

Gaseous Tropylium, Benzyl, Tolyl, and Norbornadienyl Cations^{1,2}

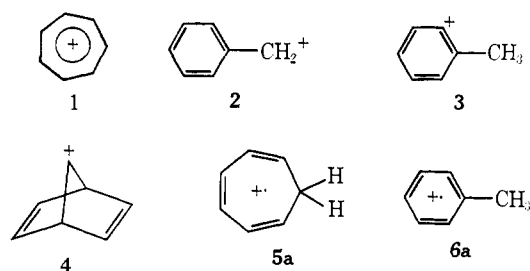
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Abstract: Collisional activation (CA) spectra are used to show that gaseous $C_7H_7^+$ ions can be formed in a variety of isomeric structures that are stable for at least 10^{-5} sec. Such isomers include tropylium (1), benzyl (2), *o*-tolyl (3), *m*- and *p*-tolyl (9), and norbornadienyl (4) ions. A variety of isomerization pathways are indicated for these ions and their precursors. The lowest energy cycloheptatriene and toluene ions losing hydrogen equilibrate rapidly, so that either forms approximately equal quantities of 1 and 2. Although 1 and 2 ions of low internal energies are stable, high energy nondecomposing 1 or 2 ions rapidly equilibrate to a mixture in which $[1]/[2] \geq 3$; earlier identifications of $C_7H_7^+$ ions from various sources as either 1 or 2 based on kinetic energy released during metastable decomposition are incompatible with CA data. Stable 3 and 9 ions can be prepared from $CH_3C_6H_4X$ compounds where $X = I$ or an electron-withdrawing group; other $CH_3C_6H_4X^+$ ions apparently isomerize to cycloheptatriene and, possibly, methylenecyclohexadiene derivatives which serve as precursors of the 1 and 2 ions, respectively, which are observed. CA spectra of $C_7H_7^+$ ions from 60 compounds are reported.

Gaseous $C_7H_7^+$ ions, such as isomers 1–4, have been the subject of a wide variety of studies^{3,4} since the provocative proposal by Meyerson and his coworkers that both cycloheptatriene (5a) and toluene (6a) give the tropylium ion, 1, as the most abundant ion in their mass spectra.³ A high preference for tropylium ion formation, even where substantial skeletal rearrangement is necessary, has often been postulated to explain the isotopic distribution of products from the decomposition of $C_7H_7^+$ ions,^{3–6} although particular exceptions have been reported.^{5,7,8} These $C_7H_7^+$ ions must be formed with substantially higher average internal energy than the nondecomposing ions which give rise to the $C_7H_7^+$ peak in mass spectra. The tendency for the latter to rearrange to 1 is less clear; in particular cases lower energy benzyl^{9,10} and tolyl^{11,12} ions apparently can at least be formed without isomerization.

In an attempt to resolve these conflicting results, in this study the structures of nondecomposing $C_7H_7^+$ ions produced by electron ionization of a variety of precursors have been examined utilizing collisional activation (CA) spectra.^{1,13} In this technique ions passing



through a field-free drift region of the mass spectrometer are excited by collision with a neutral gas such as helium, and the resulting ion decomposition products are separated and measured to yield the CA spectrum. Such spectra appear to be uniquely useful for the characterization of ion structure because the relative ion abundances are independent of the internal energy of the precursor ion examined.¹³

Experimental Section

The apparatus, procedures, and conditions are generally the same as those described previously.¹³ Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer of reversed geometry.¹⁴ An ion accelerating potential of 3.8 kV, ionizing electrons of 100 μ A and 70 eV (or lower where noted), and sample reservoir and ion source temperature of 200° were used. The desired precursor ion is selected by proper choice of the magnetic field value; unimolecular metastable decompositions of these ions occurring in the field-free drift region between the magnetic and electrostatic (ESA) analyzers are measured by scanning the ESA potential. The pressure in this field-free drift region is then increased with helium until the precursor ion intensity is reduced to 10% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan. The peaks which are of appreciable abundance in the MI spectrum have been omitted from the CA spectral data, as their abundances can be affected by ion internal energy as well as ion structure.¹³ Peak abundances have not been corrected for overlap in neighboring peaks due to poor resolving power; m/e 77 contributes ~11% of its abundance to m/e 78. Peaks of minor abundance have been omitted, and the data were normalized so that the sum of the peaks

(1) Metastable Ion Characteristics. XXXI. For a preliminary communication (Paper XXX), see J. Winkler and F. W. McLafferty, *J. Amer. Chem. Soc.*, **95**, 7533 (1973).

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Table I. Collisional Activation Spectra of $C_7H_7^+$ Ions

Compound	Electron energy, eV	Relative abundance ^a									% benzyl ^c
		<i>m/e</i> 39	41	50 ^b	51	63	74 ^b	75 ^b	76 ^b	77	
Cycloheptatriene	70	24	4.5	11	19	31	2.0	2.6	2.2	3.7	25
	12.5 ^d	22	3.7	12	19	30	2.2	3.0	3.2	5.5 ^e	45
Toluene	70	23	4.4	12	19	31	2.3	2.6	2.5	3.7	25
	13.5 ^d	21	3.4	13	18	29	1.9	3.1	3.7	6.1 ^f	50
1,2-Diphenylethane	70	23	4.9	11	19	28	2.1	2.5	2.8	7.2	65
	11.5 ^d	22	4.8	10	18	28	2.1	2.2	3.6	9.7 ^g	90
1,2-Diphenylethane- α - <i>d</i> ₄	70						1.7	2.1	3.1	5.4 ^h	
	70	23	5.5	12	18	33	2.6	2.7	2.0	1.7	
<i>o</i> -Nitrotoluene	17.5	22	5.6	12	18	33	2.5	2.7	2.0	1.8	
	70	22	5.8	14	17	29	4.2	3.8	3.4	1.2	
<i>m</i> -Nitrotoluene	70	22	5.3	13	17	31	4.0	3.4	2.8	1.4	
	20	23	4.9	13	18	29	4.4	4.1	3.3	1.2	
<i>p</i> -Nitrotoluene	70	22	5.3	13	17	31	4.0	3.4	2.8	1.4	
	20	23	4.9	13	18	29	4.4	4.1	3.3	1.2	
2,5-Norbornadiene	70	24	4.3	11	19	29	2.3	2.8	2.5	3.8	(25)

^a Based on sum for these peaks = 100%. MI spectral peaks at *m/e* 65, 89, 90 omitted; also smaller peaks omitted including *m/e* 26 (1.1), 27 (1.2), 85 (0.9), 86 (1.7), 87 (2.5), and 88 (7). ^b Poorly resolved. ^c Based on $[m/e 77] = 1.5\%$ for pure tropylium ions, 10.5% for pure benzyl ions; see text. ^d Data of lower reproducibility (± 5 -10%). ^e Value at 16.5 eV, 4.7%. ^f Value at 16.5 eV, 5.5%. ^g Value at 20 eV, 9.1%; at ~ 10.5 eV, $\sim 10.6\%$. ^h *m/e* 78, 1.5; *m/e* 79, 0.7.

included in Table I is 100%. The spectra shown are the computer averaged results of at least ten separate scans; 50-100 scans were used for low-voltage data. Separate redetermination of key spectra showed that the data were reproducible within $\pm 5\%$ (relative) except for the least abundant peaks or where otherwise indicated. Change of the electron gun filament can cause larger variations;¹³ the largest observed here was a change from a value of 1.1% for *m/e* 77 from *p*-nitrotoluene to a value of 1.7%. In most cases related compound were run with the same filament. Typical CA spectra are shown in Figure 1 and ref 1.

Compounds used, except as listed below, were obtained commercially and purified by preparative gas chromatography where necessary. Deuterium-labeled compounds obtained from Merck and Company were of 99+ % purity. *tert*-Butylbenzene- β -*d*₃ was a generous gift from Dr. N. M. M. Nibbering, University of Amsterdam; *d*₁, 0.4%; *d*₂, 4.7%; *d*₃, 94.9%. The 1,2-diphenylethane-1,1,2,2-*d*₄ used is described in ref 10b.

7-X-Cycloheptatrienes. Compounds for which X = methyl, *n*-butyl, and methoxy were prepared¹⁵ from tropylium tetrafluoroborate and methyllithium, *n*-butyllithium, and sodium methoxide, respectively.

***p*-Xylene- α -*d*₃.** Following procedures described previously,⁵ methyl *p*-toluate was treated with LiAlD₄, and the resulting alcohol was converted to the chloride with SOCl₂, and treated again with LiAlD₄ to give *p*-CH₃C₆H₄CD₃: *d*₂, 2.2%; *d*₃, 97.8%.

***o*- and *p*-Nitrotoluene-*d*₇, α -*d*₃, -ring-*d*₄.** These were prepared by nitration of the corresponding labeled toluenes obtained commercially; for the ring-deuterated compounds, D₂SO₄/D₂O/KNO₃ was used.

Results and Discussion

The CA spectra of the $C_7H_7^+$ ions in the mass spectra of cycloheptatriene (5a), toluene (6a), 1,2-diphenylethane, *o*-, *m*-, and *p*-nitrotoluene, and norbornadiene, at 70 eV and low-electron energy, are given in Table I. The most structurally significant peaks are at *m/e* 74-77; data for these CA spectral peaks for $C_7H_7^+$ ions from a variety of other compounds are given in Table II. The remaining peaks for these compounds exhibit the abundances of Table I within experimental error, except *m/e* 41, for which the values show a range of $\pm 15\%$. Partial CA spectra of deuterated analogs of several compounds are shown in Figure 1 and ref 1.

The Benzyl Ion (2). Variations in the CA spectral data with the origin of the $C_7H_7^+$ ions indicate that distinctly different ion structures can be formed which are stable for the $\sim 10^{-5}$ sec required for the ions to reach the collision region. The similarity in *m/e* 74-79 from the $C_7H_5D_2^+$ ions of $C_6H_5CD_2CD_2C_6H_5^+$ with *m/e* 74-79 of the $C_7H_7^+$ ions from $C_6H_5CH_2CH_2C_6H_5^+$ strongly

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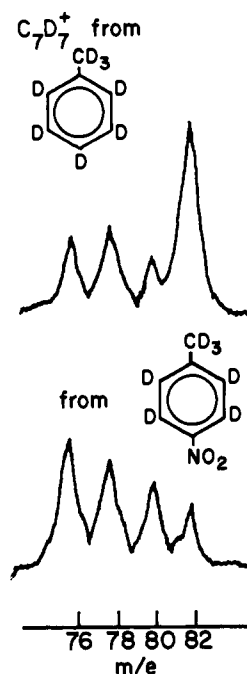


Figure 1. Partial CA spectra of $C_7D_7^+$ ions from $CD_3C_6D_3$ and $CD_3C_6D_4NO_2$. (The reaction endothermicity causes the peaks to appear below the ESA voltage corresponding to the product mass (ref 13).

supports the benzyl structure for the majority of these ions; the benzylic hydrogens must be lost specifically in the formation of these peaks in the CA spectrum. The increase in the relative abundance for the *m/e* 77 peak in the low voltage CA spectra of $C_7H_7^+$ from compounds such as $C_6H_5CH_2I$ and $C_6H_5CH_2CH_2C_6H_5$ is consistent with an increase in the relative proportion of benzyl ions. An estimate of this amount can be made from the relative abundance of $C_6H_5D_2^+$ in the spectrum of $C_7H_5D_2^+$ from $C_6H_5CD_2CD_2C_6H_5^+$; the value of $[m/e 79]/[m/e 77]$ in this spectrum is $12 \pm 2\%$ at 70 eV, and $5 \pm 3\%$ at 12.5 eV ionizing energy (compared to 55% for $C_7H_5D_2^+$ from $C_6H_5CD_3$). This corresponds to a reduction of the proportion of $C_7H_7^+$ ions other than 2, presumably ions of structure 1, to roughly 35% of the 70 eV value at 12.5 eV, or from ~ 35 to $\sim 12\%$ of the $C_7H_7^+$ ions based on $[m/e 77] < 3.6\%$ for the CA

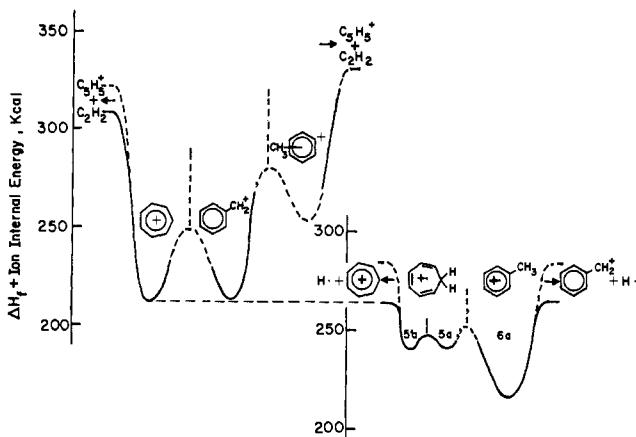


Figure 2. Energy relationships for $C_7H_7^+$ and $C_7H_7X^+$. Dashed lines on energy barrier tops indicate that isomerization reactions generally require ion energies substantially greater than E_a for significant reaction rates.

spectrum of pure 1 $C_7H_7^+$ ions.¹⁶ The tendency to form $C_7H_7^+$ isomers other than benzyl at higher energies is consistent with the complete scrambling generally found for decomposing $C_7H_7^+$ ions.^{3-6,9}

The energy diagram of Figure 2 attempts to visualize these relationships.^{9,17} The appearance potential for formation of $C_5H_5^+$ from toluene, $A(6a \rightarrow C_5H_5^+)$, corresponds to $C_7H_7^+$ ions of ~ 109 kcal internal energy and $A(5a \rightarrow C_5H_5^+)$ corresponds to $C_7H_7^+$ ions of ~ 115 kcal internal energy; the calculated activation energy, $E_a(C_7H_7^+ \rightarrow C_5H_5^+)$, is 95 kcal.¹⁷ The isomerization $2 \rightarrow 1$ (as well as $1 \rightarrow 2$) should have a relatively tight activated complex, so that $C_7H_7^+$ internal energies substantially greater than $E_a(2 \rightarrow 1)$ should be required for complete isomerization. Scheme I summarizes the postulated reactions.

The Tropylium Ion (1). The CA spectra of the $C_7H_7^+$ ions formed at 70 eV from cycloheptatriene precursors (Tables I and II) show that the bulk of these ions do not have the benzyl structure. This is also true of $C_7H_7^+$ from toluene (6a), as its behavior is identical with $C_7H_7^+$ from cycloheptatriene (5a) within experimental error. Lowering the energy of the ionizing electrons increases the abundance of the m/e 77 peak in the CA spectrum; this indicates a concomitant increase in the formation of another $C_7H_7^+$ isomer or isomers. In studies of CA spectra of pure ions (a single isomer) of a wide variety of different ion structures,^{13,18} no abundance variations¹⁹ of this magnitude due to ion internal energy changes have been observed. In further support, for the CA spectra of other $C_7H_7^+$ ions (3 and 9, *vide infra*) and of the $C_7H_8^+$ ions from 5a and

(16) The value $[m/e 77] = 1.5$ for pure 1 $C_7H_7^+$ ions, discussed below, was used to estimate $[m/e 79]/[m/e 77]$ for $C_7H_8D_2^+$ ions of structure 1 for this calculation; if $[m/e 77] = 3.0$, the calculated reduction in [1] on lowering the electron energy is to 39% of its 70-eV value. It was also assumed that pure $C_6H_5CD_2^+$ gives no m/e 79 ions in its CA spectrum; if this is incorrect, the proportion of 2 ions will be even higher.

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(19) Such abundance variations only occur for those low-energy processes giving rise to unimolecular metastable decompositions; negligible quantities of $C_6^+-C_6H_5^+$ ions are produced by metastable decompositions of $C_7H_7^+$ ions.

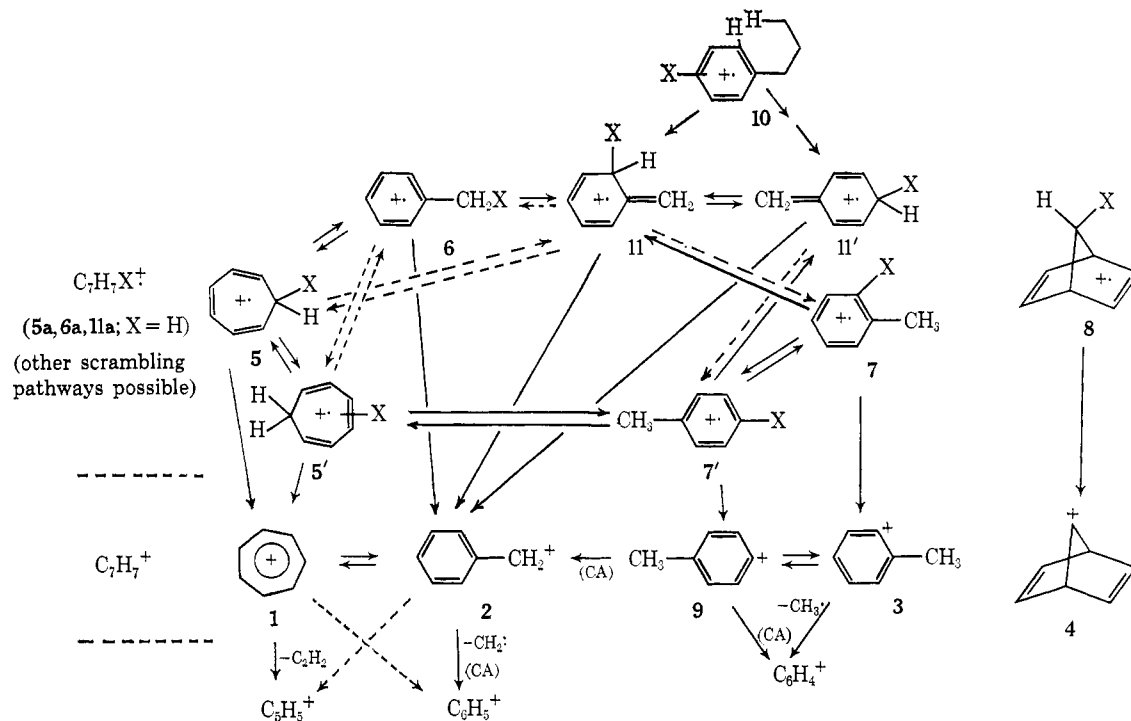
Table II. Partial CA Spectra of $C_7H_7^+$ Ions

Compound	Relative abundance, ^a 70 eV ^b				% benzyl ^c	Low energy ^d	
	m/e 74	75	76	77		eV	m/e 77
7-CH ₃ CHT ^e	2.2	2.7	2.4	3.6	25		
7- <i>n</i> -C ₄ H ₉ CHT ^e	2.3	2.5	2.7	3.8	25	12.5	4.5 ^d
7-CH ₃ OCHT ^e	2.1	2.8	2.5	3.6	25	12.5	6.2 ^d
Tropylium ⁺ BF ₄ ^{-f}	2.2	2.4	2.2	4.3	30		
C ₆ H ₅ CH ₂ CH ₃	2.4	2.9	3.2	5.1	40		
C ₆ H ₅ CH ₂ C ₂ H ₅	2.0	3.0	2.9	5.8	50		
C ₆ H ₅ CH ₂ C ₆ H ₇	2.2	3.0	2.8	5.6	45	20	5.7 ^d
C ₆ H ₅ CH ₂ CH(CH ₃) ₂	2.1	2.4	3.0	5.8	50		
C ₆ H ₅ CH ₂ C(CH ₃) ₃	2.1	2.8	3.2	5.7	45		
C ₆ H ₅ CH ₂ - <i>n</i> -C ₈ H ₁₇	2.4	2.8	2.6	5.7	45		
C ₆ H ₅ CH ₂ CH ₂ CH=CH ₂	2.2	2.9	3.3	7.0	60		
C ₆ H ₅ CH ₂ C ₆ H ₅	2.0	2.4	2.1	3.4	20	20	4.8
C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₄ - <i>p</i> -NH ₂	2.3	2.9	2.7	4.2	30	20	8.1
C ₆ H ₅ CH ₂ CH(OH)C ₆ H ₅	2.4	2.8	2.6	3.5	20		
C ₆ H ₅ CH ₂ Cl	2.2	3.0	2.7	5.7	45		
C ₆ H ₅ CH ₂ Br	2.0	3.3	2.4	5.9	50		
C ₆ H ₅ CH ₂ I	2.0	2.4	3.7	7.2	65	16	8.7
C ₆ H ₅ CH ₂ NO ₂	2.1	2.7	3.1	6.6	55		
C ₆ H ₅ CH ₂ OH ^d	2.2	2.8	2.2	3.2	20		
C ₆ H ₅ CH ₂ OCH ₃	2.6	2.7	2.5	3.9	25		
C ₆ H ₅ CH ₂ OCH ₂ C ₆ H ₅	2.2	2.7	2.4	4.5	35		
C ₆ H ₅ CH ₂ OC ₆ H ₅	2.0	2.7	3.1	7.4	65		
C ₆ H ₅ CH ₂ CH ₂ OH	2.2	2.8	2.2	4.0	30		
C ₆ H ₅ CH ₂ COC ₂ H ₅	2.6	2.9	2.5	4.8	35		
C ₆ H ₅ CH ₂ COC ₆ H ₅	2.4	2.7	2.3	4.0	30		
C ₆ H ₅ CH ₂ COOH	2.4	2.8	2.4	5.1	40		
C ₆ H ₅ CH ₂ COOCH ₂ C ₆ H ₅	2.5	3.2	3.1	6.5	55		
<i>o</i> -CH ₃ C ₆ H ₄ CH ₃	2.1	2.7	3.0	6.0	50		
<i>o</i> -CH ₃ C ₆ H ₄ I	3.0	3.1	2.7	2.4			
<i>o</i> -CH ₃ C ₆ H ₄ OCH ₃	2.7	3.0	2.9	4.2	(30)	16.5	8.1
<i>o</i> -CH ₃ C ₆ H ₄ COCH ₃	3.1	3.3	3.1	2.3			
<i>o</i> -CH ₃ C ₆ H ₄ COC ₆ H ₅ ^g	3.0	3.3	3.0	2.6			
<i>o</i> -CH ₃ C ₆ H ₄ COOCH ₃	3.5	3.6	3.2	2.2			
<i>m</i> -CH ₃ C ₆ H ₄ Br	2.3	2.7	2.2	3.9	25		
<i>m</i> -CH ₃ C ₆ H ₄ I	4.1	3.5	2.3	1.4			
<i>m</i> -CH ₃ C ₆ H ₄ OCH ₃	2.0	3.1	2.2	4.0	30		
<i>m</i> -CH ₃ C ₆ H ₄ COC ₆ H ₅	4.6	4.1	3.8	1.4			
<i>m</i> -CH ₃ C ₆ H ₄ COOCH ₃ ^g	3.7	3.2	2.7	1.2			
<i>p</i> -CH ₃ C ₆ H ₄ CH ₃ ^d	2.4	2.9	2.7	5.3	40	16.5	7.0
<i>p</i> -CH ₃ C ₆ H ₄ CD ₃ ^d	2.3	3.2	2.8	5.8	50		
<i>p</i> -CH ₃ C ₆ H ₄ CH(CH ₃) ₂	2.5	3.0	3.1	5.3	40	25	5.6
<i>p</i> -CH ₃ C ₆ H ₄ C(CH ₃) ₃	2.1	2.8	2.6	4.1	30		
<i>p</i> -CH ₃ C ₆ H ₄ C ₆ H ₅ ^d	1.6	2.2	1.9	3.7	25		
<i>p</i> -CH ₃ C ₆ H ₄ Cl ^d	2.3	2.7	2.1	4.4	30	16.5	5.9
<i>p</i> -CH ₃ C ₆ H ₄ Br	2.4	2.6	2.2	4.1	30		
<i>p</i> -CH ₃ C ₆ H ₄ OCH ₃	1.9	3.0	2.1	3.4	20		
<i>p</i> -CH ₃ C ₆ H ₄ COCH ₃	4.1	3.6	3.1	1.6			
(<i>p</i> -CH ₃ C ₆ H ₄ CO) ₂	4.9	4.6	3.8	1.7			
7-C ₆ H ₅ NBD ^g	2.3	2.7	2.3	3.4	(20)		
7-(CH ₃) ₃ CONBD	2.1	2.6	2.9	5.6	45		
7-CH ₃ COONBD	2.3	2.6	2.1	2.6			
7-C ₆ H ₅ COONBD	2.3	2.5	1.7	2.0			
C ₆ H ₅ C(CH ₃) ₃	2.6	3.2	3.3	5.7	45	18.5	6.9
C ₆ H ₅ CHClCH ₂ CH ₃	2.5	3.0	3.7	7.0	60		
2,5-(CH ₃) ₂ C ₆ H ₃ CHO	2.8	3.2	3.1	4.6	35		
Tetralin	2.3	2.9	3.1	6.6	55		
5-Methylene-2-norbornene	2.4	2.6	2.6	5.2	40		

^a Based on sum of m/e 39, 41, 50, 51, 63, 74, 75, 76, and 77 = 100%. ^b Ionizing electron energy. ^{c,d} See Table I. ^e CHT \equiv cycloheptatriene. ^f Salt, pyrolyzed. ^g NBD \equiv norbornadiene.

norbornadiene, $[C_6H_5^+]$ is unaffected by electron energy. On an energetic basis (lowest heat of formation) 2 should be the most favorable alternative product; further, as will be shown, 3, 4, and 9 give lower abundances for m/e 77 in their CA spectra. We thus conclude that an appreciable fraction of the $C_7H_7^+$ ions formed from cycloheptatriene derivatives have the benzyl structure.

Scheme 1



The relative proportions of **1** and **2** in the $C_7H_7^+$ ions can be estimated using CA spectral abundances for m/e 77 of $1.5 \pm 1.0\%$ ²⁰ for pure **1** and $10.5 \pm 1.0\%$ for pure **2** (based on the low voltage data for $C_7H_7^+$ from $C_6H_5CH_2CH_2C_6H_5$); these choices are also justifiable by the consistency of the results discussed later. On this basis the benzyl ion content at 70 eV and low voltages, respectively, are for $C_7H_7^+$ ions from **5a** 24 ± 10 and $44 \pm 10\%$, and from $C_6H_5CH_2CH_2C_6H_5$ 63 ± 10 and $91 \pm 10\%$ (11.5 eV); note the similarity of the latter values to those for the labeling data of $C_6H_5CD_2^+$ ions from $C_6H_6CD_2CD_2C_6H_5$.

The conclusion that nearly equivalent proportions of benzyl and tropylium ions are formed from toluene and from the cycloheptatriene compounds at threshold ionizing energies apparently has not been anticipated in previous studies.³⁻⁶ The benzyl ions cannot arise by equilibration after formation of the low energy $C_7H_7^+$ ions because of the high energy requirement for **2** \rightarrow **1** shown above; however, equilibration of the $C_7H_8^+$ molecular ions prior to decomposition will account for the data. Because of the equivalent heats of formation of the products of **5a** \rightarrow **1** + $H\cdot$, and **6a** \rightarrow **2** + $H\cdot$, approximately equal abundances for **1** and **2** should actually be expected for threshold energy decompositions, if these decompositions are slow in comparison to the equilibration **5a** \rightleftharpoons **6a**. Although $E_a(\mathbf{5a} \rightarrow \mathbf{6a}) \ll E_a(\mathbf{6a} \rightarrow \mathbf{5a})$, so that at equilibrium $[\mathbf{6a}] \gg [\mathbf{5a}]$, the densities of states of the reactants and activated complexes for the competing decompositions should be similar, predicting²¹ equivalent rates of formation of **1** and **2** from a rapidly equilibrating mixture of **5a** and **6a** of energies near the decomposition threshold.²² This

(20) Because a sizable quantity of **2** is present at 13 eV, an appreciable amount must be formed at 70 eV, so $[m/e\ 77] \ll 3.6\%$ for pure **1** ions. Because of the similarity in the CA spectra of the isomeric $C_7H_7^+$ ions, it seems reasonable that $[m/e\ 77] > 0$.

(21) P. F. Bente, III, manuscript in preparation; we are indebted to Dr. Bente (Cornell University) for communicating these results in advance of publication.

agrees with the $[2]/[1]$ values near unity calculated for the low energy CA spectra of **5a** and **6a**.

The decrease in $[2]/[1]$ with increasing $C_7H_8^+$ internal energy is consistent with the looser activated complex expected for **5a** \rightarrow **1** than for **6a** \rightarrow **2**.²³ The close similarity of the 70 eV CA spectra of **5a** and **6a** is consistent with the high degree of scrambling (92 and 90%, respectively) preceding decomposition.⁹ Supporting this, the CA spectra in the C_6 region for $C_7H_5D_2^+$ ions from $C_6H_5CD_3$ and from $C_6H_5CD_2C_6H_5$, and $C_7H_2D_5^+$ from $C_6D_5CH_3$ indicate complete scrambling within relatively large uncertainties; further, for the CA spectrum of $C_7H_2D_5^+$ ions from $C_6D_5CH_3$ the m/e 79:80:81 abundances at 16.5 eV (35:43:22) are the same as those at 70 eV (33:44:23) within experimental error. The reduced scrambling for higher internal energy $C_7H_8^+$ ions is expected because the possible isomerization reactions,⁹ including **5a** \rightarrow **6a** and **6a** \rightarrow **5a**, have much tighter activated complexes than either **5a** \rightarrow **1** or **6a** \rightarrow **2**. However, the higher energy $C_7H_7^+$ ions equilibrate sufficiently rapidly so that **5a** and **6a** again produce nearly the same proportion of **1** and **2**.

This general scheme also provides a rationale for the strikingly similar behavior of the other cycloheptatriene derivatives. Although *n*-butylcycloheptatriene might be expected to show a lower E_a value for tropylium ion formation than does **5a**, isomerization apparently is still competitive with $H\cdot$ loss; **5** \rightarrow **5'** \rightarrow $CH_3C_6H_4CH_2C_6H_7^+$ (**7**) is indicated by the formation of $C_8H_9^+$ as the fragment ion of second highest abundance ($C_7H_7^+$, the most abundant, should be formed by

(22) Thus the fact that $E_a(\mathbf{5a} \rightarrow \mathbf{1}) \ll E_a(\mathbf{6a} \rightarrow \mathbf{2})$, which at low energies means $k(\mathbf{5a} \rightarrow \mathbf{1}) \ll k(\mathbf{6a} \rightarrow \mathbf{2})$, offsets the fact that $[\mathbf{5a}] \ll [\mathbf{6a}]$ at equilibrium.²¹

(23) As shown for the analogous benzylic cleavage of 1,2-diphenylethane,^{10c} formation of the activated complex for **6a** \rightarrow **2**, $C_6H_5\cdots CH_2\cdots H$, should involve an increase in the bond order of the ring-methylene bond, lowering the number of free rotors of the activated complex in comparison to that for the allylic C-H bond cleavage in **5a** \rightarrow **1**.

5 \rightarrow 1 and 5 \rightarrow 6 \rightarrow 2). Although addition of the *n*-butyl group should also lower E_a (6 \rightarrow 2), the value of [2]/[1] at low electron energies is not as large as for 5a and 6a, consistent with the competition of 5 \rightarrow 5' \rightarrow 7 with 5 \rightarrow 6. Nibbering²⁴ has demonstrated that similar isomerizations are facile for 7-methyl-*d*₃-cycloheptatriene especially at low energies (Table III). Thus

Table III. Isotopic Scrambling Accompanying Methyl Loss from *p*-Xylene- α -*d*₃ and 7-Methyl-*d*₃-cycloheptatriene

Compd, ionization conditions	CD ₃ <i>m/e</i> 91	CHD ₂ 92	CH ₂ D 93	CH ₃ 94
<i>p</i> -Xylene- α - <i>d</i> ₃				
70 eV	33	15	12	40
12 eV	30	18	16	36
MI ^a	7	21	38	35
7-Methyl- <i>d</i> ₃ -CHT ^b				
70 eV	79	5	4	12
15 eV	64	9	8	19
MI ^c	~55	~11	~14	~20
Complete scrambling	1	18	53	29

^a Metastable ion spectrum, reversed geometry instrument. ^b Data of ref 24. ^c Metastable decompositions in the second drift region. ^d Calculated values assuming no isotope effects.

preparation of pure tropylium ions has not been possible here because none of the derivatives used apparently speed up 5 \rightarrow 1 sufficiently relative to competing pathways such as 5 \rightarrow 6 \rightarrow 2.²⁵

C₇H₇⁺ Ions from Benzyl Compounds. Scheme I also rationalizes the variety of [2]/[1] values observed for C₇H₇⁺ ions from benzylic precursors, with 1 formed either by rearrangement of the low energy molecular ions, 6 \rightarrow 5, or of the higher energy C₇H₇⁺ ions, 2 \rightarrow 1. For C₆H₅CH₂X compounds such as X = I, CH₂CH=CH₂, CH₂C₆H₅, and OC₆H₅, E_a (6 \rightarrow 2) is lowered so that loss of X is favored over the rearrangement 6 \rightarrow 5 even at low energies (note for the latter two compounds that this is the conclusion reached previously from substituent effect studies¹⁰). The formation of nearly all 2 at low electron energies must thus be due to the elimination of the isomerization pathway 2 \rightarrow 1. In general, E_a (6 \rightarrow 2) should decrease with increased stability of the radical product and with lower relative dissociation energies for the C-X bond. With rearrangement 6 \rightarrow 5 eliminated, the proportions of 1 and 2 will still depend on the distribution of internal energy values, $P(E)$, of the molecular ions, as these will determine the $P(E)$ of the 2 ions formed, and thus affect their tendency to rearrange to 1. By analogy to the behavior of C₆H₅CH₂CH₂C₆H₅⁺, the rearrangement 6 \rightarrow 5 should be eliminated in C₆H₅CH₂CH₂C₆H₄-*p*-NH₂⁺ and C₆H₅CH₂CH(OH)C₆H₅⁺. The much higher proportion of 1 in their C₇H₇⁺ ions suggests that these are of much higher average energy on formation, which is consistent with the appearance potential (15 eV for C₆H₅CH₂CH₂C₆H₄-*p*-NH₂^{10a}) caused by the competing formation of the more stable substituted benzyl ions. This conclusion is confirmed by the dramatic increase of the proportion of 2 in the C₇H₇⁺ ions from C₆H₅-

(24) A. Venema, N. M. M. Nibbering, and Th. J. de Boer, *Tetrahedron Lett.*, 2141 (1971).

(25) As discussed above, 5 \rightarrow 1 should be more favored over 5 \rightarrow 6 \rightarrow 2 at higher energies; thus a cycloheptatriene derivative with a more favorable low-energy pathway to some other ion could still allow 5 \rightarrow 1 at higher energies to give more pure 1 ions; compare the behavior of C₆H₅CH₂CH₂C₆H₄-*p*-NH₂ discussed below.

CH₂CH₂C₆H₅-*p*-NH₂ on lowering the electron energy; this proportion is still less than that from C₆H₅CH₂-CH₂C₆H₅ at the same electron energy, consistent with the lower average energy expected for C₇H₇⁺ ions from the latter compound. The much smaller increase in [2] with the decreasing electron energy for compounds such as C₆H₅CH₂C₃H₇ and C₆H₅CH₂C₆H₅, as well as 5a and 6a, is probably due to major formation of 1 through low energy isomerization pathways such as 6 \rightarrow 5.

The data for C₆H₅CH₂CH(OH)C₆H₅ show that the high energy equilibration 2 \rightarrow 1 substantially favors 1, [1]/[2] \geq 3.²⁶ Since the heats of formation of 1 and 2 are nearly equivalent, this suggests that there is a significant difference in the density of states of 1 and 2 ions.²¹

For the alkylbenzenes the bond dissociation energy for C₆H₅CH₂R should decrease substantially from R = H to R = CH₃, and from R = CH₃ to R = C₂H₅, consistent with the increasing 2 content in C₇H₇⁺ from these compounds. Further increases in the size of R (10) produces an increasing abundance of methylene-cyclohexadiene C₇H₈⁺ ions (11a) from rearrangement,²⁷ but no significant increase in [2]; the decomposition 11a \rightarrow 2 apparently is not important, consistent with previous conclusions.^{4,27}

Kinetic Energy Release Data. This mechanistic picture is not supported, however, by the recent study of Cooks and coworkers on the structure of C₇H₇⁺ ions undergoing metastable loss of C₂H₂.⁸ The kinetic energy released during decomposition was found to vary for C₇H₇⁺ ions from different sources; from these results the implication was drawn that 5a and 6a gave mainly 1 ions; that C₆H₅CH₂OCH₃, C₆H₅CH₂C₃H₇, and C₆H₅CH₂Cl gave mainly 2 ions; and that tropylium methyl ether and *o*-, *m*-, and *p*-CH₃C₆H₄OCH₃ gave a mixture of 1 and 2.⁸ Such C₇H₇⁺ ions undergoing metastable decomposition should have internal energies of \sim 100 kcal (Figure 2), the upper limit of energies of the C₇H₇⁺ ions studied here by CA. From our conclusions above, ions of this energy prepared as either 1 or 2 should rapidly equilibrate, and so should lose C₂H₂ from the same structure or mixture of structures, independent of the identity of the original molecular ion. This is supported by the complete scrambling of isotopic labels that have been observed for C₇H₇⁺ ions from most sources studied. Reported exceptions involve C₇H₇⁺ ions from C₆H₅CH₂C₆H₅⁵ and C₆H₅CH₂-COOCH₂C₆H₅.^{7,28} To characterize further C₇H₇⁺ ions of internal energies equivalent to those studied by Cooks,⁸ we have measured the isotopic distribution of the products from the metastable loss of C₂H₂ from C₇H₇⁺ formed from a variety of labeled precursors (Table IV) using the reversed geometry instrument.¹⁴ The data indicate a small (\sim 5%) isotope effect favoring the loss of C₂H₂; with this, the results show essentially

(26) This is consistent with the conclusion that 5a gives \sim 75% 1 at 70 eV, despite the fact that low energy 5a ions isomerize to 6a, while the maximum [2] in C₇H₇⁺ ions at 70 eV is \sim 65% when the low-energy isomerization of the molecular ions is negligible.

(27) K. Levsen, F. W. McLafferty, and D. M. Jerina, *J. Amer. Chem. Soc.*, **95**, 6332 (1973); for R = C₂H₅, C₃H₇, CH(CH₃)₂, and C₃H₇ the [C₇H₈⁺]/[C₇H₇⁺] values in the 70 eV mass spectrum are 0.04, 0.63, 0.52, and 1.1, respectively.

(28) Although the (¹²C,¹³C)₅H₅⁺ ions from norbornadiene-2,3-¹³C are not completely scrambled, this probably arises by C₇H₈⁺ \rightarrow C₅H₅⁺ \rightarrow C₃H₃⁺; R. A. Davidson and P. S. Skell, *J. Amer. Chem. Soc.*, **95**, 6843 (1973).

Table IV. Metastable Decompositions of Labeled $C_7H_7^+$ Ions

Compound	Precursor	$C_6(H,D)_6^+$ products, % ^a		
		$-C_2D_2$	$-C_2HD$	$-C_2H_2$
Toluene- α - d_3	$C_7H_5D_2^+$	4.9 (4.8) ^b	44.8 (47.6)	50.2 (47.6)
	$C_7H_4D_3^+$	14.2 (14.3)	54.8 (57.1)	31.1 (28.6)
Toluene-ring- d_5	$C_7H_3D_4^+$	27.2 (28.6)	56.6 (57.1)	16.2 (14.3)
	$C_7H_2D_5^+$	45.1 (47.6)	48.9 (47.6)	6.0 (4.8)
<i>p</i> -Xylene- α - d_3	$C_7H_4D_3^+$	15.4 (14.3)	55.4 (57.1)	29.2 (28.6)
1,2-Diphenylethane- α - d_4	$C_7H_5D_2^+$	5.0 (4.8)	45.7 (47.6)	49.2 (47.6) ^d
<i>p</i> -Nitrotoluene- α - d_3	$C_7H_4D_3^+$	13.1 (14.3)	56.6 (57.1)	30.3 (28.6)
<i>p</i> -Nitrotoluene-ring- d_4	$C_7H_3D_4^+$	26.7 (28.6)	57.5 (57.1)	15.8 (14.3)
<i>o</i> -Nitrotoluene-ring- d_4	$C_7H_3D_4^+$	27.3 (28.6)	57.6 (57.1)	15.1 (14.3)
<i>tert</i> -Butylbenzene- β - d_3	$C_7H_6D^+$		30.0 (28.6)	70.0 (71.4)
Diphenylmethane- α - d_2	$C_7H_5D_2^+$	5.0 (4.8)	45.4 (47.6)	49.4 (47.6)
	$C_7H_5D_2^{+c}$			56.2 (47.6) ^d
	$C_7H_5D_2^{+e}$			51.9 (47.6)

^a Relative reproducibility generally better than $\pm 5\%$ except for low abundance peaks. ^b Values in parentheses are results calculated assuming complete scrambling and no isotope effects. ^c Data of ref 5 for $C_6H_5D_2^+$ ions in the normal mass spectrum based on 87.2% label retention of $C_6(H,D)_7^+$ species and $[C_6H_5^+]$ in the mass spectrum of the unlabeled compound. ^d Value is 57.1% when calculated assuming formation of tropylium-1,2- d_2 ions. ^e Data for normal ions determined in this study calculated as described in footnote c.

complete scrambling in the variety of precursors studied, and support the mechanism postulated above involving rapid equilibration among isomeric $C_7H_7^+$ ions with such internal energies.²⁹ We conclude that the differences in values of kinetic energy release observed by Cooks⁸ for $C_7H_7^+$ ion from different precursors are *not due to differences in structure*, but are due to different distributions of the internal energy values of the $C_7H_7^+$ ions undergoing decomposition. Thus the use of kinetic energy release values³⁰ for the determination of ion structures appears to be subject to the same ambiguities^{18,31} as the use of other metastable ion characteristics.³⁰

Tolyl Ions. The CA spectral data (Figure 1, Tables I and II) indicate that the $C_7H_7^+$ ions from *m*- and *p*- $CH_3C_6H_4X$ compounds, where $X = NO_2, I, COCH_3, COC_6H_5, COC_6H_4CH_3,$ and $COOCH_3$, contain a substantial proportion of ions of structures other than **1** or **2**; presumably these are *m*- and/or *p*-tolyl ions (**9**). The spectra of these ions also are distinguishable from those of the $C_7H_7^+$ ions, presumably of the *o*-tolyl structure (**3**), from *o*- $CH_3C_6H_4X$, where $X = NO_2, I, COCH_3, COC_6H_5,$ and $COOCH_3$ (note $[m/e 74]/[m/e 75]$ and $[m/e 76]/[m/e 77]$). The $m/e 77$ abundance shows that the proportion of **2** in these $C_7H_7^+$ ions containing **3** and **9** is small ($\ll 20\%$); for the meta and para precursors the $m/e 74$ (and, less clearly, $m/e 75$) abundance shows that some isomer besides **1** must be present (see also Figure 1). That the fraction of **1** must be small, and that **3** and **9** are not substantially equilibrated, are demonstrated by the CA spectra of the $C_7H_3D_4^+$ ions from *o*- and *p*- $NO_2C_6D_4CH_3$ (Table V). No interchange of ring and α hydrogens apparently takes place before decomposition for a major portion of the *o*- $CH_3C_6D_4^+$ ions undergoing CH_2 loss, and of the *p*- $CH_3C_6D_4^+$ ions undergoing both CH_2 and CH_3 loss;³²

(29) Our values for the normal (ion source formation) $C_6(H,D)_6^+$ ions from $C_6H_5CD_2C_6H_5$ are somewhat lower than those reported by Meyerson⁵ (Table IV) but do not eliminate the possibility of a substantial proportion of tropylium-1,2- d_2 in the precursor ions. The CA results on $C_6H_5CH_2COOCH_2C_6H_5$ do call into question the labeling studies on this compound,⁷ for which corrections apparently were not made for the contributions of $C_6(H,D)_6^+$ and $C_6(H,D)_4^+$ to the $[C_6(H,D)_6^+]$ values; high-resolution measurements would be appropriate.

(30) T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5021 (1966).

(31) J. Occolowitz, *J. Amer. Chem. Soc.*, **91**, 5202 (1969).

(32) Although interpretation is more difficult than for the labeled **2** ions due to the isobaric multiplets arising from the similar relative

Table V. Partial CA Spectra of $C_7H_3D_4^+$ Ions from *o*- and *p*-Nitrotoluene-ring- d_4

m/e	$-\% \Sigma(m/e 75-81)^a$			
	Ortho	Random ^b	Para	Random ^b
75	18	18	11	22
76	20	20	23	21
77	15	18	14	18
78	12	15	15	16
79	9	14	8	13
80	12	12	19	8
81	14	2	10	2

^a Not corrected for overlapping peaks due to variable peak widths and poor resolution. ^b Calculated from the corresponding $C_7H_7^+$ spectra assuming complete randomization of H-D before decomposition of the $C_7H_3D_4^+$ ions.

it is difficult to envision a mechanism for these losses from **1** which would not show nearly complete scrambling. Note that a logical intermediate for the loss of CH_2 from decomposing *o*- and *p*- $CH_3C_6D_4^+$ is the benzyl ion.

The surprising stability of the tolyl ions with respect to isomerization to **1** or **2** is further underscored by the relatively high internal energies of some of these ions. Apparent heats of formation (Table VI) for the $C_7H_7^+$

Table VI. Apparent Heats of Formation of $C_7H_7^+$ Ions from Tolyl Precursors

Precursor	A, eV^a	Lit.	$\Delta H_f(C_7H_7^+),$ kcal/mol ^b
<i>p</i> -Methylacetophenone	13.8		285
<i>o</i> -Nitrotoluene	13.1		305
<i>m</i> -Nitrotoluene	12.1		280
<i>p</i> -Nitrotoluene	12.3		285
<i>p</i> -Chlorotoluene	11.5	11.7 ^c	240
<i>p</i> -Bromotoluene	11.1	11.4 ^c	245
<i>m</i> -Iodotoluene	11.0	11.3 ^c	260
<i>p</i> -Phenyltoluene	13.7		275
<i>p</i> -Xylene	11.5	11.6 ^d	235

^a Appearance potential, $\pm 0.3 eV$. ^b Calculated from $A(C_7H_7^+)$ and values in ref 17. ^c Reference 11. ^d Reference 17.

abundances of the unlabeled peaks, the data for the labeled **3** ions can be rationalized by assuming that approximately one-third of $C_6(H,D)_6^+$, two-thirds of $C_6(H,D)_4^+$, and all of $C_6(H,D)_3^+$ and $C_6(H,D)_2^+$ ions are scrambled before or during decomposition, and the data for labeled **9** by assuming one-third of $C_6(H,D)_6^+$ and $C_6(H,D)_4^+$ and two-thirds of the other ions are scrambled.

ions from $\text{CH}_3\text{C}_6\text{H}_4\text{X}$ for $\text{X} = p\text{-CH}_3\text{CO}$, o -, m -, and $p\text{-NO}_2$, and $m\text{-I}$ indicate that a major portion of these ions correspond energetically to the **1** and **2** ions which were shown above to undergo rapid equilibration. Although the reactions **3** or **9** \rightarrow **1** or **2** should be exothermic, apparently they have lower rate constants (to give products of equivalent internal energy) than $\mathbf{1} \rightleftharpoons \mathbf{2}$ (Figure 2). Several tolyl precursors that instead produce **1** and **2** ions, such as $\text{X} = p\text{-Cl}$, $p\text{-Br}$, and CH_3 , actually show lower apparent heats of formation for C_7H_7^+ (Table VI), implying that in these cases rearrangement must occur before C_7H_7^+ formation such as by the isomerization of **7** or $\mathbf{7}' \rightarrow \mathbf{5}$, **6**, or **11**. For the chlorotoluenes Williams has previously postulated¹¹ that ring expansion to **5** precedes loss of chlorine. For the meta and para isomers in which the CA m/e 77 shows the formation of appreciable quantities of **2**, the CA m/e 74 indicates that most of the balance of the C_7H_7^+ are not **9**, and so presumably are **1**. However, the $\text{CH}_3\text{C}_6\text{H}_4\text{X}^{\cdot+}$ isomerization must involve the formation of a **2** precursor, as lowering the electron energy (Tables I and II) generally increases [**2**]; $\sim 75\%$ of C_7H_7^+ from $o\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_3$ at 16.5 eV have structure **2**.³³ If the **3** and **9** ions had isomerized initially to **1**, there should be an increase in the proportion of **1** on lowering the electron energy, as this decreases the high energy ions which undergo the equilibration $\mathbf{1} \rightleftharpoons \mathbf{2}$. Further, this equilibration gives [**2**] $\leq 25\%$ (*vide supra*), so that additional **2** had to be formed to account for many of the data.

In considering a mechanism for benzyl ion formation through initial isomerization of the $\text{CH}_3\text{C}_6\text{H}_4\text{X}$ molecular ions, the direct migration of the ring substituent to the α position is not intuitively appealing because concomitant displacement of an α hydrogen would be involved. A possible alternative involves isomerization to a methylenecyclohexadiene isomer, $\mathbf{7} \rightarrow \mathbf{11}$; loss of X from **11** would also produce **2** directly. A lower isomerization proclivity for **11** ions is indicated by the observation that high energy **11** ions (those with sufficient energy to form C_7H_7^+ ions which undergo metastable decomposition to C_5H_5^+) are $\sim 56\%$ scrambled, compared to 88 and 78% for analogous **1** and **2** ions, respectively.²⁷ The possibility that other $\text{C}_7\text{H}_7\text{X}^{\cdot+}$ isomers serve as intermediates in the formation of **2** from **7** cannot be discarded, however.

Pathways in addition to $\mathbf{2} \rightleftharpoons \mathbf{1}$ must also be operative for tropylium ion formation from **7**. Several compounds giving C_7H_7^+ ions with relatively low values for the apparent heat of formation of C_7H_7^+ (Table VI) give high proportions of **1**, showing that **1** must be formed directly from $\text{C}_7\text{H}_7\text{X}^{\cdot+}$ (presumably **5**). Note that the isomerization $\mathbf{7}$ or $\mathbf{7}' \rightarrow \mathbf{5}'$ is directly analogous to the toluene isomerization $\mathbf{6a} \rightarrow \mathbf{5a}$ (identical with it for $\text{X} = \text{H}$) shown to be facile for low energy **6a** ions. Harrison has given strong evidence for such a mechanism for methylethylbenzene ($\text{X} = \text{C}_2\text{H}_5$),³⁴ while

(33) The values for the proportion of benzyl ions can be checked by measurements of a labeled compound similar to those of $\text{C}_6\text{H}_5\text{CD}_2\text{-CD}_2\text{C}_6\text{H}_5$ above. Using this procedure the $\text{C}_7\text{H}_4\text{D}_3^+$ ions from $p\text{-CH}_3\text{C}_6\text{H}_4\text{CD}_3$ give a CA spectrum consistent with 45% of the ions losing CD_2 without scrambling, which compares favorably with the value of 40% found for C_7H_7^+ from $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$ based on [m/e 77]. However, a similar determination on the $\text{C}_7\text{H}_4\text{D}_3^+$ ions produced at 16.5 eV electron energy corresponds to 50% unscrambled ions, a smaller increase than that reflected by the 60% value based on [m/e 77]. Isotopic scrambling by pathways such as $\mathbf{7}' \rightleftharpoons \mathbf{5}'$ at low energies would explain this discrepancy.

Meyerson³⁵ found for p -xylene- $\alpha\text{-d}$ -, $-\alpha, \alpha\text{-d}_2$ -, $o\text{-d}$ -, and $-\alpha\text{-}^{13}\text{C}$ that isotopic scrambling accompanies loss of methyl. We examined this same system using p -xylene- $\alpha\text{-d}_3$; data at 70 and 12 eV electron energy and metastable ion decompositions, compared in Table IV to those of Nibbering for 7-methyl- d_3 -cycloheptatriene, are at least consistent with a substantial portion of common isomerization pathways for $\mathbf{7}'$ and **5** when $\text{X} = \text{CD}_3$. Scrambling increases in both systems with decreasing ion internal energy. Although the 66% ($2 \times 33\%$) fraction of unscrambled ions from the former compound is less than the 79% fraction from the latter, the proportion of benzyl ions indicated by the CA m/e 77 peak is larger for the xylene precursor (40%:25%), again consistent with the initial isomerization $\mathbf{7}' \rightarrow \mathbf{11}'$ for a substantial fraction of the $\text{CH}_3\text{-C}_6\text{H}_4\text{X}$ ions. Further, an even higher fraction (50%) of **2** ions is formed by the loss of CD_3 from $p\text{-CH}_3\text{C}_6\text{-H}_4\text{CD}_3$; $\text{C}_8\text{H}_7\text{D}_3^{\cdot+}$ ions undergoing CD_3 loss should arise mainly from $\mathbf{7}'$ ions that have isomerized to $\mathbf{11}'$ without isomerization to $\mathbf{5}'$. Evidence was presented above that the equilibrium $\mathbf{5a} \rightleftharpoons \mathbf{6a}$ should substantially favor **6a**; by analogy in many cases $\mathbf{5}' \rightleftharpoons \mathbf{7}'$ should favor $\mathbf{7}'$, especially at low ion energies. At least this provides a rationalization for the observations that lowering the electron energy increases both the proportion of benzyl ions (Table II) and the scrambling (Table IV), by further favoring of reaction $\mathbf{5}' \rightarrow \mathbf{7}'$ over $\mathbf{5}' \rightarrow \mathbf{5}$. Lowering the electron energy should also lower the importance of reaction $\mathbf{2} \rightarrow \mathbf{1}$ (*vide supra*).

There remains the question of the favored formation of the stable tolyl ions by the loss of NO_2 , **1**, COC_6H_5 , $\text{COC}_6\text{H}_4\text{CH}_3$, and COOCH_3 groups, which are the most weakly bonded and/or strongly electron withdrawing of the substituents examined. Not only should this lower E_a ($\mathbf{7}$ or $\mathbf{7}' \rightarrow \mathbf{3}$ or **4**), but some of these substituents could also increase E_a ($\mathbf{7}$ or $\mathbf{7}' \rightarrow \mathbf{5}$ or $\mathbf{5}'$) and E_a ($\mathbf{7}$ or $\mathbf{7}' \rightarrow \mathbf{11}$ or $\mathbf{11}'$). The relatively high appearance potentials for some of these C_7H_7^+ ions (Table VI) indicate that the latter effect can be important.

Previous Tolyl Ion Identifications. Characteristics of the metastable decompositions of C_7H_7^+ ions ($\text{C}_7\text{H}_7^+ \rightarrow \text{C}_5\text{H}_5^+$) from $p\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2$ have been used as evidence for the formation of **9**.¹² Although the CA data (Table I) indicate that the stable C_7H_7^+ ions from this compound indeed have this structure, the complete scrambling found to accompany this metastable decomposition for both $p\text{-CD}_3\text{C}_6\text{H}_4\text{NO}_2$ and $p\text{-CH}_3\text{C}_6\text{-D}_4\text{NO}_2$ (Table III) again indicates that the differing metastable characteristics observed are due to differences in internal energies of the C_7H_7^+ ions, and not to the presence of a major fraction of **9**.

Appearance potential data have been used as evidence that chlorotoluenes, but not bromo- and iodotoluenes undergo molecular ion isomerization (such as $\mathbf{7} \rightarrow \mathbf{5}$) prior to loss of halogen;¹¹ this is consistent with our results for the chloro- and iodotoluenes but not the bromotoluenes. Such appearance potential studies should only be indicative of the processes producing the lowest energy C_7H_7^+ ions, while the CA spectra should be characteristic of stable C_7H_7^+ ions over their whole range of possible internal energies. However, this is

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probably not the cause of the discrepancy, as higher energy $\text{CH}_3\text{C}_6\text{H}_4\text{Br}^+$ ions should have even less tendency to undergo the tight-complex isomerization reaction than the loose complex $\text{CH}_3\text{C}_6\text{H}_4\text{Br}^{\cdot+}$ reaction. It would appear that the energy requirements for the reactions 7 or $7' \rightarrow 5 \rightarrow 1$ and 7 or $7' \rightarrow 11$ or $11' \rightarrow 2$ are higher than that for $6 \rightarrow 2$, but still lower than that for 7 or $7' \rightarrow 3$ or 9 .

Norbornadienyl Ions. The CA spectra of C_7H_7^+ ions from 7-acetoxy- and, especially, 7-benzyloxynorbornadiene also appear to be distinctive, although the dif-

ferences are less pronounced. The CA m/e 74 peak is smaller than that found for the tolyl ions, and the m/e 77 peak is smaller than in the CA spectra of **1** and **2**; we conclude that a major portion of the C_7H_7^+ ions have the norbornadienyl structure, **4**. Norbornadiene and the other derivatives studied give C_7H_7^+ CA spectra indicating that appreciable quantities of **2** ions are formed, although the remaining C_7H_7^+ ions could be **1** and/or **4**. Labeling experiments of Skell²⁸ show that the norbornadiene cation can undergo a specific elimination of C_2H_2 .

1-Phosphabicyclo[2.2.1]heptane 1-Oxide and 1-Phosphabicyclo[2.2.2]octane 1-Oxide. Syntheses and Some Properties Relative to Their Monocyclic and Acyclic Analogs¹

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Abstract: 1-Phosphabicyclo[2.2.1]heptane 1-oxide (**1**) was prepared in 11% yield by Grignard cyclization of diethyl 5-bromo-3-bromoethylpentylphosphonate (**13**) in refluxing tetrahydrofuran. In an analogous fashion, 1-phosphabicyclo[2.2.2]octane 1-oxide (**2**) was prepared in 6% yield. The sublimable solids were characterized by elemental analyses, mass spectral fragmentation patterns, and by both proton and carbon-13 nmr spectroscopy. The proton nmr spectra at 60 MHz of both **1** and **2** were resolved using the shift reagent tris(dipivalomethanato)-europium(III). The lanthanide-induced shifts for the α protons of **1** and **2** are discussed with respect to the corresponding shifts of various acyclic and monocyclic phosphine oxide analogs. The $J_{\text{P-}^1\text{H}}$ coupling constant to the proton on the bridgehead carbon of **1** was unusually large (28 Hz). In the proton-decoupled ^{13}C nmr spectra of **1** and **2** each of the different types of carbons appeared as doublets due to coupling to phosphorus. The $J_{\text{P-}^{13}\text{C}}$ values for coupling between bridgehead atoms in **1** and **2** were 35 and 47 Hz, respectively, the unusually large magnitudes of which suggest a Karplus relationship for correlation of $J_{\text{P-}^{13}\text{C}}$ values. The infrared spectra of **1**, **2**, and an isoelectronic series of acyclic and monocyclic phosphine oxides were determined at various percentages of ^{18}O enrichment. The natural abundance spectra of **1** and 1-ethyl-2,2,3-trimethylphosphetane 1-oxide (**3**) showed multiple bands attributable to the phosphoryl stretch, presumably due to Fermi resonance. The phosphoryl-stretching frequencies of this group of compounds, as well as of other phosphine oxides reported in the literature, indicate a correlation between ring strain and phosphoryl bond energy.

Studies on bicyclic compounds with carbon at the bridgehead position have led to useful generalizations^{3,4} about geometrical requirements for certain reactions involving carbon. Similar studies have been carried out with bicyclic compounds having silicon⁵ and sulfur⁶ at the bridgehead position. Since phosphorus, like silicon and sulfur, is a second row element which can utilize d orbitals to form pentavalent compounds⁷ and intermediates^{8,9} with trigonal-bipyramidal struc-

tures, we anticipated that by constraining the geometry of the substituents around phosphorus certain modes of reactivity and spectral properties characteristic of monocyclic and acyclic analogs might be altered for the corresponding bicyclic compounds. Moreover, as discussed in an accompanying paper,¹⁰ we anticipated that certain recent ideas about geometrical constraints on stereomutation, or positional interchange, of pentavalent intermediates in reactions at phosphorus^{8,9,11} might be testable experimentally.

In this paper we describe the syntheses and some of the spectral properties of 1-phosphabicyclo[2.2.1]heptane 1-oxide (**1**)¹² and 1-phosphabicyclo[2.2.2]octane 1-

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