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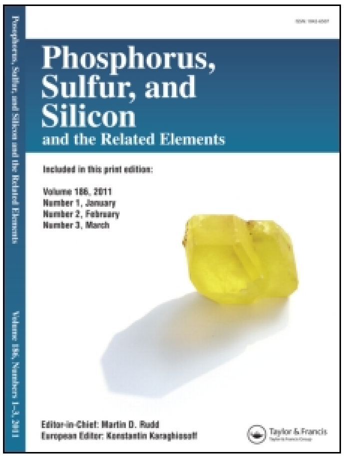

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New Reactions with Thioaldehydes and Thienium Cations

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NEW REACTIONS WITH THIOALDEHYDES AND THIENIUM CATIONS.

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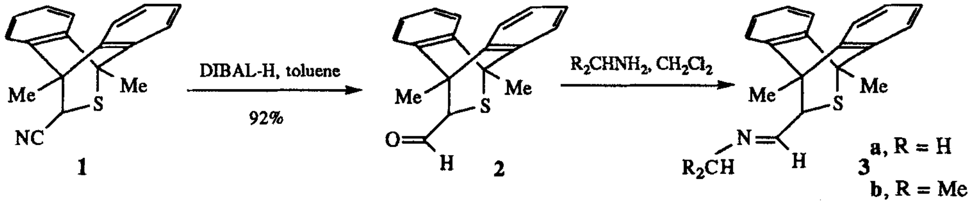
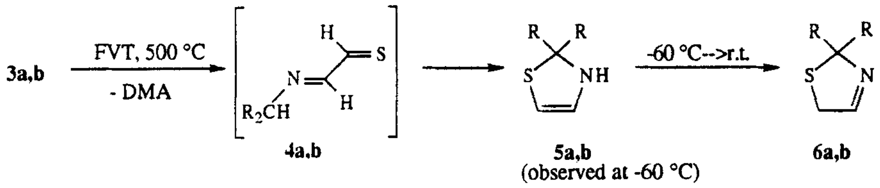
Abstract i) When generated under FVT conditions α-imino-thioaldehydes undergo a cyclization to dihydro-1,3-thiazoles. ii) Thienium cations, generated during a Pummerer reaction, can be trapped with dienes.

α-IMINO-THIOALDEHYDES

Thioaldehydes bearing an electron-withdrawing group α to the C=S group are useful intermediates in the Diels-Alder reaction. Thioxoethanal (HCSCHO)[1], thioformyl cyanide (NCCHS)[2] and various α-thioxoacetates ($HCSCO_2R$)[3] have already been generated *in situ* or by FVT and trapped with various dienes. In this communication we present our first results concerning our attempts to caracterize previously unknown α-imino-thioaldehydes.

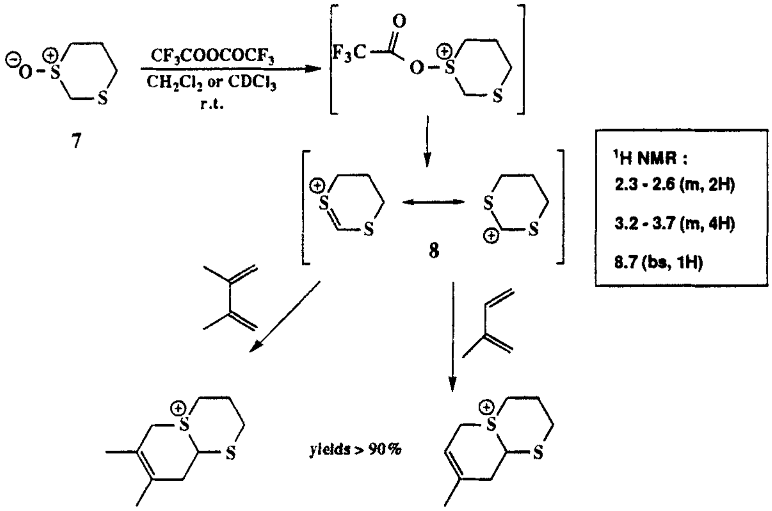
The thioformyl cyanide-dimethylanthracene adduct **1** was reduced to the corresponding aldehyde **2**, which was treated with amines to give the imines **3a,b**. Upon thermolysis in the gas phase at 500 °C, these imines gave DMA and volatile products which were trapped on a cold finger and analysed by ^{1}H and ^{13}C NMR. The obtained spectra were in agreement with structures **5a,b**. The secondary enamines **5a,b** were found to be poorly stable and gave the corresponding imines **6a,b** at room temperature. The multistep process leading from **4a** to **5a** has been investigated by theoretical *ab initio* calculations.





THIENIUM CATIONS

It has been proposed that the Pummerer rearrangement involves the formation of a transient thienium cation.[4] This type of cation should be able to undergo [4 + 2] cycloaddition with electron-rich dienes. We have treated the sulfoxide **7** by trifluoroacetic anhydride. Under these conditions, the transient cation **8** is formed and we have been able to trap it with isoprene and dimethylbutadiene.



^{1}H NMR :
2.3 - 2.6 (m, 2H)
3.2 - 3.7 (m, 4H)
8.7 (bs, 1H)

references

1. M. Torres, A. Clement, O. P. Strausz, *Nouv. J. Chem.*, **7**, 269-270 (1983). F.Bourdon, J. L. Ripoll, Y. Vallée, S. Lacombe, G. Pfister-Guillouzo, *J. Org. Chem.*, **55**, 2596-2600 (1990).
2. G. Pfister-Guillouzo, F. Gracian, A. Sennio, F. Bourdon, Y. Vallée, J. L. Ripoll, *J. Am. Chem. Soc.*, **115**, 324-327 (1993).
3. E. Vedejs, T. H. Eberlein, D. J. Mazur, C. K. McLure, D. A. Perry, R. Ruggeri, E. Schwartz, J. S. Stults, D. L. Varie, R. G. Wilde, S. Wittenberg, *J. Org. Chem.*, **51**, 1556-1562 (1986). C. M. Bladon, I. E. G. Ferguson, G. W. Kirby, A. W. Lochead, D. C. McDougall, *J. Chem. Soc. Perkin Trans. 1*, 1541-1545 (1985). T. Takahashi, N. Kurose, T. Koizumi, *Heterocycles*, **36**, 1601-1616 (1993).
4. O. De Lucchi, U. Miotti, G. Modena, *Organic Reactions*, **40**, 157-405 (1991).