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CONDENSATION OF FURAN WITH NITRILE OXIDES

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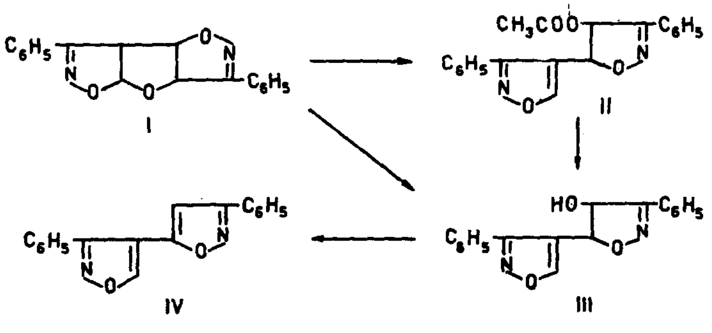
The double bonds of furan and thiophene have been reported[1] to be inert towards benzonitrile oxide, at least in ethereal solution and with equimolecular ratios of reactants.

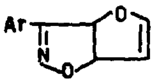
However, when benzonitrile oxide was prepared in situ by slow addition of triethylamine to a solution of benzohydroxamyl chloride in a large excess of furan, besides a nearly quantitative yield of triethylamine hydrochloride and large amounts of diphenylfuroxan, a low yield of a product, m.p. 196-198°, could be isolated from the reaction mixture. This product was assigned the structure I on the basis of ultraviolet (λ_{max}^{EtOH} 259 mμ, log ε 4.45) and chemical evidence. Acidic cleavage of I gave III, m.p. 162-163°, which could also be obtained through its acetylderivative II, m.p. 125°, prepared by treatment of I with acetic anhydride and boron trifluoride. In marked contrast with the very easy dehydration of 5-hydroxy-2-isoxazolines in acidic conditions,[2] the 4-hydroxy-2-isoxazoline III lost one molecule of water only by prolonged



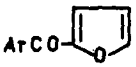
heating at 160-180° with potassium pyrosulfate. The resulting 3,3'-diphenyl-4,5'-biisoxazole (IV), m.p. 99°, was identical with a sample synthesized by an independent, unequivocal route.[3]

From structure I, an initial attack of the electrophilic carbon of benzonitrile oxide to the α-position of furan can be inferred, followed by condensation of a second molecule of nitrile oxide to the cyclic ethylenic ether system thus formed.

The reactions of furan with p-nitro- and m-nitro-benzonitrile oxides stopped at the first step, and adducts Va, m.p. 145-146°, resp. Vb, m.p. 113°, could be separated from the reaction mixture. Their structures were confirmed through acidic hydrolysis, which gave the 2-nitrobenzoylfurans VI a-b and not the isomeric 3-aroylfurans, as independent syntheses of the ketones VI a-b from furan and nitrobenzoic acids could demonstrate.



V



VI

a: Ar = p-$NO_2C_6H_4$
b: Ar = m-$NO_2C_6H_4$

Further work on the condensation between nitrile oxides and furan derivatives, as well as other heterocyclic ring systems, is in progress.

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