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Reaction of the Benzene Radical Cation with Neutral Cyclopropane and Cyclobutane

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Abstract: The adduct ions formed in the gas-phase ion–molecule reactions of the benzene radical cation with neutral cyclopropane and cyclobutane were investigated by using tandem mass spectrometry (MS/MS) and Fourier transform mass spectrometry. The adduct ions exist initially as distonic radical cations. The distonic benzene/cyclopropane radical cation adduct isomerizes via competitive free-radical-driven processes to the *n*-propylbenzene and 8,9-dihydroindan radical cations. The initially formed distonic benzene/cyclobutane radical cation adduct undergoes a more complex isomerization to give probably three adducts: *n*-butylbenzene, 9,10-dihydrotetralin, and 5-(3-butenyl)-1,3-cyclohexadiene radical cations. The results establish further the unusual reactivity of the benzene radical cation with respect to neutral benzene and illustrate that distonic radical cations possess an interesting duality that is based on both free-radical and carbenium ion properties.

The elucidation of the chemical properties of reactive intermediates such as free radicals, carbanions, and carbocations (carbonium and carbenium ions) has been a long-term goal in chemistry. The bimolecular reactivity and unimolecular isomerizations of these reactive intermediates are generally well-characterized.

The characterization of the properties of radical ions (radical cations and radical anions) has historically drawn less attention. Recent developments of methods for generating and observing these transient reactive intermediates, however, have made radical ion chemistry an active area of research. Advances in experimental methods such as the capability of studying radical cations in inert matrices and the further development of spin-trapping and various in situ EPR and NMR techniques have greatly facilitated the study of condensed-phase radical ions. The growing interest in the chemistry of radical ions can be gauged by the many and varied publications appearing on the subject. Some of this research has been highlighted in a recent symposium in print.[1]

The understanding of gas-phase radical cation chemistry has also grown in proportion to the development of mass spectrometric instrumentation. High-pressure (0.1–1.0 Torr) ionization sources, such as those used in conventional chemical ionization[2a] mass spectrometers, are being utilized for conducting gas-phase bimolecular reactions of radical cations and neutral molecules. Complementary studies can be done at lower pressures ($<10^{-6}$ Torr) on ion cyclotron resonance and Fourier transform mass spectrometers.[2b] Structural elucidation of the product ions has been greatly facilitated by the evolution of mass spectrometric techniques such as metastable ion[3-5] and kinetic energy release measurements[5-7] and collisional activation.[8-10] Of particular interest to us are those otherwise inert systems, such as that of benzene and cyclopropane or cyclobutane that can be turned reactive by ionizing one of the partners. In particular, we are endeavoring to determine the reactivities of these ionized species by their gas-phase reactions with appropriate neutral molecules.[11-16]

Another area of interest is distonic radical cations. These are species whose charge and radical sites reside in orbitals that are not in conjugation (i.e., charge-radical site-separate radical ions[17-20]). Distonic radical cations cannot be formed via direct ionization; rather, they must be formed by isomerization[21,22] unimolecular dissociation,[23] or bimolecular reaction.[13-15,24-28] The majority of work on distonic radical cations has been conducted on ions in the gas phase although there are considerable studies of solution species. Individual citings would be too numerous to report here, and the reader is directed to an excellent review of the gas- and condensed-phase research on distonic ions.[19]

The principal aims of this study are to investigate if gas-phase reactions take place between the benzene radical cation and cyclic alkanes and, if so, to characterize the adducts. These reactions are of interest because they may be a means of producing distonic hydrocarbon radical cations (whose properties are not well-known). In addition, these reactions may serve to further the understanding

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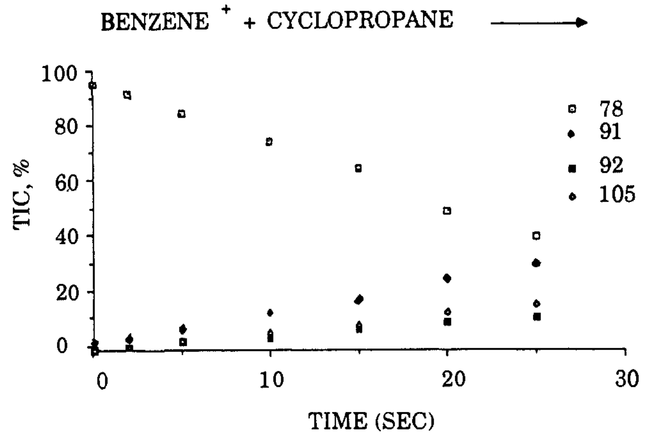


Figure 1. Kinetic plot for the reaction of the benzene radical cation with neutral cyclopropane. Data taken by FTMS. Experimental conditions are given in the Experimental Section.

of the synthetic utility of radical ion chemistry, a subject of some current interest.[1]

Results and Discussion

When the reactions in an ionized mixture of benzene and either cyclopropane or cyclobutane are conducted in the high-pressure source of a tandem mass spectrometer, adduct ion formation takes place. The following questions arise: Which of the two species (the benzene or the cycloalkane) is reacting as a radical cation? What are the relative reactivities of the various neutral reagents, and what is the nature of the bonding in the adduct ions? Finally, what are the structures of reaction products and the overall mechanism for the reactions of the benzene radical cation and cyclopropane or cyclobutane? These questions will be addressed in turn.

Identification of Reacting Species. The experimental approach chosen to address this question incorporates the use of a pulse-valve inlet system on a Fourier transform mass spectrometer.[28] This methodology allows for the formation and storage of an ion followed by subsequent addition of a neutral reagent gas. Benzene was admitted to the cell of the FT mass spectrometer and was ionized by a pulse of electrons to give its radical cation. The neutral cycloalkane was admitted to the cell via a pulsed valve, the ion and neutral were allowed to react, and a mass spectrum of the product ion was obtained. In a second set of experiments the cycloalkane was ionized and neutral benzene was admitted via a pulse valve. Only in the former experiment were the product ions observed. These experiments preclude any significant contribution to product ions from the reaction of the cycloalkane radical cation with neutral benzene, at least at low pressure ($\sim 10^{-7}$ Torr).

It is not surprising that the benzene radical cation is the reactant. The ionization potential of benzene is 9.24 eV, whereas those of cyclopropane, cyclobutane, and cyclopentane are 10.3, 10.7, and 10.9 eV, respectively. Moreover, it was previously determined that it is the benzene radical cation that is the reactive partner in the ion–molecule reaction of benzene and 1,3-butadiene.[14]

A second FTMS experiment showed that the reaction is slow ($k \approx 1 \times 10^{-11}$ cm^3 s^{-1}/molecule). A 1:1 mixture of benzene and cyclopropane was ionized at ca. 10 eV (to preclude significant ionization of cyclopropane) and allowed to react as a function of time (see Figure 1). The benzene radical cation reacts slowly to form principally $C_7H_7^+$, $C_7H_8^+$, and $C_8H_9^+$.

Because benzene is the reactive radical cation in these reactions, it is necessary that its structure be established in the gas phase. This was done in previous studies[29] in which the gas-phase benzene radical cation was shown to have the same carbon skeletal structure as its neutral precursor.

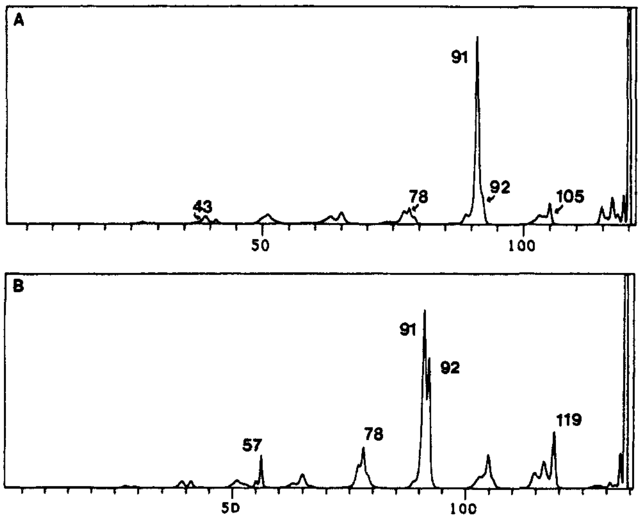
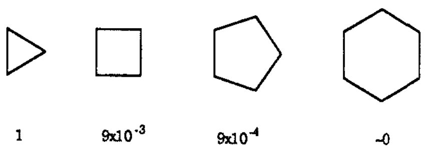


Figure 2. (A) Partial CAD spectra of the adduct formed in the reaction of the benzene radical cation with neutral cyclopropane. (B) Partial CAD spectra of the adduct formed in the reaction of the benzene radical cation with neutral cyclobutane. Experimental conditions are given in the Experimental Section.

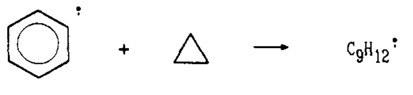
Scheme I



Adduct Ion Formation. The cyclic alkanes chosen for reaction with the benzene radical cation are cyclopropane, cyclobutane, cyclopentane, and cyclohexane. The relative reactivity of the benzene radical cation toward these cyclic alkanes was measured by conducting the reaction in the high-pressure source of a tandem mass spectrometer and determining the amount of adduct ion formed relative to the amount of unreacted benzene radical cation at constant cycloalkane partial pressure (see Experimental Section). Detectable adduct formation takes place for cyclopropane, cyclobutane, and cyclopentane. For cyclohexane, no ion–molecule adduct was observed. The following relative reactivity order is obtained.

The measurement tool is slightly flawed because the concentrations of the adducts are a function of their rates of formation and fragmentation. Nevertheless, the differences are so large that semiquantitative conclusions can be drawn. Because the radical cation acts as an electrophile in these reactions, the propensity toward adduct formation should increase with increasing nucleophilic character of the cyclic alkane. Although none of the cyclic alkanes are nucleophilic on an absolute basis, cyclopropane is considerably more nucleophilic than the higher cycloalkanes because of its special bent bonds.[30,31]

Bonding in Adduct Ions. The collision-activated decomposition (CAD) spectra of the adduct ions formed in the reaction of the benzene radical cation with neutral cyclopropane and cyclobutane (see Figure 2, A and B, respectively) illustrate that there is covalent bonding between reactants in the collisionally stabilized adducts.



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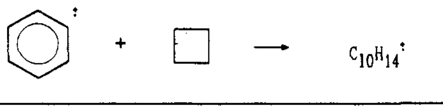

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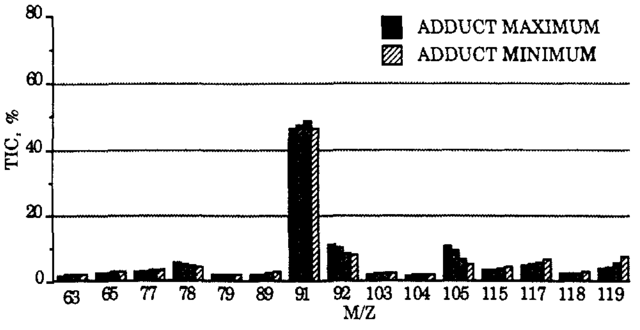
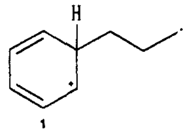


Figure 3. Histogram representing the partial CAD spectra of the adduct formed in the reaction of the benzene radical cation with neutral cyclopropane as a function of internal energy.

Gas-phase bimolecular adducts may exist as loosely bound complexes. Complexes of this nature are not expected to undergo rearrangements, and upon collisional activation they should return to starting materials. The adduct ions formed in these reactions, however, undergo multiple dissociation processes upon collisional activation. Further evidence for covalency is the fact that the metastable dissociations of these adducts resemble the CA dissociations and also do not include any significant return to starting materials.

Adduct Ion Structure. It is likely that the neutral cyclopropane ring opens when forming a covalently bonded adduct with the electrophilic benzene radical cation. Neutral cyclopropane ring does open upon attack by free radicals such as chlorine[32,33] bromine,[32,33] with carbenium ions such as the free phenylium ion,[34] and with radical cations such as the cyclopropane radical cation itself.[35] The latter species is likely to be the distonic trimethylene radical cation[27,28] although there is some disagreement on that conclusion.[36]

The initially formed adduct in the reaction with the benzene radical cation is hypothesized to be the distonic radical cation **1**.



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Such adduct formation is analogous to the distonic radical cations that form in the reactions of the benzene radical cation with 1,3-butadiene.[14] The distonic radical cation **1** may be reactive and isomerize during the 10^{-5} s between its initial formation and its detection.

A test of the hypothesis is the elucidation of the structure of the adduct. The CAD spectra of adducts were obtained as a function of internal energy, utilizing a method that has been employed successfully in previous studies.[11-14] These spectra were compared with those of model or reference compounds.

The gas-phase reactions of the benzene radical cation with neutral cyclopropane and cyclobutane were conducted in 1:1 molar mixtures in the high-pressure source of a tandem mass spectrometer. In successive experiments, the partial pressure of a third body, CS_2, was increased from zero to 40 times those of the reacting species such that the total maximum pressure was ca. 0.2 Torr. By varying the pressure of CS_2, the degree of collisional stabilization of reactants and adduct is changed.

The rationale for conducting the reactions under the above conditions is to make possible the study of gas-phase bimolecular adducts of varied and controllable amounts of internal energy. A histogram showing the relative abundances of key ions in the CAD spectra of the benzene radical cation/cyclopropane adduct as a function of internal energy (Figure 3) shows little change in going from the most to the least stabilized adduct. Therefore, the adduct must possess a stable structure.

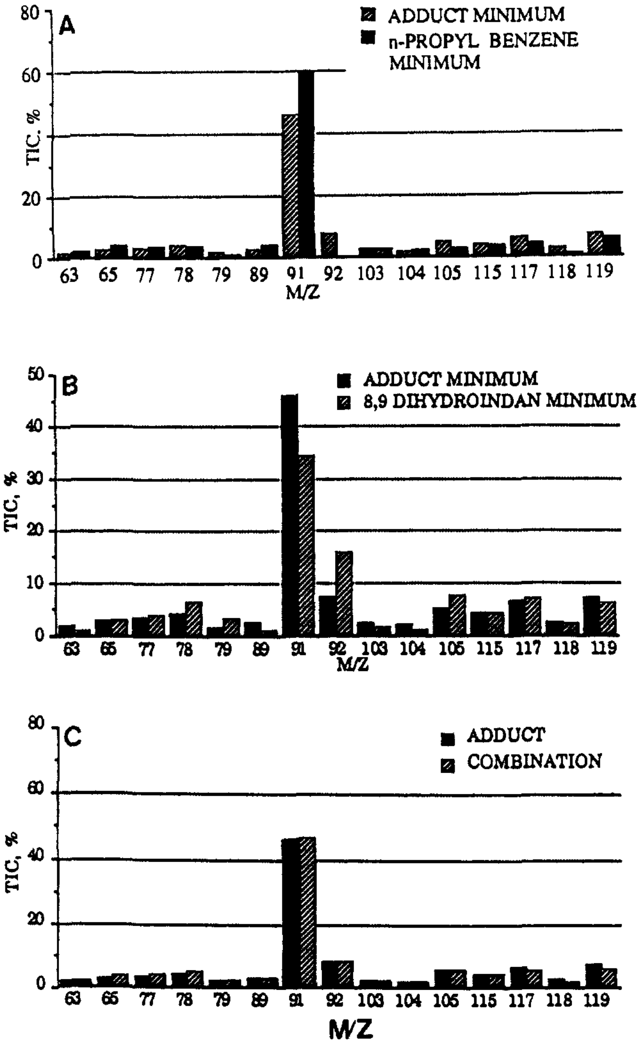
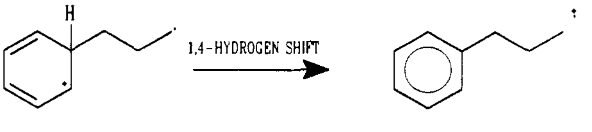


Figure 4. Histograms for comparing the partial CAD spectra of the lowest energy benzene/cyclopropane adduct with (A) the partial CAD spectra of the *n*-propylbenzene radical cation, (B) the partial CAD spectra of the 8,9-dihydroindan radical cation, and (C) a linear combination corresponding to a 48% contribution from the *n*-propylbenzene CAD spectra and 52% contribution from the 8,9-dihydroindan CAD spectra.

The actual structure or structures of the rearranged adduct can be determined from comparative CAD studies. A logical stable adduct is the *n*-propylbenzene radical cation, formed by a 1,4-hydrogen shift in **1** (eq 3). Such shifts are well-known.



(3)

A histogram comparing the predominant ions from the dissociation of the adduct with those for the *n*-propylbenzene radical cation is clear evidence that the two radical ions are different (Figure 4A). The major difference is that the adduct yields a fragment ion of *m*/*z* 92 (arising from the loss of C_2H_4), whereas this process is not detectable for the *n*-propylbenzene radical cation. In addition, the *n*-propylbenzene radical cation fragments to $C_7H_7^+$ of *m*/*z* 91 to a much greater extent than does the adduct (68% of the total ion current compared to 46%). These differences are ascribed to structural rather than internal energy factors because the CAD spectrum of the adduct is independent of the extent of collisional stabilization.

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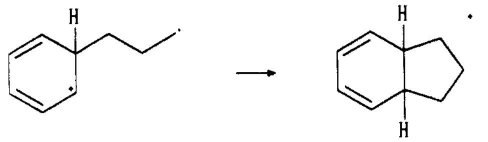
Table I. Partial CAD Spectra of Various C_9H_{12} Radical Cation Model Compounds

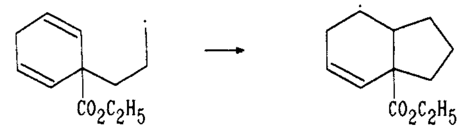
compd	119	118	117	115	105	104	103	92	91	89	79	78	77	65
sec-propylbenzene	0.9	0.5	0.9	0.9	69.5	1.2	6.7	0	6.7	0.3	0	4.0	8.9	0.9
o-ethyltoluene	12.0	4.7	2.5	1.5	54.9	3.4	5.1	0	6.4	0.8	0.4	2.1	4.2	1.2

Another possible reaction of the distonic ion **1** is a 1,5-cyclization akin to the well-known 5-hexenyl radical ring closure (eq 4).



(4)

Beckwith and co-workers[37] have long studied 5-hexenyl and related ring closure reactions and showed that such processes are quite facile. In fact, an analogy to the radical cation chemistry is given in eq 5. This ring closure occurs with a rate constant of approximately 10^5 s^{-1}.[38] Geometric constraints that exist in the transition state for intramolecular radical ring closures have been pointed to as the reason for a 1,5-hexenyl radical ring closure rather than ring closing to the thermodynamically favored six-membered-ring system.[37]



(5)

A histogram comparing the predominant ions for the dissociation of the benzene radical cation/cyclopropane adduct and those from the model 8,9-dihydroindan radical cation also illustrates that the two species are not identical (Figure 4B). The major difference is that the 8,9-dihydroindan radical cation dissociates to $C_7H_7^+$ of m/z 91 to a much less extent that does the adduct. In addition, the model loses C_2H_4 (to yield an ion of m/z 92) to a greater extent than does the adduct ion. The adduct ion, **1**, does not undergo exclusive 1,5-cyclization to the radical cation of 8,9-dihydroindan.

The benzene radical cation/cyclopropane adduct ion has properties that are intermediate between those of *n*-propylbenzene and 8,9-dihydroindan radical cations. Thus, the adduct may be comprised of two structures, and a linear combination of the two model compounds' spectra may reproduce that of **1**. To test this premise, a spreadsheet with an iterative function was used for calculating linear combinations of CAD spectra. The CAD spectra used for the linear combinations were those of the lowest internal energy model and adduct radical ions (i.e., those of the *n*-propylbenzene and 8,9-dihydroindan radical cations formed via charge exchange of the toluene radical cation with the appropriate neutral and the benzene radical cation/cyclopropane adduct formed in the presence of a 40-fold excess of CS_2).

A linear combination of CAD spectra that corresponds to a 55% contribution from the *n*-propylbenzene radical cation and a 45% contribution from the 8,9-dihydroindan radical cation matches that of the benzene radical cation/cyclopropane adduct (Figure 4C). This excellent match is evidence in support of the proposal that the initially formed distonic ion adduct **1** competitively undergoes a 1,4-hydrogen shift and 1,5-cyclization, to yield the *n*-propylbenzene and the 8,9-dihydroindan radical cations, respectively. The rates of formation of the two intermediates may not be 1:1 because the adduct ion abundances are a function of both the rates of formation and decomposition of its adducts. Nevertheless, the two processes are clearly in competition.

Other C_9H_{12} radical cations were considered as possible models for the benzene/cyclopropane adduct ion, and hence CAD spectra of the radical cation of isopropylbenzene and *o*-ethyltoluene were obtained (see Table I). These data illustrate two points. First, the isopropylbenzene or *o*-ethyltoluene radical cations are not reasonable models for the benzene/cyclopropane radical cation adduct, either on a stand-alone basis or as contributing species. Second, these C_9H_{12} isomers give distinctive CAD mass spectra, and that builds confidence in the efficacy of the methodology for determining ion structure.

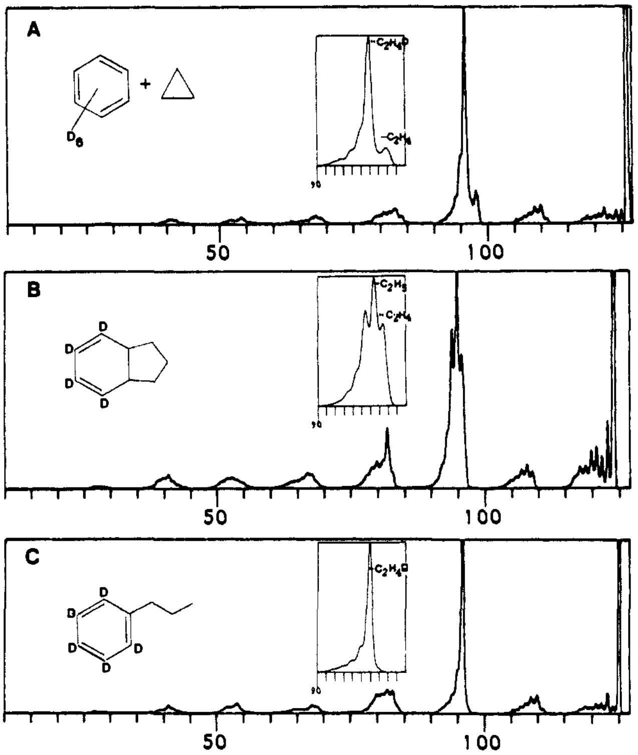


Figure 5. (A) Partial CAD spectra of the adduct formed in the reaction of the benzene-d_6 radical cation with neutral cyclopropane. (B) Partial CAD spectrum of the 8,9-dihydroindan-*2,3,4,5*-d_4 radical cation. (C) Partial CAD spectrum of the *n*-propylbenzene-d_5 radical cation.

It may be argued that the CAD spectra represent dissociations of the initial unrearranged adduct, radical cation **1**. Earlier in the discussion, we hypothesized that the adduct structures must be stable and relatively immune to isomerization because the CAD spectra of the adduct do not change significantly as a function of internal energy. Both the *n*-propylbenzene and 8,9-dihydroindan radical cations certainly fit that expectation. We may ask if the latter two radical cations are more stable than the distonic radical ion intermediate and if the intermediate is transient. On the other hand, the distonic ion may be more stable than the two reference ions, and the observed CAD spectra are of the distonic ion. The *n*-propylbenzene/8,9-dihydroindan radical cations are then transient species formed enroute to fragments.

The CAD spectra of the *n*-propylbenzene-d_5 and 8,9-dihydroindan-*2,3,4,5*-d_4 radical cations provide evidence in favor of the former possibility. A number of the losses (e.g., of C_2H_4, $C_2H_5^•$, $H^•$, and H_2) from each of the two ion species occur with considerable H/D scrambling (Figure 5). Although we have pictured the adduct as a σ-complex (**1**), this species can equilibrate with a π-complex form (**2**) (eq 6). Partial equilibration of these two

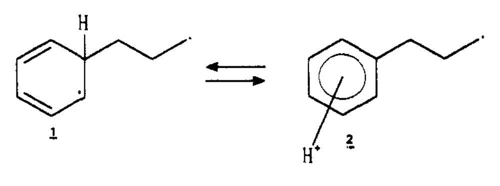


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Table II. Heats of Formation of $[C_9H_{12}]^{\bullet+}$, $[C_7H_8]^{\bullet+}$, and $[C_7H_7]^+$ Ions

ion/neutral	IE, eV	AE, eV	ΔH_f[ion], kJ mol^{-1}	ΔH_f[neutral], kJ mol^{-1}
C_6H_6			975.8^a	
C_3H_6				53.3^a
1,4-dihydroindan	8.54^b		819^b	
propylbenzene	8.75^b		849^b	
C_7H_7^{c}		9.88^b	849^a	
C_7H_7^{d}		10.17^b	849^a	
C_7H_8^{d}		11.17^b	934^a	
C_2H_5				108^a
C_2H_4				52^a

[a] Reference 72. [b] This work. [c] Generated from propylbenzene. [d] Generated from 1,4-dihydroindan.

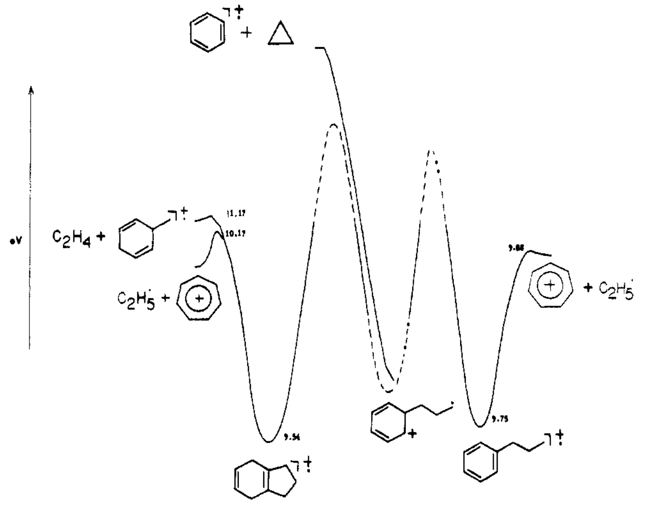


Figure 6. Schematic potential energy surface for the reaction of benzene radical cation with cyclopropane, showing the threshold energies for losses of C_2H_4 and $C_2H_5^{\bullet}$. The energy barriers for interconversion of the distonic intermediate **1** to propylbenzene and 1,4-dihydroindan are estimated.

complexes is an explanation for the H/D scrambling observed for the model compounds *n*-propylbenzene-d_5 and 8,9-dihydroindan-*2,3,4,5*-d_4. If **1** is less stable, however, then the pattern for H/D exchange of the adduct should be a composite of those of the reference compounds, provided of course the patterns are different. If **1** is more stable, the H/D exchange pattern of the reference ions should be identical and indistinguishable from that of **1**. Because the pattern of H/D exchange is composite, **1** must be transient and it undergoes competitive rearrangement to the radical cations of *n*-propylbenzene and 8,9-dihydroindan.

Potential Energy Surface. To define a potential energy surface, the appearance energies (AE) for the metastable fragment ion $C_7H_7^+$ from propylbenzene and for $C_7H_8^{\bullet+}$ and $C_7H_7^+$ from 1,4-dihydroindan (a closely related isomer of 8,9-dihydroindan) together with the ionization energies (IE) of the parent species were measured (See Table II). Heats of formation of the ions were calculated from the relationships IE = ΔH_f[ion] − ΔH_f[neutral], and AE = ΔH_f[product ion] + ΔH_f[neutral fragment] − ΔH_f[precursor].

The metastable ion peaks for the losses of C_2H_4 and $C_2H_5^{\bullet}$ are of the same Gaussian type. Energy releases from the half-height widths are 53 meV for the loss of $C_2H_5^{\bullet}$ from *n*-propylbenzene and 89 and 140 meV for the losses of C_2H_4 and $C_2H_5^{\bullet}$, respectively, from 1,4-dihydroindan. The small energy releases suggest that the reactions involve little reverse activation energy.

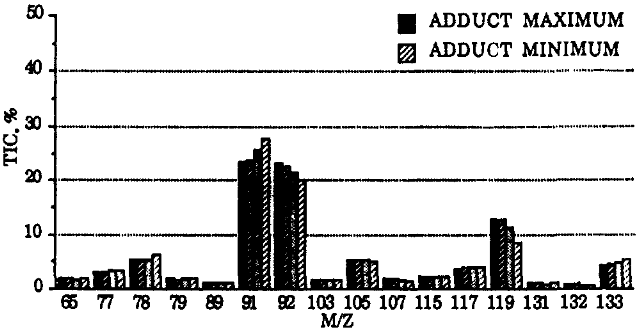
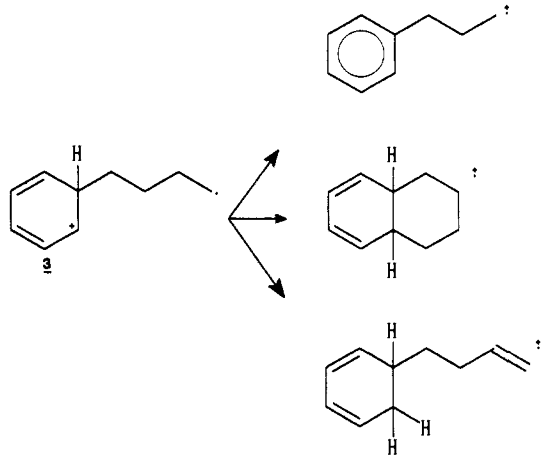


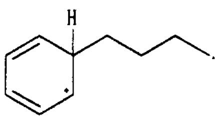
Figure 7. Histogram representing the partial CAD spectra of the adduct formed in the reaction of the benzene radical cation with neutral cyclobutane as a function of internal energy.

Scheme II



The thermochemical results are collected in a schematic potential energy surface (see Figure 6), which shows the threshold energies for the losses of $C_2H_5^{\bullet}$ and C_2H_4. The lack of equilibration between the *n*-propylbenzene and 1,4-dihydroindan radical cations requires that the magnitude of the potential barriers for rearrangement of the distonic intermediate to either *n*-propylbenzene or 1,4-dihydroindan radical cations is higher than the barriers for fragmentation of the rearranged species. Because the distonic intermediate rearranges with a slight predominance to the *n*-propylbenzene radical ion, the energy barrier for this rearrangement is lower than that for rearrangement to 1,4-dihydroindan. Moreover, the heat of formation of the distonic radical cation must also be higher than the corresponding heats of formation of either the *n*-propylbenzene or 1,4-dihydroindan radical cations, i.e. >850 kJ mol^{-1}.

Reaction with Cyclobutane. The CAD spectra of the benzene/cyclobutane adduct as a function of internal energy illustrates that this species is also stable (Figure 7). By analogy with the benzene radical cation/cyclopropane adduct, it is resonable that the initially formed adduct ion possesses the distonic structure **3**.



3

Distonic ion **3** may undergo any of three possible rearrangements. An intramolecular 1,5-hydrogen shift yields the *n*-butylbenzene radical cation, a 6-heptenyl (1,6) radical ring closure affords 9,10-dihydrotetralin, and a 1,5-hydride shift gives 5-(3-butenyl)-1,3-cyclohexadiene (Scheme II).

To test whether these products are formed, comparisons between the adduct ion's CAD spectrum and those of the model compounds *n*-butylbenzene, 9,10-dihydrotetralin, and 1-(3-butenyl)-1,4-cyclohexadiene [a closely related isomer of 5-(3-butenyl)-1,3-cyclohexadiene] were made (Figure 8). None of the spectra of the reference compounds match that of the stabilized adduct. Thus, the adduct cannot have a single structure that corresponds exclusively to any one of the reference compounds. A mixture of structures is again implicated.

Table III. Partial CAD Spectra of Various $C_{10}H_{14}$ Radical Cation Model Compounds

	m/z											
compd	133	119	117	115	105	103	92	91	89	79	78	77
sec-butylbenzene	2.2	2.2	1.5	1.5	74.3	3.7	2.1	7.4	0.7	1.5	1.1	3.0
isobutylbenzene	5.3	4.4	3.6	3.6	0.9	0.5	25.8	49.3	3.6	0.4	1.3	1.8
2-methyl-2-phenylpropane	2.8	70.4	4.2	2.8	1.4	3.5	0	7.7	1.4	2.1	2.8	0.7
1,4-dihydro-8-methylindan	3.9	20.6	4.3	8.5	5.3	1.7	23.1	18.8	1.0	3.0	3.2	3.9

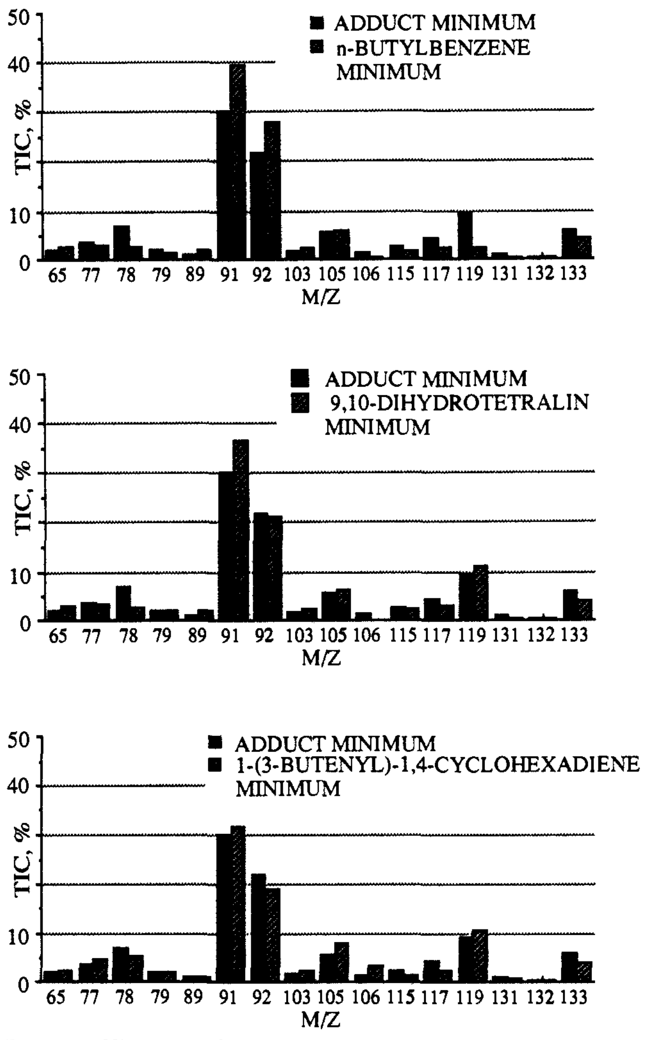


Figure 8. Histograms for comparing the partial CAD spectra of the lowest energy benzene/cyclobutane adduct with (A) the partial CAD spectra of the *n*-butylbenzene radical cation, (B) the partial CAD spectra of the 9,10-dihydrotetralin radical cation, and (C) the partial CAD spectra of the 1-(3-butenyl)-1,4-cyclohexadiene radical cation.

The best match to the benzene/cyclobutane adduct ion spectrum is a linear combination of model compound CAD spectra of the 9,10-dihydrotetralin (ca. 20%) and 1-(3-butenyl)-1,4-cyclohexadiene (ca. 75%) radical cations, with a minor contribution from the *n*-butylbenzene radical cation (ca. 5%) (see Figure 9). We do not place high confidence in the exact composition. Other linear combinations also match nearly as well because the CAD spectra of 9,10-dihydrotetralin and 1-(3-butenyl)-1,4-cyclohexadiene are quite similar. Nevertheless, all of the linear combinations that do fit well correspond to a major contribution from some combination of these two species, and a minor contribution from *n*-butylbenzene. The only fragment ions that do not match within ±5% are the ions of *m*/*z* 117 and 133, both of which are quite close to the 5% limit.

Other possible models for the benzene/cyclobutane radical cation adduct are those of *sec*-butylbenzene, isobutylbenzene, *tert*-butylbenzene, and dihydromethylindan. These ions dissociate quite differently than does the adduct and are precluded (Table III).

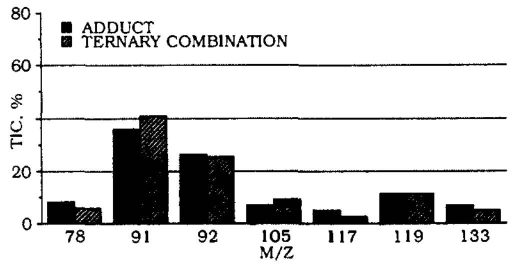


Figure 9. Linear combination corresponding to a 4:18:78 mixture of the partial CAD spectra of the *n*-butylbenzene, 9,10-dihydrotetralin, and 1-(3-butenyl)-1,4-cyclohexadiene radical cations compared to the lowest energy benzene/cyclobutane adduct ion.

Recently, Baer and co-workers[39] determined the internal energy dependence of the ratio of *m*/*z* 91 to 92 daughter ions for the *n*-butylbenzene radical cation. It was noted that as the internal energy of the *n*-butylbenzene radical cation was increased the abundance ratio of *m*/*z* 91/92 also increased. Furthermore, from these data, it is possible to determine the internal energy content of the butylbenzene ion undergoing fragmentation.

The CAD spectra reported here were acquired for ions of minimized internal energy. This was accomplished by using charge exchange with the toluene radical cation as the ionization method. Therefore, by using the *m*/*z* 91/92 abundance ratio, we can approximate the internal energy uptake of the *n*-butylbenzene radical cation as it undergoes collisional activation. The *m*/*z* 91/92 daughter ion ratio was 1.3, and thus the *n*-butylbenzene ion has accumulated on average 4.3 eV of internal energy prior to dissociation. Most of this energy is acquired during the collisional process, but an unknown small fraction is carried over from the ionization process itself.

Conclusion

The benzene radical cation is surprisingly reactive with neutral cyclopropane. The reaction proceeds via distonic radical cation **1** to yield the radical cations of *n*-propylbenzene and 8,9-dihydroindan by 1,4-hydrogen shift and a 1,5-cyclization, respectively. The benzene radical cation also reacts with neutral cyclobutane via distonic ion **3** to yield a combination of the *n*-butylbenzene, 9,10-dihydrotetralin, and 5-(3-butenyl)-1,3-cyclohexadiene radical cations. The rearrangements that lead to these species are a 1,5-hydrogen shift, a 1,6-cyclization, and a 1,5-hydride shift, respectively.

The propensity of the benzene radical cation/cycloalkane adducts to undergo competitive radical- and cation-based isomerization pathways illustrates a property that may be general for distonic radical cations. These species have the ability to express chemistry that is either free radical based or cation based. The intramolecular isomerizations of distonic radical cations **1** and **3** are identical with those observed for well-known free radical systems. It may be hypothesized that kinetic control dictates that free radical based chemistry rather than carbenium ion chemistry occurs in these intramolecular isomerizations. Further study on other systems, however, will be necessary to characterize more fully these kinetic arguments.

Experimental Section

Methods. All CAD experiments were performed on a Kratos MS 50 triple-analyzer mass spectrometer[39,40] that consists of a Nier-Johnson

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[39] Baer, T.; Dutuit, O.; Mestdagh, H.; Rolando, C. *J. Phys. Chem.* **1988**, *92*, 5674.

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 or the reference compound radical cations were then activated by collisions with helium gas in the second collision cell. The pressure of helium in the second collision cell was sufficient to produce a decrease in the main beam signal of 50%. The second ESA is scanned to give the CAD spectrum of the resulting fragment loss. 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 is approximately 5% relative as determined by replicate experiments.

The electron beam was operated at 280 eV with total emission current of 500 μA. The ion accelerating voltage was 8 kV.

Low-pressure ion–molecule reactions were carried out with a Fourier transform mass spectrometer, which consists of a Nicolet Analytical Instruments FTMS-1000 console interfaced to a custom-built spectrometer.[41] 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. A typical cell pressure was 1×10^{-7} Torr with a cycloalkane:benzene partial pressure ratio of 1:1.

The relative reactivity of the benzene radical cation was measured with the Kratos MS-50 triple analyzer. The reactions were conducted in a high-pressure chemical ionization (CI) source. The partial pressure ratio of benzene:cycloalkane in each reaction was constant at 1:1 with a total source pressure of ca. 0.01 Torr. All other source conditions (temperature, tuning, etc.) were identical and constant for each of the reactions. The composition of (or abundance of) product ions formed in the reactions, as well as any unreacted benzene radical cation, was measured in a peak matching mode by using an analogue output of the detector preamplifier.

Ionic Heats of Formation. The electron ionization and metastable-peak appearance energies were measured on a Kratos MS-50, double-focusing mass spectrometer. Ionizing-electron energies ranged from threshold to 70 eV, the source temperature was 150 °C in all cases, and the accelerating voltage was 8 keV. The metastable-peak appearance energies were measured by the method described by Burgers and Holmes.[42]

Synthesis. 8,9-Dihydroindan and 9,10-dihydrotetralin were prepared by the method of Dauben and Kellog.[43] 1-(3-Butenyl)-1,4-cyclohexadiene was prepared by the method of Birch and Mukhergee.[44] Research grade cyclopropane and cyclobutane (Matheson) were used without further purification. All other chemicals were obtained from commercial sources and used without further purification.

8,9-Dihydroindan-*2,3,4,5*-d_4 was prepared as follows by using a modification of the method of Dauben and Kellog.[43]

***endo*-10,10-Dimethoxy-1,7,8,9-tetrachlorotricyclo[5.2.1.0^{2,6}]dec-8-ene.** A mixture of cyclopentene (15.15 g, 0.22 mol) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (Aldrich) (50 g, 0.19 mol) was heated in a 500-mL bomb to 200 °C in 15 min and maintained at this temperature for 1 h. After cooling (12 h) the blackish product mixture was distilled to yield a colorless viscous liquid which was crystallized from 95% ethanol to give the tetrachloro adduct as a white crystalline solid, mp 86.0–87.5 °C (41.59 g, 66%). Anal. Found: $M^{\bullet+}$, 331.9725. Calculated for $C_{12}H_{14}O_2{}^{35}Cl_3{}^{37}Cl$: $M^{\bullet+}$ 331.9718. Mass spectrum (70 eV), *m/z* 330, 332, 334 ($M^{\bullet+}$, 0.4, 0.5, and 0.3%), 295, 297, 299 (M – $Cl^{\bullet}$, 100, 98.5, and 32.7%).

***endo*-10,10-Dimethoxytricyclo[5.2.1.0^{2,6}]dec-8-ene-*1,7,8,9*-d_4.** To a stirred, gently refluxing mixture of *tert*-butyl alcohol-*O-d* (45.53 g, 0.61 mol) and sodium pieces (39.80 g, 1.73 mol) in anhydrous tetrahydrofuran (250 mL) was added a solution of *endo*-10,10-dimethoxy-1,7,8,9-tetrachlorotricyclo[5.2.1.0^{2,6}]dec-8-ene (37.81 g, 0.11 mol) in anhydrous tetrahydrofuran (100 mL) over a period of 2.5 h. The mixture was heated under reflux for an additional 12 h. Excess sodium was removed by filtration through Celite. The filtrate was poured into water (500 mL) and extracted with diethyl ether (3 × 100 mL). The organic extract was washed with water (200 mL) and dried ($MgSO_4$), and the solvent was evaporated to give a dark brown oil. Vacuum distillation of the crude product gave *endo*-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]dec-8-ene-*1,7,8,9*-d_4 as a colorless oil, bp 58–60 °C (0.1 mm) (13.24 g, 61%). Anal. Found: $M^{\bullet+}$, 198.1559. Calcd for $C_{12}H_{14}D_4O_2$: $M^{\bullet+}$, 198.1558; d_4, 74%; d_3, 25%; d_2, 1%. Mass spectrum (70 eV), *m/z* 198 ($M^{\bullet+}$, 68%), 183 (M – $CH_3^{\bullet}$, 21%), 167 (M – $CH_3O^{\bullet}$, 44%), 151 (M – CH_3OH – $CH_3^{\bullet}$, 47%), 123 (M – CH_3OH – CO – $CH_3^{\bullet}$, 100%).

***endo*-Tricyclo[5.2.1.0^{2,6}]dec-8-en-10-one-*1,7,8,9*-d_4.** A mixture of *endo*-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]dec-8-ene-*1,7,8,9*-d_4 (10 g, 50.5 mmol) and 10% sulfuric acid solution (100 mL) was sonicated for 12 h and extracted with pentane (3 × 50 mL). The combined pentane extracts were washed with 5% sodium hydrogen carbonate (2 × 50 mL) and water (50 mL) and dried ($MgSO_4$), and the solvent was evaporated to give a semicrystalline residue. The residue was crystallized from pentane (–15 °C) to yield *endo*-tricyclo[5.2.1.0^{2,6}]dec-8-ene-*1,7,8,9*-d_4 as colorless needles (4.01 g, 52%). Anal. Found: $M^{\bullet+}$ – CO, 124.1186. Calcd for $C_9H_8D_4$: $M^{\bullet+}$ – CO, 124.1190. Mass spectrum (70 eV), *m/z* 124 ($M^{\bullet+}$ – CO, 72%), 96 ($M^{\bullet+}$ – CO – C_2H_4, 71%), 95 (M – CO – $C_2H_5^{\bullet}$, 100%).

Bicyclo[4.3.0]nona-2,4-diene-*2,3,4,5*-d_4 (8,9-Dihydroindan-*2,3,4,5*-d_4). A neat sample of *endo*-tricyclo[5.2.1.0^{2,6}]dec-8-ene-*1,7,8,9*-d_4 (1.00 g, 6.6 mmol) was heated in a nitrogen atmosphere at 190 °C until the evolution of carbon monoxide had ceased. The residue was distilled to yield bicyclo[4.3.0]nona-2,4-diene-*2,3,4,5*-d_4 as a colorless oil, bp 155–158 °C (0.63 g, 77%). Anal. Found: $M^{\bullet+}$, 124.1190. Calcd for $C_9H_8D_4$: $M^{\bullet+}$, 124.1190.

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