RING TRANSFORMATION REACTION OF HETEROCYCLIC SULFOXIDES

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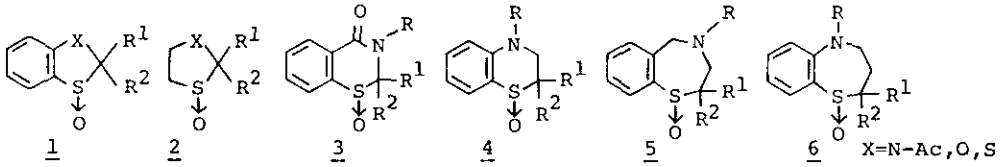
Novel ring transformation reactions of benzothiazoline sulfoxides (1, X=N-Ac) to benzothiazines in the reaction with acetic anhydride proceeded non-stereospecifically.[1)] These reactions are quite different from the similar ring transformation, Morin rearrangement of penicillin sulfoxides to cephalosporins in the standpoint of the stereospecificity.

We investigated the ring transformation of various 5-, 6-, and 7-membered heterocyclic sulfoxides (1-6), in order to elucidate the factors of non-stereospecificity in this unique ring transformation of benzothiazoline sulfoxides, and we found that sulfoxides (1, 2, and 3) bearing a heteroatom at β-position to the sulfinyl group reacted non-stereospecifically with Ac_2O or p-TsOH, as well as benzothiazoline sulfoxides, while sulfoxides (4, 5, and 6) bearing a heteroatom at γ- or δ-position underwent the stereospecific ring transformation in the reaction with p-TsOH.

Furthermore, it was clarified that the non-stereospecific ring transformation proceeds by the mechanism involving a sulfonium ion intermediate: for example, when the sulfoxides, cis-2a [X=S, R^1=Me(cis to the sulfinyl group), R^2=Ph (trans to the sulfinyl group)] was stirred with excess D_2O in benzene at room temperature, no deuterium incorporation at methyl group was observed, indicating no formation of a sulfenic acid intermediate. However, when 2a was stirred in the presence of p-TsOH in benzene at the same temperature, the reaction proceeded non-stereospecifically to give the ring transformation product along with isomerization of cis-2a to trans-2a.



1) a)M.Hori, T.Kataoka, H.Shimizu, and Y.Imai, Chem. Pharm. Bull.(Tokyo), 27, 1982(1979).
b)M.Hori, T.Kataoka, H.Shimizu, and N.Ueda, Tetrahedron Lett., 22, 1701(1981).