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MASS SPECTRAL STUDIES OF SUBSTITUTED CYCLOHEPTATRIENES I. 3,4-DICHLOROCYCLOHEPTATRIENE

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The structure of the $C_7H_7^+$ ion generated upon electron impact from numerous precursors has occupied the attention of mass spectrometrists for many years.[3,4] Originally the ion as formed from a variety of benzyl derivatives was thought to result from simple β-cleavage,

$$\phi\text{-}CH_2\text{-}X]^{+\cdot} \rightarrow \phi CH_2^+ + X\cdot,$$

however early deuterium labeling experiments indicated that the ion characteristics could most easily be explained in terms of a symmetrical structure--the tropylium ion.[5] Subsequent efforts have examined the conditions and process for the formation of the ring expanded ion. For example, benzyl-α-$d_2$chloride and bibenzyl-α,β-d_4 apparently form a tropylium ion by random insertion,[6] while diphenylmethane-α-d_2 forms tropylium-1,2-d_2. More recent mass spectral studies of toluene-α,1-$^{13}C_2$[7] and toluene-2,6-$^{13}C_2$[8] indicate that those $C_7H_7^+$ ions which possess sufficient energy to decompose, also have sufficient energy to undergo complete skeletal scrambling. No explanation or mechanism has been offered to explain these startling results, although Harrison had earlier[9] postulated isomerization within the toluene molecular ion to form a cycloheptatriene molecular ion. This conclusion has recently been supported by a study of the relationship of the degree of scrambling and variation of isotope effect with internal energy[10] for cycloheptatriene and toluene. In opposition, however, a recent Ion Cyclotron Resonance (ICR) study of the C_7H_8 isomers[11] shows that the isomerization (ring expansion) does not take place within those toluene molecular ions with sufficient energy to take part in an ion-molecule reaction but insufficient energy to decompose within the 10^{-3} sec ion lifetime in ICR, a far longer lifetime than is required for scrambling to take place in a conventional mass spectrometer.

The application of simplified quasi-equilibrium theory to the loss of H· from cycloheptatriene and toluene indicates that in both systems the reaction is not a simple cleavage but rather a more complex rearrangement.[12,13] These results are in accord with the loss of H/D, from 7-deuterocycloheptatriene, as well as those observed from metastable intensities, isotope effects, and labeling studies on both toluene and cycloheptatriene suggest that a unified mechanistic scheme exists for these compounds.

In the absence of data on the mass spectral decomposition reactions of $^{13}C_2$-cycloheptatriene,[14] we have isolated 3,4-dichlorocycloheptatriene,[15] formed along with other dichlorocycloheptatrienes by carbene insertion into o-dichlorobenzene and have examined its 70 eV mass spectra.[16] The compound exhibits mass spectral behavior consistent with a cycloheptatriene structure, and shows peaks which correspond (1) to loss of H to form a dichlorotropylium ion and (2) loss of Cl· to form a chlorotropylium ion. As can be seen from the data in Table I, loss of Cl· is favored over loss of H· and is consistent with an apriori assessment of the relative stabilities of the chlorotropylium and dichlorotropylium ions. The relevant data for 2,6-dichlorotoluene is also shown for comparison. The major difference in the 70 eV mass spectra of these compounds is in the stability of the molecular ion.

Table I. Relative Intensity of Molecular Ion and Ions Formed in Primary Decompositions at 70 eV

	3,4-dichlorocycloheptatriene	2,6-dichlorotoluene
$M^{\cdot +}$	11.3	38
$[M-H\cdot]^+$	5	5.4
$[M-Cl\cdot]^+$	100	100

The mass spectra of I shows further decomposition peaks which correspond to loss of C_2H_2, C_2HCl, and C_2Cl_2 from substituted tropylium ions. As no second field free region metastables were observed for these decomposition pathways, the values of the relative intensities of the product ions corresponding to these losses has no quantitative meaning. The relative intensities of these peaks (Table II) do not agree with those found earlier by Rinehart or Siegel for their carbon-13 labeled toluenes, nor should they be expected to be comparable. The substitution of a chlorine atom for a hydrogen not only destroys the symmetry properties of any tropylium ion formed but presumably also changes the energetics of the decomposition pathways available.

Table II. Relative Intensities of Decomposition Products of Substituted Tropylium Ions.[a]

	3,4-dichlorocycloheptatriene	2,6-dichlorotoluene
$C_5H_3Cl_2^+$	20.3	24.5
$C_5H_4Cl^+$	100	100
$C_5H_5^+$	17.4	15.2

a. The absolute intensity of these peaks relative to the base peak (m/e=135) is greater by a factor of two in the 3,4-dichlorocycloheptatriene.

The mass spectral reactions of 2,6-dichlorotoluene were also studied at 70 eV. This compound undergoes the same decomposition reactions as the 3,4-dichlorocycloheptatriene having peaks which correspond to lose of C_2H_2, C_2HCl, and surprisingly, $\underline{C_2Cl_2}$, from the substituted tropylium ions. The data presented in Tables I and II for 2,6-dichlorotoluene is quite similar to that of the 3,4-dichlorocycloheptatriene and suggests that almost complete equilibration of structure has occurred in these two systems after decomposition of the molecular ion. The scrambling in the 2,6-dichlorotoluene system appears to be analogous to that observed earlier by Siegel using ^{13}C labels, and assuming that the chlorines do not themselves participate in some rearrangement process, is consistent with skeletal scrambling occurring through norcaradienyl-like structures.[13]

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15. The structure determination, NMR, and mass spectral reactions of several dichlorocycloheptatrienes will be presented in the full paper. M. K. Hoffman, J. V. Paukstelis, and T. L. Amos, to be published.

16. An AEI MS9 double-focusing mass spectrometer was used. To prevent possible thermal rearrangements, mass spectra were obtained at a source temperature of 80-90° C.