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UNEXPECTED REARRANGEMENTS OF A (Z)-KETOVINYLAZIRINE. C-C VERSUS C-N BOND CLEAVAGE.

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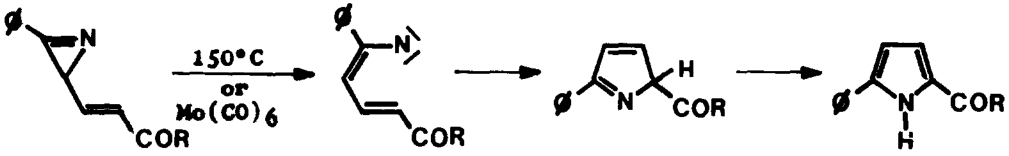
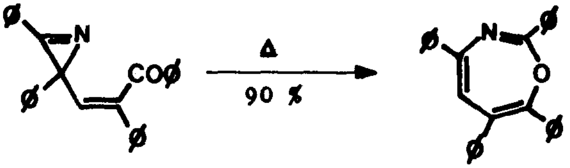
Padwa has noted that thermolysis of (E)-ketovinylazirines (1) leads to carbon-nitrogen bond cleavage whereby butadienyl nitrenes (2) are formed which cyclize to afford pyrrole derivatives (4) via pyrrolenine intermediates (3)[1]. This rearrangement can also be carried out at room temperature in the presence of molybdenum hexacarbonyl[2].



1 2 3 4

In striking contrast, Le Roux has shown that heating the tetraphenyl (Z)-ketovinylazirine (5) at 100°C provides 1,3-oxazepine (6) in 90% yield[3].



5 6

These results prompted me to investigate more closely the chemistry of the tetraphenylazirine derivative (5) which is the only known stable (Z)-ketovinylazirine[4].

Treatment of a solution of (5) in anhydrous tetrahydrofuran with one equivalent of $Mo(CO)_6$ for 30 hours at room temperature under a nitrogen atmosphere leads to a reaction mixture from which compounds (6) to (9) have been isolated and identified[5]. Both the 1,3-oxazepine (6) and the N-benzoylpyrrole (8) are inert under these reaction conditions.

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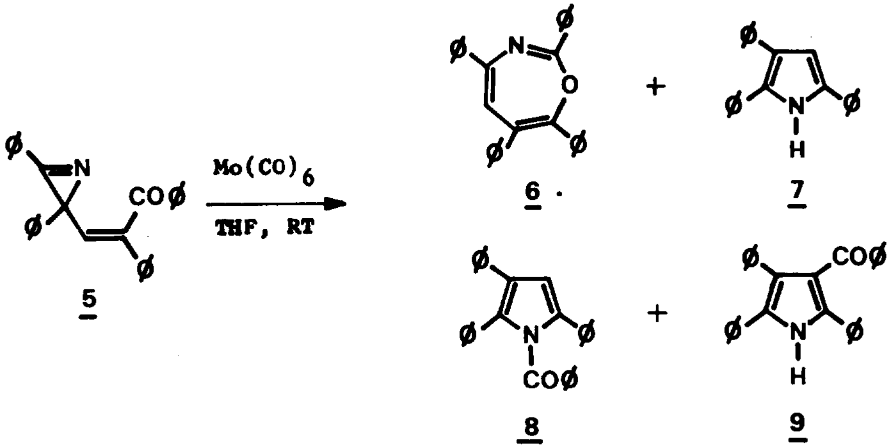
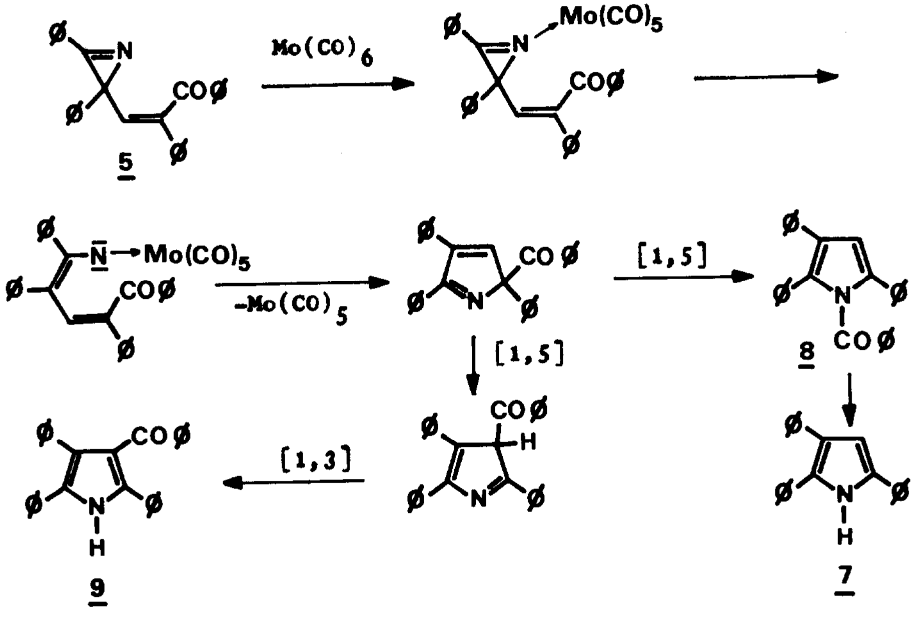


The formation of products (7), (8) and (9) can be rationalized by the mechanism depicted in Scheme 1. It is to be noted that the molybdenum hexacarbonyl induced rearrangement and the thermal rearrangement of (5) follow different pathways, a fact which is rather unexpected.

Scheme 1



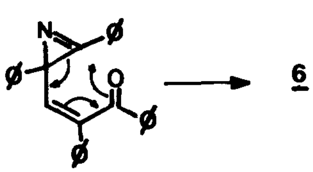
The formation of 1,3-oxazepine (6), which is purely a thermal process, involves a C-C bond cleavage in the azirine (5). Although such thermal C-C bond cleavages have already been reported, only a few of them are known[6,7] ; they usually require high temperatures of up to 400°C[8].

This C-C bond cleavage is usually obtained upon irradiation of an azirine and leads to a 1,3-dipolar species, a nitrile-ylide, which can be trapped with dipolarophiles[9].

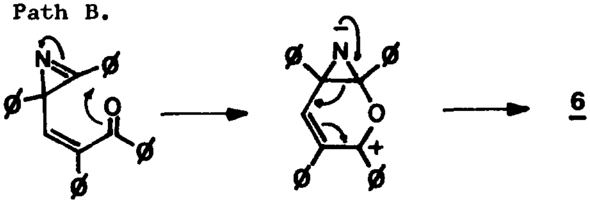
Low temperature U.V. irradiation of (5) leads to the corresponding 1,3-oxazepine (6) in 90% yield[10]. In both thermal and photochemical reactions all attempts to trap any dipolar species with methylacrylate remained unsuccessful[11].

This last result clearly indicates that, if any nitrile-ylide is formed at all during the rearrangement of (5), it reacts much faster intramolecularly to give (6) than intermolecularly with methylacrylate.

It is believed that the above described rearrangement involves a novel reaction pathway in the chemistry of azirines. Due to the peculiar stereochemistry of azirine (5), a concerted mechanism may take place (Path A). An alternative mechanism is depicted in Path B.



Path A



Path B

Further investigations are presently being conducted in our laboratory in order to determine the mechanism of this rearrangement. The synthesis as well as the chemical and photochemical behavior of other (Z)-ketovinylazirines are also under investigation[12].

References and notes

1. A.Padwa, J.Smolanoff and A.Tremper, J.Am.Chem.Soc., 97, 4682 (1975)
2. H.Alper, J.E.Prickett and S.Wollowitz, J.Am.Chem.Soc., 99, 4330 (1977)
3. J.P.Le Roux, J.C.Cherton and P.L.Desbene, C.R.Acad.Sc., 280, 37 (1975)
4. Two other Z-ketovinylazirines have been reported by T.Mukai as unstable compounds : T.Mukai, T.Kumagai and O.Seshimoto, Pure and Appl. Chem., 49, 287 (1977)
5. All compounds have been identified by comparison with authentical samples obtained by independent synthesis : C.L.Pederson and O.Buchardt, Acta. Chem.Scand., 27, 271 (1973) and references cited therein.
6. L.A.Wendling and R.G.Bergman, J.Org.Chem., 41, 831 (1976)
7. A.Demoulin, H.Garissen, A.M.H.Frisque and L.Gosez, J.Am.Chem.Soc., 97, 4409 (1975)
8. I have noted that the tetraphenylazirine (5) already rearranges to (6) in solution at room temperature.
9. For recent reviews see : A.Padwa, Acc.Chem.Res., 9, 371 (1976) and P.Gilgen, H.Heimgartner, H.Schmid and H.J.Hansen, Heterocycles, 6, 143 (1977)
10. This reaction cannot be a thermal one since the azirine (5) is indefinitely stable in solution at -10°C.
11. Methylacrylate has been used by A.Padwa for the trapping of the nitrile-ylides formed during the irradiation of some E-ketovinylazirines[16]. In these cases the efficiency of the trapping was about 80%.
12. I am grateful to Professor R.K.Murray, Department of Chemistry of the University of Delaware, for some fruitful discussions.

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