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# MASS SPECTROMETRY-III:

## FURTHER STUDIES OF THE UNIMOLECULAR DECOMPOSITION OF ACETOPHENONE AZINE IN THE GAS PHASE INDUCED BY ELECTRON-IMPACT

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Abstract—Mass spectra of acetophenone azine- $d_{10}$  (II) and acetophenone azine- $d_6$  (III) were obtained to ascertain the validity of the proposed mass spectral fragmentation mechanisms proposed for acetophenone azine (I). Data from II and III reveal that the [M - 1] ion in the spectrum of I is formed via loss of ring hydrogen. Within experimental uncertainty the major fragmentation reactions of the molecular ion of I, the [M - 1] ion, and the [M - 15] ion occur without loss of structural identity of the phenyl and methyl moieties. Ionization of I occurs with a high degree of structural integrity.

### INTRODUCTION

RECENTLY we reported that rearrangement processes involving the migration of phenyl, methyl and hydrogen accompany the unimolecular decomposition of acetophenone azine (I) induced by electron-impact.<sup>1</sup> Rearrangement-fragmentation mechanisms were postulated from a) high resolution data, b) metastable peaks, and c) analogies drawn from mass spectral literature. The data were interpreted in terms of multicentered rearrangements (1, 3; 1, 4; 1, 5) from carbon to nitrogen or carbon to carbon.

Rearrangements accompanying mass spectral fragmentation reactions are important both in the deduction of structure and in the analysis of ion energetics.<sup>2</sup>

To examine the validity of the proposed fragmentation reactions of I, we have studied the electron-impact-induced decompositions of acetophenone azine- $d_{10}$  (II), ring-deuterated, and acetophenone azine- $d_6$  (III), methyl-deuterated.<sup>3</sup>

The mass and metastable spectra of I along with other azines were reported by Cooks and Tam.<sup>4</sup> More recently Zeeh and Beutler have reported on the mass spectra of azines and phosphazines.<sup>5</sup>

## **RESULTS AND DISCUSSION**

Nominal structures are given in Table 1 for those ions of interest in the spectra of I, II and III.

As a first approximation ions in the spectra of II and III were corrected for contributions arising from incomplete deuteration by assuming a) absence of hydrogen scrambling prior to their formation, and b) absence of primary isotope effects. The high isotopic purity of II results in small correction factors. The differences between corrected and experimental intensities are appreciable, however, in the spectra of III, e.g. at 70 eV the experimental intensity at m/e 224 is 224(LKB 9000) and the intensity arising from loss of CD<sub>3</sub> from the  $d_6$  molecular ion is calculated to be 171. The corrected intensities normalized to the molecular ions are listed in Table 2 (data from LKB 9000) and 3 (data from CEC 21-110B).

Relevant metastable transitions in the spectra of I are listed in Table 4.

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TABLE 1. NOMINAL ION STRUCTURES



m/e	Cmpd. I $(d_{-0})$	Cmpd. II (d-10)	Cmpd. III (d-6)
246		100.0	
245		0.7	
244		13.3	
243		0.1	
242			100.0
241			20.2
240			1.3
239			0.9
238			0.4
236	100.0		
235	23.0		
234	0.4		
231		184.0	
230		0.6	
229		0.7	
226			0.3
225			0.5
224	0.2		171.0
223	-0.2		-1.6
222	1.2		0.1
221	179.0		
220	1.1		
219	1.0		
205		2.5	
204		3.1	
203		6.4	
202		0.4	
201		0.2	
200			0.1
199			0.2
198	0.1		4.6
197	0.1		8.2
196	0.1		2.8
195	3.6		0.9
194	11.0		0.7
193	1.0		
192	0.4		
19 <b>0</b>		14.4	
189		0.6	
188		0.6	
182	0.1		0.1
181	0.3		0.7
180	18·6		18.5
179	0.2		0.2
178	0.8		0.2
166		0.2	
165		0.6	37.9
164		34-3	<b>−0</b> ·1
163		0.2	-0.5
162		0.6	0.4
161	0.1		0.3
160	0.1		
159	35.4		
158	0.6		
157	0.3		

Table 2. Partial Spectra of Acetophenone Azines at 70 eV  $$\rm Relative\ Intensities^{3}$$ 

m/e	Cmpd. I (d-0)	Cmpd. II (d-10)	Cmpd. III (d-6)
246		100.0	
245		0.4	
244		11.2	
243		0.1	
242		• •	100.0
241			18.5
240			0.6
239			0.1
238			0.4
236	100.0		• • •
235	19.7		
231	177	136.0	
230		1.9	
229		0.5	
226		0.5	0.4
225			2.3
224			128.0
223	0.3		1200
223	1.6		0.5
222	120.0		05
220	1.20 0		
210	0.8		
219	0.3		
205	0.2	2.2	
203		2.2	
204		5.3	
203		0.4	
202		0.4	
100		0.3	0.2
199			0.2
190			5.4
197	0.2		0.1
190	0.2		2.4
195	2.3		0.0
194	8.1		0.2
193	0.8		
192	0.2	11.4	
190		11.4	
109		0.3	
188	0.0	0.4	0.2
182	0.2		0.3
181	0.2		0.0
180	13.7		14.9
179	0.5		0.4
1/8	0.9		0.3
166		0.2	22.7
165		0.7	33.1
164		31.0	-0.8
163		0.7	0.1
162	~ ~	0.4	0.2
161	0.1		<b>−</b> 0·1
160	0.2		
159	28.4		
158	0.6		
157	0.5		

Table 3. Partial spectra of acetophenone azines at 70 eV relative intensities  $^{\rm 36}$ 

<sup>a</sup> Spectra recorded on CEC 21-110B.

IN THE SPECIRUM OF I					
[M]* <sup>a</sup>	Transition				
234.00 206.95 170.30 166.15 161.12	$\begin{array}{c} 236^{+\cdot} \rightarrow 235^{+} + 1 \\ 236^{+\cdot} \rightarrow 221^{+} + 15 \\ 221^{+} \rightarrow 194^{+} + 27 \\ 195^{+\cdot} \rightarrow 180^{+} + 15 \\ 236^{+\cdot} \rightarrow 195^{+} + 41 \end{array}$				
146.61	$221^+ \rightarrow 180^+ + 41$				

TABLE 4. METASTABLE TRANSITIONS IN THE SPECTRUM OF I

<sup>a</sup> These were also reported by Cooks and Tam, see Ref. 4.

The mechanism of formation of the [M - 15] ion (V) was envisioned as simple carbon-carbon bond cleavage in the molecular ion of I (IV).<sup>1</sup> The following evidence confirms that the molecular ions of II (IVa) and III (IVb) lose protated and deuterated methyl radicals,\* respectively: a) the isotopic purities of II and III as calculated from the ion intensities in the [M - 15] and [M - 18] regions of their respective spectra (see Experimental), b) the shift in the metastable peak to m/e 216.9 and 207.3, in spectra of II and III, c) the good agreement between the intensities at m/e 229 and 230 in the spectra of II with 219 and 220 in the spectra of I, Tables 2 and 3, and d) the absence of an ion at m/e 227 and the small intensities at m/e 226 and 225 in the spectra of III. If protium and deuterium scrambling occurred prior to loss of methyl, appreciable intensities would have been observed at masses less than 231 and greater than 224 in spectra of II and III respectively. The fragmentation IV to V is indicated to involve loss of an original methyl group of I.

The [M - 1] ion (VI), m/e 235, is seen to be nearly or completely shifted to m/e244 and 241 in the spectra of II and III. Deuterium loss from IVa and protium loss from IVb indicate that the major if not the exclusive process leading to the [M - 1]ion (VI) is loss of a ring hydrogen from IV, contrary to the original suggestion<sup>1</sup> but substantiating the proposal of Cooks and Tam.<sup>4</sup> Metastable peaks were observed at m/e 242.0 for deuterium loss from IVa and at m/e 240.0 for protium loss from IVb. An isotope effect<sup>6</sup> is indicated by the reduction in the intensity at m/e 244 compared to the intensity at either m/e 241 or 235. The small residual intensity at m/e 245 (Tables 2 and 3) corresponding to protium loss from IVa indicates a second process involving loss of methyl hydrogens leading to the [M - 1] ion. A residual intensity of 0.82  $\pm$ 0.32 was obtained from spectra recorded in 0.2 eV intervals from 16 to 9.6 eV(LKB 9000). The fraction of II containing nine deuteriums, however, calculated from the 70 eV spectrum of II recorded on the CEC instrument is sufficient to account for this residue (see Experimental and Table 6). This result could be an artifact since a) it is based upon data from one spectrum, and b) the percentage of II calculated to contain nine deuteriums is an upper limit. This second process requires some loss of deuterium from IVb producing ions at mass 240. Convincing evidence for it is not provided by spectra of III recorded on both mass spectrometers. The small residual intensity observed at m/e 240 in the 70 eV spectrum of III recorded on the LKB instrument must be balanced against the small negative intensity observed in the 70 eV

\* For purposes of discussion protium and deuterium refer to the specific isotopes and hydrogen to both.

spectrum of III recorded on the CEC 21-110B. Furthermore, a corrected intensity of  $-1.3 \pm 1.0$  was obtained from spectra of III recorded from 16 to 9.2 eV.

The inherent difficulty in obtaining highly accurate ion intensities and the percentage of III containing 5 deuteriums complicate the analysis. Nevertheless, the following conclusions are clearly warranted: a) the predominant if not exclusive pathway leading to the [M - 1] ion, m/e 235, involves loss of ring hydrogen, and b) a second pathway involving methyl hydrogens must be at best a minor process.

The C<sub>14</sub>H<sub>13</sub>N ion (VII), m/e 195, was suggested to arise via a 1,3-phenyl shift in IV concomitant with loss of acetonitrile. The shift of m/e 195 to 205 in the spectrum of II

$$V \xrightarrow{\bullet} C = N - C_6 H_5 \xrightarrow{+} + C H_3 C N$$
(1)  
$$C_6 H_5$$

(VII) m/e 195 nitrilo from IVo

demonstrates loss of protated acetonitrile from IVa with retention of the ten ring deuteriums. Loss of deuterated acetonitrile from IVb is indicated by the shift of m/e 195 to 198 and by the small intensities at m/e 199 and 200. These last two intensities are seen to be very similar to those at m/e 196 and 197 in the spectrum of I. Such an observation is not expected if scrambling of aromatic and methyl hydrogens occurs in IV prior to loss of acetonitrile. These observations together with the shift in the metastable peak to m/e 170.8 and 162.0 in the spectra of II and III demonstrate that the acetonitrile produced in the formation of VII contains a methyl group originally present in I. Thus the results are consistent with the proposed fragmentation mechanism.

Comparison of the intensities from m/e 182 through 178 reveals that the  $C_{13}H_{10}N$  ion (VIII), m/e 180, in the spectrum of I is formed in the spectrum of III without deuterium incorporation. The agreement between the intensities at m/e 180 and m/e 190 demonstrates retention of all ten deuteriums in the corresponding ion in the spectrum of II. The postulated<sup>1</sup> loss of acetonitrile from V producing VIII is confirmed by the appropriate metastable transition. Another metastable transition confirms that VIII is formed from VII via loss of a methyl radical. Metastable peaks were observed at m/e 156·3 and 144·6 for loss of protated acetonitrile from Va, m/e 231, and for loss of deuterated acetonitrile from Vb, m/e 224. Loss of a protated methyl radical from VIIa, m/e 205, and a deuterated methyl radical from VIIb, m/e 198, is confirmed by metastable peaks at m/e 176·1 and 163·6 in the spectra of II and III. Consequently structures of V, m/e 221, and VII, m/e 195, are required which will maintain structural integrity of the remaining methyl group.

A metastable transition<sup>4</sup> confirms that IV fragments via loss of a  $C_6H_5$  radical producing an ion at m/e 159 (IX). The following evidence confirms that the  $C_6H_5$  radical lost contains the original hydrogens of one of the two phenyl rings of IV: a) m/e 159 is shifted within experimental uncertainty to 164 in the spectra of II, corresponding to loss of  $C_6D_5$  from IVa, b) loss of  $C_6H_5$  from IVb is confirmed by the shift of m/e 159 to 165 in the spectrum of III; the equivalent conclusion can be drawn from the calculated isotopic purity of III based on ions at m/e 161 through 165, vide post, and c) the absence of protium-deuterium scrambling in IVa prior to fragmentation is indicated by the fact that the intensities at m/e 165 and 166 do not exceed those for m/e 160 and 161 in the spectrum of I.

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The specificity observed in the cleavages of the  $\alpha$ -carbon—methyl-carbon bond and the  $\alpha$ -carbon—phenyl-carbon bond suggest a high if not total retention of structure upon formation of the molecular ion.

The ion at m/e 194 (X),  $C_{14}H_{12}N$ , was shown by a metastable transition to be formed from V, m/e 221, via loss of hydrogen cyanide and postulated to arise via loss of acetonitrile from VI, m/e 235.<sup>1</sup> The appropriate metastable peak confirms the second pathway. The loss of hydrogen cyanide from V was envisioned as occurring by a double rearrangement mechanism involving a 1,5 migration of methyl hydrogen to  $\alpha$ carbon followed by either a 1,3 or 1,5 migration of phenyl to either nitrogen or carbon.<sup>1</sup> The mechanism proposed for the second pathway is invalidated by the error in the proposed mechanism leading to the [M - 1] ion. Metastable peaks were observed at 168.9 and 180.2 in spectra of II corresponding to loss of protated acetonitrile from the [M - 2] ion producing m/e 203 and to loss of protium cyanide from the [M - 15] ion producing m/e 204. The agreement between the intensity at m/e 194, 11.0 (LKB) and 8.1 (CEC), with the sum of the 203 and 204 intensities, 9.5 (LKB) and 7.8 (CEC), indicates that 194 is shifted to m/e 203 and 204 in the spectra of II. The analogous loss of deuterated acetonitrile from the [M - 1] ion and deuterium cyanide from the [M - 18] ion in the spectrum of III producing ions at m/e 197 and 196 respectively is deduced as follows: a) metastable peaks were observed for loss of  $CD_aCN$  from VIb and DCN from Vb at m/e 161.0 and 171.5 respectively, and b) agreement was observed between the intensity at m/e 194, 11.0 and 8.1, with the sum of the intensities at m/e 196 and 197, 11.0 and 9.1. The hydrogen cyanide produced in the formation of m/e 194 from m/e 221 is indicated to contain one of the original methyl hydrogens present in I; this is consistent with the required retention of integrity of the methyl group in V. These results are in qualitative agreement with the mechanism proposed for the fragmentation of V to X. The acetonitrile formed, when VI fragments producing 194, carries off one of the original methyl groups present in I. At least one of the methyl groups present in the azine must then retain its identity when the [M - 1] ion is formed from the molecular ion. The percentage contributions of V, m/e 221 and VI, m/e 235, to the formation of X, m/e 194, were calculated from the intensities at m/e 204 and 203 in the spectra of II and from the intensities at m/e 196 and 197 in the spectra of III. The results are given in Table 5. At 70 eV approximately 25 to 32 percent of the 194 ion intensity is calculated to arise from m/e221 based upon spectral data from II and III. This discrepancy may result from an isotope effect which might favor loss of protium cyanide from Va over deuterium cyanide from Vb and/or the correction of the experimental intensities at m/e 196 and 197 which may introduce a systematic error into the data from III. The percentage contribution of each process to the intensity at m/e 194 was determined as a function of ionizing energy. Within experimental uncertainty the relative contributions are seen to be independent of electron energy from 70 eV to values close to the appearance potential of the 194 ion. From 16 to 10.2 eV the standard deviation in the percentage contribution for each pathway was calculated to be 3 percent from the composite data from spectra of II. From 16 to 10.8 eV the data from spectra of III also yielded a standard deviation of 3 percent. At electron energies very close to the appearance potential of X the data in Table 5 indicate but clearly do not prove that the contribution of the process leading from the 235 ion to the 194 ion increases. The uncertainty is shown by the results from two 10 eV spectra of III which indicate 71 and 100

	Cmpd. II	(Ring $d_{-10}$ )	Cmpd. III (Methyl d-6)		
eV	% 194 from 221ª	%194 from 235 <sup>b</sup>	% 194 from 221°	% 194 from 235 <sup>d</sup>	
70	32·7(31·6) <sup>g</sup>	67·3(68·4) <sup>g</sup>	25·4(26·1) <sup>g</sup>	74.6(73.9) <sup>g</sup>	
20	34.0	66·0	23.3	76.7	
16.0 to 10.2 <sup>e</sup>	$34.4 \pm 2.7^{t}$	$65.6 \pm 2.7^{ m f}$			
16.0 to 10.8 <sup>e</sup>			$26\cdot2\pm2\cdot9^{ m f}$	$73.8 \pm 2.9^{ m f}$	
10.6			11.8	88.2	
10.4			7.4	92.6	
10.2			27.2	72.8	
10.0	48.9	51.1	29.2(0)	70.8(100)	
9.8	16.0	84·0	10.8	89.2	

Table 5. Percentage contribution of m/e 221 and 235 to m/e 194 as a function of electron energy

a 100  $I_{204}/(I_{203} + I_{204})$ 

<sup>b</sup> 100  $I_{203}/(I_{203} + I_{204})$ 

 $^{\rm c}$  100 I<sub>196</sub>/(I<sub>196</sub> + I<sub>197</sub>)

<sup>d</sup> 100  $I_{197}/(I_{196} + I_{197})$ 

 $\Delta eV = 0.2$ 

f Std. Dev.

<sup>g</sup> data from spectra recorded on CEC 21-110B.

percent contribution from this process. The observed insensitivity in the relative contributions of the 235 and 221 ions to the 194 ion to changes in beam-energy is analogous to the observation that two processes<sup>7</sup> the relative contributions of which are essentially beam-energy-independent\* are involved in the loss of hydroxyl radical from the molecular ion of benzoic acid.<sup>†</sup> The loss of water from 6-phenylhexanoic acid and of methanol from methyl 6-phenylhexanoate has been shown to involve multiple paths with essentially equal energy requirements.<sup>8</sup>

#### EXPERIMENTAL

Acetophenone- $d_3$ . The methyl hydrogens of acetophenone were exchanged by heating the ketone at 65° with a threefold excess of deuterium oxide in *p*-dioxane (distilled from calcium hydride) containing a small quantity of dried potassium carbonate. The atom % deuterium of the crude ketone after 3 exchanges was calculated to be approximately 90% by rough n.m.r. measurement. The ketone was then purified by distillation under reduced pressure, b.p. 86 to 87° at 25 mm.

Bromobenzene- $d_5$ . Benzene- $d_6$  (Merck, Sharp and Dohme, indicated isotopic purity 99.5 atom %d), 10 g (0.119 moles), was treated with 19.1 g (0.119 moles) of bromine in the presence of iron. The crude product was taken up in ether and washed with water, saturated sodium bicarbonate solution, and water, dried and freed of ether under reduced pressure. Distillation at 70 mm gave 10.9 g of bromobenzene- $d_5$ , 64% yield, b.p. 83 to 85°. One gram of p-dibromobenzene- $d_4$  (recrystallized from ethanol) was obtained.

Acetophenone- $d_5$ . Acetaldehyde (1.24 g, 0.031 moles) dissolved in 10 ml of ether (distilled from lithium aluminum hydride) was added to phenyl-magnesium bromide- $d_5$  prepared from 5 g (0.032 moles) of bromobenzene- $d_5$  and 0.8 g (0.033 moles) of magnesium in 40 ml of ether (distilled from lithium aluminum hydride into the reaction flask under argon). The addition product was hydrolyzed by pouring the reaction mixture onto 40 ml of crushed ice and water containing a few ml of conc hydrochloric acid. The crude 1-phenylethanol- $d_5$  was extracted with ether and oxidized at low

\* Private communication from S. Meyerson.

† Yeo, Cooks, and Williams (A. N. H. Yeo, R. G. Cooks, and D. H. Williams, J. Chem. Soc. (B), 149 (1969)) also found two processes leading to [M - OH] in the spectrum of benzoic acid. However, their data suggest that the two processes respond differently to changes in beam energy. The origin of the difference between their findings and those of Meyerson has not been clarified.

temperatures in acetone with chromium trioxide.<sup>9</sup> Distillation at reduced pressure yielded 1.2 g, 30%, of acetophenone- $d_5$ .

Acetophenone Azine- $d_6$ . Acetophenone- $d_3$  (2 g, 0.016 moles) and hydrazine hydrate- $d_6$  (Merck, Sharp and Dohme) were refluxed in ethanol-O-d containing one drop of glacial acetic acid. Recrystallization three times from ethanol yielded 1.4 g of azine, 71%, m.p. 121.5 to 122.5°, lit 124°.10

Acetophenone Azine- $d_{10}$ . Acetophenone- $d_5$  was converted to the azine by the previous procedure using 95% hydrazine and ethanol as the solvent, m.p. 121 to 122°, lit 124°.<sup>10</sup>

Mass Spectra. Spectra were recorded using the LKB 9000 Prototype and CEC 21-110B mass spectrometers. Spectra taken with the CEC 21-110B instrument were obtained with an all-glass probe at 70°. The source temperature was 170°. The electron-beam current was 100  $\mu$ a. Spectra obtained by introducing samples into the ion source of the LKB either by direct probe or via the separators were within experimental uncertainty identical. Since the latter technique (separators) afforded very uniform and reproducible sample pressures, it was used thereafter, the separators and the oven being maintained at the same temperature. The source temperature was 310° and the trap current 65  $\mu$ a. Low-voltage spectra were recorded with the extraction plates near the block potential.

All spectra were corrected<sup>11</sup> for natural abundance of <sup>13</sup>C, <sup>2</sup>H, and <sup>15</sup>N using an IBM 360-50 computer.

The presence of an [M - 1] ion in the spectrum of I at all adequate values of the ionizing energy prevented direct determination of the isotopic purity of II and III. Practical reasons dictated calculation of the isotopic purity of II from low-voltage spectra of *p*-dibromobenzene-*d*<sub>4</sub> obtained from the bromination of benzene-*d*<sub>8</sub>. The results are given in column 2 of Table 6. The atom percent deuterium in the *p*-dibromobenzene-*d*<sub>4</sub> was assumed to be equal to that in the bromobenzene-*d*<sub>5</sub> in the calculation. Since a primary kinetic isotope effect has been observed in the bromination of bromobenzene-4-*t* and benzene-*t* ( $k_{\rm H}/k_{\rm T} = 1.64$ ),<sup>12</sup> an independent determination of the isotopic purity of II appeared desirable in spite of its indicated high value. The [M - 15] ion in the spectrum of I is extremely intense even at low values of the ionizing voltage. The isotopic purity of

Acetophenone Azine- $d_{10}$ (II) Cmpd.		$R_1CH_3C = NN = CCH_3R_2$ % at eV <sup>b</sup>			
R <sub>1</sub>	. R <sub>2</sub>	0/a	70	15	12.5
$C_6D_5$	$C_6D_5$	93.70	93·06(92·20) <sup>r</sup>	93·21	93·47
C <sub>6</sub> D <sub>5</sub> C <sub>6</sub> D <sub>5</sub>	C <sub>6</sub> D <sub>4</sub> H C <sub>6</sub> D <sub>9</sub> H	6·12 0·080	6·40(7·26) <sup>t</sup>	6.39	6.15
C₅D₄H	C <sub>6</sub> D <sub>4</sub> H	0.099	0·54(0·54) <sup>t</sup>	0.40	0.38
atom %	d	<del>9</del> 9·4			

TABLE 6. ISOTOPIC PURITY DATA

Cmpd.		% at eV <sup>d</sup>					
R <sub>1</sub>	R <sub>2</sub>	%°	70	15	12.5	°∕°	
CD3	CD <sub>3</sub>	58.33	58·7(57·8) <sup>t</sup>	58.5	57.9	$58\cdot2\pm1\cdot1$	
$CD_3$	CD₂H	32-28				$31.7 \pm 0.7$	
$CD_3$	$CDH_2$	4.47				93101	
CD₂H	CD <sub>2</sub> H	3.81				$8.2 \pm 0.1$	
$CD_{2}H$	$CDH_2$	1.05				$1.6 \pm 0.1$	
$CDH_2$	$CDH_2$	0.06				$0.3 \pm 0.2$	

Acetophenone Azine- $d_6$  (III)  $R_1C_6H_5C=NN=CC_6H_5R_2$ 

<sup>a</sup> Calculated from isotopic purity of *p*-dibromobenzene- $d_4$ ; 97.66%  $d_4$ , 2.09%  $d_3$ , 0.25%  $d_2$ 

<sup>b</sup> calculated from intensities at m/e 229, 230 and 231

° calculated from isotopic purity of acetophenone- $d_3$ ; 76·37% $d_3$ , 21·13% $d_2$ , 2·49% $d_1$ 

<sup>d</sup> calculated from intensities at m/e 222, 223 and 224

<sup>e</sup> calculated from intensities at m/e 161 through 165

<sup>1</sup> Data from CEC 21-110B

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II was calculated from the intensities at m/e 231, 230 and 229 in the spectra of II by assuming that a) the intensities arise solely from incomplete deuteration in II and b) hydrogen scrambling does not occur prior to loss of a methyl radical from the molecular ion of II. The first assumption places an upper limit on the percentage of species containing 8 and 9 deuteriums and a lower limit on the species containing 10 deuteriums. The results in columns 3, 4, and 5 of Table 6 are in good agreement with the values derived from *p*-dibromobenzene- $d_4$ . The isotopic purity of III was calculated from low-voltage spectra of acetophenone- $d_3$  (Table 6, Column 2). The percentage of II containing six deuteriums was calculated from the spectrum of III by assuming a) the intensities at m/e 224, 223 and 222 arise entirely from species containing six or fewer deuteriums, b) hydrogen scrambling prior to loss of a methyl radical is absent, and c) there is no isotope effect on the fragmentation. This percentage was computed from the intensity at m/e 224 corresponding to the loss of CD<sub>3</sub> from the  $d_{-6}$  analog (calculated from the total intensity at m/e 224 and the isotopic distribution of III based upon data for the ketone) and the sum of the intensities at m/e 224, 223 and 222. The agreement is seen to be excellent: see Table 6, Columns 3, 4 and 5.

Assuming structural integrity in the loss of  $C_6H_5$  from the molecular ion, the isotopic distribution of III is given by the intensities at m/e161 through 165 uncorrected for any contributions corresponding to ions at m/e 158 and 159 in the spectrum of I. The composition of III (Column 6) based upon intensity data from four 70 eV spectra (3LKB 9000 and 1 CEC 21-110B) and three 20 eV spectra (LKB 9000) is in excellent agreement with the results in Column 2.

Ions of interest in the spectra of II and III were corrected for contributions from incomplete labeling. As an illustration, the equations derived to correct the experimental intensities at m/e 229 through 231 and 222 through 224 in the spectra of II and III are given below.

Let  $Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$  correspond to the variously ring deuterated azines given in order of entry in Table 6 with the percentages normalized to a  $Y_1$  value of 100. The corrected intensities at m/e 230 and 229 are given by eqns. (2) and (3).

$$\mathbf{I}_{230}^{\text{Corr.}} = \mathbf{I}_{230}^{\text{Exp.}} - \mathbf{I}_{231}^{\text{Exp.}} (Y_2 / Y_1)$$
(2)

$$I_{229}^{\text{Corr.}} = I_{229}^{\text{Exp.}} - I_{231}^{\text{Exp.}} ((Y_3 + Y_4)/Y_1)$$
(3)

Let  $X_1, X_2, \ldots, X_6$  correspond to the variously methyl-deuterated azines given in order of entry in Table 6 with the percentages normalized to an  $X_1$  value of 100. The calculated intensity at m/e 223 and 222 is given by eqns. (4) and (5). The corrected 223 and 222 intensities are given by eqns. (6)

$$I_{223}^{\text{Calc.}} = \left[ (0.5X_2 + X_3 + 0.5X_5) / (X_1 + 0.5X_2 + 0.5X_4) \right] I_{224}^{\text{Exp.}}$$
(4)

$$I_{222}^{\text{Calc.}} = \left[ (0.5X_4 + 0.5X_5 + X_6) / (X_1 + 0.5X_2 + 0.5X_4) \right] I_{224}^{\text{Exp.}}$$
(5)

and (7). The intensity of m/e 224 due solely to the  $d_6$  azine is given

$$\mathbf{I}_{223}^{\text{Corr.}} = \mathbf{I}_{223}^{\text{Exp.}} - \mathbf{I}_{223}^{\text{Calc.}}$$
(6)

$$\mathbf{I}_{222}^{\text{corr.}} = \mathbf{I}_{222}^{\text{Exp.}} - \mathbf{I}_{222}^{\text{Calc.}}$$
(7)

by eqn. (8).

$$I_{224}^{D6} = I_{224}^{Exp} / [1 + 1/(X_1/(0.5X_2 + 0.5X_4))]$$
(8)

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