

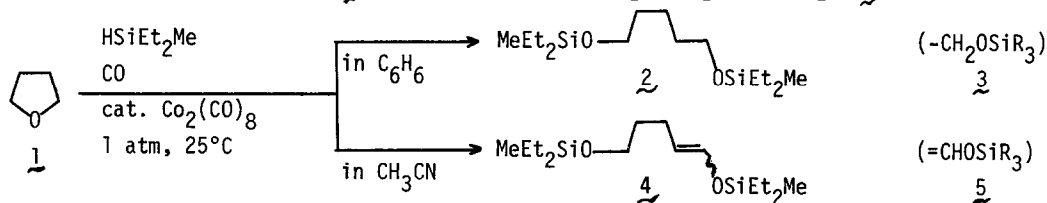
COBALT CARBONYL CATALYZED REACTION OF TETRAHYDROFURANS WITH A HYDROSILANE
 AND CARBON MONOXIDE. A NEW REACTION PATHWAY LEADING TO ENOL SILYL ETHERS.

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Summary: Cobalt carbonyl catalyzed reaction of tetrahydrofurans with HSiEt_2Me and CO (1 atm) took a new reaction pathway leading to enol silyl ethers when acetonitrile was employed as the solvent.

During the course of our study on the cobalt carbonyl catalyzed reactions of oxygen-containing compounds with a hydrosilane and carbon monoxide,¹ we have recently found that some reactions proceed under exceptionally mild reaction conditions for a reaction of carbon monoxide.^{1a,b} For example, the reaction of tetrahydrofuran (1)^{1b} with HSiEt_2Me and CO in the presence of $\text{Co}_2(\text{CO})_8$ occurs at 1 atm and 25°C using C_6H_6 or CH_2Cl_2 as the reaction solvent. The product of this reaction is 1,5-disiloxypentane (2), into which reactant CO is incorporated as the oxymethyl group (3).

We wish to report a new reaction of 1 leading to 1,5-disiloxy-1-pentene (4), an enol silyl ether. The complete change in the product distribution has been brought about by simply changing the reaction solvent from C_6H_6 to CH_3CN . In the present reaction, carbon monoxide has ended up in the form of an oxymethylidene group (5) instead of the oxymethyl moiety (3).


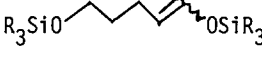
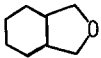
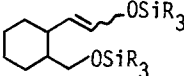
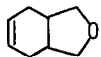
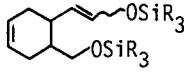

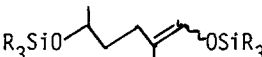

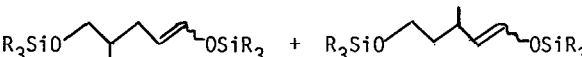
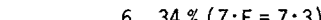
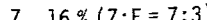

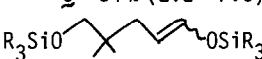


To a mixture of $\text{Co}_2(\text{CO})_8$ (0.08 mmol) and HSiEt_2Me (7.5 mmol) was added CH_3CN (2.5 mL) and tetrahydrofuran (1, 2.5 mmol) under CO (1 atm). The solution was stirred at 25°C for 20 h under CO (1 atm). The products formed were

a stereoisomeric mixture (57% yield) of (Z)- and (E)-**4** (3:1) and a small amount of **2** (3% yield). The reaction also proceeded in a mixed solvent of $\text{CH}_3\text{CN}-\text{C}_6\text{H}_6$ (1:1, 5 mL) to give **4** (66%, Z:E=3:1) and **2** (0.3%).

The results obtained for some substituted tetrahydrofurans in CH_3CN are given in Table 1. Although the yields are only moderate, the selective formation of enol silyl ethers (in CH_3CN) seems of general for tetrahydrofurans.² The function of CH_3CN is not understood yet. There exist many possibilities: acetonitrile may act as a ligand for a cobalt intermediate, as a base for proton abstraction from an intermediate, or as a solvent to stabilize a carbocationic intermediate. It has been reported that an enol silyl ether similar to **4** was found among the products when $\text{Me}_3\text{SiCo}(\text{CO})_4$ was decomposed in tetrahydrofuran (1).³

Table 1. Cobalt Carbonyl Catalyzed Reaction of Tetrahydrofurans with HSiEt_2Me and CO in CH_3CN ^{a)} Products, Yields, and Physical Properties.

tetrahydrofuran	product($\text{R}_3\text{Si} = \text{MeEt}_2\text{Si}$)		bp (°C/mmHg)	¹ H NMR for -CH=COSi
		57 % (Z:E = 3:1)	77/0.3	Z 4.35 E 4.82
		50 % (Z:E = 1:1)	140/0.5	Z 4.46 E 5.06
		41 % ^{b)} (Z:E=1:1)	113-115/0.7	Z 4.42 E 4.89
		16 % (Z:E = 1:1) (50 %) ^{d)}	106-110/0.5	- ^{c)}
		 6 34 % (Z:E = 7:3)  7 16 % (Z:E = 7:3)	93-102/0.6	^{e)} 6-Z 4.43 6-E 4.93 7-Z 4.63 7-E 5.11
		40 % (Z:E = 7:3)	120/0.8	Z 4.32 E 4.86

a) Under conditions given in the text. GLC yields. Anal.(C,H,±0.4%) as the mixture of isomers.

b) With $\text{Co}_2(\text{CO})_8$ 0.4 mmol. c) Stereochemistry of the isomers has not been determined yet.

d) With $\text{Co}_2(\text{CO})_8$ 1.25 mmol. e) By 270 MHz ¹H NMR of the mixture of the four isomers.

1) (a) T. Murai, S. Kato, S. Murai, T. Toki, S. Suzuki, and N. Sonoda, J. Am. Chem. Soc., **106**, 6093(1984). (b) T. Murai, Y. Hatayama, S. Murai, and N. Sonoda, Organometallics, **2**, 1883(1983). (c) N. Chatani, S. Murai, and N. Sonoda, J. Am. Chem. Soc., **105**, 1370(1983).

2) In CH_3CN , oxetanes gave a mixture of products corresponding to **2** and **4** in a nonselective manner, whereas oxiranes afforded many products in low yields.

3) W. M. Ingle, G. Preti, and A. G. MacDiarmid, J. Chem. Soc., Chem. Commun., 497(1973).

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