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A FACILE SYNTHESIS OF SULFINYL CHLORIDES FROM THIOLACETATES

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Summary: Alkyl and aryl thiolacetates are converted smoothly into sulfinyl chlorides by sulfuryl chloride in the presence of acetic anhydride.

Although sulfinyl chlorides are the key intermediates in the synthesis of a number of different sulfinyl derivatives (e.g. sulfinate esters, sulfinamides etc.),[1] methods currently available for their synthesis suffer from some drawbacks.[2] The appearance in the recent literature of reports suggesting the use of sulfuryl chloride instead of gaseous chlorine in the conversion of disulfides[3] and thiols[4] into sulfinyl chlorides prompts us to disclose our own results in this field.

We have found that alkyl and aryl thiolacetates are transformed into the corresponding sulfinyl chlorides in high yields through the reaction with sulfuryl chloride in the presence of acetic anhydride according to the following equation:

$$\text{(Ar)R-S-Ac} + \text{Ac}_2\text{O} + 2\text{SO}_2\text{Cl}_2 \longrightarrow \text{(Ar)R-SO-Cl} + 3\text{AcCl} + 2\text{SO}_2$$

Results are shown in the Table. Reaction progress was easily monitored by ^{1}H n.m.r. spectroscopy (by following the appearance of the AcCl signal and the disappearance of the Ac_2O signal) which showed that a clean, quantitative reaction took place in most cases. The only exceptions were t-butyl and allyl thiolacetates, which did not yield the corresponding sulfinyl chlorides. ^{1}H n.m.r., i.r. and elemental analysis data were consistent with the proposed structures.

The main advantages of the present method are:

i) The sole reaction by-products are SO_2 and acetyl chloride. The disadvantage of other methods represented by the production of large volumes of gaseous HCl is thus avoided.

ii) Since alkyl thiolacetates can be obtained directly from alcohols in a highly efficient and stereoselective way,[5] the unpleasant manipulation of thiols can be often avoided. Furthermore, non-racemic sulfinyl chlorides containing chiral centres in the alkyl group should be obtained with equal ease, the only limit being the availability of the starting chiral alcohol. Only few optically active thiols or disulfides are commercial products, while a much larger number of optically active alcohols are commercially available.

TABLE

R(Ar)	Reaction time (h)[a]	Yield %[b]	b.p.(°C) /mm Hg
C_6H_5-	8	89	71-73/1.5[c]
o-$CH_3C_6H_4$-	26	92	96-98/3[d]
$CH_3(CH_2)_3$-	0.5	86	76-77/7[e]
$C_2H_5CHCH_3$	0.5	94	f
-$(CH_2)_3$-	1.5	94	f
$CH_3(CH_2)_{11}$-	1	97	f,g
CH_2=$CHCH_2$-		h	
$(CH_3)_3C$-		h	

a: Time required for the Ac_2O peak to disappear from the ^1H n.m.r. spectrum of the reaction mixture. b: Based on the isolated material. c: Lit 71-72/1.5 (I.B. Douglass *et al.*, *J. Org. Chem.* **26**, 1996 (1971)). d: Lit. 97-98/3 (E.S. Levchenko, N.Y. Derkach, A.V. Kirsanov, *Zhur. Obshchei Khim.* **31**, 1971 (1961)). e:Lit. 76/7 (I.B. Douglass *et al.*, *J. Org. Chem.* **22**, 536 (1957)). f: Product identified as the anilide (^1H n.m.r. and i.r. spectroscopy). g: m.p. 78-80°C; lit. 78-80°C (M. Uchino, K. Suzuki, M. Sekiya, *Chem. Pharm. Bull.* **27**, 1199 (1979)). h: No sulfinyl chloride was formed over a 24 h period.

A typical experiment is described below.

Dodecanesulfinyl chloride.

Sulfuryl chloride (2.7 g, 20 mmol) was added dropwise to an efficiently stirred mixture of dodecyl thiolacetate (2.24 g, 10 mmol) and acetic anhydride (1.08 g, 10 mmol) at -10°C over a period of 30 min. Stirring was continued for additional 30 min at the same temperature. During the addition the colour became yellow at first, then it turned to deep orange, and finally to pale yellow. Removal of acetyl chloride under reduced pressure at room temperature left dodecanesulfinyl chloride (2.4 g, 97% yield)in a virtually pure state, as judged from ^1H n.m.r. spectroscopy. Conversion of the sulfinyl chloride to the anilide was accomplished through standard procedure.

We are currently investigating both the mechanistic and stereochemical aspects of this reaction.

References and notes

1) E. Krauthausen in 'Houben-Weil's Methoden der organische Chemie,' E11 (1), 638 (1985).
2) The most commonly used methods for the synthesis of sulfinyl chlorides involve treatment with thionyl chloride of sulfinic acids or sulfinate salts (which are generally unavailable as commercial products) or treatment of a stoicheiometric mixture of disulfides or thiol esters and acetic acid or anhydride with chlorine (which is difficult to measure and to handle). For a review see: M. Kee, I.B. Douglass, *Org. Prep. Proc.* 2, 235 (1970).
3) J. Youn, R. Herrmann, *Tetrahedron Lett.* 27, 1493 (1986).
4) J. Youn, R. Herrmann, *Synthesis* 72, (1987).
5) R.P. Volante, *Tetrahedron Lett.* 22, 3119 (1981).

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