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α -Oxo Sulfines and their Synthetic Behaviour

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α -Oxo sulfines and their synthetic behaviour

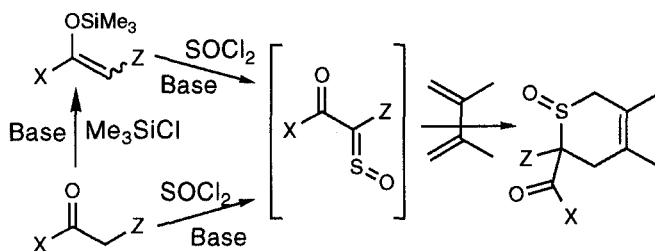
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Sulfines are reactive heterocumulenes which have been under investigation in our laboratory for a number of years¹. In this communication some new features of the chemistry of α -oxo sulfines are discussed.

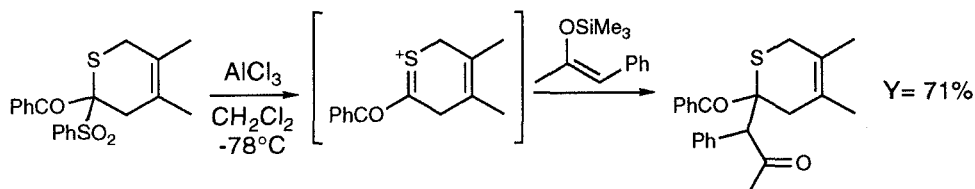
α -Oxo sulfines are readily prepared either from silyl enol ethers or from doubly-activated methylene compounds. Because of the instability of these sulfines bearing an adjacent electron-withdrawing group, they are usually trapped in an Diels-Alder reaction as dihydrothiapyran S-oxides¹.



Scheme 1

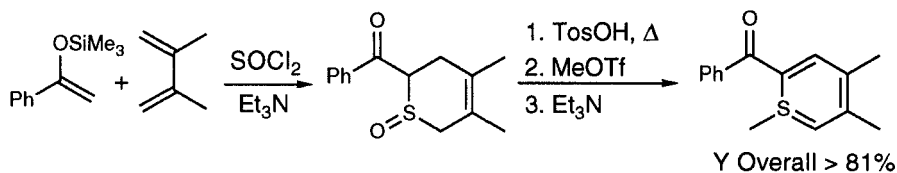
The sulfoxide function in the cycloadducts can conveniently be reduced with trifluoroacetic anhydride and sodium iodide in acetone² yielding dihydrothiapyrans in good yields. When the Z substituent is a sulfonyl group these dihydrothiapyrans can undergo a nucleophilic substitution reaction analogous to those described by Ley *et al*³ for sulfonyl substituted tetrahydropyrans.

In scheme 2 an example of such a substitution reaction is given using a silyl enol ether as the nucleophile. It is assumed that reaction with AlCl_3 generates a thioxonium intermediate which is attacked by the nucleophile to give the substituted thiapyran in a good yield.



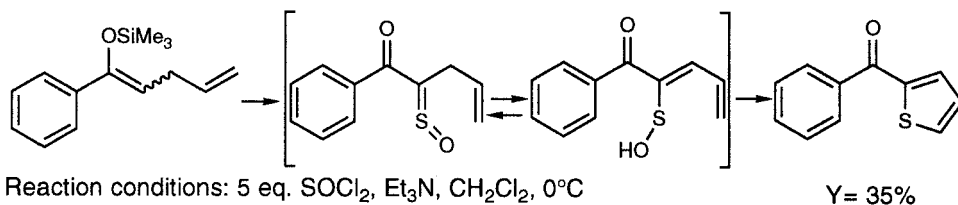
Scheme 2

An interesting application of the chemistry of α -oxo sulfines was found in the synthesis of thiabenzene in analogy with a sequence described recently by Hori *et al*⁴. Scheme 3 illustrates the manner in which the cycloadducts of α -oxo sulfines can be converted in these intriguing thiabenzene in excellent yields.



Scheme 3

The second topic of this communication concerns the intramolecular trapping reaction of α -oxo sulfines. For this purpose an α -oxo sulfine was prepared which can undergo enethiolization to give a vinyl sulfenic acid. Intramolecular reaction of this sulfenic acid with the built in olefin leads to a thiophene derivative, as depicted in scheme 4. This thiophene formation is unprecedented.



Scheme 4

References

1. B. Zwanenburg, *Phosphorus, Sulfur and Silica* **43**(1), 1 (1989).
2. J. Drabowicz and S. Oae, *Synthesis*, 404 (1977).
3. D.S. Brown, M. Bruno, R.J. Davenport and S.V. Ley, *Tetrahedron* **45**, 4293 (1989).
4. H. Shimizu, N. Kudo, T. Kataoka and M. Hori, *Tetrahedron Lett.* **31**, 115 (1990).