NEW ANNELATION METHODS FOR HETEROAROMATICS

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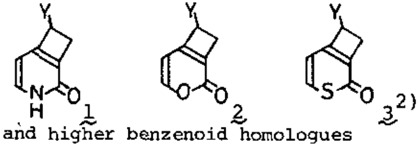
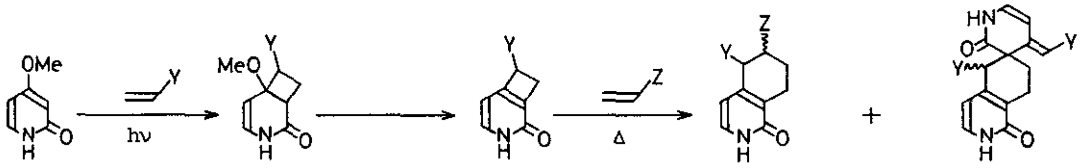
Heteroaromatics involving a β-alkoxy enone function in their ring system react photochemically with alkenes, and elimination of the alcohol from the adduct provides a new synthetic method for cyclobutane-fused heteroaromatics[1] (1, 2, and 3). These cyclobutenes are versatile synthetic intermediates 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.



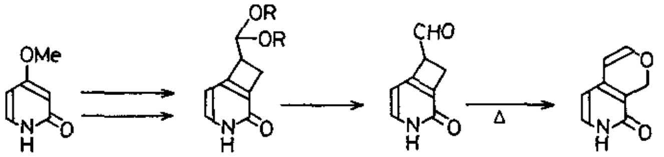
1 2 3[2]
and higher benzenoid homologues

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

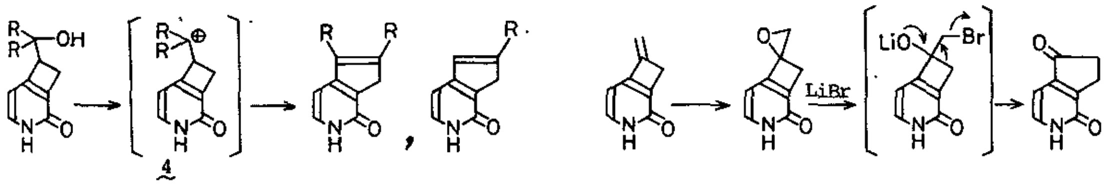
Intermolecular: the electronic demands depend upon the kind of 1-substituents.



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 carbonium ion at an adjacent carbon (e.g. 4).



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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.