

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### Sulfoxylic Acid Derivatives as Novel Sulfenylating Reagents

Sergey Z. Vatsadze<sup>a</sup>; Nikolay S. Zefirov<sup>a</sup>; Nikolay V. Zyk<sup>a</sup>; Andrey G. Kutateladze<sup>b</sup>

<sup>a</sup> Department of Chemistry, Moscow State University, Moscow, Russia <sup>b</sup> Department of Chemistry, University of Madison, Madison, USA

**To cite this Article** Vatsadze, Sergey Z. , Zefirov, Nikolay S. , Zyk, Nikolay V. and Kutateladze, Andrey G.(1994) 'Sulfoxylic Acid Derivatives as Novel Sulfenylating Reagents', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 95: 1, 333 — 334

**To link to this Article:** DOI: 10.1080/10426509408034225

**URL:** <http://dx.doi.org/10.1080/10426509408034225>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## SULFOXYLIC ACID DERIVATIVES AS NOVEL SULFENYLATING REAGENTS

SERGEY Z. VATSADZE, NIKOLAY S. ZEFIROV, NIKOLAY V. ZYK,  
ANDREY G. KUTATELADZE\*

Department of Chemistry, Moscow State University, Moscow, Russia

\*Department of Chemistry, University of Madison, Madison, USA

**Abstract** New electrophilic reagents were obtained from N,N'-thiobisamines by use of new strategy of weak electrophile activation by SO<sub>3</sub>. Addition reactions of these compounds have unexpected stereochemistry and show the unique electrophilic properties of the reagents.

### INTRODUCTION

Until recently thiobisamines were known to be the non-electrophilic reagents towards alkenes. A new strategy for the activation of these weak electrophiles through their reaction with sulfur trioxide has been developed<sup>1</sup> and now the addition chemistry of thiobisamines is available for thorough investigation.

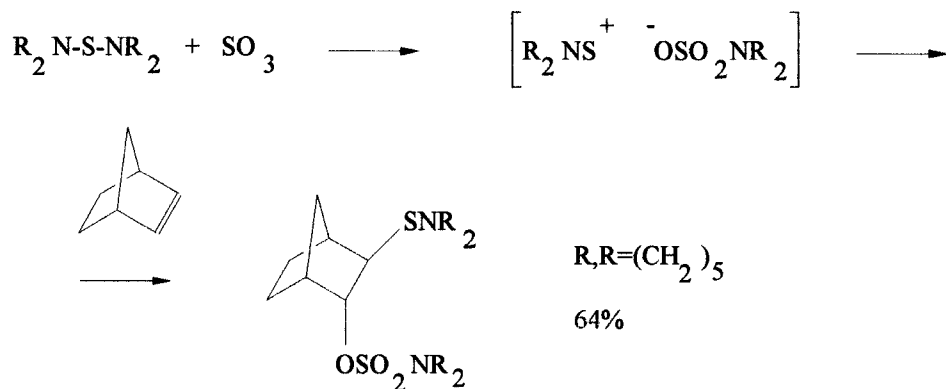
### ELECTROPHILIC BEHAVIOUR OF SULFOXYLIC ACID AMIDES

#### Addition to a double bond

Reactions of thiobisamines with two mol. equivalents SO<sub>3</sub> and then with rigid olefins lead to the formation of sulfides containing two sulfamate groups. In contrast, the reactions with terminal alkenes furnish diaminosulfides<sup>1</sup>.

It was found that sulfur trioxide activation of one S-N bond is also possible. We succeeded in obtaining the products of electrophilic addition of these reagents to

alkenes. For example, reaction of thiobispyridine with norbornylene leads to 1,2-*trans*-sulfonylamidosulfamate which is the only product:



The absence of rearrangement products shows the low effective electrophilicity of the new reagents and the unique properties of electrophilic species  $[R_2NS]^+(A)$ . As general other sulfonylating reagents in the presence of sulfur trioxide provide a large amount of rearrangement products<sup>1</sup>. It seems likely that the presence of the nitrogen atom connected to the cationic centre influences the charge distribution.

The electron structure of A may be similar to that of aminosulfonylchlorides and aminosulfenates  $R_2N-S-Z$  ( $Z=Cl$  or  $OR$ ) where the electron density transfer from N to Z is proposed from the PES-data<sup>2</sup>. But our preliminary *ab initio* calculations made in the 3-21G basis do not confirm these observations. That's why the experimental proofs for the electron structure of A are the matter of investigation.

Our first step in this field gave the unexpected results. N-Nitrosopiperidine was obtained by the reaction of piperidinesulfonylchloride with silver nitrate. This result shows that the cation A, formed by elimination of silver chloride, is easily oxidised by the nitrate anion. Therefore it is worth using silver salts with non-nucleophilic and non-oxidative anions (for example,  $BF_4^-$ ).

## REFERENCES

1. A.G.Kutateladze, N.S.Zefirov, and N.V.Zyk, *Sulfur Reports*, **11**, 2, 233-252 (1992).
2. V.V.Zverev, B.M.Musin, personal communication, (1994).