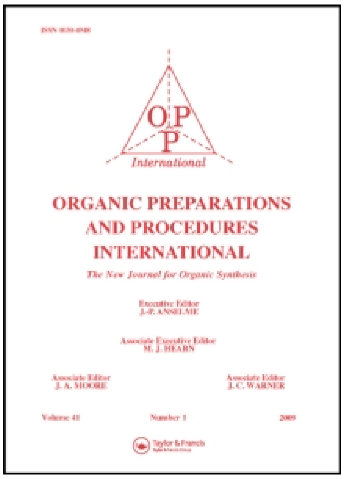
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

THE SYNTHESIS OF SULFINYL CHLORIDES. A REVIEW

Moh-Lian Kee[a]; Irwin B. Douglass[a]
[a] Department of Chemistry, University of Maine, Orono, Maine

To cite this Article Kee, Moh-Lian and Douglass, Irwin B.(1970) 'THE SYNTHESIS OF SULFINYL CHLORIDES. A REVIEW', Organic Preparations and Procedures International, 2: 3, 235 — 244
To link to this Article: DOI: 10.1080/00304947009458665
URL: http://dx.doi.org/10.1080/00304947009458665

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ORGANIC PREPARATIONS AND PROCEDURES 2(3), 235-244 (1970)

THE SYNTHESIS OF SULFINYL CHLORIDES. A REVIEW.

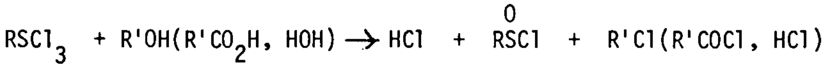
Moh-Lian Kee and Irwin B. Douglass [1]

Department of Chemistry
University of Maine
Orono, Maine 04473

Downloaded At: 13:52 27 January 2011

Previous reports from this laboratory have indicated that sulfinyl chlorides can be prepared by a variety of methods: (1) by the solvolysis of organosulfur trichloride, $RSCl_3$[2], (2) by the action of chlorine on a stoichiometric mixture of disulfide and glacial acetic acid[3], or by an even better method, (3) the action of chlorine on a mixture of disulfide and acetic anhydride[4].

In method 1, hydroxylic solvents (water, alcohols or carboxylic acids) react with organosulfur trichlorides to form hydrogen chloride, a sulfinyl chloride, and a chlorinated product. (Equation 1)



$$RSCl_3 + R'OH(R'CO_2H, HOH) \rightarrow HCl + R\overset{O}{S}Cl + R'Cl(R'COCl, HCl) \qquad (1)$$

The greatest difficulty with this method involves isolating the extremely labile organosulfur trichlorides.

In method 2, the actual isolation of the organosulfur trichloride is avoided. In fact, one can only assume that it is formed as an intermediate in the reaction. Apparently, it solvolyzes as soon as formed and never accumulates in sufficient concentration to form crystals. The over-all reaction is shown in Equation 2.

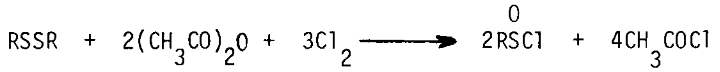
Copyright © 1970 by Marcel Dekker, Inc.

$$RSSR + 2CH_3COOH + 3Cl_2 \longrightarrow 2HCl + 2CH_3COCl + 2R\overset{O}{S}Cl \qquad (2)$$

Carboxylic acids are the only hydroxylic solvents which can be employed in method 2. Chlorination of a mixture of water and a disulfide results in the formation of either a thiolsulfonate, RSO_2SR, or a sulfonyl chloride, RSO_2Cl. The reaction can follow a number of pathways as illustrated in Figure 1. All of the steps indicated have been fully substantiated by isolated experiments.[5-8]

When a mixture of an alcohol and a disulfide is chlorinated, the product is a mixture of a sulfinyl chloride and a sulfonyl chloride with an alkyl chloride being a by-product. Figure 2 shows the various reactions which may be taking place in the reaction mixture. Again, all of the postulated steps have been verified by individual experiments.[5-9]

A problem associated with both methods 1 and 2 is the disposal of the large volume of hydrogen chloride formed in the reactions. Method 3 eliminates this difficulty since no gaseous products are formed. (Equation 3)



$$RSSR + 2(CH_3CO)_2O + 3Cl_2 \longrightarrow 2R\overset{O}{S}Cl + 4CH_3COCl \qquad (3)$$

The reaction is readily followed visually since the initial reaction of chlorine with the disulfide produces a highly colored sulfenyl chloride. When the reaction has been completed, the color has disappeared or has reached a minimum.

In both methods 2 and 3, it is extremely important that the disulfide and the acetic acid or acetic anhydride be present in stoichiometric proportions. An excess of disulfide leads at the end of the reaction to the presence of sulfenyl chloride or organosulfur trichloride in the reaction mixture. Both of these products would decompose during work-up and would contaminate the product with colored material.

Downloaded At: 13:52 27 January 2011

FIG. 1

The Aqueous Chlorination of Methyl Disulfide

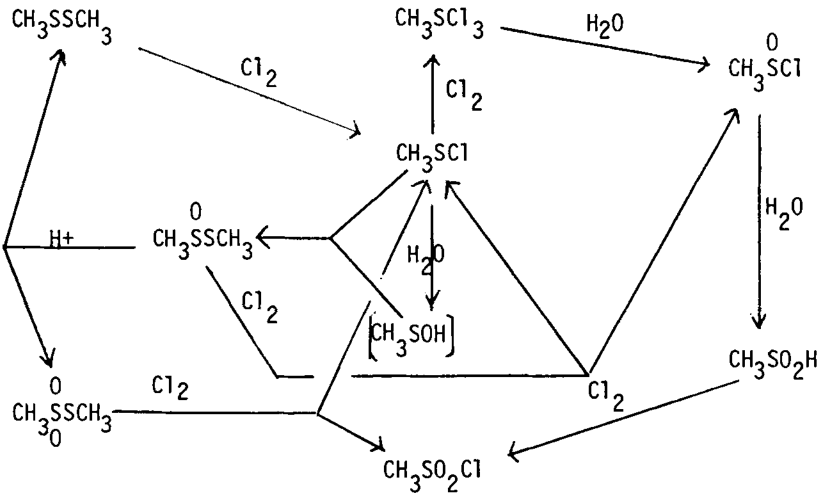
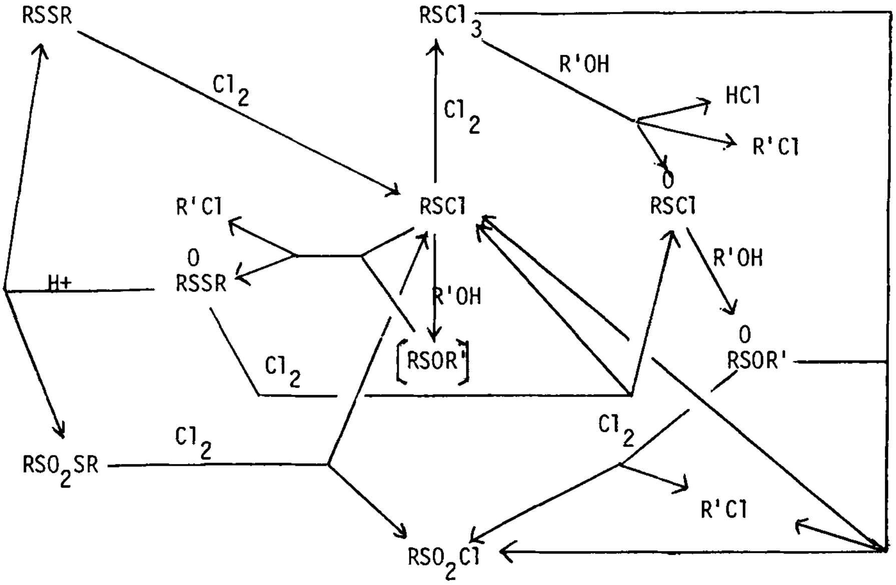


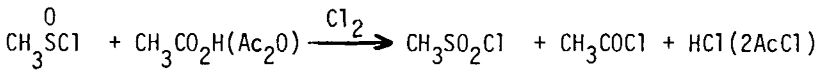
FIG. 2

The Alcoholic Chlorination of a Disulfide



Downloaded At: 13:52 27 January 2011

An excess of the acid or anhydride would cause problems because, if chlorine was also used in excess, some of the sulfinyl chloride would be converted to the sulfonyl chloride. (Equation 4)



$$CH_3\overset{O}{S}Cl + CH_3CO_2H(Ac_2O) \xrightarrow{Cl_2} CH_3SO_2Cl + CH_3COCl + HCl(2AcCl) \qquad (4)$$

If the chlorine was not in excess, the unchanged acid or anhydride would be difficult to remove from the product.

None of the methods work with all types of mercaptans or disulfides. In some compounds the action of chlorine cleaves the carbon-sulfur rather than the sulfur-sulfur bond and the yield of sulfinyl chloride has been poor. Thus, benzyl disulfide gives only a poor yield of α-toluenesulfinyl chloride, and no sulfinyl chlorides can be obtained by these methods from dithiodiacetic acid or from t-butyl disulfide.

In extending method 3, we have observed that the chlorination of an alkyl or aryl thiolester in the presence of acetic anhydride also forms sulfinyl chlorides in high yield. By this method we have been able to prepare methane-, ethane-, 2-propane-, benzene- and α-toluenesulfinyl chlorides.

Table I lists the yields of sulfinyl chlorides from thiolesters. Results from method 3 using disulfides are also listed for comparison. In spite of the nearly quantitative yields of sulfinyl chlorides from methyl thiolacetate, S,S'-dimethyl dithiocarbonate, ethyl thiolacetate, S,S'-diethyl dithiocarbonate, 2-propyl thiolacetate, phenyl thiolacetate, and benzyl thiolacetate, attempts to prepare 2-methyl-2-propanesulfinyl chloride from *t*-butyl thiolacetate and from *t*-butyl thiolchloroacetate were unsuccessful. In both cases t-butyl chloride was found to be the major product indicating cleavage of the bond between the alkyl group and the sulfur rather than the bond between the carbonyl group and sulfur.

Downloaded At: 13:52 27 January 2011

TABLE I

Preparation of Sulfinyl Chlorides

Sulfinyl Chloride Prepared	Reagents: Thiolester (moles)	Reagents: Acetic Anhydride (moles)	% Yields	% Yields of Sulfinyl Chloride by method 3 from Disulfides
CH_3SOCl	CH_3COSCH_3 0.25	0.25	82.9, 81.7	83-86
CH_3SOCl	$CO(SCH_3)_2$ 0.10	0.20	79.7, 80.6	
CH_3CH_2SOCl	$CH_3COSCH_2CH_3$ 0.25	0.25	90.0, 91.6	86
CH_3CH_2SOCl	$CO(SCH_2CH_3)_2$ 0.05	0.10	91.5, 87.8	
$(CH_3)_2CHSOCl$	$CH_3COSCH(CH_3)_2$ 0.05	0.05	73.0, 69.5	
C_6H_5SOCl	$CH_3COSC_6H_5$ 0.20	0.20	99.1, 98.1	99
$C_6H_5CH_2SOCl$	$CH_3COSCH_2C_6H_5$ 0.10	0.10	98.5, 94.6	

In carrying out a preparation, an excess of thiolester or acetic anhydride should be avoided. Any excess of the thiolester, like an excess of disulfide in methods 2 and 3, will lead to an excess of the organosulfur trichloride which will undergo a spontaneous decomposition during work-up. Such decomposition results in a complex mixture containing chloromethane-

Downloaded At: 13:52 27 January 2011

sulfenyl chloride, methanesulfenyl chloride and numerous other compounds.[10] An excess of acetic anhydride, on the other hand, will react with sulfinyl chloride in the presence of chlorine to form the sulfonyl chloride and acetyl chloride, as discussed above. (Equation 4)

As pointed out previously,[4] due to the tendency of the aromatic sulfinyl chlorides to decompose, they should not be distilled unless the distillation is carried out at a low pressure (<2 mm). There are no indications, however, that any hazard exists if distillation is avoided and the preparation is carried out at moderate temperature. Alkanesulfinyl chlorides should not be stored for long periods in sealed containers at room temperature.[11] Disproportionation of the sulfinyl chloride (Equation 5) and subsequent decomposition of the alkanesulfenyl chloride may develop

$$2\ RSOCl \longrightarrow RSCl + RSO_2Cl \tag{5}$$

high pressure within the container. Under refrigeration, however, alkanesulfinyl chlorides can be stored for several months without appreciable decomposition.

Downloaded At: 13:52 27 January 2011

EXPERIMENTAL

Preparation of Methanesulfinyl Chloride from Methyl Thiolacetate

Methyl thiolacetate (22.5 g, 0.25 mole) and acetic anhydride (25.5 g, 0.25 mole) were placed in a three-neck flask fitted with a chlorine inlet tube, stirrer, thermometer, and gas outlet tube connected to a calcium chloride tube. The reaction mixture was cooled to -10° in a Dry Ice bath and chlorine was passed in at such a rate that the temperature was held between 0° and -10°. At first the color of the mixture turned yellow, then reddish as methanesulfenyl chloride formed. On continued passage of chlorine the color faded and the solution then became colorless when 0.75 mole of chlorine had been added. At this point the reaction mixture was transferred to a distilling flask attached to a short fractionating column, and distilled under the reduced pressure of a water pump. At 24 mm the mixture boiled below 0° and held near this temperature until most of the acetyl chloride had distilled and collected in the Dry Ice trap. The pot temperature then gradually rose and finally methanesulfinyl chloride distilled at 55-56° (23 mm) as a colorless liquid with n_D^{25} 1.5024 (lit.[1] n_D^{25} 1.5038). Its infrared spectrum was identical to that of an authentic sample prepared by the method of Douglass and Norton.[4] The yield was 19.6 - 19.8 g (81.7 - 82.9%).

This procedure, with only minor variations, was used in the preparation of sulfinyl chloride from S, S'-dimethyl dithiocarbonate, ethyl thiolacetate, S,S'-diethyl dithiocarbonate, 2-propyl thiolacetate, reported in Table I.

TABLE II

Chemical Shifts and Coupling Constants of Some Sulfinyl Chlorides[a]

	NMR Data	
Sulfinyl Chloride	Chemical Shift[b] ppm	Coupling Constant cps
Methanesulfinyl Chloride	3.37 (s)	
Ethanesulfinyl Chloride	1.49 (t) 3.36 (q)	7 7
2-Propanesulfinyl Chloride	1.29 (d) 3.30 (h)	6.5 6.5
Benzenesulfinyl Chloride	7.55 ± 0.25 (m)	
α-Toluenesulfinyl Chloride	4.58 (s) 7.29 (m)	

a Nmr spectra were obtained by the use of a Varian Associates Model A-60 spectrometer.

b Down field from internal tetramethylsilane

s	Singlet	q	Quartet
d	Doublet	h	Heptuplet
t	Triplet	m	Multiplet

Downloaded At: 13:52 27 January 2011

Preparation of Benzenesulfinyl Chloride from Phenyl Thiolacetate

A mixture of phenyl thiolacetate (30.4 g, 0.2 mole) and acetic anhydride (20.4 g, 0.2 mole) was chlorinated at -10° to 0°. As chlorine was added, the colorless mixture first changed to yellow, then to a reddish color and, after about 45 minutes of reaction, to pale yellow. The reaction mixture never became completely colorless as more chlorine was added. After removal of the acetyl chloride and excess chlorine at reduced pressure (26 mm) the residue in the pot was heated to 80° and held at this temperature until boiling ceased. The liquid remaining in the pot was identified as benzenesulfinyl chloride by comparing its infrared and nmr spectra to those of an authentic specimen synthesized according to the method of Douglass and Norton.[4] The liquid, without further purification, had n_D^{25} 1.6036 (lit.[2] n_D^{25} 1.6062). The yield was 31.5 - 31.8 g (98.1 - 99.1%).

Preparation of α-Toluenesulfenyl Chloride from Benzyl Thiolacetate

A mixture of benzyl thiolacetate (10.6 g, 0.1 mole) and acetic anhydride (10.2 g, 0.1 mole) was chlorinated at 0° to -10° with 14.2 g, 0.2 mole of Cl_2. Nmr analysis of the resulting mixture, before removal of any acetyl chloride, indicated the formation of 25 mole % of α-toluenesulfinyl chloride (a singlet at δ4.58 ppm and a multiplet at ca. δ7.29 ppm). Removal of acetyl chloride by distillation at 20 mm and heating to 60° led to a pale yellow liquid with refractive index of n_D^{25} 1.5872. At this point, nmr analysis indicated that acetyl chloride had been removed and the residual liquid gave only the nmr δ signals indicated above. An infrared spectrum showed a strong absorption at 1140 cm^{-1}. The yield was 16.5 - 17.2 g (94.6 - 98.5%). Heating of the liquid to 100° led to decomposition into benzyl chloride and sulfur dioxide. The identity of the crude α-toluenesulfinyl chloride was established by causing a portion to react

Downloaded At: 13:52 27 January 2011

with dilute sodium bicarbonate. The resulting solution was divided and one portion boiled with benzyl chloride, yielding dibenzyl sulfone which melted at 150-151° and unchanged when mixed with an authentic sample. The other portion of the solution was acidified and treated with chlorine. Solid α-toluenesulfonyl chloride separated which melted at 91-92° and unchanged when mixed with a sample prepared by the aqueous chlorination of benzyl isothiourea hydrochloride according to the method of Johnson and Sprague.[12]

Attempts to Prepare 2-Methyl-2-Propanesulfinyl Chloride from t-Butyl Thiolacetate and t-Butyl Thiolchloroacetate

When a mixture of *t*-butyl thiolacetate and acetic anhydride (0.1 mole of each) was chlorinated at 0° to -10°, no sulfinyl chloride was formed. A similar result was obtained when a mixture of *t*-butyl thiolchloroacetate and acetic anhydride was chlorinated. In each case nmr analysis indicated that *t*-butyl chloride was formed in high yield.

ACKNOWLEDGMENT: Financial assistance from the National Air Pollution Control Administration, United States Public Health Service under Grant No. AP-00383 is gratefully acknowledged.

Downloaded At: 13:52 27 January 2011

REFERENCES

1. To whom inquiries may be directed.
2. I. B. Douglass and D. R. Poole, J. Org. Chem., 22, 536 (1957).
3. I. B. Douglass and B. S. Farah, Ibid., 23, 330 (1958); Org. Syntheses, 40, 62 (1961).
4. I. B. Douglass and R. V. Norton, Ibid., 33, 2104 (1968).
5. I. B. Douglass, Ibid., 24, 2004 (1959).
6. I. B. Douglass and B. S. Farah, Ibid., 24, 973 (1959).
7. C. J. M. Stirling, J. Chem. Soc., 1957, 3597.
8. R. V. Norton, Ph.D. Thesis, Univ. of Maine, 1967.

9. I. B. Douglass, J. Org. Chem. 30, 633 (1965).

10. I. B. Douglass, R. V. Norton, R. L. Weichman and R. B. Clarkson, Ibid., 34, 1803 (1969).

11. I. B. Douglass and D. A. Koop, Ibid., 29, 951 (1964).

12. T. B. Johnson and J. M. Sprague, J. Am. Chem. Soc., 58, 1348 (1936).

(Received January 15, 1970)

Downloaded At: 13:52 27 January 2011