

FRAGMENTATION OF NAPHTHOXAZOLES UNDER ELECTRON IMPACT

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The mass spectra of seven naphthoxazole derivatives were examined. Of these compounds, only phenylnaphthoxazole and 2-*p*-(aminophenyl) naphthoxazole were characterised by a prominent molecular ion (often responsible for the base peak) and also the presence of doubly charged ions with high relative abundance. One of the main features of decomposition of the parent naphthoxazole is the elimination of carbon monoxide and hydrogen cyanide. A mechanism for these fragmentations has been proposed.

INTRODUCTION

During our work on heterocyclic compounds, we have prepared a large number of naphthoxazole compounds with the object of their use for the preparation of various types of dyes and finishing products as well as for biological assays. In the course of these studies, many synthetic methods were used [1-5]. However, in many cases, determination of the mass spectra of such compounds gave a full picture of the behaviour of such compounds under electron impact.

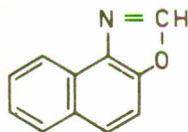
The compounds presented in the present study were selected to cover different types of naphthoxazoles and their derivatives and thus offer a rather complete survey on the subject.

The compounds which were studied are as follows:

- (1) Naphtho-[1,2-*d*]-oxazole (I); (2) 2-phenylnaphtho-[1,2-*d*]-oxazole (II); (3) 2-*p*-(nitrophenyl)-naphtho-[1,2-*d*]-oxazole (III); (4) 2-*p*-(nitrophenyl)-[1,2-*d*]-oxazole-5-sulphonic acid (IV); (5) 2-*p*-(aminophenyl)-naphtho-[1,2-*d*]-oxazole-5-sulphonic acid (V); (6) 2-*p*-(aminophenyl)-naphtho-[1,2-*d*]-oxazole (VI); and (7) 2-*p*-(aminophenyl)-naphtho-[2,1-*d*]-oxazole (VII).

The following is the detailed study of the mass spectra of such compounds:

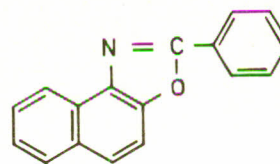
The first compound in the series is the parent compound, naphtho-[1,2-*d*]-oxazole (I) prepared by fusion of 1-amino-2-naphthol hydrochloride with formamide.



(I)

The behaviour of this molecule under electron impact is characterised by a molecular ion with m/z 169 which is not the base peak but represents a good relative abundance (24.6%). The fragmentation is based mainly on the ejection of carbon monoxide [6] followed by ring expansion then elimination of hydrogen cyanide [7]. The pattern of fragmentation of this compound can be represented by Scheme 1 (cf. Fig. 1).

The second compound in this series is 2-phenylnaphtho-[1,2-*d*]-oxazole (II) which is stable towards electron impact. This is indicated by the presence of a doubly charged ion [8] at mass number 122.5 which represents a very high relative abundance (98.6%). The molecular ion at m/z 245 represents the base peak. The decomposition of this molecular ion under electron impact can be shown as indicated in Scheme 2 (cf. Fig. 2).



(II)

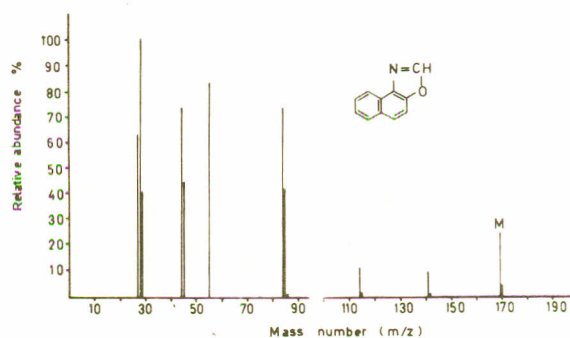
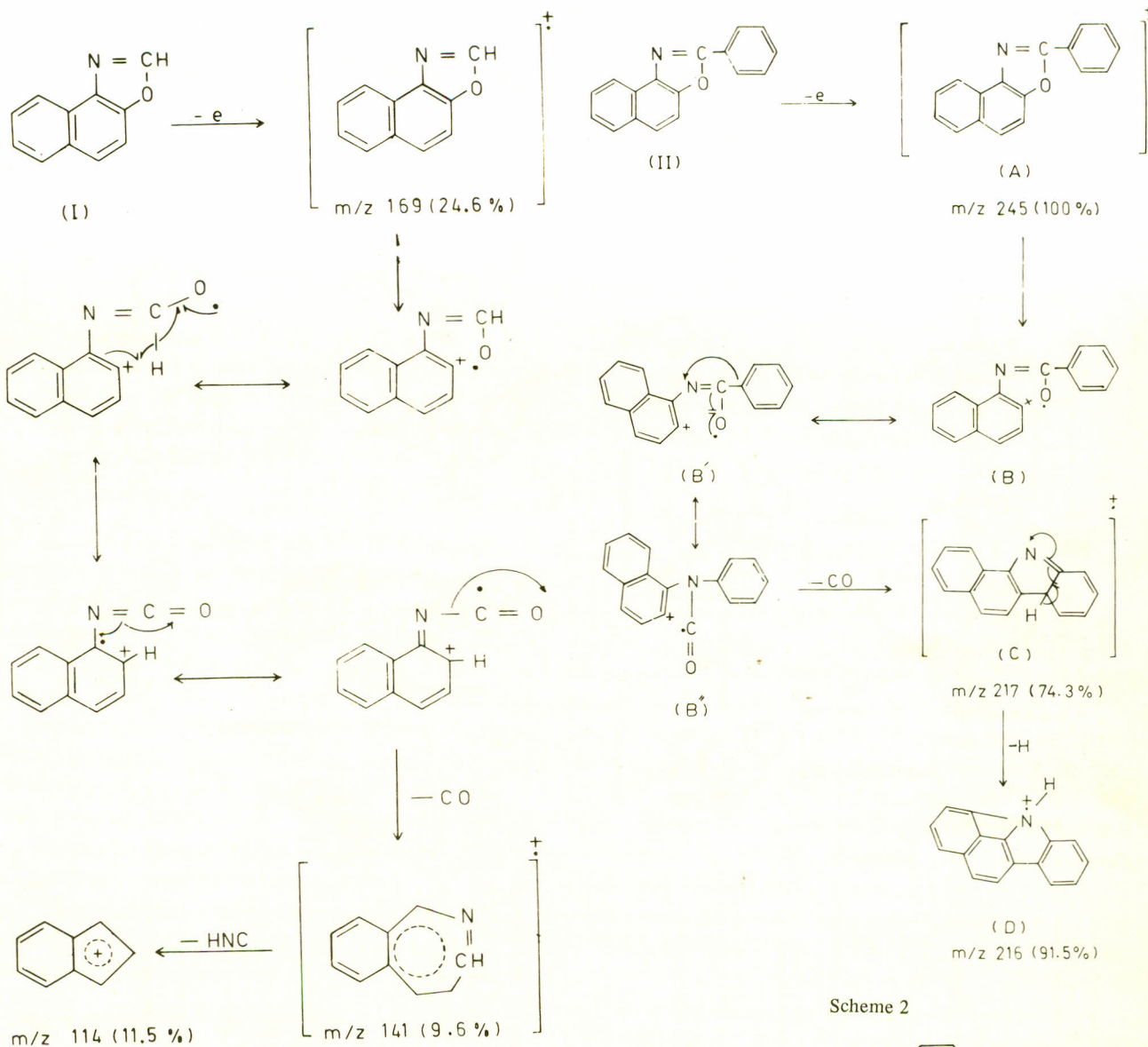


Fig. 1.



Scheme 1

Scheme 2

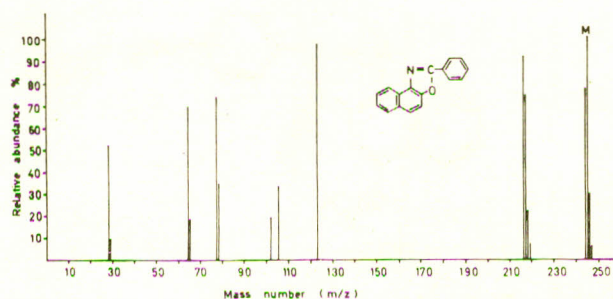
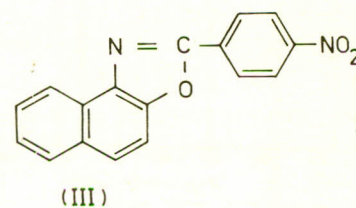
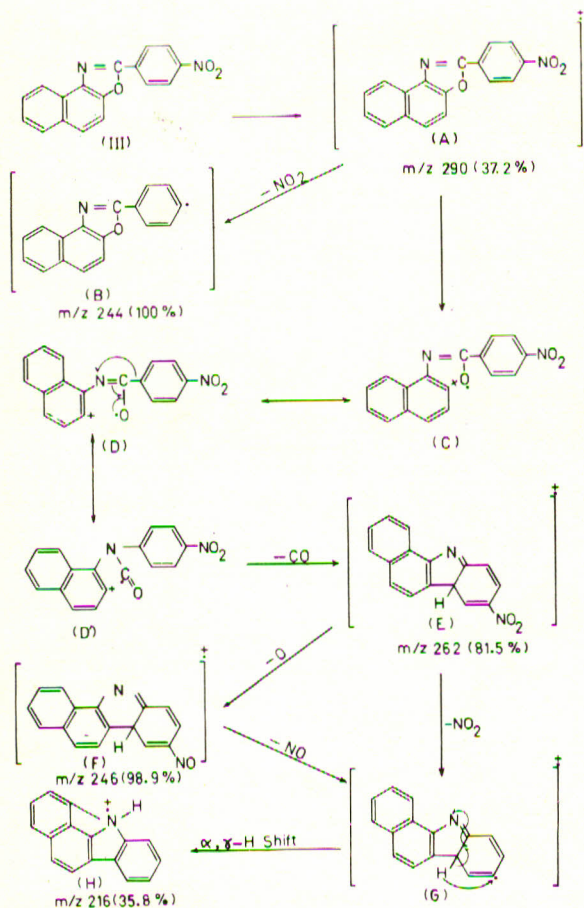


Fig. 2.

The third compound is a naphthoxazole derivative namely 2-*p*-(nitrophenyl)-naphtho-[1,2-*d*]-oxazole (III), which demonstrates the influence of the electron-attracting nitro group on the fragmentation behaviour of such compounds.



The behaviour of this molecule under electron impact is as follows: The molecular ion (A) at m/z 290 is not the base peak and is of 37.2% relative abundance. This ion can lose the nitro group [8] to give ion (B) with m/z 244 which is the base peak. The molecular ion (A) can go through another route of fragmentation by opening of the oxazole ring to give ion (C) which ejects carbon monoxide [6] via rearrangement to (D) and (D) to give the stable ion (E) with m/z 262 and of high relative abundance equal to 81.5%. The latter ion either loses oxygen to give the nitroso ion [8] (F) having m/z 246 and 98.6% as a relative



Scheme 3

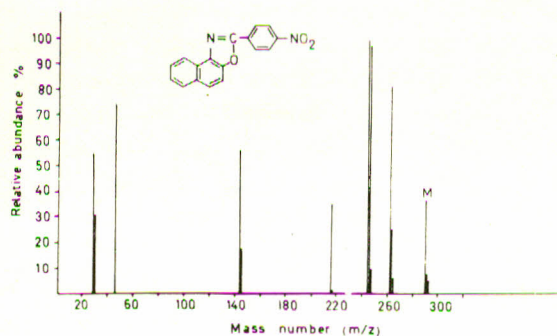
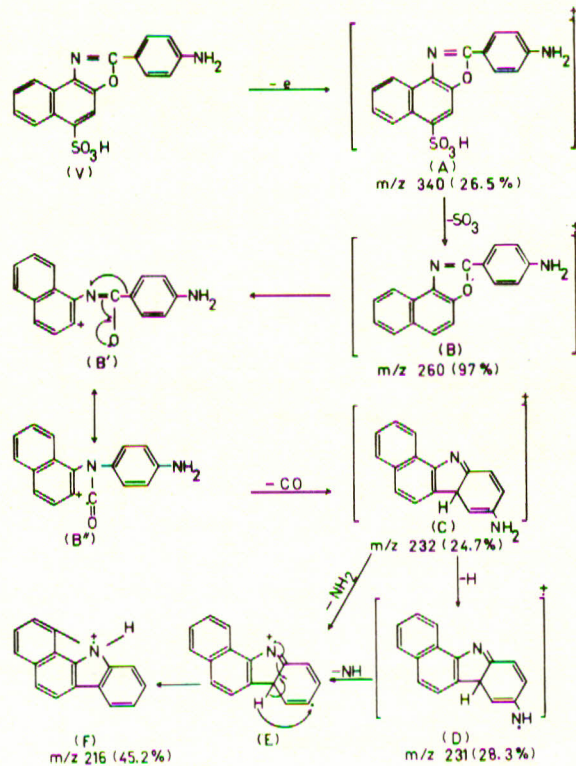


Fig. 3.

abundance or loses the nitro group [9] to give ion (G) which undergoes α, γ -hydrogen shift [9] to give ion (H) with m/z 216 and relative abundance of 35.8%.

This fragmentation pattern is represented in Scheme 3 (cf. Fig. 3).

With respect to the fragmentation pattern of 2-(nitrophenyl)-naphtho[1,2-d]-oxazole-5-sulphonic acid (IV), the molecular ion is not seen in the spectrum probably due to desulphonation of this product prior to electron impact. The heaviest ion seen corresponds to a molecular ion that has lost sulphur trioxide, i.e. ion (A) of m/z 290



Scheme 4

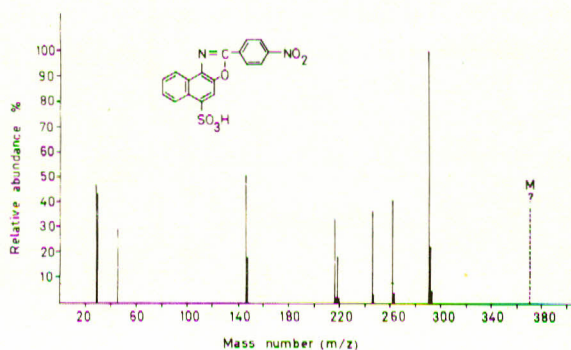
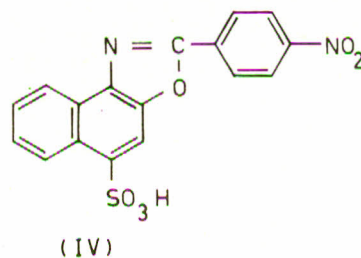


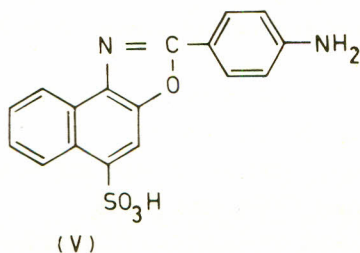
Fig. 4.



which represents the base peak. This ion undergoes fragmentation in the same manner as indicated in the case of the nitro compound (III) (Scheme 3) but shows different relative abundance of the resultant fragment ions (cf. Fig. 4).

In contrast to the previous compound, 2-(aminophenyl)-naphtho[1,2-d]-oxazole-5-sulphonic acid (V) gave

clearly the molecular ion (A) with m/z 340 and representing 26.5% relative abundance.



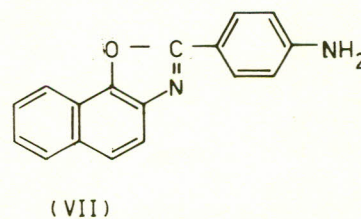
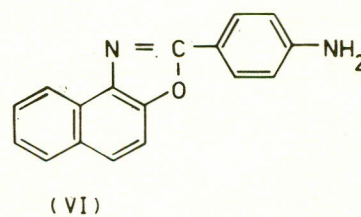
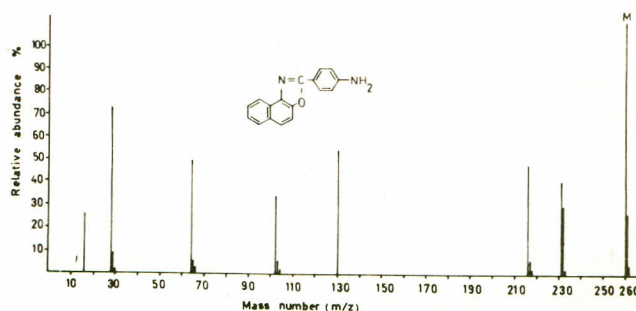
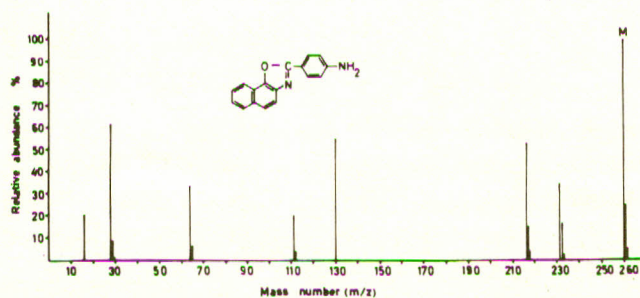
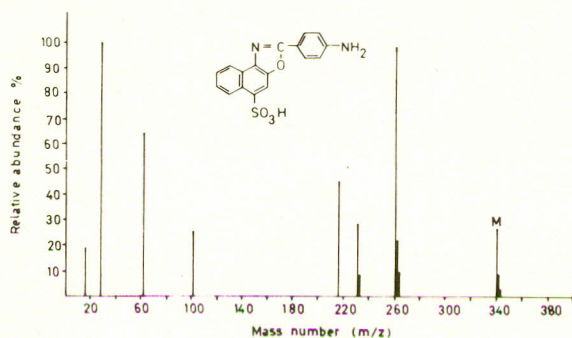
This may be due to the stabilisation of the ionic charge due to the presence of the amino group [10]. This molecular ion loses sulphur trioxide to give ion (B) with m/z 260 of 97% as relative abundance. Ion (B) undergoes fragmentation through ring opening and rearrangement to eject carbon monoxide giving rise to the imino ion (D) [11] with m/z 231 and 28.3% as relative abundance. Ion (D) loses the imino group [11] to give ion (E) which is stabilised via α,γ -hydrogen shift [9] to give the stable ion (F) with m/z 216 and relative abundance 45.2%.

This type of fragmentation is shown in Scheme 4 (cf. Fig. 5).

The last two derivatives are 2-(aminophenyl)-naphtho[1,2-*d*]-oxazole (VI) and its [2,1-*d*] isomer (VII).

The fragmentation of the two compounds are characterised by the following:

(1) The molecular ion m/z 260 is the base peak (100% relative abundance). (2) The presence of a doubly charged



ion at m/z 130. (3). The fragmentation of these two derivatives is the same as indicated in the previous compound 2-(aminophenyl)-naphtho[1,2-*d*]-oxazole-5-sulphonic acid (V) after desulphonation. These derivatives also indicated the α,γ -hydrogen shift to give the stable ion (F) m/z 216 (cf. Scheme 4) which is present in all compounds from II to VII. Figs. 6 and 7 indicate the relative abundance of the fragment ions for compounds (VI) and (VII), respectively.

EXPERIMENTAL

The mass spectra of the seven naphthoxazole derivatives (I–VII) were measured using an A.E.I. MS. 9 operating at an ionisation potential of 70 eV, 8 kV acceleration voltage and 100 μ A trap current. Samples were introduced by way of heated inlet system at ca. 200 $^{\circ}$, with the ion block temperature at ca. 190 $^{\circ}$.

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