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INTRAMOLECULAR PHOTOCHEMICAL AND THERMAL CYCLIZATION REACTIONS OF 2-VINYL SUBSTITUTED 2H-AZIRINES

Albert Padwa*, Joel Smolanoff, and Alan Tremper

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

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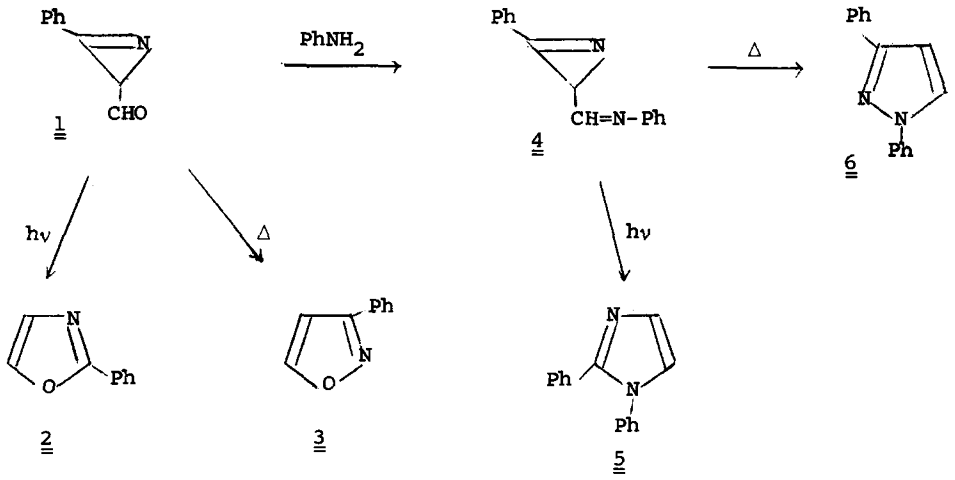
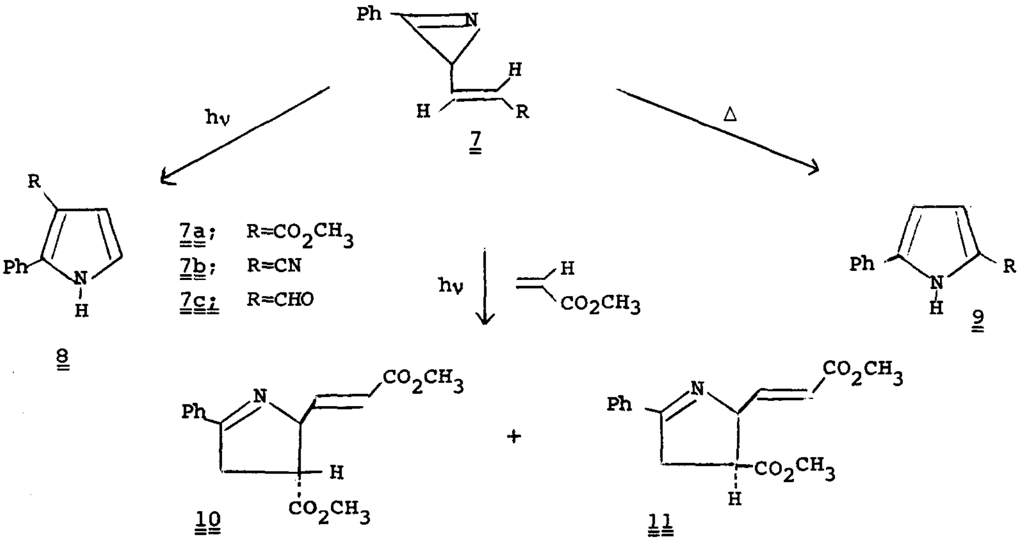
Several in-depth studies from these laboratories have demonstrated that arylazirines undergo photocycloaddition with electron deficient olefins.[1-3] It has been suggested that these reactions proceed by way of irreversible opening of the three-membered ring to form a nitrile ylide intermediate which is subsequently trapped by a suitable dipolarophile.[4] The purpose of the present study was to investigate the generality of the photoaddition when the double bond and the azirine ring were constrained to be within the same molecule. In this communication we describe some novel reactions that 3-phenyl-2-formyl-2H-azirine (1) and some of its derivatives undergo when subjected to both ultra-violet and thermal excitation. Our results are also of some interest in connection with recent accounts concerning the role of azirines as reactive intermediates in the oxazole-isoxazole transformation.[4-10]

Addition of iodine azide to the dimethylacetal of cinnamaldehyde followed by dehydrohalogenation, thermolysis, and aqueous hydrolysis afforded 3-phenyl-2-formyl-2H-azirine (1), mp 45-47°, in good yield:(ir (KBr) 5.60 and 5.85; nmr (100 mHz) τ 7.10 (1H, d, J = 7.0Hz), 2.3-1.8 (5H,m), and 1.03 (1H, d, J = 7.0Hz)).[11] When a solution of 1 in benzene was irradiated through a Vycor filter, the only product isolated was 2-phenyloxazole (2). Heating azirine 1 for 148 hr in benzene at 200° afforded 3-phenylisoxazole (3) in high yield (80%).

Azirine 1 could be smoothly converted to the corresponding N-phenylimine 4, which gave 1,3-diphenylpyrazole (6) upon heating in xylene. This stands in marked contrast to the photochemical reaction of 4, which afforded 1,2-diphenylimidazole (5) as the exclusive photoproduct.



Reaction of 1 with carbomethoxymethylenetriphenylphosphorane in benzene at 60° produced a quantitative yield of methyl (E)-3-phenyl-2*H*-azirine-2-acrylate (7a).[11] A similar set of Wittig reactions gave azirines 7b and 7c. Irradiation of azirines 7a-7c in benzene afforded 2,3-disubstituted pyrroles[12] 8a-8c while thermolysis of these compounds in xylene gave 2,5-disubstituted pyrroles 9a-9c.[11]



The best available evidence indicates that the photorearrangement of arylazirines 1, 4 and 7 proceeds by a mechanism which involves a nitrile ylide intermediate. This conclusion was reached by carrying out the irradiation of 7a in the presence of a trapping agent. Photolysis of a mixture of 7a and excess methyl acrylate in benzene gave cycloadducts 10 and 11 in high yield.[11] Under these conditions the formation of 8a, which is formed in high yield in the absence of a trapping reagent, is entirely suppressed. The formation of products 10 and 11 can readily be interpreted in terms of a 1,3-dipolar addition of the initially produced nitrile ylide with the added dipolarophile.

The thermal transformations observed with these systems can be rationalized in terms of an equilibration of the 2*H*-azirine with a transient vinyl nitrene which subsequently rearranges to the final product. Nishiwaki has recently demonstrated that a vinyl nitrene can be generated and trapped during the thermolysis of a substituted 2*H*-azirine.[13] Several examples are also available in the literature which provide good analogy for the cyclization of a butadienyl nitrene to a five-membered ring.[14]

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*Alfred P. Sloan Foundation Fellow, 1968-1972; National Institute of Health Special Postdoctoral Fellow 1972-1973; Address inquiries to this author.

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11. All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given in our full manuscript.

12. Irradiation of *trans*-azirine **7c** afforded 2-phenyl-3-formyl-pyrrole as the exclusive photoproduct. It is interesting to note that the cis isomer of azirine **7c** has been suggested as an intermediate in the photoconversion of 4-phenyl-2,3-oxazabicyclo[3.2.0]hepta-3,6-diene to 2-phenyl-1,3-oxazepine.[9] All attempts to generate the cis azirine of **7c**, to verify this claim, have failed. These experiments will be described in detail in our full manuscript.

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