

# Synthesis and Cathodic Cleavage of an Eight-membered Cyclic Sulfone, 3,4,5,6-Tetrahydro-2*H*-benzo[*b*]-thiocin-1,1-dioxide

BO LAMM\* and CARL-JOHAN AURELL

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

Some years ago, the cathodic cleavage of a series of cyclic sulfones illustrated in Scheme 1 was studied.<sup>1,2</sup> For  $n=2$  and 3, the upper route was exclusively followed, whereas for  $n=4$ , an 85:15 ratio between the upper and the lower route was observed. It was suggested<sup>2</sup> that the dihedral angle between the sulfonyl group and the benzene ring determines the cleavage mode. In the compound with  $n=2$ , this angle is  $90^\circ$  different from its value in methyl phenyl sulfone, which upon cleavage gives methane, and no benzene.<sup>3</sup> In the seven-membered ring compound, the angle is probably intermediary between the two extremes, and aryl-sulfonyl as well as alkyl-sulfonyl cleavage is observed. Inspection of a Dreiding model of the hitherto unknown member of the series,  $n=5$ , suggested that the conformation would be similar to that of an open alkyl phenyl sulfone. One would then predict that the cathodic cleavage of the eight-membered ring compound should follow the lower route in Scheme 1.

We now report an efficient synthesis of the eight-membered ring compound and its cathodic cleavage at mercury. The route is shown in Scheme 2. The crucial step, reduction of a disulfide and intramolecular displacement of a mesylate under high-dilution conditions, was inspired by recent Japanese work,<sup>4</sup> and gave in the present case 79% yield.

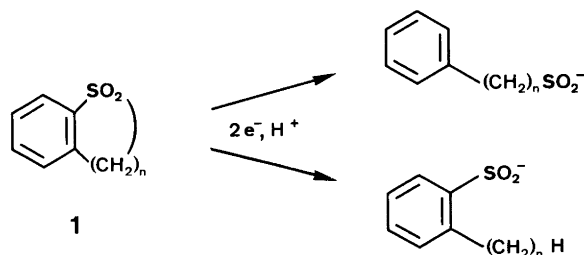
\* To whom correspondence should be addressed.

The sulfinate ions formed upon cathodic cleavage were converted into sulfones through reaction with iodomethane. By comparison with authentic material, methyl 5-phenylpentyl sulfone and methyl *o*-pentylphenyl sulfone, respectively, it could be shown that the reaction had taken entirely the lower path in Scheme 1, *i.e.*, alkyl-sulfonyl cleavage.

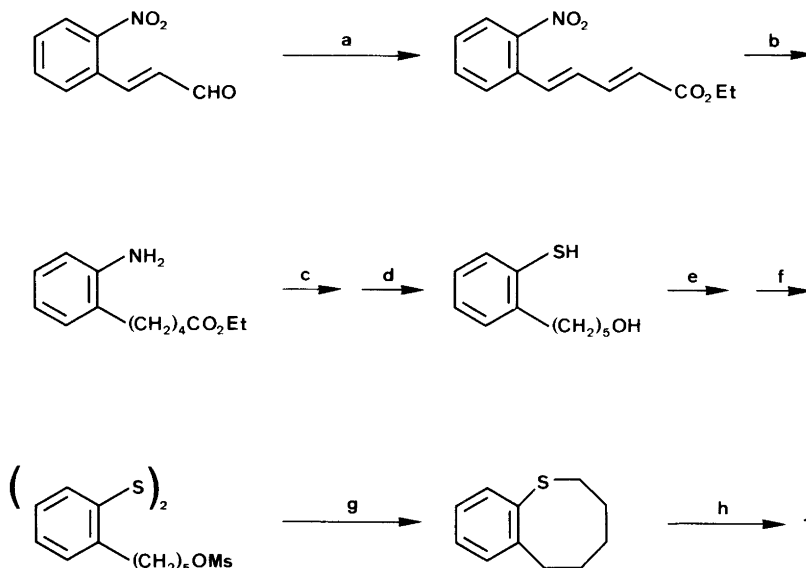
A single-crystal X-ray diffraction study of the title compound showed<sup>5</sup> the dihedral angle between the benzene ring plane and the C-S-C plane in the thiocin ring to be  $71^\circ$ , not far from the predicted  $90^\circ$ . The present work thus supports the stereoelectronic argument presented earlier<sup>2</sup> to explain the different cleavage mode for cyclic and non-cyclic sulfones.

**Experimental. Syntheses.** All steps in Scheme 2 represent well-known reactions, the conditions for which were taken from literature procedures for analogous compounds. The structures of all intermediates were verified by  $^1\text{H}$  NMR spectroscopy. Since the eight-membered ring sulfide and sulfone represent unusual heterocycles, their data are given. For 3,4,5,6-tetrahydro-2*H*-benzo[*b*]thiocin, b.p.  $120^\circ\text{C}$  at 0.1 mmHg (Kugelrohr),  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.29–1.41 (2 H, m), 1.65–1.77 (4 H, m), 2.70 (2 H, t,  $J$  5.7 Hz), 3.13 (2 H, t,  $J$  6.4 Hz), 7.07–7.29 (3 H, m), 7.58 (1 H, d,  $J$  8 Hz). MS IP 50 eV;  $m/e$  (% rel. int.): 179 (15), 178 (100, M), 177 (91), 149 (14), 137 (18), 135 (54), 123 (20), 121 (13), 117 (18), 91 (34). Mol. wt., obs. 178.0817, calc. for  $\text{C}_{11}\text{H}_{14}\text{S}$  178.0817. The sulfone, 3,4,5,6-tetrahydro-2*H*-benzo[*b*]thiocin-1,1-dioxide, forms colourless crystals, m.p.  $96-97^\circ\text{C}$  (Kofler Hot Stage).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.25–1.37 (2 H, m), 1.73–1.85 (2 H, m), 1.95–2.07 (2 H, m), 3.15 (2 H, t,  $J$  6 Hz), 3.37 (2 H, t,  $J$  6 Hz), 7.25–7.59 (3 H, m), 8.09 (1 H, d,  $J$  8 Hz). Anal.  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$ : C, H, S.

**Cathodic reduction.** An H-type cell with an AMFion® type C-100 ion exchange membrane was used. The electrolyte was 0.5 M tetramethylammonium chloride in methanol, the cathode a 20  $\text{cm}^2$  mercury pool, and the anode a carbon rod. At a potential of  $-2.5$  V vs.  $\text{Ag}/0.01$  M  $\text{AgNO}_3/0.1$  M tetraethylammonium perchlorate in DMF,<sup>6</sup> twice the amount of electricity calculated for a two-



Scheme 1. Aryl-sulfonyl (upper path) and alkyl-sulfonyl (lower path) cleavage of cyclic sulfones at mercury.



Scheme 2. Synthesis of 3,4,5,6-tetrahydro-2H-benzo[b]thiocin-1,1-dioxide. Reagents: *a*, NaH,  $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{COOEt}$ ;<sup>7</sup> *b*,  $\text{H}_2/\text{Pd}$ ; *c*,  $\text{HNO}_2$ , then  $\text{KSC}(\text{S})\text{OEt}$ ; *d*,  $\text{LiAlH}_4$ ;<sup>8</sup> *e*,  $\text{I}_2$ ; *f*,  $\text{MeSO}_2\text{Cl}$ ,  $\text{Et}_3\text{N}$ ;<sup>9</sup> *g*,  $\text{NaBH}_4$ , high dilution;<sup>4</sup> *h*,  $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$ .

electron process was introduced. The catholyte was evaporated to a small volume and heated with a tenfold molar excess of iodomethane at reflux for 2 h. The next day, it was worked up through distribution between dichloromethane and water. The sulfone formed was shown to be identical to authentic methyl *o*-pentylphenyl sulfone by comparison of the 270 MHz  $^1\text{H}$  NMR spectra, and the absence of methyl 5-phenylpentyl sulfone was demonstrated by GLC analysis; detection limit estimated at 2%.

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