NEW THERMAL RING EXPANSION REACTIONS OF 2H-AZIRINES ——EFFECTS OF O- AND S-FUNCTIONS ON RECYCLIZATION OF VINYL NITRENES

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New types of cyclization reaction to form 1,2-thiazine and 1-azaphenalene, found in thermal rearrangement of 2H-azirines having O- and S-functions, are discussed with their reaction pathways.

1) Benzofuran and benzothiophene system

Thermal rearrangement reactions of ethyl 2-(3-arylbenzofuran-2-yl)-2H-azirine-3-carboxylates gave benzofuroazepines, exclusively. However, benzothiophene analogues gave nitriles, formed by rearrangement of ethoxycarbonyl group, as well as azepines at higher temperatures. These differences are explained in terms of degree of resonance stabilization of benzofuran and benzothiophene ring and in terms of the bond length of C-O and C-S. The cyclic N-S ylides, which were expected to be formed in thermal rearrangement of benzothiophene derivatives, were not found.

2) Methoxy- and Methylthionaphthalene system

Thermal rearrangement of ethyl 2-(2-methylthio-1-naphthyl)-2H-azirine-3-carboxylate in benzene under reflux for 0.5 hr gave ethyl 1-methylnaphtho[1,2-e]-1,2-thiazine-3-carboxylate, quantitatively. Under the same conditions, ethyl 2-(2-methoxy-1-naphthyl)-2H-azirine-3-carboxylate was stable but on heating in refluxing heptane for 10 hr gave ethyl 4-methoxy-1-azaphenalene-2-carboxylate (51%) and nitrile (14%), formed by rearrangement of ethoxycarbonyl group.

The naphthothiazine may be formed by C-N bond fission of 2H-azirine to form vinyl nitrene followed by attack of the nitrene at S-atom and is stabilized by participation of d-orbital. In the case of methoxy derivative attack of the nitrene at O-atom does not give stable compound then the nitrene attack the peri-position to form 1-azaphenalene. This reaction might be assisted by the methoxy group to stabilize the intermediate to form azaphenalene.