

reaction mixture was allowed to warm to room temperature and then heated at reflux. When the reduction was found to be incomplete by GC analysis after 6 h, an additional 10 mL (2.9 mmol) of the BMPA solution was added. The reaction mixture was then heated an additional 3 h and the reduction then was found to be complete. After addition of diethyl ether (100 mL) and careful quenching with saturated aqueous NaCl (20 mL) and 10% H₂SO₄ (30 mL), the phases were separated. The aqueous layer was washed with ether (2 × 100 mL), and the combined organic extracts were then washed with 2 N NaOH (2 × 15 mL), 2 N HCl (2 × 25 mL), and saturated aqueous NaCl (25 mL). After drying over Na₂SO₄, evaporation of the ether in vacuo gave 350 mg of *l*-perillaldehyde (78%; purity >99% by GC and GC-MS).

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Registry No. LiAlH₄, 16853-85-3; BMPA, 54709-78-3; citro-nellic acid, 502-47-6; perillic acid, 7694-45-3; tiglic acid, 80-59-1; hexadecanoic acid, 57-10-3; benzoic acid, 65-85-0; 1-naphthalenecarboxylic acid, 86-55-5; 3-furancarboxylic acid, 488-93-7; (+)-citronellal, 2385-77-5; hexadecanal, 629-80-1; perillal, 2111-75-3; tiglial, 497-03-0; benzaldehyde, 100-52-7; 1-naphthalenecarboxaldehyde, 66-77-3; 3-furancarboxaldehyde, 498-60-2.

A Novel, Useful, and Inexpensive Preparation of *S*-Methyl Methanesulfonothioate

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As part of a more general program for devising new synthetic procedures that are selective, efficient, mild, easy to run, and inexpensive, we report preparation of the title compound CH₃SSO₂CH₃. This sulfonate, which is available commercially, has many uses. Among these, introduction of SCH₃ groups in aromatic rings,^{1,2} thiomethylation of exposed activated C-H and S-H bonds in organic molecules and in proteins,³⁻⁵ and substitution by the SCH₃ group into the four- or the six-membered ring of cephalosporin antibiotics and into the four-membered ring of penicillin derivatives have been especially frequent in recent years.⁶⁻¹¹

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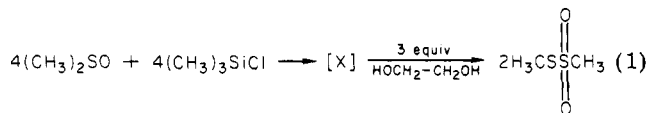
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Our preparation of this useful reagent improves upon previous methods¹¹⁻¹⁴ by requiring only inexpensive starting materials, by its easy implementation, and by its very good overall yield (80-85% isolated yield).

We have no indications yet on the mechanism of this intriguing reaction; optimization of the reaction conditions (heating temperature and duration, reactant ratios) is consistent with the following empirical equation



which corresponds to an 80% isolated yield, and we plan to make the appropriate experiments for studying it. We discovered it in serendipitous manner when preparing formaldehyde acetals from alcohols and chlorotrimethylsilane in the presence of Me₂SO.¹⁶ Subsequently, we found that using Me₂SO also as the solvent led to a much improved yield.

Experimental Section

In a 500-mL two-necked flask fitted with a magnetic stirrer, an addition funnel, and reflux condenser, both fitted with CaCl₂ drying tubes, 250 mL of Me₂SO was introduced with ice bath cooling during ca. 10 min. Chlorotrimethylsilane (0.64 mol) was then added as a rapid drip through the addition funnel. The reaction was slightly exothermic, and a white solid appeared. The mixture was stirred for 20 min while the temperature was maintained close to 0 °C, and 0.48 mol of ethylene glycol was added as a rapid drip through the addition funnel. The reaction mixture was allowed to warm to room temperature over a period of about 2 h. This mixture was heated at 60 °C (the solid redissolved) for 18 h, followed by 42 h at 110 °C. After the solution cooled to room temperature, it was poured into a mixture of 200 mL of water and 200 mL of methylene chloride. The organic layer was then extracted three times with water, dried over anhydrous MgSO₄, filtered, and concentrated. Distillation gave *S*-methylmethanesulfonothioate as a colorless oil: 32 g (80% isolated yield); bp 67-70 °C (0.4 mmHg) [lit.¹⁴ bp 122 °C (16 mm)]; ¹H NMR (CCl₄) δ 3.3 (s), 2.7 (s) (lit.¹⁵ δ 3.28, 2.69); IR (neat) 1305 (s, SO₂), 1130 (s, SO₂), 960 (s), 745 (s) cm⁻¹ (lit.¹⁴ 1310, 1130 cm⁻¹); MS, *m/e* 126 (M⁺, 100), 111 (M⁺ - Me, 7), 79 (M⁺ - SMe, 84). Anal. Calcd C, 19.04; H, 4.79. Found: C, 19.15; H, 4.98.

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Registry No. Me₂S=O, 67-68-5; Me₃SiCl, 75-77-4; HO(C-H₂)₂OH, 107-21-1; CH₃SSO₂CH₃, 2949-92-0.

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