

6-(Methylthio)hexanoic Acid (1) and **6-(Methylsulfinyl)hexanoic Acid (2)** were synthesized as described previously.²

Poly(ethylene glycol) Bis(6-(Methylthio)hexanoate) (4). A solution of PEG-2000 (10.0 g, 5.0 mmol), sulfide acid **1** (2.80 g, 17.5 mmol), and DMAP (0.21 g, 1.7 mmol) in dichloromethane (50 mL) was treated with DCC (3.60 g, 17.5 mmol) and stirred overnight. The white urea precipitate was removed by filtration through Celite and washed with CH₂Cl₂. The filtrate was concentrated to ~15 mL, and diethyl ether (150 mL) was added with vigorous stirring to precipitate the polymer. The precipitation was enhanced by stirring in an ice bath for 2 h. The precipitate was removed by filtration, washed with diethyl ether, and dried in vacuo to give 11.17 g (98%) of polymer-bound sulfide **4** as a white solid: IR (CH₂Cl₂ cast) 1733 (m), 1113 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.21 (t, 2H, *J* = 4.8 Hz), 3.64 (s, 88H), 2.48 (t, 2H, *J* = 7.3 Hz), 2.33 (t, 2H, *J* = 7.4 Hz), 2.08 (s, 3H), 1.63 (m, 4H), 1.42 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 173.44, 70.45, 69.06, 63.30, 33.90, 28.65, 28.09, 24.37, 15.39.

Poly(ethylene glycol) Bis(6-(Methylsulfinyl)hexanoate) (5). A solution of **4** (10.5 g, 4.6 mmol) in methanol (80 mL) and water (20 mL) at 0 °C was treated with 0.50 M sodium metaperiodate (19.4 mL, 9.7 mmol) overnight, during which time a white precipitate formed. The methanol was removed in vacuo below 10 °C, and the residue was extracted with CH₂Cl₂ (5 × 50 mL). Combined extracts were dried (Na₂SO₄) and evaporated to give 10.6 g (99%) of polymer-bound sulfoxide **5** as a white solid: IR (CH₂Cl₂) 1732 (m), 1114 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.20 (t, 2H, *J* = 4.7 Hz), 3.61 (s, 88H), 2.66 (m, 2H), 2.53 (s, 3H), 2.33 (t, 2H, *J* = 7.3 Hz), 1.76 (m, 2H), 1.65 (m, 2H), 1.48 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 173.08, 70.37, 68.93, 63.30, 54.17, 38.44, 33.56, 27.99, 24.20, 22.09.

General Procedure for the Modified Swern Oxidation. A solution of **5** (1.74 g, 0.75 mmol) in dichloromethane (30 mL) is cooled to -50 to -60 °C, oxalyl chloride (0.098 mL, 1.125 mmol) is added dropwise, followed after 15 min by a solution of the alcohol (0.75 mmol) in CH₂Cl₂ (5 mL). The mixture is stirred for 45 min, triethylamine (0.63 mL, 4.5 mmol) is added, and the

solution is kept at -45 °C for 2.5 h before warming to room temperature. Workup involves concentration of the reaction mixture to approximately 10 mL, followed by addition of diethyl ether (100 mL) to precipitate the polymer. The precipitation is accelerated by cooling to -20 °C for 10 min. After filtration the filtrate is concentrated in vacuo to give the oxidized product, which typically contains a trace of polymer contamination (1%). This is easily removed by passing an ethereal suspension through a pad of silica. The solid polymer reagent, which is a 1:1 mixture of the sulfide and sulfoxide, is contaminated with triethylammonium hydrochloride. Although this does not affect the subsequent periodate oxidation, it can be removed by washing a dichloromethane solution with water to give recovered polymer-bound reagent in a 98% yield. The product was analyzed by ¹H NMR spectrometry, which showed complete oxidation with no trace of alcohol. All the carbonyl products obtained from the Swern oxidation were characterized by comparing chromatographic and/or spectral properties (¹H NMR, IR, MS) with the authentic samples or literature.

In experiments to determine the recyclability of the PEG-bound sulfoxide, limiting conditions were used. Thus, 1 equiv of *endo*-borneol was used for the reaction with 0.6 equiv of polymer-supported sulfoxide **5** and 1.1 equiv of oxalyl chloride: 96% of the alcohol was oxidized to give camphor with 4% left unchanged. The polymer-bound reagent recovered was a 6:1 mixture of sulfide:sulfoxide. It was reoxidized by the above procedure for periodate oxidation, giving a 91% recovery of PEG-bound sulfoxide **5**.

Acknowledgment. These investigations were supported by Merck Frosst Ltd., the Natural Sciences and Engineering Research Council of Canada, and the Alberta Heritage Foundation for Medical Research (postdoctoral fellowships J.M.H. and M.D.A.). Y.L. acknowledges support from an Izaak Walton Killam Scholarship.

JO972304I

(9) *Purification of Laboratory Chemicals*, 3rd ed.; Perrin, D. D., Armarego, W. L. F., Ed.; Pergamon: New York, 1988.

Additions and Corrections

Vol. 62, 1997

Matthias Köck* and Jochen Junker. How Many NOE Restraints Are Necessary for a Reliable Determination of the Relative Configuration of an Organic Compound: Application to a Model System.

Page 8614. The configuration of compound **1** is correctly designated as *1R,6R,8R,11R,12S,16R* in the text. The centers 6, 8, 11, and 12 should be switched in the 2D drawing of **1**.

JO984000H

S0022-3263(98)04000-6

Published on Web