

A MILD AND CONVENIENT PREPARATION OF SULFENYL CHLORIDES FROM THIOLACETATES

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Summary: Sulfenyl chlorides are obtained easily and in good yields through the reaction of thiolesters and sulfuryl chloride.

In the course of our studies on the reaction of thiolacetates with sulfuryl chloride in the presence of acetic anhydride, which affords sulfinyl chlorides in high yields,¹ we have found that simple addition to thiol esters of SO_2Cl_2 (in equimolar amount, rather than in a two-fold excess) leads smoothly and cleanly to the corresponding sulfenyl chlorides.²



Reactions can be carried out either in CCl_4 solution or in the absence of solvent. As a general rule, aliphatic thiolacetates were best treated in solution, while the less reactive aryl thiolacetates gave quite satisfactory results when treated with neat SO_2Cl_2 .

^1H n.m.r. spectroscopy was used routinely to follow the progress of the reaction by monitoring the decrease of the CH_3 signal of the thiolacetates and the increase of the signal of the acetyl chloride product.

Sulfenyl chlorides were isolated from the reaction mixture by removing CH_3COCl (and the solvent, if present) by careful rotaevaporation of the reaction mixture at 0°C . Identification of the sulfenyl chlorides was carried out through their reaction with cyclohexene and/or phthalimide (see footnotes g, h, i to the Table for details). Unless otherwise stated, yields reported in the Table are referred to the isolated cyclohexene adducts or phthalimido derivatives and therefore represent a lower limit to the actual yield of sulfenyl chlorides. Owing to the remarkable volatility of methanesulfenyl chloride,³ the yield was assessed by ^1H n.m.r. spectroscopy, by converting it into methyl disulfide without isolation from the reaction solution (see footnote k to the Table).

Generally, formation of by-products was not observed during the reaction, the only exception being t-butyl thiolacetate, which gave rise to a considerable (c.a. 50%) amount of t-butyl chloride, together with the expected t-butylsulfenyl chloride.

We would like to point out that the advantages of the use of thiolesters and SO_2Cl_2 , as was indicated previously,¹ are also valid in the present case

(e.g. facile transfer of chiral centres to sulfenyl chlorides from alcohols through the easily accessible alkyl thioacetates;⁴ avoiding the handling of chlorine, etc.).

Considerable attention has been focused on the synthesis and utility of sulfenyl chlorides in recent years.^{5,6} We believe that the present reaction is useful extension to the methods already available for the synthesis of sulfenyl chlorides (mainly, chlorolysis of disulfides and thiols).⁵

TABLE^a

R(Ar)	Reaction time	Identification method ^b	% Yield
CH ₃ ^c	1 h	M.D.	k
n-C ₄ H ₉ ^c	2 h	C.A. + P.D. ⁱ	80
s-C ₄ H ₉ ^c	2 h	C.A. + P.D. ⁱ	70
t-C ₄ H ₉ ^c	1 h	-	c.a. 50 ^f
C ₆ H ₅	e	C.A. ^h	80 ^l
o-CH ₃ C ₆ H ₄ ^d	e	P.D. ^g	92
C ₆ H ₅ CH ₂ ^d	e	C.A. ^h + P.D. ⁱ	80
p-NO ₂ C ₆ H ₄ ^d	15 h	C.A.	j

a: Thiolester 0.5 g; SO₂Cl₂ 1 equiv., unless otherwise stated. b: Abbreviations: M.D.: methyl disulfide; C.A.: cyclohexene adduct; P.D.: phthalimido derivative. c: CCl₄ was employed as solvent, room temperature. d: Solvent absent, 0°C. e: No substrate was present at the end of the addition of SO₂Cl₂. f: Formation of *t*-butyl chloride and of *t*-butylsulfenyl chloride in similar amount was observed. g: The unknown phthalimido derivative gave satisfactory elemental and spectroscopic analyses. h: ¹H n.m.r. spectra of the cyclohexene adducts corresponded to those reported by M.Uchino and M.Sekiya, *Chem. Pharm. Bull.*, **28**, 126 (1980). i: M.p. values matched with those reported for the same derivatives by M.Behforouz and J.E.Kerwood, *J. Org. Chem.*, **34**, 51 (1969). j: Reaction run on ¹H n.m.r. scale. The yield of *p*-nitrobenzenesulfenyl chloride (identified as its cyclohexene adduct) was almost quantitative. k: Methanesulfenyl chloride was converted into methyl disulfide by adding an equivalent amount of methyl thioacetate to the reaction mixture according to I.B.Douglass, *J. Org. Chem.*, **24**, 2004 (1959). The yield (assessed by ¹H n.m.r. spectroscopy) was virtually quantitative. l: Yield based on the cyclohexene adduct.

References and notes

- 1) S. Thea, G. Cevasco, *Tetrahedron Lett.* **28**, 5193 (1987).
- 2) Perusal of the literature revealed that there are only two precedents to this reaction: W.H. Mueller, M. Dines, *J. Het. Chem.* **6**, 627 (1969); T.P. Vasil'eva, M.G. Lin'kova, O.V. Kil'di sheva, I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.* **209**, (1973) (*Chem. Abstr.* **78**, 123945e (1973)).
- 3) E. Schneider, *Chem. Ber.* **84**, 911 (1951).
- 4) R.P. Volante, *Tetrahedron Lett.* **22**, 3119 (1981).
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- 6) Y.C. Aggarwal, S. Warren, *Tetrahedron Lett.* **27**, 101 (1986); E.M. Gordon, M.A. Ondetti, J. Pluscec, C.M. Cimarusti, D.P. Bonner, R.B. Sykes, *J. Amer. Chem. Soc.* **104**, 6053 (1982), and references cited therein.

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