DIELS-ALDER REACTION OF OXAZOLES

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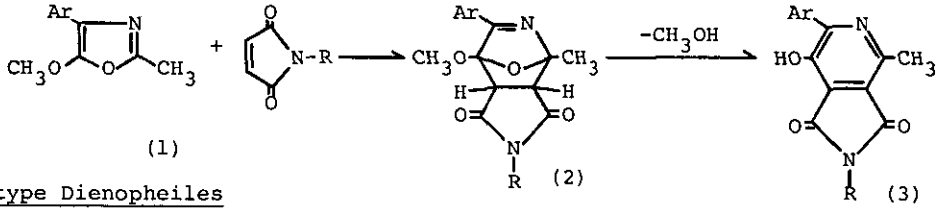
General synthetic method of oxazoles by the BF_3-catalyzed reaction of diazo carbonyl compounds with nitriles has previously been reported from this laboratory.

In order to develope the synthetic utilization of various oxazoles obtained by the method, Diels-Alder reaction of oxazoles with ethylenic, acetylenic and azo-type dienophiles. In the many oxazoles obtained 5-alkoxyoxazoles were found to be most reactive to the dienophiles.

Ethylenic Dienophiles

2-Methyl-5-methoxy-4-p-nitrophenyloxazole (1) was reacted with maleimide derivatives. N-Methyl-, N-ethyl-, and unsubstituted maleimide gave corresponding exo- and endo-adducts (2) at 50-80°C in good yields. Endo-adducts were main products in each cases. Reaction at high temperature (120°C) gave 3-hydroxy pyrizine derivatives (3) besides exo- and endo-adducts. N-Phenylmaleimide did not give adduct and (1) was recovered other non-cyclic dienophiles such as dimethyl fumalate, dimethyl maleate, and trans-1,2-dibenzoylethylene were found to be unreactive toward (1) even at high temperature of 120°C, 50 hours.



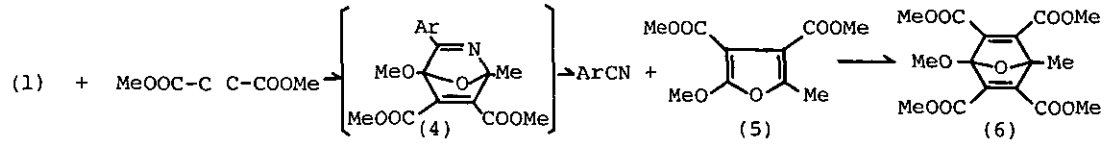
(1) (2) (3)

Azo-type Dienopheiles

Dimethyl azodicarboxylate and 4-phenyl-1,2,4-triazoline-3,5-dione gave adducts in 91 % and 67 %, respectively.

Acetylenic Dipolarophile

The reaction of (1) with dimethyl acetylenedicarboxylate at 100°C did not give adduct (4), but gave its decomposition products, p-nitrobenzonitrile, furan derivative (5) and its secondary adduct (6) with dimethyl acetylenedicarboxylate.



(4) (5) (6)