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An Alternative Method for the Synthesis of S-Methylmethanethiosulfonate

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Abstract

DMSO is converted to S-Methylmethanethiosulfonate in good yields in the presence of catalytic amount of $TiCl_4$. It provides the first example of conversion of DMSO to S-Methylmethanethiosulfonate catalysed / promoted by $TiCl_4$. The product has been characterised by ^{1}H- and ^{13}C-n.m.r. spectroscopy and mass spectrometry.

Keywords: DMSO; S-Methyl methanethiosulfonate; $TiCl^4$

Abbreviations: DMSO : dimethyl sulfoxide

Introduction

DMSO and other sulfoxides are widely used in organic synthesis [1-4]. The presence of metal complexes in such reactions often results in oxidation of sulfoxides and sometime it results even in activation of Carbon-Sulfur bond of sulfoxides giving unexpected products which might lead to confusion [5]. In a similar way, a reaction of DMSO in presence of $TiCl_4$ in 1,2-Dichloroethane resulted in the formation of S-Methylmethanethiosulfonate. S-Methylmethanethiosulfonate is a very useful sulfenylating reagent for organic synthesis as well as for biological applications [6-15]. Particularly, it is used for introduction of SCH_3 groups in aromatic rings and other organic compounds including biologically active molecules. In general, thiosulfonic S-esters are stable and reactive species; however their use has been limited by the lack of easy and practical preparations. A number of methods are known for the preparation of S-Methylmethanethiosulfonate which involves harmful toxic reagents or typical lengthy work-up which distract the interest of chemists [16-24]. Herein, we report a novel and very simple method for the synthesis of the title compound.

Results and Discussion

Conversion of DMSO (1) to S-methylmethanethiosulfonate (2) is attained selectively at reflux conditions in 1,2-dichloroethane in presence of $TiCl_4$ (Equation 1). The progress of the reactions is monitored by TLC and it takes 2-3 hrs for completion.

$$\underset{(\mathbf{1})}{2\ Me_2SO} \xrightarrow[\text{Reflux, 2-3 hrs}]{TiCl_4\text{, Solvent}} \underset{(\mathbf{2})}{MeSO_2SMe} \qquad \text{(Eq.1)}$$

During usual work up of the reaction some brownish impurities are developed which can be easily removed by short path distillation under vacuum and as a result a neat colorless liquid (2) is obtained in 79% yield. The ^{1}H NMR of this compound shows two peaks as singlet at 2.71 and 3.32 ppm corresponding to chemically two different methyl groups indicating that the two methyl groups are low field shifted compared to DMSO which shows a single peak at 2.62 ppm. Similarly, ^{13}C NMR spectrum of 2 shows two peaks at 18.2 and 48.8 ppm corresponding to two different methyl groups and non-decoupled 13C-nmr spectrum further shows two methyl carbon as quartet indicating the presence of three coupling protons on each carbon atoms. The fragmentation pattern of 2 obtained by EI (30 eV) shows major products corresponding to 126(M+), 111(CH_3SO_2S+), 79(CH_3SO_2+), 63(CH_3SO+), and 47(CH_3S+) respectively. The fragment (M= 63) is also generated in thermolysis of DMSO due to loss of methyl radical from the molecular ion [25].

Attempts will be made to explore the potential of S-Methylmethanethiosulfonate towards various organo-phosphorus compounds.

Experimental

Caution: This sulfenate should be handled carefully as it possesses a pungent smell and may cause vomiting and headache).

Synthesis of Compound (2): A mixture of DMSO (23.4 g, 0.30 mol) and $TiCl_4$ (0.190 g, 0.009 mol) in 100 mL of freshly distilled 1,2-dichloroethane was heated at reflux for 2-3 h. After completion of the reaction (marked by a single spot of S-methylmethanethiosulfonate on TLC), the reaction mixture was cooled to room temperature and then washed with water. The 1,2-dichloroethane solution was dried (anhydrous Na_2SO_4) and evaporated on a rotary evaporator to give a light brown liquid which became dark on exposure to air. This product 2 was distilled by short path distillation under vacuum (13.60 g, 70.6%; b.pt. 80-82 ºC/ 0.05 mmHg) as a neat colorless liquid. Calcd. Anal.: C, 19.03; H, 4.79; Found: C, 18.99; H, 4.78. ^1H NMR(300 MHz, $CDCl_3$) 2.71(s,3H), 3.32(s,3H); ^{13}C NMR(75 MHz, $CDCl_3$)18.2, 48.8; MS (EI, 30 eV)m/z= 126 (62%, M+), 111(10%, CH_3SO_2S+), 79(60%,CH_3SO_2+) 63 (61%, CH_3SO+), 47(100%,CH_3S+).

(P.S.: 1,2-Dichloroethane was used as freshly distilled. DMSO and $TiCl_4$ were used as received).

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