Stereochemical Tests of Cyclic 1,1-Dialkyldiazene Fragmentation Reactions. Thermal Decomposition of *N*-(*cis*-(and *trans*-)2,3-(and 2,5-)Dimethylpyrrolidine)-nitrenes[1,2]

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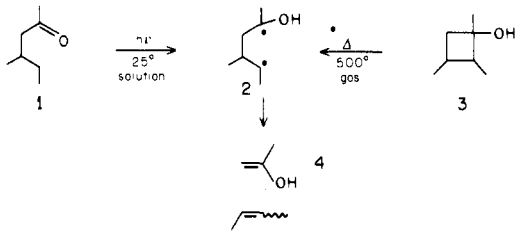
Abstract: The thermal decompositions of presumed 1,1-diazenes, *N*-(*cis*-(and *trans*-)2,5-dimethylpyrrolidine)nitrenes (**30**), generated from the base-induced decomposition of *N*-benzenesulfonamido-*cis*-(and *trans*-)2,5-dimethylpyrrolidines (**28**) in octane (and diglyme) at 120 °C, afford propene, 1,2-dimethylcyclobutanes, and 1-hexene. The retention/inversion (*r*/*i*) ratios of closure products are higher than those found from the corresponding 1,2-diazenes in the gas phase at 306 and 439 °C. The thermal decompositions of presumed 1,1-diazenes, *N*-(*cis*-(and *trans*-)2,3-dimethylpyrrolidine)nitrenes (**31**), generated from the base-induced decomposition of *N*-benzenesulfonamido-*cis*-(and *trans*-)2,3-dimethylpyrrolidine (**29**) in octane (and diglyme) at ≤120 °C, afford 2-butenes and 1,2-dimethylcyclobutanes. The stereospecificity in the 2-butanes and 1,2-dimethylcyclobutanes is high. Analysis of the data indicates a 51% direct cleavage pathway to *trans*-2-butene and ethylene and 49% 1,4-biradical pathway from the decomposition of *N*-(*trans*-(2,3-dimethylpyrrolidine)nitrene (*trans*-**31**). Similarly, *N*-(*cis*-(2,3-dimethylpyrrolidine)nitrene (*cis*-**31**) affords a 38% direct cleavage pathway to *cis*-2-butene and ethylene and 62% 1,4-biradical pathway. Whether this stereospecific cleavage reaction is a concerted cycloreversion or results from a diazenyl biradical precursor cannot be distinguished from the data. The relative rates of rotation, cleavage, and closure for 3-methyl-1,4-pentanediyl (**35C** and **35T**) generated from the corresponding tetramethylene-1,1-diazenes (**31**) in octane at ≤120 °C were determined. From **35C**, k(cleavage)/k(closure) = 1.6, k(closure)/k(rotation) = 4.9. From **35T**, k(cleavage)/k(closure) = 4.7 and k(closure)/k(rotation) = 3.1. Thermal decomposition of *N*-methanesulfonamido-*cis*-(and *trans*-)2,3-(and 2,5-)dimethylpyrrolidines (**39** and **38**, respectively) in the gas phase at 306 and 439 °C affords hydrocarbon products consistent with the intermediacy and subsequent decomposition of 1,1-diazenes (**30** and **31**). The retention/inversion ratios in the closure products suggest that 1,4 biradicals generated from cyclic 1,1-dialkyldiazene decompositions in the gas phase at 306 and 439 °C behave much like those from cyclic 1,2-diazene decompositions under similar conditions. 1,4 biradicals with secondary radical centers generated from the same 1,1-diazenes behave more stereospecifically in solution at lower temperatures (120 °C).

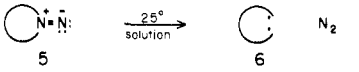
Introduction

Comparisons of stereochemical tests directed toward an understanding of the behavior of 1,4 biradicals generated by very different methods have been complicated by the lack of examples in the literature where the type of substituents, degree of substitution, and reaction conditions are the same. Frequently, experimentally observed differences in the behavior of similarly substituted biradicals from thermal and photochemical routes[4] are not easily assigned to differences in mode of generation because of the superimposed differences in reaction conditions. For example, a stereochemical test[5] was carried out to determine whether the photochemically generated intermediate (from **1**) is identical with the species generated by the thermal cleavage of an appropriately substituted cyclobutanol **3**. The observed *cis*-/*trans*-2-butene product



ratios were different from each route, the thermal result being less stereospecific. One explanation assigns the different stereochemical behavior to excess energy associated with the photochemical route.[5] The alternative explanation, that the differences in stereochemical outcome are due to the reaction conditions, requires that 1,4 biradicals with secondary radical centers behave more stereospecifically at lower temperatures in solution.

One fragmentation reaction that appears to generate biradicals by a thermal route at lower temperatures (25 °C) in solution is the decomposition of 1,1-dialkyldiazenes (aminonitrenes) **5**.[6] Unlike their more stable 1,2-diazene isomers



(azo compounds), the 1,1-diazenes are not usually isolated or characterized by physical means but rather are assumed intermediates based on a substantial body of chemical evidence (e.g., several independent methods of generation afford similar decomposition products).[6,7]

Overberger, Valentine, and Anselme found that the reaction of *N*-amino-*cis*-(and *trans*-)2,5-diphenylpyrrolidine (**7** and **8**, respectively) with mercuric oxide in ethanol afforded *cis*-(and *trans*-)1,2-diphenylcyclobutanes (**9** and **10**, respectively) and styrene **11**.[8] The results are consistent with the formation and subsequent decomposition of a 1,1-diazene **12** to 1,4-diphenyl-1,4-butanediyl (**13**). Kopecky and Soler found that the thermal decomposition of *cis*-(and *trans*-)3,6-diphenyl-3,4,5,6-tetrahydropyridazines (**14** and **15**, respectively) in benzene at 63 °C affords the same products but different ratios[9] (Table I).

N-(Pyrrolidine)nitrenes **16** may be sensitive to substitution and not simply afford 1,4 biradicals and nitrogen on decomposition. The thermal decomposition of the unsubstituted tetramethylene-1,1-diazene (**16**), generated from the corre-

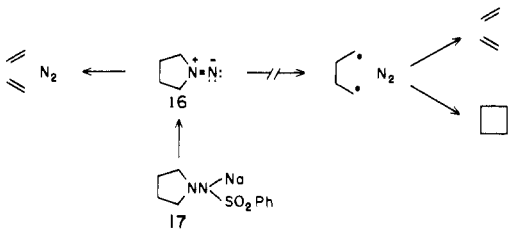


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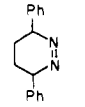
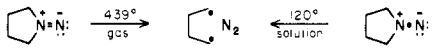
Table I

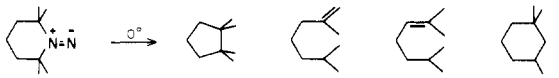
		temp, °C	Ph, Ph	Ph, Ph	Ph
	*cis*-**7**	25	6.5	66.0	12.6
	trans-**8**	25	8.5		12.4
	*cis*-**14**	63	14.6	30.1	55.3
	trans-**15**	63	39.2	1.7	59.1

sponding sulfonylhydrazine salt (**17**), was reported by Lemal and co-workers[10] to afford ethylene as the only hydrocarbon product. The absence of cyclobutane was cited as evidence that fragmentation of tetramethylene-1,1-diazene (**16**) may be concerted, i.e., does not proceed via a 1,4-biradical intermediate. The experimental benefit derived from the thermal lability of cyclic 1,1-dialkyldiazenes as sources of biradicals at low temperatures in solution will be complicated by the need to distinguish in 1,1-diazene decompositions concerted direct fragmentation pathways, presumably important in the unsubstituted case **16**, in competition with the biradical-forming pathways, presumably important in the diphenyl-substituted case **12**.

The stereochemistry of the cleavage reaction in the tetramethylene-1,1-diazene decomposition has not been examined. We describe here the syntheses and decomposition of the appropriately substituted precursors for this stereochemical test. Direct olefin-forming reactions will be separated from the 1,4-biradical pathway in the *N*-(pyrrolidine)nitrene fragmentation. In completing this assignment the behavior of a 1,1-diazene-generated 1,4 biradical in solution at relatively low temperatures will be available. We report here (a) the relative rates of rotation, cleavage, and closure for 3-methyl-1,4-pentanediyl in solution at approximately 120 °C, and (b) efforts to generate these 1,1-diazenes at 439 °C in the gas phase. A comparison of the stereospecificities of similarly substituted 1,4 biradicals generated from similar precursors (1,1-diazenes) at different temperature and phase will allow a test of the importance of these variables with regard to 1,4-biradical behavior.



Recently, evidence for the direct observation of a 1,1-dialkyldiazene has been reported.[11] Reaction of 1-amino-2,2,6,6-tetramethylpiperidine (**18**) with *tert*-butyl hypochlorite and triethylamine in diethyl ether at −78 °C affords an intense purple solution which is stable for hours at −78 °C, but decolorizes in minutes at 0 °C, affording hydrocarbon products **20–23** consistent with the formation and subsequent decomposition of a 1,1-dialkyldiazene intermediate **19**. The electronic



spectrum of this purple solution at −78 °C reveals the n → π* electronic transition (λ_{max} 541 nm in CH_2Cl_2), for *N*-(2,2,6,6-tetramethylpiperidine)nitrene (**19**). The infrared spectrum provides evidence that this 1,1-diazene **19** has considerable N=N double bond character in the ground state (N=N stretch at 1595 cm^{-1}).

Table II

reactant	conditions	% yields[a] 2			
cis-**28**	*b*	78.0	4.2	17.8	0.1
	c	77.6	5.0	17.1	0.3
trans-**28**	*b*	83.8	13.1	1.7	1.3
	c	86.2	10.5	2.2	1.1

[a] Percent yield based on total hydrocarbon product. [b] In diglyme with sodium butoxyethoxide at ≤120 °C[15] for 30 min. Typical absolute yields from **28** and **29** are 67–99%. [c] In *n*-octane with dry sodium methoxide at ≤120 °C[15] for 30 min. Typical absolute yields from **28** and **29** are 38–73%.

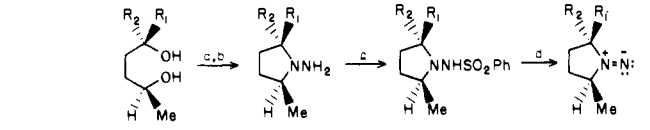
Table III

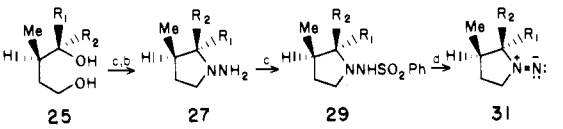
reactant	conditions	% yields[a]			
cis-**29**	*b*	1.2	87.5	0.9	10.5
	c	1.9	86.5	1.2	10.4
trans-**29**	*b*	79.3	1.8	18.6	0.4
	c	79.0	2.8	17.6	0.6

[a-c] See footnotes *a–c* of Table II.

Results and Discussion

Synthesis of *N*-Amino-*cis*-(and *trans*-)2,3-(and 2,5-)dimethylpyrrolidines (27 and 26, Respectively) and the Corresponding Benzenesulfonamides. Successive treatment of each of four isomeric diols (*dl*- and *meso*-2,5-hexanediol **24**[12] and *threo*- and *erythro*-3-methylpentane-1,4-diol **24**)[13] with methanesulfonyl chloride and hydrazine hydrate afforded stereospecifically the four *N*-aminodimethylpyrrolidines **26** and **27** (~97% isomerically pure).[14] These were further puri-

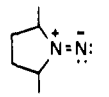
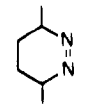
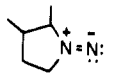
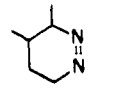




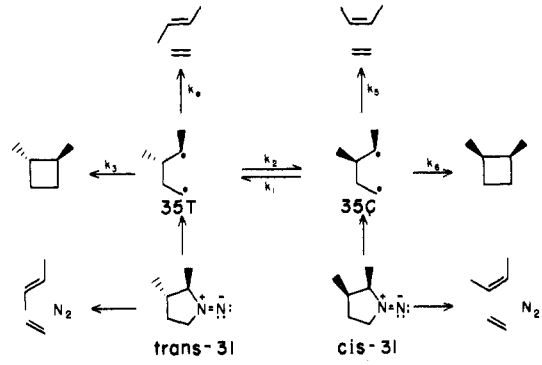
a) MsCl b) H_2NNH_2 c) $PhSO_2Cl$ d) RONa

fied (≥99.5% isomerically pure) by preparative vapor phase chromatography (Pennwalt-223 amine packing). Treatment of each of these *N*-aminodimethylpyrrolidines **26** and **27** with benzenesulfonyl chloride afforded the *N*-benzenesulfonamido-*cis*-(and *trans*-)2,3-(and 2,5)-dimethylpyrrolidines (**29** and **28**, respectively). Reaction of these benzenesulfonamides in *n*-octane (and diglyme) at ≤120 °C[15] in the presence of base afforded hydrocarbon products in absolute yields of 38–99%. Product ratios were determined by electronically integrated analytical vapor phase chromatography (VPC) analysis. Conditions and results from the pyrolyses are listed in Tables II and III.

Table IV. Retention/Inversion Ratios in Closure Products from Similarly Substituted 1,1- and 1,2-Diazenes at Different Temperature and Phase

		conditions	r/i
	*cis*-**30**	≤120 °C/solution	3.42
	trans-**30**	≤120 °C/solution	4.77
	*cis*-**32**	439 °C/gas	1.68
	trans-**32**	439 °C/gas	1.67
	*cis*-**31**	≤120 °C/solution	8.67
	trans-**31**	≤120 °C/solution	29.33
	*cis*-**33**	439 °C/gas	2.29
	trans-**33**	439 °C/gas	7.76

Scheme I



From Table II, the decomposition of the presumed *N*-(2,5-dimethylpyrrolidine)nitrenes (**30**) affords propene, 1,2-dimethylcyclobutanes, and 1-hexene. Whether all (or only part) of the propene is derived from a 1,4-biradical intermediate, 2,5-hexanediyl, cannot be determined from this experiment. However, the retention/inversion (*r/i*) ratios of closure products, presumably derived from 2,5-hexanediyl, are higher than those found from the corresponding 1,2-diazenes in the gas phase at higher temperature.[16] If the mode of generation, 1,1- vs. 1,2-diazene precursors, is not important, we have the qualitative finding that 2,4-hexanediyl behaves more stereospecifically at low temperature in solution that at high temperature in the gas phase (Table IV).

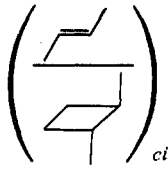
From Table III, the decomposition of the presumed *N*-(2,3-dimethylpyrrolidine)nitrenes (**31**) affords 2-butenes and 1,2-dimethylcyclobutanes. The stereospecificity in the 2-butenes and 1,2-dimethylcyclobutanes is high. In agreement with the "symmetrically" substituted series **30**, stereochemical retention in the closure products is higher from the 1,1-diazene route in solution at ≤120 °C than the corresponding 1,2-diazene route[16] in the gas phase at 439 °C (Table IV).

Examination of the data in Table III reveals that the ratio of *trans*-2-butene/*trans*-1,2-dimethylcyclobutane is higher from the *N*-(*trans*-2,3-dimethylpyrrolidine)nitrene (**31**) precursor than from the *cis*-1,1-diazene precursor **31** (at ≤120 °C in octane, 4.49 vs. 1.58). Similarly, the ratio of *cis*-2-butene/*cis*-1,2-dimethylcyclobutane is higher from the *N*-(*cis*-2,3-dimethylpyrrolidine)nitrene (**31**) precursor than from the *trans*-1,1-diazene precursor **31** (at ≤120 °C in octane, 8.32 vs. 4.67). Thus, there is an *extra component at stereospecific cleavage of retained* stereochemistry from each *N*-(2,3-dimethylpyrrolidine)nitrene, *cis*- and *trans*-**31.**

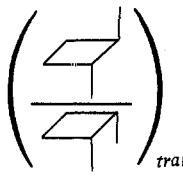
Table V. Relative Rates of Rotation, Cleavage, and Closure for 3-Methyl-1,4-pentanediyl at ≤120 °C in Octane

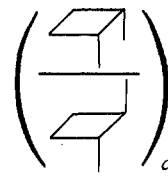
$\frac{k_4}{k_3}$	1.6	$\frac{k(\text{cleavage})}{k(\text{closure})}$	4.7	$\frac{k_5}{k_6}$
$\frac{k_3}{k_2}$	4.9	$\frac{k(\text{closure})}{k(\text{rotation})}$	3.1	$\frac{k_6}{k_1}$

Consider the following kinetic scheme (Scheme I). From Table III $k(\text{cleavage})/k(\text{closure})$, $k_5/k_6 = 4.67 = R_2$ and $k_4/k_3 = 1.58 = R_1$. Using the same kinetic equations for a steady-state treatment of a similar scheme,[13] one can solve for $k(\text{closure})/k(\text{rotation})$, i.e., k_3/k_2 and k_6/k_1. From Table III four experimental ratios are used:

$R_1 =$  $= \frac{k_4}{k_3} = 1.6$ *cis*-31

$R_2 =$  $= \frac{k_5}{k_6} = 4.7$ *trans*-31

$R_3 =$  $= 29.3$ *trans*-31

$R_4 =$  $= 8.7$ *cis*-31

These four experimental ratios R_1 to R_4 allow one to solve for $k_6/k_1 = 3.10$ and $k_3/k_2 = 4.87$. The relative rates of rotation, cleavage, and closure for 3-methyl-1,4-pentanediyl generated from a 1,1-diazene at ≤120 °C in octane are shown in Table V.

In order to determine the direct cleavage component we calculate the *trans*-/*cis*-2-butene ratios expected from the 1,1-diazene generated 1,4 biradicals:

$$\text{let } R_5 = \left(\text{  }\right) = \frac{k_4}{k_2}\left(\frac{k_1}{k_5} + 1 + \frac{k_5}{k_6}\right)$$

Then $R_5 = 7.8(0.07 + 1 + 0.21) = 10.0$, the *trans*-/*cis*-2-butene ratio expected from exclusive 1,4-biradical formation from *trans*-1,1-diazene **31**.

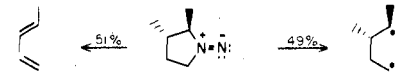
Similarly, let

$$R_6 = \left(\text{  }\right) = \frac{k_5}{k_1}\left(\frac{k_3}{k_4} + 1 + \frac{k_2}{k_4}\right)$$

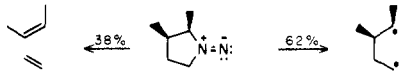
Then $R_6 = 14.48(0.63 + 1.0 + 0.13) = 25.5$, the *cis*-/*trans*-2-butene ratio expected from exclusive 1,4-biradical formation from *cis*-1,1-diazene **31.**

The experimental ratio of *trans*-/*cis*-2-butene from *trans*-1,1-diazene was 79.0/2.8. The calculated *trans*-2-butene

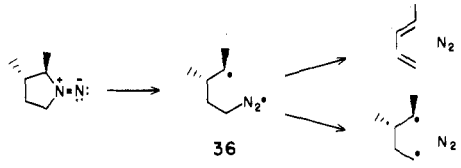
should be only 10.0 times *cis*-2-butene or (10 × 2.8 = 28.0). Therefore, the *extra* component of stereospecific cleavage superimposed on the 1,1-diazene-generated biradical is 79.0 − 28.0 = 51%.



Similarly, the experimental ratio of *cis*-/*trans*-2-butene from *cis*-1,1-diazene was 86.5/1.9. The calculated *cis*-2-butene from exclusive 1,1-diazene generated biradical should only be 25.5 times the *trans*-2-butene (25.5 × 1.9 = 48.4). Therefore, the extra component of stereospecific cleavage superimposed on the 1,1-diazene derived biradical is 86.5 = 48.4 = 38.1%.



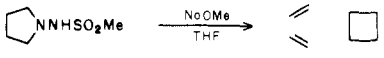
The direct stereospecific cleavage reaction may be a concerted cycloreversion in competition with the 1,4-biradical-forming pathway. An alternative explanation involves initial one-bond scission to a diazenyl radical **36,** which subsequently



36

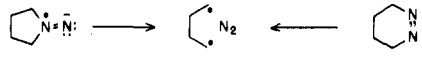
decomposes to olefin and 1,4 biradical competitively. The kinetic analysis only distinguishes a direct stereospecific olefin-forming pathway from the 1,4-biradical pathway. Whether the precursor to the stereospecific pathway is a diazenyl radical that cleaves to olefin plus nitrogen faster than loss of stereochemical integrity or a concerted cycloreversion cannot be distinguished from these data.

The energy gap between the direct stereospecific reaction and the 1,4-biradical pathway is ~30 to 388 cal (from direct/1,4-biradical path ratios of 1.04 and 0.61 at ~120 °C from *trans*- and *cis*-1,1-diazenes **31,** respectively). If the 2-methyl substituent in the 2,3-dimethyl-1,1-diazene **31** system stabilizes the 1,4-biradical pathway more than the direct olefin-forming reaction, the concerted cycloreversion might predominate in the parent system, consistent with Lemal's finding.[10] Any trace of cyclobutane in the unsubstituted 1,1-diazene decomposition would provide some idea of the relative competition between these two pathways. We have repeated the base-induced decomposition of the corresponding *N*-methanesulfonamidopyrrolidine (**37**) in THF at ≤120 °C and find a 98/2 ratio of two ethylenes/cyclobutanes.[17]



37

1,1-Diazene Decompositions in the Gas Phase at High Temperatures. We have the general finding that the similarly substituted 1,4 biradicals generated from 1,1-diazenes in solution at 120 °C behave more stereospecifically than those generated from 1,2-diazenes in the gas phase at 439 °C (Table IV). One final piece of data that is necessary is some evidence that the differences in stereospecificities are not due to the differences in mode of generation, 1,1- vs. 1,2-diazenes. One needs to compare 1,1- and 1,2-tetramethylenediazene de-



compositions at the same temperatures in the gas phase. To our knowledge, there is no method reported in the literature for the thermal generation of 1,1-dialkyldiazenes in the gas phase. A precursor is needed which will afford a 1,1-dialkyldiazene in a unimolecular reaction. Known methods for

Table VI

		% yield			
	T, °C	2			
NNHSO₂Me	306	74.0	9.1	16.2	0.7
	439	72.8	9.3	15.8	2.1
cis-**38**					
NNHSO₂Me	306	79.7	13.1	6.2	1.0
	439	76.0	14.5	7.9	1.6
trans-**38**					

Table VII

		% yield				
	T, °C					
NNHSO₂Me	306	2.4	79.9	3.4	14.3	
	439	3.1	80.7	3.2	12.6	0.4
cis-**39**						
NNHSO₂Me	306	66.6	3.3	26.5	3.4	0.2
	439	67.1	7.6	21.6	3.2	0.5
trans-**39**						

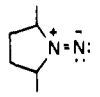
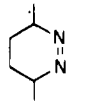
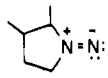
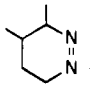
generating 1,1-dialkyldiazenes require bimolecular chemistry and are carried out in solution (e.g., base-induced α eliminations of sulfonamides, and oxidation of *N*-amino precursors with HgO or $Pb(OAc)_4$ at 25–120 °C). We find that *N*-methanesulfonamidopyrrolidines on thermal decomposition in the gas phase afford hydrocarbon products consistent with the intermediacy of 1,1-diazenes.

Treatment of *N*-amino-*cis*-(and *trans*-)2,3-(and 2,5-)dimethylpyrrolidines (**27** and **26,** respectively) with 1 equiv of methanesulfonyl chloride and triethylamine in methylene chloride (−78 °C) afforded the corresponding methanesulfonamides **39** and **38.** For pyrolyses, 20 μL of a 0.1 M freshly prepared solution of each methanesulfonamide in benzene was injected into an evacuated Pyrex chamber preheated at 306 and 439 °C. The hydrocarbon products were collected in a trap at −196 °C. Product ratios were determined by electronically integrated analytical VPC analysis. Results of the pyrolyses are listed in Tables VI and VII.

Assuming the stereochemistry of the ring-closure products reflects the 1,4-biradical behavior from the 1,1- and 1,2-diazene decompositions in the gas phase, we make the comparison of the retention/inversion ratios (*r*/*i*) in Table VIII. We conclude that 1,4 biradicals generated from cyclic 1,1-dialkyldiazene decompositions behave much like those from cyclic 1,2-diazene decompositions in the gas phase at the same temperatures (306 and 439 °C).

In summary, this work has shown, from the thermal decomposition of *N*-(2,5-(and 2,3-)dimethylpyrrolidine)nitrene (**30** and **31**) decompositions, (a) that 1,4 biradicals with secondary radical centers are more stereospecific in solution at ≤120 °C than in the gas phase at 439 °C; (b) evidence for a direct pathway to cleavage products in the decomposition of *N*-(2,3-dimethylpyrrolidine)nitrenes; (c) the relative rates of

Table VIII. Retention/Inversion Ratios in Closure Products from Similarly Substituted 1,1- and 1,2-Diazenes at the Same Temperature and Phase

	isomer	conditions	r/i
	*cis*-**30**	439 °C/gas	1.70
	trans-**30**	439 °C/gas	1.84
	*cis*-**32**	439 °C/gas	1.68
	trans-**32**	439 °C/gas	1.67
	*cis*-**31**	439 °C/gas	3.94
	trans-**31**	439 °C/gas	6.75
	*cis*-**33**	439 °C/gas	2.29
	trans-**33**	439 °C/gas	7.76

rotation, cleavage, and closure for 3-methyl-1,4-pentanediyl in solution at ≤120 °C; (d) that retention/inversion ratios of ring closure products from similarly substituted 1,1- and 1,2-diazenes in the gas phase at the same temperature are similar. The relative importance of phase on the behavior of 1,4 biradicals remains unanswered. In addition, the development of more unambiguous methods from the generation of 1,1-diazenes in a unimolecular reaction is needed.

Experimental Section

Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Infrared spectra (IR) were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates A-60A and are uncalibrated. Chemical shifts are given as parts per million (ppm) downfield from Me_4Si in δ units and coupling constants in hertz (Hz). Nuclear magnetic resonance data are reported in the order: chemical shift; multiplicity, s = singlet, d = doublet, t = triplet, m = multiplet; number of protons; coupling constants; assignment. Electronic spectra were recorded on a Cary Model 14 spectrophotometer.

For analytical vapor-phase chromatography (VPC), a Hewlett-Packard 5700A gas chromatograph, equipped with flame ionization detector and nitrogen carrier gas, was used. The 0.125-in. packed stainless steel columns used in this instrument are listed in Table IX. Quantitative VPC analysis was accomplished using a Hewlett-Packard 3370A electronic digital integrator. For preparative VPC, a Varian Aerograph Model 920 instrument, equipped with thermal conductivity detector and helium carrier gas, was used. The 0.375-in. packed aluminum columns used in this instrument are listed in Table IX.

Most reagent grade chemicals were used without further purification. Diglyme and tetrahydrofuran were distilled from lithium aluminum hydride, and pyridine from barium oxide.

***N*-Amino-*trans*-2,3-dimethylpyrrolidine (*t*-27).** To a solution of 5.13 g (44.2 mmol) of *erythro*-3-methylpentane-1,4-diol, obtained from the hydroboration/oxidation workup of 3-methyl-*cis*-penta-1,3-diene, in 15 mL of anhydrous triethylamine and 50 mL of anhydrous dichloromethane was added dropwise 12.8 g (88.6 mmol) of freshly distilled methanesulfonyl chloride at −20 °C. The reaction mixture was allowed to stir and warm to 0 °C. After standing at 0 °C for 12 h, the reaction mixture was filtered to remove the triethylammonium chloride. The filtrate was washed with water, 10% HCl, and saturated sodium bicarbonate solution. The organic extract was dried ($CaCl_2$) and concentrated, affording a yellow oil which was subsequently allowed to react at 55 °C with 12 mL of hydrazine hydrate and 7 mL of anhydrous hydrazine for 20 h under a nitrogen atmosphere. The products were extracted with two 50-mL portions of ether. The ethereal extracts were combined and concentrated. Distillation of the residue afforded 2.8 g (54%) of a colorless oil: bp 25–30 °C (2 mm). The product was shown by analytical vapor phase chromatography (Pennwalt, 180 °C) to consist of 97.7% *N*-amino-*trans*-2,3-dimethylpyrrolidine and 2.3% cis isomer. Preparative vapor phase chromatography (Pennwalt, 160 °C) afforded pure trans isomer (>99.8%): IR ($CHCl_3$) 3700–3000 (b), 2960 (s), 2924 (m), 2865 (m), 1600 (m), 1460 (sh), 1435 (m), 1378 (m), 1250 (m), 1125 (m), 940 (m), 905 (m); NMR ($CDCl_3$) δ 1.0–1.25 (m, 6), 1.3–2.6 (m, 5), 2.91 (br s, 2), 3.0–3.5 (m, 1). Anal. Calcd for $C_6H_{14}N_2$: C, 63.11; H, 12.36; N, 24.53. Found: C, 63.04; H, 12.38; N, 24.46.

Table IX. VPC Columns

column designation	description
DBT	20 ft × 0.125 in., 10% dibutyl tetrachlorophthalate in 100/120 Chromosorb P
Pennwalt	10 ft × 0.125 in., Pennwalt 223 amine packing (Applied Sciences Laboratories, Inc.)
FFAP	10 ft × 0.375 in., 25% FFAP on 60/80 Chromosorb W
Pennwalt	10 ft × 0.25 in., glass, Pennwalt 223 amine packing (Applied Sciences Laboratories, Inc.)

***N*-Amino-*cis*-2,3-dimethylpyrrolidine (*c*-27).** The same procedure used for *t*-**27** was followed. From 3.18 g (27 mmol) of *threo*-3-methylpentane-1,4-diol, obtained from the hydroboration/oxidative workup of 3-methyl-*trans*-penta-1,3-diene, was obtained 0.87 g (27%) of isomerically pure (>99.9%) *N*-amino-*cis*-2,3-dimethylpyrrolidine (*c*-**27**): IR (CCl_4) 3340 (w), 3175 (w), 2960 (s), 2865 (m), 2780 (m), 1580 (w), 1373 (m), 907 (m), 870 (m); NMR ($CDCl_3$) δ 0.81–1.5 (m, 7), 1.8–2.5 (m, 4), 2.96 (br s, 2) 3.05–3.4 (m, 1). Anal. Calcd for $C_6H_{14}N_2$: C, 63.11; H, 12.36; N, 24.53. Found: C, 62.91; H, 12.32; N, 24.44.

***N*-Amino-*trans*-2,5-dimethylpyrrolidine (*t*-26).** In a procedure similar to that employed for the synthesis of the 3,4-**27** isomers, reaction of *dl*-2,5-bismethanesulfonyloxyhexane with hydrazine hydrate/anhydrous hydrazine afforded the known compound, *N*-amino-*trans*-2,5-dimethylpyrrolidine (*t*-**26**). This was purified further (>99.9%) by preparative vapor phase chromatography (Pennwalt, 160 °C): NMR ($CDCl_3$) δ 1.06 (d, 6, J = 6.4 Hz), 1.2–2.3 (m, 4), 2.7–3.3 (m, 4). Picrate: mp 163–165 °C (lit. 162–164 °C).

***N*-Amino-*cis*-2,5-dimethylpyrrolidine (*c*-26).** In a procedure similar to that employed for the syntheses of the 3,4-**27** isomers, reaction of *meso*-2,5-bismethanesulfonyloxyhexane with hydrazine hydrate/anhydrous hydrazine afforded the known compound, *N*-amino-*cis*-2,5-dimethylpyrrolidine (*c*-**26**). This was purified further (≥99.8%) by preparative vapor phase chromatography (Pennwalt, 160 °C): NMR ($CDCl_3$) δ 1.17 (d, 6, J = 5.8 Hz), 1.25–2.4 (m, 6), 2.80 (br s, 2). Picrate: mp 156–157 °C (lit. 154–156 °C).

***N*-Benzenesulfonamido-*trans*-2,3-dimethylpyrrolidine (*t*-29).** To a solution of 424 mg (3.7 mmol) of *N*-amino-*trans*-2,3-dimethylpyrrolidine (*t*-**26**) (≥99.8% isomeric purity) and 380 mg (3.7 mmol) of anhydrous triethylamine in 6 mL of dry methylene chloride under a nitrogen atmosphere at −20 °C was added 655 mg (3.7 mmol) of benzenesulfonyl chloride via syringe. After stirring for 15 min, the reaction mixture was allowed to warm to 0 °C and stand at 0 °C for 12 h. The reaction mixture was diluted with 20 mL of methylene chloride and extracted with water, 10% HCl, and saturated aqueous sodium bicarbonate. The organic layer was concentrated affording a pale yellow solid. Recrystallization from benzene–cyclohexane gave 552 mg (59%) of fine colorless needles, *t*-**29**: mp 105.5–106.5 °C; IR ($CDCl_3$) 1353, 1330, 1180, 1165 (SO_2N); NMR ($CDCl_3$) δ 0.75–1.0 (m, 6, singlet at 0.78), 1.0–2.6 (m, 5), 2.8–3.2 (m, 1), 5.2–5.5 (br s, 1), 7.3–7.65 (m, 3), 7.85–8.15 (m, 2). Anal. Calcd for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.01. Found: C, 56.65; H, 7.12; N, 10.96.

***N*-Benzenesulfonamido-*cis*-2,3-dimethylpyrrolidine (*c*-29).** Employing a procedure identical with that used for the preparation of the trans isomer (*t*-**29**), the reaction of *N*-amino-*cis*-2,3-dimethylpyrrolidine (*c*-**26**) (≥99.9% isomeric purity) with benzenesulfonyl chloride afforded *N*-benzenesulfonamido-*cis*-2,3-dimethylpyrrolidine (*c*-**29**). Recrystallization from benzene–cyclohexane gave colorless needles of *c*-**29** (51%): mp 80–80.5 °C; IR ($CHCl_3$) 1375, 1340, 1324, 1308, 1165 (SO_2N); NMR ($CDCl_3$) δ 0.6–3.1 (m, 12), 5.1–5.5 (br s, 1), 7.3–7.7 (m, 3), 7.8–8.1 (m, 2). Anal.

Calcd for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.01. Found: C, 56.68; H, 7.09; N, 10.99.

***N*-Benzenesulfonamido-*trans*-2,5-dimethylpyrrolidine (*t*-28).** Employing a procedure identical with that used for the preparation of the trans isomer (*t*-**29**), the reaction of *N*-amino-*trans*-2,5-dimethylpyrrolidine (*t*-**26**) (≥99.9% isomeric purity) with benzenesulfonyl chloride afforded *N*-benzenesulfonamido-*cis*-2,3-dimethylpyrrolidine (*t*-**28**). Recrystallization from benzene–cyclohexane gave *t*-**28** (28%): mp 94.5–95.5 °C; IR ($CHCl_3$) 1394, 1375, 1365, 1340, 1330, 1308, 1176, 1165 (SO_2N); NMR ($CDCl_3$) δ 0.84 (d, 6, J = 6.3 Hz), 1.0–2.2 (m, 4), 2.7–3.3 (m, 2), 5.81 (br s, 1), 7.25–7.75 (m, 3), 7.75–8.1 (m, 2). Anal. Calcd for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.01. Found: C, 56.67; H, 7.16; N, 11.00.

***N*-Benzenesulfonamido-*cis*-2,5-dimethylpyrrolidine (*c*-28).** Employing a procedure identical with that used for the preparation of trans isomer *t*-**29**, the reaction of *N*-amino-*cis*-2,5-dimethylpyrrolidine (*c*-**26**) (≥99.8% isomeric purity) with benzenesulfonyl chloride afforded *N*-benzenesulfonamido-*cis*-2,5-dimethylpyrrolidine (*c*-**28**). Recrystallization from benzene–cyclohexane gave *c*-**28** (38%): mp 111.5–112.5 °C; IR ($CHCl_3$) 1372, 1342, 1315, 1163 (SO_2N); NMR ($CDCl_3$) δ 0.82 (d, 6, J = 5.8 Hz), 1.0–2.1 (m, 4), 2.2–2.9 (m, 2), 5.51 (br s, 1), 7.25–7.75 (m, 3), 7.75–8.1 (m, 2). Anal. Calcd for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.01. Found: C, 56.64; H, 7.10; N, 11.15.

***N*-Methanesulfonamido-*cis*-(and *trans*-)2,3-(and 2,5-)dimethylpyrrolidines (39 and 38, Respectively). General Method.** To a solution (0.01 M) of each isomerically pure (≥99.8%) *N*-amino-2,3-(and 2,5-)dimethylpyrrolidine (**27** and **26**) and 1.1 equiv of anhydrous triethylamine in methylene chloride at −78 °C was added 1.0 equiv of freshly distilled methanesulfonyl chloride over a period of 5 min. After stirring 10 min, the reaction mixture was allowed to warm to room temperature and stand 30 min. The reaction mixture was diluted with two equivalent volumes of methylene chloride. This was extracted with 10% HCl, and saturated aqueous sodium bicarbonate. The organic layer was dried ($MgSO_4$) and concentrated, affording pale yellow crystals which were recrystallized from benzene/hexane (1:5) and gave colorless fine needles (40–60%).

***trans*-39**: mp 86.5–88 °C; IR ($CHCl_3$) 1390, 1372, 1340, 1326, 1148 (SO_2N); NMR ($CDCl_3$) δ 1.02 (d, 3, J = 5.6 Hz), 1.17 (d, 3, J = 5.6 Hz), 1.25–2.8 (m, 5), 3.02 (s, 3), 3.4–3.8 (m, 1), 4.85–5.15 (br s, 1). Anal. Calcd for $C_7H_{16}N_2SO_4$: C, 43.72; H, 8.39; N, 14.57. Found: C, 43.81; H, 8.37; N, 14.62.

***cis*-39**: mp 91.0–92.5 °C; IR ($CHCl_3$) 1393, 1379, 1330, 1153 (SO_2N); NMR ($CDCl_3$) δ 0.96 (d, 3, J = 6.4 Hz), 1.07 (d, 3, J = 6.4 Hz), 1.2–3.0 (m, 5), 3.00 (s, 3), 3.1–3.3 (m, 1), 5.0–5.25 (br s, 1). Anal. Calcd for $C_7H_{16}N_2SO_4$: C, 43.72; H, 8.39; N, 14.57. Found: C, 43.74; H, 8.41; N, 14.49.

***trans*-38**: mp 75.5–77 °C; IR ($CHCl_3$) 1394, 1370, 1335, 1322, 1315, 1152 (SO_2N); NMR ($CDCl_3$) δ 1.12 (d, 6, J = 6.4 Hz), 1.25–3.2 (m, 4), 3.01 (s, 3), 3.1–3.5 (m, 2), 5.25–5.7 (br s, 1). Anal. Calcd for $C_7H_{16}N_2SO_2$: C, 43.72; H, 8.39; N, 14.57. Found: C, 43.77; H, 8.32; N, 14.56.

***cis*-38**: mp 77.5–79 °C; IR ($CHCl_3$) 1382, 1373, 1342, 1328, 1156 (SO_2N); NMR ($CDCl_3$) δ 1.23 (d, 6, J = 6.0 Hz), 1.2–2.2 (m, 4), 2.5–2.9 (m, 2), 3.01 (s, 3), 5.0–5.15 (br s, 1). Anal. Calcd for $C_7H_{16}N_2SO_2$: C, 43.72; H, 8.39; N, 14.57. Found: C, 43.63; H, 8.19; N, 14.33.

Thermal Reactions in Solution. Base-Induced Decomposition of the *N*-Benzenesulfonamido-2,3-(and 2,5-)dimethylpyrrolidines (29 and 28) in Diglyme. Into a glass ampule (1.2 × 7 cm), equipped with a 14/35 male glass joint, 3 cm of tublature at the narrow end, and serum cap, was placed 1 mL of a 0.05 to 1.2 M solution of each *N*-benzenesulfonamidodimethylpyrrolidine (**29** and **28**) in anhydrous diglyme via a syringe. Nitrogen gas was bubbled through the solution for 15 min at 0 °C. The reaction mixture was frozen in a liquid nitrogen bath and 0.1 mL of 2 N sodium 2-butoxyethoxide in 2-butoxyethanol was added via syringe. The pyrolysis tube was sealed immediately and immersed in a constant temperature oil bath at 120 ± 2 °C for 30 min. The pyrolysate was frozen in a liquid nitrogen bath and the tube was opened. The opened tube was connected immediately to a trap-to-trap distillation apparatus attached to a high vacuum line (10^{-4} mm) and all of the pyrolysate was distilled and collected in a small glass tube. This tube was sealed and removed. The contents were frozen in liquid nitrogen, the tube was opened, and 200 μL of toluene with cyclohexane (9.25×10^{-2} M) as an internal standard was added. This was analyzed three times by analytical vapor phase chromatography (DBT, 25 °C). The results are listed in Tables II and III. Typical yields of hydrocarbon products were 67–99%.

Based-Induced Decomposition of *N*-Benzenesulfonamido-2,3-(and 2,5)-dimethylpyrrolidines (29 and 28) in *n*-Octane. Into a glass ampule (0.8 × 10 cm), equipped with a 14/20 glass joint, 3 cm of tublature at the narrow end, and serum cap, was placed 0.5 mL of 0.03–0.05 M solution of each *N*-benzenesulfonamidodimethylpyrrolidine (**29** and **28**) in *n*-octane via a syringe. The reaction mixture was frozen in a liquid nitrogen bath and 20–25 equiv of sodium methoxide was added. The pyrolysis tube was connected immediately to a high vacuum line (10^{-4} mm), degassed, and sealed. The sealed tube was immersed in a constant temperature oil bath at 120 ± 2 °C for 30 min. The pyrolysate was frozen in a liquid nitrogen bath and the tube was opened. The opened tube was connected immediately to a trap-to-trap distillation apparatus attached to a high vacuum line (10^{-4} mm) and all of the pyrolysate was distilled and collected in a small glass tube. This tube was sealed and removed. The contents were frozen in liquid nitrogen, the tube was opened, and 200 μL of toluene with cyclohexane (9.25×10^{-2} M) as an internal standard was added. This was analyzed three times by analytical vapor phase chromatography (DBT, 25 °C). The results are listed in Tables II and III. Typical yields of hydrocarbon products were 38–73%.

Controls. (a) Sulfonamide, *trans*-**28**, was treated with sodium methoxide in methanol at 50 °C for 20 min. The major product was the hydrazone, 3,6-dimethyl-2,3,4,5-tetrahydropyridazene (58.5%). (b) The pyrolysate of *trans*-**28** with sodium methoxide in *n*-octane was analyzed by analytical vapor phase chromatography (Pennwalt, 200 °C). 3,6-Dimethyl-2,3,4,5-tetrahydropyridazene was not detected (<1%). (c) Pyrolysis of sulfonamide, *trans*-**28** in diglyme *without base* at 120 °C for 30 min in a sealed tube afforded no hydrocarbon products by analytical vapor phase chromatography (DBT, 25 °C).

Thermal Reactions in the Gas Phase. The pyrolyses were carried out in a 2.8 × 30 cm cylindrical Pyrex tube, with a 0.6 × 3 cm injector port with serum cap, mounted in a Hoskins type FD 303A tube furnace. The other end of the tube was connected via a 6-mm bore stopcock (A) to a high vacuum line equipped with two liquid nitrogen cooled U-shaped traps plus a small receiving tube. The temperature was measured by a thermometer inserted into the furnace or an iron-constant thermocouple connected to a potentiometer. Before pyrolysis the tube was evacuated and stopcock A was closed.

In a typical run, 20 μL of 0.1–0.3 M methanesulfonamide **38** and **39** in benzene, with cyclohexane as an internal standard, was injected into the pyrolysis tube through a serum cap via a gas-tight syringe. After pyrolysis times of 5 (at 439 °C) to 30 s (at 308 °C), stopcock A was opened and the pyrolysate was collected in the liquid nitrogen cooled traps. The hydrocarbon contents of the traps were transferred to the receiving tube which was sealed with a torch and removed for analysis.

The pyrolysate tube was cooled to 77 K and opened and the contents diluted with 20 μL of toluene. The products were analyzed immediately by analytical vapor phase chromatography (DBT, 25 °C). Assignment of the product peaks was carried out by coinjection techniques using authentic samples. Relative retention times are as follows (DBT, 25 °C): ethylene (0.101), propylene (0.123), *trans*-2-butene (0.211), *cis*-2-butene (0.233), *trans*-1,2-dimethylcyclobutane (0.650), 1-hexene (0.944), *cis*-1,2-dimethylcyclobutane (1.00). Each sample was pyrolyzed at least three times. Analytical VPC analysis was carried out at least twice on each run. Typical yields were 18–40% at 308 °C and 15–39% at 439 °C.

Controls. (a) The products, 1,2-dimethylcyclobutanes and 2-butenes, were shown to be stable to isomerization under the pyrolysis conditions. (b) Surface effects were checked by repeating all the pyrolyses with the pyrolysis tube filled with glass chips. The yields increased (at 439 °C, 34–49%), but there was no change in product distribution.

References and Notes

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Electrocyclic Ring Opening of the Cyclobutene Radical Cation

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Abstract: The electrocyclic ring opening of cyclobutene to give 1,3-butadiene is a well-understood chemical isomerization. The process occurs with a lower than anticipated activation energy presumably because it is an "allowed" reaction. In order to ascertain whether the electrocyclic ring opening occurs for the gas-phase cyclobutene radical cation, we have undertaken a comparative study of the chemical properties of ionized cyclobutene and 1,3-butadiene. Both ions exhibit nearly identical chemical reactivities with a variety of neutral molecules including methyl vinyl ether, furan, ethene, propene, isomeric butenes, and isomeric pentenes. The explanation proposed to account for these results is that the cyclobutene ion rapidly undergoes (within less than 2 ms) an electrocyclic isomerization to give the 1,3-butadiene ion. The maximum activation energy for this process is estimated to be less than 7 kcal/mol. The chemical properties of the molecular ions of 1,2-butadiene, 1-butyne, and 2-butyne were determined using the same reactant neutral molecules, and they differ considerably from the 1,3-butadiene and cyclobutene ions. The results are interpreted to exclude other isomeric $[C_4H_6^{+}\cdot]$ species in the electrocyclic reaction.

The ring opening of cyclobutene to produce 1,3-butadiene serves as the classic example of the application of principles of orbital symmetry control to electrocyclic reactions.[1] It is now well established that the transformation occurs in a conrotatory manner for the thermal process. The activation energy for the ring opening of the neutral cyclobutene has been determined to be 33 kcal/mol, which is approximately 15 kcal/mol lower than a "some nonallowed pathway."[2] This latter quantity can be assigned as the energy advantage for the allowed process.

In this paper, we report a study of the 1,3-butadiene and the cyclobutene radical cations designed to establish whether the cyclobutene ion isomerizes to 1,3-butadiene and to estimate the activation energy required for the process. Obviously, these are the first pieces of information that are needed to test the applicability of various selection rules to the chemistry of isolated radical ions in the gas phase.

Mass spectrometric techniques are the methods of choice for investigating gas-phase ions, and we have chosen ion cyclotron resonance spectrometry for this study. The strategy is to develop highly specific reactions of the various C_4H_6 radical cations which can be employed as structural probes.

Various authors have considered the applicability of orbital symmetry rules for reactions of open-shell systems (radical cations) in a mass spectrometer source.[3-8] However, it is not clear what the effect of removal of one electron should be on orbital symmetry considerations. In fact, recent studies of various substituted cyclobutene radical cations are indicative of contradictory experimental results. Similarities found in ionic fragmentations for the isomeric cyclobutenedicarboxylic acids and the corresponding muconic acids have been interpreted to indicate electrocyclic interconversions via electronically excited states (a photochemical analogy).[8] The quantities of kinetic energy released in the decompositions of isomeric 1,2,3,4-tetramethylcyclobutenes have been compared to the 3,4-dimethyl-2,4-hexadienes, and a similar conclusion was reached.[9] However, the results of a study of the dimethyl esters of cyclobutenedicarboxylic acids and the corresponding ring-opened 1,3-butadienes show that *no* correlation exists between the behavior of the radical cations and the photochemical or thermal reactivities of the neutral molecules.[10] That is, the cyclobutene ions refrain from ring opening, and the 1,3-butadienes do not ring close even when the ions are sufficiently excited to decompose.

In a recent study, Werner and Baer[11] have investigated the unimolecular decompositions of energy-selected C_4H_6 ions from 1,3-butadiene, cyclobutene, and other isomers using the elegant technique of photoelectron–photoion coincidence spectroscopy. They conclude that all the isomeric C_4H_6 ions rearrange to a common structure prior to dissociation. Because these data were taken at energies above the dissociation limit for $[C_4H_6]^{+}\cdot$, they tell us nothing about isomerization at low internal energies, nor do they provide an answer to the question we have posed concerning the specific ring opening of the cyclobutene ion to give 1,3-butadiene.

Results and Discussion

To answer the question we have raised, it is necessary to compare the physical or chemical properties of ionized cyclobutene and 1,3-butadiene. As a strategy, we have chosen to determine the chemical reactivities of the various isomeric C_4H_6 radical cations which are prepared by direct ionization of 1,3-butadiene and cyclobutene. In addition, $[C_4H_6]^{+}\cdot$ will be generated from 1,2-butadiene, 1-butyne, and 2-butyne. Using the technique of ion cyclotron resonance spectrometry

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