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Sulfinyl Chlorides Through the Oxidative Chlorination of Sulfenyl Derivatives with Trimethylsilyl Acetate/Sulfuryl Chloride System

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SULFINYL CHLORIDES THROUGH THE OXIDATIVE CHLORINATION OF SULFENYL DERIVATIVES WITH TRIMETHYLSILYL ACETATE/SULFURYL CHLORIDE SYSTEM*

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Abstract: A new and useful procedure for the synthesis of sulfinyl chlorides is described involving a combined action of trimethylsilyl acetate and sulfuryl chloride as a oxidative chlorination system on sulfenyl derivatives.

Sulfinyl chlorides are widely used as key substrates for the preparation of racemic and optically active sulfinyl derivatives such as sulfinates, thiosulfinates, sulfinamides and sulfoxides¹. Among methods which have been used for their preparation the most commonly used synthesis is based on the oxidative chlorination of sulfenyl derivatives in the presence of acetic acid or acetic

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anhydride^{1b}. The original procedure developed as early as 1961 by Douglass and coworkers² utilized chlorine as the chlorination agent. In 1978 Schenk and Müller³ reported a very useful modification of this procedure in which chlorine was replaced by sulfuryl chloride. It should be noted that this report disclosed only in the experimental part of the Schenk's paper remained unnoticed and after 8 years another authors⁴ have rediscovered this modification.

The main drawback of this modification constitutes the relatively long reaction time. Thus, for example, conversion of arenethiols into the corresponding sulfinyl chlorides is accomplished only after 16 hours at room temperature⁵.

Here we would like to report a new useful and convenient modification of this procedure which allows more rapid conversion of sulfenyl derivatives into the corresponding sulfinyl chlorides. It is based on the use of trimethylsilyl acetate⁶ which serves simultaneously as the oxygen donor and the chloride anion acceptor. These conversions, which are described by the general equations 1 and 2, occur at room temperature within minutes for aliphatic derivatives 1 and take less that 5 hr in the case of arenethiols. The yields of the crude products are quantitative $(^{1}H-NMR \text{ analysis})$ and the pure sulfinyl chlorides <u>2</u> are isolated in yields exceeding 80% (see Table 1) by simple distillation of the residue left after removing highly volatile the by-products.^{8,10} Only in the case of benzyl mercaptane <u>li</u> the corresponding sulfinyl chloride 2f is formed in ~50% yield and the presence of three other products is indicated by the ¹H-NMR spectrum of the crude reaction mixture.



Fig.1. ¹H-NMR spectrum of the crude reaction product between t-butyl mercaptane and trimethylsilyl acetate/sulfuryl chloride system.

When this procedure is applied for t-butyl mercaptane, the ¹H-NMR spectrum of the crude reaction product (Fig.1) clearly indicates that it has the structure of the mixed sulfenyl-carboxylic anhydride <u>3</u>.

This anhydride was found to be relatively stable in the reaction medium. However all attempts to isolate it were

Table 1. Preparation of Sulfinyl Chlorides, RS(O)Cl-2; by the Oxidative Chlorination of Sulfenyl Derivatives, RSX-1 with Trimethylsilyl Acetate and Sulfuryl Chloride

| Sul | fenyl Derivat | ive | | | | |
|------------|------------------------------------|-------|----------|---------|--------------------|-----------|
| No | R | x | <u>2</u> | Time[h] | Yield[%] | B.p. |
| | | | | | ¹ H-NMR | (°C/mmHg) |
| | | | | | (isolated) | |
| la | Me | SMe | a | 0.5 | 100 | |
| 1b | n-Pr | н | b | 0.5 | >95 | |
| 1c | i-Pr | н | c | 0.5 | 100 | |
| | | | | | (80) | 67-68/20 |
| 1d | i-Pr | Si-Pr | C | 0.5 | 100 | |
| le | n-Bu | н | d | 2 | 100 | |
| | | | | | (83) | 84-86/20 |
| 1f | n-Bu | MeCO | d | 1 | 100 | |
| 1g | n-C ₂₀ H ₄₁ | н | e | 1 | 100 | |
| lh | PhCH ₂ | н | f | | ~50 | |
| 1 i | Ph | н | à | 5 | >95 | |
| | | | | | (91) | 69-70/0.1 |
| 1j | p-Tol | н | h | 4 | 100 | |
| | | | | | (91) | 70-71/0.1 |
| 1k | pMeO-C ₆ H ₄ | н | i | 4 | 100 | |

SULFINYL CHLORIDES

unsuccessful and led to its rapid decomposition. For this reason the anhydride $\underline{3}$, which most probably is formed according to the general equation 3, could not be fully analyzed at the moment.

t-BuSH + MeCO₂SiMe₃ + SO₂Cl₂
$$\xrightarrow{}$$
 $\frac{3}{}$ (3)
+ SO₂ + HCl

The above discussed observations made on the reaction course with either benzyl or t-butyl mercaptane clearly indicate that the results reported earlier^{4a} should be again checked.

Experimental

General experimental procedure: To a mixture of equimolar amounts of the sulfenyl derivative $\underline{1}$ and trimethylsilyl acetate chilled to a 0°C two equivalent of sulfuryl chloride (for mercaptans) or three equivalent of sulfuryl chloride (for disulfides) were added dropwise with stirring. After addition had been completed, the reaction mixture was allowed to reach room temperature and was analysed by ¹H-NMR spectroscopy after appropriate time. After removing the volatile by-products the residue was distilled to give the pure sulfinyl chlorides <u>2</u> in yields given in Table 1.

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- According to ref. 4a these reactions were finished after 4 hr.
- This compounds is commercialy available (Aldrich, Fluka). It can also be conveniently prepared by the silylation of acetic acid⁷.
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- 8. All sulfinyl chlorides exhibited satisfactory ${}^{1}H-NMR$ data. For example the spectrum of isopropylsulfinyl chloride <u>2c</u>

shows the magnetic nonequivalence of the geminal methyl groups⁹. Structures of some of them ($\underline{2d}$ and $\underline{2h}$) were further confirmed by the conversion into the corresponding O-methyl n-butanesulfinate and O-methyl p-toluenesulfinate.

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