# NOVEL SYNTHESIS OF HETROCYCLIC COMPOUNDS HAVING ANGULAR NITROGEN ATOM BY INTRAMOLECULAR DIELS-ALDER REACTION OF 1-AZADIENES

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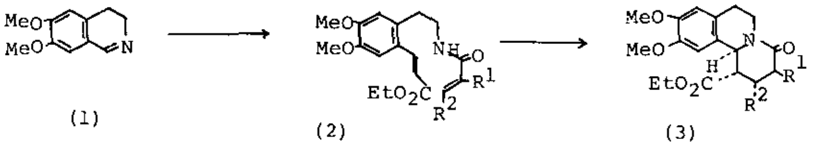
Intramolecular Diels-Alder reaction is one of the most powerful methods for synthesis of polycyclic ring system with stereocontrol. It is expected that the intramolecular cycloaddition of 1-azadienes provides a useful tool for the construction of heterocyclic compounds having angular nitrogen atom, common frameworks of many alkaloids. We have investigated the formation of such system from α,β-unsaturated amides and the subsequent cycloaddition.

(A) Synthesis of Benzo[a]quinolizidines

The 3,4- dihyroisoquinoline(1) was converted into the α,β-unsaturated amides (2) which were heated in the presence of trimethylchlorosilane, triethylamine, and zinc chloride to give benzo[a]quinolizidines(3).



(1) (2) (3)

a: $R^1=R^2=H$
b: $R^1=H, R^2=Me$
c: $R^1=H, R^2=Ph$
d: $R^1=R^2=Me$

(B) Synthesis of Indolo[a]quinolizidines

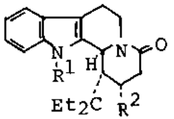
According to the similar procedure, 3,4-dihydro-β-carboline was transformed into indolo[a]quinolizidines(4), one of which (4b) is a potential synthetic intermediate of eburnamonine.

(C) Synthesis of Indolizidines

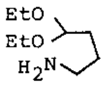
The α,β-unsaturated esters, derived from the amino-acetal(5), was submitted to the intramolecular cycloaddition to afford indolizidines(6).

(D) Synthesis of Quinolizidines: Stereoselective Synthesis of (±)-Epilupinine

Reduction of the lactam(8), synthesized from the alcohol(7), gave (±)- epilupinine(9).



(4)a: $R^1=H, R^2=Me$
b: $R^1=Bn, R^2=H$



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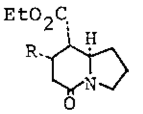
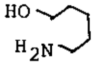


(6)a: R= H
b: R=Me
c: R=Ph



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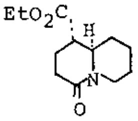

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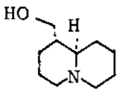

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