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SYNTHESIS OF N-HETEROCYCLES THROUGH N-OXA-ACYLIMINIUM IONS

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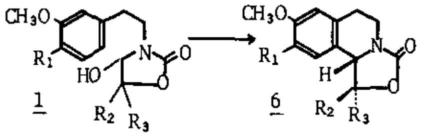
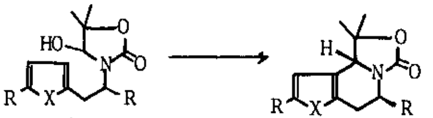
π-Cyclization of N-acyliminium ions has proven to be an important synthetic method for a wide variety of heterocyclic systems. Several kinds of N-acyliminium ions have been used for this purpose. In view of importance to develop novel methods for the controlled synthesis of condensed N-heterocycles, we examined a cyclization of N-oxa-acyliminium ions, a new type of N-acyliminium ions. By this method, isoquinoline, thieno[3,2-c]pyridine, furo[3,2-c]pyridine and piperidine derivatives fused with oxazolidinone skeleton were synthesized. The desired starting materials (1-5) were prepared by reduction of the corresponding N-substituted 2,4-oxazolidinediones with DIBAH and cyclization was carried out in formic acid at room temperature. Cyclization of 1a and 2a gave the isoquinoline (6a) and the thieno[3,2-c]pyridine (7a), respectively. Cyclization of 2b and 2c afforded 7b and 7c, respectively, with high stereoselectivity and a formation of the alternative stereoisomers was not observed. The relative configuration of 1-H and 10b-H in 6b and 6c, obtained from 1b and 1c, respectively, was indicated to be cis. Cyclization of 3a gave 8a. 8b and 8c were obtained as diastereoisomeric mixtures from 3b and 3c, respectively. This cyclization reaction was applied to a synthesis of 13-aza-16-oxa-estratetraene system (9). Cyclization of 5 gave 10 as a mixture of diastereomers.



1 6

a: R_1=OCH_3, R_2=R_3=CH_3
b: R_1=R_2=H, R_3=C_6H_5
c: R_1=OCH_3, R_2=H, R_3=C_6H_5



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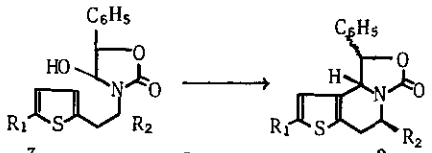
a: R=H, X=S
b: R=CH_3, X=S
c: R=CH_3, X=O



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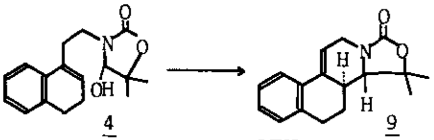
a: R_1=R_2=H
b: R_1=H, R_2=CH_3
c: R_1=R_2=CH_3



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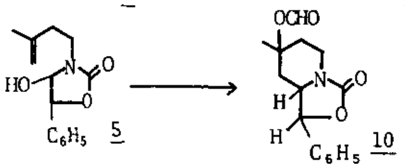

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