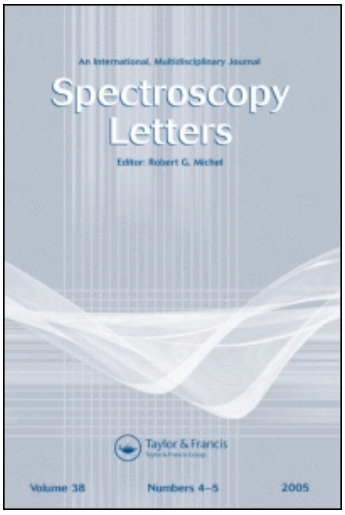

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Mass Spectral Studies of Biheteroaryls: Part 2. Diheteroarylalkanes

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To cite this Article Osborne, Alan G.(1985) 'Mass Spectral Studies of Biheteroaryls: Part 2. Diheteroarylalkanes', Spectroscopy Letters, 18: 1, 15 — 34
To link to this Article: DOI: 10.1080/00387018509438132
URL: http://dx.doi.org/10.1080/00387018509438132

SPECTROSCOPY LETTERS, 18(1), 15-34 (1985)

MASS SPECTRAL STUDIES OF BIHETEROARYLS.
Part 2. DIHETEROARYLALKANES.[1]

KEY WORDS : Mass spectra, dipyridylmethane, dipyridylethane, fragmentation

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Abstract : The mass spectral fragmentation patterns of a series of dipyridylalkanes (methanes, ethanes, propanes, butanes) are discussed. Di-2-pyridylethanes fragment by asymmetric cleavage whilst di-3- and di-4- pyridylethanes exhibit symmetrical cleavage.

Recent work in these laboratories necessitated the identification of mixtures of biheteroaryl derivatives obtained from the homolytic methylation of the lutidines. In the absence of authentic samples of the potential dimethyldipyridylethane products, gas chromatography - mass spectrometry (GC-MS) was chosen for assignment purposes. The present paper describes the behavoir of some dipyridyl- and diquinolyl- ethanes under electron impact, and has been extended to include a brief report of the dipyridyl- methane, propane and butane series.

The only substantiative investigations in this area to date have been performed[2-4] upon a series of stilbene analogues (1) - (3).

$$Ar\,CH = CHAr'$$

(1) Ar = Ar' = Ph

(2) Ar = Ph
Ar' = 2-, 3-, 4- Py

(3) Ar = Ar' = 2-, 3-, 4- Py

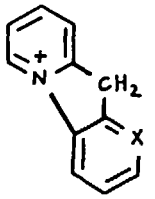
0038-7010/85/1801-0015$3.50/0

In this series the observed spectra reflected the competing fragmentations which were possible as the number of hetero groups was increased. As an illustration, since the elimination of a methyl radical from (1) required about 4.1 eV,[5] whilst elimination of HCN from pyridine required only 3.2 eV,[2] consequently the former process became progressively less significant as the number of pyridyl groups increased. In the present work the MS fragmentation patterns of the appropriate diarylalkane, aralkylheterocycle and diheteroarylalkane have been compared for increasing lengths of the central alkyl bridge.

METHANES

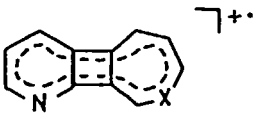
Diphenylmethane, studied by Eland and Danby,[6] was particularly resistant to electron bombardment, as shown by the formation of doubly[6] and triply[7] charged molecular ions. The only significant fragmentation processes were losses of one, two and three hydrogen atoms to form a cluster of peaks in the molecular ion region.[6] Loss of one hydrogen gave the diphenylmethyl cation, or phenyl tropylium ion, whilst ejection of two further hydrogens led to the fluorenyl cation.[8] The $(M - 1)^+$ ion also lost a methyl radical to give the biphenylene system.[8,9] Rupture of a central bond to produce the tropylium ion was a secondary process.

The MS of the benzylpyridines have attracted some interest.[10,11] As with diphenylmethane losses of multiple numbers of hydrogen atoms produced a cluster of peaks in the molecular ion region. The $(M - 1)^+$ peak, represented by the pyridyltropylium ion, was much more significant for the 2-isomer, due to the additional presence of the tricyclic ion (4a).[10]

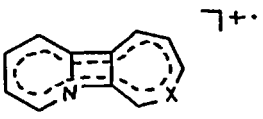


(4) a X = CH
b X = N

Loss of further hydrogen atoms led to cyclic ions (5a) for 3- and 4-benzylpyridine and (6a) for 2-benzylpyridine, the abundance being ca. 30% in each case.[10]



(5)



(6) a X = CH
b X = N

Unlike diphenylmethane loss of a methyl radical from the pyridyltropylium ion did not occur, compare the stilbene series.[2]

Since the loss of the elements of HCN dominates the spectrum of pyridine[12] this process was also significant for the benzylpyridines. Ejection of HCN occurred from the $(M - 1)^+$ and $(M - 2)^+$ ions of 3- and 4-benzylpyridines.[10] However, such losses did not occur with 2-benzylpyridine since the stable fragment tricyclic ions (4a) and (6a) each involved the nitrogen atom. Indeed, ion (6a) was so stable that a significant doubly charged species at m/z 83.5 (9%) was detected.[10] Rupture of a central bond to produce the tropylium ion at m/z 91 occurred with all the benzylpyridine isomers to a variable degree (4 - 26%, 3 - 12%, 2 - 7%), however, formation of the appropriate picolyl cations did not occur to any significant extent.

The present work has been extended to include the dipyridylmethane series. Although no samples of these compounds were available for study, a discussion of the reported[13] MS of di-4-pyridylmethane is appropriate. Although the spectrum (see Figure 1 and Scheme 1) showed some of the characteristics of diphenylmethane, such as the cluster of peaks in the molecular ion region, it was more reminiscent of 4-benzylpyridine.[10] Unlike diphenylmethane there was no $(M - 3)^+$ peak, which would give the diazafluorene species, nor any loss of a methyl radical from the $(M - 1)^+$ ion to form an azabiphenylene. As in the stilbene series[2] these high energy

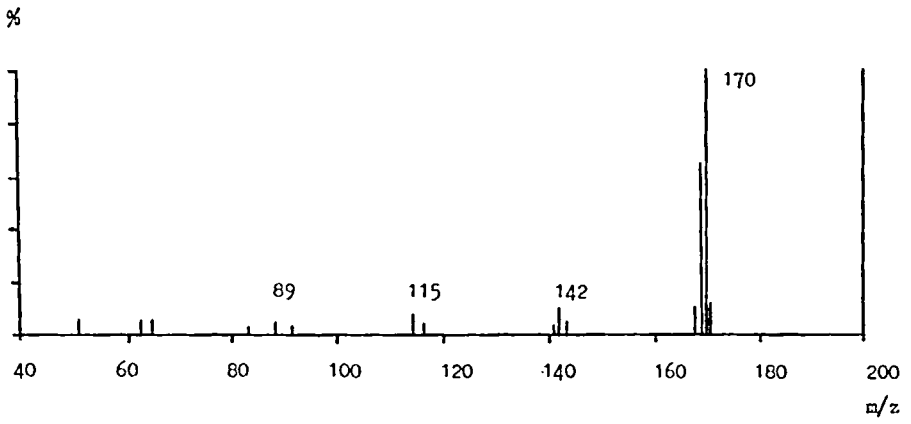


Figure 1 MS of di-4-pyridylmethane (from ref. 13)

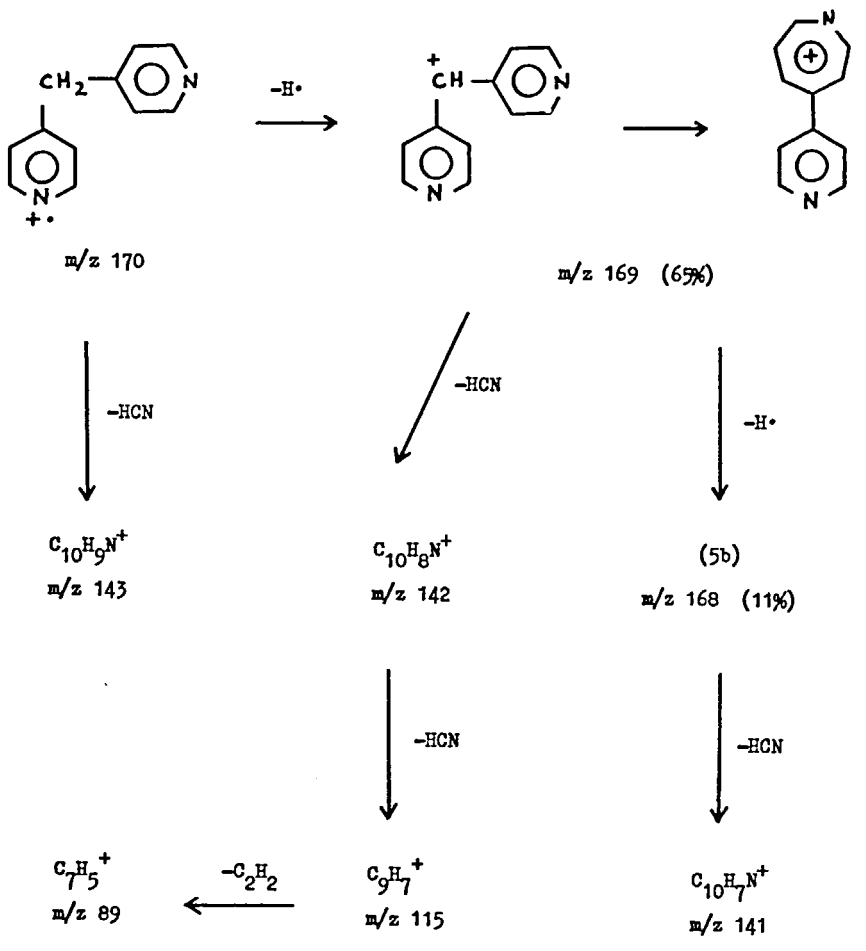
processes did not occur with the hetero derivatives. In common with the benzylpyridines ejection of the elements of HCN was again a significant process. Rupture of one of the central bonds to form the 4-picolyl cation was not favoured ; although such a rupture did occur with the benzylpyridines formation of the tropylium ion rather than the picolyl cation was preferred.[10]

Although no sample of di-2-pyridylmethane was available, the major features of the MS of the compound may be postulated based on the behavoir of related compounds. Ejection of one and two atoms of hydrogen to form ions such as (4b) and (6b) would be expected to dominate the spectrum. However, unlike 2-benzylpyridine loss of HCN from these tricyclic ions could occur utilising the second nitrogen atom not situated at the ring junction. Central bond rupture to form the 2-picolyl cation would only be a minor process.

ETHANES

Increasing the alkyl bridge between phenyl rings is known[14,15] to lower the molecular stability towards electron bombardment. Moreover, although diphenylmethane has many doubly charged peaks, bibenzyl has very few.[6]

Bibenzyl[6] shows the expected facile cleavage of the doubly activated central bond to form the tropylium ion as the bease peak at m/z 91. The MS



Scheme 1

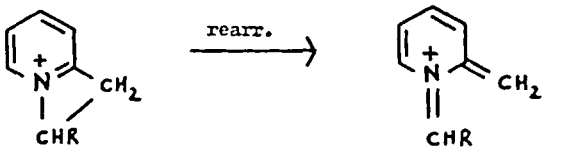
of the phenylethylpyridines* have been studied by Schwarz et al.[16] and by Budzikiewicz and Besler,[11] however, the results for the 2-isomer appear to be at variance, we have re-determined the spectrum (see Table 2) as part of

---

NOTE (*) - Throughout this paper phenylethylpyridine refers to the 2-phenylethyl derivative, viz :

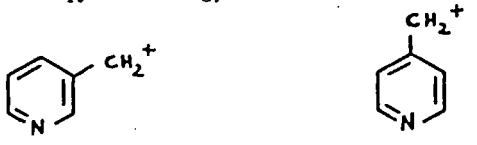
$$C_6H_5\overset{2}{C}H_2\overset{1}{C}H_2 -$$

the present study and support the work of Budzikiewicz and Besler.[11] The MS of these compounds show great similarity to those of the ethylpyridines discussed by Biemann[17] and by Porter and Baldas.[12] The base peak of 2-ethylpyridine was the $(M - 1)^+$ ion formed by γ-cleavage of a hydrogen atom with stabilisation of the resultant fragment by ring formation to give the bicyclic ion (7a).



(7) a R = H c R = 2-Py
b R = Ph d R = 3-Py

There was very little β-cleavage in 2-ethylpyridine to give an $(M - 15)^+$ ion. In contrast, loss of a methyl radical represented the base peak for the 3-isomer, a reflection of the high electron density at position 3 in the pyridine ring, which stabilised the azabenzyl cation (8).

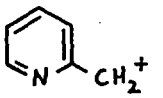


(8) (9)

The molecular ion was the base peak of 4-ethylpyridine, with β-cleavage to give the $(M - 15)^+$ ion as the most prominent fragmentation, however, since the resultant azabenzyl cation (9) was less stable than (8), the intensity was diminished. The MS of 2-, 3- and 4-ethylquinoline have been reported by Draper and MacLean,[18] and exhibited a similar pattern of behavior, although with certain differences in fragment ion intensities.

Returning to the phenylethylpyridines, the MS of the 2-isomer (see Table 2) showed prominent fragment ions at m/z 182 (100%) and m/z 106 (71%) both of which resulted from a γ-cleavage with subsequent cyclisation to

form the ions (7b) and (7a) respectively. The other significant fragmentation involved a β-cleavage which gave the tropylium ion at m/z 91 (67%); β-cleavage of a benzyl radical was not favoured, since the resultant azabenzyl cation (10) is not stabilised, as previously found for 2-ethylpyridine.[12,17]



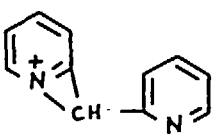
(10)

Since the total extent of γ-cleavage was in excess of that of β-cleavage this demonstrated the stability of the cyclic ions (7a) and (7b) and the favourable nature of such fragmentations.

The MS of 4-phenylethylpyridine[16] (see Table 2) was more characteristic of an α-substituted toluene derivative, and exhibited characteristic β-cleavages only. The preferential formation of the tropylium ion (100%) indicated its greater stability over the azabenzyl cation (9).

Previous studies of the MS of dipyridylethane derivatives have been restricted to reports of their molecular ions only for identification purposes.[19-21] The MS of 1,2-di-2-pyridylethane is given in Figure 2 and Table 2 and the major fragmentation pathways shown in Scheme 2.

Very little symmetrical β-cleavage occurred since the formation of the azabenzyl cation (10) was not preferred.[12,17] Instead, as with 2-phenylethylpyridine,[11,16] γ-cleavage was the main fragmentation pathway which gave ions (7c)(30%) and (7a)(100%), the latter by expulsion of a 2-pyridyl radical. There was also a minor fragmentation process leading to an $(M - 15)^+$ ion for which structure (11) is tentatively proposed. Since this fragmentation did not occur with either the 3- or 4- dipyridylethane isomers the ring nitrogen must be involved, although the precise mechanism remains obscure.



(11)

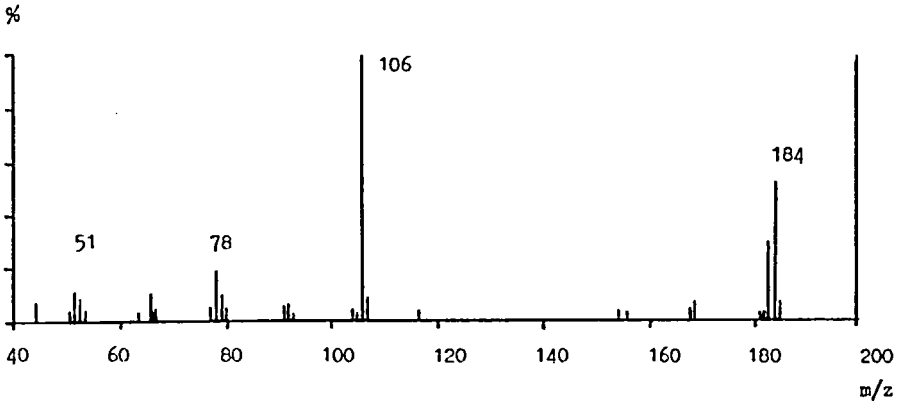
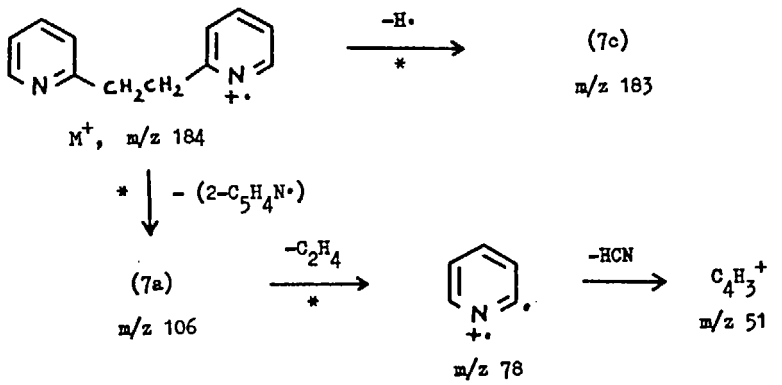


Figure 2 MS of 1,2-di-2-pyridylethane



Scheme 2

The MS of 1,2-di-2-quinolylethane (see Table 2) was similar and again featured asymmetric α-cleavage to give the base peak at m/z 156, however, the intensity of the $(M - 1)^+$ ion was much reduced, in contrast to 2-ethylquinoline in which this fragment represented the base peak.[18]

The MS of 1,2-di-3-pyridylethane is given in Figure 3 and Table 2 and the major fragmentation pathways shown in Scheme 3.

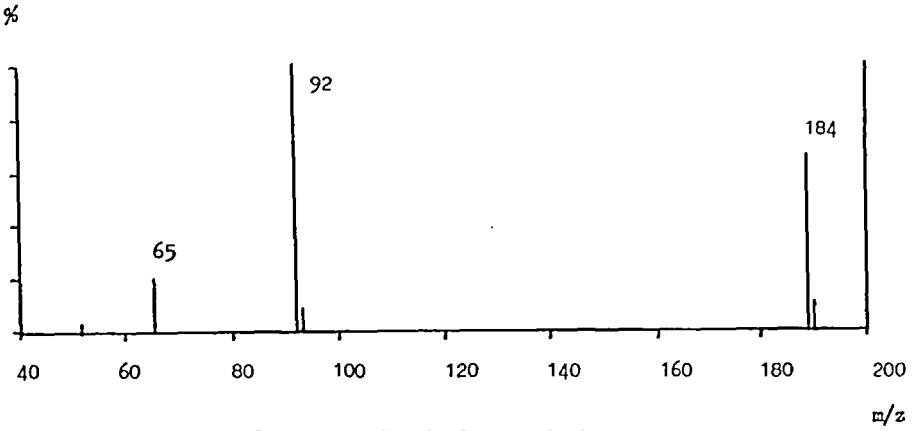
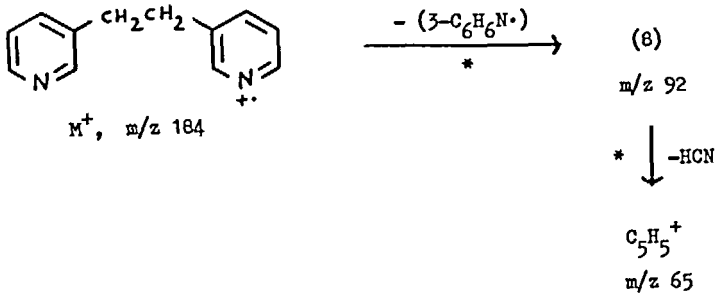


Figure 3 MS of 1,2-di-3-pyridylethane



Scheme 3

Symmetrical β-cleavage occurred with ejection of a 3-picolyl radical to produce the stabilised[17] azabenzyl cation (8) as the base peak. The MS of 1,2-di-4-pyridylethane (see Table 2) was similar except that the ion (9) was less intense in accordance with its reduced stability.[17] 1,2-Di-4-quinolylethane (see Table 2) also exhibited symmetrical cleavage to give m/z 142 as the base peak. For all of the 3- and 4- isomers, α-cleavage occurred to a very minimal extent only.

The MS of the asymmetrical dipyridylethane, 1-(2-pyridyl)-2-(3-pyridyl)ethane (12) has also been studied (see Figure 4 and Table 2).

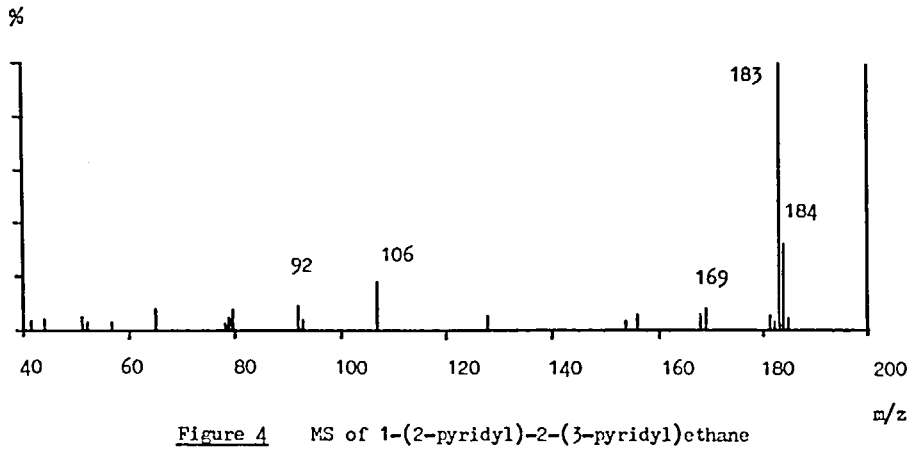
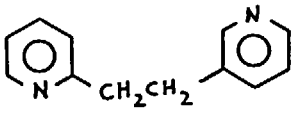


Figure 4 MS of 1-(2-pyridyl)-2-(3-pyridyl)ethane

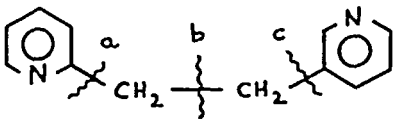


(12)

For this compound the comparative stability of the azabenzyl cations and favourability of the ejected radicals were particularly important. From the studies of the symmetrical dipyridylethanes, ions (7a), (8) and (9) were favoured which required the ejection of the 2-pyridyl and 3- and 4- picolyl radicals respectively. Rupture of the central alkyl bridge of compound (12) could take place at either a, b or c, however, in each case such fragmentations require either ejection of a less favourable radical or formation of a destabilised ion as summarised in Table 1. Accordingly, central bond ruptures to produce the ions (8) and (7a) occurred to a much reduced extent since such fragmentation pathways were unfavourable to half of the molecule. The most favoured pathway, which did not involve the ejection of an undesirable radical nor the formation of a destabilised ion, was therefore loss of a single hydrogen atom to form the $(M - 1)^+$ ion (7d) (100%). A small $(M - 15)^+$ fragment ion, as found with 1,2-di-2-pyridyl-ethane was also present. Similar considerations would also be expected to

Table 1

Possible central bridge rupture modes for compound (12)



No.	Position of Rupture	Ion Formed	F or NF	Radical Ejected	F or NF
1	a	3-EtPy$^+$	NF	2-Py•	F
2	b	2-Pic$^+$ (10)	NF	3-Pic•	F
3	b	3-Pic$^+$ (8)	F	2-Pic•	NF
4	c	2-EtPy$^+$ (7a)	F	3-Py•	NF

NOTES

Py - pyridyl (C_5H_4N)

Pic - picolyl (C_6H_6N)

EtPy - ethylpyridyl (C_7H_8N)

F - favoured

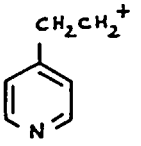
NF - not favoured

apply to other mixed 2,x-dipyridylethane derivatives, however, for a mixed 1-(3-pyridyl)-2-(4-pyridyl)ethane significant symmetrical cleavage would still occur as favoured by both portions of the molecule.

There was no significant loss of HCN in the high mass region of any of the dipyridylethane derivatives, since this characteristic fragmentation process of pyridine derivatives required a much higher energy.[2] This was in direct constrast to the situation experienced with the dipyridylmethanes.

PROPANES

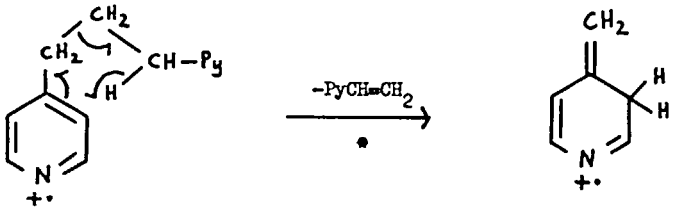
Only one compound, 1,3-di-4-pyridylpropane, was available for study, the MS is shown in Figure 5 and in Table 2. As previously suggested by Polyakova et al.[14] the compound was less stable to electron bombardment than 1,2-di-4-pyridylethane since the molecular ion no longer represented the base peak. Since symmetrical cleavage of the three carbon propyl chain was impossible, the preferred rupture involved loss of a 4-picolyl radical to give the azaphenylethyl ion (13). There was no evidence of alternative



(13)

simple ruptures to produce ions at m/z 92 or m/z 106. In contrast, 1,3-diphenylpropane exhibited two simple benzylic cleavages to give the $C_7H_7^+$ and $C_8H_9^+$ ions.[22,23] That only one such rupture occurred with 1,3-di-4-pyridylpropane may be due to the favoured ejection of a 4-picolyl radical, as previously found for 1,2-di-4-pyridylethane.

The base peak at m/z 93 resulted from a McLafferty rearrangement with consequent loss of 4-vinylpyridine. Such rearrangements have previously been observed for alkylbenzenes with three carbon side chains,[22-4] and also for 4-n-propylpyridine.[25] Although this rearrangement was insignificant for n-propylbenzene,[22] introduction of an aryl or heteroaryl group in the γ-position increased the formation of the rearrangement products considerably.[22,25]



m/z 93 (14)

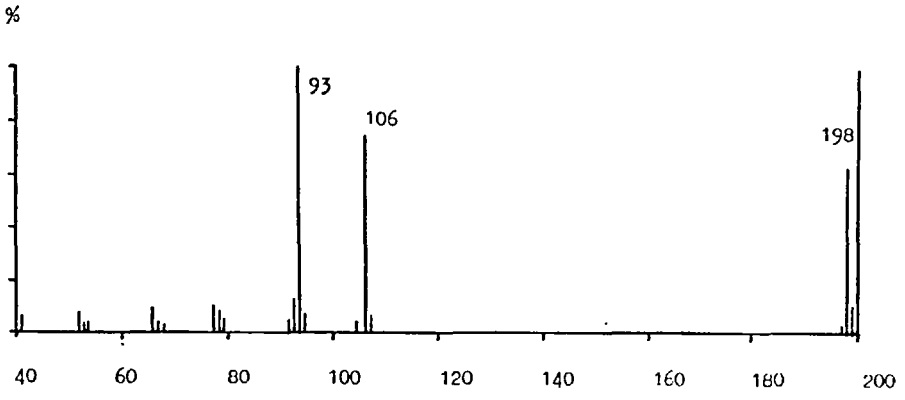
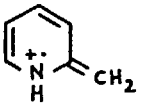


Figure 5 MS of 1,3-di-4-pyridylpropane

Budzikiewicz and Besler[11] have reported the MS of 2-(3-phenylpropyl)-pyridine, which was dominated by the McLafferty rearrangement product (15),



(15)

with a small contribution from the bicyclic ion (7a).

BUTANES

Two compounds from this series were available for study, kindly supplied by Dr. D. H. Richards,[26] their MS are shown in Figures 6 and 7 and in Table 2. With their extended alkyl bridges, these compounds were again less stable to electron bombardment, such that the 2-pyridyl isomer exhibited only a very small molecular ion. For the 4-isomer, although the molecular ion represented the base peak, the total ion current carried by the combined rupture fragment ions was greater.

The McLafferty rearrangement dominated both spectra leading to the ions at m/z 93; viz (15) for the 2-isomer and (14) for the 4-isomer, in common with such rearrangements previously found for n-butylbenzene[24] and for the n-butylpyridines.[11,27]

Table 2

Mass Spectral Results

m/z	A	B	C	D	E	F	G	H	J	K	L	M	N
39	6	6	17	8	9	11	8	4	3	7	9	6	17
40					5						4		
41			4							4	8		6
43									3				
44					6					3			6
47		5											
48		3											
50			3		3								3
51	9	9	15	6	10	3	5	4		4	8	6	10
52			13		9					3	4	4	6
53			14		4						4	3	4
54		3									3		3
57										3			
63	5	5		3	3			3	3				3
64			3										
65	10	11	43	19	11	22	16		3	8	12	8	22
66			4		3						5	6	5
67											3		
69													4
74		3											
75								3	3				
76								3					
77		3	11	4	5			8		3	11		9
78	3		17		19					5	9	10	7
79			41		11					8	5	6	5
80			10		5							3	4
82		24											
83		26											
85		15											
87		3										3	
89	5	5	5					3	6				
90			3										
91	9	28	67	100	6				3		3		6
92		3	10	9	6	100	59			9	12	9	31

Table 2 (Continued)

m/z	A	B	C	D	E	F	G	H	J	K	L	M	N
93			3		4	9	6			3	100	100	68
94											7	12	6
101								6					
102								6					
103			4					3					
104			4		4						2		3
105			4		3								4
106			71		100		4			19	75	40	55
107			6		9						6	19	22
115	4	9	3					7	33				
116								4	7				
117					4							4	4
118												12	9
119												14	4
120												93	28
121												9	3
127								3	3				
128								22		5			
129								9					
130								6					
139	4												
140								4	4				
141	4	7						5	4				
142		9						7	100				
143		21						6	15				
144		9											
152			3										
154		6	4		4			4	3	3			
155			3					4					
156					3			100		4			
157								13					
166	5	5											
167	29	29	18										
168	100	74	10		4					6			
169	23	100			6					8			
170		30											

(Continued)

Table 2 (Continued)

m/z	A	B	C	D	E	F	G	H	J	K	L	M	N
180			11										
181			5		4					4			
182			100		3					3			
183			86	32	30		5			100			4
184			13	5	52	66	100			32		3	4
185					7	10	14			3			
197											3		
198											64		
199											10		
211												2	5
212												1	100
213													17
269								6	4				
281								4					
282								3					
283								18	4				
284								58	69				
285								13	16				

Compounds

A : 2-benzylpyridine
B : 4-benzylpyridine
C : 2-phenylethylpyridine
D : 4-phenylethylpyridine
E : 1,2-di-2-pyridylethane
F : 1,2-di-3-pyridylethane
G : 1,2-di-4-pyridylethane
H : 1,2-di-2-quinolylethane
J : 1,2-di-4-quinolylethane
K : 1-(2-pyridyl)-2-(3-pyridyl)ethane
L : 1,3-di-4-pyridylpropane
M : 1,4-di-2-pyridylbutane
N : 1,4-di-4-pyridylbutane

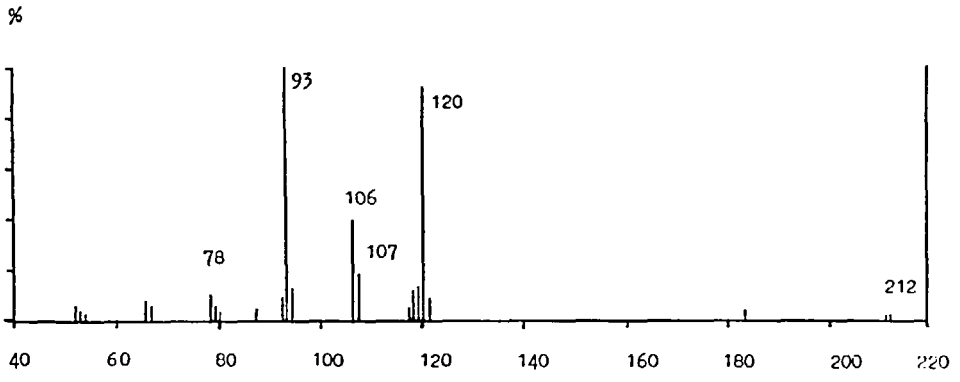


Figure 6 MS of 1,4-di-2-pyridylbutane

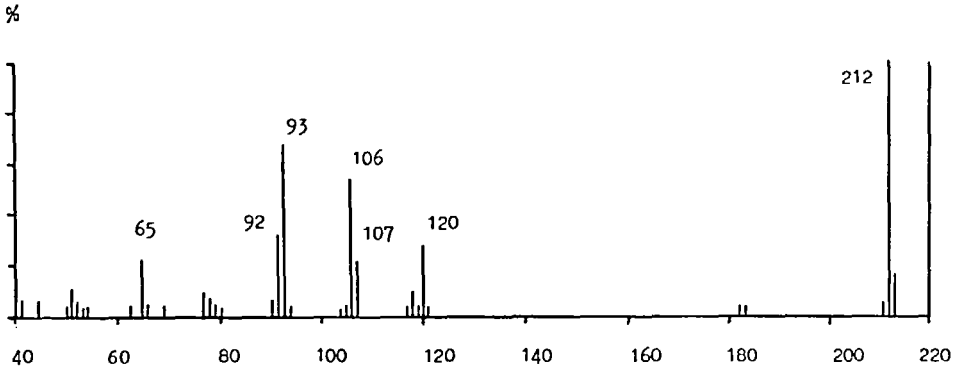
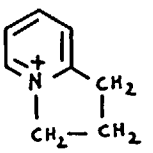


Figure 7 MS of 1,4-di-4-pyridylbutane

The lower mass regions of the dipyridylbutanes were somewhat similar to those of the respective n-butylpyridines,[27] although there were significant differences in the peak intensities. However, the general rule established for the dipyridylethanes such that the 2-isomers preferentially fragmented through asymmetric benzylic cleavage to produce an $(\frac{M}{2} + 14)^+$ ion, whilst the 4-isomers underwent symmetric cleavage still applied. Thus the symmetric rupture product ion at m/z 106 was favoured by both 4-n-butylpyridine and 1,4-di-4-pyridylbutane, whilst the asymmetric rupture product ion (16) predominated in the respective 2-pyridyl series. In the dimers,



(16)

however, the proportion of simple benzylic cleavage was more significant, and the less favourable benzylic cleavage process did still occur to a detectable degree ; thus whilst m/z 120 was not detected in the spectrum of 4-n-butylpyridine[27] it did occur in the MS of 1,4-di-4-pyridylbutane to the extent of 28% of the base peak.

For both series of compounds another fragment ion at m/z 107 also appeared in the spectra which was not present in the spectra of the appropriate monomers.

EXPERIMENTAL

2- And 4- benzylpyridine and 1,3-di-4-pyridylpropane were commercially available (Aldrich Chemical Co. Ltd., Gillingham, Dorset). 1-(2-pyridyl)-2-(3-pyridyl)ethane was also commercially available (Alfred Bader Library of Rare Chemicals, through Aldrich Chemical Co. Ltd., lit.[28,29]). Samples of 1,4-di-2-pyridylbutane and 1,4-di-4-pyridylbutane were kindly provided by Dr. D. H. Richards.[26]

2-Phenylethylpyridine[30] (b.p. 155-60°/14 mm.), 4-phenylethylpyridine[30] (m.p. 70-1°), 1,2-di-2-pyridylethane[31] (m.p. 49-50°), 1,2-di-3-pyridylethane[32] (m.p. 35-6°), 1,2-di-4-pyridylethane[32] (m.p. 114°); 1,2-di-2-quinolylethane[33] (m.p. 165°) and 1,2-di-4-quinolylethane[34] (m.p. 176°) were synthesised by established procedures. The identity and purity of all samples was checked by ^{1}H NMR spectroscopy before use.

Mass spectra were determined on an A.E.I. model MS902 spectrometer (70 eV, direct insertion), all spectra were measured by the Physico Chemical Measurements Unit, Harwell to whom we are indebted.

Mass spectra are given in Table 2, intensities of ions above 3% of the

base peak only are shown, with certain exceptions, ions below m/z 39 are not included.

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Received: 09/21/84
Accepted: 10/22/84