

# Comparative Studies of Electron Impact and Thermolytic Fragmentation of 3-phenyl-4-(Anilinomethylene)-5-Isoxazolone

AMJAD HUSSAIN

*Government College of Science Multan, Pakistan*

(Received 10th December, 1997, revised 19th September, 1998)

**Summary:** It has been observed that correlation exist between the electron impact-induced fragmentation of a molecule and its thermolysis products

## Introduction

One of the earliest and most explicit comparisons of electron-impact and pyrolytic fragmentation was due to Cava and co-workers [1] who studied aromatic and heteroaromatic anhydrides. For example, the pyrolysis of pyridine-2,3-dicarboxylic anhydride gave  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{HC}\equiv\text{C}-\text{CHCN}$  (M.W. 77). (Eq. No. 2) by a process which appears very similar to the major mass spectral pathway as in (Eq. No. 1).

In order to explore further the potentiality of using the mass spectrum of a compound as a basis for predicting its thermolysis products, we have undertaken a comparative study using 3-phenyl-4-(anilinomethylene)-5-isoxazolone. The 70 eV mass spectrum of 3-phenyl-4-(anilinomethylene)-5-isoxazolone, shows an initial loss of  $\text{CO}_2$  and followed by loss of phenyl cyanide (Eq. No. 3).

The low resolution mass spectrum does not directly provide information on the structure of ions formed.

However, scheme 1 outlines a possible fragmentation path which suggests that thermolytic path

might provide a synthetic route to anilinomethylenecarbene (Eq. No. 4).

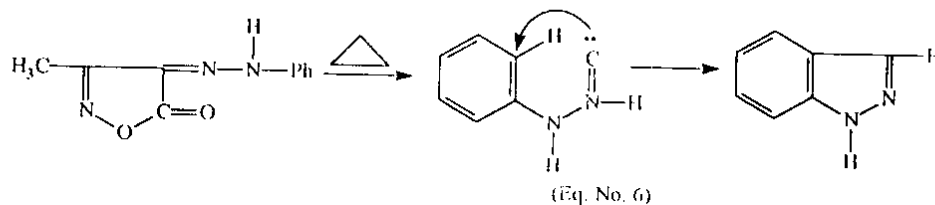
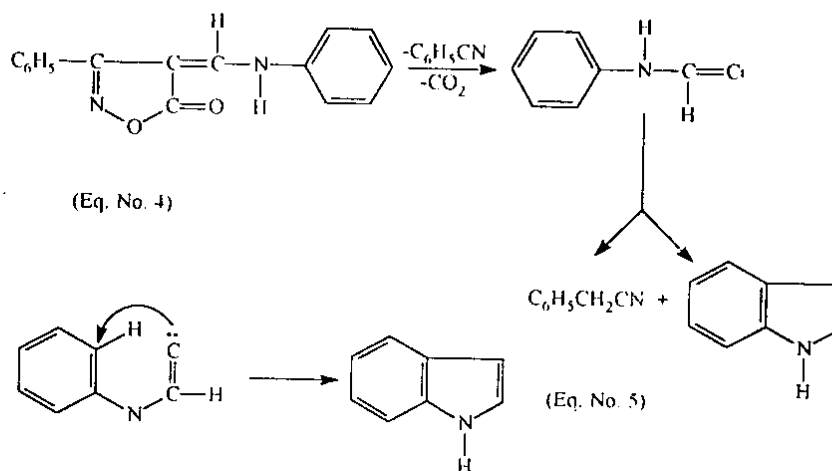
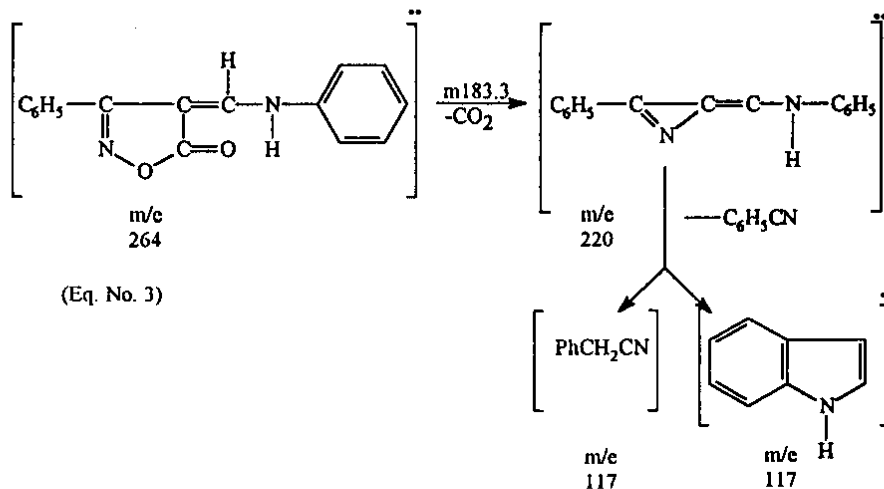
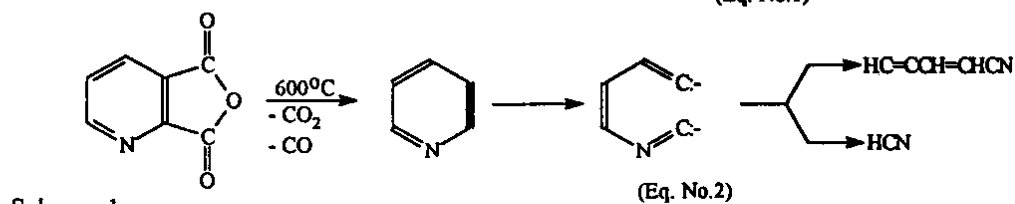
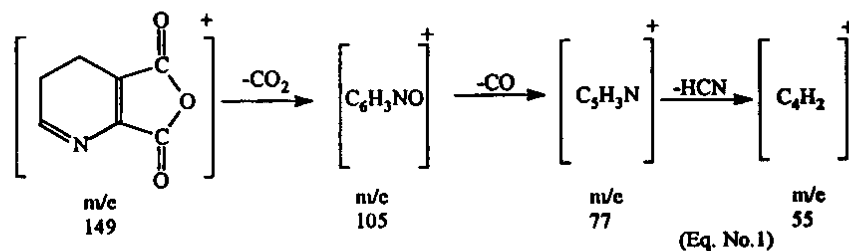
When 3-phenyl-4-(anilinomethylene)-5-isoxazolone was thermolysed at about  $700^\circ\text{C}$  and 0.1 mm Hg pressure the product contained phenyl cyanide (25%), indole (3%) and benzyl cyanide (Scheme 2).

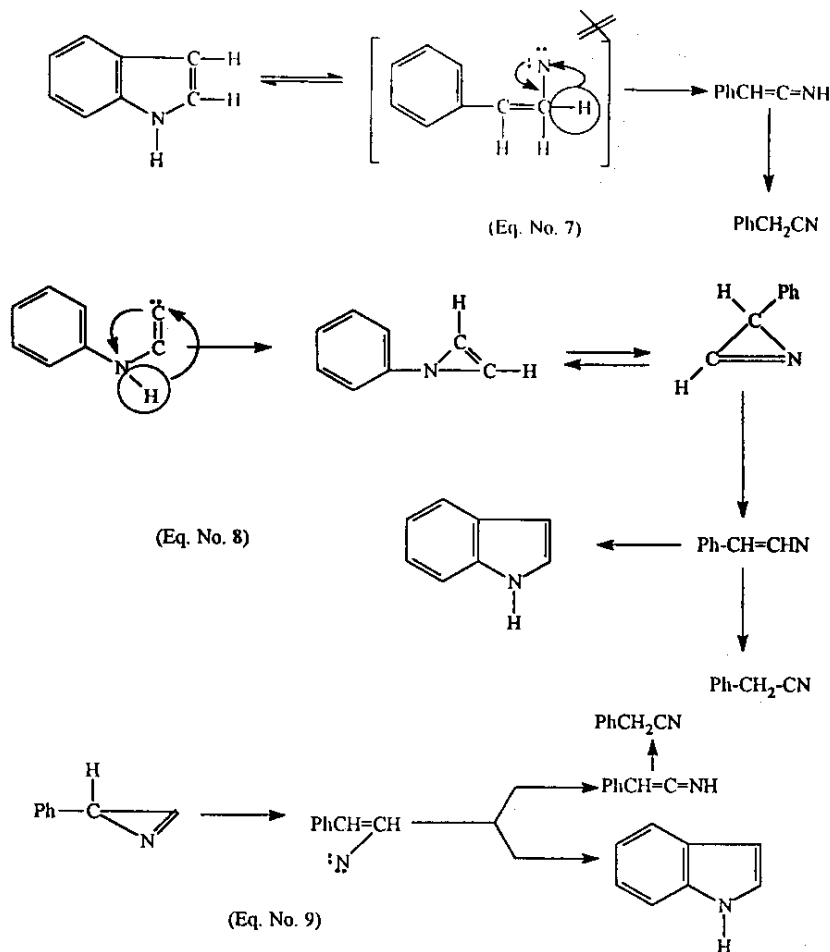
The formation of indole and benzyl cyanide may involve the generation of carbene.

Formation of indole (Eq. No. 5) may be due to the intramolecular insertion of the carbene into the C-H bond of the benzene ring [2].

The above mechanism is supported by the work of Wentrup's group. For example, 4-(phenylhydrazonyl) isoxazolones undergo thermal fragmentation into  $\text{Ph-NH-N}=\text{C}:$ , which rearranges to indazole [3]. (Eq. No. 6).

The formation of the benzylcyanide, may be due to the decomposition of the first formed indole





into unsaturated nitrene, by the fission of the aryl-N bond to give the benzyl cyanide (Eq. No.7).

An alternative and more likely explanation for the formation of benzyl cyanide and indole also involves the formation of carbenes insertion into the N-H bond to form an azirine, which is converted into benzyl cyanide and indole via the generation of nitrene as an intermediate (Eq. No. 8). The above mechanism is supported by the work of Isomura and co-workers [4] who pyrolysed 3-phenyl-1-azirine to obtain a mixture of benzyl cyanide and indole via the formation of a nitrene as an intermediate (Eq. No.9).

### Experimental

#### Flash vacuum pyrolysis apparatus

The apparatus consisted of a quartz tube 55 cm long, 17 mm i.d, packed with quartz ring for 30 cm of its length. The packed volume was heated in a

furnace at the quoted temperature. The sample, contained in a flask connected to one end of the quartz tube, was vapourised by a secondary furnace into the reaction zone. The pressure was 0.1 mm Hg in each case and the pyrolysate was collected in traps cooled with liquid nitrogen. The IR and NMR spectra were recorded on Unicam SP-200 and on Varian T 60 spectrometers, respectively. Melting points were determined by Gallenkamp melting point apparatus.

Mass spectra were recorded at 70 eV with an AEI MS 902 mass spectrometer and elemental analysis were performed on Carlo Erba model 1106.

#### Preparation of 3-phenyl-4-(Anilinoethylene)-5-isoxazolone

A solution of the 3-phenyl-5-isoxazolone (3.22 g) in ethanol was added dropwise to the

solution of N-phenylformimidate (2.98 g) in ethanol. After the addition was completed, the mixture was refluxed for an hour. The solvent was removed under vacuum and the residue was crystallised from ethanol (4g, 76% yield) [5]. M.P. 140-141°C max(KBr)17100 cm<sup>-1</sup> (CO str); H-NMR (CDCl<sub>3</sub>) 60 MHz): 7 to 7.7 (m, 10H) 9 (Broad singlet, N-H, disappear on D<sub>2</sub>O exchange).

*Flash vacuum thermolysis of 3-phenyl-4-(anilino-methylene)-5-isoxazolone*

The isoxazolone (1. g) was heated to 200°C at 0.08 mmHg. and evaporised into a hot tube at 550°C. The pyrolysate (0.61 g) was collected and

analysed by GC/MS. The main products indole, benzyl cyanide and phenyl cyanide were identified by comparison with authentic samples.

**References**

1. M.P. Cava, M.J. Mitchell, D.C. Dejongh and R.Y. Van Fossen, *Tetrahedron Letters*, 2947 (1966).
2. C. Wentrop, *Chimica*, **31**, 258 (1977).
3. W. Reichen and C. Wentrop, *Helv. Chim. Acta*, **59**, 2618 (1976).
4. K. Isomura, S. Kobayashi and H. Tangiguchi, *Tetrahedron Letters*, 3499 (1968).
5. F.B. Dains and E.L. Griffins, *J. Am. Chem. Soc.*, **35**, 959 (1913).