reactions. We were also able to show the $C_4H_4^{+\cdot}$ cluster ion in acetylene is >90% cyclic isomer and the $C_4H_4^{+\cdot}$ ion from methylene-2,3-dimethylcyclopropane is 72 ± 10% cyclic isomer. Also, the $C_4H_4^{+\cdot}$ ion originating from the metastable reaction of benzene parent ion is 82 ± 10% cyclic $C_4H_4^{+\cdot}$. Finally, it was possible to infer that linear $C_4H_4^{+\cdot}$ reacts very much faster than cyclic $C_4H_4^{+\cdot}$ with acetylene.

2. The ion chemistry of l-$C_4H_4^{+\cdot}$ reacting with acetylene was explored by using the tandem ICR. The total rate constant for reaction of l-$C_4H_4^{+\cdot}$ was measured to be $(3 \pm 1.5) \times 10^{-10}$ cm^3/s. The rate constant for the cyclic isomer with acetylene was immeasurably slow ($<10^{-11}$ cm^3/s). With use of C_2D_2 it was possible to show acetylene "catalyzed" the isomeric conversion reaction

$$\text{l-}C_4H_4^{+\cdot} + C_2H_2 \rightarrow \text{c-}C_4H_4^{+\cdot} + C_2H_2$$

with a rate constant of $\sim 1 \times 10^{-10}$ cm^3/s. A complete product distribution for reaction of l-$C_4H_4^{+\cdot}$ is reported.

3. The techniques of collision-induced dissociation and tandem ion cyclotron resonance are complimentary and allow determination of the isomeric content in $C_4H_4^{+\cdot}$ beams and information on the mechanism of formation and reactivity of $C_4H_4^{+\cdot}$ ions.

Acknowledgment. The support of the National Science Foundation under Grant CHE80-20464 is gratefully acknowledged. One of us (W.W.R.) wants to thank the Deutsche Forschnungsgemeinschaft for a Fellowship.

Registry No. I, 79105-72-9; II, 59699-48-8; vinylacetylene, 689-97-4; benzene, 71-43-2; methylene-2,3-dimethylcyclopropane, 62338-02-7; acetylene, 74-86-2.

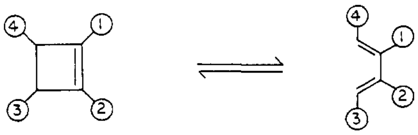
Electrocyclic Ring Opening of 1-Phenylcyclobutene and 3-Phenylcyclobutene Radical Cations

Chhabil Dass and M. L. Gross*

Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588. *Received December 10, 1982*

Abstract: The 1-phenyl- and 3-phenylcyclobutene radical cations have been studied by mass spectrometry/mass spectrometry (MS/MS) techniques to determine the effect of substitution on the electrocyclic ring opening of cyclobutene radical cation. Substitution at the double bond of cyclobutene stabilizes the cyclobutene radical cation compared to the unsubstituted moiety, whereas phenyl substitution at the 3-position enhances the rate of the electrocyclic reaction. The activation energy for the ring opening of the 1-phenylcyclobutene radical cation is estimated to be less than 14 kcal mol^{-1}, whereas that for the 3-phenylcyclobutene radical cation is close to the threshold for ionization. Raising the internal energy of the ions causes the two phenyl-substituted cyclobutenes and their ring-opened isomers to rearrange to a stable structure or a mixture of structures. The probable ultimate structure is assigned as that of the radical cation of 3-methylindene on the basis of the thermochemical measurements and the CAD spectra of other isomeric $[C_{10}H_{10}]^{+\cdot}$ radical cations.

The electrocyclic ring opening of thermally activated neutral cyclobutene and its derivatives to the corresponding 1,3-butadienes is a well-established phenomenon (eq 1). The transformation takes place in a stereospecific conrotatory manner for the thermally allowed process and in a disrotatory manner for the photochemical process.[1] The experimental activation energy is 32.9 kcal mol^{-1} for the thermal process[2] occurring for the parent compound.



(1)

The effects of substituents on the electrocyclic interconversion of the neutral cyclobutene and 1,3-butadiene pair have been the subject of many theoretical and experimental investigations.[3-8] By use of a theoretical model proposed by Carpenter,[3] it can be qualitatively predicted that any substituent at the double bond of cyclobutene should decrease the rate of conrotatory ring opening. On the other hand, substitution at the 3- and 4-positions should increase the rate of the reaction. These predictions have received considerable experimental support.[4,5,8] More recently, Wilcox and Carpenter[6] were able to predict quantitatively the relative activation enthalpies for the ring opening of various substituted cyclobutenes.

Although understanding of the electrocyclic ring opening of closed shell systems is quite well developed, relatively little is known of similar ring-opening processes of open shell systems. One approach has been to search for correlations between the chemistry of the gas-phase ions with the thermal and photochemical processes of neutrals.[9-16] Johnston and Ward[9] presented evidence that some mass spectral fragmentations take place through the electronically excited state (a photochemical analogy), whereas Bishop and Fleming[11] concluded that prediction of the stereochemical path for the ions is not straightforward, and both allowed and forbidden processes may be observed. Thus, the effect of removal of an electron on the course of most electrocyclic reactions is still not understood.

Recently, we have reported the ring opening of low internal energy cyclobutene radical cations.[17] Our conclusion was that the isomerization to the 1,3-butadiene radical cation is essentially complete at less than 0.6 eV above threshold. The corresponding activation energy was estimated to be less than 0.3 eV, which is much smaller than the activation energy needed for the similar ring opening of neutral cyclobutene.[2] Similar conclusions were drawn by Haselbach and co-workers[18] on the basis of theoretical studies. Thus, the effect of ionization is to reduce the energy

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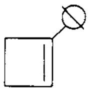
Table I. Partial 70-eV Mass Spectra of $[C_{10}H_{10}]^{+\cdot}$ Isomers[a]

	m/z																			
compd	131	130	129	128	127	126	116	115	102	91	89	78	77	76	75	74	65	64	63	51
I	8	80	100	38	16	2	6	55	38	12	2	5	16	6	3	3	4	8	6	2
II	10	94	100	46	19	2	6	63	15	17	3	7	15	4	3	3	5	9	7	2
III	8	79	100	46	19	2	5	50	5	4	2	4	8	2	3	2	5	8	5	6
IV	9	86	100	48	20	2	5	49	5	4	3	4	8	2	2	2	6	9	6	4
V	9	85	100	51	21	2	5	51	6	5	3	5	9	3	2	3	6	8	7	2
VI	21	100	82	42	16	3	9	42	4	2	2	3	5	2	2	2	4	11	6	9
VII	10	100	76	31	13	3	9	89	4	1	5	2	5	2	3	2	5	10	8	9
VIII	11	100	70	31	14	3	8	81	4	1	3	2	5	2	2	2	5	11	7	9
IX	10	100	60	30	14	3	8	77	4	1	3	3	6	2	2	2	4	9	6	9
X	10	100	88	39	18	3	7	67	5	5	3	3	7	3	3	2	5	14	9	5

[a] The mass spectra of I, II, IV, and VI have also been reported earlier (ref 21).

barrier of the electrocyclic ring opening of cyclobutene. However, unanswered questions still remain: what is the effect of substitution on the electrocyclic reaction of cyclobutene ions, and do the effects correlate with the behavior of the corresponding neutral molecules?

In this paper, we report the first investigation of possible ring-opening reactions of gas-phase substituted cyclobutenes, namely the 1-phenylcyclobutene (I) and 3-phenylcyclobutene (III) radical cations. Mass spectrometric techniques are the methods of choice for investigating the gas-phase ions, and we have selected MS/MS for the present work. The strategy is to form stable ions, i.e., the ions that do not decompose or isomerize in the mass spectrometric time frame of $<10^{-5}$ s, obtain their collisionally activated dissociation (CAD)[19] spectra, and then compare the spectra with those of the corresponding ring-opened radical cations. In order to gain additional insight into the nature of the structure of these gas-phase ions, we have also investigated other $C_{10}H_{10}$ isomers, including 1,2-dihydronaphthalene (VI), 1-methylindene (VII), 3-methylindene (VIII), 1-methyleneindan (IX), 2-methyleneindan (X), and benzobicyclo[2.1.1]hex-2-ene (XI). The choice of these isomers was governed by similarities in their structures and fragmentation patterns as shown by their conventional mass spectra.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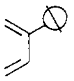
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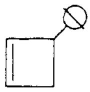
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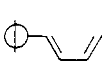
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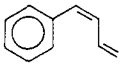
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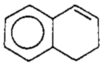
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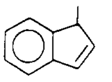
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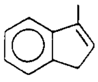
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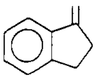
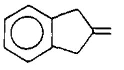

IX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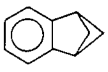
XI

Derocque and Jochem[20] previously investigated the gas-phase ions of I and 2-phenyl-1,3-butadiene (II) in terms of their slow or metastable decompositions in a double-focussing mass spectrometer with a view to establish whether the two ions fragment via a common structure. Their conclusion was that the losses of H and CH_3 radicals from $[I]^{+\cdot}$ and $[II]^{+\cdot}$ occur from a common intermediate whereas the consecutive losses of H_2 and C_2H_2 proceed by different pathways. However, their study does not explicitly tell us if $[I]^{+\cdot}$ undergoes reaction to $[II]^{+\cdot}$ or about the energy barrier for the electrocyclic reaction.

Results and Discussion

Our first aim was to determine if the 1-phenylcyclobutene and 3-phenylcyclobutene radical cations undergo a ring-opening reaction. These investigations may permit extrapolation of the conclusion for the cyclobutene radical cation, which was based on different type of evidence, and reveal the effect of phenyl substitution on the electrocyclic ring opening. Our second goal was to determine the ultimate structures of the rearranged ions, if ring opening and further isomerization did occur.

Mass spectra of the $C_{10}H_{10}$ isomers under investigation are quite similar (Table I). Upon ionization with 70-eV electrons, ions with a wide range of internal energies (1–8 eV)[22] are formed. Thus, it is likely that the initially-formed molecular ions rearrange to various isomeric structures before decomposition. Few other conclusions are possible based on these data.

To study the structure of the initially-formed molecular ions, we chose to obtain their CAD spectra.[19] In that way, ions with internal energies ranging from zero up to the lowest threshold for decomposition can be investigated. If the ions exist in a deep potential energy well and the isomerization threshold is comparable to that for the lowest energy decomposition, then we would expect to deal with stable ions. If, on the other hand, the barrier for isomerization is very low, then the abundance of stable or unisomerized ions may be so feeble that their contribution to the CAD spectra will be negligible. On lowering the ionizing energy, ions are formed with lower and more narrow distributions of internal energies, thereby increasing the probability of detecting a stable structure.

The specific strategy we have chosen for determining the structures of isomeric pairs of radical cations is based upon these arguments and can be outlined as follows. Ions with various internal energy distributions (near threshold for ionization, producing stable ions, and above the isomerization barrier) were generated by using a variety of ionizing energies such as low-energy electrons, 70-eV electrons, and low- and high-energy charge exchange (CE). The ions of interest were then selected by using high mass resolution capability of MS-I of a triple analyzer MS/MS instrument.[23] The high resolution ensured that there is no contribution of ^{13}C from $[M - H]^{+\cdot}$ ions, whose intensities are quite comparable to those of molecular ions in the normal mass spectra (Table I). CAD spectra of the radical cations were then taken and interpreted in terms of structure.

1-Phenylcyclobutene and 2-Phenyl-1,3-butadiene Radical Cations. The CAD spectra of the two ions, formed by 70-eV electron ionization of I and II, are qualitatively similar but not superimposable (Table III). When normalizing the CAD spectra, we excluded those ions that have significant (10–60%) metastable contributions because the abundances of the ions formed by unimolecular decompositions are variable depending on the internal energy distribution. The contribution of metastable ions to the abundance of m/z 115 has been ignored because the contribution is so small (<5%) that we would not expect it to affect our results.

The major difference in the spectra is that the abundance of m/z 102 is about 30% higher for the ring-closed isomer. Other than that the spectra are nearly identical. On the basis of the

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Table II. Partial CAD Spectra of $[I]^{+\cdot}$ and $[II]^{+\cdot a,b}$

		m/z							
ionization	compd	115	102	91	89	77	75	63	51
low eV	I	22.2	23.3	2.50	5.3	9.0	9.2	10.6	11.8
	II	26.7	13.7	2.50	6.5	10.9	7.5	11.6	12.5
$[\text{toluene}]^{+\cdot}$	I	27.2	18.5	2.63	6.1	10.6	7.0	10.4	11.5
CE	II	30.6	15.2	3.14	5.7	11.3	6.0	10.6	11.7
$[NO]^{+\cdot}$	I	28.6	17.9	2.68	5.7	9.6	7.3	10.4	10.8
CE	II	34.7	14.0	2.88	5.9	10.3	5.8	10.6	10.0
70 eV	I	34.3	16.9	2.20	6.3	7.9	7.8	10.1	10.1
	II	34.7	13.3	2.62	6.7	8.3	7.1	11.3	10.5
$[CS_2]^{+\cdot}$	I	38.6	12.0	1.35	7.7	7.5	7.0	11.4	8.8
CE	II	38.4	10.7	1.26	7.9	6.9	7.3	12.6	8.8
$[N_2]^{+\cdot}$	I	36.7	11.1	1.60	7.5	9.4	6.4	11.9	9.2
CE	II	36.1	11.4	2.06	7.1	9.5	6.6	12.1	10.3

[a] Relative intensities are based on area measurement. [b] Relative to sum of all the ions excluding ions above *m/z* 115.

Table III. Partial CAD Spectra of $[C_{10}H_{10}]^{+\cdot}$ Isomers[a,b,c]

	m/z								
compd	115	102	91	89	77	75	63	51	R[d]
I	34.3	16.9	2.20	6.3	7.9	7.8	10.1	10.1	2.0
II	34.7	13.3	2.62	6.7	8.3	7.1	11.3	10.5	2.6
III	42.7	10.6	0.81	7.9	6.6	6.7	11.5	8.4	4.0
IV	34.6	11.8	1.24	8.0	8.2	7.5	12.1	10.2	2.9
V	39.0	10.4	1.25	7.7	6.6	7.7	11.4	9.3	3.8
VI	35.8	11.2	0.65	7.6	6.8	8.1	12.2	9.6	3.2
VII	44.1	9.6	0.67	8.2	5.9	7.2	11.2	7.6	4.6
VIII	43.3	10.3	0.67	8.1	5.8	7.1	11.2	7.6	4.2
IX	44.4	10.0	0.88	7.9	6.9	5.3	10.4	7.3	4.4
X	41.2	10.5	1.01	7.7	7.1	5.9	10.6	8.2	3.9
XI	40.0	10.3	1.00	7.7	7.0	7.0	11.0	8.7	4.0

[a,b] See Table II. [c] Ionization by 70-eV electrons. [d] *R* is the ratio of abundances of *m/z* 115 over *m/z* 102.

Table IV. Partial CAD Spectra of $[C_{10}H_{10}]^{+\cdot}$ Isomers[a,b,c]

	m/z								
compd	115	102	91	89	77	75	63	51	R[d]
I	22.2	23.3	2.50	5.3	9.0	9.2	10.6	11.8	1.0
II	26.7	13.7	2.50	6.5	10.9	7.5	11.6	12.5	2.0
III	38.8	11.8	1.20	7.7	8.3	6.5	11.0	8.2	3.3
IV	28.0	12.8	1.68	8.6	10.5	7.0	11.6	11.8	2.2
V	31.4	12.9	1.82	8.2	11.8	5.3	11.9	10.3	2.4
VI	28.3	12.4	1.05	7.7	8.0	8.9	14.7	10.9	2.3
VII	42.9	10.3	1.04	8.5	6.1	7.8	11.1	7.1	4.2
VIII	40.8	10.2	0.54	8.3	6.2	7.2	11.8	7.7	4.0
IX	41.2	10.3	0.84	8.0	6.4	6.8	11.9	7.9	4.0
X	38.9	10.1	0.81	8.1	7.7	6.2	12.6	9.2	3.9
XI	40.4	10.5	1.00	7.2	7.3	6.9	10.9	8.8	3.9

[a,b] See Table II. [c] Ionization by low-energy electrons. [d] See Table III.

arguments presented earlier, we postulate that the ions produced by 70-eV electron ionization of I are characteristic of some rearranged structure at least in part.

Since the above results do not permit us to assign actual structures or even to rule out the possibility of partial isomerization to a mixture of ion structures, we decided to obtain the CAD spectra as a function of ionizing energy. Ionization of the parent molecule was carried out by low-energy electrons (the electron energy was reduced such that the molecular ion beam was 1% of its maximum value) and by CE with the molecular ions of toluene, nitric oxide, carbon disulfide, and nitrogen. Internal energy of the ions formed by CE is the difference in recombination energy (RE) of the reagent gas (which is normally close to its ionizing energy) and ionizing energy (IE) of the molecule being ionized. The RE of $[NO]^{+\cdot}$ has been reported to be 9.25[24] and 8.3 eV[25] (IE = 9.26 eV[26]) and that of $[CS_2]^{+\cdot}$ and $[N_2]^{+\cdot}$ to be ≃10[27] (IE = 10.1 eV[26]) and 15.3 eV[27] (IE = 15.58 eV[26]), respectively. The RE of $[\text{toluene}]^{+\cdot}$ is taken as 8.82 eV (its IE[26]). Thus, by proper choice of the reagent ions, $[C_{10}H_{10}]^{+\cdot}$ ions of various, well-defined energies can be formed initially.

The following observations are made from the CAD spectra taken of the ions with various internal energies (Table II). At lower ionizing energies: (1) the abundance of ions representing loss of CH_3 radical (*m/z* 115) decreases for both $[I]^{+\cdot}$ and $[II]^{+\cdot}$ but the change is more drastic for the ring-closed isomer, (2) there is a significant increase in the abundance of *m/z* 102 for $[I]^{+\cdot}$, and (3) the remainder of the spectral features remain relatively unchanged. The greater abundance of *m/z* 102 can be attributed to the loss of C_2H_4 from the cyclobutene structure, a cycloreversion reaction. At higher ionizing energies, the spectra of the two ions become more similar and ultimately become superimposable when $[N_2]^{+\cdot}$ was used as the CE reagent. In that case, about 7 eV can be initially deposited in the molecular ions. Because the CAD spectra vary with the ionizing energy, it is concluded that the ions are isomerizing as a function of the internal energy. The CAD spectra of the ions formed near the threshold are, to a large extent, characteristic of the unisomerized structures, whereas increasing the internal energy of the ions not only causes the two isomeric ions to interconvert but also causes them to rearrange to some other more stable isomeric structure or a mixture of structures (vide infra).

Although a precise estimate of the activation energy for the ring opening of $[I]^{+\cdot}$ cannot be made on the basis of these data, we can arrive at a conservative estimate using the following reasoning. If we linearly extrapolate the CAD spectra of $[I]^{+\cdot}$ produced by CE to the threshold energy for ionization, the relative abundances of *m/z* 115 and 102 can be estimated to be approximately 21.5 and 22.5, respectively, which are approximately the same as that in the CAD spectrum of the ions produced by low-energy electrons (see Table II). This suggests that the latter spectrum is characteristic of the ions having retained the structure of the neutral precursor. If we assume that at high internal energies, $[I]^{+\cdot}$ has interconverted to a thermodynamically stable structure such as $[VIII]^{+\cdot}$ (vide infra), then it can be estimated that <30% of $[I]^{+\cdot}$ has isomerized when ionization was carried out by CE with $[\text{toluene}]^{+\cdot}$. A maximum of 0.6 eV can be transferred to I by CE with $[\text{toluene}]^{+\cdot}$. Since one of the consequences of quasi-equilibrium theory[28] of mass spectrometry is that the activation energy for a unimolecular dissociation is less than the internal energy of the decomposing ions, we conclude that the activation energy for the electrocyclic ring opening is less than 0.6 eV or 13.8 kcal mol^{-1}. The value could be as low as 7.0 kcal mol^{-1}, which was estimated for the electrocyclic ring opening of unsubstituted cyclobutene radical cation.[17] Thus, substitution of phenyl at the 1-position has little or no effect in stabilizing the cyclobutene radical cation with respect to the electrocyclic ring opening.

3-Phenylcyclobutene and 1-Phenyl-1,3-butadiene Radical Cations. Our next goal was to investigate the influence of substitution of phenyl at the 3-position of cyclobutene radical cation on the electrocyclic ring opening. This problem was also studied in terms of differences in the CAD spectra of $[III]^{+\cdot}$ and its ring-opened isomers. Neutral III is thermally unstable, and even at about 75 °C, it is converted mainly to *trans*-1-phenyl-1,3-butadiene (IV).[5] The CAD spectra of the ions $[III]^{+\cdot}$ and $[IV]^{+\cdot}$ formed near the threshold for ionization are not similar (Table IV). Even when the ionization was carried out by 70-eV electrons, the spectra of the two ions are not identical (Table III). On the other hand, the CAD spectra of $[III]^{+\cdot}$ and $[V]^{+\cdot}$ formed at 70-eV ionizing energy are nearly identical, but they are quite distinctive for the

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ions formed near the threshold for ionization.

An interpretation of these observations is that there are two possibilities for the structure of ionized 3-phenylcyclobutene. Either (a) it is a stable structure because it gives a unique CAD spectrum at low ionizing energy or (b) $[III]^{+\cdot}$ is thermodynamically unstable and the energy barrier for the electrocyclic ring opening (or other isomerization) is so small that it not only has undergone reaction 1, even at low ionizing energy, but has also rapidly rearranged to some more stable isomeric structure or a mixture of structures. The second possibility is more plausible considering the low thermodynamic stability of $[III]^{+\cdot}$ (see latter discussion of the mechanism). Moreover, on raising the ionizing energy to 70 eV or ionizing by energetic CE with $[CS_2]^{+\cdot}$ and $[N_2]^{+\cdot}$, we notice small changes in the spectrum of $[III]^{+\cdot}$, whereas the spectra of $[IV]^{+\cdot}$ and $[V]^{+\cdot}$ change considerably and ultimately tend toward that of another structure (such as ionized VIII). These results indicate that the ions having the structure of precursor III are quite unstable. One contributing factor to the low stability of III is the lack of conjugation of the cyclobutene double bond with the phenyl ring.

We did not obtain as complete a set of CAD spectra of $[III]^{+\cdot}$, $[IV]^{+\cdot}$ and $[V]^{+\cdot}$ as a function of ionizing energy, as was done in the case of $[I]^{+\cdot}$ and $[II]^{+\cdot}$, because the results have already given us the proof of isomerization of $[III]^{+\cdot}$ even at the lowest ionizing energy.

Although it is not possible to determine the precise energy onset of the isomerization reaction of the 3-phenylcyclobutene radical cation, it can be pointed out that the energy barrier for the transformation is close to the threshold for ionization and is lower than that for the corresponding reactions of the cyclobutene and 1-phenylcyclobutene radical cations.

Ultimate Structure of $[C_{10}H_{10}]^{+\cdot}$ Ions. Based on the results in Table II, we interpreted that at low ionizing energies $[I]^{+\cdot}$ and $[II]^{+\cdot}$ represent two distinct structures which isomerize to some more stable structure or a mixture of structures at high internal energy. The data for $[III]^{+\cdot}$, $[IV]^{+\cdot}$ and, $[V]^{+\cdot}$ showed that these ions also rearrange to another structure. Losses of CH_3 and C_2H_4 are distinguishing features of the CAD spectra of all these compounds. Therefore, the ratio of relative abundances of m/z 115 and 102 should be a sensitive probe for discerning the various ion structures. The major change in the spectra of the ions formed at high ionizing energy compared to those of ions formed near threshold is that the methyl loss becomes more and more facile, while the C_2H_4 loss becomes less probable. A plausible explanation is that all the $[C_{10}H_{10}]^{+\cdot}$ radical cations rearrange to a structure which has greater propensity to lose a methyl radical. Johnstone and Ward[29] invoked a cyclic structure when accounting for the significant loss of CH_3 radical from ionized stilbene and 1,4-diphenylbutadiene.

To investigate the nature of the ultimate structure formed from these $C_{10}H_{10}$ radical cations, compounds VI–X were chosen for further study because (1) they give mass spectra similar to I–V, (2) they can be shown to be thermodynamically stable with respect to I–V, (3) analogous isomerizations are known for the neutral molecules, and (4) they possess structures which should readily lose a methyl radical (except VI).

Weber and co-workers[30] have shown that pyrolysis of IV leads to the formation of largely VI. A similar observation was made by Padwa et al.[31] while studying thermolysis of 2-phenyl-1,3,4-oxadiazolinone. II was the major product along with IV, VI, and 1-phenyl-3-buten-1-one. Thus, $[VI]^{+\cdot}$ may be a likely stable structure.

We have calculated ΔH_f's of all the radical cations of I–X from their experimental IE's and from estimates of the ΔH_f's of neutrals. The results (Table VI) show that $[VI]^{+\cdot}$ and $[VIII]^{+\cdot}$ are the most stable structures. The heats of formation of $[C_{10}H_9]^+$ fragment ions formed from $[I]^{+\cdot}$ and $[II]^{+\cdot}$ are similar to that formed from $[VIII]^{+\cdot}$.[20] This indicates that isomerization to a stable structure is occurring for $[I]^{+\cdot}$ and $[II]^{+\cdot}$.

Table V. Partial CAD Spectra of $[C_{10}H_{10}]^{+\cdot}$ Isomers[a,b]

	m/z							
compd	115	102	91	89	77	75	63	51
I, *c*	38.6	12.0	1.35	7.7	7.5	7.0	11.4	8.8
d	36.7	11.1	1.60	7.5	9.4	6.4	11.9	9.2
II, *c*	38.4	10.7	1.26	7.9	6.9	7.3	12.6	8.8
d	36.1	11.4	2.06	7.1	9.5	6.6	12.1	10.3
III, *c*	41.9	9.9	1.00	8.1	7.4	6.4	11.1	8.4
d	39.5	10.2	1.39	7.4	8.0	7.0	12.3	9.2
IV, *c*	38.8	10.2	0.91	8.1	7.4	7.4	12.0	8.7
d	36.3	11.6	1.56	8.1	9.8	6.1	11.4	10.0
VI, *c*	30.9	12.0	0.94	7.5	7.1	9.1	13.5	10.8
d	34.2	10.1	1.22	7.6	7.5	8.6	12.9	9.9
VII, *c*	41.1	9.5	0.74	8.3	7.3	6.6	11.2	8.7
d	42.7	10.1	1.04	8.0	6.1	6.8	11.6	7.3
VIII, *c*	41.1	9.5	0.70	8.1	6.6	6.6	11.7	8.4
d	42.0	9.7	1.11	8.6	6.4	6.5	11.9	8.4

[a,b] See Table II. [c] Ionization by CE with $[CS_2]^{+\cdot}$. [d] Ionization by CE with $[N_2]^{+\cdot}$.

Table VI. Ionizing Energies[a] and Heats of Formation[b] of $[C_{10}H_{10}]^{+\cdot}$ Isomers

compd	$IE[M]^{+\cdot}$	$IE[M]^{+\cdot}$[c]	ref	$\Delta H_f[M]$[d]	$\Delta H_f[M]^{+\cdot}$
I	8.24	8.20	20	59.7	250
		8.22	26		
II	8.19	8.10	20	48.7	238
		8.57	26		
III	8.42			63.7	258
IV	8.06	8.10	32	48.8	235
		7.95	26		
V		8.39	26	49.8	243
VI	8.14	8.00	32	30.3[e]	218
VII	8.27			35.2	226
VIII	8.05	8.10	32	33.3	219
IX	8.28	8.00	26	35.6	227
X	8.34			38.1	231
XI	8.26			64.1	255

[a] Expressed in eV. [b] Expressed in kcal mol^{-1}. [c] Literature values. [d] $\Delta H_f(298)$ (except for VI) were calculated according to the group additivity rule by using the scheme of Benson and Buss.[33] [e] Reference 34.

The 1-methylindene radical cation may also be a likely ultimate structure because it also should show abundant methyl loss initiated by the double bond of the indene ring. However, the ease of mobility of the double bond from one carbon to another in the five-membered ring will allow the interconversion of the structures of VII–X ions, which is indeed the case as manifested by the similarity of the CAD spectra of these compounds (Tables III–V).

The CAD spectra of $[VI]^{+\cdot}$–$[X]^{+\cdot}$ are in accord with the hypothesis that they are the likely candidates. Specifically, the CAD spectra of $[VII]^{+\cdot}$–$[X]^{+\cdot}$ are nearly identical and not a strong function of the ionizing energy. Therefore, these structures must be the most stable of all the isomers studied, which is consistent with the thermochemical measurements. Comparing their spectra with those of $[I]^{+\cdot}$–$[V]^{+\cdot}$ we find that the spectra of $[I]^{+\cdot}$, $[II]^{+\cdot}$, $[IV]^{+\cdot}$, and $[V]^{+\cdot}$, although distinctive at low ionizing energy, become nearly identical and have changed to resemble the CAD spectra of the indene-type structures when the ionizing energy is raised. The spectrum of $[III]^{+\cdot}$ may be interpreted as a mixture of the spectra of $[IV]^{+\cdot}$ and $[VIII]^{+\cdot}$ even for the ions formed near the threshold for ionization. The ratio of relative abundances of m/z 115 and 102 for $[III]^{+\cdot}$ is 3.3 compared to 2.2 and 4.0 for $[IV]^{+\cdot}$ and $[VIII]^{+\cdot}$, respectively. Our interpretation of these observations is that $[I]^{+\cdot}$–$[V]^{+\cdot}$ isomerize to stable indene-like structures.

It is unlikely that $[VI]^{+\cdot}$ is an ultimate structure, because its spectrum changes with the internal energy and because of the lower probability of methyl loss from this structure.

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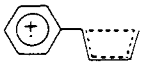
(31) Padwa, A.; Caruso, T.; Nahm, S.; Rodriguez, A. *J. Am. Chem. Soc.* **1982**, *104*, 2865.

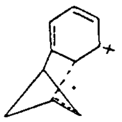
Our conclusions are supported by photochemical studies carried out by Andrew et al.[35] on matrix-isolated radical cations. Allylbenzene and 1-phenyl-2-butene ions rearrange to indan and methylindan ions, respectively, probably because of interaction between the olefin π system and the positive aromatic π system. Koppel et al.[36] have also given evidence in favor of a cyclic structure (indanyl cation) for $[C_9H_9]^+$ ions derived from phenylpropene. Further support comes from the observation that the CAD spectra of $[C_9H_7]^+$ and $[C_{10}H_8]^{+\cdot}$ fragment ions obtained at 70 eV from all the $[C_{10}H_{10}]^{+\cdot}$ under investigation are identical.[37]

Tautomeric rearrangement of neutral VII to VIII is well documented.[38] Palensky and Morrison[39] have observed that photochemical rearrangement of VII leads to 2-methylindene, while the latter compound gives VII and VIII. VIII is stable under these conditions. X should be less stable due to the lack of conjugation of the exocyclic double bond with the phenyl ring. If we argue that the order of stability of these compounds is maintained upon ionization, then the structure of $[VIII]^{+\cdot}$ appears to be the most stable one. The thermochemical measurements indicate that indeed this is true.

Mechanism for Isomerization of 3-Phenylcyclobutene Radical Cation. Unlike $[I]^{+\cdot}$, the evidence for the electrocyclic ring-opening reaction of $[III]^{+\cdot}$ is not clear. The lowest activation energy process of $[III]^{+\cdot}$ is isomerization to the $[VII]^{+\cdot}$–$[X]^{+\cdot}$ manifold either by direct means or by involving an intermediate of thermodynamic stability between that of $[III]^{+\cdot}$ and $[VIII]^{+\cdot}$. The most probable route of $[III]^{+\cdot}$ to $[VIII]^{+\cdot}$ is the electrocyclic ring opening to give $[IV]^{+\cdot}$. This mechanism seems to be reasonable because (a) it involves a loose transition state, a, in which stretching of the bond in the reaction coordinate occurs with subsequent relief of the ring strain and (b) there are analogies with the electrocyclic ring opening of 1-phenylcyclobutene (present work) and cyclobutene[17] radical cations and with thermally activated neutral III.[5] The CAD spectrum of low internal energy $[III]^{+\cdot}$, however, does not resemble that of low internal energy $[IV]^{+\cdot}$. The likely explanation for this obliquity is that the isomerization of $[III]^{+\cdot}$ to $[IV]^{+\cdot}$ generates $[IV]^{+\cdot}$ in a highly excited vibrational state; i.e., the internal energy of $[IV]^{+\cdot}$ thus formed is higher ($\simeq$23 kcal mole^{-1}) than the internal energy of $[IV]^{+\cdot}$ formed directly by near-threshold ionization of neutral IV. This excess internal energy causes $[IV]^{+\cdot}$ to rapidly cascade to the more stable structure $[VIII]^{+\cdot}$.



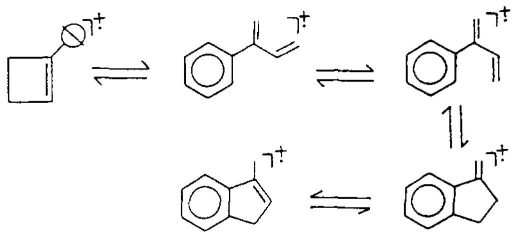
a



b

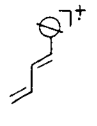
The possibility of another route for the rearrangement of $[III]^{+\cdot}$ to $[VIII]^{+\cdot}$ cannot be ruled out a priori. A chemically reasonably intermediate is $[XI]^{+\cdot}$, as suggested by one of the reviewers. We have synthesized this compound and studied its CAD spectrum (see Tables III and IV). The spectrum resembles very closely that of $[VIII]^{+\cdot}$ and does not change with internal energy. This is also in accord with an isomerization of $[XI]^{+\cdot}$ to the stable $[VIII]^{+\cdot}$. The CAD spectra of low internal energy $[III]^{+\cdot}$ and $[XI]^{+\cdot}$ are qualitatively similar but not superimposable. The ratios of the abundances of m/z 115 and 102 are 3.3 and 3.9, respectively. These data also cannot be used to prove unequivocally isomerization of $[III]^{+\cdot}$ to $[VIII]^{+\cdot}$ via structure $[XI]^{+\cdot}$. However, $[XI]^{+\cdot}$ could exist as a transitory intermediate, but only if its stability is between $[III]^{+\cdot}$ and $[VIII]^{+\cdot}$.

Scheme I

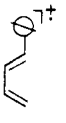


An estimate of the heat of formation of $[XI]^{+\cdot}$ can be made to examine the stability of this radical cation by using the experimental IE of XI and a calculation of the ΔH_f of neutral XI.[40] The ΔH_f of $[XI]^{+\cdot}$ is equal within experimental error to that of $[III]^{+\cdot}$ (Table VI). The relative instability of this ion is not surprising because of the overlap repulsion of the π orbitals of the phenyl ring and the e_s orbital of the cyclobutane moiety.[41] Therefore, there is little driving force for $[III]^{+\cdot}$ to isomerize to $[XI]^{+\cdot}$ en route to $[VIII]^{+\cdot}$. Furthermore, we should expect isomerization of $[III]^{+\cdot}$ to $[XI]^{+\cdot}$ to have a high entropy of activation because a tight transition state, b, is required. Finally, the spectrum of $[III]^{+\cdot}$ should resemble that of $[XI]^{+\cdot}$, if isomerization occurs, because $[XI]^{+\cdot}$ so formed does not contain significant amount of excess internal energy as does $[IV]^{+\cdot}$ formed from $[III]^{+\cdot}$. This is clearly not the case. Likewise the direct isomerization of $[III]^{+\cdot}$ to $[VIII]^{+\cdot}$ will also involve a tight activated complex and therefore is unlikely.

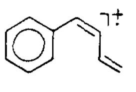
On comparing the CAD spectra of the ions formed at intermediate energies (e.g., 70 eV; see Table III), we find that $[V]^{+\cdot}$ more readily isomerizes to $[VIII]^{+\cdot}$ than does $[IV]^{+\cdot}$. This may be attributed to the fact that a large proportion of $[V]^{+\cdot}$ exists in the s-trans configuration which is expected to be an immediate precursor to $[VIII]^{+\cdot}$. The relative abundance of *s-cis*-$[V]^{+\cdot}$ compared to *s-trans*-$[V]^{+\cdot}$ is expected to be extremely low, due to steric repulsion of π orbitals of the phenyl ring and those of the butadiene moiety. Threfore, $[V]^{+\cdot}$ is expected to have a larger energy barrier to rotation of the central bond in the diene moiety; as a result isomerization to $[VI]^{+\cdot}$ is not expected or observed. On the other hand, interconversion of s-cis and s-trans forms of $[IV]^{+\cdot}$ is easily achieved. Consequently the proportion of *s-cis*-$[IV]^{+\cdot}$ at intermediate energies is quite significant, and the spectrum of $[IV]^{+\cdot}$ has features characteristic of $[VIII]^{+\cdot}$ and of unisomerized $[IV]^{+\cdot}$ (a 50:50 mixture; see Table III).[42]



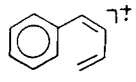
s-trans-$[IV]^+$



s-cis-$[IV]^+$



s-trans-$[V]^+$



s-cis-$[V]^+$

At high internal energies the CAD spectrum of $[VI]^{+\cdot}$ also has features of $[VIII]^{+\cdot}$, suggesting a partial rearrangement of $[VI]^{+\cdot}$ to $[VIII]^{+\cdot}$. The energy barrier for such a rearrangement may be as high as 43 kcal mol^{-1} on the basis of the observation that the spectrum of $[VI]^{+\cdot}$ begins to show features of $[VIII]^{+\cdot}$ when ionization was carried out by CE with $[CS_2]^{+\cdot}$. Under these conditions of ionization, 1.86 eV excess energy can be transferred. A closely related interconversion of tetralyl and methylindanyl radicals has been reported by Franz and Camaioni.[43]

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[32] Koppel, C.; Schwarz, H.; Bohlman, F. *Org. Mass Spectrom.* **1974**, *9*, 324.

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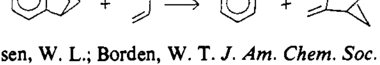
[36] Koppel, C.; Schwarz, H.; Bohlmann, F. *Org. Mass Spectrom.* **1974**, *8*, 25.

[37] Dass, C.; Gross, M. L. *Org. Mass Spectrom.*, in press.

[38] Bergson, G.; Weidler, A.-M. *Acta Chem. Scand.* **1963**, *17*, 862, 1798; **1964**, *18*, 1483, 1487, 1498. Bergson, G. *Ibid.* **1963**, *17*, 2691. Weidler, A.-M. *Ibid.* **1963**, *17*, 2724.

[39] Palensky, F. J.; Morrison, H. A. *J. Am. Chem. Soc.* **1977**, *99*, 3507.

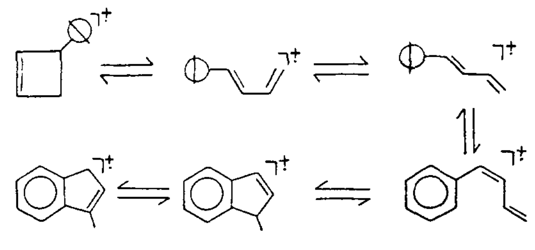
[40] The ΔH_f of neutral XI was calculated for the following isodesmic reaction, which according to Jorgensen and Borden[41] is exothermic by −12 kcal mol^{-1}.



[41] Jorgensen, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1973**, *95*, 6649.

[42] When *s-cis*-$[V]^{+\cdot}$ is energetically accessible, the spectrum of $[IV]^{+\cdot}$ in addition may also have features of that of $[VI]^{+\cdot}$.

Scheme II



Conclusions

From the results of this study we have demonstrated that 1-phenylcyclobutene radical cation formed near threshold for ionization can be distinguished from the corresponding ring-opened isomer, [II]$^{+\cdot}$. However, as the ionizing energy is increased, [I]$^{+\cdot}$ undergoes electrocyclic ring opening to [II]$^{+\cdot}$ and ultimately rearranges to stable [VIII]$^{+\cdot}$ (Scheme I).

3-Phenylcyclobutene radical cation also isomerizes to [VIII]$^{+\cdot}$. This isomerization occurs even more readily and involves electrocyclic ring opening to highly activated [IV]$^{+\cdot}$, which is rapidly transformed to [VIII]$^{+\cdot}$ via the s-trans form of *cis*-1-phenyl-1,3-butadiene radical cation (Scheme II).

The energy barrier for the elctrocyclic ring opening of [I]$^{+\cdot}$ was estimated to be between 7 and 13.8 kcal mol^{-1}. In the case of [III]$^{+\cdot}$, the ring opening is essentially complete at energies close to the threshold for ionization. Evidently, substitution of phenyl at the 3-position has destabilized the cyclobutene radical cation compared to substitution at the 1-position.

Based on these observations, we conclude that there exists an energy advantage for the electrocyclic reaction of the ionized cyclobutenes; i.e., the effect of removing a bonding electron from the HOMO of the cyclobutenes is to reduce the energy barrier for the electrocyclic process in accord with the recent theoretical predictions.[18,44,45] However, the questions of stereochemistry and the applicability of the Woodward–Hoffmann rules still remain unanswered.

Experimental Section

All CAD experiments were performed with a Kratos MS-50 triple analyzer, which has been described elsewhere.[23] The instrument is a high-resolution mass spectrometer of Nier–Johnson geometry to which has been added a third sector, an electrostatic analyzer. The CAD spectra were acquired by adjusting the first two sectors to pass the ions of interest to the collision chamber located in the third field free region. Helium was employed as collision gas at a pressure to effect a 50% suppression of the main beam intensity.

Ionization was carried out at 70-eV, low electron energy and by charge exchange with the molecular ions of toluene, nitric oxide, carbon disulfide, and nitrogen at a partial pressure of ca. 20 mtorr in the ion source. All the reagent gases were ionized by using a 280-eV electron beam. The total emission current was 500 μA and the accelerating voltage was 8000 V. The ions formed were selected at a resolution of ca. 30 000 (for 70-eV ionization) and ca. 5000 (low-energy electron ionization or CE). The sample probes were kept below 65 °C in order to avoid thermal isomerization. The ion source was maintained at 100 °C for the same reason. The CAD spectra are averages of 3–5 determinations, each of which was the result of 10–40 computer-averaged scans (on a Data General Nova 4X computer). The measurement precision is better than ±5% (RSD) for the major peaks.

All ionization potential measurements were carried out on a Kratos MS-50 double analyzer equipped with a low-eV[46] ion source. Phenol and deuterated benzene were used as reference compounds. The ion intensities were recorded at increments of 0.1 eV and processed as semilog plots. Each IE value is an average of at least three measurements with a standard deviation of better than ±0.1 eV.

All 70-eV mass spectra were taken on a Kratos MS-50 double analyzer. Each spectrum is an average of 10 scans.

All the compounds were purified by preparative gas chromatography using the following columns: (A) 2 m × 6 mm column packed with 4% SE 30/6% SP 2401 on 100/120 Supelcoport (for I and II), (B) 2 m × 6 mm column packed with 5% SE 30 on 45/60 Chromosorb PNAW (for III and XI), and (C) 2 m × 6 mm 10% SP 2100 on 100/120 Supelcoport (for IV–X). Helium was used as carrier gas.

Compounds I,[47] II,[21] III,[48] IV,[49] V,[50] VI,[21] VII,[51] IX,[52], and XI[48] were synthesized as reported in the literature. Their purity was checked by ^{1}H NMR and mass spectrometry. The spectra were consistent with the assigned structure.

3-Methylindene was prepared by thermal isomerization of VII on column C. Typical column conditions were as follows: injector at 330 °C, detector at 195 °C, column at 165 °C, and helium flow rate at 22 mL min^{-1}. Under these conditions two peaks were observed; the one with a retention time of 4.2 min was the starting material and that at 5.0 min was confirmed to be VIII by its ^{1}H NMR and mass spectra.

2-Methyleneindan was synthesized from 2-indanone by the Wittig reaction with the procedure reported for IX.[52]

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Registry No. I, 3365-26-2; I$^{+\cdot}$, 86549-86-2; II, 2288-18-8; II$^{+\cdot}$, 86549-87-3; III, 20211-64-7; III$^{+\cdot}$, 86549-88-4; IV, 16939-57-4; IV$^{+\cdot}$, 86594-44-7; V, 31915-94-3; V$^{+\cdot}$, 86594-45-8; VI, 447-53-0; VI$^{+\cdot}$, 86562-98-3; VII, 767-59-9; VII$^{+\cdot}$, 86594-46-9; VIII, 767-60-2; VIII$^{+\cdot}$, 86549-89-5; IX, 1194-56-5; IX$^{+\cdot}$, 86549-90-8; X, 68846-65-1; X$^{+\cdot}$, 86549-91-9; XI$^{+\cdot}$, 86549-92-0; 2-indanone, 615-13-4.

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