Organic Mass Spectrometry, 1973, Vol. 7, pp. 65 to 71. Heyden & Son Limited. Printed in Northern Ireland

FRAGMENTATION OF REDUCED DIBENZO[b, f][1,4]-DIAZOCINES, -OXAZOCINES AND -THIAZOCINES ON ELECTRON-IMPACT

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(Received 12 June 1972; accepted 3 August 1972)

Abstract—An investigation of the mass spectral behaviour of the title compounds is reported. Two processes have been studied by deuterium labelling. One, which occurs with all three ring systems, results in the loss of a C_7H_7 radical, whilst the other, which occurs only in the dibenzothiazocine, leads to the loss of a C_6H_6N radical.

ALTHOUGH extensive investigations of hydrogen scrambling in the molecular ions of monocyclic¹ to 4</sup> and bicyclic^{4,5,6} heterocyclic systems have been carried out, tricyclic systems in which a carbon bridge is lacking between the two rings have not been studied. Since as a result of synthetic studies^{7a} derivatives of 5,6,11,12-tetrahydro-dibenzo[b,f][1,4]diazocine (III) were available, it was considered of interest to investigate the behaviour of these derivatives and two analogous compounds 11,12-dihydro-6*H*-dibenz[b,f][1,4]oxazocine (II) and 11,12-dihydro-6*H*-dibenz[b,f][1,4]-thiazocine (I)⁸ in the mass spectrometer. The mass spectra of these compounds are given in Table 1. The availability of the deuterium labelled analogues (Ia),⁹ (Ib),

TABLE 1. MASS SPECTRA OF THE DIBENZOTHIAZOCINE (I), THE DIBENZOXAZOCINE (II) AND SOME DIBENZODIAZOCINE DERIVATIVES (m/e values are followed by intensity (%) in parenthesis)

11,12-Dihydro-6H-dibenzo[b,f][1,4]thiazocine (I)

229(6), 228(16), 227(90), 226(45), 211(3), 210(6), 195(18), 194(100), 193(20), 178(7), 165(8), 137(9), 136(67), 135(60), 134(12), 118(18), 109(17), 104(12), 103(17), 91(13), 78(13), 77(13), 65(13), 51(9), 39(9).

11,12-Dihydro-6H-dibenz[b,f][1,4]oxazocine (II)

212(13), 211(85), 210(100), 196(9), 195(14), 194(40), 183(5), 182(20), 181(4), 180(5), 168(3), 167(6), 166(2), 165(6), 153(1), 152(2), 138(3), 137(6), 136(8), 135(4), 120(19), 118(16), 117(6), 116(6), 105(11), 104(52), 103(35), 102(6), 91(14), 90(6), 89(7), 78(40), 77(24), 76(5), 65(22), 64(6), 63(11), 51(8), 39(6).

5,6,11,12-*Tetrahydrodibenzo*[b,f][1,4]*diazocine* (III)

211(4), 210(42), 209(40), 194(20), 193(46), 146(8), 145(9), 120(9), 119(100), 118(7), 105(8), 104(10), 103(8), 93(6), 92(12), 91(6), 78(6), 77(7), 65(12), 51(9), 39(6).

5,6,11,12-Tetrahydro-2-methoxydibenzo[b,f][1,4]diazocine

241(4), 240(29), 239(20), 224(16), 223(19), 208(8), 181(5), 180(7), 150(9), 149(100), 134(7), 118(6), 104(7), 103(9), 91(6), 79(6), 78(11), 77(8), 52(8), 51(7), 39(6).

 ${\tt 5,6,11,12-} Tetrahydro-{\tt 2-trifluoromethyldibenzo[b,f][1,4]} diazocine$

279(5), 278(30), 277(35), 262(15), 261(44), 188(10), 187(100), 118(9), 105(6), 104(8), 103(9), 91(12), 90(5), 89(6), 78(11), 77(8), 65(5), 63(5), 51(6), 39(5).

5,6,11,12-Tetrahydro-5-methyldibenzo[b,f][1,4]diazocine (IV)

225(12), 224(57), 223(36), 209(26), 208(17), 207(26), 206(8), 194(44), 193(64), 192(11), 180(12), 179(6), 178(5), 165(7), 134(14), 133(100), 132(9), 131(10), 119(18), 118(12), 106(16), 105(10), 104(14), 103(14), 92(17), 91(14), 78(19), 77(24), 65(20), 63(10), 52(9), 51(16), 39(14).

(IIa), (IIb) and (IIIa),⁹ and the methyldibenzodiazocines (IV),^{7b} (IVa)⁹ and (IVb) has thrown light on one fragmentation process common to all these systems and on another process which occurs only in the dibenzothiazocine molecule. Partial mass spectra showing the intensities of the ions in the relevant regions of the spectra at 70 and 12 electron volts beam energy are given in Tables 2 and 3, respectively. For each spectrum

m e	(I)	(Ia)	(Ib)	(II)	(IIa)	(11b)	(III)	(IIIa)	(IV)	(IVa)	(IVb)
118				39.4	12.3	18.6		·			
119				3.5	22.8	20.4	100	44.5			
120				57.1	31.2	3.0		26.0			
121					18.1	58·0		29.5			
122					15.6						
133									100	75.4	51.6
134	10.9	1.6	0.8							18.6	48.4
135	38.8	5.6	30.4							6·0	
136	50.3	26.6	31.6								
137		44·3	37.2								
138		21.9									
Та	BLE 3. P.	ARTIAL	MASS SPI	ECTRA AT	12 eV	(CORRE	CTED FO	or ¹³C a	ND ³⁴ S	ISOTOPES)
m e	(I)	(Ia)	(Ib)	(II)	(IIa)	(IIb)	(III)	(IIIa)	(IV)	(lVa)	(IVb)
119							100	34.9			
120				100	79·5	9.9		30.4			
101					40 -	004					

TABLE 2. PARTIAL MASS SPECTRA AT 70 eV (CORRECTED FOR ¹³C AND ³⁴S ISOTOPES)

Table 3. Partial mass spectra at 12 eV (corrected for $^{13}\mathrm{C}$ and $^{34}\mathrm{S}$ isotopes)											
m e	(I)	(Ia)	(Ib)	(II)	(IIa)	(IIb)	(111)	(IIIa)	(IV)	(lVa)	(IVb)
119							100	34.9			
120				100	79 ·5	9.9		30.4			
121					10.5	90.1		34.7			
122					10.0						
133									100	61.9	63·8
134										34.2	36.2
135										3.9	
136	100	73.8	38.0								
137		15.5	62.0								
138		10.7									

the ion intensities have been normalised to give a total of 100%. The compositions of these ions have been confirmed by accurate mass measurement at high resolution.



In each of the unlabelled compounds a fission process occurred which resulted in the loss of a C_7H_7 radical. This radical appears to consist of ring B and one of the

attached methylene groups together with an additional hydrogen atom, since dibenzodiazocines with a substituent in ring A in the 2-position (methoxy or trifluoromethyl) still lose a C_7H_7 radical (Table 1).

In the thiazocine (I) the loss of a C_7H_7 radical gives an ion of m/e 136, due to $[C_7H_6NS]^+$. In the labelled compound (Ia) at 70 eV, m/e 136 has been split into two ions at m/e 136 and 138, shown by accurate mass measurement to be $[C_7H_6NS]^+$ and $[C_7H_4D_2NS]^+$, with intensities in the ratio of 54.8:45.2. There is no ion of composition $[C_7H_5DNS]^+$ at m/e 137. It follows that fission of the molecule can occur in the two ways (a) and (b) and that (b) is slightly favoured. Furthermore the absence of m/e 137 shows firstly that in fission (a) the seventh hydrogen required to make up the C_7H_7 radical which is eliminated does not come from the methylene group which is retained in the ion and secondly that there is no hydrogen scrambling in the molecular ion prior to this elimination. At 12 eV the m/e 136 ion is split into three, at m/e 136, 137 and 138, in the ratio of 73.8:15.5:10.7. Thus fission (b) shows even greater predominance at low electron volts, while the presence of the ion at m/e 137 shows that a significant degree of hydrogen/deuterium scrambling is occurring.



The monodeuterated compound (Ib) gives results in good agreement with this view. If in the fission (a) the seventh hydrogen/deuterium in the C_7H_7 radical lost is the deuterium atom, then the ratio of the fissions (a) and (b), which give the ions at m/e 136 and 137, respectively is virtually the same as for Ia, being 46.0:54.0. Furthermore in fission (b) the deuterium atom is retained in the m/e 137 ion, so it seems likely that the seventh hydrogen lost comes from the methylene group adjacent to the sulphur atom, although it could come from ring A. At 12 eV the ratio becomes 38.0:62.0, again showing that fission (b) predominates at low electron volts, although this ratio has probably been reduced by partial hydrogen scrambling (*cf.* Ia) towards the value of 46.2:53.8 required for complete equilibration of the deuterium atom throughout the molecule.

Loss of a C_7H_7 radical from the molecular ion of the dibenzoxazocine (II) gives an ion at m/e 120, due to $[C_7H_7NO]^+$. It is not possible to draw any conclusions about this process from the 70 eV spectra of the labelled compounds (IIa and IIb), because of the presence of interfering ions $[C_7H_6NO]^+$ and $[C_7H_5NO]^+$ at m/e 119 and 118. At 12 eV, however, these ions are not present. The compound IIa gives peaks at m/e 120, 121 and 122 in the ratio of 79.5:10.5:10.0, which indicates that as for the sulphur analogue, fission (b) is the process which is favoured. The occurrence of an ion at m/e 121 again shows that some degree of scrambling is occurring, although



this is only slight, since complete equilibration of the deuterium atoms throughout the molecule would result in a ratio of $19 \cdot 2 : 53 \cdot 9 : 26 \cdot 9$ for $m/e \ 120 : 121 : 122$. The spectrum of the N-deuterated compound (IIb) supports this, the deuterium being largely retained in the charged fragment to give ions at $m/e \ 120$ and 121 in the ratio of $9 \cdot 9 : 90 \cdot 1$ at 12 eV.

The *N*-methyldibenzodiazocine (IV) loses a C_7H_7 radical to give an ion at m/e 133 due to $[C_8H_9N_2]^+$. The deuterated compound (IVa) gives ions at m/e 133, 134 and 135 in the ratio 75.4:18.6:6.0, showing that fission (a) is the favoured process.



Since m/e 134 is more intense than m/e 135, it appears that if fission (b) is occurring a deuterium atom is transferred from the methylene group, rather than a hydrogen atom being transferred from elsewhere in the molecule. Both m/e 134 and 135 could be the result of some scrambling occurring prior to fission (a) however. As expected¹⁰ there is an increase in this scrambling at 12 eV, since the intensity of m/e 134 is reduced. The N-deuterated compound (IVb) gives results which at first sight seem anomalous, the ratio of the ions at m/e 133 and 134 being 51.6:48.4. In the absence of scrambling fission (b) would lead to m/e 134, since it is unlikely that the N—D bond would be broken as well as the ND—CH₂ bond. Fission (a) would give m/e 133 if deuterium is transferred and m/e 134 if hydrogen is transferred. From the behaviour of IVa fission (a) should be preferred, so the similar intensities of m/e 133 and 134 can be explained in two ways. Either there are two mechanisms, where deuterium is shifted from the nitrogen and hydrogen from say the methylene group to a similar extent, or there is one mechanism with significant scrambling prior to transfer. In the latter case the position from which the deuterium/hydrogen is transferred can be inferred from the low eV data. At 12 eV there is an increase in the proportion of m/e 133, i.e. an increase in the amount of deuterium transferred. Therefore deuterium/ hydrogen is not transferred from the nitrogen atom, since scrambling would lead to a decrease in the amount of deuterium transferred. The methylene group would appear to be the origin of the transferred atom in this case.



In the unsubstituted labelled dibenzodiazocine (IIIa), the two fissions will not



necessarily occur to the same extent, since the deuterium atoms may exert a secondary isotope effect, thus rendering the methylenes non-equivalent. If, however, there is little scrambling at 70 eV, the ratio of the ions at m/e 119, 120 and 121, namely 44.5:26.0:29.5, indicates that the fissions take place to approximately equal extents, and that in (b) the 'seventh' hydrogen/deuterium of the radical lost can come from either the nitrogen or the carbon of the NH—CD₂ group. At 12 eV the ions are in the ratio 34.9:30.4:34.7. This ratio could arise from a combination of two factors, one being a partial scrambling of the hydrogen and deuterium atoms. Complete equilibration would give a ratio of 23.1:53.8:23.1, so partial scrambling would serve

to decrease the abundance of the ions at m/e 119 and 121 and increase that of m/e 120, in comparison to the results at 70 eV. Secondly, increased transfer of the hydrogen rather than the deuterium from the NH--CD₂ group would increase the abundance of m/e 121 at the expense of m/e 120. A suitable balance of these two processes would result in the observed decrease in m/e 119 and increases in m/e 120 and 121.

In the mass spectrum of the dibenzothiazocine (I) an ion occurs at m/e 135, due to $[C_7H_6NS]^+$. This occurs by a process not observed with the other ring systems, elimination of the radical C_6H_6N . from the molecular ion. In the labelled compound (Ia) this ion is shifted to m/e 137, both the deuterium atoms being retained in the ion. In the compound IVb the ion remains at m/e 135, as would be expected. Possible mechanisms for the fragmentations discussed are shown below, using the labelled dibenzothiazocine (Ia) as the example.



EXPERIMENTAL

Mass spectra were obtained on an AEI MS-902 mass spectrometer using a direct insertion probe. The source temperature was 220°C and the beam energy 70 and 12 eV. Accurate mass determinations were carried out at a resolving power of 20,000 (10% valley definition) and observed values were within 5 parts per million of calculated values.

Deuterium exchange

N-deuterated compounds were prepared by recrystallising the unlabelled material three times from *O*-deuteromethanol. The mass spectra were obtained without delay by direct insertion into the source previously equilibrated with deuterium oxide.

11,12-Dihydro-6H-dibenz[b,f][1,4]oxazocine (II). A solution of 11,12-dihydro-11-oxo-6H-dibenz[b,f][1,4]oxazocine¹¹ (0.5 g) in dry tetrahydrofuran (40 ml) was added slowly to a stirred suspension of lithium aluminium hydride (0.25) in tetrahydrofuran (10 ml) under nitrogen. The mixture was heated under reflux for 12 hrs. To the cooled solution were added water (0.5 ml),

sodium hydroxide solution (10%, 0.5 ml) and water (1.5 ml). The mixture was filtered and the solid mass extracted with boiling ether (15 ml). The ethereal solutions were combined and dried (MgSO₄) and the solvent was removed. Crystallisation of the residue from benzene-cyclohexane gave the dibenzoxazocine (0.26 g, 56%), m.p. 135° (Found: 211.0997. $C_{14}H_{13}NO$ requires 211.0997).

The 11,11-*dideutero-derivative* was prepared similarly from the 11-oxodibenzoxazocine by reduction with lithium aluminium deuteride.

Acknowledgement-The authors thank Mr D. Carter for the determination of the mass spectra.

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