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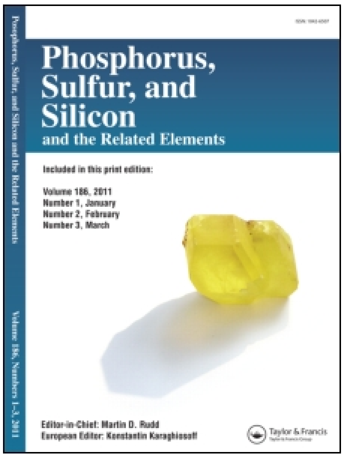

Phosphorus, Sulfur, and Silicon and the Related Elements

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Spectral and Chemical Studies on the Protonation of Sulfinamides

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SPECTRAL AND CHEMICAL STUDIES ON THE PROTONATION OF SULFINAMIDES

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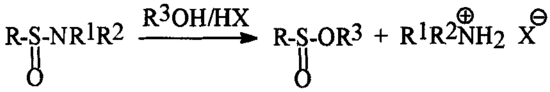
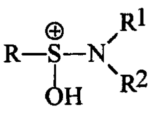
The acid-catalyzed reaction of sulfinamides with alcohols has been found to be the method of choice for the preparation of a variety of sulfinic acid esters.[1] (eq.1).



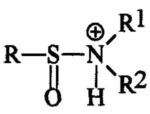
$$R\text{-}\underset{\overset{\|}{O}}{S}\text{-}NR^1R^2 \xrightarrow{R^3OH/HX} R\text{-}\underset{\overset{\|}{O}}{S}\text{-}OR^3 + R^1R^2\overset{\oplus}{N}H_2\ \overset{\ominus}{X} \qquad \text{(eq.1)}$$

It is obvious that protonation of the sulfinamide molecule allows its further reaction with an alcohol nucleophile.

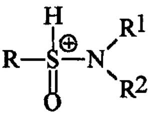
Sulfinamide molecule contains three basic sites located on the sulfinyl oxygen atom, tricoordinated nitrogen atom and sulfinyl sulfur atom, respectively. Therefore, theoretically each of the above mentioned atoms in sulfinamides can be protonated upon treatment with a protonic acid to afford the corresponding protonated species A, B and C.



A



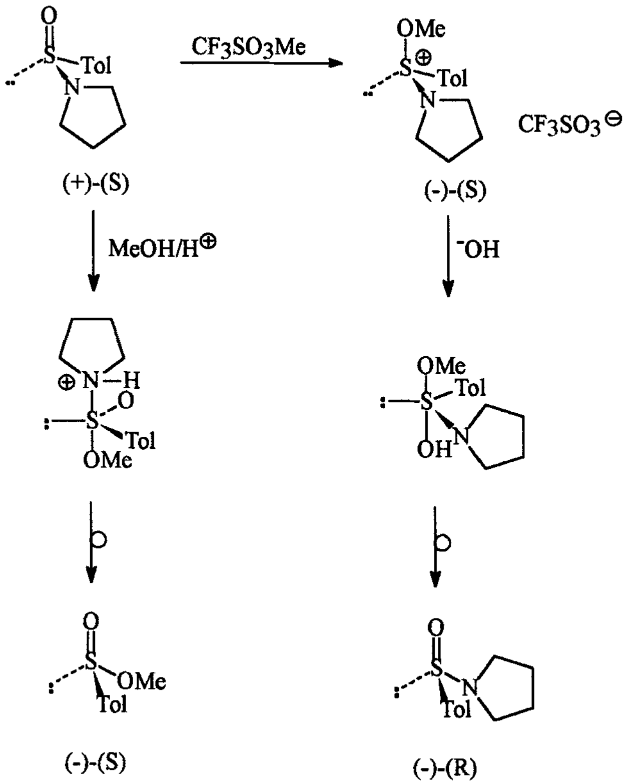
B



C

Here we would like to the present results of our spectroscopic studies (IR, UV, NMR) which indicate that the tricoordinated nitrogen atom in sulfinamides is a major site (it not exclusive) of the protonation. For example, a substantial shift of the IR absorption of the S=O group towards higher wave number observed for the protonated N,N-diethyl-p-toluenesulfinamide (1160 cm^{-1} in comparison with 1060 cm^{-1} and 1080 cm^{-1} for the free amide) may be considered as strongly indicative of protonation at nitrogen, because only in this case the strength of the S=O bond increases.

An additional support for the N-protonation of sulfinamides is provided by comparison of the reaction course of the acid-catalyzed methanolysis of (+)-(S)-N--pyrrolidine-p-toluenesulfinamide and alkaline hydrolysis of (+)-(S) methoxy-p-tolyl-N--pyrrolidinesulfonium trifluoromethanesulfonate (see Scheme I).



Scheme I

References:

1. a. M.Mikołajczyk, J.Drabowicz, B.Bujnicki, J.S.C.Chem.Commun., 568 (1976).
   b. M.Mikołajczyk, B.Bujnicki, J.Drabowicz, Bull. Acad.Polon,Sci., 25, 267 (1979), M.Mikołajczyk, J.Drabowicz, Topics in Stereochemistry, 13, 333 (1982).
   c. M.Mikołajczyk, J.Drabowicz, B.Bujnicki, Tetrahedron Lett., 26, 5699 (1985).
   d. M.Mikołajczyk, Perspectives in the Organic Chemistry of Sulfur, ed. B.Zwanenburg, A.J.H.Klunder, Elsevier, 1987, p.23.
   e. J.Drabowicz, P.Kiełbasiński, M.Mikołajczyk, The Chemistry of Sulfinic Acids, Esters and their Derivatives, Ed. S.Patai, J.Wiley and Sons, 1990, 351.
   f. M.Mikołajczyk, Phosphorus and Sulfur, 27, 31 (1986).