

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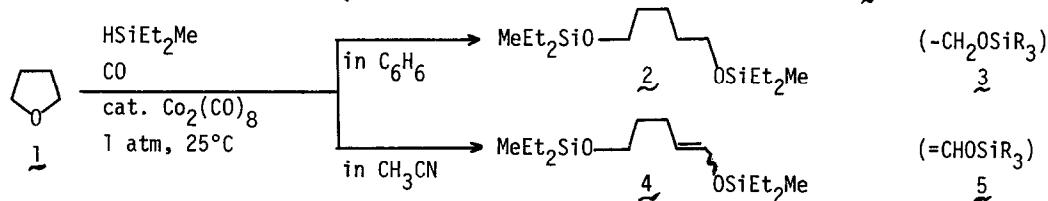
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Summary: Cobalt carbonyl catalyzed reaction of tetrahydrofurans with HSiEt_2Me and CO (1 atm) took a new reaction pathway leading to enol silyl ethers when acetonitrile was employed as the solvent.

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-disiloxylpentene (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 $\text{CH}_3\text{CN}^{\text{a})}$ Products, Yields, and Physical Properties.

tetrahydrofuran	product ($\text{R}_3\text{Si} = \text{MeEt}_2\text{Si}$)	bp (°C/mmHg)	^1H 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)}
	+	93-102/0.6	$\underline{\text{Z}}\text{-Z}$ 4.43 ^{e)} $\underline{\text{Z}}\text{-E}$ 4.93 $\underline{\text{Z}}\text{-Z}$ 4.63 $\underline{\text{Z}}\text{-E}$ 5.11
		34 % (Z:E = 7:3) 16 % (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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