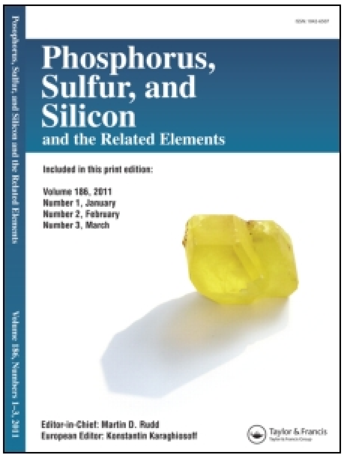

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A Novel Synthesis of Thioaldehyde S-Oxides Via an Unusual β-Elimination of Chloroform From Allylic and Benzylic Trichloromethyl Sulfoxides

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A NOVEL SYNTHESIS OF THIOALDEHYDE S-OXIDES VIA AN UNUSUAL β-ELIMINATION OF CHLOROFORM FROM ALLYLIC AND BENZYLIC TRICHLOROMETHYL SULFOXIDES

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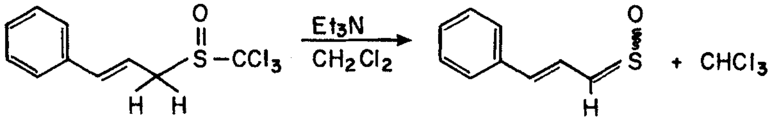
Abstract: A new method for the synthesis of thioaldehyde S-oxides including α,β-unsaturated derivatives, by mild base-induced elimination of chloroform from readily available allylic and benzylic trichloromethyl sulfoxides is described.

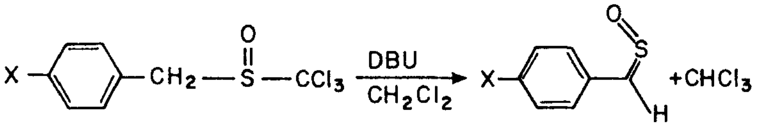
Allylic trichloromethyl sulfoxides are readily prepared by the well-known [2,3]-sigmatropic rearrangement of the corresponding sulfenate esters,[1a] and have played a central role in the discovery and elucidation of the mechanism of this rearrangement.[1b] We now wish to report, that in contrast to the unsubstituted allyl trichloromethyl sulfoxide which yields the corresponding vinyl sulfoxide on stirring overnight with Et_3N in CH_2Cl_2, treatment of cinnamyl sulfoxide under the same conditions leads to an unexpected, and apparently unprecedented, β-elimination of chloroform and formation of thiocinnamaldehydes S-oxide, in practically quantitative yield (eq. 1). Similarly, we have found that γ,γ-dimethylallyl trichloromethyl sulfoxide also undergoes β-elimination of chloroform under the same conditions and affords the corresponding conjugated vinyl sulfine.



(1)

During the past three decades a large variety of substituted sulfines, including some conjugated vinyl thioketone S-oxides, has been reported.[2] However, the method described above provides an easy and direct access to α,β-unsaturated thioaldehyde S-oxides which have never been reported before. In order to check the generality of the new reaction we have tested the reactivity of benzylic trichloromethyl sulfenates as well. Interestingly, with these sulfoxides, Et_3N or DABCO are not sufficiently basic to bring about elimination of $CHCl_3$. However, the use of a stronger base such as DBU, results in a fast reaction and affords the expected thiobenzaldehyde S-oxides in high yield (eq. 2, X=H, OMe).

It is worthwhile noting that in all cases studied we could only detect one of the two possible stereoisomers. In the case of the aromatic derivatives the stereochemistry has been determined by comparison of the NMR spectral data with those previously reported by Bonini, who obtained both isomers.[3]



(2)

A preliminary mechanistic study indicates that, as expected, the conversion of sulfoxide to sulfine proceeds by a reversible E1cB mechanism and not by a concerted E2 elimination. Thus, on treatment of the cinnamyl sulfoxide with Et_3N in the presence of D_2O, the rate of hydrogen-deuterium exchange is faster than the rate of sulfine formation. The observed stereospecifity is therefore quite striking.

Although elimination of HCl is one of the oldest approaches to sulfine synthesis,[2] the present study on the elimination of chloroform (pKa=24) is rather surprising not only in the context of sulfine formation, but as β-elimination reactions in general. However, the elegant and detailed studies by Kice in recent years[4] have demonstrated that methoxide-induced eliminations of other weak acids such as alcohols, amines, sulfones and fluorene from the corresponding sulfinyl derivatives, are also suitable for sulfine formation.

It is interesting to add, that in spite of the apparent lack of previous documented examples of β-elimination of chloroform in the literature, the α-elimination of chloroform has been thoroughly studied and extensively used for the generation of dichlorocarbene in the past. Similarly, the leaving group ability of the trihalomethyl anion is well demonstrated by the old haloform reaction, whereby the trihalomethyl group of a trihalomethyl ketone is substituted by a two-step nucleophilic addition-elimination mechanism. We are presently exploring the application of chloroform and haloform eliminations in general, for the synthesis of various other heterocumulenes.

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