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MASS SPECTROMETRY—II: THE UNIMOLECULAR DECOMPOSITION OF BENZALDEHYDE AZINE IN THE GAS PHASE INDUCED BY ELECTRON-IMPACT

STUART E. SCHEPPELE, RONALD D. GRIGSBY*, KEITH F. KINNEBERG, EARL D. MITCHELL, and CLAUDE A. MANNAN[†] Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074, USA

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Abstract—The mass spectra of benzaldehyde azine- $\alpha, \alpha' d_2$ (III) and benzaldehyde azine- d_{10} (IV) reveal that both ring and α hydrogen are lost from the molecular ion of benzaldehyde azine (II) in forming the [M - 1] ion. Data from the spectra of III and IV at 70 eV and reduced ionizing voltages are consistent with the existence of two competing pathways producing [M - 1] ions. Rearrangement ions are observed in the spectra of II. Randomization is unimportant in the electron-impact-induced fragmentation reactions of II. The rearrangement-fragmentation reactions for II in general parallel those previously observed for acetophenone azine (I).

INTRODUCTION

REARRANGEMENTS accompanying electron-impact-induced fragmentation reactions are important both in analysis of ion energetics and in structure determination.¹

The mass spectrum of acetophenone azine (I) showed evidence for the occurrence of phenyl, methyl and hydrogen migrations.² The data were interpreted in terms of multicentered rearrangements (1,3; 1,4; 1,5) from carbon to nitrogen or carbon to carbon. Electron delocalization in the precursor and rearranged ions and the formation of stable neutral molecules appeared to contribute part of the driving force for the rearrangement processes.

To test the generality and effect of substitution on the proposed rearrangementfragmentation scheme for aromatic azines,² the mass spectra of benzaldehyde azine (II), benzaldehyde azine- α , α' - d_2 (III), and benzaldehyde azine- d_{10} [‡] (ring-deuterated) (IV) have now been examined. Since extensive mass spectral data for the parent aldehyde³ and its phenylhydrazone,⁴ anil⁵ and nitrone⁶ derivatives are available,



conclusions concerning the effect of a functional group upon electron-impact-induced decomposition appear feasible. During the course of this investigation mass spectra of $II^{7,8b}$, III^7 and IV^8 appeared in print.

* Texas A and M University, College Station, Texas 77843.

† Undergraduate Research Participant.

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RESULTS AND DISCUSSION

Ion intensities, which are normalized to a molecular ion value of 100, from spectra of II and III and from II, III and IV corrected for naturally occurring heavy isotopes of carbon, nitrogen and hydrogen, but not for incompletely labeled species, are tabulated in Tables 1 and 2 respectively. Fragment ion intensities are seen to increase

	Relative Intensity	n n' d	
mje		<i>a</i> , <i>a</i> - <i>u</i> ₂	
210		100.0	
209		59.3	
208	100.0	18.5	
207	74.2	1.3	
206	1.1		
182		15.1	
181	13.6	18.2	
180	28.8	14.3	
133		123.0	
132		5.3	
131	109.0		
130	3.0		
79		9.2	
78	8.7	4.9	
77	64.4	58·0	

TABLE 1. PARTIAL SPECTRA OF BENZALDEHYDE AZINES AT 70 eV*†‡

* Spectra recorded on CEC 21-110B. † Ion source temp. 165°.

‡ Spectra uncorrected for presence of incompletely labeled III.

			Relative I	ntensities			
	Cmpd. II unlabeled		Cmpd. II	$[\mathbf{I} \alpha, \alpha' - d_2]$	Cmpd. IV ring-deuterated Ion Source Temp. °C		
	Ion Source	Ion Source Temp. °C		Temp. °C			
m e	215	310	215	310	215	310	
218					100.0	100.0	
217					35.4	46.7	
216					54.3	68.5	
215					4∙0	4.9	
214					1.3	2.0	
210			100.0	100.0			
209			65.4	89.1			
208	100.0	100.0	19.7	27.7			
207	87·2	122.0	1.8	2.2			
206	3.1	4.4					
205	1.3	1.8					
191					11.7	15.8	
190					15.7	22.4	
189					14.6	19.7	
182			14.1	19.2			
181	12.7	16· 0	18.8	26.8			
180	27.6	38.7	17.7	24.8			
136					144·0	186.0	
133			138.0	196· 0			
131	122.0	173·0					

Table 2. Partial spectra of benzaldehyde azines at $70 \text{ eV}^{*\dagger}$

* Data from LKB 9000. † Spectra uncorrected for incompletely labeled III and IV.

with increasing source temperature. This is the result of decreasing molecular ion stability with increasing source temperature, e.g. the percents ionization ($\%\Sigma_{25}$) for the molecular ion of II are 14.9, 13.4 and 9.6 at source temperatures of 165, 215 and 310 degrees.

The pertinent metastable transitions in the spectra of II are listed in Table 3. Not all such transitions were observed with both mass spectrometers. The spectrum of II

M*	Transition	Observed (eV)
206.0	$208^+ \rightarrow 207^+ + 1$	70 to 10
179·0	181+ -→ 180+ + 1	70 to 10
177·0	$181^+ \rightarrow 179^+ + 2$	70 to 12
157.5	$208^+ \rightarrow 181^+ + 27$	70 to 12
156.5	$207^+ \rightarrow 180^+ + 27$	70 to 12
82.5	$208^+ \rightarrow 131^+ + 77$	70 to 12

TABLE 3. METASTABLE TRANSITIONS OBSERVED IN THE MASS SPECTRUM OF BENZALDEHYDE AZINE

TABLE 4. PEAKS MEASURED AT HIGH RESOLUTION IN THE MASS SPECTRUM OF BENZALDEHYDE AZINE AT 70 eV

m e	$\Delta m/e imes 10^3$	Composition
181.0883	-0.8	C ₁₃ H ₁₁ N
1 80·0 806	-0.7	$C_{13}H_{10}N$
131.0609	0.0	$C_8H_7N_2$

recorded with the LKB instrument shows a broad metastable peak of moderate intensity in the mass range 156 to 158. The appropriate mass shifts were observed for the metastable peaks in the spectrum of III, which reveals a broad unresolved metastable peak in the mass range 155 to 158. Equivalent results were obtained for IV.

Elemental compositions for ions in the spectra of II and III are listed in Tables 4

		,		
Exp. m/e	Possible Composition	Calc. <i>m</i> /e	$\Delta m/e imes 10^3$	Assumed Composition
211.1155	$C_{14}H_9N_2D_3$	211.1189	3.4	
	${}^{12}C_{13}{}^{13}C_{1}H_{10}N_{2}D_{2}$	211.1159	0.4	${}^{12}C_{13}{}^{13}C_1H_{10}N_2D_2$
210.1123	$C_{14}H_{10}N_2D_2$	210.1126	0.3	$C_{14}H_{10}N_2D_2$
209.1041	$C_{14}H_{11}N_{2}D$	209.1063	2.2	
	$C_{14}H_9N_2D_2$	209.1048	0.7	$C_{14}H_{9}N_{2}D_{2}$
208·0987	$C_{14}H_{12}N_2$	208.1000	1.3	
	$C_{14}H_{10}N_{2}D$	208.0985	−0·2	$C_{14}H_{10}N_{2}D$
182.0964	$C_{13}H_{10}ND$	182.0954	-1.0	$C_{13}H_{10}ND$
	C13H12N*	182.0970	+0.6	
	$C_{13}H_8ND_2$	182.0939	-2.5	
181.0883	C ₁₃ H ₉ ND	181.0876	0.7	C13H9ND
	C ₁₃ H ₁₁ N*	181.0891	0.8	
180.0801	C ₁₃ N ₈ ND	180.0798	0.3	C ₁₃ H ₈ ND
	$C_{13}H_{10}N$	180.0813	+1.5	$C_{13}H_{10}N$

Table 5. Peaks measured at high resolution in the mass spectrum of benzaldehyde azine- α , α' - d_2

* Insufficient number of hydrogens in molecular ion eliminates this composition.

and 5. Because of the presence of deuterium, multiple compositions have been given for the experimentally measured masses together with calculated masses and errors. The most probable compositions are listed separately.

The molecular ion of II (V) loses hydrogen to form the prominent [M - 1] ion (VI). The following spectral features show that both deuterium and protium* are lost from the molecular ion of III (Va): (a) the relative intensities of the 209 and 208 ions in the spectrum of III, Table 1, (b) the elemental compositions of the 209 and 208 ions, Table 5, and (c) the metastable peaks at m/e 208·0 and 206·0 for formation of 209 and 208 respectively from 210. Equivalent data confirm loss of both protium and deuterium from the molecular ion of IV (Vb). Similar results were reported by Cooks and Tam⁷ and Zeeh and Beutler.^{8b} This finding contrasts with the formation of the [M - 1] ion from the molecular ion of benzaldehyde exclusively via loss of α hydrogen,³ of benzaldehyde anil via loss of α hydrogen (>90%),^{5b} and of the *p*-chlorophenyl nitrone via loss of a ring hydrogen exclusively (presumably producing a five-membered ring).⁶ The unique formation of VI from V may result from properties peculiar to the azine structure.

The ratio of protium to deuterium loss, P/D, and the percent protium loss, PPL, from the molecular ions of III and IV are $3 \cdot 4 \pm 0 \cdot 2$ and 77 ± 1 , and $0 \cdot 61 \pm 0 \cdot 04$ and 38 ± 1 at 70 eV independent of the source temperature and type of mass spectrometer. The average standard deviations are approximately one-third those estimated for any one scan. These values are in reasonable agreement with the reported P/D loss ratio of 4 for Va⁷ and $0 \cdot 75$ for Vb.^{8b} To arrive at the P/D loss ratios the intensities at m/e208 and 216 in the spectra of III and IV were corrected for protium loss from the molecular ions of III and IV containing one and nine deuteriums (see Experimental) but not for molecular hydrogen loss from Va nor the metastable peaks for protium loss from 210 and 218. Assuming that the intensity at m/e 206 in the spectrum of II is a measure of the magnitude of these factors in the spectrum of III, the P/D loss ratio from Va is raised to 4 within experimental uncertainty. Similarly, any correction, while difficult to estimate, would raise the P/D loss ratio from Vb.

Values of the percentage protium loss from Va and Vb are plotted as a function of electron energy in Figs. 1 and 2. The standard deviation in these values is estimated to be 3 to 5 percent.

The remaining spectral data, *vide post*, appear to demand maintenance of structural integrity about at least one α carbon in the molecular ion. For reasons of symmetry only one such α carbon and the associated groups need be considered in a discussion of the mechanism leading to VI.

Let j be the factor by which loss from an α position is preferred over that from a ring position, l be the factor by which protium loss is favored over that of deuterium, and n be the number of equivalent ring positions for purposes of this reaction. Equations (1) and (2) relating to the percentage protium loss from Va and Vb respectively can then be written

$$j/(j+nl) = 1 - (PPL^{Va} \times 10^{-2})$$
(1)

$$jl/(jl+n) = PPL^{Vb} \times 10^{-2}$$
⁽²⁾

where

$$PPL^{Va} = (I_{209}/(I_{208} + I_{209})) \times 10^2,$$

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



FIG. 1. Plot of Percentage Protium Loss as a Function of Electron Energy, solid circles, data for Vb, open circles, data for Va, ion source temperature 215°.

and

$$PPL^{Vb} = (I_{217}/(I_{217} + I_{216})) \times 10^2.$$

The existence of kinetic isotope effects upon the electron-impact-induced cleavage of carbon-hydrogen bonds⁹ argues for including *l* as a factor in determining *PPL*. Table 6 presents values of *l* and *j* as a function of *n* calculated at selected values of the ionizing voltage. Actual experimental values of *PPL*^{Va} and *PPL*^{Vb} rather than data from the curves in Fig. 1 were used to calculate values of *l* and *j*. As might be anticipated,^{9b} *l*, which is independent of *n*, increases with decreasing electron voltage. At any given value of the ionizing voltage *j* is seen to be strongly dependent on *n*, but for any given value of *n*, *j* is seen to increase with decreasing voltage. The probability of loss from a ring position is both different from that for the α position and dependent on beam energy. The same conclusion is drawn from Figs. 1 and 2, which show that the percentage loss of α -deuterium from Va and α -protium from Vb increases at beam energies less than 13 to 14 eV. Comparison of the data in Figs. 1 and 2 reveals that an increase in source temperature from 215 to 310° reduces the probability of loss from the α position at electron energies close to the appearance potential of the



FIG. 2. Plot of Percentage Protium Loss as a Function of Electron Energy, solid circles, data for Vb, open circles, data for Va, ion source temperature 310°.

	TABLE 6								
	<u></u>		<u>-</u> -	·	j for values of n				
eV	$PPL^{VB} imes 10^{-2}$	$PPL^{Vb} imes 10^{-2}$	I	1	2	3	4	5	
70.0	0.77	0.38	1.4	0.4	0.9	1.3	1.7	2.1	
12.0	0.80	0.44	1.8	0.4	0.9	1.3	1.8	2.2	
11.0	0.79	0.52	2.0	0.2	1.1	1.6	2.2	2.7	
10.0	0.65	0.60	1.7	0.9	1.8	2.7	3.6	4.5	
9.2	0.73	0.86	4 ∙0	1.5	3.0	4.5	6.0	7.6	

[M - 1] ion. There appears to be no line of reasoning from the present data to a mechanism for formation of the [M - 1] ion involving scrambling of aromatic and α hydrogens as suggested by Cooks and Tam.⁷ For example, such a mechanism would require the values of PPL^{Va} and PPL^{Vb} to be such that for the true value of *n* and *l*, *j* must equal 1, most reasonably at all values of the electron energy. Loss from a ring or α position should be equally probable once an α position is scrambled with *n* ring positions. This is contrary to the observed results.

Mass spectrometry-II

The data of Figs. 1 and 2 and Table 6 are consistent with a two-pathway mechanism leading to the [M - 1] ion. Meyerson¹⁰ has recently shown that two pathways, each responding differently to changes in beam energy, are involved in the loss of a methyl radical from the molecular ion of methylcyclopentane. Specific loss of α hydrogen (eqn. 3a), which is consistent with preference for loss from the α position and its energy dependence, would constitute one path. The details of the second pathway (eqn. 3b) cannot be clearly delineated at this time. This path might link an

$$[C_{14}H_{12}N_2]^+ \xrightarrow{k_{\mathrm{H}}\alpha} [C_{14}H_{11}N_2]^+ + H^{\cdot}$$

$$V m/e \ 208 \qquad VI \ m/e \ 207 \qquad (3a)$$

$$\underbrace{ \begin{array}{c} \underbrace{k_1} [C_{14}H_{12}N_2]^{+,*} \xrightarrow{k_H^R} [C_{14}H_{11}N_2]^+ + H \\ \hline k_2 \end{array}}_{k_2} V' \xrightarrow{VI \ m/e \ 207} (3b)$$

ortho carbon with an α carbon (forming a six-membered ring) or with nitrogen (forming a five-membered ring) suggested as a minor pathway leading to the [M - 1] ion.⁷ The presence of two isomeric [M - 1] ions at m/e 207 is a reasonable possibility.

It is appropriate to consider the nature of the isotope discrimination factor l of eqns. (1) and (2). Equations (3a) and (3b) represent general mechanisms for formation of the [M - 1] ion. We assume (a) the formation of only one intermediate, V', preceding loss of a ring hydrogen, (b) no isotope effect on k_1 , and (c) the formation of V from V', if it occurs, does so without scrambling of the α and ring hydrogens. The kinetic expressions appropriate to protium and deuterium loss from $C_6D_5CH = N-N = CDC_6H_5$, which is seen to be a hypothetical combination of azines III and IV, are given by eqns. (4) and (5)

$$w_1/w_2 = (k_{\rm H}/k_{\rm D})_{\alpha}$$
 (4)

$$w_3/w_4 = (k_{\rm H}/k_{\rm D})_{\rm R}(k_2 + k_{\rm D})_{\rm R}/(k_2 + k_{\rm H})_{\rm R}$$
(5)

where w_1 and w_2 and w_3 and w_4 are the intensities for protium and deuterium loss from the α and ring positions respectively. Equation 6 can then be derived which expresses *l* in terms of the rate constant ratios of eqns. (4) and (5). Equation 6 reveals that *l* is the geometric mean of the

$$l = [(k_2 + k_D)/(k_2 + k_H)]_R^{1/2} [(k_H/k_D)_\alpha (k_H/k_D)_R]^{1/2}$$
(6)

isotope effects for loss of protium from the α and ring positions times the square root of the factor which partitions the intermediates V'- d_0 (no ring deuterium) and V'- d_5 (5 ring deuteriums) between products and reactants. For the case in which loss of ring hydrogen is rate-determining, $k_2 \gg k_D$ or k_H , *l* is just the geometric mean of the two isotope effects. This is also the case if no intermediate(s) are involved. If the formation of the intermediate(s) is rate-determining, $k_2 \ll k_D$ or k_H , *l* is seen to be equal to the square root of the isotope effect on loss from the α position.

The increased tendency for the molecular ion of o, o'-dichlorobenzaldehyde azine compared to the *meta* and *para* isomers to lose chlorine provides indirect evidence in support of the mechanism.⁷ Loss of ring hydrogen as a contributing mechanism for formation of the [M - 1] ion parallels the loss of ring hydrogen in the formation of the [M - 1] ion in the spectrum of I.¹¹ Direct loss of an α hydrogen, however, parallels loss of an α methyl and an α phenyl from the molecular ion of I.²

The appropriate metastable transition (Table 3) confirms the formation of the m/e 131 ion (VII), via loss of a C₆H₅ radical from V, eqn. (7). The atoms of an original phenyl ring of the azine are indicated to be present in the C₆H₅ radical since the

$$\begin{array}{ccc} [C_{14}H_{12}N_2]^+ & & & \\ (V) \ m/e \ 208 & & (VII) \ m/e \ 131 \end{array}$$

intensity shift of VII to m/e 133 and 136 is quantitative within experimental uncertainty and the metastable transition is shifted to m/e 84·2 and 85·6 in the spectra of III and IV respectively. A metastable transition confirms that VII fragments to produce the $[C_6H_5]^+$ ion.⁷ Although a metastable transition was not observed, the molecular ion, (V), also appears to be a reasonable precursor to $[C_6H_5]^+$.

$$[C_{8}H_{7}N_{2}]^{+} \xrightarrow{*} [C_{8}H_{6}]^{+} \longleftarrow [C_{14}H_{12}N_{2}]^{+}$$
(8)
(VII) m/e 131 (VIII) m/e 77 (V) m/e 208

The intensities at m/e 77 and 78 in the spectrum of III (Table 1), reveal that the $[C_6H_5]^+$ ion is formed with less than 10% incorporation of deuterium. These results, especially the fragmentation sequence V to VII to VIII, support structural integrity of one and probably both phenyl rings in the molecular ion.

The elemental composition (Table 4), reported metastable transition,⁷ and the apparent metastable peak recorded at m/e 157.5 reveal that a rearrangement process is involved in the loss of hydrogen cyanide from V producing m/e 181 (IX) C₁₃H₁₁N. The hydrogen cyanide produced in this fragmentation contains an α hydrogen and

$$\begin{array}{ccc} [C_{14}H_{12}N_2]^+ & \stackrel{*}{\longrightarrow} & [C_{13}H_{11}N]^+ & + & HCN \\ (V) & m/e & 208 & (IX) & m/e & 181 \end{array}$$

carbon of the azine, since (a) within experimental error m/e 181 is shifted to m/e 182 in the spectrum of III (Tables 1 and 2) and to m/e 191 in the spectrum of IV (Table 2), (b) the elemental composition of m/e 182 is $C_{13}H_{10}ND$, and (c) apparent metastable peaks exist at m/e 157.7 and m/e 167.3 in the spectra of III and IV respectively. The results are consistent with a mechanism involving a 1,3-phenyl shift from α carbon to nitrogen concomitant with loss of hydrogen cyanide.^{7,8b}

Hydrogen loss from IX producing m/e 180 is confirmed by the metastable peak at

$$[C_{13}H_{11}N]^+ \xrightarrow{*} [C_{13}H_{10}N]^+ + H^{\cdot}$$
(10)
(IX) m/e 181 m/e 180

m/e 179.0. The one at m/e 178.0 in the spectrum of III is consistent with loss of both deuterium and molecular hydrogen from m/e 182, IXa. Molecular hydrogen is lost from m/e 181, IX (Table 3). In the spectra of IV a metastable peak at m/e 189.0 was observed for loss of protium from m/e 191, IXb. Since metastable peaks were not observed for protium loss from IXa and deuterium loss from IXb, which would correspond to loss from ring position, the results strongly imply that the hydrogen which is lost from IX, m/e 181, was the remaining α hydrogen of the azine.

The apparent metastable peak at m/e 156.5 in the spectrum of II, reported by Cooks and Tam,⁷ confirms that the [M - 1] ion fragments with loss of hydrogen cyanide producing m/e 180, X. The elemental composition of the 181 ion in the

$$\begin{array}{c} [C_{14}H_{11}N_2]^+ \xrightarrow{*} [C_{13}H_{10}N]^+ + HCN \\ (VI) \ m/e \ 207 \qquad (X) \ m/e \ 180 \end{array}$$
(11)

spectrum of III was found to be $C_{13}H_9ND$ (Table 5). Although some ambiguity

exists in the high resolution data for the ion at m/e 180 (Table 5) the results are not inconsistent with the presence of two ions having elemental compositions $C_{13}H_8ND$ and $C_{13}H_{10}N$. The origin of the $C_{13}H_{10}N$ has been discussed. These data, together with the agreement of the sum of the 180 and 181 ion intensities in the spectrum of III with the intensity of the 180 ion in the spectrum of II, and the apparent metastable peaks at m/e 155.8 and 156.8 indicate loss of deuterium cyanide from both the [M - 1], m/e 209 and [M - 2], m/e 208, ions in the spectrum of III. The analogous loss of protium cyanide from the [M - 1] ion, m/e 217 and [M - 2] ion, m/e 216, in the spectrum of IV is deduced from both (a) the intensities at m/e 190 and 189 respectively

	Relative Intensity at m/e^{++}								
	181	180	182	181	180	191	190	189	
eV	Cmp	od. II	Cmpd. III			Cmpd. IV			
15.0	10.5	10.9	10.2	7.2	5.8	9.0	6.6	4.6	
14.0	11.2	6.6	9.4	3.8	3.1	9.2	4-5	2.8	
13.0	8.6	4.3	8 ∙0	2.7	2.0	6.3	3.2	2.6	
12.8			7.8	2.4	1.3	8.0	4 ∙0	1.3	
12.6			7.8	2.5	1.6	7-2	3.2	1.8	
12.5	7.4	3.1							
12.4			6.7	1.9	1.6	6.4	3-2	1.9	
12.2	8.1	2.4	6.3	1.8	1.4	7.3	2.8	1.5	
12.0			5.8	1.7	0.8	5-1	1.8	1.0	
11.9	7.8	2.0							
11.8			5.6	1.4	0.8	5.2	1.8	1.1	
11.6	5.7	1.7	6.8	1.5	1.0	5.6	1.9	1.1	
11.4			5.9	0.8	0.2	4.9	1.6	1.2	
11.3	7.3	1.5							
11.2			4∙5	0.9	0.4				
11.0	6.2	1.3	4.7	0.7		4.5	1.6	0.7	
10.8	5.7	1.2	5.3	1.0		5.4	1.4		
10.6	5.8	1.3	3.8	1.1					
1 0·4	4.2	1.5	3.6	1.1		3.4			
10.2	4.3		3.8						
10.0	3.4		3.4			3-4			

TABLE 7. PARTIAL SPECTRA OF BENZALDEHYDE AZINES

* Data from LKB 9000.

† Ion source temp. 215°.

and (b) the apparent metastable peaks at m/e 166.4 and 165.4. The hydrogen cyanide produced in the fragmentation VI to X, eqn. (11), is indicated to contain one of the original α -hydrogens and carbons of the azine. Therefore, the structure of the [M - 1] ion must be such that one hydrogen 'remembers' that it was an α hydrogen in the azine.

The observation at 12 eV of ions at m/e 180 and 181 in the spectrum of II and at 182 in the spectrum of III, but the absence of ions at m/e 180 and 181 in the spectrum of III, were considered evidence for randomization of hydrogens in the molecular ion prior to hydrogen loss but not prior to expulsion of hydrogen cyanide.⁷ Table 7 tabulates relative abundances for these ions and the corresponding ones in the spectra of IV computed from spectra of II, III and IV recorded under nearly identical instrument settings as a function of electron energy at a source temperature of 215°. Equivalent results were obtained at a source temperature of 310° and from spectra of II and III recorded using the CEC 21-110B. These results, which contrast markedly

with those of Cooks and Tam,⁷ suggest that m/e 180 and 181, in the spectrum of III and 189 and 190 in IV disappear at the same beam energy as m/e 180 in the spectrum of II. The ions at m/e 180 and 189 apparently disappear at somewhat higher beam energies than the 181 and 190 ions in the spectra of III and IV. This difference, if outside of experimental uncertainty, is consistent with the dual pathway mechanism for formation of the [M - 1] ion. Also, metastable peaks were observed in the spectra of III down to 12 eV for the loss of deuterium from m/e 182 and deuterium cyanide from m/e 208 and 209 as were the corresponding metastables in the spectra of II and IV.

Mass spectral fragmentation reactions involving loss of hydrogen cyanide are important for benzaldehyde anils⁵ and heteroaromatic compounds such as phthalazines,¹² pyrido[2,3-d]pyridine,¹² quinoxalino[2,3-d]pyridazine¹² and 1- and 2-naphthonitriles.¹³

Benzaldehyde azine, like benzaldehyde,³ fragments to produce $[C_6H_6]^+$. The shift of m/e 78 to m/e 79 in the spectrum of III is in accord with the formation of $[C_6H_5D]^+$ and hence involvement of α hydrogen in the fragmentation.

It is interesting to note that rearrangement processes in the spectrum of benzaldehyde phenylhydrazone account for approximately 15% of the ion current (estimated ion intensities $\%\Sigma_{40}$)⁴ whereas only 3 to 5% of the ions in the spectrum of II result from rearrangements.

The electron-impact-induced rearrangement fragmentation reactions of benzaldehyde azine parallel in general those suggested for acetophenone azine. The data support the absence of any appreciable randomization accompanying these fragmentations. The data from III and IV when examined collectively are inconsistent with randomization in the molecular ion preceding formation of the [M - 1] ion but are consistent with a two-pathway mechanism for its formation. Since these results do not clearly delineate the details of this mechanism further studies are in progress

EXPERIMENTAL

Benzaldehyde Azine. A solution of benzaldehyde (150 g, 1.60 mol) and 85% hydrazine hydrate (45.7 g, 0.77 mol) in abs. ethanol (150 ml) containing 10 drops of glacial acetic acid was refluxed for 9 hours. Recrystallization of the crude product, obtained by filtration of the reaction mixture cooled to 0° followed by trituration with water, from ethanol yielded 139 g of azine (86%), m.p. 91.8 to 92.6° , lit. 92 to $93^{\circ}.^{14}$

Benzaldehyde Azine- $\alpha, \alpha'-d_2$. Benzaldehyde- α -d was prepared by the method of Brown and Tsukamoto.¹⁵ N,N-Dimethylbenzamide (17·7 g, 0·10 mol) was dissolved in 125 ml of ether (distilled from lithium aluminum hydride into the reaction flask under argon) and the solution cooled to 0°. Lithium aluminum deuteride (1·35 g, 0·032 mol) was added. The reaction mixture was stirred under an argon atmosphere for 4 hours at 0°. The reaction mixture was hydrolyzed at 0° by addition of water followed by addition of a saturated solution of Rochelle salt. The aqueous layer was extracted with peroxide-free ether. The combined ether fractions were washed with 10% aq. hydrochloric acid, saturated sodium bicarbonate solution, and water, dried (MgSO₄), and concentrated. Distillation under reduced pressure (20 mm) yielded 3 fractions. The first fraction (1·98 g) contained 68% aldehyde (20%) and 32% benzyl alcohol- α, α - d_2 by v.p.c. analysis using a 5% SE-30 column. The aldehyde (1·22 g, 0·014 mol) was converted to the deuterated azine by the previous procedure using anhydrous hydrazine (95%) (0·192 g, 0·007 mol), 5 ml of absolute ethanol and 3 drops of glacial acetic acid. The crude azine from evaporation of the ethanol was taken up in ether and washed with sodium bicarbonate solution and water. Recrystallization from abs. ethanol yielded 1·0 g of III, m.p. 92·5 to 93·7°. The second fraction (1 g) was shown to contain deuterated benzyl alcohol (95%) and benzaldehyde-d (5%). An n.m.r. analysis of the third fraction indicated its composition to be approximately 75% unreacted amide and 25% alcohol.

Mass Spectra. Spectra were recorded using the LKB 9000 and CEC 21-110B mass spectrometers. Spectra taken with the CEC 21-110B instrument were obtained with an all-glass probe at temperatures from 40° to 80°. The source temperature ranged from 150° to 180°. Except for low voltage measurements the electron-beam current was held constant at 100 μ a. Samples were introduced into the ion source of the LKB 9000 either by direct probe or via the separators. Since the latter technique afforded very uniform and reproducible sample pressures, the data reported were obtained from spectra recorded using this technique maintaining the separators and the oven at the same temperature, approximately 165°. Spectra were recorded at source temperatures of 200 to 230° and 310° and with trap currents of 65 and 20 μ a. Low voltage spectra were recorded with the repeller plates (CEC 21-110B) and extraction plates (LKB 9000) near the block potential.

The presence of an [M - 1] ion in the spectrum of benzaldehyde prevented determination of the isotopic purity of benzaldehyde- α -d.³ The presence of an [M - 1] ion in the spectrum of II at all values of the ionizing voltage great enough to produce a useful intensity of the molecular ion prevented measurement of the isotopic purity of III and IV. The isotopic purity of III and IV was calculated from the molecular-ion-less-phenyl region of the spectrum. The spectra of II recorded in 0.2 eV intervals from 10 to 12 eV exhibited an intense 131 ion and ions with small residual intensities at m/e 129 and 130. The intensities at m/e 129 and 130 normalized to m/e 131 were found (a) to be invariant to electron energy from 10 to 12 eV, and (b) to decrease with increase in sample pressure, *i.e.* increasing the sample pressure by a factor of 2 doubled the absolute intensity at m/e 131 but did not alter the intensities at m/e 129 and 130. Analogous behavior to changes in electron energy and sample pressure was observed for the ions at m/e 131 and 132 and 133, 134 and 135 in the spectra of III and IV respectively. An explanation, other than peculiarity of the ion source and/or the compound, for this phenomenon is not obvious. Isotopic purities were calculated from the average of 3 partial spectra of II, III and IV recorded in 0.2 eV intervals from 10 to 12 eV under nearly identical conditions by (a) subtracting the sum of the intensities at m/e 131 and 132 and 133, 134 and 135 in the spectra of III and IV from the sums of the intensities at m/e 129 and 130 in the spectra of II and (b) assuming the residuals represent the intensities of the molecular ions of III and IV containing 1 and 9 deuteriums respectively. The isotopic purities so obtained are $98.5 \pm 0.5\% d_2$, $1.5 \pm 0.5\%$ d_1 , or 99.3 \pm 0.5 at. $\frac{9}{2}$ d for III and 93.8 \pm 0.4 $\frac{9}{2}$ d_{10} , 6.2 \pm 0.4 $\frac{9}{2}$ d_9 or 99.4 \pm 0.6 at. $\frac{9}{2}$ d for IV. A check on the validity of this method was made by calculating the isotopic purity of III from the benzyl alcohol = $\alpha, \alpha - d_2$ formed in the preparation of benzaldehyde- $\alpha - d$. Since the low voltage spectrum of N,N-dimethylbenzamide revealed a complete absence of fragment ions in the region of the molecular ion of the alcohol, fraction 3, vide supra, was used to determine the isotopic purity of the alcohol at reduced voltage. Isotopic purity so measured was $98\cdot3 \pm 0\cdot3\% d_2$, $1\cdot67 \pm 0\cdot32\% d_1$ or $99\cdot2 \pm 0\cdot4$ at. % d. Assuming the atom percent deuterium in the aldehyde to be equivalent to that in the alcohol, the isotopic purity of III was calculated to be $98.3 \pm 0.7\% d_2$, $1.6 \pm 0.7\% d_1$ and $0.07 \pm 0.003\% d_0$, or 99.2 ± 0.8 at.% d in reasonably good agreement with the previous results. Correction of the intensities at m/e 209 and 217 in the spectra of III and IV for contributions from molecular ions of III and IV containing 1 and 9 deuteriums is independent of the mechanism for formation of the [M - 1] ion. Since in principle this situation is not valid for protium loss from the [M + 1] and [M + 9] species, the intensities at m/e 208 and m/e 216 were corrected assuming two different mechanisms.

Assuming a partial scrambling mechanism eqns. (12) and (13) were derived to correct the experimental relative intensities at m/e 209 and 208 in the spectrum of III for the presence of [M + 1] and [M] species and for hydrogen loss from the [M + 1] species where X_1 is the intensity at m/e 210, 100, X_2

$$X_3 = X_2 - 1.68_3 \tag{12}$$

$$X_{5} = X_{\rm Va} - [(1.68_{3})(X_{3})/2X_{1}][((1 + N_{\rm H}^{\rm Va}(k_{\rm H}/k_{\rm D}))/N_{\rm H}^{\rm Va})(k_{\rm D}/k_{\rm H}) + 1] - 0.007_{1}$$
(13)

and X_4 and X_3 and X_5 are the experimental and corrected intensities at m/e 209 and 208 respectively, $N_{\rm H}^{\rm Va}$ are the number of ring hydrogens scrambled with one α deuterium, 1.68₃ and 0.007₁ are the fractional percent d_1 and d_0 species normalized to a d_2 value of 100, and $k_{\rm H}/k_{\rm D}$ is the isotope effect. Assuming $k_{\rm H}/k_{\rm D} = 1$ and $N_{\rm H}^{\rm Va} = 4$, eqn. (13) reduces to eqn. (14). With equivalent assumptions

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eqns. (15) and (16) appropriate

$$X_5 = X_4 - \left[(1.68_3)(9)(X_3)/(8)(100) \right] - 0.007_1 \tag{14}$$

to the spectrum of IV can be derived where X_6 and X_8 and X_7 and X_9 are the

$$X_7 = X_6 - 6.57_2$$
(15)

$$X_{9} = X_{8} - (7)(6.57_{2})(X_{7})/(5)(100)$$
(16)

experimental and corrected intensities at m/e 217 and 216 respectively, 6.57_2 is the fraction of d_9 species with the d_{10} normalized to 100, and 100 is the intensity at m/e 218. Values of the percentage hydrogen loss and the P/D loss ratio were calculated from the corrected intensities. Although the value assigned to N might be considered arbitrary the values of X_5 and X_9 were found to be within experimental uncertainty independent of N. Within experimental uncertainty the values of X_5 are independent of $k_{\rm H}/k_{\rm D}$. The standard deviation in these values was computed assuming a 5% standard deviation in the absolute intensities at m/e 210, 209, 208, 218, 217 and 216.

For a two-pathway mechanism eqns. (3a) and (3b) eqns. (12) and (15) remain valid. For this mechanism eqns. (17) and (18) can be derived to correct intensities at m/e 208 and 216 where the X's have the previous

$$X_{5} = [X_{4} - 0.007_{1} - 1.68_{3}X_{3}/X_{1}]/[1 + (1.68_{3})(k_{\rm H}/k_{\rm D})^{\alpha}/200]$$
(17)

$$X_{9} = [X_{8} - 6.57 X_{7}/X_{1}] / [1 + (1.68) (k_{\rm H}/k_{\rm D})_{\rm R}/1000]$$
(18)

meaning and $(k_{\rm H}/k_{\rm D})_{\alpha}$ and $(k_{\rm H}/k_{\rm D})_{\rm R}$ are the isotope effects on α and ring protium loss. To assess the effect of $(k_{\rm H}/k_{\rm D})_{\alpha}$ and $(k_{\rm H}/k_{\rm D})_{\rm R}$ two procedures were employed. An iterative procedure revealed that X_5 and X_9 were independent of the isotope effects and within experimental uncertainty equal to the values computed from eqns. (14) and (16). Assigning a value of 10 to each isotope effect produces only a five percent change in the values of X_5 and X_9 . Consequently the correction to the experimental intensities at m/e 208 and 216 is independent of assumed mechanism and reflects the high isotopic purity of III and IV.

The standard deviations in these functions were calculated from equations derived by the usual method.¹⁶ The usual methods were used to correct for natural abundance ¹³C, ²H and ¹⁵N.¹⁷

All computations were made using an IBM 360-50 computer.

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