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MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS—CCXXXI[1]

DIFFERENTIATION BETWEEN TAUTOMERIC ION STRUCTURES (PHENOL *vs.* CYCLOHEXADIENONE)

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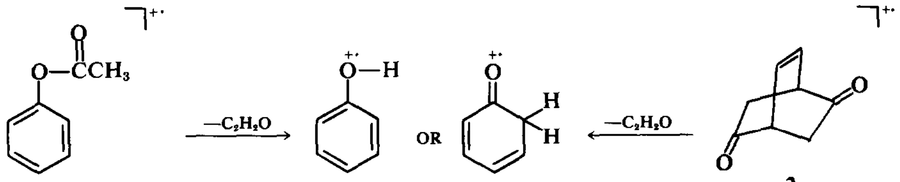
Abstract—Ionized phenol and ionized cyclohexadienone can be distinguished on the basis of ion-molecule reactions of unlabeled and deuterium-labeled substrates. Application of these results to the $C_6H_6O^+$ ion from phenyl acetate shows that this ion possesses the phenol structure.

The question whether the $C_6H_6O^+$ ion generated by electron impact induced expulsion of ketene from phenyl acetate (**1**) has a phenol structure (**a**) or the tautomeric cyclohexadienone structure (**b**) has been a topic of much interest in recent years.[2]



1 **a** **b** **2**

In connection with our work on mass spectral fragmentation mechanisms we have been involved for some time in elucidating the structures of ions based on their reactivity in ion-molecule reactions as observed by ion cyclotron resonance spectrometry.[3] We now describe the application of the techniques of ion cyclotron resonance spectrometry and pulsed double resonance spectrometry to the elucidation of the $C_6H_6O^+$ ion from phenyl acetate.

To determine the unknown structure of an ion on the basis of its ion-molecule reactions, the reactions of ions of known structure must first be determined. Phenol, of course, was chosen to determine the reactivity of $C_6H_6O^{+\cdot}$ ions possessing structure **a**. Bicyclo[2.2.2.]oct-2-en-5,7-dione (**2**) was chosen as a precursor of cyclohexadienone ions (**b**) because upon electron impact (for ICR spectrum see Fig 1) **2** expels ketene to form **b**. The fragment ion **b** decomposes further by expulsion of CO (as evidenced by the appropriate metastable ion) to form the base peak of the spectrum as well as by loss of methyl (*m/e* 79).

The large abundance of the mass 66 and mass 79 ions relative to the mass 94 ion in **2** in comparison (Table 1) to that observed for phenol gives credence to the assignment of a non-phenolic structure to the mass 94 ion in **2**.

Both **a** and **b** were observed by pulsed double resonance to donate a proton to neutral 4-heptanone (**3**). We expected proton transfer from phenol to specifically involve the hydrogen on oxygen. To determine the validity of this assumption the proton transfer reactions of phenol-O-d_1 (**4**) and phenol-d_5 (**5**) to 4-heptanone (**3**) were investigated. The pulsed double resonance spectra of the M+1 and M+2 ions of **3** indicate that predominant transfer of the phenolic H atom occurs (Eq 1). Deuterium transfer from **4** is much less favorable than proton transfer from **a** indicating a large isotope effect for the proton transfer reaction. We have also observed H transfer from the aromatic ring of the $C_6H_6O^+$ ion. In light of Nibbering's recent report[4] in which no proton transfer from the aromatic ring of the $C_6H_6O^+$ ion derived from phenetole was observed, this implies that some isomerization of **a** to **b** may be occurring in our time scale.†

Table 1. Relative abundances of some fragment ions in the ICR spectra of phenol and bicyclo[2.2.2.]oct-2-en-5,7-dione at 20 eV

	Relative abundance	
Ion	Phenol	Bicyclo[2.2.2.]oct-2-en-5,7-dione
m/e 94	100	100
m/e 79	0	86
m/e 66	10	438

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†Alternatively in the absence of absolute intensities, our data could be due to our observing ring hydrogen donation at much more sensitive settings than Nibbering used.

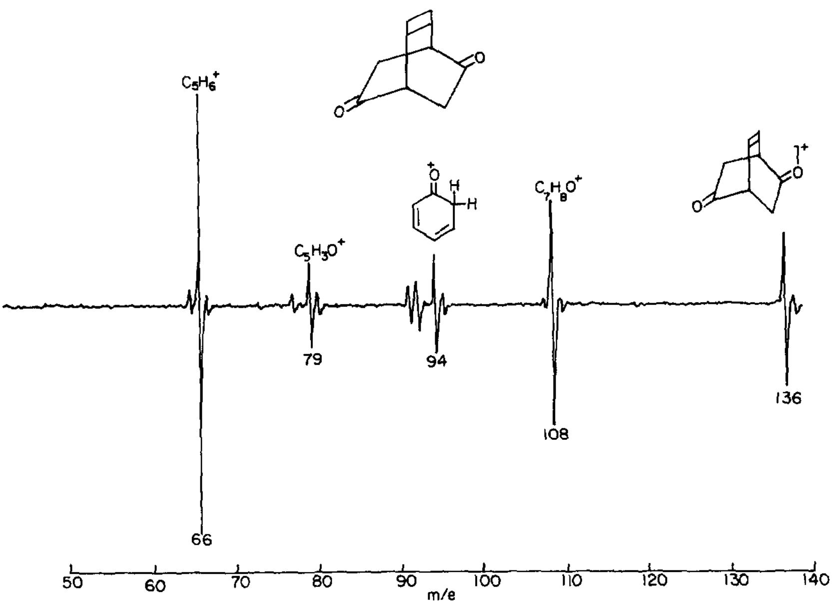
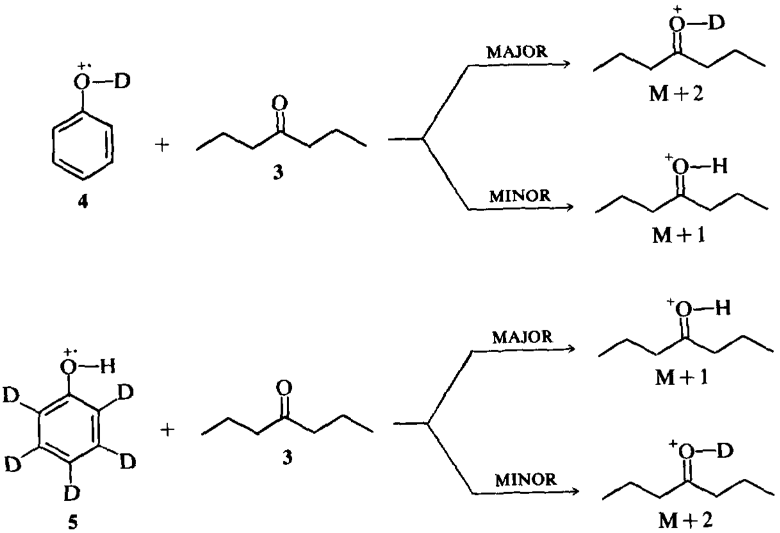


Fig 1. Ion cyclotron resonance spectrum of bicyclo[2.2.2]oct-2-en-5,7-dione, 20 eV, 8×10^{-6} t.



(1)

We have observed in previous studies[3] that ionized enols condense with 1-methylcyclobutanol (**6**) while the keto tautomer does not. The ICR spectrum (Fig 2) of a mixture of phenol and **6** shows the presence of two new peaks at *m/e* 162 (**c**) and 134 (**d**). The pulsed double resonance spectra showed that the mass 94 ion is the precursor ion in accordance with the formulation depicted in Eq 2 (R = H).

Confirmation of this mechanism was obtained by examining the single resonance spectra of phenol-O-d_1 (**4**) and phenol-d_5 (**5**) in the presence of 1-methylcyclobutanol (**6**) in which only the hydrogen on oxygen is lost in the formation of the condensation products (Eq 2 (R = D) and 3). The pulsed double resonance spectra of the product ions confirmed the identity of **4** and **5** as the reactant ions.

However, the ICR spectrum of a mixture of bicyclo[2.2.2.]oct-2-en-5,7-dione (**2**) and 1-methylcyclobutanol (**6**) also displays peaks at *m/e* 134 and 162. The pulsed double resonance spectra confirmed that the mass 94 ion was the precursor ion. Since Bursey *et al.*[5] have shown that cyclic enol ions can undergo tautomerization to their keto form on the ICR time scale, it is possible that a significant fraction of the cyclohexadienone ions (**b**) from **2** tautomerize to the phenol structure (**a**) followed by subsequent condensation with **6**. Thus, the non-

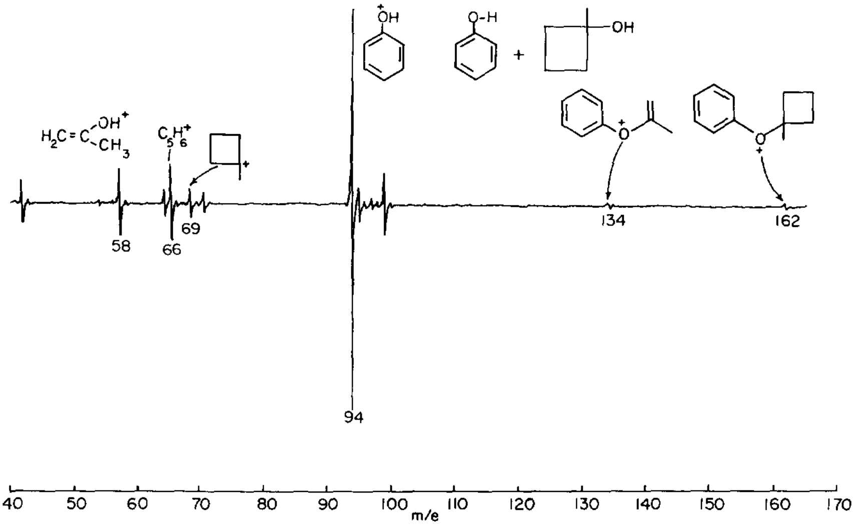
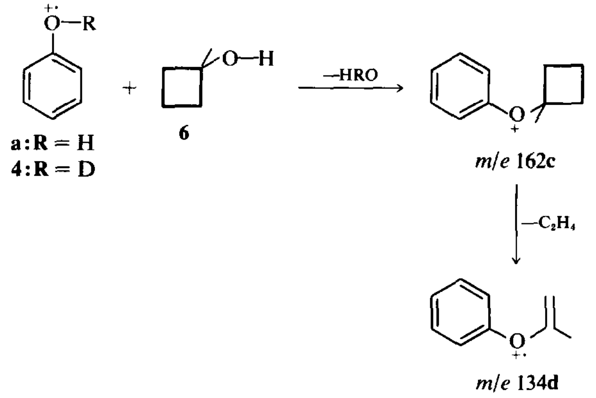
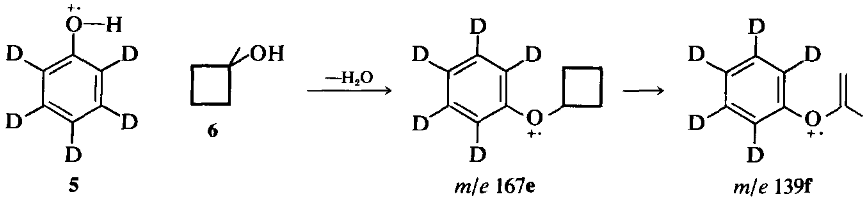


Fig 2. Ion cyclotron resonance spectrum of a mixture of phenol and 1-methylcyclobutanol, 20 eV, 7×10^{-6} t.



(2)



(3)

decomposing mass 94 ions from **2** may not be a suitable model for the keto form.

Even though **b** appears to condense with **6**, the ion-molecule reactions leading to the appearance of **c** and **d** can be used to determine the structure of the $C_6H_6O^+$ ion derived from phenyl acetate, provided deuterium labeled compounds are used. Phenyl acetate-d_3 (**7**) will give rise to a mass 95 ion which will react to form ions of mass 162 and 134 if it has the phenol structure **4** (Eq 4). On the other hand, if the mass 95 ion initially possesses the d_1-cyclohexadienone structure (**g**), ions of mass 162, 163, 134 and 135 will result (Eq 5).

Similarly phenyl acetate-d_5 (**8**) will form ions of mass 167 and 139 if it possesses the phenol structure **5** (Eq 6), whereas ions of mass 166, 167, 138 and 139 will be produced from a d_5-cyclohexadienone precursor **h** (Eq 7).

The ion cyclotron resonance spectrum (Fig 3) of a mixture of **7** and **6** showed the presence of only mass 162 and 134 ions (corresponding to Scheme 4). The pulsed double resonance spectra of these ions showed that the mass 95 ion was the precursor.* The ICR spectrum (Fig 4) of a mixture of **8** and **6**

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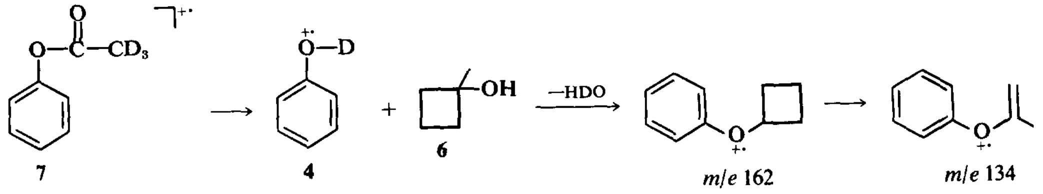
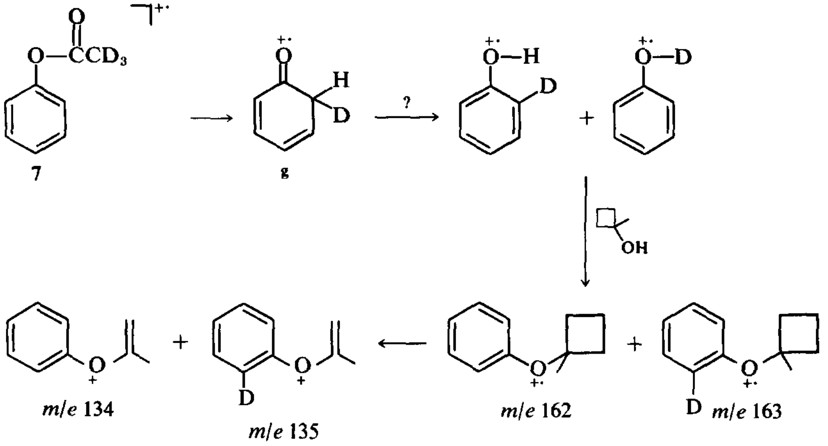
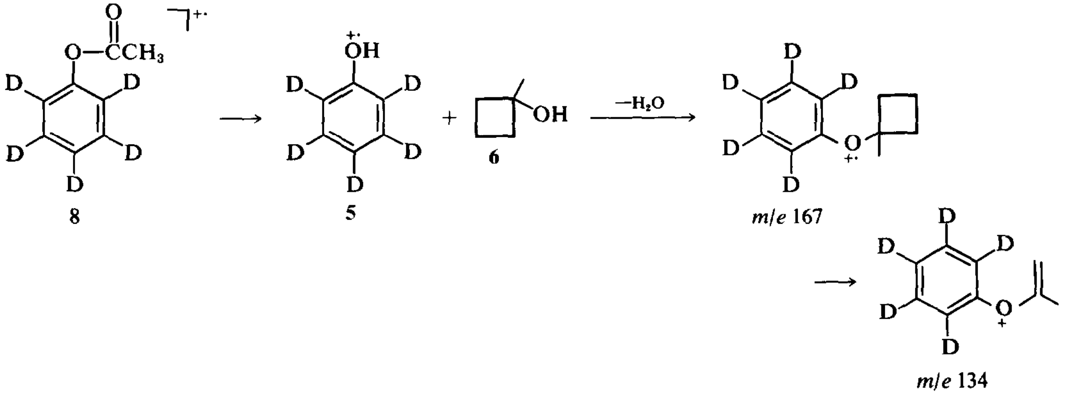
*The mass 94 ion arises from protonated **8**. The *m/e* 94 and 95 signals in the pulsed double resonance spectra of **a** and **b** were in the same ratio as the single resonance peaks.


7
4
6
OH
CD3
O—D
—HDO
m/e 162
m/e 134

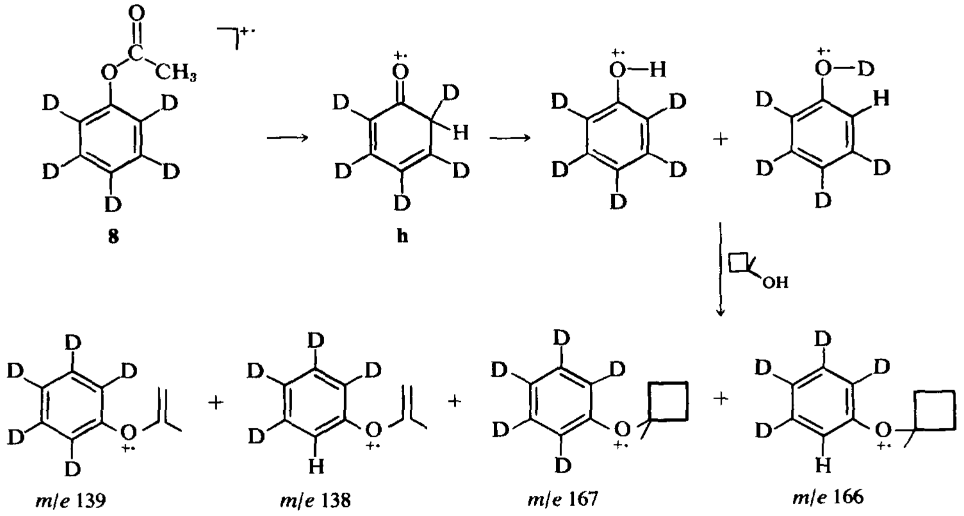
(4)


7
g
CCD3
O—H
O—D
H
D
?
OH
m/e 134
m/e 135
m/e 162
m/e 163

(5)


8
5
6
CCH3
OH
—H2O
D
m/e 167
m/e 134

(6)


8
h
CH3
O—H
O—D
D
H
OH
m/e 139
m/e 138
m/e 167
m/e 166

(7)

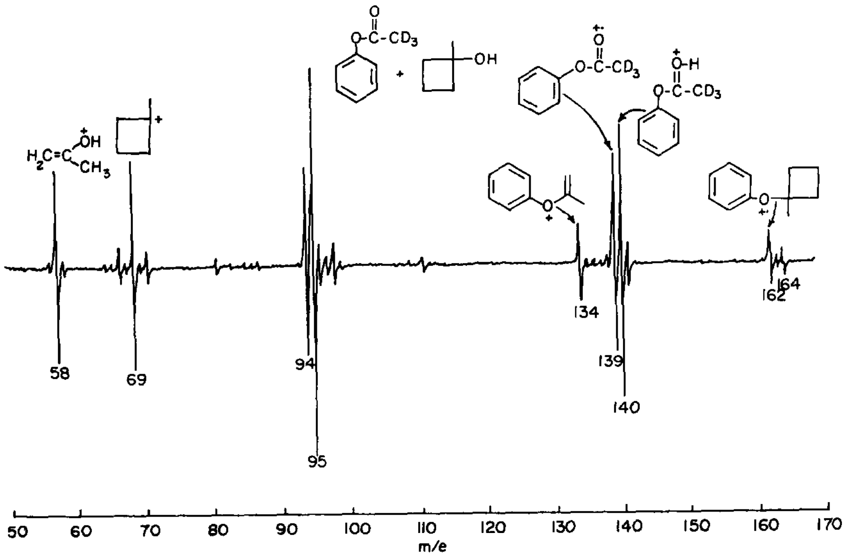


Fig 3. Ion cyclotron resonance spectrum of a mixture of phenyl acetate-d_3 and 1-methylcyclobutanol, 20 eV, 4×10^{-6} t.

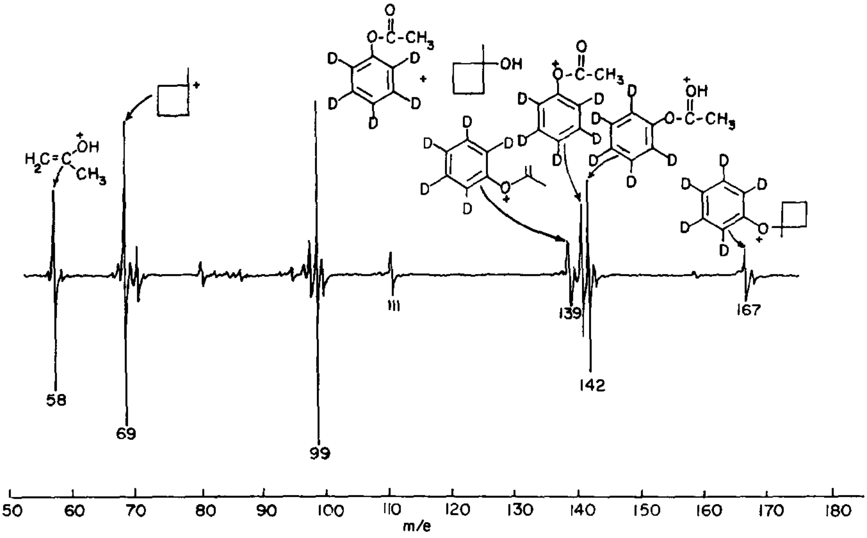
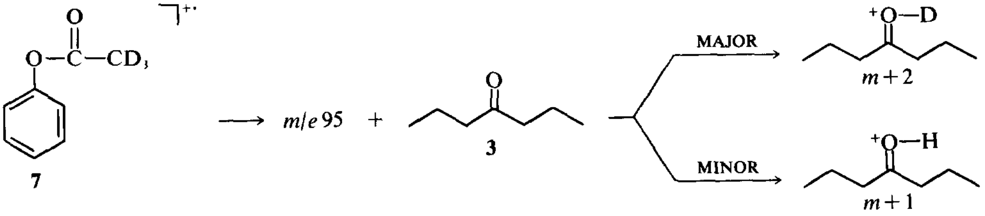


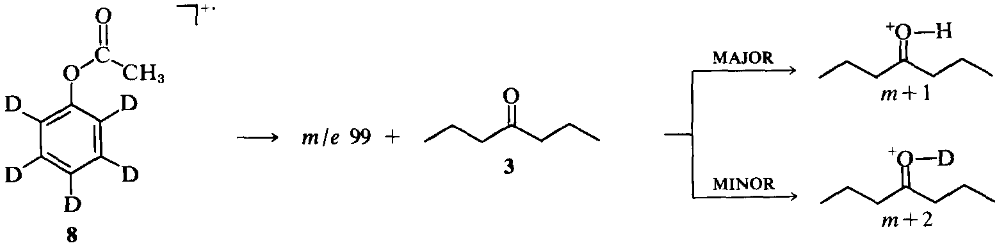
Fig 4. Ion cyclotron resonance spectrum of a mixture of phenyl acetate-d_5 and 1-methylcyclobutanol, 20 eV, 7×10^{-6} t.

showed only the presence of the mass 167 and 139 ions (corresponding to Scheme 6). The pulsed double resonance spectra again confirm that the mass 99 ion was the precursor of both species. These results are identical to that observed for phenol-O-d_1 and phenol-d_5 and are not the same as that expected for a cyclohexadienone-d_1 ion. These results are consistent only with the view that the $C_6H_6O^+$ ions formed by expulsion of ketene from phenyl acetate initially possess the phenol structure.

These results were confirmed by the proton transfer results. The pulsed double resonance spectra of the M+1 and M+2 ions of 4-heptanone (3) in the presence of phenyl acetate-d_3 (7) show that the *m/e* 95 ion donated predominantly a deuterium atom (Eq 8). The pulsed double resonance spectra of the M+1 and M+2 ions of 4-heptanone (3) in the presence of phenyl acetate-d_5 (8) demonstrated predominant proton transfer from the mass 99 ion (Eq 9). the ratio of the *m/e* 95 or *m/e* 99 peaks to the *m/e* 71 peak from 4-heptanone in the pulsed double resonance spectra of the M+1 and M+2 ions of 4-heptanone in the presence of



(8)



(9)

phenyl acetate-d_3 or phenyl acetate-d_5 is the same as this ratio (corrected for the relative intensities of the single resonance peaks) in the pulsed double resonance spectra of the M+1 and M+2 ions of 4-heptanone in the presence of phenol-O-d_1 or phenol-d_5. Thus the fragment ions behave similarly to the corresponding phenol.

In summary the ion-molecule reactions of the $(\text{M-ketene})^+$ ion from phenyl acetate demonstrate again the power of the ICR technique for shedding light on ion structures and thus on the mechanism of mass spectral fragmentation processes.

EXPERIMENTAL

The basic spectrometer used in this study is the Varian V-5900 spectrometer fitted with a dual inlet system with the addition of a third inlet directly into the analyzer. The spectrometer, the method, and applications of single and double resonance have been described.[5]

Phenyl acetate-d_3 was prepared by the reaction of acetyl chloride-d_3 with phenol in pyridine. The product was purified by GLC. Phenyl acetate-d_5 was prepared by the reaction of Ac_2O with phenol-d_6 (Bio-Rad) in pyridine. The product was purified by GLC. Phenol-O-d_1 was prepared in the inlet by exchange with D_2O Bicyclo-[2.2.2.]oct-2-en-5,7-dione was prepared according to the methods of Takeda, *et al.*[7] and Grob and Weiss.[8]

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