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% H_2SO_4 (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 Na_2SO_4, 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. $LiAlH_4$, 16853-85-3; BMPA, 54709-78-3; citronellic 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; tiglal, 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 $CH_3SSO_2CH_3$. This sulfonate, which is available commercially, has may uses. Among these, introduction of SCH_3 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 SCH_3 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]

Our preparation of this useful reagent improves upon previous methods[11–14] 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

$$4(CH_3)_2SO + 4(CH_3)_3SiCl \longrightarrow [X] \xrightarrow[HOCH_2-CH_2OH]{3\ equiv} 2H_3CS\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}CH_3 \quad (1)$$

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 Me_2SO.[16] Subsequently, we found that using Me_2SO 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 $CaCl_2$ drying tubes, 250 mL of Me_2SO 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 $MgSO_4$, filtered, and concentrated. Distillation gave *S*-methyl-methanesulfonothioate 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 (CCl_4) δ 3.3 (s), 2.7 (s) (lit.[15] δ 3.28, 2.69); IR (neat) 1305 (s, SO_2), 1130 (s, SO_2), 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. $Me_2S{=}O$, 67-68-5; Me_3SiCl, 75-77-4; $HO(CH_2)_2OH$, 107-21-1; $CH_3SSO_2CH_3$, 2949-92-0.

(1) Bosscher, J. K.; Kraak, E. W. A.; Kloosterziel, H. *J. Chem. Soc. D* **1971**, *21*, 1365.
(2) Dunbar, J. E.; Harris, R. F.; McCarthy, J. R. U.S. Patent 3 847 927, 1972; *Chem. Abstr.* **1975**, *82*, 72796e.
(3) Ogura, K.; Itoh, H.; Morita, T.; Sanada, K.; Iida, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1216–20.
(4) Whitesides, G. M.; Lamotte, A. L.; Adalsteinsson, O.; Baddour, R. F.; Chmurny, A. C.; Colton, C. K.; Pollak, A. *J. Mol. Catal.* **1979**, *6*, 177–98.
(5) Smith, D. J.; Maggio, E. T., Kenyon, G. L. *Biochemistry* **1975**, *14*, 766–71.
(6) Applegate, H. E.; Cimarusti, C. M.; Dolfini, J. E.; Funke, P. T.; Koster, W. H.; Puar, M. S.; Slusarchyk, W. A.; Young, M. G. *J. Org. Chem.* **1979**, *44*, 811–18.
(7) Jen, T.; Frazee, J.; Hoover, J. R. E. *J. Org. Chem.* **1973**, *38*, 2857–9.
(8) Numata, M.; Yamaoka, M. Eur. Patent 6011, 1979; *Chem. Abstr.* **1980**, *93*, 46699h.
(9) Dolfini, J. E.; Slusarchyk, W. A.; Koster, W. H. Ger. Offen. 2 360 945, 1974; *Chem. Abstr.* **1974**, *81*, 77939t.
(10) Dolfini, J. E.; Slusarchyk, W. A.; Koster, W. H. U.S. Patent 3 868 365, 1975; *Chem. Abstr.* **1975**, *83*, 9273r.
(11) Slusarchyk, W. A.; Applegate, H. E.; Funke, P.; Koster, W.; Puar, M. S.; Young, M.; Dolfini, J. E. *J. Org. Chem.* **1973**, *38*, 943–50.
(12) Bentley, M. D.; Douglas, I. B.; Lacadie, J. A. *J. Org. Chem.* **1972**, *37*, 333–4.
(13) Backer, H. J. *Bull. Soc. Chim. Belg.* **1953**, *62*, 3–9.
(14) Palumbo, G.; Caputo, R. *Synthesis* **1981**, *11*, 888–90.
(15) Norton, R. V.; Beverly, G. M.; Douglas, I. B. *J. Org. Chem.* **1967**, *32*, 3645–7.
(16) Bal, B. S.; Pinnick, H. W. *J. Org. Chem.* **1979**, *44*, 3727–8.

0022-3263/84/1949-2281$01.50/0