

# Chemical Activation as a Probe of Reaction Mechanism. Synthesis and Thermal Decomposition of 2,3-Diazabicyclo[2.1.1]hex-2-enes

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**Abstract:** Gas-phase thermolysis of 2,3-diazabicyclo[2.1.1]hex-2-ene (**1**) produces highly vibrationally excited (chemically activated) bicyclo[1.1.0]butane (**2**). The excited **2** rearranges to butadiene, in competition with collisional deactivation by a bath gas. Quantitative modeling using RRKM theory and a stepladder model for collisional deactivation indicates that, of the substantial amount of excess energy available to the products of thermolysis of **1**, the great majority lies in the hydrocarbon fragment (**2**). Within the framework of a mechanistic criterion developed previously by Bauer, this result suggests that **1** decomposes by a stepwise, one-bond cleavage involving an intermediate diazenyl diradical. The synthetic approach to structures such as **1** is developed, as are certain other aspects of the chemistry of **1** and its dimethyl derivative **7**.

The mechanism of the thermal decomposition of 1,2-diazenes (azoalkanes) has long been a subject of controversy, and a wide variety of techniques has been applied to this problem.<sup>2</sup> The central issue is whether the cleavage of two C-N bonds occurs synchronously with direct extrusion of N<sub>2</sub> or whether the cleavage is sequential and produces a diazenyl radical as an intermediate.

Some time ago, Bauer proposed that the distribution of excess energy among the products of such a fragmentation reaction could be used as an operational criterion for discerning mechanism.<sup>3</sup> The present work applies this criterion to the thermolysis of the symmetrical bicyclic diazene 2,3-diazabicyclo[2.1.1]hex-2-ene (**1**).<sup>4</sup> When **1** is decomposed thermally, highly vibrationally excited (chemically activated) bicyclo[1.1.0]butane (**2**) is produced. Through the application of RRKM theory and a multistep collisional deactivation scheme, we have been able to obtain a quantitative estimate of the energy distribution between **2** and N<sub>2</sub>, and thus to apply the Bauer postulate to the decomposition of **1**.

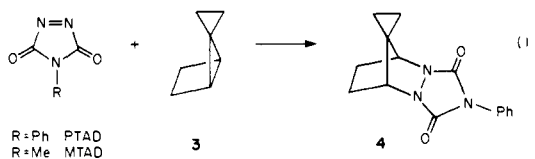


We also describe herein our synthetic approach<sup>4b</sup> to structures such as **1** and several other aspects of their thermal chemistry. Our synthetic route provides the first entry into this fundamental, highly strained azoalkane ring system, and it should be applicable to a variety of interesting new structures.

## Synthesis

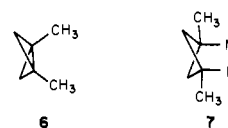
The synthesis of cyclic and polycyclic azoalkanes continues to be an area of active interest due to the utility of such structures as precursors to interesting diradicals and strained ring systems.<sup>5</sup> A wide variety of such structures has been prepared, and it may at first glance seem surprising that the fundamental ring system represented by **1** had not been prepared previously. However, the major synthetic route to polycyclic diazenes uses a Diels-Alder reaction to incorporate the nitrogens. Since there are no six-membered rings in **1**, such a route is not applicable.

Our synthesis of **1** was inspired by Roth's observation (eq 1) that 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) reacts with spirobicyclo[2.1.0]pentane-5-cyclopropane (**3**) in acetone at 20 °C to give adduct **4** in practically quantitative yield.<sup>6</sup> Given the

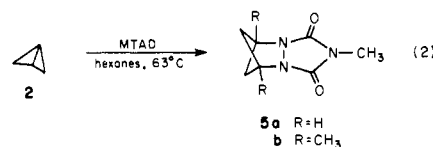


known thermal additions of electron-deficient olefins to bicyclobutanes to give both bicyclo[2.1.1]hexanes and 3-substituted cyclobutenes ("ene" products),<sup>7</sup> the reaction of triazolinedione with bicyclobutane (**2**) seemed feasible.

In practice, reaction of PTAD or MTAD with bicyclobutane (**2**) in acetone, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, or THF is quite rapid at room temperature, as monitored by the disappearance of the red color of the TAD. However, an extremely complex mixture of products was produced (>9 spots by TLC), which contained <5% of the desired adduct. On changing to a nonpolar solvent (*n*-hexane),



two changes were observed. First, the disappearance of MTAD (preferred over PTAD because of its greater solubility in nonpolar solvents) occurred at a much slower rate, and thus an elevated temperature (63 °C) was necessary. Second, NMR of the crude reaction products revealed that only adduct **5a** and a presumed polymer of MTAD were present (eq 2). Flash chromatography



gave pure **5a** in 40% yield based on **2**. Reaction of 1,3-dimethylbicyclobutane (**6**) with MTAD in hexanes occurred smoothly, although less cleanly, at room temperature to give a 12% isolated yield of the dimethyl adduct **5b**. Hydrolysis-oxidation of **5a** and **5b** by standard procedures produced **1** and the dimethyl derivative **7** in good yields.

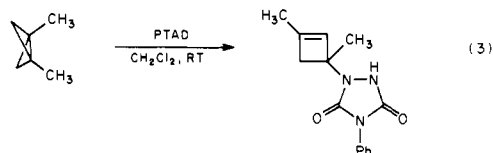
The synthesis of **5** raised some interesting questions. It is known that in the reactions of electron-deficient olefins with strained C-C bonds, the rates are essentially independent of solvent polarity, and the stereochemistry of addition is from the endo direction.<sup>7</sup> This suggested the formation of a diradical intermediate that either ring closed to give a bicyclohexane or hydrogen abstracted to give

(1) Fellow of the Alfred P. Sloan Foundation, 1983-1985.  
(2) For an excellent overview of azoalkane chemistry, see: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99-150.  
(3) Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 3688-3689.  
(4) Preliminary reports: (a) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 1131-1132. (b) Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092-4093.  
(5) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762-779.

(6) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695-4698.  
(7) Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128-136.

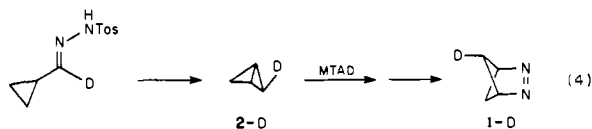
"ene" product. The fact that PTAD also reacted with **3** from the endo face suggested a similar mechanism.<sup>6</sup> However, the dramatic solvent effect on both the rate and the product composition in the reaction of **2** with MTAD and the absence of "ene" products in the reaction in *n*-hexane suggested the possibility of a change in mechanism.

One unambiguous indication of a change in mechanism would be a change in reaction stereochemistry. Concurrent with our original synthetic work,<sup>4b</sup> Amey and Smart had isolated both cycloaddition and "ene" adducts from the reactions of triazolinedione with 1-methyl-3-*R*-bicyclobutanes (*R* = CH<sub>3</sub>, CONH<sub>2</sub>, CO<sub>2</sub>CH<sub>3</sub>, CN) in CH<sub>2</sub>Cl<sub>2</sub>.<sup>8</sup> For the 1,3-dimethyl compound, only "ene" product was obtained (eq 3), in contrast to our results in

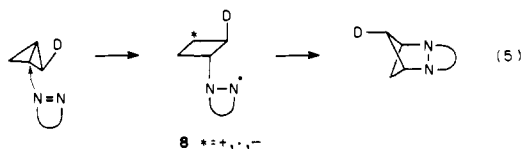


hexanes. Their observations led Amey and Smart to suggest the possibility of exo attack, perhaps via a dipolar intermediate analogous to that proposed by Greene in the reaction of TAD with olefins.<sup>9</sup> Another feasible alternative mechanism would involve initial electron transfer from **2** to TAD followed by collapse of the radical ion pair.<sup>10</sup> Such a reaction might also proceed via exo attack.

We therefore prepared stereospecifically <sup>2</sup>H-labeled **2** (**2-D**) using the procedure of Wiberg (eq 4).<sup>11</sup> Analysis of the product by 77.775-MHz <sup>2</sup>H NMR revealed that of the total <sup>2</sup>H present in the molecule, 75% was exo, 16% was endo, and 9% was at the bridgehead. Similar exo/endo ratios were observed by Wiberg<sup>11</sup> using <sup>1</sup>H NMR, but no bridgehead <sup>2</sup>H was detected. For the present purposes we shall refer to **2-D** as exo labeled, but all stereochemical analyses took into account the full labeling pattern.



Reaction of **2-D** with MTAD is completely stereospecific. The product is **5a** and, ultimately, **1** with the <sup>2</sup>H exo (eq 4). Thus, the triazolinedione attacks from the endo direction, presumably in a stepwise manner (eq 5). The nature of the intermediate **8**



is uncertain, but the substantial solvent effect on the reaction would appear to indicate some zwitterionic character. It is not clear why **8** does not hydrogen abstract to produce "ene" product in *n*-hexane, while the substituted bicyclobutanes studied by Amey and Smart<sup>8</sup> do give "ene" products in CH<sub>2</sub>Cl<sub>2</sub>.

#### Solution-Phase Thermal Chemistry

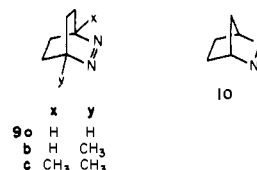
**Kinetics.** Thermal decomposition of **1** in C<sub>6</sub>D<sub>6</sub> produces bicyclobutane (**2**) as the sole detectable product. Similarly, dimethyl derivative **7** produces only **6** on thermolysis. Surprisingly, the thermolysis rate of substituted derivative **7** is slower than that of **1** by roughly a factor of 3. We have determined activation parameters for both processes (Table I), and we find that the rate difference results from a roughly 1-kcal/mol difference in  $\Delta H^\ddagger$ . The closest analogy to the present case is the diazabicyclo-

**Table I.** Activation Parameters for Thermolysis of Bicyclic Azoalkanes

compd	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	$k_{rel}^a$
<b>1</b>	33.7 ± 0.2	10.0 ± 0.3	1.0
<b>7</b>	34.5 ± 0.2	10.2 ± 0.5	0.396
<b>10</b>	36.2 <sup>b</sup>	6.1 <sup>b</sup>	0.0057
<b>9a</b>	44.3 <sup>b</sup>	9.5 <sup>b</sup>	10 <sup>-6</sup>

<sup>a</sup> Relative rates (s<sup>-1</sup>) at 120 °C calculated from data of the previous two columns. <sup>b</sup> Average of values in ref 2.

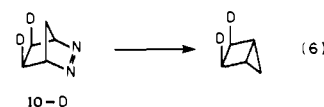
[2.2.2]octyl system **9**.<sup>12</sup> Methyl substitution facilitates deazetation in that case, such that the relative rates for **9a**, **9b**, and **9c** at 230 °C are 1.0, 2.2, and 5.3, respectively. The rate enhancement,



however, is quite small in **9** compared to that in acyclic azoalkanes. It is interesting to note that, using the empirical force field (EFF) of Kao,<sup>13</sup> we calculate that our dimethyl compound, **7**, is 3.4 kcal/mol less strained than **1**. The absolute accuracy of the EFF method as applied to azoalkanes remains to be determined, but there are other indications in the literature that bridgehead methyl substitution can stabilize strained rings.<sup>12</sup> Thus, it seems possible that a ground-state stabilization effect is responsible for the rate retardation in **7**.<sup>14</sup> In fact, precisely such an effect was proposed to account for the unusually small rate acceleration due to methyl substitution in **9**.<sup>12</sup>

Also listed in Table I are activation parameters for the next higher homologues of **1**: **10** and **9a**. EFF calculations<sup>13</sup> indicate that **1** is 31 kcal/mol more strained than **10**. However, this substantial increase in strain on going from **10** to **1** is accompanied by only a modest decrease (<3 kcal/mol) in  $\Delta H^\ddagger$  for N<sub>2</sub> loss. Clearly, most of the strain in **1** is still present in the transition state, in the form of the four-membered ring. As discussed below, this result has significant implications for the gas-phase thermal chemistry of **1**.

**Stereochemistry.** One of the most fascinating, if not bizarre, aspects of azoalkane chemistry is the stereochemistry of N<sub>2</sub> loss from monocyclic and polycyclic pyrazolines.<sup>2,15</sup> For the present case the most relevant example is from the [2.2.1] ring system, **10**. Both Roth and Allred have shown that the dominant pathway for N<sub>2</sub> loss leads to a double inversion of the hydrocarbon frame (e.g., eq 6).<sup>16</sup> In monocyclic pyrazolines, double inversion, single inversion, and double retention have all been observed.<sup>15</sup>



Thermolysis of **1-D** allows the determination of the stereochemistry of N<sub>2</sub> extrusion in only the second simple bicyclic

(12) Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 7102-7107.

(13) Kao, J.; Huang, T.-N. *J. Am. Chem. Soc.* **1979**, *101*, 5546-5557.

(14) There is precedent for methyl substitution slowing a pyrazoline decomposition. 3,3,5,5-Tetramethyl-4-isopropylidene-pyrazoline decomposes much more slowly than 4-isopropylidene-pyrazoline. This effect results from steric congestion in the transition state, as the development of a trimethylenemethane biradical-like structure leads to a more nearly planar carbon framework. See ref 2 and Engel et al.: Engel, P. S.; Soltero, L. R.; Baughman, S. A.; Nalepa, C. J.; Cahill, P. A.; Weisman, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 1698-1700. It is difficult to see any analogous interactions in **7**.

(15) Dervan, P. B.; Dougherty, D. A. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982; pp 107-149.

(16) Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1-7. Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 6766-6775.

(8) Amey, R. L.; Smart, B. E. *J. Org. Chem.* **1981**, *46*, 4090-4092.

(9) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384-6385.

(10) Hoyer, T. R.; Bottorff, K. J.; Caruso, A. J.; Dellaria, J. F. *J. Org. Chem.* **1980**, *45*, 4287-4292.

(11) Wiberg, K. B.; Lavanish, J. M. *J. Am. Chem. Soc.* **1966**, *88*, 5272-5275.

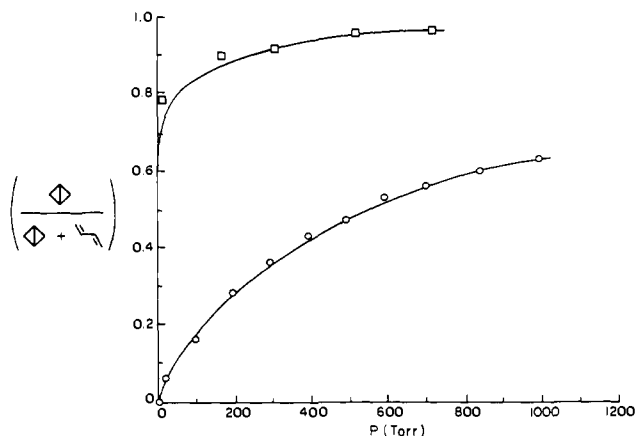
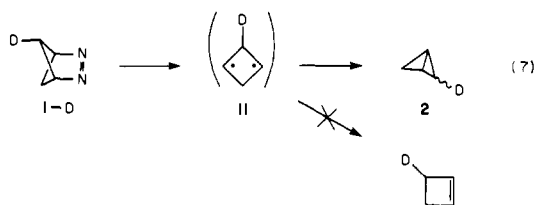


Figure 1. Product composition from gas-phase thermolysis of **1** as a function of pressure: (O)  $N_2$  as bath gas; (□)  $C_6H_6$  as bath gas.

pyrazoline ring system. We find that the bicyclobutane produced is equally labeled exo and endo (eq 7). Since Wiberg has pre-



viously demonstrated<sup>11</sup> that exo/endo interconversion does not occur in **2-D**, our results indicate that  $N_2$  loss leads to stereorandomization, in contrast to the variety of other pyrazolines previously studied. The simplest explanation of this result is that 1,3-cyclobutanediyl (**11**) is formed as a planar or rapidly inverting intermediate (eq 7).

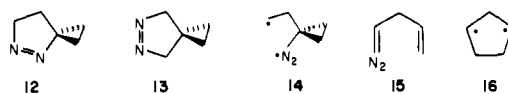
It is interesting that in this simple 1,3-diradical, a 1,2-hydrogen shift to give cyclobutene is *not* competitive with ring closure (eq 7). We estimate that we could have detected as little as 0.2% cyclobutene by 500-MHz  $^1H$  NMR of the thermolysis mixture. Such a H shift is well-precedented in 1,3-diradical chemistry.<sup>17</sup> For example, decomposition of diazene **10** always produces both bicyclo[2.1.0]pentane (eq 6) and cyclopentene. In the present system, we ascribe the lack of such a reaction to a stereoelectronic effect. In our previous ab initio theoretical study<sup>18</sup> of 1,3-diradicals such as **11** we showed that the interaction between the radical orbitals and the intervening  $CH_2$  group (through-bond coupling) is significantly diminished as the C-C-C angle at the  $CH_2$  group is decreased. This is because the  $\pi_{CH_2}$  orbital is significantly distorted toward the hydrogens of the  $CH_2$  group. Since overlap between the radical orbitals and the  $\pi_{CH_2}$  orbital is certainly crucial to the H-shift reaction, the smaller C1-C2-C3 angle in **11** relative to 1,3-cyclopentenediyl or the parent trimethylene will retard the reaction.

### Gas-Phase Thermal Chemistry

Thermolysis of **1** in the gas phase is remarkably different from that in solution. Both bicyclobutane (**2**) and 1,3-butadiene are produced, and, as shown in Figure 1, the product composition is strongly dependent on pressure. At low pressures butadiene is the dominant and ultimately the exclusive product when  $N_2$  is the bath gas. With benzene as the bath gas, a much smaller but still significant amount of butadiene is formed (Figure 1). Since it is known that bicyclobutane thermally rearranges to butadiene ( $E_a = 40.6$  kcal/mol),<sup>19</sup> the results of Figure 1 suggest that thermolysis of **1** produces highly vibrationally excited (chemically activated) bicyclobutane. It is well-known that  $N_2$  is much less

efficient at collisionally deactivating vibrationally excited molecules than benzene. Thus, the difference between the two curves in Figure 1 is understandable. Similarly, 1,3-dimethylbicyclobutane (**6**) can rearrange to 2,3-dimethylbutadiene, with activation parameters quite similar to those of the unsubstituted system.<sup>20</sup> However, in striking contrast to the results for **1**, gas-phase thermolysis of dimethyldiazene **7** produces no diene—only **6** is produced even at very low pressures.

The apparent observation of a "hot molecule" effect from **1** is also remarkable in that only one other well-documented example of chemical activation from thermolysis of an azoalkane has been reported. Bergman found that pyrolysis of pyrazoline **12** at 1 atm produced 98% spiroentane, but at 0.2 torr this value dropped to 81%, with the remainder being "hot molecule" products.<sup>21</sup> Interestingly, the isomeric, symmetrical pyrazoline **13** did not produce a "hot molecule" effect. This result was rationalized<sup>21</sup> with reference to earlier work by Bauer<sup>3</sup> in which it was proposed that the distribution of excess energy among the products of a reaction could be used as a probe of mechanism. In the symmetrical diazene **13**, the  $N_2$  was presumed to be extruded in a symmetrical fashion. The N-N bond is much longer in the diazene than in  $N_2$ , and the N-N stretching mode is essentially perpendicular to and therefore weakly coupled to the reaction coordinate. Thus, the  $N_2$  is expelled with a stretched N-N bond, i.e., in a highly vibrationally excited state. Most of the excess energy of the reaction is therefore carried off by the  $N_2$ , and the hydrocarbon is not chemically activated. In contrast, the unsymmetrical diazene **12** cleaves unsymmetrically to produce an intermediate diazenyl diradical (presumably **14**). Vibrational coupling between the  $N_2$  and the hydrocarbon fragment can be efficient in this intermediate, and thus the hydrocarbon can be chemically activated.



The results of Figure 1 suggested that the *symmetrical* diazene **1** produced a much greater "hot molecule" effect than **12**, a seeming contradiction to the above analysis. We therefore felt it was important to rule out alternative sources of butadiene. As described above, diradical **11** could in principle undergo a 1,2-hydrogen shift to produce cyclobutene, which could then thermally rearrange to butadiene over a much smaller barrier than the bicyclobutane to butadiene conversion. Alternatively, allyldiazomethane (**15**) could be formed by a formal retro[3 + 2] cycloaddition of **1**, a process which is observed upon photochemical excitation.<sup>22</sup> Under the reaction conditions, **15** would likely lose  $N_2$  to form a carbene which would predominantly rearrange to butadiene.

Thermolysis of **1-D** allows for a differentiation among the three mechanisms. Shifts of  $^1H$  and  $^2H$  in diradical **11** would produce both [1- $^2H$ ]- and [3- $^2H$ ]cyclobutene in a ratio between 1:2 and 1:3, depending on the kinetic isotope effect (KIE). These would then produce [2- $^2H$ ]- and [1- $^2H$ ]butadiene, respectively. Diazoalkene **15** would be labeled equally in the allylic and the vinylic  $CH_2$  groups (ignoring the secondary KIE). This would lead to a mixture of [2- $^2H$ ]- and [1- $^2H$ ]butadiene, with the ratio between 1:1 and 1:3, depending on the KIE on the carbene insertion reaction. However, it has been demonstrated<sup>11</sup> that [2- $^2H$ ]bicyclobutane (**2-D**) produces only [1- $^2H$ ]butadiene on thermal rearrangement. We find that gas-phase thermolysis of **1-D** produces exclusively [1- $^2H$ ]butadiene, consistent only with the chemical activation mechanism.

**Thermochemistry.** Some qualitative insights into the reasons for the highly efficient chemical activation of bicyclobutane on its formation from **1** can be gained with reference to Figure 2. We have included in Figure 2 data for **1** and for azoalkane **10**,

(17) See, for example: Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533-6542 and references therein.

(18) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284-290.

(19) Frey, H. M.; Stevens, I. D. R. *Trans. Faraday Soc.* **1965**, *61*, 90-94.

(20) Chesick, J. P. *J. Phys. Chem.* **1964**, *68*, 2033-2034.

(21) Shen, K. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1655-1657.

(22) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333-2334.

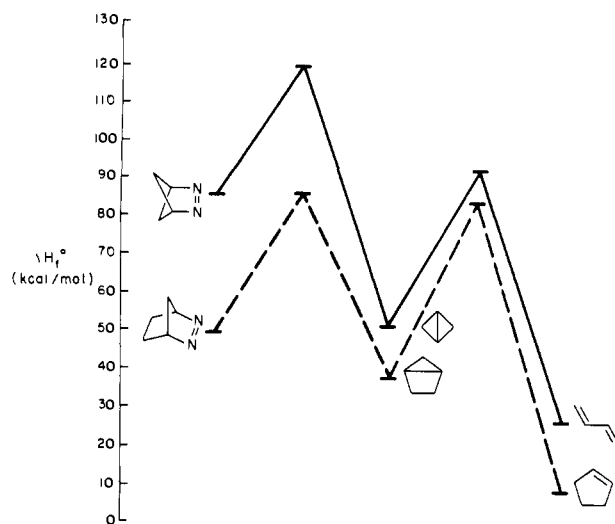


Figure 2. Energetics of the thermal decomposition of **1** and **10**.

as an example of a well-characterized, fairly typical pyrazoline. The heats of formation are known for all structures shown<sup>23</sup> except **1**, for which the EFF value<sup>13</sup> was used. Transition-state heats of formation were determined from the known activation parameters.<sup>24</sup>

Both **1** and **10** decompose to hydrocarbons which have available to them a subsequent thermal rearrangement pathway. However, a major difference between **1** and **10** arises in the energy of the transition state for N<sub>2</sub> loss relative to that for the hydrocarbon rearrangement. Because **1** is highly strained, and this strain is not relieved in the transition state for N<sub>2</sub> loss (see above), the deazetation transition state lies very high in energy. This leads to a substantial amount of excess energy in the products (**2** and N<sub>2</sub>) beyond that necessary for the bicyclobutane-to-butadiene rearrangement. Even if the N<sub>2</sub> carries away a large amount of excess energy, as the Bergman/Bauer analysis would predict, there still could be enough energy left in the hydrocarbon fragment for rearrangement to occur. In contrast, the deazetation transition state for **10** is roughly equienergetic with the hydrocarbon rearrangement transition state, and therefore the hydrocarbon cannot be generated with an energy significantly above this barrier. Thus, the qualitative observation of chemical activation for **1** does not necessarily contradict the Bergman/Bauer analysis.

Another ambiguity in Figure 2 is the question of how much of the excess energy of the reaction ( $E_{xs}$ ) is available to the N<sub>2</sub> fragment when it is expelled. If one considers the products to be bicyclobutane and N<sub>2</sub>, then all of  $E_{xs}$ , which is equal to the  $\Delta H_f^\circ$  of the deazetation transition state minus  $\Delta H_f^\circ$  of bicyclobutane (since  $\Delta H_f^\circ$  of N<sub>2</sub> is zero) could end up as vibrational excitation in N<sub>2</sub>. From Figure 2,  $E_{xs}$  is approximately 68 kcal/mol, and thus the N<sub>2</sub> could be very highly excited. However, the stereochemical scrambling observed on thermolysis of 1-D (see above) suggests that the products are actually N<sub>2</sub> and 1,3-cyclobutanediyl (**11**). In this case, not all of  $E_{xs}$  would be available to the N<sub>2</sub>, because of the high energy content of **11**. The maximum vibrational energy available to the N<sub>2</sub> would be equal to  $E_{xs} - \Delta H_f^\circ(\mathbf{11})$ . If this is the case, quantitative analysis would require an evaluation of  $\Delta H_f^\circ$  of diradical **11**. The uncertainties in evaluating  $\Delta H_f^\circ$  of diradicals are many, and in the case of **11** there is the additional problem of choosing a value for the ring strain energy. However, it seems highly likely that  $\Delta H_f^\circ$  of **11** is greater than  $\Delta H_f^\circ$  of the bicyclobutane-to-butadiene transition state. Ring inversion (exo/endo isomerization) in **2** is not competitive with rearrangement to butadiene.<sup>11</sup> All recent results indicate that in the

Table II. Unimolecular Rate Constants for **2** and **6** from RRKM Calculations

$E^*$ , kcal/mol	$k(E^*)$ , s <sup>-1</sup>	
	<b>2</b>	<b>6</b>
5.0	$2.2 \times 10^6$	$3.9 \times 10^2$
10.0	$2.4 \times 10^7$	$9.7 \times 10^3$
15.0	$1.3 \times 10^8$	$9.5 \times 10^4$
20.0	$4.7 \times 10^8$	$5.6 \times 10^5$
25.0	$1.3 \times 10^9$	$2.4 \times 10^6$
30.0	$3.1 \times 10^9$	$8.0 \times 10^6$
35.0	$6.5 \times 10^9$	$2.3 \times 10^7$
40.0	$1.2 \times 10^{10}$	$5.5 \times 10^7$
45.0	$2.1 \times 10^{10}$	$1.2 \times 10^7$
50.0	$3.5 \times 10^{10}$	$2.5 \times 10^8$
55.0	$5.4 \times 10^{10}$	$4.6 \times 10^8$

closely related bicyclo[2.1.0]pentane system, singlet diradical **16** is most likely a ring-inversion transition state or lies in a very shallow minimum.<sup>15</sup> If, by analogy, we rule out the possibility of a very deep well for **11**, then, like the ring inversion transition state, it must lie above the rearrangement transition state. Using the most recent values for C-H bond dissociation energies<sup>25</sup> and assuming a reasonable ring strain energy,<sup>26</sup> thermochemical estimates<sup>27</sup> predict that **11** lies 6 kcal/mol above the rearrangement transition state, consistent with this analysis.

The important consequence of this result is that even if *all* of the available excess energy is carried away by N<sub>2</sub>, leaving behind diradical **11** in its ground vibrational state and satisfying the Bergman/Bauer analysis of the results for **12** and **13**, the energy content of the bicyclobutane which is formed upon ring closure of **11** could still be above the rearrangement transition state. Thus, the chemical activation process we are observing could actually be the ring closure of diradical **11**, not the deazetation of **1**.

**RRKM Calculations.** The thermochemistry of Figure 2 allows one to conclude that there is potentially much more excess energy available to the products in the decomposition of **1** than in typical diazenes. This could provide a rationalization of the observation of chemical activation. However, from Figure 2 alone one cannot evaluate the distribution of  $E_{xs}$  between the fragmentation products. In order to apply the Bauer criterion to this system one must know how much of the available  $E_{xs}$  is carried away by N<sub>2</sub> and how much by the hydrocarbon. In principle, one can solve this problem by using RRKM theory to evaluate the rate of rearrangement as a function of the energy content of the bicyclobutane,  $k(E^*)$ , where  $E^*$  is the energy content of the bicyclobutane *above* the threshold (activation) energy. Application of a multistep collisional deactivation scheme then allows one to determine which value of  $E^*$  is required to reproduce the data of Figure 1. In such a treatment all that matters is the value of  $E^*$  once the bicyclobutane is formed, regardless of whether it was formed directly from diazene **1** or from diradical **11**. The absolute amount of vibrational energy carried away by N<sub>2</sub> could then be calculated by subtracting  $E^*$  and the hydrocarbon rearrangement threshold energy from  $E_{xs}$ .

The application of RRKM theory to the rearrangement of bicyclobutane to butadiene is straightforward.<sup>28</sup> A high-quality, completely analyzed vibrational spectrum of **2** is available,<sup>29</sup> thereby providing excellent vibrational frequencies for the ground

(25) Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279-5283.

(26) We chose a ring-strain correction that is intermediate between those proposed<sup>27</sup> for cyclobutane and cyclobutene. Diradical **11** should be more strained than cyclobutane because of the introduction of two sp<sup>2</sup> centers into a four-membered ring but less strained than cyclobutene because of the diminished number of H-H eclipsing interactions. While one can only obtain an approximate value for  $\Delta H_f^\circ(\mathbf{11})$ , it seems certain that this value lies well below the deazetation transition state. Thus, there must be a significant amount of excess vibrational energy available to the system.

(27) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(28) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: New York, 1972; p 64.

(29) Wiberg, K. B.; Peters, K. S. *Spectrochim. Acta Part A* **1977**, *33A*, 261-271.

(23) See ref 2 and: Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. Turner, R. B.; Goebel, P.; Mallon, B. J.; Doering, W. von E.; Coburn, J. F., Jr.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315-4322.

(24) See ref 2, 4b, and: Willcott, M. R.; Cargill, R. L.; Sears, A. B. *Prog. Phys. Org. Chem.* **1972**, *9*, 25-98.

state. The conversion of **2** to butadiene was considered to be a concerted, [ $\sigma_{2s} + \sigma_{2a}$ ] reaction.<sup>30</sup> Thus, for modeling the reaction transition state, we have chosen symmetry coordinate  $S_{10}$  (frequency no. 11), in Wiberg's notation,<sup>29</sup> as the reaction coordinate. This motion corresponds to a stretching of the two C-C bonds that are broken in the reaction and a compression of the bonds that become double bonds. The reaction pathway was assigned a degeneracy of 2, as there are two equivalent sets of bonds that can cleave to give butadiene. The remaining C-C vibrational frequencies of **2** were lowered in the transition state so as to reproduce the high-pressure Arrhenius pre-exponential term for the rearrangement.

The results from the RRKM calculations are the unimolecular rate constants for the rearrangement of **2** for various values of the energy content of **2**. A sampling of the data can be seen in Table II. When one considers that at ca. 500 torr of  $N_2$  as bath gas, where roughly equal amounts of **2** and butadiene are formed, the collision frequency is ca.  $2.4 \times 10^{10} \text{ s}^{-1}$ ,<sup>31</sup> it can immediately be seen that **2** must be formed with a substantial amount of excess energy in order for rearrangement to compete with collisional deactivation.

Also shown in Table II are the results of a comparable RRKM calculation on the rearrangement of 1,3-dimethylbicyclobutane (**6**) to 2,3-dimethylbutadiene. Appropriate corrections were made to the list of ground-state and transition-state vibrational frequencies to account for the replacement of the bridgehead hydrogens of **2** by methyls. A dramatic decrease in  $k(E^*)$  occurs upon methyl substitution. Such an effect has been observed previously and results from the greatly increased number of oscillators into which vibrational energy may flow, which thereby decreases the probability of accumulation of energy into the reactive mode. The data of Table II clearly show why no chemical activation is seen from diazene **7**. Quantitative modeling using the multistep collisional deactivation techniques described below predicts <0.5% diene even at very low pressures.

In order to reproduce Figure 1, we must explicitly consider the collisional deactivation of vibrationally excited **2**, which involves two adjustable parameters. The first is the initial energy content of the bicyclobutane once it is formed from **1** (expressed as  $E^*$ ). The other is the amount of vibrational energy removed by the bath gas per collision,  $\langle \Delta E \rangle$ . We initially assumed,<sup>32</sup> and our subsequent modeling confirmed, that benzene is a strong collider in this system. That is, in a single collision with vibrationally excited bicyclobutane, a benzene molecule removed enough energy to drop the bicyclobutane down below the reaction threshold energy. We were unable to reproduce the data of Figure 1 without this assumption of benzene as a single-step, hard-collision deactivator. Thus, by using benzene as the bath gas, only one adjustable parameter ( $E^*$ ) remains.

As shown in Figure 3, the best fit to the benzene data of Figure 1 is obtained with a value of 25 kcal/mol for  $E^*$ . The highest possible value for  $E^*$ , i.e., the difference between the deazetation and rearrangement transition states ( $E^*_{\text{max}}$ ) is 28 kcal/mol (Figure 2). Thus, essentially all of the excess energy from the deazetation of **1** is carried off by the bicyclobutane.

Having established a value of  $E^*$ , we can now fit the  $N_2$  deactivation data. It is established that  $N_2$  is a relatively weak collider,<sup>32</sup> and we have applied the standard stepladder model<sup>33</sup> to evaluate its efficiency as a deactivator. As shown in Figure 3, the best fit to the data is obtained with a value of 0.35 kcal/mol ( $120 \text{ cm}^{-1}$ ) for  $\langle \Delta E \rangle$  for  $N_2$ . The fit of the data is not precise, and it has often been noted that it is difficult to obtain one set of parameters that mimics both the high- and low-pressure regions.<sup>34</sup> We have chosen to emphasize the high-pressure region,

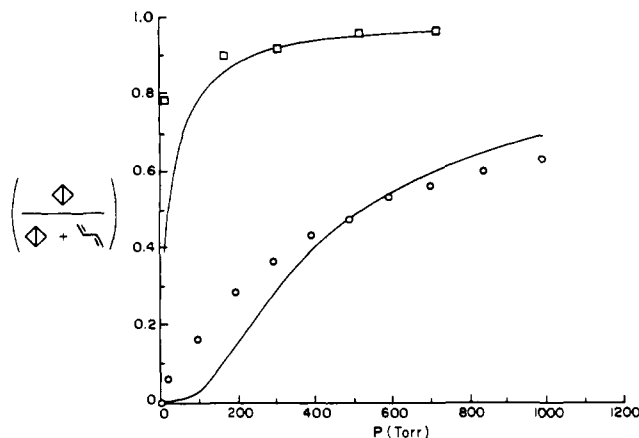


Figure 3. Theoretical fits to product composition data from gas-phase thermolysis of **1**. Single points are experimental data [(O)  $N_2$  bath gas; (□)  $C_6H_6$  bath gas]; solid lines are theoretical curves obtained as described in the text.

as we feel that these data are more accurate.

The value of 0.35 kcal/mol for  $\langle \Delta E \rangle$  for  $N_2$  is relatively small compared to values obtained from other studies using  $N_2$ .<sup>32</sup> It has been shown that for a given collider,  $\langle \Delta E \rangle$  varies from system to system. A smaller value of  $\langle \Delta E \rangle$  is obtained in those systems for which  $E^*$  is smaller, and in the present system,  $E^*$  is smaller than, for example, in the extensively studied<sup>35</sup> dimethylcyclopropane system. For the present system the important point is that any upward revision of  $\langle \Delta E \rangle$  for  $N_2$  will also require an increase in  $E^*$ . For example, with a  $\langle \Delta E \rangle$  of 1.0 kcal/mol, a number more consistent with other studies of  $N_2$  as a collisional deactivator, a value for  $E^*$  of 29 kcal/mol gives a fit to the experimental data as good as that of Figure 3. Thus, the  $N_2$  data suggest that the 25-kcal/mol estimate of  $E^*$  from the benzene data should be viewed as a lower limit.

**Mechanistic Implications.** Before discussing the implications of our results for the mechanism of diazene decomposition, it is perhaps worthwhile to consider possible uncertainties in the above analysis. The three critical quantities are  $E^*_{\text{max}}$ ,  $k(E^*)$ , and the efficiency of collisional deactivation as determined primarily by  $\langle \Delta E \rangle$ . The quantity  $E^*_{\text{max}}$  is derived from Figure 2, and the only value that could have a substantial uncertainty is  $\Delta H_f^\circ$  for **1**. The EFF method was parametrized<sup>13</sup> to precisely reproduce  $\Delta H_f^\circ$  of **10**, and thus it should be fairly reliable for **1**. Perhaps a value of  $28 \pm 3 \text{ kcal/mol}$  would be appropriate for  $E^*_{\text{max}}$ . The unimolecular decomposition rate,  $k(E^*)$ , derives from RRKM theory. It would seem that the bicyclobutane-to-butadiene rearrangement is an ideal candidate for RRKM. The small size and well-understood vibrational spectrum for **2** along with the relatively constrained nature of the transition state would seem to diminish some of the uncertainties associated with the method. Concerning the collisional deactivation data, the fit for the benzene curve is fairly good, but the range in measured product ratios is relatively small. The fit for the  $N_2$  data is poorer, but it does seem to provide a viable lower limit to  $E^*$ . From evaluation of the range of  $E^*$  values that can give an acceptable fit to the experimental curves, we conclude that  $E^*$  is  $25 \pm 2 \text{ kcal/mol}$ .

We feel that the above-mentioned error bars are quite generous. For the present purposes, though, there is no need to fine tune the values any further. Since the amount of vibrational energy in the  $N_2$  equals  $E^*_{\text{max}} - E^*$ , the qualitative result is clear-cut. The vast majority of the excess energy from the decomposition of **1** is absorbed by the hydrocarbon fragment **2**. Remembering that one quantum of vibrational energy in  $N_2$  is worth ca. 6.7 kcal/mol ( $2345 \text{ cm}^{-1}$ ), any hot  $N_2$  is at best in the  $\nu = 1$  vibrational state, and it seems quite possible that only a fraction of the ejected  $N_2$  molecules are "hot" at all. Within the framework of the Bauer postulate,<sup>3</sup> then, we conclude that  $N_2$  loss from **1** occurs in a

(30) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 45 and 46.

(31) See ref 28, p 164.

(32) Chan, S. C.; Rabinovitch, B. S.; Bryant, J. T.; Spicer, L. D.; Fujimoto, T.; Lin, Y. N.; Pavlou, S. P. *J. Phys. Chem.* **1970**, *74*, 3160-3176.

(33) Hoare, M. J. *Chem. Phys.* **1963**, *38*, 1630-1635.

(34) McCluskey, R. J.; Carr, R. W., Jr. *J. Phys. Chem.* **1976**, *80*, 1393-1398.

(35) Rynbrandt, J. D.; Rabinovitch, B. S. *J. Phys. Chem.* **1970**, *74*, 1679-1685 and references therein.

stepwise fashion, via an intermediate diazenyl diradical. The requirement of a diazenyl diradical as a true intermediate is brought about by the need to allow statistical energy redistribution to occur prior to release of N<sub>2</sub>.

Several recent studies<sup>36</sup> have presented evidence for stepwise, one-bond cleavage in highly unsymmetrical trans, and certain symmetrical cis, acyclic diazenes and for 4-alkylidene-pyrazolines. A recent kinetic study<sup>12</sup> of the bicyclic system **9** was unable to distinguish between simultaneous, two-bond scission and reversible one-bond cleavage. The present work provides the first clear-cut evidence favoring the one-bond cleavage mechanism in a simple pyrazoline and the first time that the distribution of excess energy between the products of such a reaction has been used as a mechanistic probe. In light of the present results, the observation of a very small amount of chemical activation in the unsymmetrical structure **12**, but none in the symmetrical **13**,<sup>21</sup> does not justify the proposal of different mechanisms for the two. Perhaps the thermochemistries of **12** and **13** are slightly different, thereby providing the products from **12** with slightly more excess energy. Consistent with this interpretation is the fact that the activation energy for decomposition of **12** is ca. 3–4 kcal/mol greater than that for **13**.<sup>21</sup>

### Conclusions

Thermal addition of MTAD to bicyclobutanes in a nonpolar solvent provides a convenient entry into the 2,3-diazabicyclo[2.1.1]hex-2-ene system. This fundamental azoalkane ring system is highly strained but relatively thermally stable. Thermolysis in solution produces 1,3-cyclobutanediyls which undergo exclusive ring closure to bicyclobutanes.

Gas-phase thermolysis of the parent structure produces N<sub>2</sub> and highly vibrationally excited bicyclobutane. Quantitative analysis based on the reaction thermochemistry, RRKM theory, and a standard collisional deactivation scheme indicates that of the substantial amount of excess vibrational energy available to the products, the great majority lies in the hydrocarbon fragment. Given this result and Bauer's analysis<sup>3</sup> of the distribution of excess energy among the products of fragmentation reactions, we conclude that the thermal deazetation of **1** occurs by a stepwise, one-bond cleavage mechanism.

### Experimental Section

**General.** <sup>1</sup>H NMR spectra were recorded on a Varian EM-390 spectrometer. Fourier transform NMR spectra (<sup>1</sup>H and <sup>13</sup>C) were recorded on a JEOL FX-90Q or a Varian XL-200 spectrometer. <sup>2</sup>H NMR (77.8 MHz) and 500-MHz <sup>1</sup>H NMR spectra were recorded on a Bruker WM-500 spectrometer. UV spectra were recorded on a Beckman Model 25 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 257 grating spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI, or by the Caltech Analytical Facility. Mass spectra were also obtained by the Caltech Analytical Facility. Analytical gas chromatography was performed on a Hewlett-Packard 5840A chromatograph equipped with a flame ionization detector. Preparative gas chromatography was performed on a Varian Aerograph Model 920 chromatograph with a thermal conductivity detector.

**4-Methyl-2,4,6-triazatricyclo[5.1.1.0<sup>2,6</sup>]nonane-3,5-dione (5a).** A solution of 1.00 g (18.5 mmol) of bicyclobutane<sup>37</sup> in 1.5 L of *n*-hexane was placed in a 2-L two-necked round-bottomed flask equipped with a dry ice-acetone condenser and an addition funnel. This solution was heated to 63 °C and then, under an atmosphere of nitrogen, 2.20 g (19.5 mmol) of MTAD<sup>38</sup> in 200 mL of diethyl ether was added dropwise over a period of 4 h with vigorous magnetic stirring. The reaction mixture was then stirred at 63 °C for another 6 h and finally cooled to room temperature. Removal of solvents on a rotary evaporator left a pale yellow residue which was flash chromatographed<sup>39</sup> (3:1 v/v of CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O as eluent)

on 70–230 mesh silica gel. White crystalline **5a** (*R*<sub>f</sub> = 0.7) was obtained: 1.23 g (7.37 mmol, 39.8% yield); mp 134–134.5 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.75 (dd, 2 H, H<sub>a</sub>), 2.30 (m, 2 H, H<sub>b</sub>), 3.08 (s, 3 H), 4.70 (t, 2 H, H<sub>c</sub>); complete spectral simulation gives *J*<sub>aa'</sub> = 6.5, *J*<sub>ab</sub> = 8.4, *J*<sub>bc</sub> = 2.0 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 25.74 (CH<sub>3</sub>), 40.55 (CH<sub>2</sub>), 62.32 (CH), 161.30 (C=O); IR (CHCl<sub>3</sub>) 3040, 2990, 1780, 1720, 1455, 1400, 1275, 1125, 1015, 980, 940, 895 cm<sup>-1</sup>.

Anal. Calcd for C<sub>7</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: C, 50.30; H, 5.43; N, 25.14. Found: C, 50.24; H, 5.40; N, 24.94.

**2,3-Diazabicyclo[2.1.1]hex-2-ene (1).** An adaptation of literature procedures<sup>40</sup> was used for the hydrolysis-oxidation of **5a** to **1**. Potassium hydroxide (3.5 g, 53 mmol, 85%) in 25 mL of 2-propanol (previously flushed with nitrogen for 10 min) was heated in a 200-mL round-bottomed flask and 1.2 g (7.2 mmol) of **5a** was added. The reaction mixture was brought to reflux under a nitrogen atmosphere for 1.5 h. A heterogeneous mixture was obtained. This was cooled in an ice-water bath and then acidified to a pH of 2 with 3 N hydrochloric acid. After being warmed to 40 °C for about 10 min, the acidic mixture was neutralized at room temperature with 1 N ammonium hydroxide. A solution of 4.0 g (18 mmol) of cupric bromide in 25 mL of water was added dropwise to the reaction mixture which was then kept at ambient temperature for 2 h. A dark-brown copper complex precipitated and was filtered. Ammonium hydroxide (4 mL, 1 N) was then added to the filtrate and the solution gently stirred at room temperature to give more dark-brown precipitate. The combined copper complex was washed with distilled water (2 × 20 mL), methanol (1 × 20 mL), and diethyl ether (2 × 20 mL) and air dried to give 1.6 g of a solid which was suspended in 180 mL of diethyl ether. Ammonium hydroxide (63 mL, 1 N) was added dropwise in an ice bath with vigorous stirring. The ether layer was separated and the aqueous layer extracted with diethyl ether (3 × 50 mL). The combined organic layer was dried over magnesium sulfate, and the ether was slowly distilled with use of a 20-cm Vigreux column. After being condensed to about 2 mL, the ether was completely removed by a liquid nitrogen trap in a vacuum manifold (at 0 °C and 100 torr). The product was then transferred into a gas storage bulb in a vacuum manifold (at 0.05 torr and room temperature) with the aid of liquid nitrogen to give 381 mg (4.64 mmol, 64% yield) of the white crystalline 1,2-diazene: mp (sealed tube) 63–64 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.22 (m, 2 H), 1.60 (d d, 2 H), 4.40 (t, 2 H); spectral simulation gives coupling constants essentially identical with those for **5a**; <sup>13</sup>C NMR (CCl<sub>4</sub>) δ 59.01 (CH<sub>2</sub>), 76.36 (CH); IR (CCl<sub>4</sub>) 3020, 2960, 2870, 1475, 1430, 1260, 1210, 1100, 1015, 960 cm<sup>-1</sup>; UV (*n*-hexane) λ<sub>max</sub> 331 nm (ε 1360), 325 (ε 143), 320 (ε 186), 316 (ε 124); mass spectrum (degassed sample, 15 eV) *m/e* 54 (98), 39 (100), 28 (55).

**1,3-Dimethylbicyclo[1.1.0]butane (6).** A slight modification of the procedure reported in the literature<sup>41</sup> was adopted. 1,3-Dibromo-1,3-dimethylcyclobutane (**17**)<sup>42</sup> (6.0 g, 25 mmol) in 10 mL of DMF was added dropwise over a period of 1 h to a suspension of 19.1 g (54.6 mmol) of 2% lithium amalgam<sup>43</sup> in 15 mL of DMF at room temperature. The reaction mixture was then stirred for another 2 h. The product was isolated by fractional distillation under reduced pressure to give 1.82 g (21.9 mmol, 88% yield) of **6**.

**1,4,7-Trimethyl-2,4,6-triazatricyclo[5.1.1.0<sup>2,6</sup>]nonane-3,5-dione (5b).** In a 2-L, two-necked, round-bottomed flask fitted with a dry ice-acetone condenser and pressure equalizing addition funnel was placed a solution of 1.83 g (21.9 mmol) of **6** in 1.5 L of hexane. At room temperature and under a slow stream of nitrogen, a solution of 2.75 g (23.9 mmol) of MTAD in 200 mL of diethyl ether was added dropwise over a period of about 3 h. A white insoluble material was filtered off and the filtrate concentrated on a rotary evaporator. The resulting yellow oil was subjected to flash chromatography<sup>39</sup> on 70–230 mesh silica gel with a 5:1 mixture of CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O as eluent. **5b** (510 mg, 2.61 mmol, 12% yield) in the form of a yellow oil (*R*<sub>f</sub> 0.55) was obtained: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 0.98 (m, 2 H), 1.36 (m, 2 H), 1.51 (s, 6 H), 2.58 (s, 3 H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 15.7 (CH<sub>3</sub>), 25.0 (N-CH<sub>3</sub>), 47.4 (CH<sub>2</sub>), 69.9 (bridgehead), 160.3 (C=O).

Anal. Calcd for C<sub>9</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C, 55.37; H, 6.71; N, 21.53. Found: C, 55.17; H, 6.80; N, 21.55.

**1,4-Dimethyl-2,3-diazabicyclo[2.1.1]hex-2-ene (7).** To a hot solution (40–45 °C) of 1.2 g (19 mmol, 87.2%) of potassium hydroxide in 20 mL of 2-propanol (previously flushed with nitrogen for 10 min) was added

(36) Porter, N. A.; Dubay, G. R.; Green, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 920–925. Green, J. G.; Dubay, G. R.; Porter, N. A. *Ibid.* **1977**, *99*, 1264–1265. Neuman, R. C., Jr.; Binigar, G. A. *Ibid.* **1983**, *105*, 134–135. Neuman, R. C., Jr.; Lockyer, G. D., Jr. *Ibid.* **1983**, *105*, 3982–3987. Engel, P. S.; Gerth, D. B. *Ibid.* **1983**, *105*, 6849–6851. Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529–4534. Crawford, R. J.; Chang, M. H. *Tetrahedron* **1982**, *38*, 837–842.

(37) Lampman, G. M.; Aumiller, J. C. *Org. Synth.* **1971**, *51*, 55–59.

(38) Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121–127.

(39) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925. (40) Gassman, P. G.; Mansfield, K. T. *Org. Synth.* **1969**, *49*, 1–6. Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806–4809. Jösel, R.; Schröder, G. *Liebigs Ann. Chem.* **1980**, 1428–1437.

(41) Griesbaum, K.; Butler, P. E. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 444–445.

(42) Griesbaum, K.; Naegele, W.; Wanless, G. G. *J. Am. Chem. Soc.* **1965**, *87*, 3151–3158.

(43) Alexander, J.; Krishna Rao, G. S. *J. Chem. Educ.* **1970**, *47*, 277.

468 mg (2.40 mmol) of **5b**, and the mixture was refluxed under nitrogen for 1 h and subsequently cooled in an ice-water bath. The reaction mixture was acidified using 3 N hydrochloric acid, warmed to about 40 °C for 10 min, cooled to room temperature, and neutralized with 1 N ammonium hydroxide. A solution of 1.3 g (6.0 mmol) of cupric bromide in 15 mL of water was added dropwise with gentle stirring. The pH was adjusted to 6 using 1 N ammonium hydroxide and the reaction flask kept at room temperature for 1 h. Reddish-brown crystals of the copper complex appeared and were filtered, washed (with water, methanol, and diethyl ether), and air dried. To a suspension of the complex in 30 mL of diethyl ether was added 25 mL of 1 N ammonium hydroxide at 0 °C with vigorous stirring. The ethereal layer was separated and the aqueous layer extracted with ether. The combined organic phase was dried over magnesium sulfate. After filtration, the ether was distilled off through a 10-cm Vigreux column. Care was taken not to heat the solution above 40 °C. When about 1.5 mL of the solution remained, the distillation was stopped, and pure **7** was isolated by preparative gas chromatography. A 10 ft  $\times$  1/4 in. column of 10% UCW-982 on Chromosorb WAW-DMCS mesh size 80/100 was used. At a column temperature of 55 °C and a helium flow of 120 mL/min, the retention time for **7** was 13 min. A total of 114 mg (1.04 mmol, 41.7% yield) of the product **7** was isolated: mp (sealed tube) 47–48 °C;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.00 (m, 2 H), 1.51 (s, 6 H), 1.83 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  15.57 ( $\text{CH}_3$ ), 64.45 ( $\text{CH}_2$ ), 83.48 (bridgehead); IR ( $\text{CCl}_4$ ) 2995, 2980, 2940, 2875, 1445, 1422, 1380, 1285, 1150, 995  $\text{cm}^{-1}$ ; UV (*n*-hexane)  $\lambda_{\text{max}}$  341 nm ( $\epsilon$  1320), 334 ( $\epsilon$  270), 330 ( $\epsilon$  226), 325 ( $\epsilon$  270); mass spectrum *m/e* 82 (30), 67 (60), 41 (67), 39 (60), 28 (100).

**Kinetic Measurements.** All kinetic experiments in the solution-phase thermal decompositions of **1** and **7** were conducted in sealed NMR tubes in a well-insulated silicone oil bath at temperatures between 80 and 125 °C. A Bayley Model 253 proportional temperature controller was used. Accurate measurements of the temperature were made by using an iron-constantan thermocouple connected to a digital voltmeter. Stock solutions of 240 mg of **1** in 25  $\mu\text{L}$  of benzene and 3 mL of benzene- $d_6$  and 43 mg of **7** in 5 mL of benzene- $d_6$  were prepared. A number of NMR samples were then prepared from these solutions by degassing (3 freeze-pump-thaw cycles) and sealing the tubes under vacuum. Reactions were followed by 90-MHz  $^1\text{H}$  NMR spectroscopy using multiple integrations. Because of the intense, well-separated NMR signals in **1** and **7** and their products, quite accurate quantitative analysis by NMR was possible. All rate plots and the Arrhenius and Eyring plots gave linear correlation coefficients of 0.9997 or better. For **1**: rate constant  $\times 10^5 \text{ s}^{-1}$  (*T*, °C), 0.321  $\pm$  0.006 (84.98), 1.20  $\pm$  0.03 (95.04), 4.20  $\pm$  0.08 (104.97), 13.5  $\pm$  0.4 (115.06);  $E_a = 34.4 \pm 0.2$  kcal/mol;  $\log A = 15.50 \pm 0.09$ . For **7**: rate constant  $\times 10^5 \text{ s}^{-1}$  (*T*, °C), 0.866  $\pm$  0.007 (100.83), 2.25  $\pm$  0.01 (108.49), 3.765  $\pm$  0.0065 (112.93), 6.05  $\pm$  0.05 (116.65), 9.31  $\pm$  0.09 (120.38), 13.96  $\pm$  0.09 (124.18);  $E_a = 35.3 \pm 0.2$  kcal/mol,  $\log A = 15.6 \pm 0.13$ .

Gas-phase thermal studies were conducted in a 2-L Pyrex vessel fitted with a vacuum stopcock. The vessel was treated with  $\text{Et}_3\text{N}$  for a day at

120 °C and then evacuated. Samples (1–2 mg) of **1** or **7** were introduced along with measured amounts of bath gas. The vessel was then heated at 120 °C for typical time periods of 6 h. The products were condensed with liquid nitrogen, and solvent was transferred in. Analyses were performed both by  $^1\text{H}$  NMR spectroscopy and by gas chromatography on either a 20 in.  $\times$  1/4 in. UCW-982 column on Chromosorb WAW-DMCS or on a 30 m  $\times$  1/4 mm DB-17 capillary column. Control experiments revealed that bicyclobutane and 1,3-dimethylbicyclobutane were stable to the reaction conditions. Addition of glass beads to increase the surface-to-volume ratio by a factor of 7 did not produce any significant change in the product ratio.

**Calculations.** The Hase-Bunker program<sup>44</sup> was used for RRKM studies of the decomposition of **2** to butadiene and **6** to 2,3-dimethylbutadiene. For **2**, the necessary vibrational frequencies were obtained as described in the text, and for **6**, they were obtained by appropriate adjustment of the frequencies for **2** in a manner similar to cyclopropane and 1,2-dimethylcyclopropane.<sup>45</sup> The Whitten-Rabinovitch algorithm<sup>46</sup> was used to calculate the sums and densities of states. All rates were obtained assuming harmonic oscillations. No internal rotors were considered, and contributions from external rotations were also ignored. The moments of inertia in the ground and transition states were taken to be the same, while the frequencies of the transition state were related to those of the ground state by the high-pressure Arrhenius pre-exponential term by

$$A = \frac{\prod_i \nu_i}{\prod_i^{\ddagger} \nu_i^{\ddagger}}$$

Here *s* is the total number of ground-state oscillators and  $\ddagger$  indicates the transition state, which has one less vibrational mode.

The multistep collisional deactivation scheme assumed a stepladder model.<sup>33</sup> Collision diameters of 3.68 Å for nitrogen and 4.8 Å for benzene were used.<sup>32</sup> The values used for **2** (5.9 Å) and **6** (7.0 Å) were obtained by examining molecular models and by comparison with literature values<sup>35,47</sup> for similar structures. Hoare's deactivation scheme<sup>33</sup> yielded the theoretical product distribution as a function of pressure (Figure 3).

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(44) Hase, W. L.; Bunker, D. L. *QCPE* 1973, 11, 234.

(45) Durig, J. R.; Nease, A. B.; Milani-Nejad, F. *J. Mol. Struct.* 1981, 72, 57–72.

(46) Whitten, G. Z.; Rabinovitch, B. S. *J. Chem. Phys.* 1963, 38, 2466–2473.

(47) Dorer, F. H. *J. Phys. Chem.* 1969, 73, 3109–3114.