The Preparation of β-Oxo Sulfoxides from Sulfinyl Chlorides and Trimethylsilyl Enol Ethers

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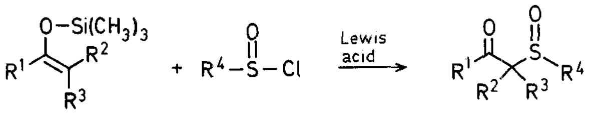
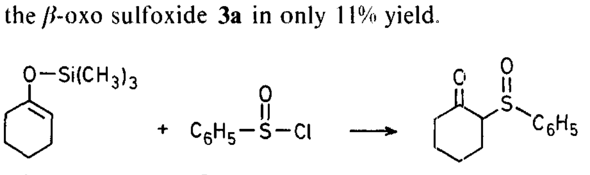
β-Oxo sulfoxides **3** have proven to be versatile synthetic intermediates in organic chemistry and a number of preparative procedures have been developed[1]. We report on a quick and efficient approach to this class of compound that involves the Lewis acid-mediated interaction of sulfinyl chlorides **2** with trimethylsilyl enol ethers **1**[2].



1 **2** **3**

Although the addition of sulfenyl chlorides and sulfonyl chlorides to trimethylsilyl enol ethers to give β-oxo sulfides[3] and β-oxo sulfones[4], respectively, was investigated some years ago, the reaction of sulfinyl halides with silyl enol ether derivatives has attracted attention only recently[5]. Sergeev and co-workers reported[5] that exposure of sulfinyl halides to acyclic silyl enol ether derivatives afforded β-oxo sulfoxides in good to excellent yields. However, in our hands, admixture of benzenesulfinyl chloride (**2**; $R^4 = C_6H_5$) and 1-trimethylsilyloxycyclohexene (**1a**) under the conditions described by Sergeev furnished the β-oxo sulfoxide **3a** in only 11% yield.



1a **2** ($R^4 = C_6H_5$) **3a**

We have found that the introduction of a Lewis acid into the reaction mixture markedly promotes the desired reaction. Thus, treatment of equimolar quantities of trimethylsilyl enol ethers **1** and benzenesulfinyl chloride (**2**; $R^4 = C_6H_5$) in dichloromethane at −78 °C with one equivalent of tin(IV) chloride generally affords high yields of the corresponding β-oxo sulfoxides **3** (see Table). The reaction is quick (complete in <30 min at −78 °C) and clean and the products can conveniently be purified by column chromatography or by extraction into 5% potassium hydroxide solution[6] when necessary. The use of catalytic amounts of Lewis acid led to a substantial reduction in the yield. This is presumably due to the formation of a complex between the β-oxo sulfoxide **3** and the Lewis acid.

2-Phenylsulfinylcyclohexanone (3a); Typical Procedure:

Benzenesulfinyl chloride[9] (**2**; $R^4 = C_6H_5$; 500 mg, 3.1 mmol) in dichloromethane (3 ml) is cooled to −78 °C and added in one portion to a stirred solution of 1-trimethylsilyloxycyclohexene[2] (**1a**; 530 mg, 3.1 mmol) in dichloromethane (10 ml) maintained at −78 °C under an atmosphere of argon. Tin(IV) chloride (809 mg, 0.35 ml, 3.1 mmol) is added dropwise from a syringe and the mixture is stirred at −78 °C for 30 min before being poured into water (15 ml). The organic layer is separated and the aqueous layer extracted with dichloromethane (3 × 15 ml). The combined extracts are dried with sodium sulfate and the solvent evaporated to give an oily residue which is purified by column chromatography on silica gel (Method A) to give **3a**; yield: 625 mg (90%) or by extraction into 5% potassium hydroxide solution (3 × 15 ml) followed by neutralization with dilute hydrochloric acid and extraction with dichloromethane (3 × 20 ml) (Method B) to give

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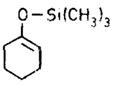
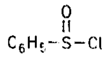
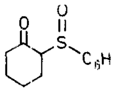
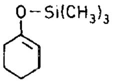
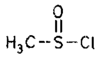
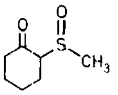
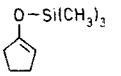
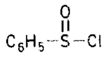
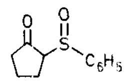
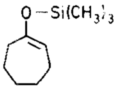
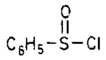
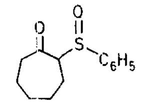
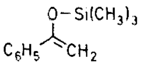
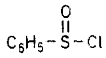
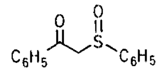
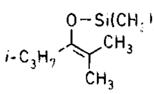
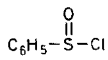
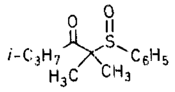
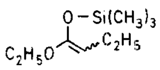
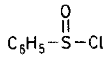
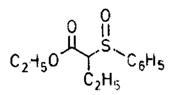
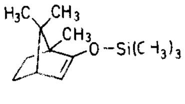
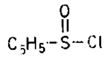
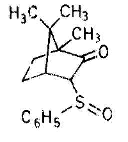
Table. β-Oxo Sulfoxides **3a–h**

Silyl Enol Ether **1**	Sulfinyl Halide[a] **2**	Product		Yield [%] A[b]	Yield [%] B[c]	m.p. [°C]	Remarks
	 $C_6H_5-\overset{O}{\overset{\|}{S}}-Cl$		**3a**	90	87	108–109°	Lit.[8], m.p. 104–105 °C
	 $H_3C-\overset{O}{\overset{\|}{S}}-Cl$		**3b**	—	61	oil[1]	~3 : 1 Diastereomeric mixture; ^{1}H-N.M.R. (CDCl$_3$): δ = 2.62, 2.55 ppm (2s, 3H); I.R. (film): ν = 1705 (C=O); 1030 cm^{-1} (S=O)
	 $C_6H_5-\overset{O}{\overset{\|}{S}}-Cl$		**3c**	87	83	oil[12]	I.R. (CHCl$_3$): ν = 1740 (C=O); 1040 cm^{-1} (S=O)
	 $C_6H_5-\overset{O}{\overset{\|}{S}}-Cl$		**3d**	74	—	oil[13]	I.R. (film): ν = 1700 (C=O); 1050 cm^{-1} (S=O)
	 $C_6H_5-\overset{O}{\overset{\|}{S}}-Cl$		**3e**	94	77	70–71°	Lit.[8], m.p. 70–71 °C
	 $C_6H_5-\overset{O}{\overset{\|}{S}}-Cl$		**3f**	53	—	oil[d]	I.R. (CHCl$_3$): ν = 1695 (C=O); 1030 cm^{-1} (S=O)
	 $C_6H_5-\overset{O}{\overset{\|}{S}}-Cl$		**3g**	78	—	oil[14]	I.R. (film): ν = 1720 (C=O); 1052 cm^{-1} (S=O)
	 $C_5H_5-\overset{O}{\overset{\|}{S}}-Cl$		**3h**	49	—	127–129°	Lit.[8], m.p. 112–113 °C

[a] Benzenesulfinyl chloride (**2**; R^4 = C$_6$H$_5$) prepared according to Lit.[9]; methanesulfinyl chloride (**2**; R^4 = CH$_3$) according to Lit.[10].

[b] After column chromatography.

[c] After extraction into 5% potassium hydroxide solution.

[d] Hygroscopic; oxidized with *m*-chloroperoxybenzoic acid to 2,4-dimethyl-2-phenylsulfonyl-3-pentanone; m.p. 52–53 °C.

$C_{13}H_{18}O_3S$	calc.	C 61.42	H 7.09
(254.3)	found	61.49	7.12

I.R. (CHCl$_3$): ν = 1705 (C=O); 1320, 1138 cm^{-1} (SO$_2$).
^{1}H-N.M.R. (CDCl$_3$): δ = 1.12 (d, J = 7 Hz, 6H); 1.52 (s, 6H); 3.50 (quin, 1H); 7.4–7.9 ppm (m, 5H).

3a; yield: 600 mg (87%); m.p. 108–109 °C (needles from dichloromethane/hexane) (Lit.[8], m.p. 104–105 °C).

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