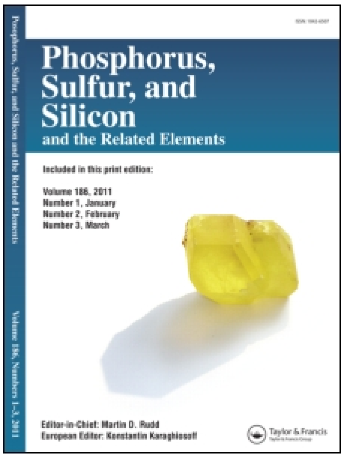

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Sulfoxylic Acid Derivatives as Novel Sulfenylating Reagents

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SULFOXYLIC ACID DERIVATIVES AS NOVEL SULFENYLATING REAGENTS

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Abstract New electrophilic reagents were obtained from N,N'-thiobisamines by use of new strategy of weak elestrophile activation by SO_3. Addition reactons of these compounds have unexpected stereochemistry and show the unique electrophilic properties of the reagents.

INTRODUCTION

Untill 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[1] and now the addition chemistry of thiobisamines is available for thorough investigation.

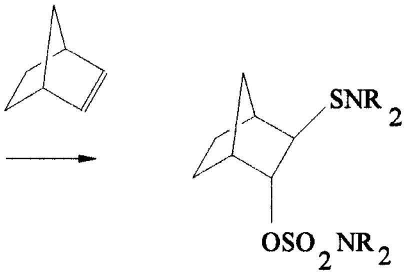
ELECTROPHILIC BEHAVIOUR OF SULFOXYLIC ACID AMIDES

Addition to a double bond

Reactions of thiobisamines with two mol. equivalents SO_3 and then with rigid olefins lead to the formation of sulfides containing two sulfamate groups. In contrast, the reactions with terminal alkenes furnish diaminosulfides[1].

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 thiobispiperidine with norbornylene leads to 1,2-*trans*-sulfenylamidosulfamate which is the only product:

$$R_2N\text{-}S\text{-}NR_2 + SO_3 \longrightarrow \left[R_2NS^{+}\ \ {}^{-}OSO_2NR_2\right] \longrightarrow$$



R,R=$(CH_2)_5$

64%

The absense of rearrangement products showes the low effiective electrophilicity of the new reagents and the unique properties of electrophilic spiecies $[R_2NS]^+$(A). As general other sulfenylating reagents in the presence of sulfur trioxide provide a large amount of rearrangement products[1]. 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 aminosulfenylchlorides and aminosulfenates $R_2N\text{-}S\text{-}Z$ (Z=Cl or OR) where the electron density tranfer from N to Z is proposed from the PES-data[2]. 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 piperidinesulfenylchloride 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).

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