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KINETICS OF DIMERIZATION OF BENZONITRILE N-OXIDES TO DIPHENYLFUROXANS

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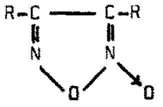
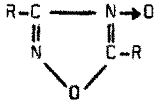
Among the reactions exhibited by benzonitrile N-oxides (I)(1), the dimerization is well known to take place leading to diphenylfuroxans (II) (2,3) in neutral medium and to azoxime (III) (4) in acidic medium.

$R{-}CN{\rightarrow}O$

(I)



(II)



(III)

We have undertaken a kinetic investigation of the dimerization of benzonitrile N-oxides to furoxans with the aim of elucidating the reaction mechanism. Some semiquantitative data were published previously by Speroni (5). We report here the preliminary results concerning the dimerization of p-OCH_3, p-CH_3, p-Cl and m-Cl benzonitrile N-oxides.

Benzonitrile N-oxides in anhydrous CCl_4 at 40°C yield almost quantitatively the corresponding diphenylfuroxans (II). The reaction was followed by infrared absorption measurements of the $C\equiv N$ stretching band (in the neighbour of 2290 cm^{-1}) (6,7). The phenylfuroxans do not absorb in this spectral region as observed by previous authors (6,8).

The reaction of dimerization in the concentration range employed in the present investigation (0.004 - 0.03 $mol.l^{-1}$) takes place with a clean second order kinetic. The rate constants for the compounds investigated, average of at least ten independent runs, are listed in table 1,

TABLE 1

Rate constants for dimerization of benzonitrile N-oxides in CCl_4 (at 40 ± 1°C)

Compound		$K.10^3$ ($l\ mol^{-1} sec^{-1}$)	log K	(σ) (c)
(p)$H_3CO-C_6H_4-CNO$	(a)	2,37 ± 0,09	- 2,63	- 0,27
(p)$H_3C-C_6H_4-CNO$	(b)	3,06 ± 0,13	- 2,51	- 0,17
(p)$Cl-C_6H_4-CNO$	(b)	6,68 ± 0,40	- 2,18	+ 0,23
(m)$Cl-C_6H_4-CNO$	(b)	8,53 ± 0,34	- 2,07	+ 0,37

a) Product prepared for the first time starting from the corresponding hydroxamyl chloride and triethylamine in anhydrous ether at 0°C: white needles, crystallized from ether/ /light petroleum (-70°C), m.p. 69-70°C.

b) The m.p.'s agree with those reported in the literature (5).

c) From J.Hine (9).

Although the data at our disposal are few, a correlation seems to exist between the reactions rates and Hammett's sigma constants of the substituents in the phenyl ring ($\rho \approx + 0{,}9$).

Further work is in progress.

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