# Pyrolysis of 3-Phenyl-4-(2-methoxyphenylmethylene)-5-isoxazolone to give *O*-Methoxyphenylacetylene, Benzofuran and Phenylcyanide

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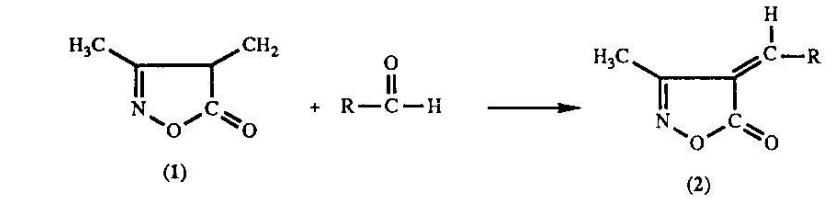
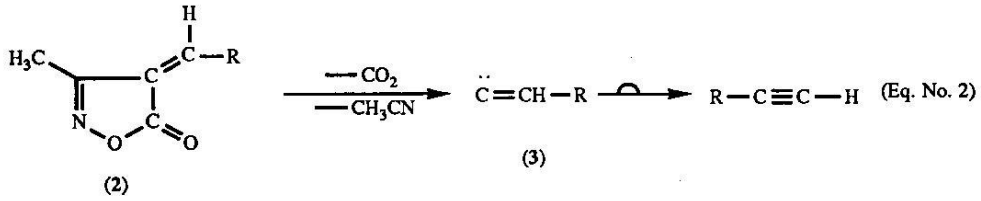
**Summary:** Pyrolysis of 3-phenyl-4-(2-methoxyphenylmethylene)-5-isoxazolone produces *o*-methoxy -phenylacetylene, benzofuran and phenylcyanide.

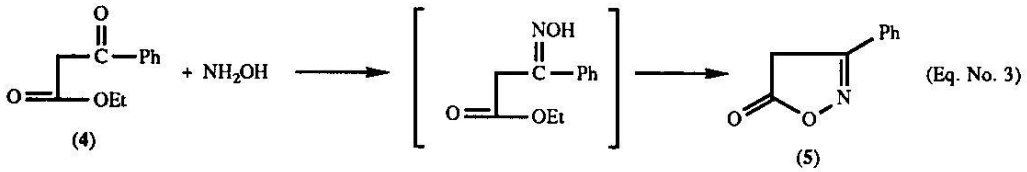
## Introduction

Wentrup *et al.* [1] observed that flash vacuum thermolysis of certain 4-substituted isoxazolones gave unsaturated carbenes of the type Ar-CH=C which, after rearrangement, gave heterocyclic or carbocyclic substituted acetylenes (Eq. No. 3). The compounds required for pyrolysis were obtained by condensation of the corresponding aldehydes with 3-methyl-5-(4H)-isoxazolone in etha- nol (Eq. No. 1).

To explore the pyrolysis reactions and to study the mechanism in more detail, the compound 3-phenyl-4-(2-methoxyphenylmethylene)-5-isoxazolone was prepared by condensing 3-phenyl-5-isoxazolone with *o*-anisaldehyde. Flash vacuum pyrolysis at 700°C and 0.1mm Hg pressure gave *o*-methoxyphenylacetylene 11%, benzofuran 20% and phenylcyanide 17% (Eq. No. 6).




Phenylcyanide is thermodynamically more stable compared to methylcyanide and might lead to a cleaner reaction process. Keeping this fact in view, 3-phenyl-5-(4H)-isoxazolone (5) was obtained by interaction of ethyl benzoylacetone (4) with hydroxylamine hydrochloride and base (Eq. No. 3).

## Results and Discussion

The *o*-methoxyphenylacetylene was identified by the presence of a peak at 2100 $cm^{-1}$ in the I.R. spectrum, which is expected for the -C=C stretching frequency.

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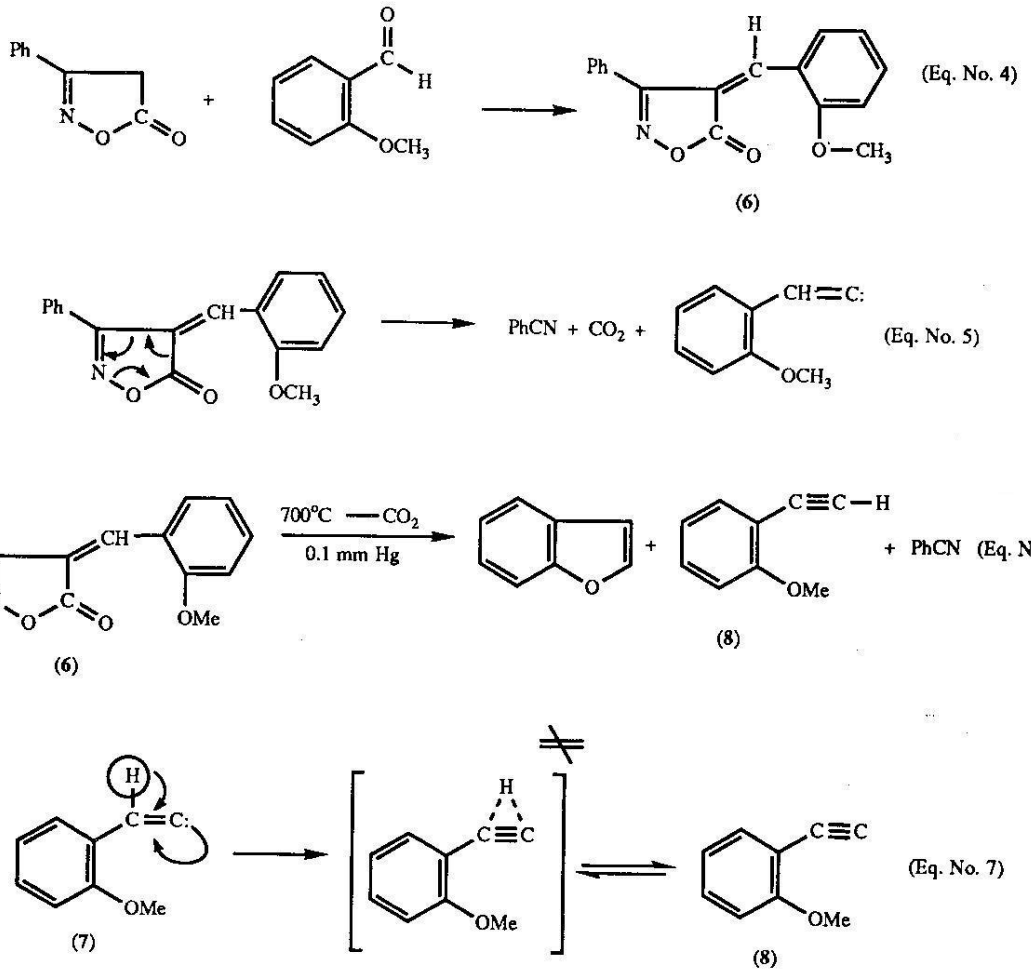



The NMR spectrum showed the presence of a methyl group by a singlet at δ 3.5 ppm and also the mass spectrum showed the presence of expected molecular ion peak at m/z 132. The mechanism to explain the formation of *o*-methoxyphenylacetylene is shown in Eq. No. 7.

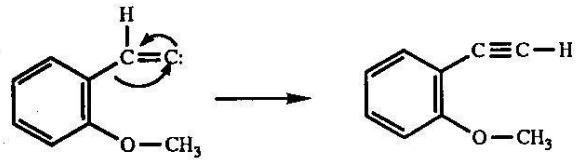
The intermediate unsaturated carbene of the type (7) undergoes skeletal rearrangement i.e. 1,2-hydrogen shift, to give *o*-methoxypheny- lacetylene (8) (Eq. No. 7) the other possibility is instead of a shift of hydrogen, migration of methoxyphenyl group has takes place (Eq. No. 8). The two mechaisms may occur are supported by the work of R.F.C. Brown and co-workers [3], who pyrolysed a labelled phenylacetylene at 700°C/0.2mmHg, and found that the pyrolysate contained an equal mixture of Ph-$C^{13}$=C-H and Ph-C=$C^{13}$C-H (Eq. No. 9).

The migratory tendency of cyclopropyl group was also observed in the carbenes of the type (10), that were formed from the nitrosooxazolidones [4] (9) (Eq. No. 10).

*2-Formation of benzofuran*

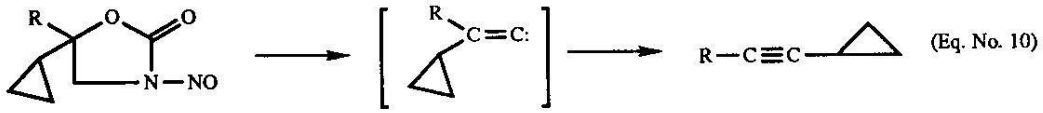
It seems likely that the reaction mechanism for the formation of benzofuran involves the action of HCl (a product of the pyrolysis of $CHCl_3$) either on the methoxyl group of the isoxazolone (or the carbene) to give the hydroxyl compound, which then undergoes a carbene insertion into the O-H bond, resulting in the benzofuran (Eq. No. 11-12).

Alternatively, it is possible that a methyl group is lost from the oxonium ion intermediate formed due to the nucleophilic attack of oxygen on the carbene.



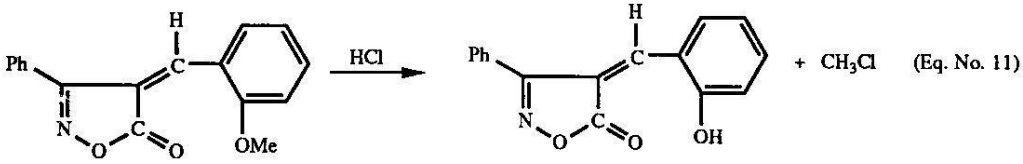
(Eq. No. 8)

(Eq. No. 9)



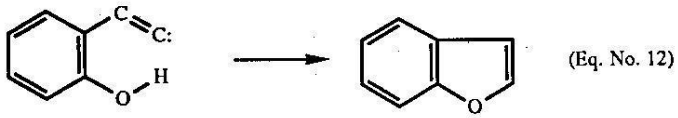
(Eq. No. 10)

(9) (10)



(Eq. No. 11)

(12)



(Eq. No. 12)

(12)

The methyl group is lost from the oxonium ion intermediate by the attack of $Cl^-$ ion (Eq. No. 13-15). Moreover there are evidences [5-8] for intramolecular insertion of carbenes at an oxygen atom have taken place. Also, examples of intramolecular insertion of carbenes into a C-H bond are well known [9]. Here, non-formation of compounds like (14 and 15) from (7) are due to the greater stability of benzofuran because of its more aromatic character (Eq. No. 18).

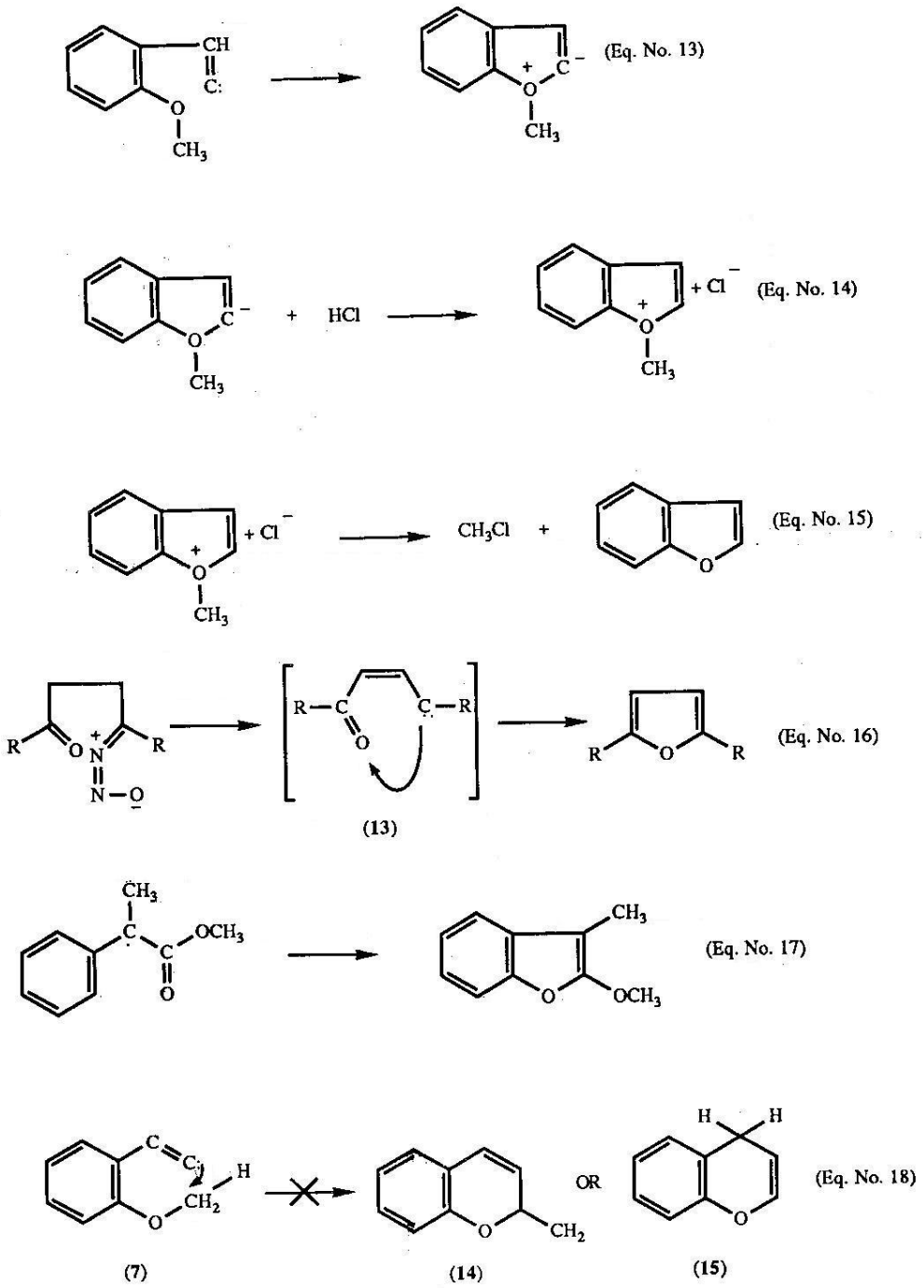
## Experimental

*Flash vacuum pyrolysis apparatus*

The apparatus consisted of a quartz tube 55 cm long, 17 mm i.d., packed with quartz rings 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 furance into the reaction zone. The pressure was 0.1 mm. Hg., in each case and the pyrolysate was collected in traps cooled with liquid $N_2$.

The IR and NMR spectra were recorded on Unicam SP200 and on Varian T60 spectrometer 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 analyses were performed on Carlo Erba model 1106.




*Preparation of 3-Phenyl-4-(2-methoxyphenyl methylene)-5- isoxazolone*

3-Phenyl-5-isoxazolone (0.745 mole) in ethanol (20 $cm^3$) was mixed with a solution of *o*-anisaldehyde (0.644 mole) in ethanol (20 $cm^3$) and few drops of piperidine. The mixture was refluxed for 2 hours and the solvent removed. The residue was crystallized from ethanol as pale yellow crystals (50%) m.p. 115-116°C. (Found; C, 73.10; H, 4.6; N, 5.0%. $C_{17}H_{13}NO_3$. Requires : C, 73.11; H, 4.65; N, 5.01%). $\lambda_{max}$ (KBr) 1725 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$, 60 MHz): 3.8 (s, $OCH_3$), 6.6 to 7.6 (m, 9H), 8.2 (s, =CH).

*Flash vacuum thermolysis of 3-phenyl-4-(2-methoxy phenyl methylene)-5-isoxazolone*

The isoxazolone (1) (1g., 0.35 mole) was heated to 200°C at 0.08 torr and vapourised into a hot tube at 700°C. The pyrolysate (0.45 g) was collected and analysed by GC/MS and by separation of the components by preparative G. L. C. with carbowax 20M as the stationary phase at 150°C. Three products benzofuran, *o*-methoxyphenylacetyelene and phenylcyanide were shown to be present by analysis of the NMR spectra of the separated components.

**References**

1. C. Wentrup and H. W. Wintor, *Angew. Chem. Internat. Ed.* (English) **17**, 609 (1978).
2. R. Schiff and M. F. Betti, *Ber.*, **30**, 1337 (1897).
3. R. F. C. Brown and F. W. Eastwood and K. J. Harrington, *Aust. J. Chem.*, **27**, 2339 (1974).
4. M. S. Newman and S. J. Gromelski, *J. Org. Chem.*, **37**, 3220 (1972).
5. K. B. Tomer, N. Harrit, I. Rosenthal, O. Buchardt, P. L. Kumler and D. Creed, *J. Amer. Chem. Soc.*, **95**, 7402 (1973).
6. G. L. Closs, L. R. Kaplan and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967).
7. M. E. Hendrick, *J. Amer. Chem. Soc.*, **93**, 6337 (1971).
8. H. Durr and L. Schrader, *Chem. Ber.*, **103**, 1334 (1970).
9. R. A. Walish and A. T. Bottini, *J. Org. Chem.*, **35**, 1086 (1970).