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THE THERMAL DECOMPOSITION OF 1,1'-AZO-4,4'-DI (N-METHYLANILINO) PYRIDINIUM DIBROMIDE DIHYDRATE AND 1,1'-AZO-3,3'-DIMETHYL-2,2'-DIPHENYLIMIDAZO [1,2-*a*] PYRIMIDINIUM DIBROMIDE TETRAHYDRATE*

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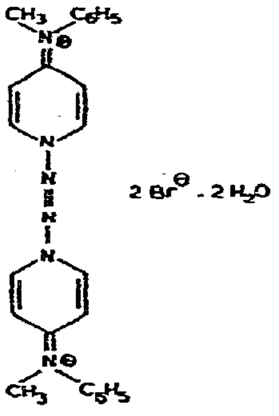
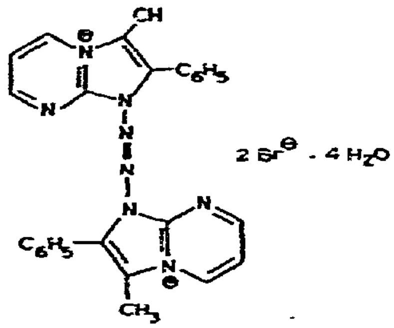
ABSTRACT

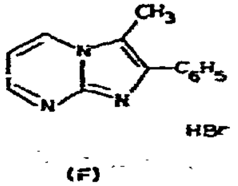
The thermal decomposition of 1,1'-azo-4,4'-di(N-methylanilino) pyridinium dibromide dihydrate (A) and 1,1'-azo-3,3'-dimethyl-2,2'-diphenylimidazo [1,2-*a*] pyrimidinium dibromide tetrahydrate (B), and the mass spectra of their volatile products, are described. The results show that the water of crystallisation can be



(A)



(B)



(F)

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removed from (A) without causing rupture of the tetrazene linkage, but that loss of water from (B) caused breakdown of the molecule. 4-(N-methylanilino)pyridine hydrobromide was the major product formed from (A) after the rupture of the tetrazene linkage, and 3-methyl-2-phenyl imidazo [1,2-*a*] pyrimidine hydrobromide (F) was formed from (B).

INTRODUCTION

1,1'-Azoimidazo [1,2-*a*] pyridinium salts have been found to exhibit non-depolarising neuromuscular blocking activity[1, 2] as have other tetrazenes such as (A)[3]. For some of these compounds, their duration of action in man is longer than that required of an ideal muscle relaxant, whereas others, although showing increased brevity of action, suffer from decreased chemical stability. This study was undertaken in order to examine, for two different types of tetrazene, their thermal stability, the way in which the water of crystallisation was lost, and to determine the compounds formed on their decomposition. No previous TG and mass spectral studies of these types of tetrazene have been reported.

EXPERIMENTAL

The decomposition reactions were studied in an atmosphere of nitrogen using a Stanton TG 750 thermobalance with sample weights of about 5 mg contained in platinum crucibles, heating rates of 2, 5, 10 and 20°C min^{-1} being used and, in addition, some samples were heated isothermally at selected temperatures. The infrared examination of the starting materials and residues from various stages of the decompositions was carried out using a Perkin-Elmer 377 spectrophotometer. The volatile fragments of the decompositions were studied using a Hitachi RMU 6D mass spectrometer with an electron impact source which was coupled to the oven of an F11 Perkin-Elmer gas–liquid chromatograph. The mass spectra were recorded for each 10°C interval of temperature rise up to 450°C. Helium was used as the carrier gas. Some mass spectra were obtained with direct entry of the samples into the mass spectrometer. Samples of compounds (A) and (B) were kindly supplied by E. E. Glover and D. Doughty who quoted the following analyses. Compound (A): C, 48.7; H, 4.4; N, 14.2%. *Calc.*: C, 48.7; H, 4.8; N, 14.2%. Compound (B): C, 46.4; H, 4.2; N, 16.5%. *Calc.*: C, 46.0; H, 4.5; N, 16.5%.

COMPOUND (A)

Results

Figure 1 shows a typical TG curve for the decomposition of compound (A). The two molecules of water present were lost in separate steps, the first by 90°C and the second by 180°C. As the water was lost the compound changed in colour from yellow to deep orange and was molten by 240°C. IR examination of samples

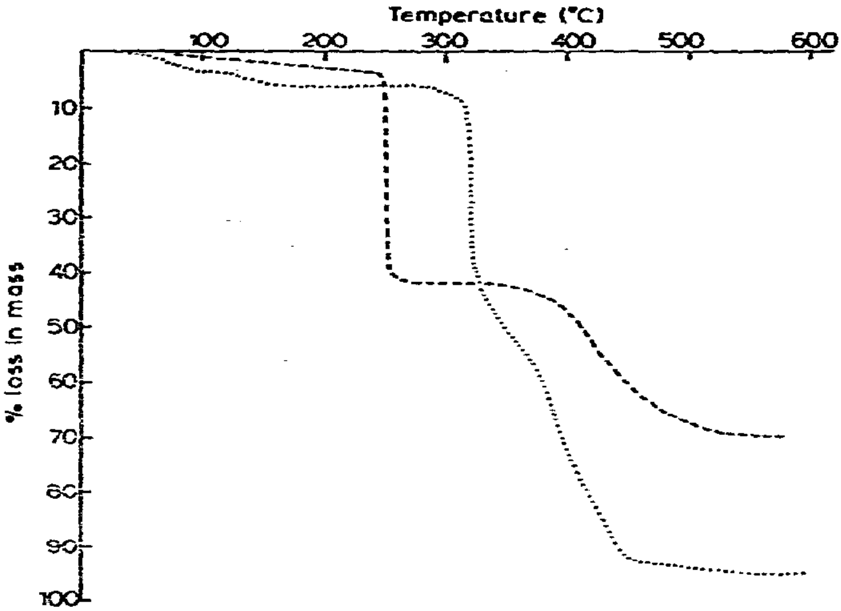


Fig. 1. Decomposition of 1,1′-azo-4,4′-di(N-methylanilino)pyridinium dibromide dihydrate (A) and 1,1′-azo-3,3′-dimethyl-2,2′-diphenylimidazo[1,2-*a*]pyrimidinium dibromide tetrahydrate (B). Heating rate, 10°C min^{-1}. Dynamic atmosphere of nitrogen, 10 cm^3 min^{-1}. Stanton TG 750 thermobalance. ·····, Compound (A); ------, compound (B).

heated to 250°C gave spectra identical with that from compound (A), except that peaks due to the water of crystallisation had been removed. Further heating gave a very rapid loss in mass in the temperature range 250–320°C, the actual temperature and the size of this step depending on the heating rate. Visual examination of the residues at the end of this stage showed that only traces of carbon were present, and the white solid produced gave an IR spectra identical with that of 4-(N-methylanilino) pyridine hydrobromide (compound (C)). The final part of the decomposition corresponded to the volatilisation of (C) and separate experiments on pure (C) showed that it volatilised, without cracking, over the same temperature range. In all cases, the amount of carbon formed as final residue was very small, and with slow heating rates the final residue was < 1% of the original mass. Table 1 shows the mass spectra of the volatile fragments from four selected regions of the decomposition of (A) corresponding to:

1. 130°C, the loss of the water molecules.
2. 255°C, the breakdown of compound (A).
3. 280°C, the volatilisation of the compounds present immediately after the breakdown.
4. 360°C, the final stages of the decomposition.

The mass spectral results are in accord with those obtained by TG. They show that at low temperatures the loss of water was the most important decomposition process, but that some breakdown of the tetrazene also occurred as indicated by the presence of a strong peak at *m/e* 28, due to N_2. All other peaks were very weak and

TABLE 1

MASS SPECTRA FROM THE DECOMPOSITION OF 1,1′-AZO-4,4′-DI(N-METHYLANILINO)PYRIDINIUM DIBROMIDE DIHYDRATE (A)

m/e	*Compound (A) in oven of gas chromatograph coupled to mass spectrometer Temp. (°C)*			
	130	*255*	*280*	*360*
14	2	3	4	
15		2	7	4
16	3		3	
17	27	8	25	17
18	100	28	97	16
27			5	4
28	42	100	97	16
29		5	5	
30		4	4	
32	15	5	5	
38			3	2
39			11	10
40	2		4	
41			6	2
42			3	
43	3	2	5	
44		7	26	7
50			9	8
51			31	31
52			6	7
53			2	2
55			4	
56			2	
57			4	
63			5	5
64			7	5
65			6	7
66			3	3
74				2
75				3
76				3
77			29	24
78			18	18
79			5	5
80			3	4
84.5			5	7
89			3	3
90			3	3
91			12	9
91.5				3
92			5	5
93			2	
94		3	5	
95			2	
96		3	5	
103			2	2

Table 1 *(continued)*

m/e	*Compound (A) in oven of gas chromatograph coupled to mass spectrometer Temp. (°C)*			
	130	*255*	*280*	*360*
104			6	5
105			5	6
106			5	6
107			2	3
114			2	2
115			7	7
116			3	4
117				2
127			2	2
128			3	3
129			2	
130			2	3
131			2	
140			4	3
141			3	3
142			2	3
143			3	5
154			5	4
155			4	3
156			4	4
157			2	2
168			5	2
169			26	15
170			9	8
182			9	7
183			19	17
184			76	98
185			100	100
186			21	23
264			21	3
265			7	
266			19	3
351				2
352				2
353				2

none were detected with *m/e* > 57. During the breakdown of the compound the evolution of nitrogen was predominant, all other peaks were small compared with it, and none could be detected with *m/e* > 96. At 280 and 360°C the most intense peaks were at *m/e* 184 and 185, corresponding to the free base of (C), and to its protonated form. Small peaks of equal size with *m/e* 264 and 266 were also present due to compound (C) itself. However, the relative intensities of some of the peaks changed with increasing temperature, and, in particular, the peak at *m/e* 169 arising from both (D) and (C) was stronger at 280°C than at 360°C.

Small peaks with *m/e* 351, 352 and 353, possibly due to compound (E) started to appear at 360°C. All of the peaks observed can be explained in terms of the breakdown pattern illustrated in Fig. 2.

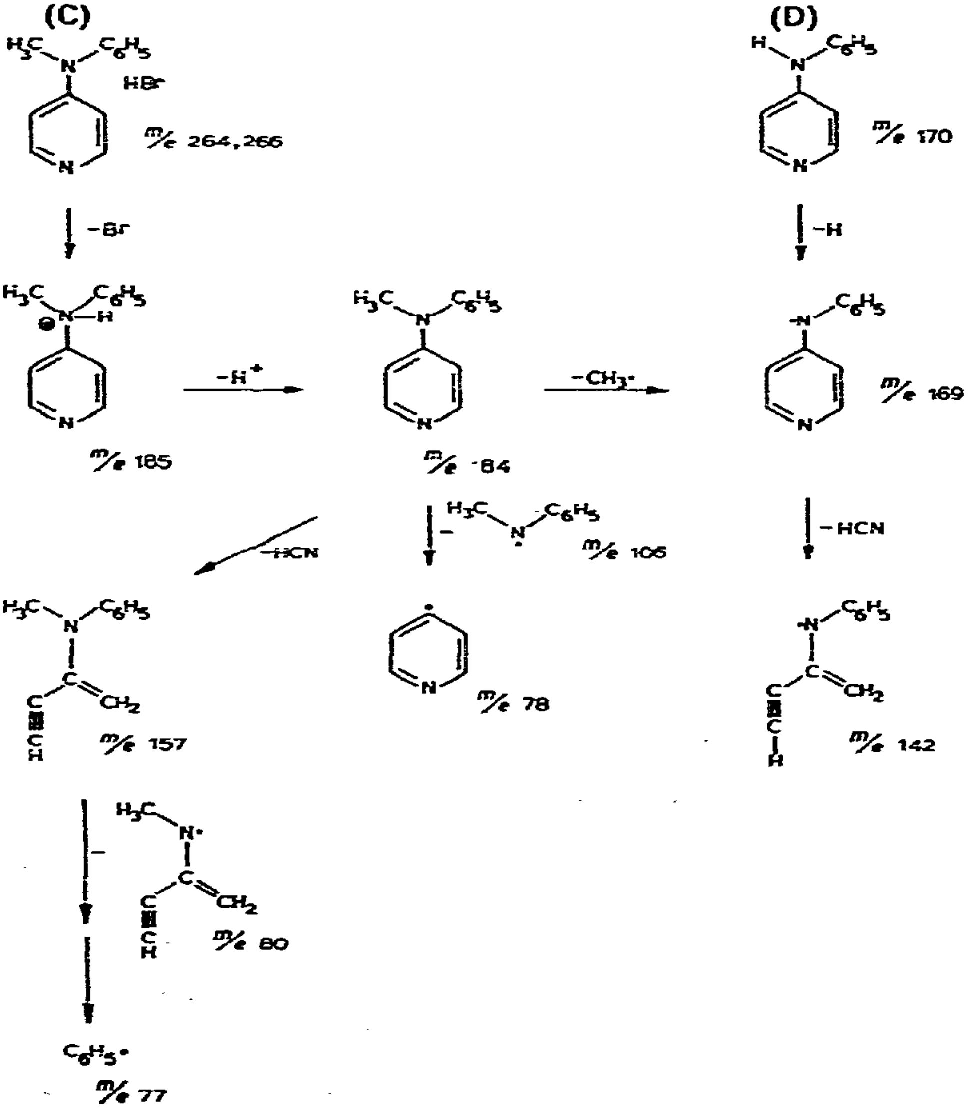
Discussion

After the loss of the water of crystallisation, compound (A) decomposed by the rupture of the tetrazene linkage and compound (C) was present in the products of reaction. The following points must be noted.

(1) The formation of (C) involves the movement of a hydrogen atom from one half of the molecule of (A) to the other half.

(2) The mass of the product after the rupture of the tetrazene linkage was always greater than that due to the formation of 1 mol (C)/mol (A).

(3) The loss in mass during the rupture was much greater than that due to



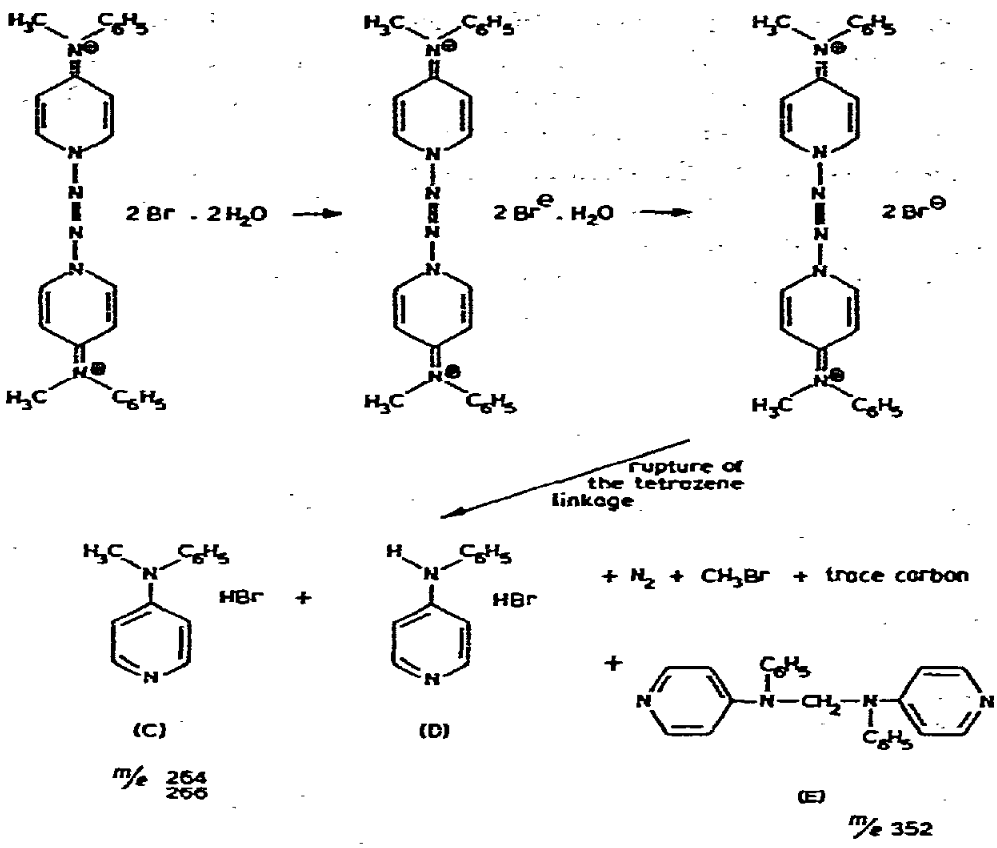


Fig. 2. Decomposition of 1,1′-azo-4,4′-di(N-methylanilino) pyridinium dibromide dihydrate (A).

nitrogen evolution alone, but no fragments of high molecular weight could be detected at this point.

(4) Very little carbon was formed during the rupture and the mass of the final residue was very small.

These facts can be explained on the assumption that one of the N methyl groups is lost whilst the sample is molten immediately before the rupture of the tetrazene linkage, and that some of the hydrogen atoms from this group were used to form (C). Small peaks of equal intensity, with *m/e* 94 and 96, corresponding to CH_3Br, were present at this point in the decomposition. It is possible that some 4-anilinopyridine hydrobromide (D) was also formed, but it would not have been detected by IR in the presence of (C). The volatilisation range of (D) is not known, but it is reasonable to assume that it would be lower than that of (C). Moreover the shape of the TG curve after the rupture of the tetrazene linkage is in agreement with the formation of both (C) and (D) since the volatilisation range of (C) agrees with the final part of the TG curve. The mass spectral results also indicate that (D) was formed in addition to (C) since the relative intensity of the peaks with *m/e* at 170, 169 and 168 were stronger at 280°C than at 360°C. Compound (D) is formed as one of the breakdown products of (C) as shown in Fig. 2. Additional evidence for the loss of an N-methyl group during the rupture of the tetrazene linkage is shown by the presence of peaks with *m/e* 351, 352 and 353, possibly due to (E), which was formed in small amounts. Figure 2 shows that the initial stages in the breakdown of 4-(N-methylanilino)pyridine hydrobromide (C) is either by the loss of HBr or of CH_3Br. Subsequently, there was loss of HCN from the heterocyclic ring, followed by breakdown of the products formed. Since no peaks were detected with *m/e* 158, due to $C_6H_5{}^{81}Br$, nor with *m/e* 108, due to 4-methylaminopyridine, it would appear that the rupture of the N–C_6H_5 bond plays only a minor role in the initial stages of the breakdown of (C).

COMPOUND (B)

Results

Figure 1 also shows a typical TG curve for the decomposition of compound (B). Some water was lost in the early stages but the amount did not correspond to the four molecules present. Between 250 and 270°C the compound decomposed rapidly without melting and considerable amounts of carbon were deposited. The infrared spectrum of the sample immediately before the rapid decomposition was identical with that of (B), and afterwards was identical with that of 3-methyl-2-phenylimidazo [1,2-*a*] pyrimidine hydrobromide (compound (F)). There was no further loss in mass until 340°C when (F) started to volatilise. Separate experiments with pure (F) showed that it volatilised, with the deposition of carbon, over the same temperature range.

Table 2 shows the mass spectra of the volatile fragments evolved from the oven of the gas chromatograph from three stages of the decomposition of (B) corresponding to:

1. 130°C, before the breakdown of (B).
2. 250°C, the breakdown of (B).
3. 405°C, the volatilisation of (F).

The results from the oven did not show any peaks due to (F) itself or to its free base. This was undoubtedly due to condensation of (F) in the line between the oven and the mass spectrometer. Because of this, the mass spectra of both (B) and the free base of (F) were also obtained with direct entry of the samples into the mass spectrometer. These results are also given in Table 2.

The results agree with those obtained by TG, and show that at low temperatures the loss of water was the most important process. During the rupture of the tetrazene linkage, the loss of nitrogen was predominant, though water continued to be evolved. Many other peaks were present, and there was a particularly strong peak at *m/e* 105, but no peaks with *m/e* > 109 were observed. The mass spectra at high temperatures can only be deduced satisfactorily from the results of direct entry of the samples into the spectrometer. The results show that (F) is the major product of the decomposition of (B), and that the free base of (F) only breaks down with difficulty in the spectrometer. The fragments observed from the oven at high temperatures may

TABLE 2

MASS SPECTRA FROM THE DECOMPOSITION OF 1,1′-AZO-3,3′-DIMETHYL-2,2′-DIPHENYLIMIDAZO [1,2-*a*] PYRIMIDINIUM DIBROMIDE TETRAHYDRATE (B) AND OF 3-METHYL-2-PHENYLIMIDAZO [1,2-*a*]PYRIMIDINE

m/e	*Compound (B) direct into mass spectrometer* *Temp (°C)*					*Compound (B) in oven of gas chromatograph coupled to mass spectrometer*			*Free base of Compound (F)*
	100	*110*	*130*	*150*	*175*	*130*	*250*	*405*	
14						4	3	4	
15		3					2	4	
16		3				4		22	
17	22	23	22	19		28	11	49	2
18	100	100	100	79	2	100	58	100	10
26		5	2	2				5	
27	2	15	7	9	3		2	16	4
28	13	30	48	98	19	72	100	74	17
29	2	13	9	11		2	4	4	4
32			2			19	6	6	
33							3	2	
36		2		6					
37			3						
38		2		4	5			5	3
39	2	15	7	9	7	2		21	6
40		4	2		2	2		6	
41	8	32	20	19	2	2		12	13
42	2	4	5	6	3			4	3
43	10	23	22	23		4		9	13
44	2	4	3	6		4	5	63	4
45			2	2			5	5	
46				2			2	2	
48								15	
50		2		2	3		2	9	
51		5	3	9	7	2	6	19	3
52		3		4	6			7	3
52.5							2		
53		6	3	6	8			4	4
54		10	4	4					3
55	9	32	27	26	10	2		4	13
56	4	15	10	11	5				6
57	13	22	29	28	12	2		4	17
58			2	2					
59							3		
60			2					2	
61							3	2	
62					2			4	
63					4			9	
64					4			36	
65		4			2			15	
66		3						5	
67	3	16	7	13	2			2	4
68	2	9	5	6				2	3

Table 2 *(continued)*

m/e	*Compound (B) direct into mass spectrometer*					*Compound (B) in oven of gas chromatograph coupled to mass spectrometer*			*Free base of Compound (F)*
	Temp (°C)								
	100	*110*	*130*	*150*	*175*	*130*	*250*	*405*	
69	9	20	18	19	3	2		2	10
70	4	12	10	9	2				6
71	7	11	16	13	2	2			9
73			3	4				2	
74								2	2
75					2			2	
76					3			5	
77	2	7	7	13	10		17	11	6
78		4	2	4	2			15	
79		9	6	13	20			4	10
80		5	5	15	24				10
81	5	13	11	13	5				6
82	2	9	10	13	11				4
83	6	12	14	13	10			2	9
83.5								4	
84	2	7	7	6				2	4
85	4	5	10	9				2	6
88					2				
89					3			6	
90								6	
91	2	13	7	6	2			74	3
91.5				4	2				4
92		6	3	4	7			57	
93		5	3	4	2			12	
94		4	3	4				4	
95	4	9	10	11				6	
96	2	6	5	6				2	
97	6	9	11	13					
98	2	5	4	6					
99	2		2	2					
102					2				
103		2		6	9			2	4
103.5				11	13				9
104		3		6	7			6	4
104.5				6	6				6
105	2	7	8	21	4		25	6	6
106		3	2	6	5		2	5	4
107		3	2	4				2	
108		2	2	2					
109	3	5	6	6					4
110	2	3	3	4					
111	4	5	7	6					4
112	2	5	4	4					
113		2	3	4					
114				2	2				
115		5	3	6	6			5	4

Table 2 *(continued)*

m/e	*Compound (B) direct into mass spectrometer*					*Compound (B) in oven of gas chromatograph coupled to mass spectrometer*			*Free base of Compound (F)*
	Temp (°C)								
	100	*110*	*130*	*150*	*175*	*130*	*250*	*405*	
116		2		2	2			4	
117		5	3	2				6	
118		2						2	
119	2	4	5	6					4
120		2	2	2					
121		2		2					
122				2					
123	2	3		4					
124		2							
125	2	3							
128		4						4	
129		4						2	
130		2						2	
131		3							
132					2				
133		2							
135		2							
137		2							
138		2							
141	3	4						2	
142		2							
149	2	2							
155					2				
156					2				
158					2				
160					4				
162					2				
166								4	
167								11	
168								35	
169								12	
170								2	
181					2				
182					2				
185	2	4							
206					4				3
207			2	11	15				9
208		2	8	64	61				70
209		2	12	100	100				100
210			10	15	27				16
289					2				
291					2				

either be breakdown products of (F) or may arise from other compounds formed in low concentrations during the rupture of the tetrazene linkage in (B).

Discussion

Compound (B) did not melt and during the rupture of the tetrazene linkage considerable amounts of carbon were produced. One half of the molecule was destroyed during the rupture as indicated by the number of peaks on the mass spectra and those at *m/e* 105 and 52.5, probably due to 2-isocyanopyrimidine. Less than one mol(F)/mol(B) was formed. The hydrogen atom required to stabilise the other half of the molecule as (F) was obtained at this point. The fact that compound (B) could only be partially dehydrated before the rupture of the tetrazene linkage would imply that the water molecules present are required to give stability to the compound. The mass spectra have confirmed that (B) breaks down into (F), water and nitrogen as the main products. However, little information has been obtained concerning the breakdown of (F). The expected route of ring expansion, as observed in other heterocyclic systems[4-8] followed by the loss of ethyne from the unsubstituted pyrimidine ring, has not been observed.

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