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PARTICIPATION OF A RING CARBON IN THE LOSS OF METHYL FROM THE MOLECULAR ION OF 7-METHYLCYCLOHEPTATRIENE

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In the formation of $XC_7H_6{}^+$-ions from substituted aromatic hydrocarbons upon electron impact, ring expansion of the molecular ions to cycloheptatriene intermediates has been proposed by some authors (1,2,3). The results of appearance potential measurements on $XC_7H_6{}^+$-ions however, have shown that the possibility cannot be excluded, that certain $XC_7H_6{}^+$-ions have retained the six-membered ring. Indeed, a ^{13}C-and ^{15}N-tracer study in our laboratory has shown, that this is true for a substantial part of the decomposing molecular ions of (o,m,p)cyanobenzylcyanide ($C_7H_6(CN)_2$) (4).

These results prompted us to study various substituted cycloheptatrienes. We can now report that the molecular ion of 7-methylcycloheptatriene (C_8H_{10}) partly seems to collapse to a six-membered ring prior to the loss of a methyl radical, as derived from the mass spectra of its 7-CD_3- and 7-$^{13}CH_3$ analogues (5). Table 1 shows the extent of label-loss in the formation of the $C_7H_7{}^+$ (M-CH_3)-ion. The data illustrate:

1° Some of the molecular ions eliminate the original methyl group almost without hydrogen scrambling (% CD_3 loss ≈ % $^{13}CH_3$ loss).

2° Other molecular ions expel a methyl group containing a ring carbon. In this reaction all hydrogens appear to participate, but the figures are not consistent with a complete hydrogen scrambling. Moreover, the participation of the ring carbon becomes more important when the molecular ions have a relatively low internal energy.

Table 1. Label loss in the formation of $C_7H_7^+$ (in %)[a] in the ion source and second field free region ("2^{nd}") of the mass spectrometer.

Labeled compound	Eliminated fragment	70 eV		15 eV	
		source	2^{nd}	source	2^{nd}
$7\text{-}CD_3\text{-}C_7H_7$	$CH_3^{\cdot}$	12	~20[b]	19	20
	$CH_2D^{\cdot}$	4	~14	8	18
	$CHD_2^{\cdot}$	5	~11	9	12
	$CD_3^{\cdot}$	79	~55	64	50
$7\text{-}^{13}CH_3\text{-}C_7H_7$	$^{12}CH_3^{\cdot}$	23	~51	33	49
	$^{13}CH_3^{\cdot}$	77	~49	67	50

[a] Average of at least five runs (estimated accuracy of 2%).

[b] Due to overlap with diffuse peaks corresponding with the loss of hydrogen from $C_6H_{(7-x)}D_x^+$ these values are rough approximations.

All these phenomena can be explained by assuming a competition between the loss of a methyl radical from the original cycloheptatriene- and from an isomeric xylene structure. The latter could be generated by an isomerization (6) of the 7-methylcycloheptatriene to one of the other methylcycloheptatrienes, followed by ring contraction. Further studies in this field are in progress.

References

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5. These compounds were prepared as described by K. Conrow, *J. Am. Chem. Soc.* 83, 2343 (1961).
6. Although thermal isomerization could occur in the heated inlet system, a mass spectrometrically induced isomerization must also occur as shown by the increase of $^{12}CH_3$-loss from the ^{13}C-labeled compound going from ion source to second field free region (Table 1).