# The Mechanisms of Decomposition of the 1and 2-Phenyltetralin Radical Cations

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Mechanisms for decomposition of 1- and 2-phenyltetralins were investigated using low resolution mass spectrometry and metastable ion techniques. Four primary decompositions were observed for 1-phenyltetralin radical cations: (1) the loss of  $C_6H_6$  via a 1,4-elimination; (2) the elimination of ethene via competing losses from carbons 3+4 and carbons 2+3; (3) the loss of  $C_8H_8$ , probably through a stepwise Diels-Alder cycloreversion to expel styrene; and (4) the loss of methyl radical involving carbon 2 and possibly carbon 4. Three major decompositions were observed for 2-phenyltetralin radical cations: (1) the loss of C<sub>8</sub>H<sub>8</sub>, possibly through a Diels-Alder cycloreversion to expel styrene; (2) the loss of  $C_6H_6$  via a 1,3 elimination; and (3) the loss of methyl radical from carbon 1. Various exchange reactions occur prior to these losses, but they proved to be incomplete even for metastable ions.

We have investigated the losses of  $C_6H_6$ ,  $C_8H_8$ , ethene and methyl radical from the 1-phenyltetralin radical cation, and the losses of C8H8, C6H6 and methyl radical from the 2-phenyltetralin radical cation. To probe the mechanisms for these losses and also the mechanisms of hydrogen isomerization prior to these losses, the deuterium labelled 1-phenyltetralins 1-6 and 2-phenyltetralins 7-11 were synthesized and studied by low resolution mass spectrometry and metastable ion techniques.



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Interest in the decomposition pathways of the 1- and 2-phenyltetralin radical cations dates back to work published in 1971 by Wilkins and Gross.<sup>1,2</sup> Using ion cyclotron resonance (ICR) spectrometry, they showed that the styrene radical cation reacts with neutral styrene to give an intermediate complex of m/z 208, which subsequently loses  $C_6H_6$  to give a fragment ion at m/z 130. Based on the evidence available then, they postulated that the collision complex had the structure of 1-phenyltetralin. Lin and Gross,<sup>3</sup> in an ICR study of the reaction of o-quinodimethane radical cation, generated from o-methylbenzyl acetate, with neutral styrene, concluded that the secondary m/z 130 ions arose from an intermediate complex which had the structure of 2-phenyltetralin, consistent with a Diels-Alder cycloaddition.

In more recent studies,<sup>4</sup> the collision complexes were produced and stabilized in the chemical ionization (CI) source of a triple analyzer mass spectrometer, and subsequently characterized by their unimolecular and collisional activation dissociation (CAD) spectra. Comparison of the spectra of the intermediate formed in the styrene ion/molecule reaction, with the spectra of authentic 1-phenyltetralin radical cations established that the collisionally stabilized adduct did not have the structure of 1-phenyltetralin. However, the o-quinodimethane/styrene intermediate does have the structure of 2-phenyltetralin radical cation.

During the course of these investigations, it became necessary to understand the mechanisms of decomposition of the 1- and 2-phenyltetralin radical cations themselves. Furthermore, since deuterium labeling was used to study the ion/molecule reactions, we also needed to understand the mechanisms of H/D exchange prior to fragmentation. Gross and Wilkins<sup>2</sup> have shown that the loss of neutral benzene from the 1-phenyltetralin radical cation is a highly regiospecific 1,4 elimination. However, no work has been published to date on the mechanisms of the losses of C<sub>8</sub>H<sub>8</sub>, ethene and methyl radical from the 1-phenyltetralin radical cation or of any of the decompositions of 2-

Co	mpound/loss	Mass spectrum	V <sup>1/2</sup> /E	MIKES	Compound/loss	Mass spectrum	V <sup>1/2</sup> /E	MIKES
2	$\xrightarrow{-C_6H_6} -C_6H_5D$ $\xrightarrow{-C_6H_4D_2}$	92 6 2	94 3 3	100 0 0	$5 \xrightarrow{-C_6H_6} -C_6H_5D$	3 2 3 10	4 5 8 18	2 5 10 19
3	$ \xrightarrow{-C_6H_6} -C_6H_5D $	89 9 2	92 4 4	<b>100</b> 0 0	$  -C_6H_2D_4 \\ \rightarrow -C_6HD_5 $	25 57	34 31	27 37
4	$\xrightarrow{-C_6H_6} -C_6H_5D$ $\xrightarrow{-C_6H_4D_2}$	0 78 22	7 72 21	14 59 27	$6 \xrightarrow{\rightarrow} -\mathbf{C}_{6}\mathbf{H}_{5}\mathbf{D}$ $6 \xrightarrow{\rightarrow} -\mathbf{C}_{6}\mathbf{H}_{5}\mathbf{D}_{2}$ $\xrightarrow{\rightarrow} -\mathbf{C}_{6}\mathbf{H}_{3}\mathbf{D}_{3}$ $\xrightarrow{\rightarrow} -\mathbf{C}_{6}\mathbf{H}_{2}\mathbf{D}_{4}$		54 23 10 7 6	67 18 9 6 0

Table	1.	Loss	of	C <sub>4</sub> H <sub>2</sub>	from	the	1-nhenvitetralin	radical	cation <sup>18</sup>
		1000	•••	~~~~	WY OTH		T-buen incertain	raura	Cauon

phenyltetralin. The only published analogies are the mechanisms of ethene and methyl losses from the unsubstituted tetralin system,<sup>5.6</sup> and of decompositions of 1- and 2-tetralol and their acetate derivatives.<sup>7-10</sup>

## **RESULTS AND DISCUSSION**

Three instrumental techniques were used to give a semi-quantitative time-resolved view of the decomposition processes. The first technique was normal mass spectrometry in which an integrated view was obtained of those ions with enough energy to decompose by approximately 1  $\mu$ s. The second technique was linked  $V^{1/2}/E$  metastable scanning, whereby the decomposition of ions in the first field free region (1st FFR) between the source and first electric sector were observed. Ions fragmenting in the 1st FFR were sufficiently energetic to fragment in 1–5  $\mu$ s but had too little energy to do so in the source. The third technique was Mass-analyzed ion kinetic energy spectroscopy (MIKES), whereby the fragmentation of the 3rd FFR of ions of even lower average internal energy was observed (10–30  $\mu$ s lifetimes).

### **1-Phenyltetralin**

The 1-phenyltetralin radical cation undergoes four principal decompositions to give fragments with the formulae  $[C_{10}H_{10}]^{++}$ ,  $[C_8H_8]^{++}$ ;  $[C_{14}H_{12}]^{++}$  and  $[C_{15}H_{13}]^{+}$ . Loss of  $C_6H_6$  is the lowest energy process with an activation energy of 0.6 eV, and the losses of  $C_8H_8$ ,  $C_2H_4$  and  $CH_3^{-+}$  are higher energy processes with activation energies of 1.4 eV, 1.4 eV and 1.5 eV, respectively.

Loss of  $C_6H_6$ . Predominantly  $C_6H_6$  was lost from 2, 3 and 6 (refer to Table 1), whereas mostly  $C_6H_5D$  was lost from 4. Thus,  $C_6H_6$  was expelled through a 1,4 elimination in agreement with the earlier study.<sup>2</sup> Furthermore, the hydrogen at C-2 and C-3 were not involved in any hydrogen interchange since 2 and 3 lost exclusively  $C_6H_6$  in the 3rd FFR. Therefore, the small nonzero percentages for loss of  $C_6H_5D$  and  $C_6H_4D_2$  from 2 and 3, as observed in their mass spectra and  $V^{1/2}/E$  spectra, must be due to some competitive 1,2 and 1,3 elimination of benzene from ions of higher internal energies and not to interchange involving the hydrogens on C-2 and C-3. By the same reasoning, we conclude that the hydrogens on C-4 were involved quite extensively in scrambling with the phenyl hydrogens and also with the hydrogens on the fused aromatic ring. Note, for example, that **4** lost not only  $C_6H_5D$  but also  $C_6H_4D_2$  and, at longer observation times,  $C_6H_6$ .

Based on these results, we propose the loss of  $C_6H_6$ from the 1-phenyltetralin radical cation proceeds as the fused cyclohexene ring orients itself in a pseudoboat configuration, a hydrogen on C-4 is transferred to the phenyl ring, and then  $C_6H_6$  is expelled (Scheme 1). In order that two deuteriums be transferred to the phenyl ring in the case of 4, the loss of benzene must be preceded by epimerization of C-1. Furthermore, the hydrogens on C-4 must also be involved in interchange with those on the fused aromatic ring in order for 4 to lose  $C_6H_6$ . The results obtained for 5 and 6 prove that such interchange does indeed occur.

Loss of ethene. We note from Table 2 that 3 lost almost exclusively  $d_2$ -ethene, whereas 2 lost predominantly  $d_0$ -ethene but also a significant amount of  $d_2$ -ethene. These results are in accord with a predominant loss of ethene involving carbons 3+4 in competition with a loss involving carbons 2+3. A competitive elimination of ethene also has been observed

Table 2. Loss of ethene from the 1-phenyl- tetralin radical cation <sup>18</sup>									
Compound/loss	Mass spectrum	V <sup>1/2</sup> /E	MIKES						
$2 \xrightarrow{\rightarrow} -C_2H_4 \\ \xrightarrow{\rightarrow} -C_2H_3D \\ \xrightarrow{\rightarrow} -C_2H_2D_2$	82	75	78						
	4	<8	5						
	14	<15	17						
$3 \xrightarrow{-C_2H_4} -C_2H_3D \\ \xrightarrow{-C_2H_2D_2} -C_2H_2D_2$	1	1	8						
	1	6	1						
	98	93	91						
$ \begin{array}{c} \bullet & -C_2H_4 \\ \bullet & -C_2H_3D \\ \bullet & -C_2H_2D_2 \end{array} $	14	18	38						
	39	55	49						
	47	27	13						



for the tetralin radical cation.<sup>5,6</sup> Unlike the loss from the tetralin radical cation, however, the competitiveness of loss involving carbons 3+4 compared with that involving carbons 2+3 of the 1-phenyltetralin radical cation depends little upon the internal energy of the ions undergoing decomposition. The interchange of the hydrogens on C-4 explains the shift towards more loss of C<sub>2</sub>H<sub>3</sub>D and C<sub>2</sub>H<sub>4</sub> for longer-lived ions of **4**, i.e. those observed in the 3rd FFR. The shift is not due to more effective competition of loss from carbons 2+3for the longer-lived ions since the corresponding percentages for **2**, in which deuteriums do not scramble, remain nearly unchanged in the ms,  $V^{1/2}/E$  and MIKE spectra.

Mechanisms which account for the loss of ethene are depicted in Schemes (2) and (3). Greater than 75% of ethene loss involves carbons 3+4 with the ion undergoing a hydrogen shift, followed by a Diels-Alder cycloreversion to give the  $\alpha$ -substituted styrene ion (Scheme 2). Loss from carbons 2+3 is a direct



Scheme 2

Diels-Alder cycloreversion to give a substituted oquinodimethane ion (Scheme 3). Based upon the stabilities of unsubstituted styrene and o-quinodimethane radical cations,<sup>11</sup> one would in fact predict that the former mechanism would dominate the latter.

Loss of  $C_8H_8$ . Compounds 2 and 3 proved to be particularly useful for unravelling the mechanism for loss of  $C_8H_8$ . Within experimental error, the molecular ions of 2 and 3 decomposing in the source, the 1st FFR and the 3rd FFR showed nearly identical losses of  $C_8H_8$  and  $C_8H_6D_2$  in the ratio 1:1, and showed



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little or no loss of  $C_8H_7D$  (see Table 3). Again, the hydrogens on C-2 and C-3 were not involved in scrambling, which allowed us to see at once that expulsion of  $C_8H_8$  proceeds via an intermediate which fragments to produce both styrene ion and styrene neutral. If this were not the case, retention of the charge by one half of the molecule would surely have been favored over retention by the other; i.e. the ratio for the loss  $C_8H_8:C_8H_6D_2$  would have been other than 1:1.

We postulate that  $C_8H_8$  is expelled as the ionized 1phenyltetralin undergoes a carbon-carbon bond scission and then a hydrogen rearrangement followed by loss of neutral styrene (Scheme 4). The results obtained for 4 and 5 again prove that the hydrogens on carbon 4 and those on the phenyl ring were involved in scrambling, and the symmetric distribution of losses (e.g. for 5 loss of  $C_8H_8 \approx loss$  of  $C_8H_3D_5$ , loss of  $C_8H_7D \approx loss$  of  $C_8H_4D_4$ , etc.) lends added support to the mechanism depicted in Scheme 4.

In addition, we hypothesize that the reaction of the styrene radical cation with neutral styrene<sup>1,4b</sup> is simply the reverse reaction which gives a product ion with structure *b*. Furthermore, since the product, when formed in a CI source, does not isomerize to the 1-phenyltetralin radical cation,<sup>4b</sup> the barrier for the tautomerization of *b* to give *a* must be substantial.

One of the referees suggested an alternative scheme in which the benzyl cation moiety of b isomerizes to a

Table 3. Loss of phenylte	of C <sub>8</sub> H <sub>8</sub> etralin radi	from ical catio	the 1.
Compound/loss	Mass spectrum	V <sup>1/2</sup> /E	MIKES
$2 \xrightarrow{\rightarrow -C_8H_8} -C_8H_7D$	49 <1 50		46 <5 48
$\begin{array}{ccc} & & \rightarrow & -C_8H_8 \\ 3 & & \rightarrow & -C_8H_7D \\ & & \rightarrow & -C_8H_6D_2 \end{array}$	49 3 48	44 <7 49	47 <6 47
$4 \xrightarrow{-C_8H_8}_{-C_8H_6D_2}$	27 50 23	23 50 27	24 52 24
$ \begin{array}{c} \rightarrow -C_8H_8 \\ \rightarrow -C_8H_7D \\ \rightarrow -C_8H_6D_2 \end{array} $ $ \begin{array}{c} 5  \longrightarrow -C_8H_5D_3 \\ \rightarrow -C_8H_4D_4 \\ \qquad $	23 19 8 18 24		8 18 25 24 18 7



tropylium ion and then undergoes either H/D exchange or loss of styrene to give a methylene cycloheptatriene radical cation. We cannot dismiss this mechanism, although it is more difficult to explain the H/D exchange of compounds **4** and **6** in terms of it.

Loss of methyl radical. Loss of unlabelled methyl radical from 2, 3 and 4 was the dominant process, and extensive scrambling was evident in both the  $V^{1/2}/E$ and MIKE spectra (Table 4). In contrast to H/D scrambling prior to loss of C<sub>6</sub>H<sub>6</sub>, C<sub>8</sub>H<sub>8</sub> or C<sub>2</sub>H<sub>4</sub>, the scrambling observed here did involve the hydrogens on C-2 and C-3. Another H/D exchange mechanism must be operating in the ring-opened ions involving the hydrogens on these carbons. In fact, the ratio for the losses of CH3'/CH2D'/CHD2' approach the statistical ratio of 65/32/3. However, the relatively large loss of  $CH_2D_2$  from 2 leads us to suggest that methyl loss involves predominantly carbon 2 (Scheme 5). However, loss from C-4 may also be important, since the extensive scrambling involving the hydrogens on C-4 would have made this process transparent.

A model for H/D exchange prior to decomposition in the 3rd FFR. Assuming for simplicity that incomplete exchange can be represented by a fraction of complete exchange, we undertook a series of calculations to establish a model for H/D exchange with which we can correlate all the results of 3rd FFR decompositions, those which reflect the most complete scrambling. We also assumed mixed exchange mechanisms were involved. At short times H/D scrambling appeared to involve predominantly the hydrogens on C-4 and the phenyl ring, since 4 lost no  $C_6H_6$ . However, significant losses of  $C_6H_6$  were observed from ions of 4 decomposing in the 1st FFR and 3rd FFR, which indicated



that interchange of the hydrogens on the fused aromatic ring with those on C-4 and the phenyl ring is important for longer-lived ions.

Prior to the 1,4 elimination of  $C_6H_6$  from the 1phenyltetralin radical cation, we assumed that 70% of the ions had completely exchanged the two C-4 hydrogens with three phenyl hydrogens and that 5/7 of those ions had also exchanged these hydrogens with three hydrogens of the fused aromatic ring. Total

	1-Phenyltetralin Mass				2-Phenyltetralin Mass		
Compound/loss	spectrum*	V <sup>1/2</sup> E	MIKES	Compound/loss	spectrum	V <sup>1/2</sup> /E	MIKES
→-CH <sub>3</sub>	_	46	64				
2 _+→-CH <sub>2</sub> D'		21	20	r→-CH <sub>3</sub>	13	15	17
-CHD <sub>2</sub>	—	33	16	8 →→−CH <sub>2</sub> D <sup>·</sup>	12	17	15
-				L→-CHD₂ <sup>°</sup>	75	68	68
r⇒−CH₃`	_	56	78				
$3 \rightarrow -CH_2D'$	_	28	16	r→-CH₃'	10	13	15
L→-CHD <sub>2</sub>		16	6	9 →→ – CH <sub>2</sub> D'	87	82	80
-				L→-CHD₂'	3 <sup>r</sup>	5	5
r→−CH₃'		63	72				
4 $\rightarrow$ $\rightarrow$ $-CH_2D'$	_	22	22	r→-CH³.	82	83	82
L→-CHD <sub>2</sub>		15	6	10 $\rightarrow -CH_2D'$	12	14	16
-				L→-CHD <sub>2</sub>	6	2	2
				r→CH₃`	85	82	78
				11 -+→-CH <sub>2</sub> D'	13	16	18
				P-CHD <sup>2</sup> .	2	2	4

\* These results are not available since interferences could not be eliminated at low ionizing energies.

Table	5.	Mathematical	model	for	H/D	exchange	in	labelled	1-phenyltetralins	prior	to
		decomposition	1 in the	3rd	FFR						

		2	2	3		4	£	5	5		6	
	Loss	а	b	а	b	а	b	а	ъ	а	ь	
	С											
	C <sub>6</sub> H <sub>6</sub>	100	100	100	100	14	11	2	0	67	54	
	C <sub>6</sub> H₅D	0	0	0	0	59	66	5	0	18	21	
	C <sub>6</sub> H₄D₂	0	0	0	0	27	23	10	4	9	21	
	C <sub>6</sub> H₃D₃							19	21	6	4	
	C <sub>6</sub> H₂D₄							27	33	0	0	
	$C_6HD_5$							37	42			
	d											
	C₂H₄	78	83	8	0	38	49					
	C <sub>2</sub> H <sub>3</sub> D	5	0	1	0	49	38					
	$C_2H_2D_2$	17	17	91	100	13	13					
	d											
	C <sub>a</sub> H <sub>a</sub>	46	50	47	50	24	25	8	7			
	C <sub>8</sub> H <sub>7</sub> D	<5	0	<6	0	52	50	18	19			
	C <sub>8</sub> H <sub>6</sub> D <sub>2</sub>	48	50	47	50	24	25	25	24			
	$C_8H_5D_3$							24	24			
	C <sub>8</sub> H₄D₄							18	19			
	$C_8H_3D_5$							7	7			
<sup>a</sup> Observe <sup>b</sup> Predicte <sup>c</sup> 30% no Hs].	ed losses. ed losses. H/D exchai	nge+2	20% [3	pheny	/I and	2 C-4	Hs]+5	0% [3	pheny	4, 2 C-	4 and 3	3 aromatic
<sup>d</sup> 10% nc	H/D exchai	nge+4	10% [3	phen	yl and	2 C-4	Hs]+5	0% [3	pheny	1, 2 C-	4 and	3 aromatic

epimerization of C-1 was also assumed to have occurred prior to fragmentation. We also assumed that 17% of the ethene loss occurred from C-2+C-3 and 83% from C-3+C-4 (vide supra) and that, prior to this loss, 90% of the ions had completely exchanged the two C-4 hydrogens with three phenyl hydrogens and that 5/9 of those ions had also exchanged these hydrogens with three hydrogens of the fused aromatic ring. The predicted results for loss of C8H8 were calculated assuming the same scrambling as that which preceded ethene loss.

Hs].

The agreement between the predicted and observed losses (see Table 5) is good, but not perfect. Nevertheless, the model is a reasonable approximation which



allows us to devise a mechanism (Scheme 6) that depicts the salient features of isomerization by hydrogen migrations prior to the losses of C<sub>6</sub>H<sub>6</sub>, ethene and C<sub>8</sub>H<sub>8</sub>. This mechanism pertains to decomposing ions with lifetimes greater than 1 µs.

Isomerization prior to methyl loss is more complex and probably involves yet another mechanism. The results do indicate that H/D exchange is a slow process which is not complete even for ions decomposing by loss of methyl in the 3rd FFR. Slow H/D exchange processes have been reported previously for tetralin<sup>6</sup> and aralkyl compounds.<sup>14,15</sup> The slow rate of H/D exchange must be due to an activation energy approaching that for fragmentation. In fact, this was the basis for the assumption that the scrambling was more complete for ions losing ethene and C<sub>8</sub>H<sub>8</sub>. The slow rate cannot be due to a tight transition state<sup>6</sup> since fast H/D exchange processes have been reported for other hydrocarbons such as cyclohexene<sup>16</sup> and alkene ions<sup>17,19</sup> for which the transition state should be of comparable tightness.

### 2-Phenyltetralin

The 2-phenyltetralin radical cation undergoes three principal decompositions to give fragments with the formulae  $[C_{10}H_{10}]^{+}$ ,  $[C_{15}H_{13}]^{+}$  and  $[C_8H_8]^{+}$  (see Fig. 1 for the 70 eV mass spectrum). Loss of  $C_6H_6$  is the lowest energy process with an activation energy of 0.3 eV, loss of CH<sub>3</sub> is intermediate with an activation energy of 1.3 eV, and loss of C<sub>8</sub>H<sub>8</sub> is the highest energy process with an activation energy of 1.9 eV.

Loss of  $C_6H_6$ . Predominantly  $C_6H_6$  was lost from 8 and 9, whereas mostly  $C_6H_5D$  was lost from 10 and a



Figure 1. Mass spectrum of 2-phenyltetralin at 70 eV of electron ionizing energy.

significant amount of  $C_6HD_5$  from **11** (see Table 6). These trends indicate that  $C_6H_6$  is lost via a highly regiospecific 1,3 elimination mechanism (Scheme 7).

Although the loss of  $C_6H_6$  appeared to become less specific for longer-lived ions, we attribute the losses of various labelled  $C_6H_6$  ions to increased H/D scrambling and not to a loss of regiospecificity. The results indicate that this scrambling involves predominantly the phenyl hydrogens and the hydrogens on C-4, and also the hydrogens on C-1 and to a small extent the hydrogens on C-3.

Loss of CH<sub>3</sub>. The results for the loss of methyl from the 2-phenyltetralin radical cation are much more easily interpreted than those for loss from the 1phenyltetralin radical cation. Predominantly CH<sub>3</sub> was lost from 10 and 11, whereas mostly CH<sub>2</sub>D was lost from 9 and CHD<sub>2</sub> from 8 (see Table 4). Cleavage of the C-1—C-2 bond, followed by a hydrogen transfer from C-3 to C-1, and expulsion of this C-1 methyl group (Scheme 8) accounts for these results. This mechanism is analogous to that proposed for the loss of methyl from cyclohexene,<sup>20,21</sup> but differs markedly from that for methyl loss from tetralin in which losses

Table 6. Loss of phenylte	i C <sub>6</sub> H <sub>6</sub>	from	the 2-
	tralin radi	ical catio	0n <sup>18</sup>
Compound/loss	Mass spectrum	V <sup>1/2</sup> /E	MIKES
$ \begin{array}{c} \bullet & -C_6H_6 \\ \bullet & -C_6H_5D \\ \bullet & -C_6H_4D_2 \end{array} $	70	72	72
	28	25	22
	2	3	6
$9 \xrightarrow{-C_6H_6} -C_6H_5D \xrightarrow{-C_6H_4D_2}$	97	91	91
	3	8	9
	<1	<1	<4
$10 \xrightarrow{\rightarrow} -C_6H_6 D_{-C_6H_5D} -C_6H_4D_2$	19	19	25
	59	55	54
	22	26	21
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} -C_{6}H_{6} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\C_{6}H_{5}D \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $	0	~0	~0
	<1	1	2
	2	5	10
	14	26	30
	47	46	41
	37	22	17



involving the four saturated carbons of the fused cyclohexene ring occur with equal probability.<sup>5</sup>

Although some nonspecificity exhibited by ions decomposing in the source may have been the result of another mechanism for methyl loss, it is more likely the result of H/D scrambling as was observed for the loss of  $C_6H_6$ . We also attribute the apparent decrease in specificity for longer-lived ions to increased H/D scrambling. The loss of methyl from the longer-lived ions of 9, 10 and 11 was ~80% specific; whereas the loss from those ions of 8 was only ~70% specific. Therefore, competing H/D scrambling mechanisms, involving the phenyl hydrogens and those on C-1 and C-4, are probably involved.



Loss of  $C_8H_8$ . If the loss of  $C_8H_8$  proceeds via a Diels-Alder cycloreversion to yield neutral styrene and the *o*-quinodimethane radical cation (Scheme 9), then **9** should have shown exclusive loss of  $C_8H_6D_2$ .

The normal mass spectrum of **9** (see Table 7) showed that there is high specificity for this loss. We interpret the 7% abundance corresponding to the loss of  $C_8H_8$  to arise from the departing styrene retaining the charge. Thus, the specificity is actually higher than indicated in Table 5. Furthermore **8** and **10** showed large losses of  $C_8H_8$ , just as anticipated for the mechanism shown in Scheme 9. However, the onset of H/D exchange of the hydrogens on the phenyl ring and those on C-1 and C-4 is also apparent. Separate mechanisms appear to be involved as the hydrogens on C-4 were seen to be more extensively exchanged than those on C-1. The results for **9** indicate that the hydrogens on C-3 are not involved to any great extent



phenylto	etralin radi	cal catio	<b>n</b> <sup>18</sup>
Compound/loss	Mass spectrum	V <sup>1/2</sup> E	MIKES
r→-C <sub>8</sub> H <sub>8</sub>	82	38	5 <b>2</b>
$8 \rightarrow \mathbf{C}_{8} \mathbf{H}_{7} \mathbf{D}$	11	45	31
$\rightarrow -C_8H_6D_2$	7	17	17
r→-C <sub>8</sub> H <sub>8</sub>	7	16	18
$9 \rightarrow -C_8H_7D$	4	25	21
$\rightarrow -C_8H_6D_2$	8 <del>9</del>	59	61
r→-C <sub>8</sub> H <sub>8</sub>	45	18	29
$10 \rightarrow -C_8H_7D$	44	56	49
$-C_8H_6D_2$	11	26	22
_→−C <sub>8</sub> H <sub>8</sub>	1	1	3
→−C <sub>8</sub> H <sub>7</sub> D	3	5	10
$\rightarrow -C_8H_6D_2$	2	9	15
$11 \rightarrow -C_8H_5D_3$	12	28	28
$\rightarrow -C_8H_4D_4$	41	43	31
$-C_8H_3D_5$	41	14	13

C<sub>8</sub>H<sub>8</sub>

from

the

2-

Table 7. Loss

of

in scrambling of short-lived ions. However, extensive H/D scrambling involving even these hydrogens was observed for ions decomposing in the 3rd FFR. The results for 11 are consistent with the others, as significant losses of  $C_8H_3D_5$ ,  $C_8H_4D_4$  and  $C_8H_5D_3$  were found.

The dominant loss of neutral styrene and formation of the o-quinodimethane radical cation is not in accord with the literature estimates<sup>11</sup> of the heat-offormation of this latter radical cation. It may be that the ion is more stable than estimates predict, and this may be due to the fact that the dominant resonance form is an aromatic system with exocyclic cation and radical sites (c). This matter is under investigation in our laboratory.



A model for H/D exchange prior to decomposition in the **3rd FFR.** We again sought a simple model for H/D exchange with which we could correlate the results of 3rd FFR decompositions for the labelled 2-phenyltetralins. The H/D exchange involved the phenyl hydrogens and those on carbons 1, 3 and 4, but did so to varying degrees. Therefore, we assumed mixed mechanisms were involved. Furthermore, it was assumed that the hydrogens of the fused aromatic ring were involved based upon results with tetralin<sup>5,6</sup> and 1-phenyltetralin, although a direct probe (i.e. 5,6,7,8 $d_4$ -2-phenyltetralin) was not used.

Prior to the 1,3-elimination of  $C_6H_6$  and the loss of methyl radical from carbon 1 from 2-phenyltetralin radical cations, we assumed all of the ions had completely exchanged the two C-4 hydrogens with three phenyl hydrogens. Furthermore, we assumed that 30% had also exchanged these with two C-1 hydrogens and that 50% had exchanged these with the four hydrogens of the fused aromatic ring.

Table 8. Mathematical model for H/D exchange in labelled 2-phenyltetralins prior to decomposition in the 3rd **FFR** 

			8			9			10			11	
Loss		а	b	С	а	b	С	а	b	С	а	ь	С
	d												
C <sub>6</sub> H <sub>6</sub>		72	74		91	100		25	18		0	0	
C₅H₅D		22	17		9	0		54	53		2	0	
C <sub>6</sub> H₄D₂		6	9		<4	0		21	29		10	7	
$C_6H_3D_3$											30	34	
$C_6H_2D_4$											41	45	
C₅HD₅											17	14	
	d												
CH₃.		17	14		15	0		82	85		78	79	
CH₂D <sup>°</sup>		15	14		80	100		16	14		18	17	
CHD₂ <sup>°</sup>		68	72		5	0		2	1		4	4	
CD₃'											0	0	
	е												
C <sub>8</sub> H <sub>8</sub>		52	79	71	18	1	10	29	30	29	3	0	1
C <sub>8</sub> H <sub>7</sub> D		31	17	17	21	10	10	49	52	52	10	0	3
C <sub>8</sub> H <sub>6</sub> D <sub>2</sub>		17	4	12	61	89	80	22	18	19	15	15	18
C <sub>8</sub> H₅D₃											28	45	42
C <sub>8</sub> H₄D₄											31	33	30
C <sub>8</sub> H₃D₅											13	7	6
<sup>a</sup> Obser	e Observed losses.												

° Predicted losses of  $C_8H_{8-n}D_n$  assuming that 10% of the departing styrene retains the charge.

<sup>d</sup> 20% [3 phenyl and 2 C-4 Hs]+30% [3 phenyl, 2 C-4 and 2 C-1 Hs]+50% [3 phenyl, 2 C-4 and 4 aromatic Hs] exchange. <sup>•</sup> 20% [3 phenyl, 2 C-4 and 2 C-3 Hs]+30% [3 phenyl, 2 C-4 and 2 C-1 Hs]+50% [3 phenyl, 2 C-4 and 4 aromatic Hs] exchange.

More extensive scrambling was evident for those highly excited ions which underwent fragmentation to lose C<sub>8</sub>H<sub>8</sub>. Scrambling involving the hydrogens on carbon 3 could not be ignored as evidenced by the 21% abundance of  $C_8H_7D$  loss from 9. Therefore, we assumed 20% of the ions also had exchanged the three phenyl and two C-4 hydrogens with two C-3 hydrogens.

The agreement between the observed and the predicted results for the losses of  $C_6H_6$  and  $CH_3$  is good, while that for loss of  $C_8H_8$  is poor (refer to Table 8). However, the agreement is improved considerably, particularly with compounds 7 and 9, when we allow for the possibility that as much as 10% of the departing styrene may have retained the charge (see column c in Table 8). Then, the model becomes a reasonable approximation to the isomerization by hydrogen migrations in the 2-phenyltetralin radical cation, for which the mechanism can be drawn (see Scheme 10). As with the 1-phenyltetralin radical cation, hydrogen isomerization in the 2-phenyltetralin radical cation is incomplete even for metastable ions.

### EXPERIMENTAL

Low resolution mass spectra, metastable spectra and appearance energy measurements (with reference to the ionization energy of  $d_6$ -benzene which was used as an internal standard) were acquired using Kratos MS-50 double and triple analyzer<sup>22</sup> mass spectrometers at a mass resolution of 2000-5000. Normal mass spectra



were acquired using both 13 eV and 70 eV nominal ionizing energies and were recorded on an oscillographic recorder. Metastable spectra were taken at 70 eV by signal averaging 6–100 scans at a repetition rate of 20 s using a Data General Nova 4X computer and software developed in this laboratory. More than 40 ADC points were acquired per unit mass. Metastable spectra were plotted using a Calcomp 1012 drum plotter.

Materials. 1-Phenyltetralin (1), 2-phenyltetralin (7), 1,1- $d_2$ -phenyltetralin (8), 2,2- $d_2$ -3-phenyltetralin (9), 1,1- $d_2$ -3-phenyltetralin (10) and 2-(phenyl- $d_5$ )-tetralin (11) were prepared according to standard literature methods.<sup>23-28</sup> The syntheses are described in detail in Ref. 4a. The 2,2- $d_2$ -1-phenyltetralin (2) was synthesized by addition of phenyl magnesium bromide to 2,2- $d_2$ - $\alpha$ -tetralone, prepared by H/D exchange from  $\alpha$ -tetralone, followed by a Birch reduction (Li/NH<sub>3</sub>) of the resulting  $2,2-d_2-1$ -phenyltetralol.<sup>23</sup> The  $3,3-d_2$ and  $4, 4-d_2-1$ -phenyltetralins (3 and 4) were prepared from 4-phenyltetralone by H/D exchange followed by reduction with AlCl<sub>3</sub>/LiAlH<sub>4</sub>, respectively.<sup>24</sup> The 4phenyltetralone was prepared from 2,2-diphenylethanol (Aldrich) by converting the alcohol to its p-toluenesulfonyl chloride derivative, followed by condensation with diethylmalonate using sodium and dry ethanol to give the diester of 4,4-diphenylbutanedioic acid. The diester was saponified and the resulting diacid then decarboxylated by heating to 180°C to give 4,4-diphenylbutanoic acid. This in turn was cyclized using polyphosphoric acid (PPA) to yield 4-phenyl tetralone.<sup>29</sup>

The 5,6,7,8- $d_4$ -1-phenyltetralin in (6) was synthesized by addition of phenyl magnesium bromide to 5,6,7,8- $d_4$ - $\alpha$ -tetralone, followed by a Birch reduction (Li/NH<sub>3</sub>) of the resulting alcohol.<sup>23</sup> The 5,6,7,8- $d_4$ - $\alpha$ tetralone was prepared in a multistep synthesis starting with the reaction of benzene- $d_6$  with succinic anhydride and AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> to give  $d_5$ - $\beta$ -benzoylpropionic acid.<sup>30</sup> Hydrogenation at 40 lb in <sup>-2</sup> over 5% Pd/C in acetic acid at 65 °C for 0.5 h gave  $d_5$ - $\gamma$ phenylbutyric acid,<sup>31</sup> which was cyclized using PPA to give the 5,6,7,8- $d_4$ - $\alpha$ -tetralone.<sup>32</sup> The 1-(phenyl- $d_5$ )tetralin (5) was prepared by the addition of phenyl- $d_5$ magnesium bromide to  $\alpha$ -tetralone, followed by a Birch reduction (Li/NH<sub>3</sub>) of the resulting alcohol.<sup>23</sup>

The phenyltetralins were purified by gas chromatography and characterized by their nuclear magnetic resonance and mass spectra. Mass spectrometric analysis of the deuterated compounds gave the following isotopic compositions: **2**: 97.5%  $d_2$ , 2.5%  $d_1$ ; **3**: 94.4%  $d_2$ , 3.7%  $d_1$ , 1.9%  $d_0$ ; **4**: 94.4%  $d_2$ , 3.8%  $d_1$ , 1.8%  $d_0$ ; **5**: 97%  $d_5$ , 2%  $d_4$ , 1%  $d_3$ ; **6**: 46%  $d_4$ , 30%  $d_3$ , 16%  $d_2$ , 6%  $d_1$ , 2%  $d_0$ ; **8**: 98%  $d_2$ , 2%  $d_1$ ; **9**: 97%  $d_2$ , 2%  $d_1$ , 1%  $d_0$ ; **10**: 95%  $d_2$ , 3%  $d_1$ , 2%  $d_0$ ; **11**: 96%  $d_5$ , 2%  $d_4$ , 2%  $d_3$ .

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