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Thermal Decomposition of a Series of 1,2-Diazetines

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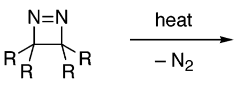
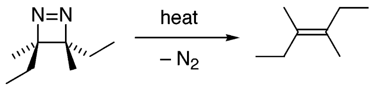
A homologous series of tricyclic diazetines (**6a**−**c**), differing by the number of methylene groups in the saturated bridges of the fused carbon bicycles, was synthesized. The $\Delta H^{\ddagger}$ of decomposition for each of the diazetines to afford N_2 and the corresponding alkene was determined experimentally: **6a**, 31.7; **6b**, 39.3; **6c**, 38.8 kcal/mol. The ground-state strain energy of each diazetine was estimated utilizing computationally obtained ΔH_f's for each of the experimentally investigated diazetines as well as several other diazetines whose $\Delta H^{\ddagger}$'s had been previously reported in the literature. The sum of the ground-state strain energies and $\Delta H^{\ddagger}$'s of decomposition for all of the diazetines was nearly constant, with an average value of 59 kcal/mol, suggesting that all of the diazetines decompose via the same mechanism. Generally, the higher the ground-state strain energy of the diazetine, the less the $\Delta H^{\ddagger}$ for decomposition. The decomposition transition states for **6a**−**c** and **7** were modeled computationally at the RB3LYP/6-311+G(3df,2p)//UB3LYP/6-31+G(d,p) level. The agreement of the experimentally determined $\Delta H^{\ddagger}$ values with transition-state energies obtained computationally supports the reaction mechanism originally proposed by Yamabe that the elimination process occurs by an unsymmetrical, yet concerted, transition state with strong biradical character.

Introduction

1,2-Diazetines are a class of strained four-membered ring azo compounds.[1] Diazetines are quite thermally robust, despite the release of strain energy that would be anticipated upon decomposition (eq 1).[1,2] Thus, although decomposition to afford N_2 and the corresponding alkene is strongly exothermic ($\Delta H \approx -50$ kcal/mol), there is a substantial activation barrier to the process ($\Delta H^{\ddagger} \approx 35$ kcal/mol).[2] The high activation barrier was initially attributed to one of two factors: (i) the significant energy "cost" required to surmount the symmetry forbiddenness of a [2s + 2s] cycloreversion or (ii) the large increase in strain energy for the molecule to adopt a transition-state geometry required for a symmetry-allowed [2s + 2a] cycloreversion.[3] An alternative, nonconcerted process was later suggested in which one C−N bond is broken to form a biradical intermediate followed by loss of the remaining N_2 fragment.[2] A crucial piece of mechanistic evidence was provided by the work of Greene who demonstrated that diazetine **2** stereospecifically afforded alkene **3** via cis elimination of N_2.[2] This finding ruled out a symmetry-forbidden [2s (N_2) + 2a (olefin)] cycloreversion as a mechanistic possibility and probably also a [2s (olefin) + 2a (N_2)] cycloreversion process based on the expectation that N_2 would not be generated in a high-energy triplet state. The nonconcerted diradical pathway was still considered viable, assuming that the loss of N_2 from the intermediate was rapid relative to the C−C bond rotation to account for the stereospecificity of the decomposition process. A final piece of mechanistic evidence was provided by Olsen who reported his studies on the decomposition of appropriately substituted mono- and dideuterated diazetines.[4] He surmised from the observed kinetic isotope effects that the transition state was unsymmetrical and strongly diradical-like.



1 a R = H
b R = CH$_3$ (1)



2 **3** (2)

More recently, a theoretical investigation of the diazetine decomposition was carried out at the CASSCF(2,2)/6-31G* level and then confirmed at higher levels of theory.[5] Studies on the hypothetical parent unsubstituted diazetine (**1a**) supported Olsen's conclusions of an unsymmetrical, yet concerted, transition state with strong biradical character. This was corroborated with the location of a similar transition-state structure for the known tetramethyldiazetine compound (**1b**) along with reasonable agreement of the computed activation energy and entropy change with those obtained experimentally

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[1] (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99−150. (b) Hogenkamp, D. J.; Greene, F. D. *J. Org. Chem.* **1993**, *58*, 5393−5399.

[2] White, D. K.; Greene, F. D. *J. Am. Chem. Soc.* **1978**, *100*, 6760−6761.

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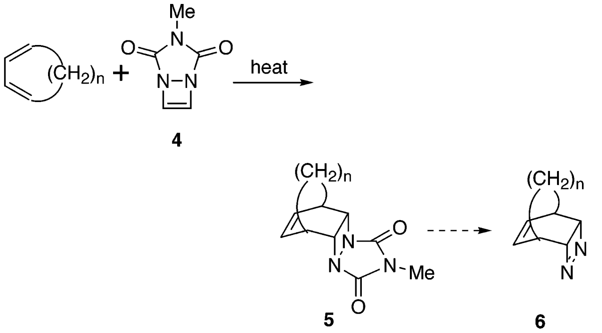
($\Delta H^{\ddagger}_{\text{calcd}} = 35.3$, $\Delta H^{\ddagger}_{\text{exp}} = 31.7$ kcal/mol; $\Delta S^{\ddagger}_{\text{calcd}} = +0.94$, $\Delta S^{\ddagger}_{\text{exp}} = +0.3 \pm 0.8$ cal/(mol K)).

Several years ago, Engel demonstrated that for a series of related acyclic and cyclic azo compounds, the sum of the ground-state strain energy and $\Delta H^{\ddagger}$ for thermolysis (the sum being referred to as the "transition-state energy for decomposition") was approximately constant (~ 43 kcal/mol).[1a,3] Thus, the more strained the azo compound in the ground state, the lower the observed $\Delta H^{\ddagger}$ for thermolysis. Tetramethyldiazetine **1b**, although formally a member of this homologous group of compounds, was observed to have a higher than expected $\Delta H^{\ddagger}$ based on its large strain energy (24.5 kcal/mol) and thus a transition-state energy (~56 kcal/mol) that was significantly higher than expected. However, to our knowledge, no further studies have been carried out to determine whether the transition-state energies for diazetine compound decompositions are likewise constant or whether strain similarly affects the $\Delta H^{\ddagger}$ of diazetine decomposition. The absence of studies may be traced to the notoriously limited methodology available for diazetine synthesis.

We recently reported a novel method for the synthesis of 1,2-diazetines based on the Diels–Alder cycloaddition of heterocyclic dienophile **4** with suitable dienes (eq 3).[6] The initially formed diazetidines (**5**) are readily converted to the corresponding diazetine compounds (**6**). We reasoned that the strain of the diazetine ring could be altered by changing the bridge size of the fused bicyclic alkane. Tightening the bridge size (ultimately from $n = 3$ to $n = 1$ in eq 3) was predicted to "pinch" the diazetine ring and increase the strain energy. In this paper, we report the synthesis of such a series of diazetines and investigate the effect of ring strain on diazetine decomposition.



4

5

a n = 1
b n = 2
c n = 3

6

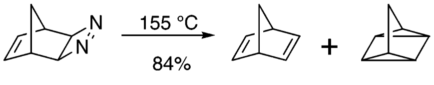
a n = 1
b n = 2
c n = 3 (3)

Results and Discussion

Synthesis of Diazetines 6a–c. Diazetines **6a–c** were synthesized utilizing a previously described method.[6] Heating dienophile **4** with 1,3-cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene afforded diazetidines **5a**, **5b**, and **5c**, respectively, via conventional Diels–Alder reactions in reasonable yields (**5a**, 74%; **5b**, 66%; **5c**, 53%). The endo isomers were observed exclusively with the exception of the reaction with 1,3-cyclopentadiene, in which small amounts of the exo isomer were formed in addition to the endo isomer (ratio of endo/exo was 9.4:1).

Hydrolysis of the urazole ring of cycloadducts **5a–c** (and the exo isomer of **5a**) with KOH in refluxing 2-propanol according to literature precedent afforded the corresponding hydrazo compounds that were not isolated.[7] Oxidation of the hydrazines to the diazetines was carried out utilizing a standard two-step method. First, treatment of the hydrazines with $CuCl_2$ resulted in oxidation to the corresponding diazetines but with anticipated formation of a complex between the diazetine and the Cu(I) ion.[7,8] Treatment of the complex with an aqueous NaOH solution released the diazetine from the complex. Published reports of similar oxidations suggested that the diazetine–Cu^+ complex that is formed could be easily isolated prior to release of the diazetine using NaOH.[7,8] However, we found it difficult to isolate these particular Cu^+ complexes and instead simply added the aqueous NaOH solution directly to the diazetine–Cu^+ complex in situ followed by extraction.[9] The yields obtained (**6a**, 60%; **6b**, 70%, **6c**, 98%; **7** [the exo isomer of **6a**], 53%) were comparable to yields published for azo compounds in which the complex was first isolated. Each of the compounds had ^1H and ^{13}C NMR data consistent with the proposed structure. Furthermore, each had a characteristic absorption in the UV spectrum attributed to the N=N double bond ($\lambda_{\max} \sim 343$ nm).[1b,3]

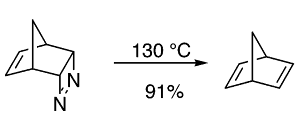
Products from the Thermal Decomposition of Diazetines 6a–c and 7. Thermal decomposition of each of the diazetines was accomplished in microscale sealed tubes in toluene as solvent (which also served as an internal standard for ^1H NMR integration). Thermolysis of the exo isomer of diazetine **6a** (i.e., **7**) at 155 °C (eq 4) for 2 h afforded a 92:8 mixture of norbornadiene and quadricyclane (analyzed by GCMS) in 84% yield (by ^1H NMR integration) in good agreement with previously reported results on this thermolysis (94:6 ratio at 111 °C in diglyme).[10] A control experiment demonstrated that quadricyclane is converted to norbornadiene at only 10% conversion under the same reaction conditions and for the same length of time.



7

92:8 (4)

Thermolysis of **6a** was carried out in a similar manner but at 130 °C for 2 h (eq 5). The only product observed under these conditions was norbornadiene (91% yield by ^1H NMR integration). No quadricyclane was observed by



6a (5)

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(6) Breton, G. W.; Shugart, J. H.; Hughey, C. A.; Perala, S. M.; Hicks, A. D. *Org. Lett.* **2001**, *3*, 3185–3187.

(7) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806–4809.

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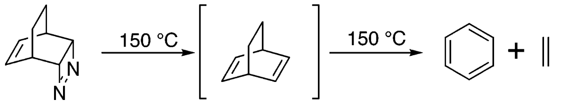
(9) See: Wildi, E. A.; Carpenter, B. K. *Tetrahedron Lett.* **1978**, 2469–2472.

(10) Rieber, N.; Alberts, J.; Lipsky, J. A.; Lemal, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 5668–5669.

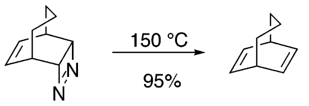
^{1}H NMR or GCMS. This finding lends support to the suggestion by Rieber that the quadricyclane formed during decomposition of the exo isomer, **7**, results from a competing [2s + 2s + 2s] retrocycloaddition process rather than via intramolecular trapping of a diradical intermediate by the C=C double bond.[10] If the latter process were active, both isomers might be expected to afford some quadricyclane whereas **6a** is geometrically incapable of taking part in a concerted retrocycloaddition process.

Diazetine **6b** was heated at 150 °C for 10 h to complete decomposition (eq 6). The reaction was followed by ^{1}H NMR spectroscopy, which revealed the loss of diazetine but no formation of the expected bicyclo[2.2.2]octa-2,5-diene product. Two singlets in the ^{1}H NMR spectrum were observed to appear, however, one corresponding to benzene (corroborated by GCMS) in approximately 68% yield and the other at ~5.4 ppm presumably due to ethylene. Bicyclooctadiene is known to undergo cycloreversion to yield benzene and ethylene.[11] Utilizing literature data, we estimated the half-life of bicyclooctadiene at 150 °C to be only ~6 min.[11] It is quite reasonable to assume, therefore, that the initially formed product of the thermolysis is bicyclo[2.2.2]octa-2,5-diene, which undergoes rapid cycloreversion to afford benzene and ethylene as final products (eq 6). As with diazetine **6a**, there was no formation of products of a tetracyclic nature.



6b (6)

Finally, diazetine **6c** decomposed within 10.5 h at 150 °C (eq 7) to afford predominantly a single product by ^{1}H NMR spectroscopy and GCMS in 95% yield (by ^{1}H NMR integration). The ^{1}H NMR spectrum, GC retention time, and MS of the product were identical to those of an authentic sample of bicyclo[3.2.2]nona-6,8-diene prepared independently.[12] As with the other two endo-substituted diazetines, no evidence for a tetracyclic product was observed.



6c (7)

Kinetics for the Decomposition of Diazetines 6a–c and 7. The kinetics for decomposition of each of the diazetines was determined employing UV spectroscopy by following the loss of the azo absorption with time (see Table 1). Clean first-order kinetics were observed in all cases. The decompositions were carried out in triplicate at three different temperatures for each of the diazetine compounds. Linear plots of ln(k/t) vs $1/T$ afforded $\Delta H^{\ddagger}$ values for decomposition of each of the diazetines (Table 1).

TABLE 1. Kinetic Data and $\Delta H^{\ddagger}$ Values for Decomposition of Diazetines 6a–c and 7

cmpd	temp (K)	$k/10^{-4}$ (s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)
7	398	0.66 ± 0.02	30.8 ± 0.8
	408	1.66 ± 0.05	
	418	4.51 ± 0.2	
6a	398	3.84 ± 0.09	31.7 ± 0.4
	408	9.75 ± 0.01	
	418	27.9 ± 0.4	
6b	418	0.51 ± 0.05	39.3 ± 1
	428	1.48 ± 0.06	
	438	4.57 ± 0.2	
6c	418	0.36 ± 0.01	38.8 ± 0.5
	428	1.11 ± 0.05	
	438	3.21 ± 0.05	

The value of $\Delta H^{\ddagger}$ (30.8 ± 0.8 kcal/mol) obtained for **7** was somewhat lower than that reported in the literature ($\Delta H^{\ddagger} = 33.1 \pm 0.5$ kcal/mol), although they are in reasonable agreement.[10] It should be noted that the literature value comes from a gas-phase determination while our data was obtained in solution. It may be observed that for the series of diazetines **6a–c**, diazetine **6a** had the lowest value of $\Delta H^{\ddagger}$ while the remaining two diazetines have values that are essentially equivalent within the limits of error. However, the difference in $\Delta H^{\ddagger}$ values between **6a** and **6c** of approximately 7 kcal/mol is significant and was the first indicator that there may be a dependence of $\Delta H^{\ddagger}$ on diazetine ring strain.

Determination of Ring Strain in Diazetines. The ring strain of several diazetines of interest was estimated according to the method of Engel in which the ΔH_f of a strain-free reference compound (calculated using Benson's group contribution method) is subtracted from the ΔH_f of the compound of interest.[13] The difference in these two values is attributed to ring strain. Values for the ΔH_f's of diazetines may be obtained experimentally (although requiring the sacrifice of precious compound!), or they may be predicted computationally with reasonable accuracy.[14] Although computational results may afford values for ΔH_f that differ from the actual values by as much as a few kcal/mol, we suspected that such errors would be systematic, and given that we were primarily interested in trends rather than absolute values, we decided to opt for the more practical computational route to ΔH_f values.

Computational values for ΔH_f may be obtained using a group-equivalent method based on computationally derived energies of suitable reference compounds according to the method of Wiberg.[14] Wiberg has reported group-equivalent energies explicitly for this purpose at the HF/6-31G* and MP2/6-31G* levels. However, there were no tabulated group-equivalent data for compounds containing N=N double bonds. Furthermore, neither of the computational levels employed for generation of the group-equivalent energies was suitable for our purposes. We had found in previous work that for strained dinitrogen heterocycles, HF methods afforded N–N bonds that were generally too short.[15] Extensive computations

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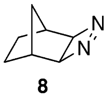
(15) Breton, G. W.; Martin, K. L. *J. Org. Chem.* **2002**, *67*, 6699–6704.

TABLE 2. Group Energy Terms at the RB3LYP/6-31G* Level

group	E (hartrees)	group	E (hartrees)
aliphatic groups			
CH_3	−39.89927	CH	−38.70984
CH_2	−39.30585	C	−38.11195
olefinic groups			
CH_2	−39.30369	C	−38.11868
CH	−38.71176		
azo group			
N_2	−109.53485		

at the MP2/6-31G* level are simply beyond our computational abilities at this time.

Previous work demonstrated that DFT methods (using the hybrid B3LYP functional) afforded values more in line with what was observed crystallographically for related strained compounds.[15] Furthermore, for our purposes, DFT calculations were more computationally affordable than MP2 methods. We, therefore, generated our own group-energy terms at the RB3LYP/6-31G* level according to the procedure (and using the same reference compounds) described by Wiberg. The calculated energies employed were obtained from the NIST Computational Chemistry Comparison and Benchmark DataBase website.[16] We obtained a group energy term for the N═N bond by including several azo compounds for which experimental ΔH_f's had already been reported and utilizing calculated energies of our own. The resulting group energy terms are recorded in Table 2 (for details of the compounds used, energies, and the method of calculation, see the Supporting Information). The terms were tested on some model compounds to ensure their robustness (Table 3). Several relevant cyclic (including the strained compounds cyclobutane and cyclobutene) and bicyclic (i.e., **11**−**14**) hydrocarbons were tested and demonstrated good agreement between the calculated and experimental ΔH_f's. The greatest deviation observed was for **14**, but the large uncertainty in the experimental value (−0.84 ± 0.55 kcal/mol) casts at least some doubt on the validity of the value. Several acyclic and cyclic azo compounds were tested, and reasonable agreement of the experimental ΔH_f's with calculated values were observed. Of particular note is that the calculated ΔH_f for tetramethyldiazetine (**1b**) of 35.2 kcal/mol agrees quite nicely with the experimental value of 35.9. Overall, the average difference between the observed and calculated ΔH_f's was an acceptable 1.4 kcal/mol. Applying these group-energy terms to the determination of ΔH_f for diazetines **6a**−**c** and **7** yielded the values in Table 3. Also in Table 3 are the calculated ΔH_f's for two other diazetines of interest, **8** and **9**, for which the experimental $\Delta H^‡$ of decomposition have already been reported.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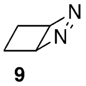
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Molecular strain energies may be computed by subtraction of the ΔH_f of a strain-free reference compound from the computationally derived ΔH_f of the diazetine.[13] Benson's method of summing group contributions to the ΔH_f provides a convenient strain-free reference value.[17] These reference values for the hydrocarbons **10**−**14** are provided in Table 4. However, the Benson group value for N_A−(C) (which is the group value for one of the azo nitrogens attached to a saturated carbon) of 32.5 kcal/mol was based on a single compound, and we opted instead to use the value employed by Engel of 27.9 kcal/mol.[13] The theoretical ΔH_f's for the strain-free reference compounds of the diazetines of interest are provided in Table 4. By subtraction of the reference ΔH_f's from the calculated ΔH_f's, strain energies were computed and are compiled in Table 4. Note that the calculated strain energy of **1b** (24.4 kcal/mol) compares very well with Engel's previously determined value of 24.5 kcal/mol. The successful prediction of both the ΔH_f and strain energy for **1b** suggested that the computational approach to obtaining strain energies for diazetines is both practical and useful.

Finally, a considerable portion of the strain inherent in these compounds is localized in the hydrocarbon backbone of the structure. Therefore, the strain energy of the relevant hydrocarbon (calculated in the same manner as for the diazetines) was subtracted from the total strain energy of each of the diazetine compounds (Table 5). The resulting strain energy difference ($\Delta E_{\mathrm{strain}}$) is an estimation of the strain localized within the diazetine ring itself. From Table 5 a few observations may be made. First, it is obvious that the diazetine ring of the endo-substituted norbornyl diazetine (**6a**) is more strained than the exo isomer (**7**), as might by expected ($\Delta E_{\mathrm{strain}} = 5$ kcal/mol). Second, there is a decrease in strain energy of the diazetine ring as the number of bridging carbons in the fused hydrocarbon bicycle increases: **6c** (21.3) < **6b** (24.1) < **6a** (29.5 kcal/mol). This is exactly the effect we predicted based on the presumption that tightening the bridge of the fused hydrocarbon bicycle would result in a "pinching" of the diazetine ring with a corresponding increase in strain energy.

Transition-State Energies. The transition-state energy for decomposition (E_{TS}) of each of the diazetines was obtained by summing the diazetine strain energies (i.e., the "diazetine"-localized portion of the strain as discussed above) and the corresponding $\Delta H^‡$ for decomposition (Table 5). The transition-state energies are fairly constant for all of the diazetines despite the estimations introduced during the calculation of strain energies and heats of formation. The average transition-state energy (59 kcal/mol) agrees well with Engel's initial estimate of the transition-state energy for the decomposition of **1b** of 56 kcal/mol.[3] The similarity of transition-state energies for all of the diazetines suggests they all decompose via the same reaction pathway.

As discussed earlier, the tricyclic series of diazetines **6a**−**c** provides a homologous series of diazetines whose ring strain methodically decreases. The overall decrease in strain energy (i.e., from **6a** to **6c**) of 8.2 kcal/mol is nearly matched by a corresponding increase in $\Delta H^‡$ of decomposition of 7.1 kcal/mol. The transition-state energy of **6b** (63.4 kcal/mol) is somewhat higher than that of both

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(16) Web address: http://srdata.nist.gov/cccbdb/Calcdata.asp.

(17) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279−324.

TABLE 3. Calculated RB3LYP/6-31G* Energies and Comparison of Calculated and Observed Heats of Formations[a]

compound	*E* (hartrees)[b]	ΔH_f(calcd)	ΔH_f(exp)[c]	diff
cyclohexane	−235.88044[d]	−28.4	−29.4	+1.0
cyclopentane	−196.55708[d]	−17.5	−18.3	+0.8
cyclobutane (**10**)	−157.21315[d]	6.4	6.8	−0.4
cyclobutene	−155.97326[d]	38.9	37.5	+1.4
bicyclo[2.2.1]heptane (**11**)	−273.96865	−12.3	−13.1	+0.8
bicyclo[2.2.1]hept-2-ene (**12**)	−272.72747	20.9	21.7	−0.8
bicyclo[2.2.2]oct-2-ene (**13**)	−312.05673	6.2	6.3	−0.1
bicyclo[3.2.2]non-6-ene (**14**)	−351.36874	2.32	−0.84	+3.2
trans-dimethyl diazene	−189.27545	36.4	35.5[e]	+0.9
trans-dipropyl diazene	−346.53594	13.1	12.4	+0.7
trans-diisopropyl diazene	−346.54252	5.7	8.6	−2.9
trans-di-*tert*-butyl diazene	−425.17025	−10.0	−8.7	−1.3
3,3,5,5-tetramethyl-1,2-diazacyclopentene (**15**)	−384.65018	7.2	9.3	−2.1
3,3,5,5-tetramethyl-1,2-diazacyclohexene (**16**)	−423.95566	7.5	10.0	−2.5
1,4-dimethyl-bicyclo[2.2.2]-2,3-diazaoct-2-ene (**17**)	−422.74872	20.1	22.1[e]	−2.0
1b	−345.29971	35.2	35.9	−0.7
6a	−380.92932	109.3		
6b	−420.26719	89.3		
6c	−459.58344	82.7		
7	−380.93734	104.3		
8	−382.17931	70.6		
9	−265.42061	91.4		

[a] Energies are in kcal/mol unless otherwise indicated. [b] Minimized at the RB3LYP/6-31G(d) level and confirmed with a frequency check (no imaginary frequencies). Values are uncorrected for zero-point energies. [c] Unless otherwise indicated, obtained from NIST Chemistry webbook (http://webbook.nist.gov/). [d] Energies obtained from NIST Computational Chemistry Comparison and Benchmark DataBase website (ref 16) and are uncorrected for zero-point energies. [e] Reference 1a.

TABLE 4. Benson Reference Heats of Formation and Calculated Strain Energies[a]

compd	ΔH_f(calc)	ΔH_f(ref)[b]	E_{strain}[c]
10	6.4	−19.8	26.2
11	−12.3	−28.6	16.3
12	20.9	−0.63	21.5
13	6.2	−5.58	11.8
14	2.32	−10.53	12.9
1b	35.2	11.5	24.4
6a	109.3	58.3	51.0
6b	89.3	53.4	35.9
6c	82.7	48.5	34.2
7	104.3	58.3	46.0
8	70.6	30.4	40.2
9	91.4	41.9	49.5

[a] All energies are in kcal/mol. [b] Theoretical unstrained ΔH_f obtained from Benson group values (ref 17). Compounds **6**−**9** include Engel's group value for the N=N group (ref 13). [c] Obtained by taking the difference between ΔH_f(calc) and ΔH_f(ref).

TABLE 5. Calculation of the Strain Energy (ΔE_{strain}) Localized in the Diazetine Ring and the Transition-State Energy (E_{TS}) for Several Diazetines[a]

compd	ref compd	ΔE_{strain}	$\Delta H^\ddagger$	E_{TS}[b]
1b		23.7	31.7[c]	55.4
6a	**12**	29.5	31.7	61.2
6b	**13**	24.1	39.3	63.4
6c	**14**	21.3	38.8	60.1
7	**12**	24.5	30.8	55.3
8	**11**	23.9	33.7[d]	57.6
9	**10**	23.3	32.9[e]	56.2

[a] All energies in kcal/mol. [b] Obtained as the sum of ΔE_{strain} and $\Delta H^\ddagger$. [c] Reference 1a. [d] Reference 10. [e] Reference 18.

6a (61.2) and **6c** (60.1), primarily due to a somewhat higher than expected $\Delta H^\ddagger$ value of decomposition at 39.3 kcal/mol (that of **6a** and **6c** are both lower [31.7 and 38.8 kcal/mol, respectively]). However, given the error limits on the $\Delta H^\ddagger$ values and the estimations used to arrive at the strain energies of the diazetine rings, we believe that at least the qualitative picture holds true; the decomposition of diazetines is affected by strain in a manner similar to that of acyclic azo compounds, i.e., increased ground-state energy induced by strain is compensated for by a decrease in $\Delta H^\ddagger$ of reaction to afford a common transition-state energy for the decomposition of diazetines.

Computational Results on Diazetine Decomposition. To supplement our experimental findings on the decomposition of diazetines, we also performed some computational modeling studies.[19] As mentioned earlier, a theoretical investigation of the decomposition of unsubstituted diazetine **1a** had been carried out at the CASSCF(2,2)/6-31G* level by Yamabe.[5] While we had no problems reproducing the reported results, we ran into unresolvable convergence problems when attempting to apply the same method to model the transition states for decomposition of some of the substituted diazetines. Yamabe had commented that HF and DFT methods (BLYP, B3PW91, and hybrid B3LYP) had been tested for a transition-state search but were found to be unsuccessful. However, we were able to locate a transition state for the decomposition of **1a** utilizing the UB3LYP/6-31+G** method (Figure 1). The transition-state structure located was in reasonable agreement with the structure

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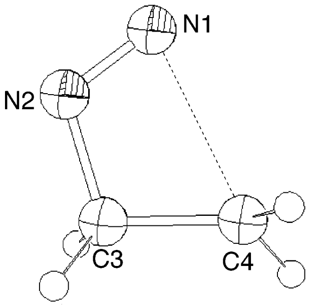

FIGURE 1. Calculated transition state structure for the decomposition of **1a** at the UB3LYP/6-31+G** level. Structural data provided in Table 6.

located by the CASSCF(2,2)/6-31G* method (Table 6). The most significant difference being that the twist of the N1−N2 fragment relative to the C3−C4 bond of the UB3LYP/6-31+G** structure as measured by the N1−N2−C3−C4 dihedral angle (6.0°) was shallower than that of the CASSCF(2,2)/6-31G* structure (14.9°). However, the calculated reaction barrier (30.9 kcal/mol) at the UB3LYP/6-31+G** level matched that reported by Yamabe (31.0 kcal/mol). It appeared, therefore, that the UB3LYP/6-31+G** method afforded reasonable results for the calculation.[20]

This computational method was next applied toward locating the transition state for decomposition of diazetines **6a**−**c**, and **7**. In each case, a transition state was successfully located (Figure 2). Each of the transition-state structures exhibited a single imaginary frequency whose animated motion was consistent with loss of N_2 from the hydrocarbon fragment. The transition-state geometries at the diazetine ring systems were remarkably similar (Table 5). As with the parent diazetine (i.e., **1a)**, each of the substituted diazetines exhibited a small N1−N2−C3−C4 dihedral angle of 4.9−5.5° such that the diazetine portion of the ring was not planar. Yamabe had previously established for **1a** that the symmetry-lowering twist of the N_2 fragment relative to the C−C diazetine bond in the transition state results in a lowering of the energy of the transition state due to dual orbital mixing effects possible for a transition state exhibiting strong biradical character. The twisted transition state is of even lower energy than a C_s-symmetric Woodward−Hoffmann "symmetry-allowed" transition-state structure.[5]

Higher-level single-point energy calculations of the transition-state structures and the corresponding ground-state diazetine structures (minimized at the B3LYP/6-31G** level) at the B3LYP/6-311+G(3df,2p) level afforded transition-state barriers for the decomposition reactions (which were corrected for zero-point energies utilizing the corresponding zero-point correction from the minimization calculation). Calculated barriers for **6a** (33.3), **6b** (36.9), **6c** (37.5), and **7** (34.6 kcal/mol) corresponded reasonably well with the experimental values (Table 1). The agreement of these calculated values with the experimental values suggests that Yamabe's proposed mechanism of an unsymmetrical, yet concerted, elimination of N_2 from diazetines is quite reasonable.

Conclusions

A homologous series of tricyclic diazetines (**6a**−**c**), differing by the number of methylene groups in the saturated bridges of the fused carbon bicycles, was synthesized. The $\Delta H^{\ddagger}$'s of decomposition for each of the diazetines were determined experimentally. The ground-state strain energy of each diazetine was estimated utilizing computationally obtained ΔH_f's for each of the experimentally investigated diazetines as well as several other diazetines whose $\Delta H^{\ddagger}$'s had been previously reported in the literature. The sum of the ground-state strain energies and $\Delta H^{\ddagger}$'s of decomposition for all of the diazetines was nearly constant, with an average value of 59 kcal/mol, suggesting that all of the diazetines decompose via the same mechanism. Generally, the higher the ground-state strain energy of the diazetine, the less the $\Delta H^{\ddagger}$ for decomposition. The agreement of the experimentally determined $\Delta H^{\ddagger}$ values with values obtained by computational modeling studies supports the reaction mechanism proposed by Yamabe that the elimination process occurs by an unsymmetrical, yet concerted, transition state with strong biradical character.

Experimental Section

Cycloadduct 5c. In a screw-cap high-pressure tube was combined **4** (0.105 g, 0.76 mmol), 1,3-cycloheptadiene (5 g, 53 mmol), and chlorobenzene (2 mL). The mixture was swirled and briefly deoxygenated with a stream of dry N_2. The tube was sealed with a teflon cap and heated at 150 °C for 48 h. After this time, the solution had darkened and some dark precipitate was apparent. The mixture was cooled and filtered into a clean round-bottomed flask, and the solvent was removed in vacuo. Column chromatography (SiO_2, 1:2 EtOAc/hexane) afforded 94.3 mg (53% yield) of **5c** as a white solid: ^1H NMR δ 6.16 (dd, $J = 4.8, 3.2$ Hz, 2H), 4.78 (br s, 2H), 3.01 (br m, 2H), 2.99 (s, 3H), 1.8−1.5 (m, 6H); ^{13}C NMR δ 162.7, 130.9, 67.4, 33.8, 25.5, 25.1, 21.9. Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.70; H, 6.57; N, 17.74.

Diazetine 6c. To a solution of **5c** (93.4 mg, 0.4 mmol) in 1.5 mL of 2-propanol was added 0.112 g (2 mmol) of freshly crushed KOH. The resulting mixture was heated to reflux for 2 h and then cooled to room temperature. A few small pieces of ice were added to the solution, and then concentrated HCl was added dropwise until a solution of pH = 2 was obtained. This solution was heated at 50 °C for 5 min and then cooled. A solution of 5 M aq NH_4OH was added dropwise to obtain a neutral solution. An aq solution of 3 M $CuCl_2$ (1 mL) was added via pipet to the stirring reaction mixture, and a dark-brownish-red precipitate formed almost immediately. Finally, sufficient 5 M aq NH_4OH was added to convert the reaction mixture to a clear-deep-blue solution. This solution was washed with 3 × 15 mL Et_2O, dried, and concentrated. Column chromatography (SiO_2, 1:1 EtOAc/hexane) afforded 58 mg (98% yield) of **6c** as a thick colorless liquid: ^1H NMR δ 5.95 (dd, $J = 5.0,3.1$ Hz, 2H), 4.43 (dd, $J = 2.2, 1.7$ Hz, 2H), 2.87 (br m, 2H), 1.9−1.1 (m, 6H); ^{13}C NMR δ 129.7, 82.7, 33.6, 25.0, 22.2. UV $_{\lambda\max}$ (N=N) = 342 nm.

General Procedure for the Thermolysis of Diazetines 6a−c and 7. A microtube was fashioned from a standard Pasteur pipet by first sealing the dispensing tip with a flame. Most of the upper portion of the pipet was cut off leaving ∼2 cm of the wider glassware attached. A solution of the diazetine (∼10 mg) in 20 μL of toluene was carefully dispensed into the sealed portion of the pipet with a syringe, being especially careful to avoid contaminating the sides of the tube where the second seal was to be made. The solution was cooled in dry ice while a vacuum was applied at the open end of the tube, and the tube was sealed at the top of the tube just below where

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[20] The spin-squared values for each of the calculations carried out using the UB3LYP method are reported in the Supporting Information.

TABLE 6. Structural and Energetic Data on the Calculated Ground State and the Calculated Transition-State Energy for the Decomposition of Selected Diazetines[a]

					bond length (Å)				
compd	SP[b]	*E*[c]	*E*[d]	E_{TS}[e]	N_1-N_2	N_1-C_4	N_2-C_3	C_3-C_4	dihedral angle (deg)[f]
1a	GS	−187.98509			1.264	1.491	1.491	1.546	0.02
	TS	−187.93584		30.9[g]	1.205	2.209	1.477	1.530	6.01
	TS	−186.84624[h]		31.0[h]	1.184	2.290	1.453	1.522	14.86
6a	GS	−380.82002	−380.91850		1.264	1.500	1.500	1.545	0.00
	TS	−380.77695	−380.86547	33.3	1.207	2.235	1.471	1.548	4.88
6b	GS	−420.13252	−420.23957		1.266	1.492	1.492	1.546	0.05
	TS	−420.08456	−420.18077	36.9	1.207	2.227	1.474	1.540	5.14
6c	GS	−459.42403	−459.53919		1.265	1.494	1.494	1.551	0.00
	TS	−459.37510	−459.47948	37.5	1.206	2.234	1.481	1.542	5.54
7	GS	−380.82818	−380.92579		1.261	1.506	1.506	1.551	0.00
	TS	−380.78339	−380.87073	34.6	1.201	2.301	1.488	1.553	1.93

[a] Energies in hartrees unless otherwise indicated. [b] SP = type of stationary point, GS = ground state, TS = transition state. [c] Minimized at the UB3LYP/6-31+G** level for TS structures and RB3LYP/6-31+G** for GS structures. All energies have been corrected for zero-point energy. [d] Single-point energy calculation at the B3LYP/6-311+G(3df,2p)//(U)B3LYP/6-31+G** level and corrected for zero-point energy using the ZPC from the B3LYP/6-31+G** calculation. [e] Calculated transition-state barrier in kcal/mol at the B3LYP/6-311+G(3df,2p)// UB3LYP/6-31+G** level unless otherwise indicated. [f] Pertaining to the N1−N2−C3−C4 dihedral angle (see Figures 1 and 2). [g] At the UB3LYP/6-31+G**// UB3LYP/6-31+G** level. [h] At the CASSCF(2,2)/6-31G(d)// CASSCF(2,2)/6-31G(d) level.

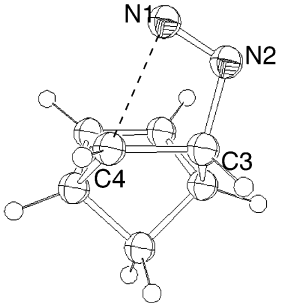

FIGURE 2. Calculated transition state structure for the decomposition of **6a** at the UB3LYP/6-31+G** level. Structural data provided in Table 6.

the wider glassware begins. The tube was carefully placed into an NMR tube, and the NMR tube was filled with CCl_4 to a level just above that of the sealed tube. A ^1H NMR spectrum was then run on the sample, and integrations of the diazetine compound versus the toluene signals were recorded. The sealed tube was removed from the NMR tube and slipped into a preheated silica gel bath at the appropriate temperature. (Sand proved to be too rough and sometimes caused the tube to rupture and explode. **CAUTION**: the sealed tubes are under pressure and have been known to explode unexpectedly while being heated. Appropriate precautions should be taken at all times.) The tube was removed at appropriate intervals and analyzed by ^1H NMR spectroscopy as described above. After complete reaction, the sealed tube was placed in a large screw-capped test tube with a small stir bar. The test tube was sealed, and the contents were shaken to break the sealed tube. A few mL of CH_2Cl_2 was added to the test tube to dissolve the contents, and the resulting solution was then analyzed by GCMS.

Kinetics Determinations. A specially designed fiber optic UV−vis system was utilized for the determinations of reaction kinetics.[21] Generally, a solution of the diazetine in hexadecane (~6 mM) in a quartz cuvette with a screw-cap seal was placed into a preheated cuvette holder at the desired temperature. The reaction was followed by taking periodic measurements of the absorbance at the maximum absorption of the azo group (**6a**, 343 nm; **6b**, 343 nm; **6c**, 342 nm; **7**, 345 nm). Three runs at each of the three different temperatures were conducted for each diazetine (see Table 1).

Computational Methods. Computations were carried out with the Gaussian98W suite of programs.[19] All points were characterized by the calculation of the vibrational frequencies at the same computational level at which the minimization were conducted (minima having no imaginary vibrational frequencies and transition states having a single imaginary vibrational frequency). All energies reported include the zero-point corrections (scaled by a factor of 0.9614) unless otherwise indicated.

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Supporting Information Available: General experimental details; data and method of calculation of the group energy equivalents at the RB3LYP/6-31G(d) level; Cartesian coordinates, total energies, and computed zero point corrections for all of the calculated structures; ^1H and ^{13}C NMR spectra for compound **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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