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NEW PERSPECTIVES IN THE CHEMISTRY OF NITRILE OXIDES

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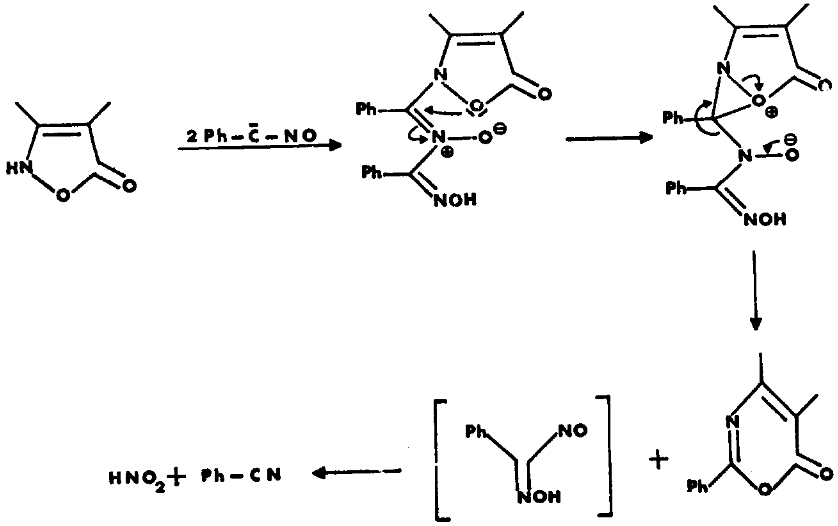
Our previous papers showed that nitrile oxides (e.g.,benzonitrile oxide = BNO), within the limits of their thermal instability, as in refluxing benzene, may react as arylnitrosocarbenes. Indeed we reacted BNO with certain C=C double bonds to give cyclopropane rings and NO (1).

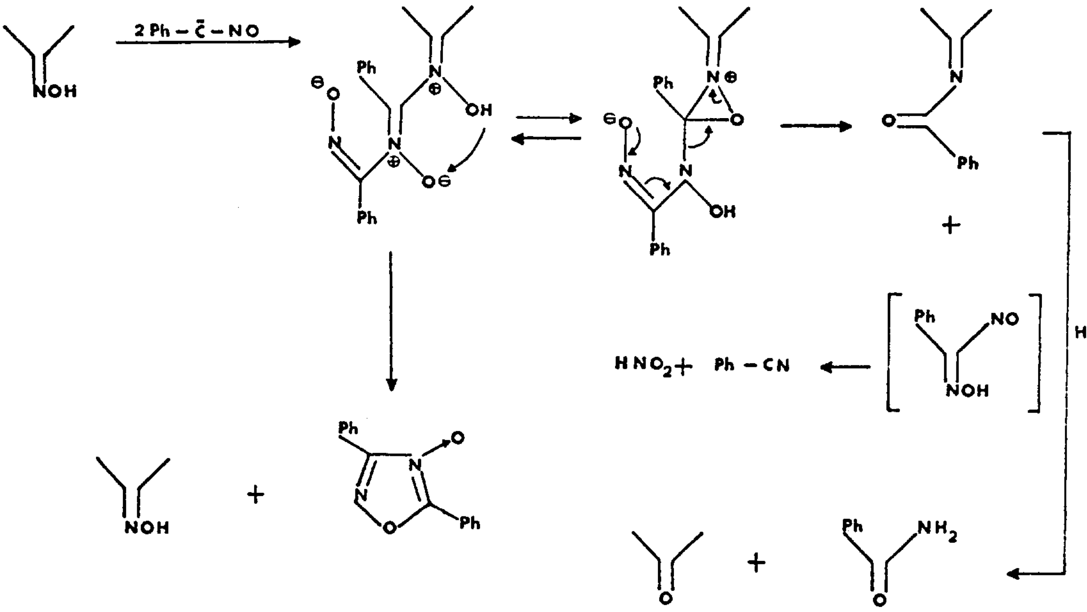
These results, especially the postulate that the carbenoid form of BNO was a key to the reaction, led us to investigate the possibility of carbenoid insertion reactions on heterocyclic rings and of inducing some otherwise difficult open-chain 1,3-addition reactions.

We have discovered that excess of BNO reacts with at the nucleophilic nitrogen atom (NH) of isoxazol-5-ones with ring expansion to give compounds 1,3-oxazin-6-ones involving loss of HNO_2 (instead of NO) and formation of Ph-CN :



Analogous behaviour of BNO was observed with unsubstituted oximes. In this case no 1,3-dipolar cycloaddition reaction occurs on the C=N double bond, as in an acid-catalysed reaction$^{(2)}$. We found the corresponding carbonyl compounds, benzamide, 3,5-diphenyl-1,2,4-oxadiazole-4-oxide and, as above, Ph-CN and HNO_2 evolution.

The carbonyl compounds and benzamide do not result from hydrolytic cleavage of the starting materials and Ph-CN, respectively, but from the intermediate benzoyl-imide derivatives:



Further results of some transformations of the above synthesized 1,3-oxazin-6-ones will be reported at a later date.

REFERENCES

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