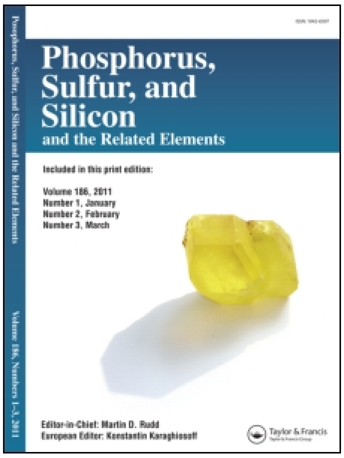

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Oxidation of Thiolates with Oxaziridines: an Efficient Method to the Preparation of Sulfoxides, Sulfones and Sulfonic Acid Derivatives

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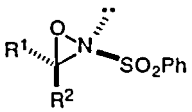
Oxaziridine-mediated oxidation reactions of thiolates into sulfenates and sulfinates are reported.

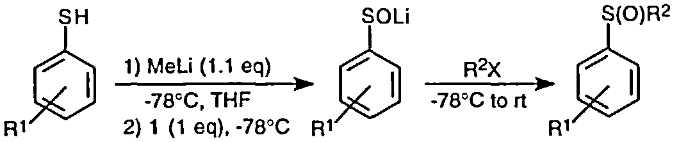
Keywords: oxaziridine; oxidation; sulfenate; sulfinate; thiolate

With only a few exceptions, the oxidation of thiolates (RS^-) into the corresponding sulfenates (RSO^-) or sulfinates (RSO_2^-) remains unexplored. This can be interpreted by the inefficiency of the oxidants tested so far. We wish to present here the surprising results we obtained using oxaziridines **1-2**.



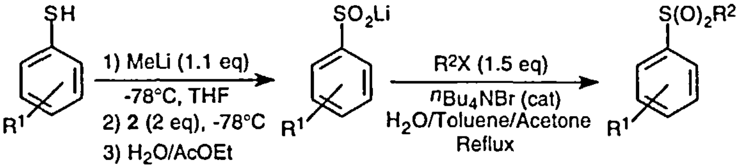
1 $R^1 = {}^tBu, R^2 = Me$
2 $R^1 = Ph, R^2 = H$

Treatment of aromatic thiolates with oxaziridine **1** gave the anticipated sulfenate anions (mono-oxidation reaction). Subsequent *in situ* trapping with various aliphatic halides led to sulfoxides in good to excellent yields.[1] The overall sequence allows a convenient approach to the synthesis of sulfoxides from thiols, with the main advantage to be performed in one pot.



a) R^1=H, R^2=Me, 89%; b) R^1=H, R^2=Et, 83%; c) R^1=2-OMe, R^2=Me, 89%

Use of oxaziridine **2** gave a different result, without any sulfenate formation at all. Instead a 1:1 mixure of sulfinate salt (double oxidation reaction) and unreacted thiolate was obtained. With two equivalents of the oxidant, the sulfinate was produced quantitatively. Isolation of the sulfinate with subsequent alkylation under phase transfer catalysis[2] afforded sulfones efficiently and cleanly. The sulfinates have also been used for the preparation of sulfonyl chlorides and sulfonamides.



a) R^1=H, R^2=Me, 70%; b) R^1=H, R^2=Et, 84%; c) R^1=2-OMe, R^2=Et, 80%

References

[1] F. Sandrinelli, S. Perrio, and P. Beslin, *J. Org. Chem.*, **62**, 8626 (1997).
[2] J. K. Crandall, and C. Pradat, *J. Org. Chem.*, **50**, 1327 (1985).