

**STUDIES ON THE REACTION
OF SUBSTITUTED N-ARYLSULFONYLAZIRIDINES
WITH ISOCYANATES AND ISOTHIOCYANATES AS
A ROUTE TO 2-IMIDAZOLIDINONES AND
2-IMIDAZOLIDINETHIONES**

by
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requirements for the
degree of*
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CERTIFICATE

This is to certify that the thesis entitled, "STUDIES ON THE REACTION OF SUBSTITUTED N-ARYLSULFONYLAZIRIDINES WITH ISOCYANATES AND ISOTHIOCYANATES AS A ROUTE TO 2-IMIDAZOLIDINONES AND 2-IMIDAZOLIDINETHIONES", being submitted by Ms. Nupur Basu, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by her. Ms. Nupur Basu 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.



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ABSTRACT

The investigations described in this dissertation were undertaken as part of a programme to develop useful synthetic methods based on elaboration of three-membered heterocycles. The present study pertains to defining the scope and limitations of the reaction of substituted N-arylsulfonylaziridines with isocyanates and isothiocyanates in the presence of NaI as a route to 2-imidazolidinones and 2-imidazolidinethiones.

It has been found that the reaction of 2- and/or 3-substituted-N-arylsulfonylaziridines with isocyanates using NaI as a catalyst is a fairly general approach to 2-imidazolidinones, which are obtained in good yield through this procedure. The method is regiospecific and the ring opening is governed by the nature of the substituent(s) at 2- and/or 3- position of the aziridine ring. Thus 2-arylaziridines give solely the product corresponding to attack at the substituted carbon whereas the 2-alkylaziridines yield exclusively the isomer corresponding to attack at the unsubstituted carbon. The regiochemistry is unaffected by the nature of the isocyanate.

The stereochemical course of the reaction has also been studied for the first time. Apparently, imidazolidinones are formed stereospecifically with the product retaining the geometry of the starting aziridine. However, the procedure fails with cis-2,3-diphenyl and cis- and trans-2,3-dialkyl-N-aryl-sulfonylaziridines.

The study revealed that imidazolidinone yields are better with 2-arylaziridines (as compared to the 2-alkyl analogues) and phenyl isocyanate (in relation to alkyl isocyanates). Also electron-donating and electron-withdrawing groups on the 2-aryl substituent do not seem to affect the course of the reaction significantly. However,

it was found that when the catalyst is changed from an alkali metal halide (like NaI) to a quaternary ammonium halide, the arylsulfonyl group is missing in the product 2-imidazolidinones.

In order to establish the regiostructure of some of the imidazolidinones, they had to be synthesised independently. This was done by treating the corresponding N-arylsulfonylaziridine with Me_3SiI . The present dissertation also includes a study of the regio- and stereo-chemical aspects of this reaction which have not been investigated before. Our results indicate that the reaction is regiospecific. Also it is stereoselective for 2,3-diphenylaziridines; with dialkylaziridines a mixture of stereoisomers is obtained.

Reaction of substituted N-arylsulfonylaziridines with isothiocyanates in the presence of NaI uncovered some interesting facts. It was found that it leads to the formation of 2-imidazolidinethiones and not to 2-iminothiazolidines as reported and that with phenyl isothiocyanate the reaction is mechanistically similar to that with isocyanates. However, with alkyl isothiocyanates a different course is followed and the imidazolidinethiones show absence of the alkyl groups present in the isothiocyanate.

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