Mass Spectral Fragmentation Mechanisms of Some Dibenzo[c,f][1,2]diazepines

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The fragmentation mechanisms of 11*H*-dibenzo[c,f][1,2]diazepine (I), its 3,8-dichloro derivative (II), 3,8-dichlorodibenzo[c,f][1,2]diazepin-11-one (III) and 3,8-dichloro-11*H*-dibenzo-[c,f][1,2]diazepin-*N*-oxide (IV) are discussed. The initial loss of molecular nitrogen is characteristic of I, II and III. Compound IV has a strong molecular ion, that competitively eliminates either NO or Cl· and N_2O. The common radical ion, m/e 166, present in the mass spectra of I, fluorene, 2-methyl-9,10-anthraquinone and 2-methylbenzo[c]cinnoline, appears to be formed in different states.

Introduction

The mass spectra of several heterocyclic systems containing two adjacent nitrogen atoms have been reported (1-6). More recently, the fragmentation patterns upon electron impact of some 1,2-diazepines have been studied (7). For some time, we have been concerned with the chemistry of the dibenzo[c,f][1,2]diazepine ring system (8-12) and this interest and the lack of information about their mass spectral characteristics prompted us to study the behavior of this system upon electron impact. It would be expected that the mass spectra of these compounds would resemble the spectra of the heteropolycyclic systems rather than those of the simple 1,2-diazepines.

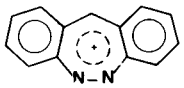
Results and Discussion

Schemes I through 4 show the fragmentation processes of four dibenzo[c,f][1,2]diazepines. These compounds represent three oxidation states of the diazepine ring: the 11*H*-dibenzodiazepines (I,II), the dibenzodiazepin-11-one (III), and the dibenzodiazepin-*N*-oxide (IV); (*) indicates the presence of supporting metastable peaks; (†) indicates that the composition of the ions was determined by high resolution measurements. Table I shows the principal peaks in the mass spectra of compounds I-IV.

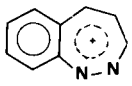
11*H*-Dibenzo[c,f][1,2]diazepine (I). (Scheme I).

Like other heterocyclic compounds containing two adjacent nitrogen atoms (1-6), I fragments primarily by loss of molecular nitrogen from the molecular ion, to produce a species **a**, m/e 166, which then readily loses a hydrogen atom to form the stable, even electron fluorene ion **b** (base peak, m/e 165).

The alternative fragmentation, involving the initial loss of a hydrogen atom from the molecular ion to give a dibenzo-1,2-diazatropilium ion, **d**, does not seem to take place since the M-1 peak is not observed. This agrees with the lack of stability postulated for the benzo-1,2-diazatropilium ion, **e** (2).



d



e

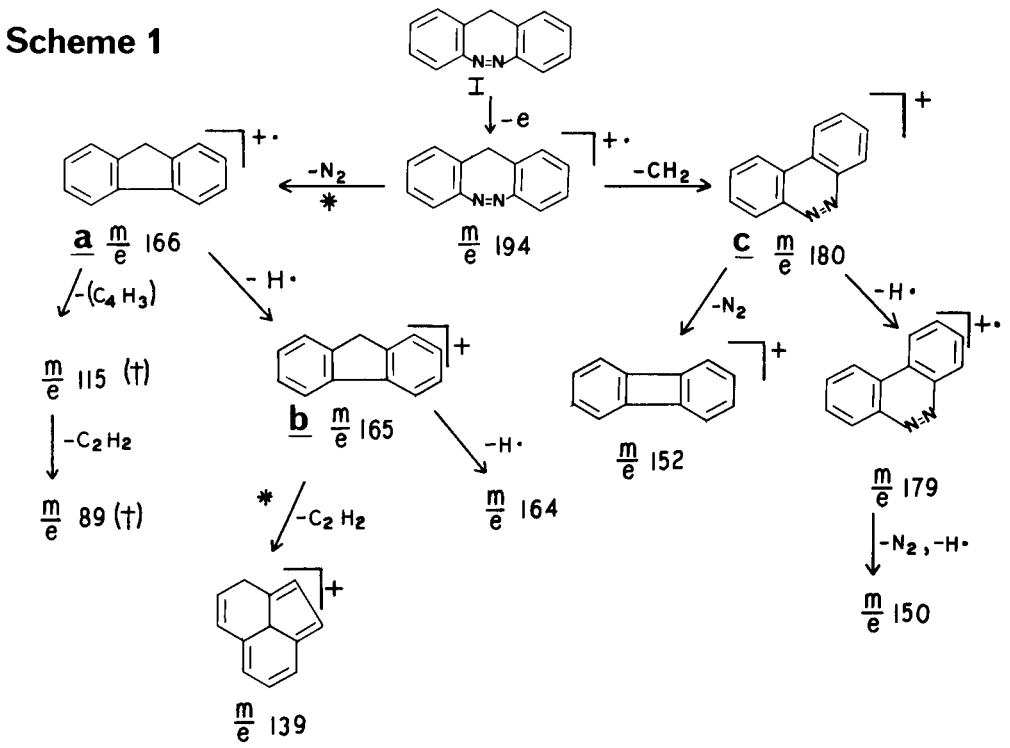
Further fragmentation of **b** follows the path discussed by Hall and Oliver (13) for a similar ion produced by electron impact on 1 and 2-methyl-9,10-anthraquinones.

The production of **c**, a benzo[c]cinnoline radical ion, is a very minor process; however, the fact that this transient species is formed is indicated by the appearance of peaks at m/e 150, m/e 126, m/e 74, corresponding to the fragmentation pattern of benzo[c]cinnoline itself (4). Other major peaks, with relative abundance, are included in Table I.

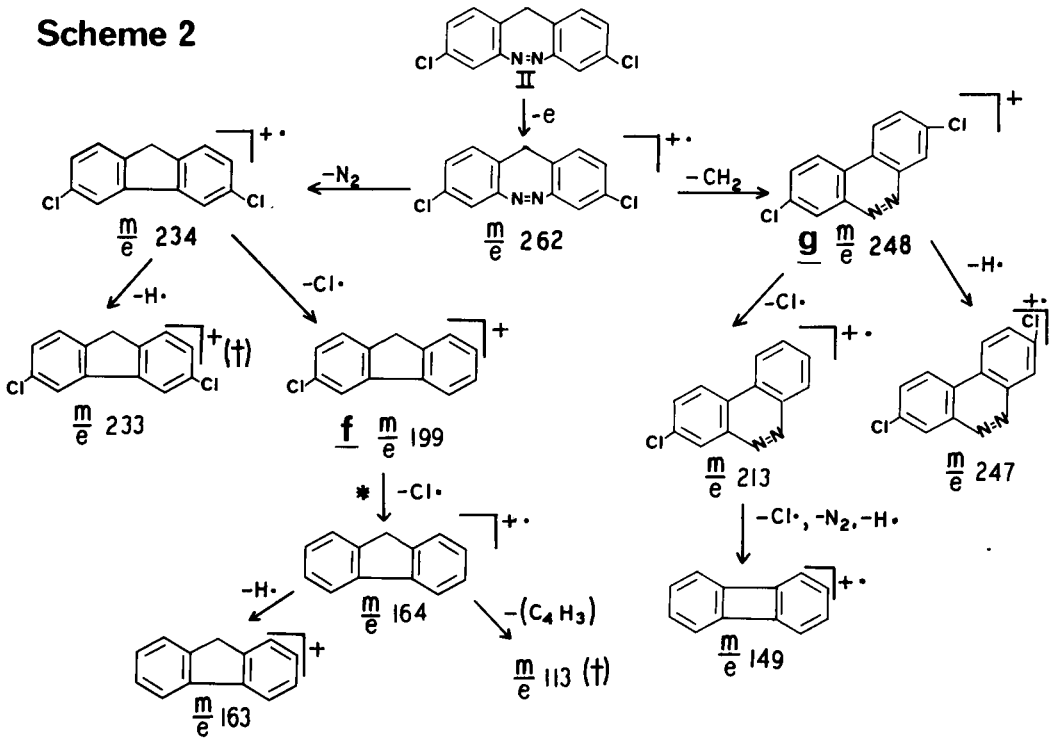
The ion m/e 166 and its -H· even electron fragment, m/e 165, have been observed as major ions in the fragmentation of similar molecules, for example fluorene (13), anthrone (13), 1-methyl-9,10-anthraquinone (13) and 2-methylbenzo[c]cinnoline (4). In the case of the fragmentation of fluorene, m/e 166 is formed by direct electron impact, while in the case of the other compounds it is the product of a series of fragmentation and rearrangement processes. In Table II a comparison is made of the ratios of the relative intensities of parent to daughter ions for some of the cited molecules.

It is easily seen that the m/e 166 ion, when obtained from fluorene, undergoes fragmentation to a much lesser degree than when obtained from the last five compounds listed in Table II, anthrone, I, the methylanthraquinones and 2-methylbenzo[c]cinnoline. These results suggest that the m/e 166 ion is formed in a different state in the

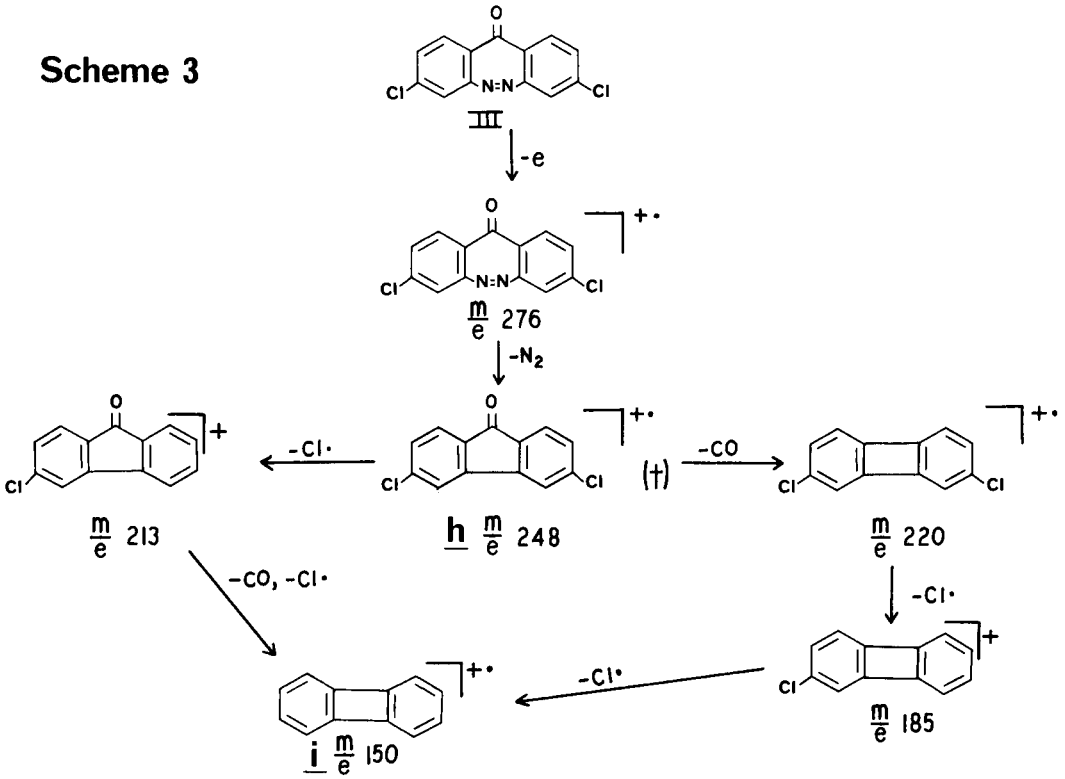
Scheme 1



Scheme 2



Scheme 3



Scheme 4

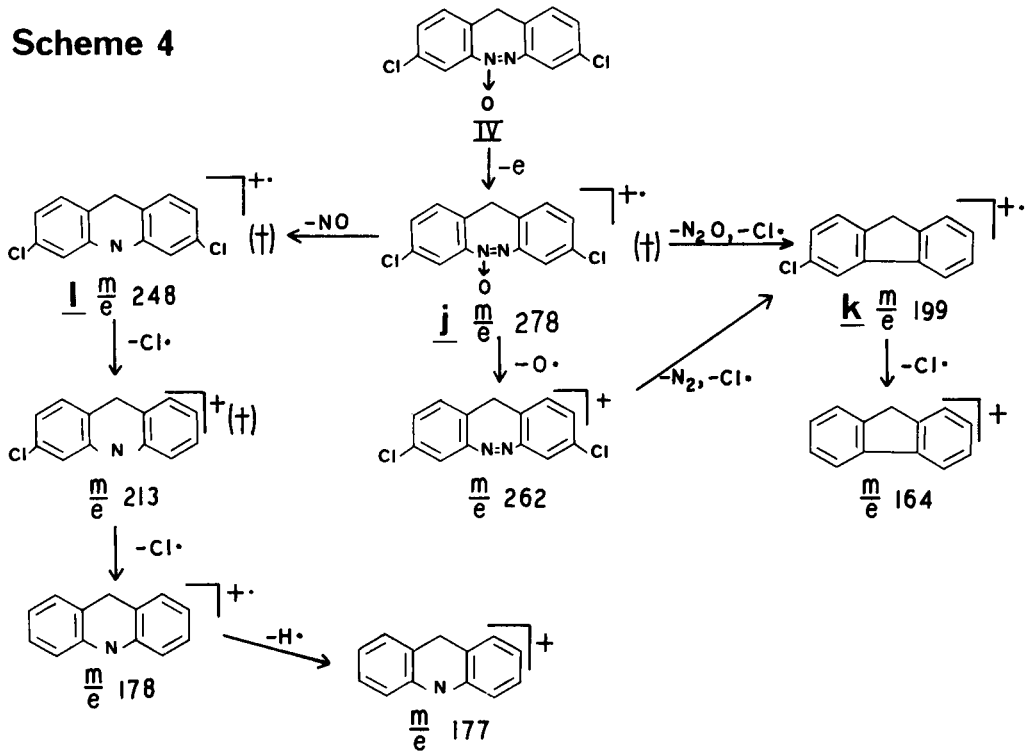


TABLE I

Principal Peaks in the Mass Spectra of Dibenzo[*c,f*][1,2]diazepines.

(All peaks greater than 5% of the base peak [100%] are recorded, except for those having a higher m/e value than the molecular peak and certain others of diagnostic value.)

11*H*-Dibenzo[*c,f*][1,2]diazepine (I).

m/e	37	38	39	40	50	51	52		
Rel. int.	7	17	43	6	29	26	12		
m/e	61	62	63	64	65	74	75		
Rel. int.	7	26	56	17	7	21	21		
m/e	76	77	82.5	86	87	88	89		
Rel. int.	14	9	6	12	19	9	22		
m/e	98	99	100	101	102	113	115		
Rel. int.	7	6	5	5	5	10	16		
m/e	126	139	140	150	162	163	164	165	
Rel. int.	7	37	7	3	5	27	19	100	
m/e	166	194(M)	195						
Rel. int.	22	29	7						

3,8-Dichloro-11*H*-dibenzo[*c,f*][1,2]diazepine (II).

m/e	63	81	81.5	87	89	99	99.5	149	
Rel. int.	8	5	11	5	5	6	6	3	
m/e	163	164	165	199	200	201	202	213	233
Rel. int.	31	16	6	100	19	35	8	3	8
m/e	234	235	247	248	262(M)	263	264	265	
Rel. int.	2	5	3	2	54	15	38	12	
m/e	266								
Rel. int.	12								

3,8-Dichlorodibenzo[*c,f*][1,2]diazepin-11-one (III).

m/e	51	53	60	61	62	63	64	74	75
Rel. int.	7	7	5	10	17	14	7	72	99
m/e	76	84	86	87	88	92	92.5	98	99
Rel. int.	14	14	10	10	5	10	5	16	17
m/e	100	110	111	112	122	123	124	138	139
Rel. int.	5	43	14	14	7	14	7	10	10
m/e	149	150	151	184	185	186	187	213	215
Rel. int.	19	100	14	14	57	12	19	29	30
m/e	220	221	222	223	224	248	249	250	
Rel. int.	86	14	57	10	10	4	7	3	
m/e	251	252	276(M)	277	278	279	280		
Rel. int.	5	5	72	12	43	10	10		

3,8-Dichloro-11*H*-dibenzo[*c*,*f*][1,2]diazepin-*N*-oxide (IV).

m/e	50	51	52	55	57	61	62	63	64
Rel. int.	20	27	6	8	6	6	20	39	6
m/e	73	74	75	76	77	81	81.5	86	87
Rel. int.	18	20	41	16	8	6	12	6	8
m/e	88	88.5	89	90	98	99	100	101	102
Rel. int.	8	6	31	6	6	6	6	6	6
m/e	111	112	113	123	124	125	126	127	137
Rel. int.	6	6	6	8	6	6	10	6	8
m/e	138	139	149	150	151	152	153	161	162
Rel. int.	8	6	10	20	24	14	8	6	10
m/e	163	164	165	175	176	177	178	179	
Rel. int.	39	24	6	6	10	43	29	12	
m/e	180	186	187	188	198	199	200	201	
Rel. int.	6	8	6	12	6	37	10	14	
m/e	212	213	214	215	216	226	243		
Rel. ing.	16	43	12	26	8	11	24		
m/e	245	247	248	249	250	251	260		
Rel. int.	8	10	26	16	24	8	10		
m/e	261	262	263	278(M)	279	280	281		
Rel. int.	8	8	8	100	20	65	12		
m/e	282								
Rel. int.	12								

TABLE II

Ratio of Parent/Daughter Ion Intensities in the Fragmentation of the m/e 166 Ion.

Molecule	I 166/I 165	I 165/I 164	I 165/I 139	I 165/I 115
Fluorene (a)	1.2	15.7	13.5	22.2
Anthrone (a)	0.2	8.8	9.8	14.7
I	0.2	5.4	2.6	6.2
1-Me-9,10-Anthraquinone (a)	0.3	5.9	3.1	–
2-Me-9,10-Anthraquinone (a)	0.3	7.1	4.0	11.1
2-Me-Benzo[c]cinnoline (b)	0.43	5.5	5.2	11.1

(a) See ref. 13. (b) See ref. 4.

cases where it is produced by ion rearrangement than in the case where it is formed by direct electron impact.

If it is assumed that there is a common structure for m/e 166, as indicated for the last five compounds on Table II, it seems then as if the overall effect of ionization → fragmentation → rearrangement is to form an ion in a higher energetic state than when it is formed from a stable molecule by direct electron impact. The excitation energy is perhaps derived from energy released by internal rearrangement preceding ion fragmentation.

3,8-Dichloro-11*H*-dibenzo[*c*,*f*][1,2]diazepine (II) (Scheme 2).

The mass spectrum of II is very similar to that of I. While the unsubstituted dibenzodiazepine (I) fragments by the process M-N_2-H·(M-N_2-H.), II reveals a related path M-N_2-Cl· (Scheme 2) probably to give **f**, m/e 199, an even electron chlorofluorene ion. Loss of CH_2 from the molecular ion leads to **g**, m/e 248, presumably a dichlorobenzo[*c*]cinnoline ion, which has the fragmentation mode characteristic of this class of compounds (4). In the mass spectrum of II, as in the spectrum of I, fragmentation through the benzo[*c*]cinnolines is not the favored path.

The dibromo analog of II behaves in the same manner as II upon electron impact, and will not be discussed further.

3,8-Dichlorodibenzo[*c*,*f*][1,2]diazepin-11-one (III) (Scheme 3).

Loss of nitrogen from the molecular ion of III precedes fragmentation with loss of CO, giving an ion that can be best represented as **h**, m/e 248, a dichlorofluorenone ion, indicating once more the tendency of the dibenzodiazepines to preferentially lose nitrogen. Consecutive loss of two chlorine atoms and CO from **h**, leads to the base peak, m/e 150, most plausibly represented as **i**, an *o*-phenylene ion.

3,8-Dichloro-11*H*-dibenzo[*c*,*f*][1,2]diazepin-*N*-oxide (IV) (Scheme 4).

The molecular ion of IV, **j**, m/e 278, is the base peak in its mass spectrum. Compound **j** fragments in two equally competitive ways. Loss of N_2O and a chlorine atom produces **k**, m/e 199, corresponding to **f** in the fragmentation of II and which fragments further in a similar manner, while loss of NO leads to an ion, m/e 248, best represented as a dihydrodichloroacridine, **l**. Consecutive loss of two chlorine atoms from **l**, gives an ion, m/e 178, probably a dihydroacridine. Elimination of oxygen from the molecular ion **j**, is a minor but noteworthy process. Azoxybenzene fragments by consecutive expulsions of 28 mass units from the molecular ion, first CO and then a nitrogen molecule (14). The appearance of a peak at m/e 250, (M-28) in the spectrum of IV would indicate a similar loss of CO. However no exact mass measurement of this peak was made and this precludes speculation as to the nature of the species eliminated.

EXPERIMENTAL

The diazepines (I-IV) were prepared by previously described methods (8,11) and were analytically pure. Mass spectra were obtained with an A.E.I. MS-902 instrument at a resolution of about 2,000, using the direct insertion probe and 70 eV electron beam. Exact masses were determined for several peaks by peak matching with a resolution of about 10,000. All compounds were run at 150°.

Note added in proof.

It has come to our attention that a paper on a similar subject by F. D. Popp, K. T. Potts, E. Brugel and R. J. Dubois is in press in *Org. Mass Spectrom.* We thank Dr. F. D. Popp for making their manuscript available to us prior to publication.

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