

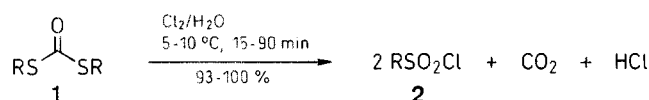
A New Application of *S,S*-Dialkyl Dithiocarbonates. A Convenient Synthesis of Alkanesulfonyl Chlorides

Margherita Barbero, Silvano Cadamuro, Iacopo Degani,* Rita Fochi, Valeria Regondi

Istituto di Chimica Organica dell'Università, Via Pietro Giuria 7, I-10125 Torino, Italy

An advantageous procedure for the synthesis of alkanesulfonyl chlorides **2** in 93–100% yield, by aqueous chlorination of readily accessible *S,S*-dialkyl dithiocarbonates **1** is reported.

Alkanesulfonyl chlorides are an important class of compounds widely utilized as reagents or intermediates in organic synthesis.¹ They are also used for various industrial and agricultural applications,² especially as wetting, emulsifying, weed-killing, fungicidal, lubricating or tanning agents. There are several methods for the preparation of alkanesulfonyl chlorides,³ Reed's reaction and its modifications, however, can be excluded as it produces mixtures of alkanesulfonyl chlorides.⁴ Amongst these methods the more important involve the aqueous chlorination of thiols and disulfides. This is principally utilized in the large-scale preparation of methanesulfonyl chloride.⁵ Similarly, various sulfur compounds have also been converted to alkanesulfonyl chlorides, e.g., sulfides, thiocyanates, isothiuronium salts, Bunte salts, sulfenyl chlorides, thioesters, sulfinyl chlorides, thiolsulfonates, and sulfinic acids.¹ However, the procedures either involve difficulties connected with the preparation of starting materials, or unsatisfactory reaction yields. Thus limiting convenient access to alkanesulfonyl chlorides. In previous work we have shown that symmetrical *S,S*-dialkyl dithiocarbonates⁶ can easily be obtained by rearrangement of the corresponding *O,S*-dialkyl dithiocarbonates. The *S,S*-dialkyl dithiocarbonates can be used as a source for alkanethiols in both laboratory and industrial preparations.⁷



1, 2	R	1, 2	R
a	CH ₃	e	(CH ₂) ₁₁ CH ₃
b	CH ₂ CH ₃	f	(CH ₂) ₁₅ CH ₃
c	(CH ₂) ₃ CH ₃	g	(CH ₂) ₁₇ CH ₃
d	(CH ₂) ₇ CH ₃	h	CH ₂ Ph

Table. Sulfonyl Chlorides **2a–h** Prepared

Prod- uct	Reaction Time (min)	Yield ^a (%)	mp (°C) (solvent) ^b or bp (°C)/mbar	Lit. mp (°C) or bp (°C)/ mbar
2a	15	95	62–63.5/23	65/31 ⁹
2b	40	95	74–75/23	74/28 ⁹
2c	80	93	97–98/23	84/13 ¹⁰
2d	60	94	145–146/23	121–122/5 ¹¹
2e	60	~100	40–41 (PE)	39.4–41.6 ¹²
2f	60	~100	56.5–57.5 (PE)	57–58 ¹³
2g	60	~100	63–64 (PE)	64–64.2 ¹⁴
2h	90	96	91–92 (PE)	92–93 ¹⁴

^a Yield of pure isolated product.

^b PE = Petroleum ether (bp 40–70°C).

We report here the conversion of *S,S*-dialkyl dithiocarbonates **1** to alkanesulfonyl chlorides **2**, by the chlorination of **1** as an emulsion in water (Table).

The method is suitable for small scale preparations, and for industrial production due to its simplicity, availability of the starting materials, excellent yields, purity of the products, and low cost. All alkanesulfonyl chlorides have been identified by comparison of their bp, mp, ¹H-NMR and IR spectra with those of authentic samples of analytical purity.

S,S-Dialkyl Dithiocarbonates **1a–h** were prepared as previously reported.⁶

Ethanesulfonyl Chloride (2b); Typical Procedure:⁸

A small stream of Cl₂ is bubbled through a well-stirred and ice-cooled emulsion of *S,S*-diethyl dithiocarbonate (**1b**; 7.50 g, 0.05 mol) in water (~30 mL), at such a rate that the temperature can be controlled between 5–10°C. The reaction is stopped after about 40 min, by which time Cl₂ is no longer absorbed and an intense yellow color appears, the temperature remaining constant. The organic layer is separated, washed with cold water (3 × 5 mL) and dissolved in Et₂O (20 mL). The Et₂O solution is washed with cold 5% aq. NaHCO₃ (3 × 5 mL), water (3 × 5 mL), and then dried (Na₂SO₄). After evaporation of the solvent, the residue is distilled to give pure ethanesulfonyl chloride (**2b**); yield: 12.21 g (95%); bp 74–75°C/23 mbar (Lit.⁹ 74°C/28 mbar); purity > 99% (Table).

This work is supported by the National Research Council of Italy (CNR), Progetto Finalizzato „Chimica Fine e Secondaria.“

Received: May 10, 1989

- (1) Langler, R.F., Marini, Z.A., Spalding, E.S. *Can. J. Chem.* **1979**, *57*, 3193, and references therein.
March, J. *Advanced Organic Chemistry*, John Wiley & Sons, New York, 1985, p. 1340, and references therein.
- (2) Tinker, J.M., Fox, A.L. *US Patent* 2174507, E.I. du Pont de Nemours & Co.; *C.A.* **1940**, *34*, 8349.
Koch, H. *Ger. Offen.* 833808 (1952), Farbwerke Hoechst vorm Meister Lucius & Bruning; *C.A.* **1953**, *47*, 3336.
Olivannan, M.S., Nayudamma, Y. *J. Sci. Ind. Res.* **1969**, *28*, 293; *C.A.* **1969**, *71*, 114168.
Krawiecki, C., Majewski, J. *Przegl. Skorzany* **1984**, *39*, 34; *C.A.* **1984**, *101*, 74697.
- (3) Ref. 2b, pp. 202–214.
Russ, C.R., Douglass, I.B., in: *Sulfur in Organic and Inorganic Chemistry*, Senning, A. (ed.) Marcel Dekker, New York, 1971, Vol. 1, p. 246.
Weickmann, A., Zeller, K.P., in: *Houben-Weyl*, Muller, E., Bayer, O. (eds.), Vol. IV/1a, Georg Thieme Verlag, Stuttgart, 1981, p. 607, and references therein.
- (4) Reed, C.F., Horn, C.L. *US Patent* 2046090 (1936); *C.A.* **1936**, *30*, 5593.
Gilbert, E.E., in: *Sulfonation and Related Reactions*, Wiley-Interscience, New York, 1965, pp. 126–131, and references therein.
Pawlenko, S., in: *Houben-Weyl*, Klamann, D. (ed.), Vol. E 11, Georg Thieme Verlag, Stuttgart, 1985, p. 1067, and references therein.
- (5) Gongora, H., Tournier-Lasserve, J. *Eur. Pat. Appl. EP* 40 560 (1981), Societ  Nationale Elf Aquitaine S.A.; *C.A.* **1982**, *96*, 70776.
Guertin, R.M. *Ger. Offen.* 2225733 (1972), Pennwalt Corp.; *C.A.* **1973**, *78*, 71432.
- (6) Degani, I., Fochi, R., Regondi, V. *Synthesis* **1981**, 149, and references therein.
- (7) Degani, I., Fochi, R., Regondi, V. *Synthesis* **1983**, 630.
Degani, I., Fochi, R., Regondi, V. *Chem. & Ind.* **1986**, 671.
Cadamuro, S., Degani, I., Fochi, R., Regondi, V. *Synthesis* **1986**, 1073.
Degani, I., Fochi, R., Regondi, V. *Eur. Pat. Appl. EP* 63327 (1982), *US Patent* 4449004, Consiglio Nazionale delle Ricerche; *C.A.* **1983**, *98*, 160238.
- (8) The synthetic method reported herein was been patented: Barbero, M., Degani, I., Fochi, R., Regondi, V. *Eur. Pat. Appl. EP* 234249 (1987), *US Patent* 4743404 (1988), Consiglio Nazionale delle Ricerche; *C.A.* **1988**, *108*, 23697.
- (9) Foon, R., Hambly, A.N. *Austr. J. Chem.* **1962**, *15*, 668.
- (10) Voigt, D., Dagnac-Amans, P., Baldazzini, E. *Bull. Soc. Chim. Fr.* **1969**, 716.
- (11) Ziegler, C., Sprague, J.M. *J. Org. Chem.* **1951**, *16*, 621.
- (12) Geiseler, G., Asinger, F. *Chem. Ber.* **1956**, *89*, 1100.
- (13) King, J.F., Aslam, M. *Synthesis* **1980**, 285.
- (14) Rieche, A., Naumann, E. *J. Prakt. Chem.* **1959**, *9*, 108.