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A VERSATILE VINYL SULPHIDE SYNTHESIS USING BENZENESULPHENYL CHLORIDE

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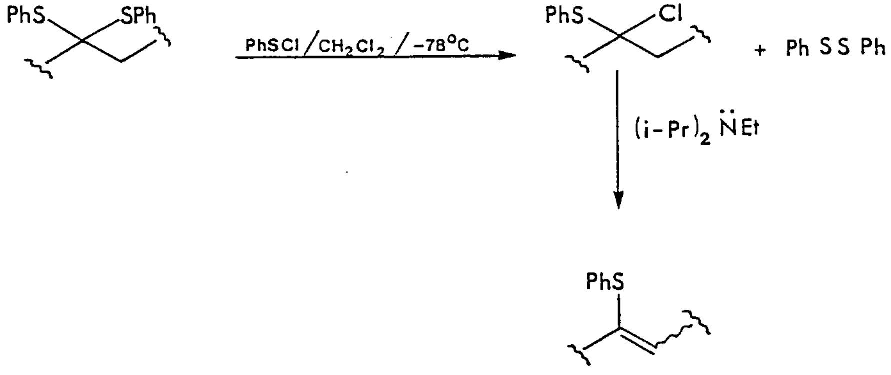
Abstract: Benzenesulphenyl chloride (PhSCl) in CH_2Cl_2 at -78°C converts thioacetals and thioketals to their α-chlorosulphides which afford vinyl sulphides on elimination. The method is compatible with a range of functionality.

Vinyl sulphides are valuable synthetic intermediates and their potential as enolate equivalents has been recently evaluated[1]. Some methods currently available for their preparation involve dehydrohalogenation of α-halosulphides[2], direct conversion from carbonyl compounds[3], use of Pummerer intermediates derived from sulphoxides[4] and thiol elimination[5] from thioacetals and thioketals. To date reagents to effect the latter include cuprous triflate[5a] (as benzene complex), mercuric trifluoroacetate/lithium carbonate[1] and diphosphorus tetraiodide[5b]. Although benzenesulphenyl chloride has emerged in recent years as a useful synthetic reagent, particularly in its reactions with alkenes[6] and allylic alcohols[7], no study[8] has been made on its use as a soft electrophile for conversion of thioacetals and thioketals to vinyl sulphides via the thio-elimination pathway. A study of the reaction[9] between methane sulphenyl chloride and 2,2-bis(methylthio) propane has been made but rapid cleavage of both carbon-sulphur bonds of the thioketal function occurs and the objective was to develop a mild deprotection method of the thioketal function. In this communication we present results to show that benzenesulphenyl chloride smoothly converts thioacetals and thioketals to their α-chlorosulphides which on elimination furnish the corresponding vinyl sulphides. Scheme 1.

Scheme 1



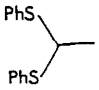
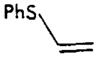
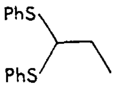
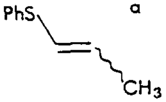
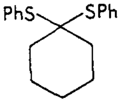
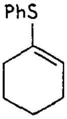
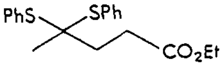
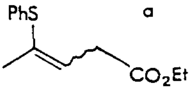
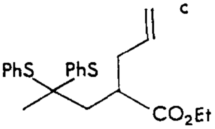
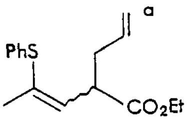
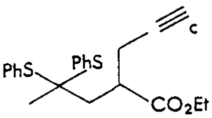
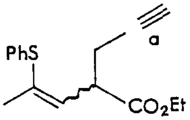
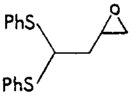
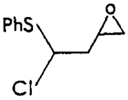
Furthermore, because of the low temperature that can be employed, we have demonstrated that the method is compatible with a broad range of other functionality. Benzeneselenenyl bromide also proved successful, producing α-bromosulphides, but it was considered less attractive in view of its expense. The phenyl group was used throughout as the sulphur protecting group though in principle other groups should be applicable to the method. The method should be of use in highly functionalised molecules where the experimental conditions of other procedures might be too harsh.

A typical experimental procedure is as follows. Benzenesulphenyl chloride (1,2 equivalents) in dry dichloromethane (1 mmole per mℓ of solvent) is syringed into a solution of thioacetal in dry dichloromethane (2 mmole in ≈ 2-3 mℓs solvent) at -78°C. The yellow colour discharges almost instantaneously and the solution is left stirring for five minutes before diisopropylethylamine (1,5 equivalents) is added whereupon the solution is allowed to warm to room temperature. On completion of the elimination (followed by NMR) the solution is extracted with ice cold HCℓ (0,1 M), the organic extracts dried and evaporated and the residue distilled or chromatographed to furnish the vinyl sulphide in good to excellent yield. The conversion of thioacetals can be monitored spectroscopically using 'H NMR by a downfield shift in the chemical shift of the methine proton ($CHCℓ_3$ as solvent at -60°C) while reaction of thioketals with α-methyl groups (see table) could also be followed using the downfield shift in the methyl signal. Excess reagent did not result in further substitution and a recent ^{13}C NMR study[10] indicates the possibility of reaction between the reagent and diphenyl disulphide to afford a sulphonium ion as a likely one at higher temperatures. The diphenyl disulphide can be isolated and re-used to prepare the reagent.

A range of substrates incorporating a varying degree of functionality were chosen so as to test out the method. Thioacetals and ketals were most conveniently prepared by reaction between carbonyl compound and thiophenol in dichloromethane in the presence of phosphorous pentoxide, and yields were very high. The elimination step in the preparation of the vinyl sulphides of ethanal and propanal[11] required refluxing temperatures while all the other compounds proceeded smoothly at room temperature. Also, the two products were isolated by distillation owing to their similar chromatographic polarities to diphenyl disulphide. By comparison, entry three in the table derived from cyclohexanone, was separated from the disulphide by lithium aluminium hydride destruction of the latter followed by a basic extraction. In the unsymmetrical cases (entries 4 - 6), elimination always gave rise to the more substituted regioisomer as a mixture of geometrical isomers. It was gratifying to establish that the method worked in molecules containing one or more of the four functional groups studied, ester, alkene, alkyne and epoxide (entries 4 - 7). In the latter case elimination couldn't be effected and the α-chlorosulphide was identified on the basis of its NMR spectrum.

In addition to providing vinyl sulphides this new method has obvious potential for production of α-chlorosulphides which have proved to be valuable compounds in synthesis and whose use in the latter has been reviewed[12]. Attempts to trap out the intermediate, (presumably the thionium ion), from reaction between the thioacetal of ethanal (entry 1) and benzenesulphenyl chloride by the enol silyl ether of cyclohexanone, resulted in phenylsulphenylation of the latter[13] demonstrating that the reactive enol is one functional group more nucleophilic towards the reagent than the thioacetal. However, use of benzenesulphenyl chloride and zinc

Table 1

	Starting thioacetal or thioketal	Product[e]	Yield
(1)			63
(2)		 [a]	64
(3)			91
(4)		 [a]	97
(5)	 [c]	 [a]	71
(6)	 [c]	 [a]	73
(7)	 [d]	 [b]	—

Notes

a: obtained as a mixture of geometrical isomers, approximately 1:1 ratio in each case.

b: obtained as a mixture of diastereomers and identified by 'H NMR.

c: synthesised by appropriate alkylation of the thioketal of ethyl laevulinate.

d: synthesised by alkylation of bis(phenylthio)methane with epichlorohydrin.

e: all compounds gave satisfactory spectroscopic data.

bromide or titanium tetrachloride[14] in a combination sequence of alkylation could provide an alternative to other Lewis acid promoted alkylations of thioketals[15a] and thioacetals[15b].

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