"STUDIES ON THE REACTION OF SULFUR YLIDES WITH AZIRIDINES AND RELATED COMPOUNDS - AN APPROACH TO AZETIDINES"

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Certificate

This is to certify that the thesis entitled, "Studies on the Reaction of Sulfur Ylides with Aziridines and Related Compounds - An Approach to Azetidines", being submitted by Raman Lata Sharma, to the Indian Institute of Technology, Delhi, for the award of the degree of 'Doctor of Philosophy' in Chemistry, is a record of bona fide research work carried out by her. Ms. Raman Lata Sharma has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or in full, to any other University or Institute for the award of any degree or diploma.

U.K. Nadir
Thesis Supervisor

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Raman

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ABSTRACT

This dissertation describes investigations undertaken to define the scope and limitations of an azetidine synthesis developed as part of a new approach to four membered rings in our laboratories. The procedure involves a methylene transfer from dimethylsulfoxonium methylide to N-arylsulfonylaziridines through an addition, 1,4- elimination process in a manner analogous to conversion of aldehydes and ketones to oxiranes, α, β - unsaturated aldehydes and ketones to α, β - unsaturated oxiranes or cyclopropyl aldehydes or ketones and other related reactions. It has been found now that the method is quite general and a number of N-arylsulfonylazetidines with different alkyl and aryl substituents can be prepared in fair to good yields. In contrast reaction with the sulfonium ylide leads only to olefins.

The regio - and stereo - chemical course of the reaction has also been studied. As expected on the basis of the rationale of this synthesis, the reaction proceeds stereospecifically with inversion at the carbon suffering nucleophilic attack by the ylide. The regiochemical course is, however, more complex. Although both electronic as well as steric effects seem to control the regiochemistry of ring opening of N-arylsulfonylaziridines by dimethylsulfoxonium methylide, in general the latter effect seems predominant.

An attempt to prepare 2-(o-hydroxyphenyl)-N-benzenesulfonylazetidine through two consecutive methylene transfers to salicylidenebenzenesulfonamide led to the synthesis of 3-benzenesulfonamido-2,3-dihydrobenzofuran.

This methodology, however, could not be used to prepare oxazetidines and cyclobutanes through reaction of an appropriate oxaziridine and cyclopropane with the ylide respectively. In the former case azetidines were the final products whereas the cyclopropanes could be recovered unchanged on treatment with dimethylsulfoxonium methylide. These results have been rationalised.

Analysis of the ^{1}H-NMR spectra of the various N-arylsulfonylazetidines reveal that the puckering in these molecules is relatively small. In the case of trans-2,3-diphenyl-N-arylsulfonylazetidines the preferred conformation has the two phenyl rings pseudo-equatorial. A comparison of the ^{1}H-NMR of cis - and trans-2,3 diphenyl-N-arylsulfonylazetidines suggests that the cis - isomers are somewhat more flat than the corresponding trans - compounds.

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