# **Electron Impact Fragmentation of** 2-Arylhydrazonopropandioic Acid Derivatives

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Examination of the mass spectra of eleven 2-arylhydrazonopropandioic acid derivatives reveals that a radical ion which is tentatively formulated as a 1*H*-diazirine species is produced in each case (except for the diphenyl ester) by more than one process. Formation of what is formally the aryl amine radical ion occurs by a novel hydrogen rearrangement. Simple cleavage of the bonds  $\beta$  to either the aromatic ring or the C=N moiety also produces abundant ions. The diphenyl ester behaves anomalously yielding the phenol ion instead of the amine. The proposed mechanisms were confirmed by metastable studies, deuterium labelling and exact mass measurements.

2-Arylhydrazonopropandioic derivatives, also known as arylhydrazones of mesoxalic acid, are not only intermediates in the synthesis of a variety of heterocyclic systems<sup>1,2</sup> but also are found to be useful in the agrochemical<sup>3</sup> and polymer<sup>4</sup> fields. Therefore, it was thought to be useful to examine the electron impact fragmentation of this hitherto unexplored class of compounds, in the expectation that they might exhibit interesting rearrangements by analogy with the enamines.<sup>5,6</sup>

# **RESULTS AND DISCUSSION**

The prominent peaks in the mass spectra of the compounds 1-11 listed below are shown in Table 1. The spectra of the deuterated species 12-14 are quoted at the appropriate places in the text.

# Formation of the 1H-diazarine system

All the esters 1-7 show abundant peaks due to the loss of 74 mass units from the molecular ion, while for

	,CO₂R′								
	Ar—N—N==(   R		O <sub>2</sub> R″						
Compoun	d Ar	R	R′	R″					
1	Ph	н	Et	Et					
2	o-MeC <sub>6</sub> H₄	н	Et	Et					
3	o-CIC <sub>6</sub> H₄	н	Et	Et					
4	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	н	Et	Et					
5	p-MeÔČ <sub>e</sub> H <sub>4</sub>	н	Et	Et					
6	p-CeHECeH	н	Et	Et					
7	2-C, H,	н	Et	Et					
8	C₌H₌	н	н	Et					
9	CrH	H	H	H					
10	p-EtOC_H	H	Ĥ	Ĥ					
11	Ph	Н	Ph	Ph					
12	C <sub>e</sub> D <sub>e</sub>	H	Et	Et					
13	C D E	н	н	H					
14	o-CIC <sub>6</sub> H₄	D	Et	Et					

<sup>†</sup> Present address: Department of Chemistry, University of Toronto, Ontario, M5S 1A1, Canada. **8–10** the corresponding loss was 46 mass units. Examination of the metastable transitions revealed that in the case of 1–7, the  $[M-74]^{++}$  ions were formed by three different processes (Scheme 1). In the case of compounds 8–10, only process A (Scheme 1) was found to occur, while for 11 the only route was formally analogous to process B (Scheme 1). However, the following argument would suggest that the ions a', b' and c' formed from 11 have structures different from ions a, b and c produced from 1–10. In the first place a' (m/z 238) has a relative intensity of only 2%.



**1-7**, R' = Et, R'' = Et; **8**, R' = H, R'' = Et; **9**, **10**, R' = R'' = H



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Scheme 1

Table 1. Mass to charge ratios and %I values (in brackets) of the prominent ions in the spectra of 1-11\*

Compound	[M]+,	a	ь	с	d	f	g	h	i	k	1
1	264(6)	190(26)	219(2)	191(7)	218(4)	118(19)	<del>9</del> 1(100)	93(13)	92(54)	65(78)	77(33)
Other peaks	44(12) 43(17)										
2	278(37)	204(48)	233(8)	205(12)	232(4)	132(24)	105(100)	107(12)	106(68)	79(60)	91(40)
Other peaks	<b>44(6) 43(8)</b>										
3	298(39)	224(57)	253(7)	225(9)	252(3)	152(36)	135(100)	127(13)	126(35)	99(53)	111(13)
Other peaks	44(	6) 43(	5)								
4	309(84)	235(51)	264(18)	236(9)	263(5)	163(81)	136(100)	138(7)	137(18)	91(60)	
Other peaks	44(	(71) 43(	(78)								
5	294(27)	220(20)	249(2)	221(4)		148(26)	121(100)	123(10)	122(65)	95(30)	107(17)
Other peaks	44(	(7) 43	(16)								
6	340(28)	266(20)	295(3)	267(4)		194(7)	167(65)	169(3)	168(19)	143(20)	153(6)
Other peaks	44(	(100) 43	(50)								
7	314(6)	240(16)	269(1)	241(3)		168(10)	141(100)	143(9)	142(45)	115(95)	127(23)
Other peaks	44(	(2) 43	(11)								
8	236(4)	190(14)		191(3)		118(18)	91(100)	93(20)	92(43)	65(95)	77(53)
Other peaks	44	(4) 43	(14)								
9	208(34)	162(50)				118(13)	91(93)	93(33)	92(43)	65(100)	77(50)
Other peaks	164	(13) 190	(6)								
10	252(11)	206(5)		<u> </u>		162(5)	135(22)	137(34)	136(30)	109(35)	121(30)
Other peaks	203	(13) 108	(100)								
11	360(11)	238(2)	267(65)	239(8)					92(100)	65(78)	77(75)
Other peaks	211	(7) 1 <del>9</del> 5	(4) 145	(7) 10	5(13) 94	4(50) 93	3(23) 91	(20)		-	

<sup>a</sup> Isotopic abundances subtracted from h and j. With 3, corresponding  $[M+2]^{++}$  isotopic ions were observed.

Second, kinetic energy releases measured for the process [PhNHNC]<sup>+,</sup> $\rightarrow$ [C<sub>6</sub>H<sub>5</sub>N]<sup>+,</sup>+HCN ([118]<sup>+,</sup> $\rightarrow$ [91]<sup>+,</sup>+27), the former ion being produced from c or c' (Scheme 2) for 1 ( $T^{50} = 57 \pm 2 \text{ meV}$ ) (see Experimen-



tal) and 11  $(T^{50} = 90 \pm 10 \text{ meV})$  are appreciably different. This suggests that m/z 239 (c') from 11 does not have the same structure as c from compounds 1-10. Since a and a' are produced, at least in part, from c and c' this would suggest that they too did not have the same structure. The elemental composition of the ions a, formulated as 1H-diazirines, was confirmed in the case of 1 by exact mass measurement. The non-participation of the aryl hydrogens in the elimination of either the alcohol (1-7) or water (8-10) was supported by the loss of CO and EtOH only from the molecular ion of 12 and the loss of CO and H<sub>2</sub>O only from that of 13. Additionally, the loss of EtOD from 14.

Further fragmentation of the ions a generated from **1–10**, leading in most cases to the base peak g, are shown in Scheme 3.

In the case of **11**, an alternative route leading to the base peak via c' is observed (Scheme 4).

Any attempt at a direct comparison between metastable molecular ions produced from an authentic sample of 1-phenyl-1*H*-diazirine and the metastable ions f produced from a in the case of **1** was impossible since 1-phenyl-1*H*-diazirine has only a transient exis-



$$[11]^{+-} \xrightarrow{-OPh} b \xrightarrow{-CO} c' \xrightarrow{-\dot{C}O_2Ph} [PhNHNC]^{+-} \xrightarrow{-HCN} [C_6H_5N]^{+-} \\ * \downarrow_{-H'} f' g \\ a' \xrightarrow{-\dot{C}O_2Ph} [C_7H_5N_2]^+$$

Scheme 4

tence.<sup>7</sup> Very few 1*H*-diazirines have been reported in the literature so far, and those have mostly been obtained in very low yields by the photolysis of heterocycles with adjacent nitrogen atoms.<sup>8-10</sup>

## Formation of the amine radical ion

All the esters 1-7 give what presumably are the corresponding arylamine radical ions h, with approximately 10% relative abundance in each case. The composition of this ion was determined for 1 by an exact mass measurement, and by the shift to m/z 98 in the mass spectrum of 12. Metastable peaks in each case indicated that these ions are produced in a one-step process from the ions c (Scheme 5). The retention



#### Scheme 5

of the amide hydrogen in h is confirmed by the shift of this peak to m/z 128 in the mass spectrum of 14. The low abundance of h made it impossible to confirm its identity by a study of the metastable characteristics. In any event, the method in this case may well have been inconclusive.<sup>11</sup>

A competing process leading to the formation of  $[C_2H_4O]^{+}$  rather than its loss may be responsible for the low abundance of h in some cases. The ion m/z 44 is very intense for 4, where the nitro- group might be expected to destabilize h. The reason for the high intensity in 6 is not clear. The structure of m/z 44 remains a mystery. Work by Holmes et al.<sup>12</sup> has established the kinetic energy release associated with various possible structures of  $[C_2H_4O]^+$ . Attempts to measure  $T_{0.5}$  (see Experimental) for  $m/z \ 44 \rightarrow m/z \ 43$ for 4 and 6 gave irreproducible results. However, for the p-nitro compound 4 the values observed ruled out the formation of  $[CH_3CHO]^+$ ,  $[CH_2-CH_2-O]^+$  and [ethylene oxide]<sup>+</sup>. by comparison with the values of Holmes et al.<sup>12</sup> It can only be concluded that a mixture of structures in formed with the  $[M-2H]^{+}$  ion from dimethyle ther predominating. The variation in the  $T_{0.5}$ values for these compounds is attributed to pyrolysis; similar effects were found for 11, where examination of the transition  $m/z \ 118 \rightarrow m/z \ 91$  showed that the intensity of an adjacent metastable varied markedly with temperature.

With **8** a much more abundant amine ion is formed (c. 20%), probably due to the more facile formation of  $c (m/e \ 191)$  by the loss of CO<sub>2</sub>H from the parent ion. With **9** and **10** still greater abundance (c. 35%) is noticed, due to the intervention of another, perhaps more facile process (Scheme 6). No amine ion is



formed from 11, m/z 93 being shown by exact mass measurements to be  $[C_6H_5O]^+$ .

# Simple cleavage

All compounds 1-14 form abundant ions corresponding to the fission of bonds  $\beta$  to the aromatic ring or to the C=N group (Scheme 7). The ion k is the base peak for 9.



#### The molecular ions

The esters studied exhibit a considerable variation in their molecular ion abundances, depending on the substituent in the aryl moiety. While the molecular ions of 1 and 7 have very low abundances, those of 2-6 have appreciably higher abundances, the maximum being shown by 4. The lowest molecular ion abundance is shown by the monoacid 8, while the diacids 9 and 10 seem to be much more stable to electron impact. The much larger abundances shown for the molecular ions of the compounds reported here compared with the esters of aliphatic diacids, may be ascribed to the resonance structure m, m' as supported by the enhanced abundances for 2, 3 and 5, which contain an electron donating substituent.



The remarkably high intensity (for a molecule with so many labile groups) of the molecular ion of **4** suggests that a different type of resonance  $n \leftrightarrow n'$ occurs in this instance. This is supported by the low abundances for h and j exhibited by **4** in comparison with other hydrazono propandioic acid esters. A similar argument applies to **6**, the molecular ion abundance of which is much greater than those of **1** and **7**, from which it can be deduced that the second phenyl group acts as an electron accepting group.



## **Miscellaneous** features

The diphenyl ester **11** displays an abundant ion at m/z 94 whose composition was determined by exact mass measurements to be C<sub>6</sub>H<sub>6</sub>O and was taken to be the phenol radical ion (Scheme 8).



The base peak in the spectrum of 10 at m/z 108 is produced by loss of ethylene from j (Scheme 9).



# CONCLUSIONS

Four conclusions follow from this study. First, the arylhydrazonopropandioic acids and their esters studied here yield the 1*H*-diazirine system on electron impact, with the possible exception of the diphenyl ester. Second, arylamine ions are formed in the order of facility diester < monoester < diacid, the diphenyl ester again forming an exception. Third, for the molecular ions the arylhydrozono tautomeric form predominates with electron releasing substituents on the aryl moiety, while the enolic tautomeric form exists to an appreciable extent with electron accepting groups on the aryl moiety. Finally, the mass spectrum of the diphenyl ester shows an abundant phenol radical ion.

## EXPERIMENTAL

All the arylhydrazono propanedioic acids, except **6** and **11**, have been reported earlier.<sup>13</sup> Compound **6** was obtained in 70% yield when diazotized benzidine was treated with malonic ester under the reported conditions, m.p. 127 °C. Compound **11** was obtained in 80% yield by an analogous procedure from diazotized aniline and diphenylmalonate, m.p. 145 °C.

## Preparation of 12

 $d_5$ -Aniline<sup>14</sup> (1.2 g) was dissolved in conc. HCl (2.5 ml) and water (2.5 ml) and the ice-cooled solution diazotized with sodium nitrite (0.7 g, in 2 ml water). The resulting diazonium solution was added dropwise over 15 min to a mixture of diethylmalonate (1.6 ml), ethanol (15 ml), sodium acetate (1.8 g) and water (3 ml) with constant stirring and cooling in freezing mixture. The stirring was continued for another 3 h while the temperature rose to 20 °C. The product was extracted with ether, the ethereal layer washed with cold water and the residue after removal of solvent recrystallized from petroleum ether (40–60), to yield a light yellow solid, m.p. 32 °C.

#### Preparation of 13

To 12 (1 g) in boiling ethanol (5 ml), heated under reflux, NaOH (2 N, 3 ml) was added dropwise during c. 10 min and the heating under refluxing continued for a further  $\frac{1}{2}$  h. The solution was acidified with dil. HCl and the resulting yellow solid recrystallized from dilute ethanol, m.p. 162 °C.

## Preparation of 14

Compound **3** (0.2 g) in dioxane (2 ml) was refluxed with  $D_2O$  (1 ml) for about 1 h and the solid resulting on cooling filtered and dried, m.p. 77 °C. Mass spectral determinations revealed 70% deuterium incorporation.

## Measurement of spectra

The low resolution spectra were recorded on an MS 12 mass spectrometer at 70 eV, using the direct inlet system and source temperatures ranging from 30–60 °C. Exact mass measurements (resolution 10 000, heptacosafluorotributylamine as reference) and determination of  $T^{50}$  or  $T_{0.5}$  values were carried out using an AEI MS 902 mass spectrometer.  $T^{50}$  is determined from measures of the width of the peak at a height such that half the peak area is above and half below.<sup>15</sup>  $T_{0.5}$  is determined from the peak width at half height.

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