Kinetics of the Reaction of a Substituted Benzonitrile Oxide with Some Arylacetylenes

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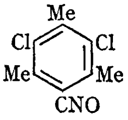
NITRILE OXIDES add on to alkenes and alkynes giving Δ^2-isoxazolines and isoxazoles respectively; in particular when a benzonitrile oxide reacts with an arylacetylene the product is a 3,5-diarylisoxazole.[1] Such a reaction, which has been classified among the "1,3-dipolar cycloadditions"[2] has now been studied kinetically in the case of the nitrile oxide (I) and the arylacetylenes (II):



(I)

p-R·C_6H_4·C≡CH

(II)

a; R=OMe b; R=Me
c; R=H d; R=Cl
e; R=NO_2

3,5-Dichloro-2,4,6-trimethylbenzonitrile oxide (I) is, like other *ortho*-disubstituted benzonitrile oxides,[3] a stable compound that does not dimerize. The reaction of (I) with compounds (II) in the presence of a few drops of alcoholic KOH gives the corresponding isoxazoles in a few minutes with good yields.

Kinetic experiments in neutral chloroform and carbon tetrachloride solutions have been followed by quantitative infrared analysis. The reaction has been shown to be of first order with respect both to (I) and to (II) in every case. The rate is slightly affected by the choice of solvent, being higher in CCl_4 than in $CHCl_3$ by a factor 1·9 for (IIa) and 3·0 for (IIe), at 24·8°.

In carbon tetrachloride at 24·8° the following rate constants have been obtained ($\text{l.mole}^{-1}\text{sec.}^{-1}$):

(IIa)	$10^4 k$ = 3·9 ± 0·2
(IIb)	3·7 ± 0·2
(IIc)	3·2 ± 0·2
(IId)	4·5 ± 0·4
(IIe)	9·6 ± 0·9

The reaction of (I) with p-dimethylaminophenylacetylene (II; R = Me_2N), while not suitable for exact measurements because of disturbing secondary reactions, has indicated that the cycloaddition has a higher rate than in the case of (IIa).

Such a mild acceleration by both electron-donating and electron-withdrawing *para*-substituents on the acetylene points rather to a concerted than to a two-step cycloaddition for nitrile oxide (I). The observed solvent effect is consistent with this suggestion.

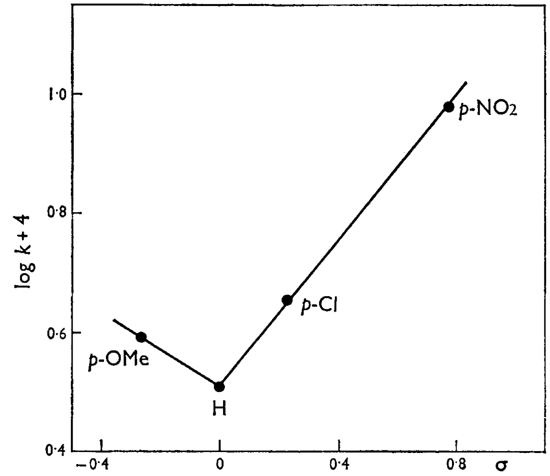


FIGURE. *Hammett plot for the cycloaddition of* (I) *to arylacetylenes* (II).

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[3] G. Speroni, *Ricerca sci.*, 1957, **27**, 1199; S. Califano, R. Moccia, R. Scarpati, and G. Speroni, *J. Chem. Phys.*, 1957, **26**, 1777; C. Grundmann and J. M. Dean, *Angew. Chem. Internat. Edn.*, 1964, **3**, 585.