

# MASS SPECTROMETRY FOR INVESTIGATIONS OF GAS-PHASE RADICAL CATION CHEMISTRY

## THE TWO STEP CYCLOADDITION OF THE BENZENE RADICAL CATION AND 1,3-BUTADIENE†

R. W. HOLMAN, M. D. ROZEBOOM and M. L. GROSS\*  
Department of Chemistry, University of Nebraska, Lincoln, NE 68588, U.S.A.

and

C. D. WARNER  
Department of Chemistry, Hastings College, Hastings, NE 68901, U.S.A.

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**Abstract**—Mass spectrometric techniques are now used extensively for the study of gas-phase radical cation chemistry. The generation and structural properties, the unimolecular and bimolecular chemistry of some representative radical cation systems, and the methods of study are reviewed. The structure of the ion-molecule adduct produced in the reaction of the benzene radical cation and neutral 1,3-butadiene was investigated by collisionally stabilizing the adduct and then acquiring its collision-activated decomposition spectrum. The CAD spectrum of the adduct changes dramatically as a function of the degree of collisional stabilization. This observation is interpreted in terms of two distinct structures for the adduct. The species that is stabilized at 0.7 Torr has a CAD spectrum similar to the 2-phenyl-2-butene radical cation. The second structure, stabilized at 0.1 Torr, has a CAD similar to that of 1-methylindan. The results of these experiments are interpreted in terms of a two-step cycloaddition mechanism for the formation of the 1-methylindan radical cation.

### INTRODUCTION

The chemistry of radical cations generated by using electrochemistry or chemical oxidation in solution is an area of research that is well accepted as an important and useful intellectual pursuit. The chemistry of gas-phase radical cations seems more esoteric even though mass spectroscopists have dealt productively with organic radical cations for over two decades. The chemistry of gas-phase radical cations was less recognized because of the limited measurement tools available in the early days of organic mass spectrometry and perhaps because of the intemperate amount of speculation on structure and properties that was characteristic of some early research efforts.

However, instrumentation developments over the past 15 years have made possible many new measurements and convincing interpretations have followed. High pressure (>0.1 Torr) sources, such as those used in conventional chemical ionization<sup>1,2</sup> mass spectrometers, make it possible to study bimolecular reactions of radical cations and neutral molecules (often called ion-molecule reactions). This capability adds a new dimension to conventional ion sources which previously only permitted observation of unimolecular dissociations of radical cations. Metastable ion methods,<sup>3-9</sup> kinetic energy release measurements<sup>4-10</sup> and collisional<sup>11-20</sup> and photoactivation<sup>21,22</sup>

are presently available for determining structures of radical cations.

The evolution of ion cyclotron resonance into Fourier transform mass spectrometry (FTMS)<sup>23-25</sup> coupled with new laser techniques as well as the emergence of tandem mass spectrometry (MS-MS)<sup>26-35</sup> have elevated mass spectrometry into position as a discipline for studying radical cation chemistry.

In this paper, some examples of unimolecular isomerization and bimolecular reactions of radical cations will be reviewed to illustrate the approach and highlight some of the chemical properties of these species. Following this introduction, the reactions of the benzene radical cation with neutral 1,3-butadiene will be discussed to show that this chemistry provides a new route to indan-type systems.

### EXPERIMENTAL METHODOLOGY

**Ionization.** Traditional ionization techniques such as electron ionization have been extremely useful for obtaining mass spectra of neutral molecules and for quantifying ultratrace levels of organic compounds. However, electron ionization suffers because it is not easy to control the amount of energy imparted to the ionized organic species.

Recent adoption of other methods of ionization, such as charge exchange ionization,<sup>36</sup> have made it feasible to study bimolecular reactions of radical cations that have been prepared with more precise and controllable amounts of internal energy. Field ionization kinetics<sup>37</sup> allows one to study fast reactions in

†This paper is dedicated to the memory of Chuck Stiefvater, the best friend and fellow graduate student of R. W. Holman.

the  $10^{-10}$  s regime. Multiphoton ionization (MPI)<sup>38,39</sup> is a new means of producing radical cations and can be used to ionize selectively one species in the presence of another.<sup>38,39</sup> Thus, the range of species that can be ionized and the control available for ionization make it possible to produce efficiently high yields of radical cations for studies of either unimolecular or bimolecular reactions.

**Monitoring gas-phase chemistry.** Historically, metastable ion methods<sup>3-9</sup> were used to elucidate mechanisms of decompositions of gas-phase radical cations. The development of tandem mass spectrometry or mass spectrometry-mass spectrometry (MS-MS) has taken metastable methods a step further. Two consecutive stages of mass analysis are utilized in MS-MS to obtain information on the ions formed in the source of a mass spectrometer.<sup>26-35</sup> A schematic diagram of a tandem system is depicted in Fig. 1. The main components include: (a) an ionization source, (b) mass spectrometer one (MS-I), (c) a field free region for ion dissociation, and (d) mass spectrometer two (MS-II).

A typical MS-MS study of a bimolecular reaction begins with conducting the reaction in a high pressure source. All product ions formed in the source are accelerated and focused through an electrostatic analyzer, ESA-I. The field of the magnetic sector is set to pass only the product ion of interest into a collision cell where it is induced to dissociate into "daughter" fragment ions. The second mass spectrometer, in this case ESA-II, is scanned to obtain the spectrum of daughter ions which is used as a fingerprint of the parent ion structure. Thus, the reaction, product isolation, and product structure determination are conducted in a single experiment.

Fourier transform mass spectrometry complements the MS-MS experiment. FTMS is well-suited to make thermochemical measurements and to conduct bimolecular reaction kinetics because of its time resolution and ion storage features (up to seconds at  $10^{-7}$  Torr). Double resonance and ion ejection experiments can be used to elucidate which ions are reacting.<sup>25</sup> Pulsed valve reagent introduction and ion manipulation techniques (excitation and ejection) allow MS-MS, and higher order (MS<sup>n</sup>) experiments;<sup>25</sup> however, these experiments are less routine with FTMS compared to tandem instruments. The FT mass spectrometer differs from a high pressure mass spectrometer because it operates best at  $10^{-7}$  Torr or lower, whereas pressures of 0.1-1.0 Torr are needed for ion-molecule reactions to occur in the  $10^{-5}$ - $10^{-6}$  s ion residence time frame of a high pressure source.

High pressure, as will be seen, is important for stabilizing adducts formed in the reactions of radical cations and neutral molecules.

**Structure determination.** Two commonly used structure determination techniques involve comparison of either ion decomposition spectra or ion-molecule reactivity. The direct comparison of the collisionally activated decomposition (CAD) and/or unimolecular dissociation (metastable) spectra of an unknown radical cation with those of known reference compounds often allows assignment of the unknown structure. Low energy spectra can be taken with the added dimension of energy resolution,<sup>40</sup> whereas the dependence of higher energy CAD spectra on angle of scattering<sup>41,42</sup> gives equivalent information.

A second major way to verify the structure of an unknown radical cation is to react it, and appropriate known model compounds, with diagnostic neutral species. To conclude that the unknown and a specific model compound have the same structure, they should exhibit the same reactivity with the same set of neutral species and react to yield adducts whose CAD spectra are identical.

Additional structurally diagnostic experiments include charge stripping mass spectrometry<sup>43,44</sup> and neutralization/reionization mass spectrometry.<sup>45,46</sup>

Some results, principally from this laboratory, are discussed below. For convenience, the investigations are divided into three categories: (1) unimolecular isomerizations, (2) dicationic ions, and (3) bimolecular reactions of radical cations. This brief review is not intended to be comprehensive but only illustrative of some of the above methods.

#### *Isomerizations of gas-phase radical cations*

Although isomerizations of closed shell, neutral systems in the condensed phase are well understood, less is known about isomerization of open shell radical cation systems. Several questions are of interest. Does the structure of a neutral precursor remain intact upon ionization? If so, will the newly-formed radical cation isomerize similarly as its neutral precursor? How do the energy requirements that govern isomerizations of radical cations compare with those of their neutral counterparts?

The thermal conrotatory electrocyclic ring opening of neutral cyclobutene to 1,3-butadiene is a good example of a condensed phase unimolecular isomerization.<sup>47</sup> The activation energy for ring opening is  $33 \text{ kcal mol}^{-1}$ , which is approximately  $15 \text{ kcal mol}^{-1}$  lower than "some non-allowed pathway".<sup>48</sup> This latter

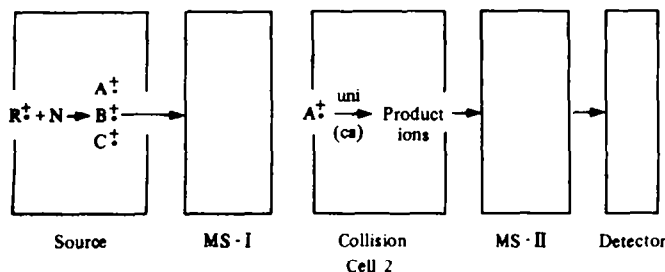


Fig. 1. Schematic diagram of a tandem mass spectrometer (MS-MS) for studying ion-molecule reactions.

quantity is the energy advantage of the allowed process. The radical cation of cyclobutene also isomerizes to 1,3-butadiene radical cation with an activation energy estimated to be less than 7 kcal mol<sup>-1</sup>.<sup>49</sup> Clearly, an additional energy advantage exists for the electrocyclic reaction of the radical cation.

The effects of substituents on the ring opening of radical cations parallel those of closed shell species.<sup>50</sup> Substitution of a phenyl<sup>50</sup> or methyl<sup>51</sup> group at the double bond of cyclobutene stabilizes the radical cation, whereas substitution at the 3-position enhances the rate of ring-opening reaction with respect to the unsubstituted system. Furthermore, the activation energies for ring openings of substituted cyclobutene radical cations are significantly lower than those of their neutral counterparts.<sup>51</sup>

On the basis of the reduced activation barriers for radical cation isomerizations, it may be expected that the isomerization of high energy radical cations will be so rapid that the structure corresponding to the neutral will not be seen. The chemical properties of both the fulvene<sup>52</sup> and benzvalene<sup>53</sup> radical cations were investigated to see if this is true. Both low energy radical cations exhibit considerably different properties than other [C<sub>6</sub>H<sub>6</sub>]<sup>+</sup> isomers, which can be interpreted in terms of unique structures, not subject to either ring opening or to isomerization to benzene. For highly activated ions, however, isomerization and/or rearrangement reactions occur because activation energies for those processes are lower than for fragmentation channels. Nevertheless, stable, low energy radical cations can be prepared and investigated.

#### Distonic ions

Distonic ions<sup>54</sup> are radical ions whose charge and radical sites are neither adjacent nor in conjugation with each other. The predicted existence of distonic ions was confirmed recently in a number of experimental studies.<sup>55,56</sup>

A prototypal example is the ion formed by ring opening of the cyclopropane radical cation. The ring openings of simple cycloalkane radical cations have been extensively studied using both experimental and theoretical methods,<sup>57-71</sup> yet it is not clear that simple trimethylene and related radical cations exist. Three gas-phase ion-molecule reactions were used to resolve this problem.<sup>72</sup> The C<sub>3</sub>H<sub>6</sub><sup>+</sup> radical cations from propene and cyclopropane were reacted in separate experiments with neutral ammonia, carbon disulfide and propene-*d*<sub>6</sub>. On the basis of reactivity comparisons, it was concluded that cyclopropane radical cations do not isomerize to propene to any appreciable extent. The differences in reactivity depend markedly on the internal excitation of cyclopropane and can be accounted for by invoking ring opening to the trimethylene radical cation, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sup>+</sup>. Only high internal energy forms of cyclopropane radical cations yield the distonic trimethylene radical cation.

#### Bimolecular reactions of radical cations

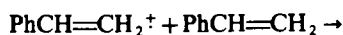
Investigations of radical cation-neutral molecule reactions in the gas phase are not complicated by issues such as choice of oxidation method or choice of solvent. The ionization methods serve as means to conduct efficient one-electron oxidations. Moreover,

the reactivities are intrinsic; i.e. they are free of any complicating solvent effects. Thus, gas-phase ion chemistry could serve as a model for solution chemistry particularly to identify systems which show considerable improvements in selectivity and reactivity as a result of ionizing one of the reacting partners. In this section, a few reactions are cited which proceed much more readily if one reagent is modified by converting it to a radical cation.

**Cycloadditions.** The butadiene radical cation reacts with neutral 1,3-butadiene to produce an acyclic intermediate which isomerizes to an activated 4-vinylcyclohexene radical cation in the absence of collisional stabilization.<sup>73</sup> As the pressure is increased, the collisional stabilization rate increases, and the acyclic product is intercepted before it can isomerize to the 4-vinylcyclohexene radical cation. Similarly, the methyl vinyl ether radical cation reacts with 1,3-butadiene to produce an acyclic structure which, in the absence of stabilizing collisions, cyclizes to an activated 4-methoxycyclohexene radical cation.<sup>74</sup> Under conditions of collisional stabilization, the initially-formed acyclic adduct can be observed.

These reactions are examples of two-step cycloadditions quite unlike the putative concerted cycloadditions of two neutral 1,3-butadiene molecules.<sup>75</sup>

The mechanism of [2+1] cycloaddition reactions occurring in the condensed phase is not fully established due to the difficulty of determining the structure of the intermediates in these reactions. Possibilities include a concerted process<sup>76</sup> and a two-step process involving an acyclic 1,4-distonic radical cation intermediate. The gas-phase reaction of the styrene radical cation and neutral styrene does not proceed through a classical cyclic intermediate, but instead an acyclic 1,4-distonic radical cation is produced (Eq. 1).<sup>77</sup> Under low-pressure (collision free) conditions and in solution, the acyclic intermediates are likely to be short-lived and, therefore, difficult to observe before they cyclize. However, the acyclic styrene dimer can be stabilized by collisions with an inert bath gas. The observation provides experimental justification for the existence of a stable distonic 1,4 radical cation;



Ketenes undergo concerted cycloadditions in an antarafacial fashion.<sup>78</sup> The ketene radical cation [CH<sub>2</sub>CO<sup>+</sup>] should be more electrophilic than neutral ketene, and its propensity to cycloadd to olefins should be enhanced.<sup>79</sup> This premise was tested by reacting the ketene radical cation and neutral ethylene.<sup>80</sup> The [2+1] cycloaddition is quite facile, whereas the corresponding reaction of neutral ketene and ethylene to form cyclobutanone was observed but only under vigorous reaction conditions. Ionization of ketene presumably lowers the energy of both its HOMO and LUMO and brings its LUMO and the HOMO of the ethylene closer, thereby enhancing the rate of the cycloaddition reaction.

**Alkylations.** A different type of adduct formation pertains to the reaction of the benzene radical cation and neutral 2-iodopropane.<sup>81</sup> The adduct is a  $\sigma$ -complex iodonium ion which subsequently expels I

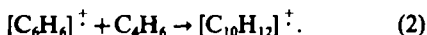
through a three-electron reductive elimination. The resulting ion is directly analogous to the Wheland intermediate seen in the condensed-phase Friedel-Crafts reaction. If this unique alkylation reaction can be extended, it may serve as a basis for using radical cation reactions as a more specific surrogate for the classic Friedel-Crafts reaction.

In summary, it is clear that gas-phase radical cations have unique and interesting chemical properties. They undergo isomerizations with an energy advantage compared to their neutral precursors. They exist in unique forms such as distonic structures. Certain reaction types such as cycloadditions are accelerated when one reactant is a radical cation, and other new reactions are opened for radical cations such as indirect alkylations of benzene. In the following section, we report new results for the reaction of the benzene radical cation and 1,3-butadiene.

## RESULTS AND DISCUSSION

### Benzene/1,3-butadiene

On the basis of the discussion in the last section, one might expect that the reaction of the benzene radical cation and 1,3-butadiene (Eq. 2) could proceed as a cycloaddition to form bicyclo[4.4.0]deca-2,4,8-triene, or yield a monocyclic material such as a phenyl-substituted butene



The reaction in a mixture of benzene and 1,3-butadiene ionized by an electron beam gives an adduct  $[\text{C}_{10}\text{H}_{12}]^{\cdot+}$  in the high pressure source (approx. 0.7 Torr) of a tandem mass spectrometer. The collisionally activated decomposition (CAD) spectrum of the adduct is shown in Fig. 2, and tabulated in Table 1.

Two distinct features are found in the CAD spectrum of the benzene-butadiene adduct. Firstly, the ion does not return to starting materials to any appreciable extent, indicating that the  $[\text{C}_{10}\text{H}_{12}]^{\cdot+}$  ion is a covalent, stable species, in contrast to a weakly

Table 1. CAD spectra of various  $\text{C}_{10}\text{H}_{12}$  radical cations\*

$\text{C}_{10}\text{H}_{12}^{\cdot+}$	Fragment ions						
	117	115	105	104	91	77	51
Adduct	100	43	7	<2	24	7	5
1	100	122	<2	451	231	53	23
2	100	21	<1	<2	17	6	<1
3	100	27	<1	<2	15	5	<1
4	100	69	<2	362	205	43	19
5	100	28	3	4	20	7	5
6	100	29	2	3	20	7	5
7	100	19	2	3	8	3	2
8	100	49	3	<2	25	9	4

\*The adduct was formed at ca 0.7 Torr in a 1:1 mixture of benzene-1,3-butadiene. The model compounds 1-8 were ionized by using toluene charge exchange.

bound  $\pi$  complex. Secondly, the predominant fragmentation pathway of the adduct is the loss of a methyl radical.

In order to elucidate the structural identity of the benzene-butadiene adduct, the CAD spectra of the tetralin 1, 2-methyl-1-phenyl-1-propene 2, 2-methyl-3-phenyl-1-propene 3, 4-phenyl-1-butene 4, 1-phenyl-2-butene 5, 1-phenyl-1-butene 6, 1-methylindan 7, and 2-phenyl-2-butene 8 radical cations were also acquired and are tabulated in Table 1.

Before discussing the results, it should be recalled that the structures of reference  $[\text{C}_{10}\text{H}_{12}]^{\cdot+}$  radical cations depend on internal energy.<sup>12</sup> To maximize the probability of obtaining CAD spectra of structures which resemble those of their neutral precursors, the  $\text{C}_{10}\text{H}_{12}$  reference compounds were ionized by low energy charge exchange with the toluene (IE = 8.82 eV) radical cation. This ionization coupled with stabilization afforded by collision of the  $\text{C}_{10}\text{H}_{12}$  ions with excess toluene molecules should yield thermally cool, non-isomerized  $\text{C}_{10}\text{H}_{12}$  radical cations.

On the basis of comparisons of CAD spectra (Table 1), it is clear that the model compound spectrum that most closely fits that of the benzene-1,3-butadiene

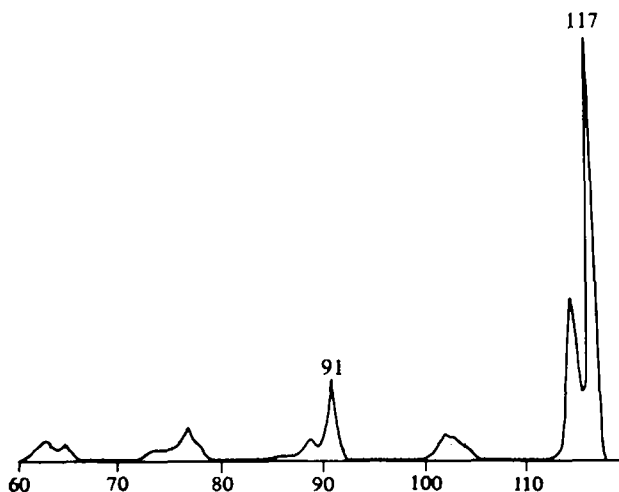
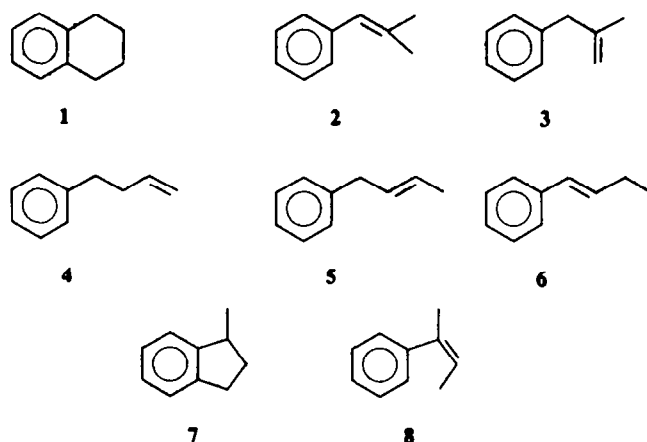


Fig. 2. Partial CAD spectra of the  $[\text{C}_{10}\text{H}_{12}]^{\cdot+}$  benzene-1,3-butadiene adduct.



adduct is that of the 2-phenyl-2-butene radical cation, **8**. The partial CAD spectra in Table 1 also serve to rule out several other mechanistic possibilities for the formation of the benzene-1,3-butadiene adduct. It is obvious that the CAD spectra of model compounds **2** and **3** differ dramatically from that of the benzene-1,3-butadiene adduct (Table 1). Structures **2** and **3** are hardly reasonable candidates for the adduct, but their spectra do serve as demonstrations that CAD spectra of isomeric  $C_{10}H_{12}$  radical cations are highly distinctive.

The benzene-1,3-butadiene adduct whose CAD spectrum is used for comparison purposes was formed in a 1:1 mixture of benzene and butadiene at a total pressure of approximately 0.7 Torr. An adduct formed at such high pressure undergoes considerable collisional stabilization. As a result, the radical cations are inherently "cool" species with little excess internal energy. Evidence that the ionic reactant is the aromatic radical cation is from FTMS experiments and will be discussed later.

As the amount of excess internal energy is increased, activation barriers for isomerizations may be surpassed and rearrangements could occur. A question

must now be addressed: Does the low internal energy benzene-1,3-butadiene adduct, which is similar to the 2-phenyl-2-butene radical cation, rearrange as its internal energy content is increased? Such a question is reasonable in view of several recent published examples of two-step, gas-phase, radical cation mechanisms whereby an initially-formed adduct rearranges to a different isomeric species as a function of internal energy.<sup>73,74,77</sup>

To test whether the adduct rearranges as a function of internal energy, the reaction was conducted at various source pressures. As the total pressure is decreased, the extent of collisional stabilization of the adduct is also reduced and its internal energy content is increased. The partial CAD spectra of benzene-1,3-butadiene adducts of varying internal energies are plotted in Fig. 3.

The CAD spectrum does change as a function of internal energy. As the internal energy is increased by decreasing the pressure, the formation of all other fragment ions becomes less competitive compared to the ion of  $m/z$  117 originating by methyl loss. At the lowest internal energy (highest pressure), the spectrum of the adduct reproduces that of the 2-phenyl-2-

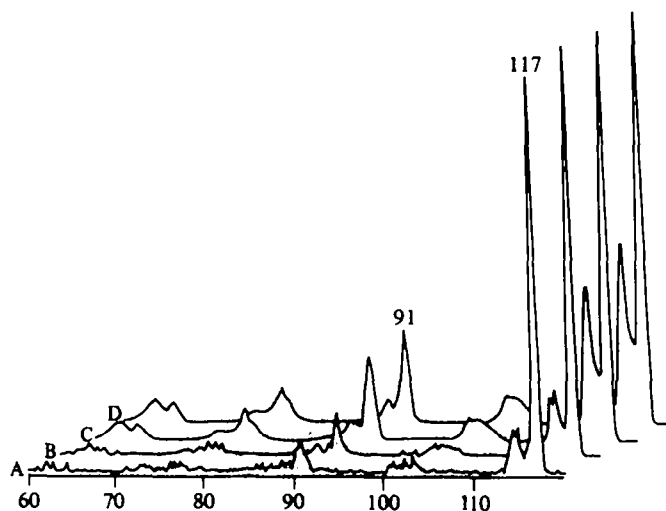


Fig. 3. Energy dependent partial CAD spectra of the benzene-1,3-butadiene adduct. Approximate total source pressures: (A) 0.1 Torr; (B) 0.25 Torr; (C) 0.5 Torr; and (D) 0.7 Torr.

butene radical cation (cf. Table 1 and Fig. 3(D)). At the highest internal energy, the CAD spectrum of the adduct is qualitatively similar to that of the 1-methylindan radical cation, **8**. As mentioned earlier, the 1-methylindan radical cation is the most thermodynamically stable of the  $[C_{10}H_{12}]^+$  isomers. Therefore, it is reasonable that the higher energy adduct isomerizes to such a species.

On the basis of the results, it is clear that a two-step mechanism must be invoked for the formation of the adduct produced in the reaction of the benzene radical cation and neutral 1,3-butadiene. A possibility for the first step is to form a monocyclic  $[C_{10}H_{12}]^+$  species resembling the 2-phenyl-2-butene radical cation. This radical cation subsequently ring closes, if internal energy is not removed, to a 1-methylindan radical cation. However, for this mechanism to be correct, a monocyclic radical cation such as **8** must also rearrange as a function of internal energy to the 1-methylindan radical cation.

The internal energy of the 2-phenyl-2-butene radical cation was controlled by varying the mode of ionization. Charge exchange by [toluene] $^+$  imparts very little excess internal energy, whereas charge exchange by  $[CS_2]^+$  deposits greater than 1.5 eV excess energy. Electron ionization at 70 eV was chosen as a third form of ionization; it produces a  $[C_{10}H_{12}]^+$  with a broad distribution of internal energies with a mean energy that is difficult to predict.

The partial CAD spectra of ionized 2-phenyl-2-butene do change with internal energy (Fig. 4). The spectrum of the highest energy species (produced by CE with  $CS_2$ ) is quite similar to that of the 1-methylindan radical cation. A more detailed comparison can be made by inspecting the tabulated ratios of abundances of the three most diagnostic ions of  $m/z$  91, 115, and 117 (see Table 2) as a function of increasing internal energy. Examination of Table 2 reveals the

Table 2. Ion abundance ratios for the CA decompositions of the benzene-1,3-butadiene adduct and the 2-phenyl-2-butene radical cations

Benzene-1,3-butadiene adduct <sup>a</sup>		2-Phenyl-2-butene <sup>b</sup>	
91/117	115/117	91/117	115/117
0.09	0.11	0.13	0.17
0.11	0.17	—	—
—	—	0.19	0.41
0.20	0.38	—	—
—	—	0.25	0.50
0.23	0.49	—	—

<sup>a</sup> Adduct formed at pressures 0.1, 0.25, 0.5, and 0.7 Torr.

<sup>b</sup> Radical cation formed by  $CS_2$  charge exchange, 70 eV EI, and toluene charge exchange.

parallel trends exhibited by the adduct and the 2-phenyl-2-butene radical cations.

The ratios of abundances for ions of  $m/z$  91/117 and  $m/z$  115/117 from 1-methylindan radical cation are 0.08 and 0.19, respectively. These abundance ratios do not change as a function of internal energy.<sup>82</sup> Therefore, the 1-methylindan radical cation retains its structural integrity over the entire internal energy range investigated here.

Although the relative internal energy scales for the adduct and the 2-phenyl-2-butene radical cations are probably not the same, two conclusions can still be drawn from the data in Table 2. Firstly, CAD spectra of the two systems are nearly identical at their low energy extremes. Secondly, the CAD spectra of both species converge with increasing internal energy to that of a new species whose collisionally activated decompositions are similar to those of the 1-methylindan radical cation, **7**.

The CAD spectra indicate that the initially formed monocyclic adduct arises via attack at C-2 of the 1,3-

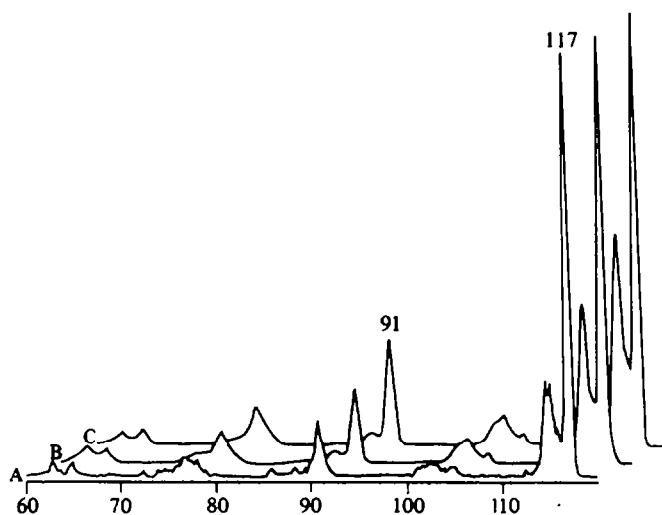


Fig. 4. Energy dependent partial CAD spectra of the 2-phenyl-2-butene radical cation. Ionization techniques: (A)  $[CS_2]^+$  CE; (B) 70 eV electron ionization; (C) [toluene] $^+$  CE.

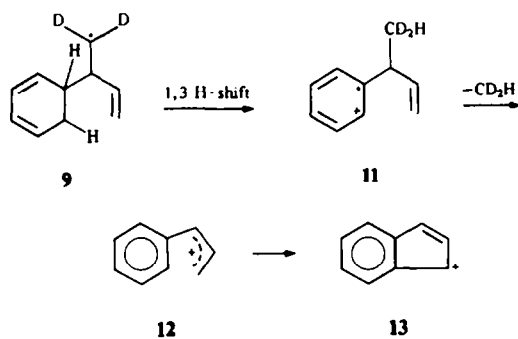
butadiene. Possibly a more reasonable point of attack would be at C-1 of the butadiene to give a monocyclic species that resembles the radical cations of model compounds 5 or 6. It was previously established that both 5 and 6 isomerize with increasing internal energy to 7.<sup>22</sup> However, these radical cations at their lowest internal energy contents differ from the low energy benzene-1,3-butadiene adduct in their production of  $C_9H_7^+$  ( $m/z$  115) (Table 1). The possibility exists that the monocyclic adduct is a mixture of 5 and/or 6 with 8. However, the only linear combinations of CAD spectra that match the spectrum of the low energy adduct are those of 8 with minor amounts of 5 or 6. In the absence of further evidence, we conclude that the initially-formed adduct predominantly resembles 8.

### Mechanism

A unifying mechanism to explain all the results involves two steps. The first step is the formation of an open-chain species followed by cyclization to a 1-methylindan radical cation species (Scheme 1). The initially-formed acyclic radical cation, 9, is not precisely 2-phenyl-2-butene but is a distonic ion which can isomerize to the 2-phenyl-2-butene ion via two 1,3-hydrogen shifts. This species, if intercepted by collisions in a high pressure system, will be sufficiently "cool" to remain as a monocyclic or ring-opened species. Its CAD spectrum is similar to that of the low internal energy ring-opened form of the 2-phenyl-2-butene radical cation; i.e. that formed via [toluene]<sup>+</sup> charge exchange (Table 1). If, however, this species is formed in the absence of stabilizing collisions (under low-pressure conditions) it will then be sufficiently energetic to undergo rapid cyclization to the bicyclic or ring-closed distonic ion, 10. The CAD spectrum of this high energy benzene-butadiene adduct is similar to that of the 1-methylindan radical cation.

The proposed cyclization of ion 9 to ion 10 is facilitated by the isolated positive charge of the initially-formed distonic species. Moreover, it is known that the favored process of high energy acyclic  $[C_{10}H_{12}]^+$  species is rapid cyclization to the 1-methylindan radical cation, which is the most thermodynamically stable  $[C_{10}H_{12}]^+$  isomer under consideration here.<sup>22</sup> Further evidence for the chemical reasonableness of the mechanism is that species containing exocyclic radical sites are known to be quite stable in both the gas and condensed phases.<sup>23,24</sup>

Both the intermediate distonic ion, 9, and the ultimate product ion, 10, show a facile loss of a methyl radical in their respective CAD spectra. Mechanistic detail about the methyl loss can be obtained by using deuterium labeling. Methyl loss from the adduct



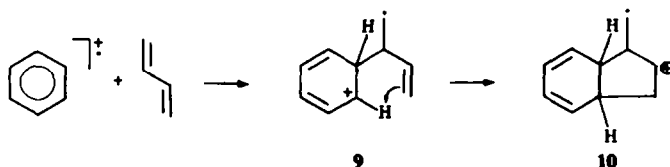
Scheme 2.

formed from the benzene radical cation and 1,3-butadiene-*d*<sub>6</sub> yielded the following results: 80% of methyl radical loss is in the form of CD<sub>2</sub>H for the low-energy, monocyclic intermediate, 9, whereas 88% of the methyl loss is CD<sub>2</sub>H for the high energy, ring-closed ultimate product ion, 10.

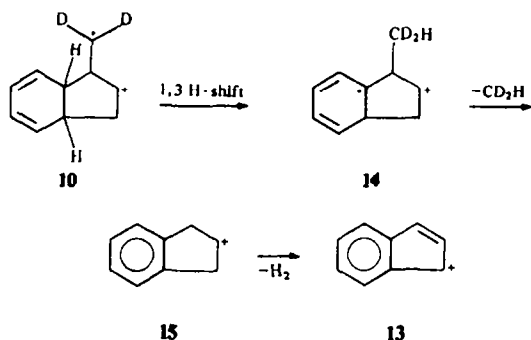
In order for the ring-opened intermediate species, 9, to undergo methyl radical loss as its most predominant fragmentation pathway, rearrangement to another species is required. The most probable rearrangement would be a 1,3-shift of a hydrogen atom from the benzene portion to the radical site on C-1 of the butadiene moiety of the adduct. Such a rearrangement would produce 11. If this rearrangement were to occur, then the rearranged species, 11, would lose CD<sub>2</sub>H (Scheme 2). The preference for loss of greater than 80% CD<sub>2</sub>H is in accord with the hypothesized mechanism proposed in Scheme 1, but this evidence does not rule out attack of the benzene radical cation on C-1 of the 1,3-butadiene.

Loss of a methyl radical from 11, leads to a phenyl-substituted allyl ion, 12, which ultimately ring closes to the indenium ion, 13. The ring closure of 12 is not surprising because it is an intramolecular analog of the bimolecular gas-phase reaction between the allyl cation and benzene, which is known to be quite exothermic.<sup>25</sup> Moreover, formation of the indenium ion is a favored process, as this ion is known to be highly thermodynamically stable.<sup>26</sup>

In order for the high energy, ring-closed adduct, 10, to undergo methyl radical loss as its most dominant fragmentation, rearrangement to another species is required. The most probable rearrangement would be a 1,3-shift of a benzene hydrogen to the exocyclic radical site of the butadiene portion of the adduct as shown in Scheme 3. This rearrangement of 10 to 14 followed by subsequent methyl loss as CD<sub>2</sub>H, is in accord with the experimental evidence that the adduct



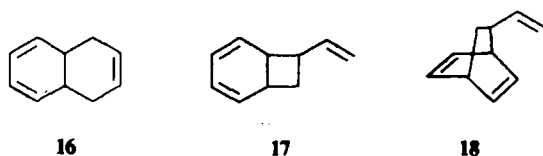
Scheme 1.



Scheme 3.

loses 88%  $\text{CD}_2\text{H}$  and 12%  $\text{CD}_3$ . Loss of methyl radical from 14 yields 15, which will lose  $\text{H}_2$  to form the indenium cation, 13. This is reasonable because of the aforementioned thermodynamic stability of the indenium ion.

An untested possibility for the reaction mechanism of the benzene radical cation and 1,3-butadiene is a radical cation analog of a [4+2] cycloaddition. The initially-formed adduct in this cycloaddition would be the bicyclo[4.4.0]deca-2,4,8-triene radical cation, 16, whose carbon skeleton is the same as that of tetralin, 1. The CAD spectrum of the adduct is considerably different from that of the tetralin radical cation (Table 1) and from that expected of the bicyclo[4.4.0]deca-2,4,8-triene radical cation. This latter substance should principally undergo a retro Diels-Alder reaction to regenerate starting materials and would not be expected to form an abundant  $\text{C}_7\text{H}_7^+$ . The benzene-1,3-butadiene adduct does not revert to starting materials to any appreciable extent, and it does decompose to form an abundant  $\text{C}_7\text{H}_7^+$  (Table 1). Other reasonable candidates for the benzene-1,3-butadiene include 7-vinyl-bicyclo[4.2.0]octa-2,4-diene, 17, and 7-vinyl-bicyclo[2.2.2]octa-2,5-diene, 18, formed via radical cation-analogs of [2+2] and [4+2] cycloadditions, respectively. However, neither of these species would be expected to undergo methyl radical loss as a major fragmentation, or to form abundant  $\text{C}_7\text{H}_7^+$  ions. It is reasonable to conclude that the benzene-1,3-butadiene adduct is not formed by any radical cation-analog of a [2+2] or [4+2] cycloaddition.

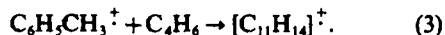


#### Results from FTMS

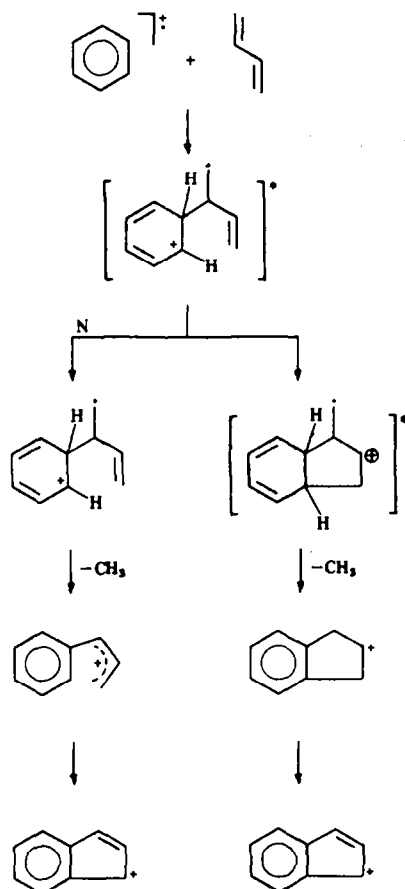
Throughout this paper we have assumed that it is the radical cation of benzene that is reacting with neutral 1,3-butadiene and not the 1,3-butadiene radical cation and neutral benzene. In order to justify this assumption, independent FTMS experiments were performed which would allow for selective formation of the radical cation of either chemical species in the presence of the other. Unfortunately, no detectable product was seen in the reaction of benzene and 1,3-

butadiene under the low pressure ( $10^{-7}$  Torr) conditions of FTMS. As a result, toluene was chosen as an example of a simple substituted benzenoid aromatic for reaction with 1,3-butadiene.

Toluene and butadiene (1:1) were admitted to the cell of the FTMS to a total pressure of  $2 \times 10^{-7}$  Torr, and the mixture was irradiated with a high power laser pulse at 266 nm. This irradiation will ionize toluene to give its radical cation; however, irradiation at 266 nm will not ionize 1,3-butadiene. Considerable  $[\text{C}_{11}\text{H}_{14}]^+$  was detected verifying that reaction between the aromatic radical cation and neutral butadiene does yield products (Eq. 3)



To verify that the 1,3-butadiene radical cation is unreactive, a pulsed-valve FTMS experiment was employed. Butadiene was admitted to the cell of the FT mass spectrometer and ionized by electron ionization to produce the radical cation. After the electron beam pulse was turned off, neutral toluene was admitted to the cell via a pulsed valve. No product was detected under a variety of experimental conditions in which the pressure of the pulsed gas and the length of time between gas pulse and detection were varied. These experiments preclude any significant contribution to product ions from the reaction of the radical cation of 1,3-butadiene and the neutral aromatic, at least at low pressure.



Scheme 4.



## CONCLUSION

The gas-phase reaction of the benzene radical cation and neutral 1,3-butadiene is a two-step cycloaddition. The first step is formation of a monocyclic radical cation, probably of the 2-phenyl-2-butene structure, and this is followed by rapid cyclization to give the bicyclic 1-methylindan radical cation (an overall reaction is depicted in Scheme 4). This system is the fifth potential radical cation cycloaddition to be investigated in this laboratory. For all systems, a cycloaddition occurs.<sup>73,74,77,80</sup> For four of the five systems, it could be proved that the cycloadditions take place as two steps.<sup>73,74,77</sup> These observations have implications for solution-phase radical cation cycloadditions.

## EXPERIMENTAL

All CAD experiments were performed on a Kratos MS50 triple analyzer mass spectrometer<sup>77</sup> which consists of a Nier-Johnson geometry high resolution mass spectrometer followed by an electrostatic analyzer (ESA). The ions formed in the source were mass selected at a mass resolution of 2500–3500 (10% valley definition) by using MS-1 (ESA-1 and the magnetic sector). The ion-molecule adduct was then activated by collisions with helium gas in the second collision cell. The second ESA is scanned to give the CAD spectrum of the resulting fragment ions. In a typical CAD experiment 20–40 scans were acquired and signal averaged by using software written in this laboratory. The precision for all peak heights reported was approximately 10% relative as determined by replicate experiments.

The CI source was operated at 280 eV with a total emission current of 500  $\mu$ A. The ion accelerating voltage was 8000 V.

Low pressure ion-molecule reactions were carried out with a Fourier transform mass spectrometer which consisted of a Nicolet Analytical Instruments FTMS-1000 console interfaced to a custom-built spectrometer.<sup>88</sup> A 5.08 cm cubic cell in a 1.2 T magnetic field was used for all experiments. The trap voltage was maintained at 1 V. Both electron ionization at low ionizing energy and multiphoton ionization (MPI) at 266 nm were used.<sup>88</sup> Typical cell pressure was  $10^{-7}$  Torr with a butadiene-benzenoid partial pressure ratio of 1:1.

The 2-phenyl-2-butene was synthesized from acetophenone using the Wittig reaction. Both *cis* and *trans* products were obtained and separated. Each of the two isomers displayed the same bimolecular chemistry and were used interchangeably. 1-Methylindan was prepared by hydrogenation of 3-methylindene at 760 Torr pressure using 10% Pd/C as catalyst and ethyl acetate as solvent. All synthetic samples were purified by using preparative GC on a 12 ft column packed with 10% SE30 on 80/100 mesh Chromosorb W.

All other hydrocarbons were obtained from commercial sources. Their purity was checked by using mass spectrometry and were used without further purification.

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