NEW ANNELATION METHODS FOR HETEROAROMATICS

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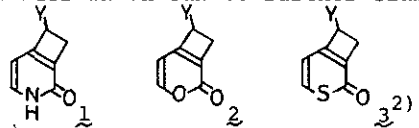
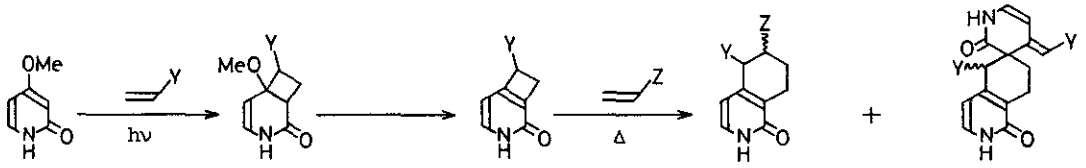
Heteroaromatics involving a β-alkoxy enone function in their ring system react photochemically with alkenes, and elimination of the alcohol from the adduct provides a new synthetic method for cyclobutane-fused heteroaromatics[1] (1, 2, and 3). These cyclobutenes are versatile synthetic intermediates which can be further elaborated in a variety of ways. Here, we report four-carbon (A) and three-carbon annelations (B) of heteroaromatics via these intermediates.



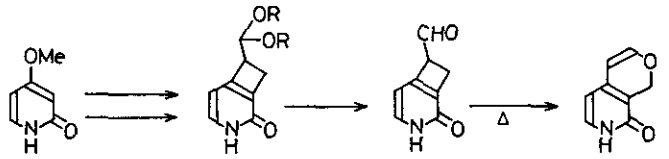
and higher benzenoid homologues [2]

A) Four-carbon annelation of heteroaromatics: The cyclobutane-fused heteroaromatics react with olefins, just like as benzocyclobutenes.

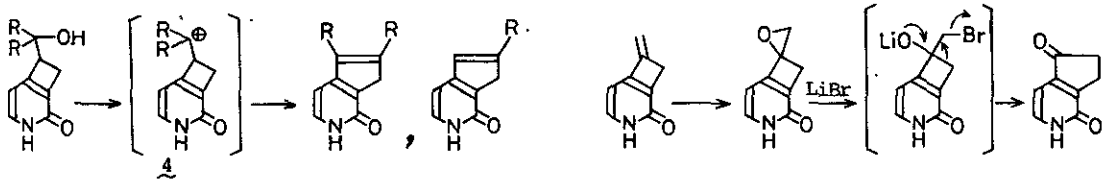
Intermolecular: the electronic demands depend upon the kind of 1-substituents.



Intramolecular: A pyran ring formation[3] is shown as an example.



B) Three-carbon annelation of heteroaromatics: Relief of the strain in the cyclobutene ring can also be accomplished by a Wagner-Meerwein rearrangement of a cyclobutane σ-bond. This ring expansion is initiated by a carbouium ion at an adjacent carbon (e.g. 4).



1) C. Kaneko and T. Naito, Heterocycles, 19, 2183 (1982).
2) C. Kaneko, T. Naito, and T. Ohashi, Heterocycles, submitted.
3) C. Kaneko, Y. Momose, and T. Naito, Chemistry Letters, 1982, 1361.