine 7b: ^1H NMR 3.30 (br s, 2H), 2.18 (br s, 4H), 2.13–1.65 (m, 20H); ^{13}C NMR 56.02, 39.63, 37.67, 36.98, 36.10, 35.78, 32.70, 27.72, 27.53, 26.85.

Reaction of Aminoaziridine 7b with *tert*-Butyl Hypochlorite. To 7b (47 mg; 0.16 mmol) in 5 mL of deoxygenated CH_2Cl_2 at −80 °C was added 2,6-di-*tert*-butylpyridine (36 μL; 31 mg; 0.160 mmol). The solution was treated with *tert*-butyl hypochlorite (19 μL; 17 mg; 0.159 mmol) added *via* syringe. Some evolution of gas occurred as the addition proceeded. The reaction was stirred at −80 °C for 4.5 h and then allowed to come to room temperature. The CH_2Cl_2 was evaporated, leaving a white solid which was chromatographed (flash silica gel; 10% ether/hexane) affording 22.3 mg (50%) of diazetine 1 ("diadamantyl") and 14.5 mg (32%) of Ad=Ad. Both products were identified by comparison with authentic samples. When the reaction was run at room temperature, the only product isolated was Ad=Ad.

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Reaction of *trans*-2,3-Diphenyl-1-aminoaziridine 9b[7b,11a] with *tert*-Butyl hypochlorite under the conditions described above for **7b** afforded only *trans*-stilbene.

Reaction of *cis*-2,3-Diphenyl-1-aminoaziridine 10 with Nickel Peroxide. Oxidation of aminoaziridine 10[7b,11a] with nickel peroxide in CH_2Cl_2 at −78 °C gave a 4:1 mixture of *trans*- and *cis*-stilbene (determined by GC, SE-30 column), with no diazetine apparent by ^1H NMR.

Reaction of 2,2,3,3-Tetramethyl-1-aminoaziridine 8 with *tert*-Butyl Hypochlorite. 2,2,3,3-Tetramethyl-1-phthalimidoaziridine was prepared by a general procedure[15] and cleaved by hydrazine hydrate[15,30] to 2,2,3,3-tetramethyl-1-aminoaziridine 8: liquid; ^1H NMR 3.07 (br s, 2H), 1.15 (s, 12H). Reaction with *tert*-butyl hypochlorite at −80 °C as described above for **7b** afforded only 2,3-dimethyl-2-butene (^1H NMR 1.65 (s)) and no tetramethyldiazetine.[2b]

Pyrazoline 6 was prepared from pyrazolidine **5** by the procedure for **3** → **4** → **1**. Compound **6** was purified by column chromatography on silica gel (ether/pet ether), 31 mg of **6**: mp 164–166 °C dec; ^1H NMR 4.40 (d, 1H), 3.30 (d, 1H), 3.04 (dd, 1H), 2.70 (br s, 1H), 2.57 (dd, 1H), 2.35–1.25 (m, 23H).

Reaction of Diazenes with Aminium Radical Cations. Reaction of Diazetine 1 ("diadamantyl") and Tris(4-bromophenyl)aminium Hexachloroantimonate.[31] To the diazetine **1** (51 mg; 0.17 mmol) and 2,6-di-*tert*-butylpyridine (20 μL; 17 mg; 0.089 mmol) dissolved in 2.0 mL of freshly distilled CH_2Cl_2 at 25 °C under nitrogen was added the aminium radical cation salt[31] (15 mg; 0.017 mmol). The blue solution started to evolve gas after ca. 15 s, lasting for ca. 30–45 s. TLC of the crude reaction showed only adamantylideneadamantane, identified by cospotting with authentic alkene. Concentration of the solvent in vacuo and filtration of the residue through a flash silica gel plug gave pure Ad=Ad, weight 41 mg (90%).

Diazetine 2 ("dinorbornyl ") and Tris-(4-bromophenyl)aminium hexachloroantimonate.[31] To the diazetine **2** (12 mg; 0.055 mmol) and 2,6-di-*tert*-butylpyridine (6 μL; 5.1 mg; 0.027 mmol) dissolved in 1.0 mL of dry CH_2Cl_2 under nitrogen was added the aminium radical cation salt (6 mg; 0.007 mmol) in one portion. After 8 h, the blue color of the reaction had faded to yellow. By TLC, the diazetine was still present with no olefin or azine. Concentration of the solvent under reduced pressure gave a light yellow solid which by ^1H NMR consisted only of tris(4-bromophenyl)amine and unreacted diazetine **2**.

Reaction of Pyrazoline 6 with Tris(4-bromophenyl)aminium Hexachloroantimonate.[31] Exposure of pyrazoline **6** to 10 mol% of tris-(4-bromophenyl)aminium hexachloroantimonate and 50 mol% of 2,6-di-*tert*-butylpyridine in CH_2Cl_2 as described for the diazetine **1** gave adamantylideneadamantane, identified by comparison to authentic material.

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