

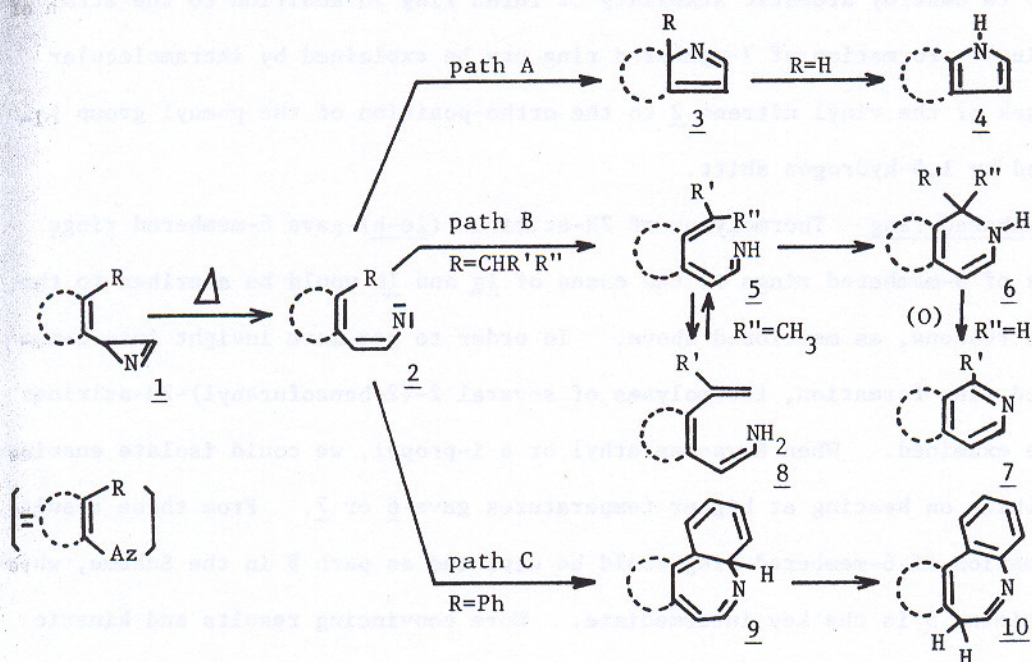
VINYL NITRENE AS VERSATILE SYNTHON; CONTROLLING FACTORS FOR SELECTIVE PREPARATION OF 5-, 6-, AND 7-MEMBERED HETEROCYCLES

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Previously, we made it clear that thermolyses of 2H-azirines gave vinyl nitrenes, which further rearranged into 6- and 7-membered rings, as well as usual 5-membered rings. In this paper, the controlling factors for the formation of 6- and 7-membered rings were explored to establish new synthetic method of heterocycles.

The reaction pathways and product distributions in thermal rearrangement reactions of 2H-azirines (1a-h) are shown in the Scheme and the Table.



Scheme

Table. Product distributions in thermal rearrangement of 2H-azirines

No	<u>1a</u>	<u>1b</u>	<u>1c</u>	<u>1d</u>	<u>1e</u>	<u>1f</u>	<u>1g</u>	<u>1h</u>
path A	100	100	60	0	85	66	0	0
path B	-	-	-	-	15	34	100	100
path C	0	0	40	100	-	-	-	-

7-Membered ring Decreased 5-membered ring formation in the case of 1c, compared with 1b, would be attributed to high strain in 3c caused by fusing two 5-membered rings. Selective 7-membered ring formation from 1d would be ascribed to suppression of 5-membered ring formation, which suffers disadvantage to destroy aromatic stability of furan ring in addition to the strain of fusing. Formation of 7-membered ring can be explained by intramolecular attack of the vinyl nitrene 2 to the ortho-position of the phenyl group followed by 1,5-hydrogen shift.

6-Membered ring Thermolyses of 2H-azirines (1e-h) gave 6-membered rings. Lack of 5-membered rings in the cases of 1g and 1h would be ascribed to the same reasons, as mentioned above. In order to get more insight into 6-membered ring formation, thermolyses of several 2-(2-benzofuranyl)-2H-azirines were examined. When R was an ethyl or a i-propyl, we could isolate enamines 8, which on heating at higher temperatures gave 6 or 7. From these results, formation of 6-membered ring would be depicted as path B in the Scheme, where the imine 5 is the key intermediate. More convincing results and kinetic aspects will also be presented.