The Question of Cyclic Versus Acyclic Ions: The Structure of $[C_{10}H_{12}]^+$ Gas Phase Ions

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The extent of isomerization of acyclic and cyclic gas phase radical cations of composition $[C_{10}H_{12}]^+$ has been investigated by using collisionally activated dissociation spectroscopy. Both electron and charge exchange ionization were employed to form the ions with various internal energies. The $[C_{10}H_{12}]^+$ ions investigated consisted of ionized phenylbutenes, ring-substituted methyl derivatives of allylbenzene and phenylpropene, 1-methyl-2-isopropenylbenzene, benzylcyclopropane, phenylcyclobutane, tetralin and 1-methylindan. The 1-methylindan and tetralin radical cations are the most stable of the $C_{10}H_{12}$ isomeric radical ions. The $[C_{10}H_{12}]^+$ formed from acyclic olefins having the double bond in conjugation with the aromatic ring retain the initial structure to a significant extent. However, ions derived from olefins with the double bond out of conjugation with the benzene ring preferentially cyclize to stable five- and six-membered cyclic ions. Ring opening of small-ring cyclic ions, such as ionized benzylcyclopropane and phenylcyclobutane, occurs, followed by ring closure to the tetralin radical cation.

It is well established that five- and six-membered cyclic compounds are the most stable of an isomeric set of compounds. The instability of small-ring cyclic compounds is reflected in part by the ring strain, three-membered cyclic structures being the most strained. Strain in a molecule is the result of distortion of bond angles which introduces unusual reactivity in the molecule. For example, ethylene oxide is more reactive than other ethers.¹ Cyclopropane easily undergoes bromination to 1,3-dibromopropane.² Thermal ring opening of cyclopropanes³ and cyclobutanes⁴ is frequently observed. Examples are also known of ring contraction of greater than six-membered cyclic compounds and of cyclization of unsaturated acyclic compounds to five- and six-membered cyclic compounds.

Similarly, processes leading to internal rearrangement of gas phase ions are often encountered. Rearrangements involving gas phase ions are thought to be facile due to charge and radical site initiated reactions. Ions containing heteroatoms retain structural identity in most cases due to charge localization, while isomerization reactions are more frequently observed for hydrocarbons.

The subject of ring opening of cyclic radical cations and the reverse process are widely debated. In a recent study, we demonstrated electrocyclic ring opening of phenyl-substituted cyclobutene radical cations and subsequent cyclization of the corresponding 1,3butadienes to a stable 3-methylindene ion.⁵ These reactions were found to be internal energy dependent. Isotopic labeling⁶ and metastable studies^{7,8} have been interpreted to show a reversible isomerization of propene and cyclopropane radical cations, whereas low-energy cyclopropane ions retain the cyclic structure.⁹⁻¹¹ Evidence also exists for retention of the intact structures in the case of $[C_4H_8]^{++,12}$ $[C_5H_{10}]^{++,13} [C_8H_8]^{++14,15}$ and $[C_9H_{10}]^{++,15,16}$ ions.

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In this paper, we wish to report a systematic investigation of the relative stabilities of various acyclic and three-, four-, five- and six-membered cyclic gas phase isomeric ions by using $[C_{10}H_{12}]^+$ ions as models. The $[C_{10}H_{12}]^+$ ions were derived from the precursors 1-methylindan (1), 1-phenyl-1-butene (2), 1-phenyl-2-butene (3), 2-methyl-1-phenyl-1-propene (4), 2-methyl-3-phenyl-1-propene (5), 2-methyl-1-allylbenzene (6), 4-methyl-1-allylbenzene (7), 1-methyl-2-isopropenylbenzene (8), tetralin (9), 4-phenyl-1butene (10), benzylcyclopropane (11) and phenylcyclobutane (12). These compounds were chosen because of the possibilities of a variety of internal rearrangement processes such as ring opening and closing, ring contraction and expansion, and double-bond migration. The ions were examined by using collisionally activated dissociation (CAD) spectroscopy,¹⁷ a well-established technique for distinguishing isomeric structures, especially if the isomers exist in shallow potential energy wells. The ions which are stable to unimolecular dissociation and possess low internal energy are preferentially sampled with this technique. These ions should have the best chance of displaying differences characteristic of the neutral precursor.

The rearrangement of phenylbutenes has been the subject of previous studies. Fu and Dunbar¹⁵ investigated the radical cations of **2**, **3**, and **10** trapped in an ion cyclotron resonance cell by obtaining their photodissociation spectra. The evidence gathered by them was interpreted to show that only a small fraction of $[3]^+$ isomerizes to $[2]^+$, the latter ion being the preferred structure due to conjugation of the double bonds of the butene moiety and the phenyl ring. Such a rearrangement was not observed for $[10]^+$. On the other hand, Andrews *et al.*,¹⁸ on the basis of a photochemical study of $[2]^+$, $[3]^+$ and $[10]^+$ trapped in a solid argon matrix, concluded that the isomerization of $[2]^+$ to $[3]^+$ and $[10]^+$ occurs. In other words, the rearrangement of a double bond away from conjuga-

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tion from the aromatic ring is also feasible. Ring closure of ionized 1-phenyl-2-butene to 1-methylindan ion was also suggested but no conclusive evidence was presented.

RESULTS AND DISCUSSION

The principal aim of this study is to discern the structures of $[C_{10}H_{12}]^{+}$ isomeric ions and thereby to investigate rearrangement reactions. Because electron ionization forms radical cations with a broad distribution of internal energies, the structure elucidation of gas phase ions in a mass spectrometer can be complicated. Therefore, we have chosen to form the [C10H12]+ ions with different energy distributions and then to obtain and compare their CAD spectra. To accomplish this, the $C_{10}H_{12}$ hydrocarbons were ionized by 70 eV and low-energy electron ionization (electron energy reduced such that the ion beam was approximately 1% of the maximum value) and by charge exchange with molecular ions of toluene and carbon disulfide. All the $[C_{10}H_{12}]^{+}$ ions formed by low-energy electron ionization of $C_{10}H_{12}$ hydrocarbons will have approximately the same amount of excess energy because the criteria for selection of ionizing energy is the same in each case. This should be the lowest energy ionization method used for most of the $C_{10}H_{12}$ hydrocarbons. Since the ionizing energy $(IE = 8.82 \text{ eV}^{19})$ of toluene is close to some of the $C_{10}H_{12}$ hydrocarbons under study (see Table 1), the charge exchange ionization by [toluene]+. will be the lowest energy ionization process for these selected hydrocarbons. This, coupled with collisional stabilization, should form thermally cool ions which should reflect more closely the properties of the initially formed structure. On the other hand, ionization by $[CS_2]^+$ ions will impart >1.5 eV excess energy, thereby promoting internal rearrangements. These ions, after collisional stabilization, may display characteristics of ground state *rearranged* structures. This was a successful strategy for investigation of the electrocyclic reactions of phenyl-substituted cyclobutene radical cations.⁵

Before discussing the results, the effect of internal energy of the ions on the abundance of the fragment ions must be addressed. In general CAD spectra are not affected by ion internal energy.^{17b} However, Bowers and coworkers have found examples of ions whose CAD spectra vary as a function of internal energy.²⁰ More pronounced changes were observed for those fragments which arise by low-energy processes. To be certain that the effects of internal energy of the $C_{10}H_{12}$ radical cations studied here have been discounted, the low-energy decompositions involving H, H₂ and H₂+ H losses are not included in the comparisons. (The relative abundances of these ions were not reproducible in experiments done on separate days possibly because of overlap with reflected main beam ions.) Moreover, the ions were formed at CS₂ bath gas pressures of 0.2-0.4 Torr in order to reduce excess internal energy by stabilizing by collisions those vibrationally and rotationally excited ions.

Based on comparisons of CAD spectra (see Tables 2–5), the $C_{10}H_{12}$ radical cations can be classified into two broad categories: (i) those which decompose principally by loss of a methyl group (1-8), and (ii) those which fragment primarily by elimination of C_2H_4 (9-12). Within each group, the spectra of the ions are qualitatively similar. However, there are significant quantitative differences in the CAD spectra of ions formed at low ionizing energies (see Tables 2 and 3) which can be used to distinguish ions. These differences can be attributed to different ion structures or at least to different mixtures of ion structures. The differences become less significant for C10H12 radical cations formed at higher ionizing energies (see Tables 4 and 5) which we interpret as an indication that isomerization to stable ion structures is nearly complete. In the following sections, the variations of CAD

Table 1. Ion ma	nizing end ution ^b of [ergies* C ₁₀ H ₁₂	and heats] ^{+:} isomers	of for-						
Compound	IE([M] ^{+*})	Ref.	$\Delta H_{f}(M)^{c}$	∆H _f ([M] ^{+*})						
1	8.47	19	38.7	856						
2	—	_		887						
3	8.48	15	105	923						
6	—			937						
7			_	920						
8	7.78	19	81.0	833						
9	8.44	19	25.1	839						
10	8.60	19	144	944						
12	8.77	19	136	982						
^a Expressed in eV. ^b Expressed in kJ mol ⁻¹ . $^{\circ}\Delta H_{f}$ (298) were calculated according to the group										

additivity rule by using the scheme of Benson and Buss.²¹ ^d See Ref. 22.

Table 2. Partial CAD spectra of $[C_{10}H_{12}]^{+}$ isomers ^{a,b}														
	m/z													
Compound	117	116	115	105	104	103	91	89	78	77	65	63	51	39
1	63	8	14	<1	1	1	6	1	1	2	1	1	1	1
2	54	8	15	<1	1	2	8	2	2	3	2	1	2	1
3	58	7	13	<1	1	2	8	1	2	2	1	1	1	1
4	35	10	22	<1	1	2	13	3	2	4	2	2	2	2
5	44	9	18	1	1	2	12	2	1	3	2	2	2	2
6	42	9	17	5	2	3	9	2	1	4	2	1	2	2
7	36	9	18	6	2	3	10	2	2	4	3	2	2	2
8	29	12	26	1	1	2	12	3	1	3	3	2	2	2
9	7	7	13	<1	31	5	21	2	1	5	2	2	2	2
10	13	5	9	<1	33	2	25	2	2	3	2	1	1	2
11	10	4	7	<1	34	2	30	1	2	2	1	1	1	1
12	16	6	9	<1	34	3	19	1	2	3	2	2	2	2
^a Relative to sum of all the ions excluding ions above m/z 117.														

Table 3.	Pa	rtial	CA	D s	pect	ra o	of [(H ₁₂]	+• i	som	ers	ı,b	
	m/z													
Compound	117	116	115	105	104	103	91	89	78	77	65	63	51	39
2	48	7	14	<1	3	3	9	2	2	3	2	2	2	1
3	51	8	13	<1	2	2	11	2	2	3	2	2	2	1
4	42	10	20	1	2	2	12	2	1	3	2	2	2	2
5	49	10	14	1	2	2	11	2	1	2	2	2	1	1
6	44	10	15	5	з	3	9	2	1	3	2	2	1	1
7	42	9	16	5	3	2	10	1	1	3	2	1	1	1
8	40	11	21	1	2	2	11	2	1	2	2	2	1	2
9	10	7	11	<1	31	4	20	2	1	4	2	2	2	2
10	7	6	8	<1	31	3	32	2	1	3	2	2	2	1
11	9	5	7	<1	31	4	35	2	2	3	2	1	1	1
12	15	7	10	<1	36	3	17	2	1	3	2	2	2	1
^a See Tab ^b Ionizatio	ole 2 on b	2. Ivy [te	olue	ne]+	' cha	arge	exc	har	nge.					

Table 4. Partial CAD spectra of $[C_{10}H_{12}]^{++}$ isomers^{a,b}

	m/z													
Compound	117	116	115	105	104	103	91	89	78	77	65	63	51	39
1	69	7	14	<1	1	1	6	1	1	1	1	1	1	
2	54	8	15	<1	<1	1	9	2	2	3	1	1	2	2
3	51	7	14	<1	1	2	10	2	2	3	2	2	2	2
4	40	10	20	1	1	2	12	2	2	3	2	2	2	2
5	49	9	17	1	1	2	10	2	2	2	2	2	2	2
6	45	10	16	4	2	3	9	2	1	3	2	1	1	1
7	42	9	17	4	2	3	9	2	1	3	2	2	2	2
8	35	11	24	<1	<1	2	12	2	2	2	2	3	2	2
9	7	6	10	<1	29	3	17	2	1	3	1	2	2	1
10	13	5	9	<1	29	3	26	2	2	3	2	1	2	1
11	10	4	7	<1	34	3	30	1	2	3	1	1	1	1
12	13	6	13	<1	34	3	20	1	2	3	2	1	1	1
^a See Tab ^b 70 eV el	^a See Table 2. ^b 70 eV electron ionization.													

spectra of each $C_{10}H_{12}$ isomer as a function of ionizing energy are discussed in detail.

1-Methylindan (1) radical cation. The radical cation $[1]^{+}$ gives a unique CAD spectrum. The major fragment ion in the spectra (Tables 2, 4 and 5) is $[C_9H_9]^+$ arising by the loss of a CH₃ radical along with low yields of other ions. The exocyclic methyl group is easily lost, especially if the fragmentation leads to a stable daughter ion, which is the case for 1-methylindan. The spectrum remains unchanged even for the ions formed by high-energy charge exchange

Table 5.	Partial CAD spectra of $[C_{10}H_{12}]^{+}$ isomers ^{a,b}													
	m/z													
Compound	117	116	115	105	104	103	91	89	78	77	65	63	51	39
1	65	8	11	<1	1	1	6	1	1	1	1	1	1	1
2	59	8	12	<1	1	2	8	1	1	2	1	1	1	1
3	61	7	12	<1	1	2	7	1	1	2	1	1	1	1
4	47	10	18	1	1	2	12	2	2	2	2	2	1	2
5	55	9	15	1	1	2	8	1	1	2	1	1	1	1
6	52	10	16	2	1	2	8	2	1	2	2	1	1	1
7	52	10	15	3	2	2	8	1	1	2	2	1	1	1
8	39	12	22	1	1	2	12	2	1	2	2	2	2	2
9	7	6	10	3	37	4	21	2	1	4	2	2	2	1
10	10	4	6	3	38	2	18	1	2	2	1	1	1	1
11	15	6	10	2	31	3	21	2	2	3	1	2	2	2
12	7	7	12	2	32	4	20	2	2	4	2	2	2	2
^a See Tab	ole 2	2.												
^b lonization by [CS ₂] ^{+.} charge exchange.														

with $[CS_2]^{+}$; thus, the methylindan radical cation is one of the most stable of all the $[C_{10}H_{12}]^{+}$ ions. This is consistent with thermochemical measurements (see Table 1). The spectrum of the ions derived from **1** is interpreted to be characteristic of the initially formed ions.

1-Phenyl-1-butene (2) and 1-phenyl-2-butene (3) radical cations. Like the 1-methylindan ion, the major fragmentation process as indicated by the CAD spectra of $[2]^{+}$ and $[3]^{+}$ formed at low ionizing energies is the loss of a CH₃ radical (Tables 2 and 3). The methyl loss from $[2]^+$ may be assumed to occur either from the original structure or from ionized 1-methylindan if isomerization of $[2]^{+}$ to $[1]^{+}$ occurs. On the basis of thermodynamic stability (Table 1), it can be concluded that a considerable fraction of [2]+. maintains the structure of the neutral precursor. Additional support for this hypothesis is found in the relatively constant abundance ratio for m/z 117 and 91 as the ionizing energy is increased. The other fragment of significant abundance (in addition to that formed by the loss of CH₃ and H₂) is the $[C_7H_7]^+$ ion. If we assume $[3]^+$ is stable to internal rearrangement, we would expect formation of the fragment ion $[C_7H_7]^+$ by α -cleavage initiated by the phenyl ring to be an important process for this ionic structure. The preponderance of loss of CH₃ can only be accounted for by rearrangement of $[3]^{+}$ to either $[2]^{+}$ or $[1]^{+}$ (Scheme 1). We postulate that $[3]^+$ formed by low-energy ionization, isomerizes to $[2]^+$. High-energy ionization by $[CS_2]^+$ probably allows interconversion of [1]⁺, [2]⁺ and [3]⁺ with preferred formation of $[1]^{+}$ (see Table 5). One tentative mechanism for the interconversion is pictured in Scheme 1.

These results are in accord with the work of Andrews *et al.*¹⁸ The reversible isomerization of $[2]^+$ and $[3]^+$ is postulated on the basis of the similarities of the CAD spectra at all ionizing energies. Our results are also evidence for isomerization of $[2]^+$ and $[3]^+$ to the stable indan structure.

$$(2)^{+} \rightleftharpoons (3)^{+} \rightleftharpoons (1)^{+}$$

Scheme 1

(1,2,3,4-tetrahydronaphthalene) (9) Tetralin radical **cation.** The tetralin radical cation, $[9]^{+}$, is the most stable of the [C₁₀H₁₂]⁺ ions considered here (see Table 1). Therefore, $[9]^{+}$ is expected to maintain the structure of the neutral precursor. This hypothesis is substantiated by the CAD spectra (Tables 2-5). The ion $[C_8H_8]^+$ is the predominant fragment ion which arises by expulsion of C_2H_4 (Scheme 2), either involving carbon atoms 1+2 (or 3+4) or carbon atoms 2+3, commonly called a retro-Diels-Alder reaction.²⁵⁻²⁸ Moreover, the CAD spectrum is not a strong function of ionizing energy ions, which is also consistent with the postulate that the nondecomposing tetralin radical cations are stable to internal rearrangements.



Scheme 2

4-Phenyl-1-butene (10) radical cation. Ionized 10 gives a CAD spectrum which is significantly different from those of the radical cations of 1, 2 and 3 (Tables 2-5). Therefore, rearrangement of a substantial fraction of $[10]^{+\cdot}$ to $[2]^{+\cdot}$ and $[3]^{+\cdot}$ by migration of the double bond is dismissed, although rearrangement of a small fraction of [10]⁺ to these ions and ultimately to [1]⁺ cannot be ruled out. The CAD spectrum of [10]+. has features which are more similar to those of the [C₁₀H₁₂]⁺ ions derived from tetralin; the only difference in the spectra of the ions formed by [toluene]+. charge exchange is that [10]⁺ shows a greater abundance of $[C_7H_7]^+$ ions which result by the loss of C_3H_5 triggered by the phenyl ring and the double bond in the side-chain. This is indicative of the fact that some unisomerized ions of structure $[10]^+$ still persist in the time-scale of c. 10^{-6} s. The other fragment ion of importance has the composition $[C_8H_8]^{+}$ (m/z 104). Formation of the $[C_8H_8]^{+}$ ion can be best explained by rearrangement to the tetralin radical cation (Scheme 2). Another possibility is cyclization to phenylcyclobutane, which seems less likely on the basis of thermodynamic instability of the cyclobutane ring.

With increases in ionizing energy, the C_3H_5 loss becomes less probable, and ultimately the spectrum of [10]⁺⁻ becomes nearly identical to that of [9]⁺⁻. The heat of formation (ΔH_f) of [10]⁺⁻ is 944 kJ mol⁻¹ compared to 839 kJ mol⁻¹ for [9]⁺⁻. The lower stability of [10]⁺⁻ supports the foregoing conclusion that ionization of 10 promotes isomerization to the stable tetralin radical cation. Ionization by [toluene]⁺⁻ charge exchange transfers ~0.2 eV energy to the molecular ions of 10. Therefore, the critical energy for ring closure of [10]⁺⁻ to [9]⁺⁻ should be less than 5 kcal mol⁻¹

Benzylcyclopropane (11) radical cation. Cyclopropane is a highly strained cyclic structure, and ring opening of the radical cation may be facile. Cleavage of the cyclopropane ring of $[11]^{++}$ can occur in three possible ways (Scheme 3). The processes *a* and *b* accompanied



by hydrogen rearrangement should yield either 2, 3 or 10 radical cations or a mixture of them. The process c_{1} , on the other hand, produces a branched acyclic product, the 2-methyl-3-phenyl-1-propene (5) radical cation. The ring-opened isomers can further rearrange to cyclic products, ionized 1-methylindan and tetralin. The occurrence of a specific process can be ascertained by examining the CAD spectra of [11]⁺⁻ formed with different internal energies. The spectra of $[11]^+$ formed at low ionizing energies (Tables 2 and 3) although qualitatively similar to those of 9, 10 and 12, are quantitatively different, which is taken to indicate that a fraction of the ions retain the cyclic structure. Two major fragmentation reactions are evident: formation of $[C_8H_8]^+$ and $[C_7H_7]^+$ resulting from elimination of C_2H_4 and C_3H_5 , respectively. A large abundance of $[C_7H_7]^+$ which presumably arises by the loss of an intact cyclopropane moiety (cleavage α to the phenyl ring) is consistent with the hypothesis that a fraction of [11]⁺⁻ retains the original structure. The predominance of $[C_8H_8]^{+}$ in the spectra is explained by the fact that cleavage of the cyclopropane ring by the process a yields the 4-phenyl-1-butene radical cation which subsequently cyclizes to ionized tetralin. Isomerization of [11]⁺⁻ to [5]⁺⁻, which may occur if rupture of the cyclopropane ring occurs by the process c, is ruled out at least to any significant extent, since $[11]^{+}$ and $[5]^{+}$ give distinct spectra. These results are in accord with the earlier studies of the cyclopropane⁶⁻¹¹ and cyclopropylbenzene¹⁶ radical cations. The latter radical cation has been shown to have a structure different from α -methylstyrene, and it undergoes isomerization to allylbenzene and probably to β -methylstyrene.

The spectrum of $[11]^{+}$ varies as a function of ionizing energy. The ions formed by $[CS_2]^{+}$ charge exchange exhibit a greater propensity to lose CH₃, whereas the extent of C_3H_5 loss is reduced (Table 5). A tentative explanation of this observation is that a small fraction of ions formed at higher ionizing energies isomerize to $[9]^{+}$ and $[1]^{+}$ via the intermediacy of $[3]^{+}$. The possibility of a small amount of ring opening to ionized 1-phenyl-1-butene ($[2]^{+}$) cannot be dismissed (Scheme 3).

Phenylcyclobutane (12) radical cation. The cyclobutane moiety of $[12]^{+\cdot}$ is expected to undergo two bond cleavage reactions: a cycloreversion reaction yielding $[C_8H_8]^{+\cdot}$ by elimination of C_2H_4 (Scheme 4)²⁵ and ring opening followed by hydrogen atom migration to form 1-phenyl-1-butene (2) or 4-phenyl-1-butene (10) radical cations (Scheme 5). Scrutiny of the CAD spectra (Table 2) reveals that the most predominant fragment

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ion is $[C_8H_8]^+$ which can arise by a cycloreversion reaction from either the ion having retained the structure of the neutral or from tetralin radical cation as noted above in Scheme 2. The CAD spectra of [12]+" and $[9]^+$ become nearly identical (see Table 5) as the ionization energy is increased except that the latter ion shows a slightly greater loss of C_2H_4 . Reasonable explanations for these observations are as follows. (i) A fraction of phenylcyclobutane ionized at low energy maintains the structure of the neutral precursor. (ii) Ring opening of the cyclobutane moiety occurs with subsequent isomerization to the tetralin radical cation. This may occur by H rearrangement following ring opening to produce an intermediate 4-phenyl-1-butene radical cation. (iii) A small portion of phenylcyclobutane ions undergo ring expansion to 1methylindan ion via the 1-phenyl-2-butene radical cation.

2-Methyl-1-phenyl-1-propene (4) and 2-methyl-3-phenyl-1propene (5) radical cations. These ions present another opportunity to investigate double-bond migration into conjugation with an aromatic ring. Possibilities for rearrangements to cyclopropane and indan rings also exist.

A careful examination of the spectra of the ions formed by low-energy ionization (Table 2) reveals that ionized 4 and 5 can be distinguished from each other. There are significant differences in the relative abundances of $[C_9H_9]^+$ and $[C_9H_7]^+$ ions (consider the differences in the abundance ratio for m/z 117: m/z 91). As the ionizing energy increases, the propensity for methyl loss from [5]⁺⁺ increases significantly and approaches that of an indan-type structure. The radical cation formed from 4 appears to be more stable (note the abundance ratio m/z 117: m/z 91 changes less than that of $[5]^+$ as the ionizing energy increases) which may be interpreted as stabilization of the double bond of [4]⁺ by conjugation with the phenyl group. If a significant fraction of [5]⁺ had retained the acyclic structure, the loss of C₃H₅ would be expected to be the dominant process resulting by the cleavage α to the phenyl ring and directed by branching on the propylene moiety. The possibility of the reaction channel involving the isomerization to a cyclic structure probably precludes rearrangement of $[5]^+$ to $[4]^+$. There is no evidence for rearrangement to the tetralin ion.

2-Methyl-1-allylbenzene (6) and 4-methyl-1-allylbenzene (7) radical cations. $[C_{10}H_{12}]^{+\cdot}$ ions derived from pre-

$$(\mathbf{0}^{+})^{\mathbf{1}^{+}} \longrightarrow \mathbf{c}_{\mathbf{8}}\mathbf{H}_{\mathbf{9}}^{\mathbf{7}^{+}} + \mathbf{c}_{\mathbf{2}}\mathbf{H}_{\mathbf{3}}$$
$$(\mathbf{6})^{+}$$

Scheme 6

cursors 6 and 7 yield almost identical CAD spectra at all ionizing energies (Tables 2-5). The spectra of these ions formed at low ionizing energies differ from those of other $[C_{10}H_{12}]^+$ ions. The loss of C_2H_3 resulting in the formation of a product of composition $[C_8H_9]^+$ is conspicuous and is of negligible importance for the other $[C_{10}H_{12}]^{+}$ ions. This fragmentation is characteristic of the intact acyclic ions $[6]^{+}$ and $[7]^{+}$ (Scheme 6). Apart from this difference, the remainder of the CAD spectra of $[6]^+$ and $[7]^+$ is identical with that of the ionized 1-methylindan. The energetic charge exchange ionization of 6 and 7 by $[CS_2]^+$ generates the ions which cease to exhibit the characteristic reaction shown in Scheme 6. On the basis of these results it can be argued that a measureable portion of low internal energy $[6]^{+}$ and $[7]^{+}$ ions retain the structure of their neutral precursors. As is the case for some of the other acyclic ions investigated here, radical ions from 6 and 7 also isomerize at higher energies to a stable five-membered cyclic structure.

1-Methyl-2-isopropenylbenzene (8) radical cation. Ionized 8 yields a CAD spectrum which can be distinguished from all the $[C_{10}H_{12}]^{+}$ ions investigated here; thus $[8]^+$ has a unique ion structure. The spectrum of $[8]^{+}$ shows that more pronounced losses of CH_4 and CH_5 ($CH_3 + H_2$) moieties occur than for any other $[C_{10}H_{12}]^{+}$ ions. The spectrum also exhibits a greater abundance of $[C_9H_9]^+$ and $[C_7H_7]^+$ ions. The loss of methyl from $[8]^{+\cdot}$ arises because of the carbon branching in 8. The methyl loss is, however, relatively low compared to the [C₁₀H₁₂]⁺⁺ ions so far discussed, thereby precluding rearrangement of [8]+ to an indantype structure, at least to any significant extent. These results are consistent with the general hypothesis that conjugation of the double bond stabilizes the molecular ion. A similar result was reported in a recent study of its lower homolog, the α -methylstyrene radical cation, which was shown to possess a unique structure distinct from several other [C₉H₁₀]⁺ isomers.¹⁶

CONCLUSION

Usually an aromatic ring of a molecule constitutes a center for stabilization of positive charge and, as a result, specific rearrangement reactions may be promoted. This fact is evident from the results obtained in this study. Olefins having the double bond in conjugation with the phenyl ring, e.g. 1-phenyl-1-butene and 1-methyl-2-isopropenylbenzene radical cations, prefer to maintain the initially formed structure. On the other hand, cyclization is a more favored rearrangement for the olefins in which a $-CH_2$ -- group is interposed between the phenyl ring and the double bond. The phenyl ring initiates migration of the double bond of 1-phenyl-2-butene radical cation into

conjugation whereas the possibility of isomerization to a stable cyclic structure favors bond formation with the ring. Ring closures of the radical cations of **3** and **10** to 1-methylindan and tetralin radical cations, respectively, are favored, perhaps because the removal of an electron from the phenyl ring gives it electrophilic properties and promotes attack on the π electrons of the carbon-carbon double bond of the side-chain.

The CAD spectra of benzylcyclopropane and phenylcyclobutane radical cations have been interpreted to show that a measurable fraction of the ions retains their cyclic structures at low ionizing energies. In addition, ring opening of these strained ring compounds to acyclic intermediates and subsequent ring closure to the ionized tetralin are observed as the energy is increased.

The present study has also served to demonstrate the efficacy of charge exchange ionization for investigation of isomerization reactions. By this approach the ions can be generated with some control of internal energy, although the control is not as sophisticated as that which can be obtained by photoion photoelectron coincidence techniques.

EXPERIMENTAL

All experiments were performed with a Kratos MS-50 triple analyser mass spectrometer.²⁹ The ions were mass-selected by using MS-I which consisted of an electrostatic analyser and a magnetic analyser. The mass-selected ions were collisionally activated using He as a neutral target in a cell located in the third field free region. The pressure of the collision gas was adjusted to reduce the ion beam intensity by half. The CAD spectra were acquired by scanning the second electrostatic analyser (the third sector). The unimolecular fragmentations in the same region were also monitored. By the time $(10-30 \ \mu s)$ the ions arrive in the third field free region of the MS-50 TA, most of the metastable ions already have decomposed. Metastable ions contributed less than 10% to any of the

signals in the CAD spectra of the ions formed at 70 eV ionizing energy. Nevertheless, we corrected the relative abundances of $[C_9H_9]^+$ and $[C_8H_8]^{+\cdot}$ for the metastable ions by acquiring the CAD and metastable spectra under the same conditions. The CAD spectra are the average of at least three measurements, each recorded by signal averaging 7–25 scans with a Data General NOVA 4X computer.

The primary ions were formed by 70 eV and lowenergy electron ionization and by charge exchange with [toluene]⁺⁻ and $[CS_2]^{+-}$. The reagent ions were generated at 280 eV in a high-pressure CI source supplied by Kratos. Mixtures of the reagent gases and $C_{10}H_{12}$ hydrocarbons (in the ratio of 10:1) were admitted to the source through separate inlets to give a total ion source pressure of 0.2–0.35 Torr. Other experimental conditions were as follows: source temperature, 100 °C; sample inlet temperature, 70 °C; accelerating voltage, 8 kV; emission current, 500 μ A.

Benzylcyclopropane was synthesized from allylbenzene by reacting it with methylene iodide in the presence of a Zn/Cu couple by using the procedure of Friedrich.³⁰ 1-Methylindan was prepared by hydrogenation of 3-methylindene at 760 Torr pressure using 10% Pd/C as catalyst and ethyl acetate as solvent.³¹ 1-Phenylcyclobutane was prepared by stirring 1-phenylcyclobutanol with NaNH₂ in liquid ammonia for 4–5 h. All synthetic samples were purified by using preparative GC and a $2 \text{ m} \times 6 \text{ mm}$ stainless steel column packed with 10% SP 2100 coated on 100/120 Supelcoport. Their purity was confirmed by using ¹H NMR and mass spectrometry.

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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