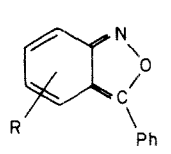
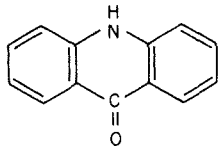
New Mass Spectra

Mass Spectra of 3-Phenyl-2,1-benzisoxazoles

We report here the electron impact (EI) mass spectra of eight 3-phenyl-2,1-benzisoxazoles (**1**), seven of which bear substituents in the benzo ring at positions 5 or 6.



1 (Ph = C_6H_5)



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The data for the unsubstituted compound (**1**, R = H) are summarized in Table 1. The origins of all these fragment ions have been established by observations of either second field-free region (2nd FFR) metastable ions (*m**) or by means of linked-scan spectra (*B/E*) from the 1st FFR. The characteristic initial fragmentations of the molecular ion are: loss of CO followed by $H^{\cdot}$; loss of C_6H_4N to leave $[C_7H_5O]^+$ (*m/z* 105); elimination of C_7H_5N to give the ion at *m/z* 92 of composition C_6H_4O; and formation of Ph^+. These fragments are significantly different from those of 2,1-benzisoxazole, which is reported[1] to lose only CO and HCN.

This mass spectrum of 3-phenylbenzisoxazole can best be understood by comparison with that of 9(10*H*)acridinone (**2**). The similarities (see Fig. 1) are striking, and the matching *m/z* values in the two spectra correspond to identical ion compositions. Figure 2 shows the linked scans (*B/E*) which identify the daughters of the two molecular ions, and again there is close correspondence. One must conclude that many of the ions produced from this benzisoxazole are identical to those produced from acridinone. The spectral similarities extend to the doubly charged ions (Table 2).

Nevertheless, the two spectra are not quite identical. The major difference is that 3-phenylbenzisoxazole loses C_6H_4N to

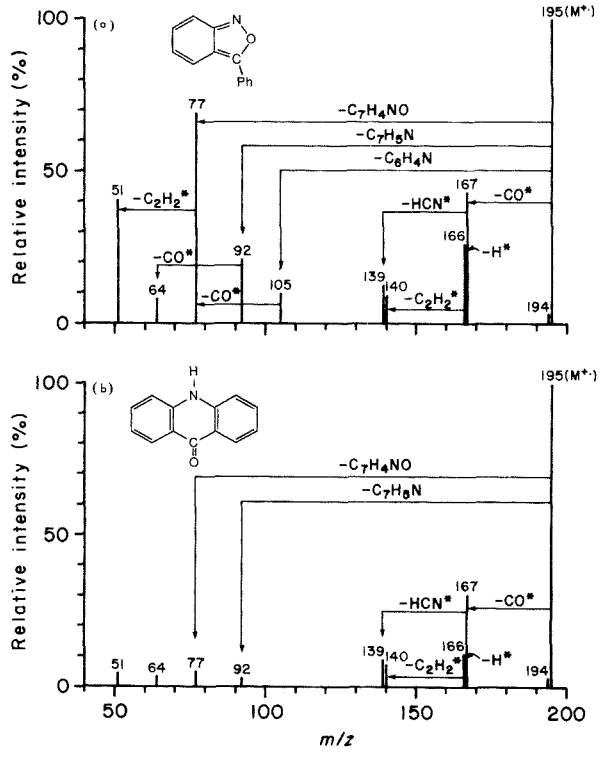


Figure 1. Fragmentation under EI of (a) 3-phenyl-2,1-benzisoxazole, and (b) 9(10*H*)acridinone.

Table 1. Identifiable fragmentations in EI mass spectrum (*z* = 1) of 3-phenyl-2,1-benzisoxazole

m/z	Ion abundance (%)	Ion composition	Origin	Metastable
195	100	$C_{13}H_9NO$	$M^{+\cdot}$	
194	3.4	$C_{13}H_8NO$	M − H	*B/E*
167	43.4	$C_{12}H_9N$	M − CO	*m** 143.0, *B/E*
166	26.3	$C_{12}H_8N$	167 − H	*m** 165.1
			M − (CO + H)	*B/E*
141	2.2	$C_{10}H_7N$	167 − C_2H_2	
140	9.0	$C_{11}H_8$[a]	167 − HCN	*m** 117.5[b]
		$C_{10}H_6N$[a]	M − (CO + H + C_2H_2)	[b]
139	12.7	$C_{11}H_7$	166 − HCN	*m** 116.5
			M − (CO + H + HCN)	*B/E*
105	10.1	C_7H_5O	M − C_6H_4N	*B/E*
92	20.9	C_6H_4O	M − C_7H_5N	*B/E*
77	69.8	C_6H_5	M − C_7H_4NO	*B/E*
			105 − CO	*m** 56.5
64	8.0	C_5H_4	92 − CO	*m** 44.6
51	40.4	C_4H_3	77 − C_2H_2	*m** 33.9

[a] These two ions, $C_{11}H_8$ and $C_{10}H_6N$, could not be resolved from one another or from $^{12}C_{10}{}^{13}C_1H_7$. The experimental mass measurement corresponded to $C_{10}H_6N$.
[b] The *B/E* linked scan (see Fig. 2) indicates that $M^{+\cdot}$ loses 55 mass units. This mass loss fits either or both of M − (CO + HCN) and M − (CO + H + C_2H_2).

0030–493X/89/010070–04 $05.00

Received 4 May 1988
Accepted 21 June 1988

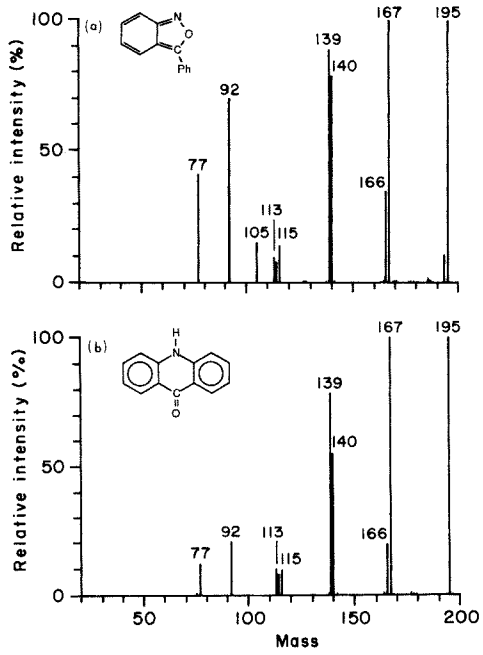


Figure 2. Linked scans (*B*/*E*) on molecular ions (*m*/*z* 195) of (a) 3-phenyl-2,1-benzisoxazole, and (b) 9(10*H*)acridinone.

yield $PhCO^+$ (*m*/*z* 105, 10.1% abundance), whereas acridinone has no significant ion here (observed abundance <0.2%). In addition, the benzisoxazole has abundant ions at *m*/*z* 92, 77, 64 and 51, whereas acridinone has such feeble ones (abundance <5%) that they were disregarded by Bowie and co-workers[2] in their published discussion of the spectrum.

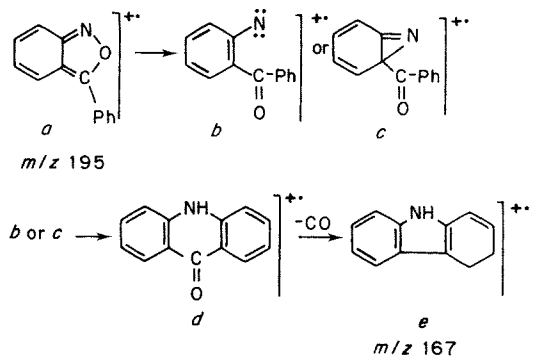
We suggest Schemes 1, 2, and 3 to accommodate all these observations. In Scheme 1, the molecular ion (*a*) of 3-phenylbenzisoxazole ring-opens to a nitrene (*b*) and then re-cyclizes via nitrene insertion into the phenyl group, thus forming the acridinone molecular ion (*d*) along the lines Hawkins and Meth-Cohn[3] have advanced for the high-temperature rearrangement of neutral 3-arylbenzisoxazoles to acridinones. The azirene ion (*c*) is an equivalent formulation of the nitrene and would likewise lead to the acridinone cation (*d*). Our observed successive losses of CO, H· and HCN are well documented for the acridinone ion;[2] our own data are shown in Figs 1 and 2. Scheme 1 includes ions (*b* or *c*) from which the observed ion $PhCO^+$ could be formed.

In Scheme 2 we show rearrangement of the ion (*a*) into the phenylimine ketene (*f*), presumably via the N—O bond cleavage and phenyl radical migration pathway which Simons *et al.*[4] have suggested for the rearrangement of simple isoxazole

Table 2. Doubly charged ions from 3-phenyl-2,1-benziosoxazole (1) and 9(10*H*)acridinone (2)

Compound	*m*/*z*	Ion abundance (%)[a]	Assignment	Observed *m**
1	97.5	4.4	M^{2+}	
	83.5	7.8	M − CO	71.5
	70.5	3.8	167 − C_2H_2	59.6
	70	1.7	167 − HCN	58.7
2	97.5	4.3	M^{2+}	
	83.5	15.5	M − CO	71.5
	70.5	5.8	167 − C_2H_2	59.6
	70	3.5	167 − HCN	58.6

[a] The abundance scale is relative to 100% for the singly charged molecular ion.



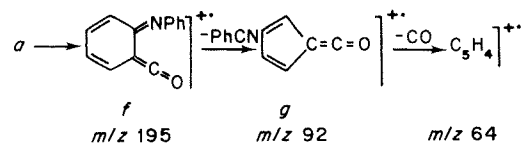
Scheme 1

ions. This ion (*f*) can clearly account for loss of C_7H_5N (presumed to be PhCN or PhNC) and the subsequent ejection of CO, but is not a plausible parent for $PhCO^+$.

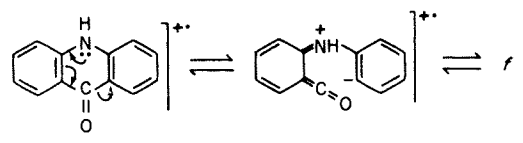
Ramana and Srinivas[5] have proposed that the phenylimine ketene ion (*f*) is a daughter in the EI spectrum of 2-phenylaminobenzoic acid, and leads to the acridinone ion (*d*). If we assume that this route (*f* → *d*) can be followed in reverse to a small extent (see Scheme 3), then the presence of low-abundance ions at *m*/*z* 92 and 64 in the mass spectrum of acridinone is explained by Scheme 2. Loss of Ph^+ from (*f*) likewise accounts for the presence of *m*/*z* 77, and its daughter at *m*/*z* 51, in the acridinone spectrum. An alternative ring-opening of the acridinone ion (*d* → *b* or *c* in Scheme 1) can be disregarded since $PhCO^+$ is not a daughter ion of acridinone.

Unlike the other benzisoxazoles reported here, the 5- and 6-methyl compounds show substantial H-atom loss from their molecular ions (see Table 3). Carbon monoxide is lost from both the $M^{+\cdot}$ and $[M - H]^+$ species. In the case of the latter fragmentation, the CO loss follows so closely upon the initial H· loss that a metastable ion is observed for the M − C'HO process. These features are also observed for C-methylacridinones,[6] which provide further strong argument that 3-phenylbenzisoxazoles and acridinones have many common ions in their EI spectra.

The overall picture for our eight 3-phenylbenzisoxazoles is that they yield a prominent molecular ion, and abundant ions at *m*/*z* 77, $[C_6H_5]^+$, and 51, $[C_4H_3]^+$. The ion at *m*/*z* 105, $[C_7H_5O]^+$, is invariably present, at modest abundance (8.8–29.7%). The other fragmentations of 3-phenylbenzisoxazole (**1**, R = H) are not so readily apparent when R is not H. The ion formed by C_7H_5N loss is abundant (20.9%) when R = H, but is of minor intensity when R is methyl or halogen, and cannot be recognized when R is 5-NO_2 or 5-COOEt (see Table 3). In all these compounds, CO loss is an important step in the fragmentation, but often yields precedence to cleavages of substituents in the benzo ring. The $[M - CO]^{+\cdot}$ ion thus appears with very variable abundance, from 43% when R = H in (**1**), to zero when R is 5-NO_2 or 5-COOEt.



Scheme 2



Scheme 3

Table 3. Mass spectra of substituted 3-phenyl-2-1-benzisoxazoles[a]

5-Methyl-3-phenyl-2,1-benzisoxazole

m/z 209 (100%, $C_{14}H_{11}NO$, $M^{+\cdot}$); 208 (29.5, M – H); 194 (3.5, M – CH_3); 181 (11.4, M – CO); 180 (51.0, M – CHO, *m** 155.1); 166 (6.7, 194 – CO or 181 – CH_3); 153 (3.0, 180 – HCN, *m** 130.0); 106 (2.6, M – C_7H_5N); 105 (12.2, M – C_7H_6N); 77 (41.5, M – C_8H_6NO and 105 – CO, *m** 56.5); 51 (16.3, 77 – C_2H_2, *m** 33.8).

6-Methyl-3-phenyl-2,1-benzisoxazole

m/z 209 (100%, $C_{14}H_{11}NO$, $M^{+\cdot}$); 208 (18.9, M – H); 194 (2.9, M – CH_3); 181 (9.7, M – CO); 180 (61.8; M – CHO, *m** 155.0; 208 – CO, *m** 155.8); 166 (2.3, 194 – CO or 181 – CH_3); 153 (2.9, 180 – HCN, *m** 130.0); 106 (1.9, M – C_7H_5N); 105 (9.9, M – C_7H_6N); 77 (61.7, M – C_8H_6NO and 105 – CO, *m** 56.5); 51 (23.3, 77 – C_2H_2, *m** 33.9).

5-Chloro-3-phenyl-2,1-benzisoxazole

m/z 231, 229 (14.7, 48.1%, $C_{13}H_8ClNO$, $M^{+\cdot}$); (230)[b], 228 (–[b], 0.9, M – H); 203, 201 (1.7, 4.7, M – CO, *m** 178.1, 176.2); 194 (29.6, M – Cl, *m** 164.5, 163.0); 166 (44.1; 194 – CO, *m** 142.0; 203 – ^{37}Cl, *m** 135.7; 201 – ^{35}Cl, *m** 137.0); 140 (8.0, 166 – C_2H_2, *m** 118.1); 139 (10.1, 166 – HCN, *m** 116.4); 128, 126 (2.2, 8.4, M – C_7H_5N); 105 (10.2, M – C_6H_3ClN); 77 (100, M – C_7H_3ClNO and 105 – CO, *m** 56.5); 51 (62.8, 77 – C_2H_2, *m** 33.8).

6-Chloro-3-phenyl-2,1-benzisoxazole

m/z 231, 229 (14.1, 36.9%, $C_{13}H_8ClNO$, $M^{+\cdot}$); 203, 201 (0.2, 0.6, M – CO, *m** 178.2, 176.0); 194 (9.7, M – Cl, *m** 164.3, 162.8); 166 (14.3, 194 – CO, *m** 142.0; 203 – ^{37}Cl, 201 – ^{35}Cl); 140 (1.5, 166 – C_2H_2); 139 (3.0, 166 – HCN, *m** 116.3); 128, 126 (1.4, 5.6, M – C_7H_5N); 105 (8.8, M – C_6H_3ClN); 77 (44.6, M – C_7H_3ClNO and 105 – CO, m* 56.5); 51 (100, 77 – C_2H_2, *m** 33.8).

5-Fluoro-3-phenyl-2,1-benzisoxazole

m/z 213 (100%, $C_{13}H_8FNO$, $M^{+\cdot}$); 185 (22.0, M – CO, *m** 160.7); 184 (19.5, 185 – H); 165 (0.5, 185 – HF, *m** 147.2, or 184 – F); 157 (7.9, 184 – HCN, *m** 134.0); 110 (5.6, M – C_7H_5N); 105 (9.7, M – C_6H_3FN); 77 (45.7, M – C_7H_3FNO and 105 – CO, m* 56.5); 51 (59.3, 77 – C_2H_2, *m** 33.8).

5-Nitro-3-phenyl-2,1-benzisoxazole

m/z 240 (87.1%, $C_{13}H_8N_2O_3$, $M^{+\cdot}$); 239 (0.1, M – H); 210 (4.1, M – NO); 194 (13.7, M – NO_2, *m** 156.8); 182 (10.2, 210 – CO, *m** 157.8); 166 (53.3, 194 – CO, m* 142.0); 140 (19.4, 166 – C_2H_2, *m** 118.0); 139 (30.6, 166 – HCN, *m** 116.4); 105 (29.7, M – $C_6H_3N_2O_2$); 77 (100, M – $C_7H_3N_2O_3$ and 105 – CO, *m** 56.5); 51 (5.0, 77 – C_2H_2, *m** 33.8).

5-Ethoxycarbonyl-3-phenyl-2-,1-benzisoxazole

m/z 267 (100%, $C_{16}H_{13}NO_3$, $M^{+\cdot}$); 239 (31.2, M – C_2H_4, *m** 214.0); 222 (92.2, M – C_2H_5O, *m** 184.8); 195 (6.0, 239 – CO_2, *m** 159.2); 194 (32.9, 222 – CO, *m** 169.5); 167 (7.2, 195 – CO, *m** 143.0); 166 (31.5, 194 – CO); 105 (22.9, M – $C_9H_8NO_2$); 77 (81.4, M – $C_{10}H_8NO_3$ and 105 – CO, *m** 56.5); 51 (64.8, 77 – C_2H_2, *m** 33.8).

[a] All assignments are supported by correct ion compositions.
[b] One (M – H) peak could not be resolved from the ^{13}C satellite of the *m/z* 229 molecular ion.

The 3-phenyl-2,1-benzisoxazoles were synthesized by pyrolysis of corresponding 2-azidobenzophenones.[7] Samples were purified by recrystallization. No impurities could be detected by thin-layer chromatography (silica gel G adsorbent, benzene or chloroform elution), or by infrared spectroscopy.

All mass spectra were obtained by EI (70 eV). High-resolution spectra were recorded with an AEI MS-30 single-beam instrument whose source operated at 200 °C. The DS-55 data-handling system derived ion compositions which fitted the measured *m/z* values closer than 4 ppm. Perfluorokerosene was used as internal standard.

Second FFR metastable ions were recorded photographically with either a VG Micromass or the MS-30 instrument. Measured values of *m** agreed within 0.2 units of calculated values. First FFR metastables were recorded by means of linked scans (*B/E*) with a VG Analytical 7070E spectrometer.

We are indebted to Mr Neil Keats for recording the MS-30 spectra, to Dr Roger Summons of the Bureau of Mineral Resources, Canberra, for recording the linked scans, and to Dr John MacLeod for the Research School of Chemistry, Australian National University, for helpful discussions.

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