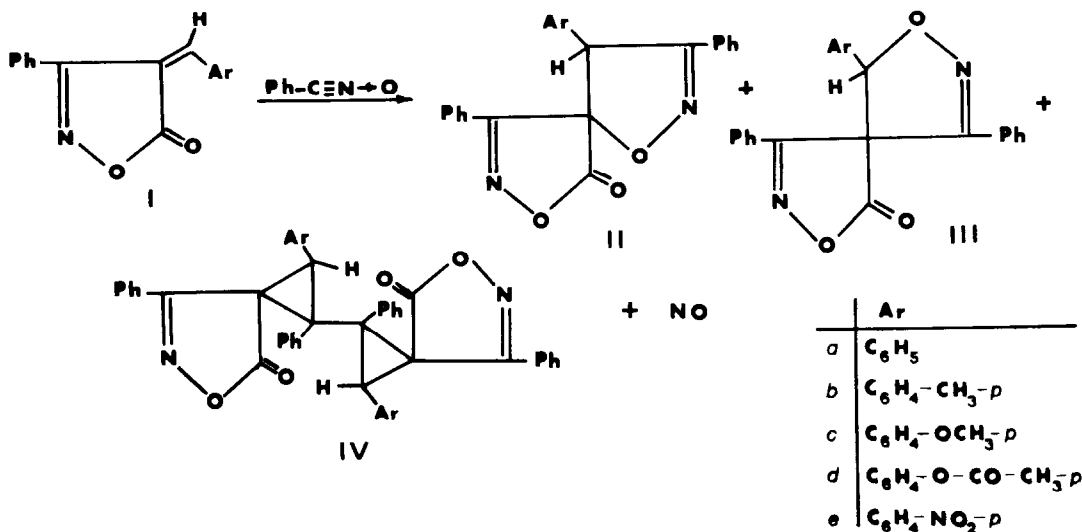


## UNUSUAL REACTION OF BENZONITRILE OXIDE AS PHENYLNITROSOCARBENE

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The cycloaddition of benzonitrile oxide to arylidenic double bond of 3-phenyl-4-arylidene-isoxazol-5-ones I in refluxing ether-acetone medium gives two isomeric types of isoxazolone-isoxazolinic spiro compounds II and III<sup>(1)</sup> and very small quantities of a colourless high melting product IV.



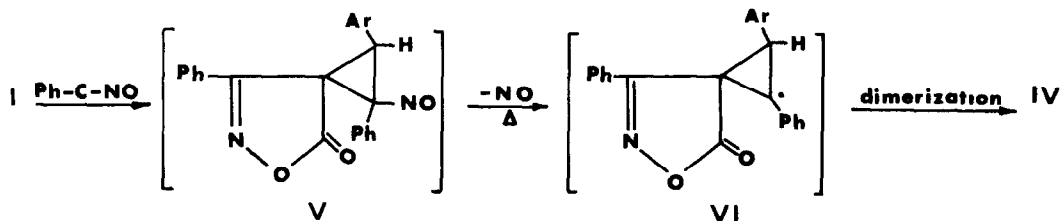
The structures IV, a - e, represent dimeric products of adducts formed from the starting isoxazolones I, a - e, and a radical or carbenoid group Ph-C $\dot{C}$ .

This unusual reaction of the benzonitrile oxide was never observed before using conjugated (or not) dipolarophile systems different from these employed here I. The phenylnitrosocarbene Ph-C-NO<sup>(2)</sup> was foreseen as resonance contributor of benzonitrile oxide.

Huisgen<sup>(3)</sup> has proposed that this carbenoid structure symbolizes the behaviour

of nitrile oxides in the dimerization to form furoxans.

Carbenoid attack to the double bond of I leads to the formation of the spiro compound V as intermediate (not isolated, but preservable for many days at low temperature) from which, by heating, nitrogen oxide is evolved<sup>(4)</sup> and the cyclopropyl radical VI rapidly dimerizes to IV.



Compound VI is stabilized by resonance with the adjacent phenyl group and it does not undergo ring opening as pointed out for other types of cyclopropyl radicals<sup>(5)</sup>.

The yield of IV is related to reaction temperature and increases proportionally to the nitrogen oxide evolution that is small in the cold and rises to 50-65% when the reagents are refluxed in benzene, ethylbenzene or cumene, whereas the amounts of the spiro compounds II and III are falling off. The reported yields are calculated with respect to the starting product I which has reacted ( $\sim 25\%$ ). It is advisable to run the reaction under nitrogen. The low solubility of IV in methanol makes it easy to separate it from the unreacted product I, the spirans II and III and diphenylfuroxan. This last is present in a large amount. By refluxing in the same solvents for several days neither the pure spiro compounds II and III nor the benzonitrile oxide liberate nitrogen oxide.

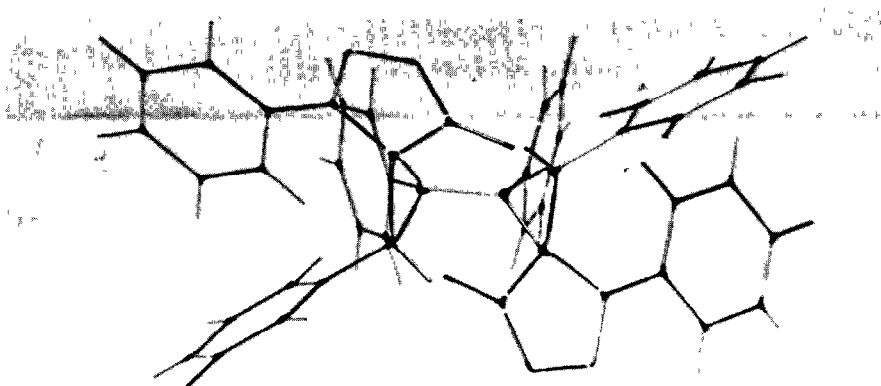
Molecular weight determinations and elemental analysis of IV, *a-e*, are in agreement with the calculated molecular formulas. These compounds possess a zero dipole moment and their molecular symmetry is also confirmed by the NMR spectra; a strong carbonyl stretching band is observed in the IR spectra at  $\sim 1743 \text{ cm}^{-1}$ . The same band was observed for the related starting isoxazolones I, *a-e*, at about  $10 \text{ cm}^{-1}$  higher frequency ( $\nu_{\text{C=O}}$ : Ia, 1755; IVa, 1740; Ib, 1752; IVb, 1743; Ic, 1745; IVc, 1743; Id, 1753; IVd, 1743; Ie, 1755; IVe, 1743). According to Maquestiau et al.<sup>(6)</sup> the considered arylidenisoxazolones I possess a *Z* type structure. This allows an interaction increasing the C=O bond length between the conjugated carbonyl oxygen and *o*-hydrogen of the coplanar aryl group. A similar interaction is observed in the compounds IV, where the two cyclopropane

protons are located in the proximity of the two carbonyl groups of the isoxazolo ne rings. Therefore, the cyclopropane protons are strongly deshielded by the carbonyl groups:  $\Delta^H$   $\tau$ IV *a* and *b* = 4,36 ppm;  $\tau$ IV *c* = 4,98 ppm.

In the IR spectra the cyclopropane ring is confirmed by the presence of the characteristic ring deformation band (one or two) near  $1020\text{ cm}^{-1}$  (7-9).

Found  $\nu\text{ cm}^{-1}$ : IV *a*, 1017; IV *b*, 1016; IV *c*, 1020, 1040; IV *d*, 1019; IV *e*, 1018; all bands of medium relative absorbance (optical density).

The following figure represents the Dreiding-stereomodel of the IV.



The 1,3-dipolar activity of benzonitrile oxide is well documented. It remains to be seen if more examples for its carbenoid activity can be uncovered.

Syntheses of other derivatives of type IV and the study of their chemical and physical properties by IR, NMR and Mass Spectrometry are in progress.

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