

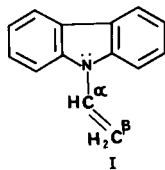
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Received May 2, 1988

Aryl substituted nitrile oxides undergo 3 + 2 cycloaddition to *N*-vinyl carbazole to afford only one regioisomer, *i.e.*, 3-aryl substituted 5-(9-carbazolyl)- Δ^2 -isoxazolines **III** in good yield.

J. Heterocyclic Chem., **26**, 255 (1989).

In continuation of our work on the dipolar cycloaddition reaction of nitrile oxides to chlorosulfonyl isocyanate, wherein nitrile oxides add selectively to C=N of isocyanate [2], it is considered of interest to investigate the 1,3-dipolar cycloaddition of nitrile oxides to *N*-vinylcarbazole (**I**) to see whether this molecule, **I** exhibits any regioselectivity in cycloaddition to the vinyl group as the electron lone pair of the ring nitrogen is conjugated with π -electrons of the vinyl double bond and also with the ring π -electron system [3].



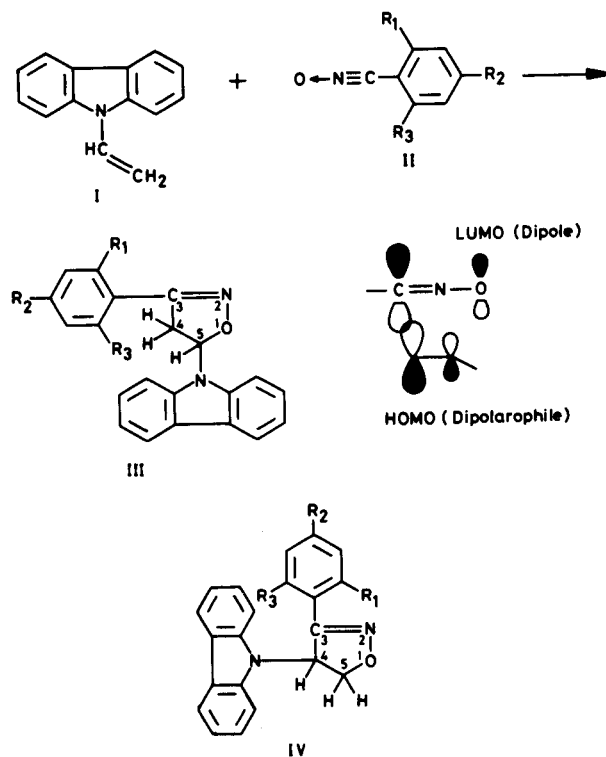
The mode and the nature of this cycloaddition reaction has been assessed on the observation that nitrile oxides are known to possess higher electrophilicity [4], hence their reaction with *N*-vinylcarbazole should be favourable due to larger coefficient at the β -carbon of the vinyl group if it is as a consequence of a strong mesomeric effect through electron lone pair of the ring nitrogen. Then according to the principle of maximal overlap [5,6] which predicts the preferred isomers of each interaction by the union of two sites of reactants having larger coefficients, the cycloaddition of nitrile oxides and *N*-vinylcarbazole may be favoured since the nitrilium carbon of the nitrile oxides is the terminus that possesses the higher coefficient in the dipole LUMOs and the β -carbon of the vinyl group of *N*-vinylcarbazole is the terminus that will have higher coefficient in the dipolarophile HOMOs if it is by mesomeric effect through ring nitrogen.

The cycloaddition reaction of nitrile oxides to *N*-vinylcarbazole did indeed proceed according to this prediction and yielded 3-aryl substituted 5-(9-carbazolyl)- Δ^2 -isoxazolines **III** as the only product up to 90% yield (Table 1). This reaction also highlights that the β -carbon of the vinyl group of *N*-vinylcarbazole has a higher coefficient due to strong mesomeric effect, thus showing regioselectivity in cycloaddition with nitrile oxides.

All the compounds are characterised by ir, pmr and mass spectral data. These compounds are shown in Table 1. In pmr spectra, H_4 protons of the isoxazoline ring are seen as a doublet between δ 3.40 and 3.50 accounting for two protons, whereas the H_5 proton merges in the aromatic region between δ 7.10 and 8.10. Mass spectral fragmentation indicated cycloreversion of the products and their subsequent fragmentations. The percentages of the major ions are shown in Table 1.

The formation of other regioisomer *i.e.*, 3-aryl substituted 4-(9-carbazolyl)- Δ^2 -isoxazoline **IV** has been excluded on the basis of the appearance of H_4 protons as a doublet accounting for two protons as seen in structure **III**, whereas the H_4 proton in structure **IV** should be seen as a doublet of doublet accounting for one proton. The

Scheme 1



$R_1, R_2, R_3 = \text{CH}_3, \text{OCH}_3 \text{ or Cl}$

Table 1

No.	Products			Yield %	mp °C	Molecular formula	Analysis Calcd./Found			Mass spectral Fragments: m/z (Relative intensities)	
	R ₁	R ₂	R ₃				C	H	N		
1	CH ₃	CH ₃	CH ₃	89	132-133	C ₂₄ H ₂₂ N ₂ O	81.33 81.17	6.26 6.21	7.90 7.98	354 (55), 188 (25), 161 (10)	193 (20), 167 (100)
2	Cl	H	Cl	90	228-230	C ₂₁ H ₁₄ N ₂ OCl ₂	66.16 66.14	3.70 3.68	7.35 7.34	380 (20), 187 (15), 167 (100)	193 (20), 167 (100)
3	OCH ₃	OCH ₃	OCH ₃	92	235	C ₂₄ H ₂₂ N ₂ O ₄	71.63 71.76	5.51 5.77	6.96 6.92	402 (10), 209 (25), 167 (100)	236 (60), 193 (30)

deep downfield shift of the H₅ proton into the aromatic region is also well justified from structure **III** due to the deshielding effect of the oxygen atom of the isoxazoline ring and also due to nitrogen of the carbazole ring. The formation of **IV** is also not favourable due to high steric crowding involved in the transition state.

Arylnitrile oxides are prepared from the corresponding oximes [7]. The nitrile oxide is dissolved in chloroform and reacted with 9-vinylcarbazole at 0-5°. The resultant products are purified by recrystallisation.

EXPERIMENTAL

Mass spectra were recorded on VG micromass 70-70H mass spectrometer. The pmr spectra were recorded on JEOL FT FX-900 spectrometer. The ir spectra were recorded on Perkin-Elmer Model 283B spectrometer. Arylnitrile oxides were prepared from the corresponding oximes by sodium hypobromite oxidation as described by Grundmann and Dean [7].

Typical Reaction Procedure.

2,4,6-Trimethylbenzonitrile oxides (3.2 g, 0.02 mole) was dissolved in

chloroform (20 ml) and cooled in ice bath for 15 minutes. To this solution was added dropwise 9-vinylcarbazole (3.86 g, 0.02 mole) in chloroform (20 ml) and the reaction mixture was stirred for 2 hours at ice bath temperature and then for 12 hours at room temperature. Later the solvent was removed under reduced pressure. The pure compound was obtained by recrystallisation from a mixture of chloroform:n-hexane (1:1).

REFERENCES AND NOTES

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