Electron Ionization and Chemical Ionization Mass Spectra of Pyridinium and Isoquinolinium Ylides

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Electron ionization (EI) spectra and both positive and negative chemical ionization (CI) spectra have been obtained for four isoquinolinium ylides and two pyridinium ylides. Electron transfer reactions dominate the CI mass spectra. The base peak in negative chemical ionization is the [M]⁻⁻ ion, formed by electron capture. In the positive methane CI spectra the molecular ion, [M]⁺, is relatively more intense than [MH]⁺ showing electron transfer to be the main positive ionization process. In the positive ammonia CI spectra, proton transfer to give [MH]⁺ is the main ionization process, but electron transfer is also observed. The EI spectra show fragmentations in which the aromatic nitrogen molety retains the charge and fragmentation is by loss of radicals or small neutral molecules from the side-chains. Radical driven reactions are proposed to explain these spectra.

INTRODUCTION

Ylides can be proton acceptors, electron acceptors or electron donors, so their behaviour under chemical ionization conditions in a mass spectrometer is of interest. In spite of this, the CI mass spectra of ylides have not been reported and there are few studies of their EI spectra.

The rearrangement of pyridinium ylides to indolizines has been studied by Poshivalov et al. using field desorption mass spectrometry, but these ylides were said to rearrange so rapidly that electron ionization showed only the spectra of the indolizines.¹ Alkylidene triphenyl phosphoranes were stable enough that they gave useful positive and negative EI spectra which contained structural information and evidence for numerous rearrangements.^{2,3} Sulphur ylides were also reported to give useful EI mass spectra,4.5 and a selenium ylide showed a strong molecular ion and fragments in which the charge stayed with the diphenylselenium moiety.

This paper reports electron ionization spectra and both positive and negative chemical ionization spectra of six nitrogen ylides. In the positive CI mode methane and ammonia were used as reagent gases. Methane was used for the negative ion CI experiments. Four isoquinolinium and two pyridinium ylides were studied (compounds 1-6).



EXPERIMENTAL

Mass spectra

Mass spectra were measured on a VG 7070F double focusing mass spectrometer with a VG 2225 data system (VG Analytical Ltd, Manchester, UK). Electron ionization spectra were measured with the electron beam at 75 V, the ion beam at 2 kV, and the source temperature at 240-260 °C. The methane chemical ionization spectra were obtained with a 100-150 V electron beam, a 2 kV ion beam and a source temperature of 200-220 °C. For ammonia chemical ionization the same conditions were used except that the source temperature was between 160-220 °C and pyridine or N,N-diethylaniline was bled into the source to give a lock mass.

Negative chemical ionization spectra were measured with the ion beam at 3 kV, and the source temperature at 198-220 °C. The trap, heater and repeller were disconnected. A mixture of chloroform, dibromobenzene and iodobenzene was used to give lock masses $(Cl^-, Br^- and I^-).$

Accurate mass measurements were made on a VG 7070E at 6 kV and 10 000 resolution. PFK was used as the reference compound.

Preparation of the ylides

Compounds 1^7 , $3^{8,9}$, 5^7 and 6^8 were synthesized according to methods given in the literature. Compounds 2 and 4 were synthesized according to the method given below and in Ref. 10.

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Preparation of ethyl methyl bromomalonate. (i) Malonic acid (104 g, 1 mol), dry ethanol (46 g, 1 mol) and sulphuric acid (1 ml) in acetone (600 ml) were mixed and left to stand for one week. Vacuum distillation gave the monoethyl malonate. Further esterification using a Dean and Stark apparatus with methanol (1 mol) in boiling benzene with a trace of sulphuric acid gave the mixed ester (b.p. 70-81 $^{\circ}C/6 \text{ mm } 10.0 \text{ g}$). (ii) The ethyl methyl malonate in carbon tetrachloride was treated with bromine (10.7 g) over 30 minutes and refluxed for a further 30 minutes. (The reaction was initiated by a 150 W light.) The yellow solution was washed with Na₂CO₃ solution and water and then dried. Distillation gave ethyl methyl bromomalonate (b.p. 104-6 °C/9 mm 12.1 g) containing some dimethyl and some diethyl ester.

Preparation of compound 2: isoquinolinium ethoxycarbonyl(methoxycarbonyl) methylide. Isoquinoline (6.45 g, 0.05 mol) and ethyl methyl bromomalonate (11.25 g, 0.05 mol) and chloroform (10 ml) were mixed and left to stand for 4 days. The mixture was diluted with more chloroform (60 ml) and treated with Na₂CO₃ solution. Addition of light petroleum to the dried chloroform layer gave the ylide, which crystallized from benzene (m.p. 175–177 °C, 11.3 g (83%)). Mass spectra indicated that the product was 90% pure and that the major impurities were about 4% each of the dimethyl (compound 1) and diethyl (compound 3) ylides.

Preparation of compound 4: isoquinolinium cyano(ethoxycarbonyl) methylide. Isoquinoline (38.7 g, 0.3 mol) and ethyl bromocyanoacetate (86 g, 0.45 mol) in diethyl ether (300 cm³) were left for 3 days; the red precipitate was washed with ether, treated with chloroform and water and excess sodium carbonate solution added. Chromatography on alumina (Laporte type H) of the chloroform extracts and crystallization from ethanol gave the ylide as long yellow needles (m.p. 146–147 °C, 32.2 g (45%; found C 69.9, H 4.9, N 11.5; $C_{14}H_{12}N_2O_2$ requires C 70.0, H 5.0, N 11.7).

RESULTS AND DISCUSSION

Electron ionization data

The electron ionization spectra of the six ylides are given in Table 1 (the four isoquinolinium ylides) and Table 2 (the two pyridinium ylides). Both groups of ylides fragment in the same way, outlined in Scheme 1 for compound 2. The fragmentations are notable because the charge stays on the aromatic ring while the radical centre dominates the reactions of the diester side-chain.

Although no MS/MS data have been obtained, the agreement among the six ylides provides strong support for the fragmentations proposed. In addition, the accurate masses of some peaks in the spectra of compounds 1, 3, 4 and 5 have been measured. These are given in Tables 3–6, along with the compositions

	quinolini	ium ylides*		
m/z	1	Relative in 2	itensity (%) 3	4
220		-	20	
220 287		2.0	15.0([M] ⁺ ′)	
274		2.2		
273	—	17.9([M]+ ⁻)	_	
260	6.7	_	—	-
259 259	39.1([M] ⁺⁺)		_	
230 243			3.6	_
242	_	5.4([M-31] ⁺)	10.8([M-45]+)	
241	_		0.9	9.5
240	_			47.3([M]+·)
230	61	18	1.9	
228	41.4([M-31] ⁺)	13.3([M−45] ⁺)	_	
217	_	_	1.6	
216	0.9	0.9	4.7	
215	_	6.3([M-58]**)) 24.8([M-72] ^{+·})	-
214		8.9	6.6	 5.4
213	_	_		15.6([M - 28] ⁺⁻)
202	6.8	5.5	_	-
201	50.3([M-58]+*)) 35.7([M – 72] ⁺))	-
200	3.7	1.8	_	—
199	1.3	2.4	2.9	-
196	1.0			3.1
195	_		_	27.9([M-45] ⁺)
188	_	_	1.9	_
187	-	1.0	3.5	-
185	10		1.7	
172	1.0	_		_
170	12.8	11.3	6.5	_
169	1.5	_	2.5	25.1
168		_	1.5	100 ([M-72] ^{+.})
167		_		25.8
165	_			36
158	1.1	-	1.9	_
157		_	1.3	_
156	1.2	_	1.8	<u> </u>
155		_		4.1
124	0.9	33	25	_
144	19.1	17.7	17.0	_
143	100	100	100	11.4
142	8.0	5.0	8.6	1.4
141	6.6 15.0	5.2	6.4	20.7
139	15.9	15.4	7.8	33.5
133	_	_	6.8	
131	1.1	-	3.0	
130	9.5	13.2	17.3	6.3
129	47.4	46.8	58.9	38.6
128	31.0	19.7	16.1	14.5
117			1.0	_
116	4.4	4.8	6.2	3.4
115.5	1.4			
115	27.1 11 7	27.8	36.8	32.4
113	5.9	5.0 4.1	10.2 3.1	2.8
105	 		1.5	
103	9.5	6.0	8.4	5.3
102	12.8	9.8	22.0	9.3

Table 1. EI mass spectra of compounds 1-4, the iso-

Table	e 1 (c	ontinued)		
		F	Relative intensity (%)	
m/z	1	2	3	4
91		2.5		-
89	3.7	2.1	3.0	6.3
88	4.1	3.9	5.2	2.1
87	2.6	4.3	2.7	3.9
86	—		2.1	
84		2.0	—	
78		—	2.5	
77	5.7	5.4	6.2	4.5
76	4.3	5.8	5.6	3.1
75	5.2	7.3	5.3	5.4
74	3.5	4.0	6.8	
70.5	2.1	6.5	3.6	
70		_	—	3.2
69		3.2	2.3	
65	2.4		2.8	3.0
64.5			2.2	-
64	2.9		—	
63	9.1	3.6	8.0	15.8
62	4.8	3.4	2.9	5.8
60	—	—	4.6	
59	9.1	2.9	—	
57	_	4.2	—	
55		3.0	_	
52	_	—	3.9	
51	8.4	6.8	9.9	6.8
50	5.4	4.7	6.4	5.1
a T L .	F 1			- (

^a The El spectra are reported above m/z 50. From m/z 50–100 relative intensities \geq 2% are reported. Above m/z 100 relative intensities \geq 0.9% are reported.

deduced for the ions and hypotheses for their fragmentation pathways.

The loss of 58 mass units from the molecular ion $(m/z \ 273 \rightarrow m/z \ 215$ in Scheme 1) might imply loss of CH₂ and CO₂, by analogy to the reaction seen for sulphur ylides.⁴ A radical driven, five-centred reaction is also possible (Scheme 2).

A six-centred reaction may explain loss of C_2H_4 from the ethyl esters (Scheme 3).

Chemical ionization data

The methane CI spectra of these nitrogen ylides are shown in Table 7. Each of the six ylides has a strong molecular ion (a radical ion). Some proton transfer is observed, but the molecular ions, formed by electron transfer reactions, are relatively more intense than the $[MH]^+$ ions.

On fragmentation the charge is retained on the aromatic nucleus, frequently giving rise to radical ions. The ester functions in the ylides are lost either as radicals RO' from $[M]^+$ or $[MH]^+$, or as the alcohol ROH from $[MH]^+$ (where R is CH₃ or C₂H₅). The data do not permit the relative importance of these reactions to be measured.

The methyl esters show an unusual fragmentation which may be concerted loss of CO_2CH_2 or may be loss of CH_2O and CO (see Schemes 1 and 2). The ethyl esters show loss of ethene followed by decarboxylation, which may be rationalized by Scheme 3. In all cases loss of both ester groups from the side-chain is observed; this gives charged fragments containing the

Table	2.	EI	mass	spectra	of	compounds	5	and	6,	the
		pyri	idininn	n vlides*						

	Relative intens	ity (assignment)
m/z	5	6
237		17.2([M]+·)
210	7.2	
209	62.8([M]+-)	
193		2.0
192		22.3([M-45] ⁺)
179	9.9	_
178	73.9([M-31] ⁺)	_
165		24.5([M-28-44]+·)
164		10.5
162	2.6	_
152	5.9	_
151	75.0([M-58] ⁺⁻)	
150	4.2	
149	5.2	<u> </u>
148	48.6([M-31-30] ⁺)	15.4([M-45-44] ⁺)
146	1.2	—
137		9.1
135	2.8	
122	1.9	—
121	1.3	
120	25.2([M-31-58] ⁺)	17.0([M-45-28-44] ⁺)
119	3.2	2.8
118	2.0	-
113	1.3	-
106	2.2	
95	3.0	
94	31.2	11.1
93	100	100
92	6.8	3.6
91	18.2	6.2
90	3.0	
80	21.1	20.1
79	36.9	17.6
78	20.6	3.1
77	1.8	
74	5.8	
71	1.1	2.7
70	 	2.0
69	3.7	3.1
67	3.2	
66	5.5	
65	30.2	28.7
64	23.0	5.5
63	22.6	3.5
62	1.3	
59	8.4	
5/	2.0	1.0
55	—	4.4
54	1.9	
53	10.0	4. <i>1</i> 67
52	10.8	D./
51	10.0	0.0
50	0.0	

^a The EI spectra are reported above m/z 50, for peaks with relative intensity $\ge 1\%$.

aromatic nucleus $(m/z \ 143$ for the isoquinolinium ylides, **1-4**, and $m/z \ 93$ for the pyridinium ylides, **5** and **6**).





Scheme 1. Fragmentation of compound 2 after electron ionization.

Ylide 4, with a nitrile group in its side-chain, shows a peak corresponding to loss of ethene from the $[M+1]^+$ ion, which agrees with the peak at m/z 212 in its EI spectrum.

Loss of ethene may be rationalized by the McLafferty rearrangement shown in Scheme 4. This presumes that the nitrile allows the molecular ion (or the $[M]^+$ ion) to have the rearranged structure (shown

in Scheme 4 for m/z 241). The rearranged ion can now lose C₂H₄ by the McLafferty rearrangement, and can then lose CO₂ to give m/z 168 (the base peak in EI) or m/z 169 (relative intensity 95% in the methane CI spectrum). This rearrangement explains the major differences between compounds 1-3 and compound 4 in both EI and CI.

Under ammonia chemical ionization conditions

Table 3. Electron ionization spectra: accurate mass data for compound 1, mol. wt 259			Table 4. Electron ionization spectra: accurate mass data for compound 3, mol. wt 287				
Observed mass	Composition	∆M (ppm) (obs.−calc.)		Observed mass	Composition	ΔM (ppm) (obs. – calc.)	
259.0862		7	[M]+·	287.1149	C ₁₆ H ₁₇ NO₄	-3	[M]+·
228.0684	C ₁₃ H ₁₀ NO ₃	10	[M−CH₃O] ⁺	215.0959	C ₁₃ H ₁₃ NO ₂	6	[M–C ₂ H ₄ –CO ₂]+·
201.0803	C ₁₂ H ₁₁ NO ₂	6	[M-CH ₂ O-CO] ⁺⁺	214.0507	C ₁₂ H ₈ NO ₃	1	$[M - C_2H_4 - C_2H_5O]^+$
198.0541	C ₁₂ H ₈ NO ₂	-7	[M−CH ₃ O−CH ₂ O] ⁺	198.0554	C ₁₂ H ₈ NO ₂	~1	[M-C2H4O-C2H5O]+.
170.0613	C, H NO	4	See Scheme 1	170.0607	C ₁₁ H ₈ NO	0	See Scheme 1
143.0732	C ₁₀ H ₀ N	-2	See Scheme 1	143.0721	C ₁₀ H ₉ N	-10	See Scheme 1
142.0643	C ₁₀ H ₈ N	-10	. —	142.0665	C ₁₀ H ₈ N	6	
140.0508	C ₁₀ H _e N	6		130.0656	C ₉ H ₈ N	0	
129.0573	C ₀ H ₇ N	-4	See Scheme 1	129.0576	C ₉ H ₇ N	-2	See Scheme 1
102.0477	C _e H _e	8	See Scheme 1	128.0481	C ₆ H ₈ O ₃	6	

Table 5. Electron ionization spectra: accurate mass data for compound 4, mol. wt 240

Observed mass	Composition	∆M (ppm) (obs.−calc.)	
240.0890	$C_{14}H_{12}O_2N_2$	3	[M]+·
212.0590	$C_{12}H_8O_2N_2$	-2	[M–C ₂ H ₄]+·
195.0549	$C_{12}H_7ON_2$	5	$[M - C_2 H_5 O]^+$
168.0699	$C_{11}H_8N_2$	-7	[M-C ₂ H ₄ -CO ₂]+·
167.0612	$C_{11}H_7N_2$	-1	$[M - C_2 H_5 O - CO]^+$
140.0488	C ₁₀ H ₆ N	8	
129.0587	C ₉ H ₇ N	-7	See Scheme 1

Table 6.	Electron	ionization	spectra:	accurate	mass	data	for
	compour	ıd 5, mol.	wt 209				

Observed mass	Composition	∆M (ppm) (obs.−calc.)	
209.0693	C ₁₀ H ₁₁ O₄N	-2	[M]+·
178.0508	C ₉ H ₈ O ₃ N	2	[M - CH ₃ O] ⁺
151.0635	C ₈ H ₉ O ₂ N	-1	[M-C ₂ H ₂ O ₂]+







 Table 7. Partial positive methane CI spectra of the nitrogen ylides

		Re	elative abur	idance ^a		
lon	1	2	3	4	5	6
[M+1] ⁺	14.0	30	15	84		15
[M]+·	57	59	43	100	34	43
[M27]+	_			10	_	
[M-31]+	54	96	_		94	19
[M+1-45]+·	_	59	19	6		19
[M45]+	_	83	100	51	—	100
[M-58]+	74	7	5		100	5
[M59]+	2	8				
[M61]+	4					
[M72] ^{+.}	—	100	60	95	—	6
[M 89]+	9	—	8		11	8
m/z 148		—	8		33	8
m/z 143	100	64		9	—	
m/z 141	2		<u> </u>	23		
m/z 140	12	—		12	—	
m/z 129	78	—	—	—	—	
m/z 93		—	—	—	67	51
^a Intensities as gas ions.	s percenta	ge of the	base pe	eak, exclu	uding re	agent



m/z 273





Scheme 3



m/z 213,[M+H-28]⁺

Scheme 4

(Table 8) there is less fragmentation; the fragments seen are those observed with methane. The reduced fragmentation may be ascribed to the reduced acidity of $[NH_4]^+$ compared to the $[CH_5]^+$ reagent ion. (NH₃ has a proton affinity of 865 kJ mol⁻¹, while the proton affinity of CH₄ is 530 kJ mol⁻¹.)¹¹ The reduced intensity of $[M]^{++}$ relative to $[MH]^+$ in the ammonia CI spectra may similarly be ascribed to the lower electron affinity of $[NH_4]^+$ compared to the $[C_2H_5]^+$ ion in the methane plasma. The importance of proton transfer to the ammonia CI spectra is also shown by the intensity of m/z 130 and m/z 80 (protonated isoquinoline and protonated pyridine, respectively).

The negative chemical ionization spectra show that electron capture by the ylides is the ionization process. The $[M]^{-1}$ ion formed is the base peak of the spectra in all cases (Table 9).

Little or no fragmentation is observed in these spectra, but ylide 4 did show a McLafferty-type rearrangement in which the charge was retained on the side-chain (Scheme 5).

In conclusion, these spectra show that the ylides **1–6** give informative EI mass spectra in which the charge is

Table 8.	. Partial	positive	ammonia	CI	spectra	of	the	nit-
	rogen	ylides						

		I	Relative abu	undance ^a		
lon	1	2	3	4	5	6
[M+1]+	100	80	25	100	100	74
[M]+·	48	29	2	66	27	25
[M-28]+·				7		
[M-31]+	69	24			66	_
[M+1-45]+·		5		1		7
[M-45]+		29	9	14		51
[M-58]+·	66	14			57	2
[M-59]+		4			1	
[M-61]+	5					
[M-72]+·		79	14	69		67
m/z 148					17	9
m/z 143	63	91	24	9		
m/z 141		—		8		
m/z 140			1	18	—	
m/z 130	32		100	30	—	
m/z 129	49	100	76	53		
m/z 120					6	11
m/z 93				3	41	100
* Intensities as	percent	age of th	ie base p	oeak, exc	luding re	agent
gas ions.						-

Table 9. P	artial negati	ive CI :	spectra o	of the	nitrogen	ylides
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lon	Relative abundance [®]					
	1	2	3	4	5	6
[M]	100	100	100	100	100	100
[M-63] ⁻						3
[M-92] ⁻						2
[M-113] ⁻	87					
[M-125] ⁻	95	—				
[M-128] ⁻				8		
* Intensities mass ions.	as percent	age of	the base	peak,	excluding	lock



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retained by the aromatic moiety and fragmentation of the ester side-chain proceeds by the loss of small neutral molecules and radicals. The radical centre is the principal driving force for fragmentation. This situation is also found in the methane CI spectra, where the abundance of radical ions (both $[M]^+$ and fragments) shows that electron transfer is important to the ionization. Electron transfer (to form $[M]^-$) also dominates the negative CI spectra. The ammonia CI spectra contain more evidence of ionization by proton transfer, with fewer radical ions and fewer radical driven fragmentations.

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