

$\text{Co}_2(\text{CO})_8$ CATALYZED REACTIONS OF STYRENE OXIDE WITH TRIALKYLSILANES

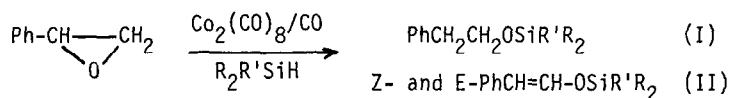
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Summary: The dicobalt octacarbonyl catalyzed reaction of styrene oxide with trialkylsilanes yields a mixture of 1-phenyl-2-trialkylsiloxyethane and Z- and E-1-phenyl-2-trialkylsiloxyethene. The ratio of these products can be controlled.

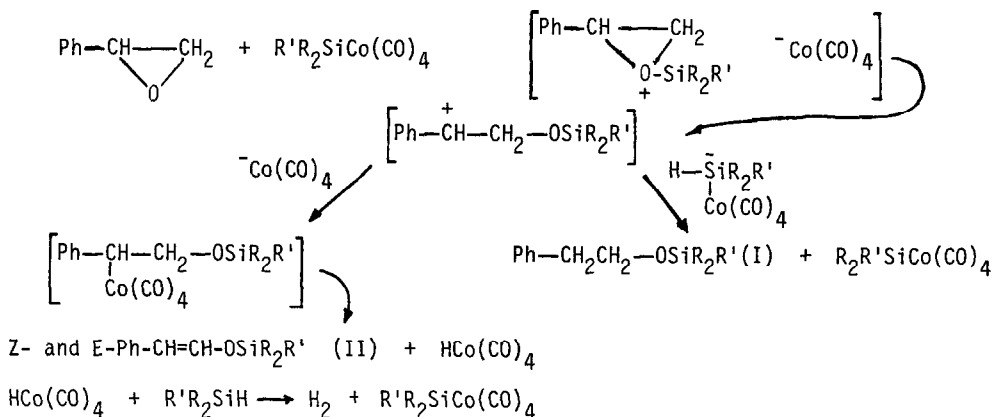
The silyl-hydroformylation reaction of aliphatic epoxides catalyzed by $\text{Co}_2(\text{CO})_8$ has recently been reported to yield silyl ethers of 1,3-diols.²

Surprisingly, we have found quite different results when we carried out a similar reaction with styrene oxide with trialkylsilanes and CO catalyzed by $\text{Co}_2(\text{CO})_8$. Specifically, with trialkylsilane we have obtained a mixture of 1-phenyl-2-trialkylsiloxyethane (I) and Z- and E-1-phenyl-2-trialkylsiloxyethene (II) in high yield. With Et_3SiH I is the major product. On the other hand, with $t\text{-Bu}(\text{Me})_2\text{SiH}$ Z-II and E-II are predominant. (See Table) Clearly, CO is not involved in these reaction.



We believe that these results can be rationalized in terms of the mechanism previously proposed with minor modifications.² Thus reaction of trialkylsilanes with $\text{Co}_2(\text{CO})_8$ is well known to yield trialkylsilyl cobalt tetracarbonyl and $\text{HCo}(\text{CO})_4$.^{3,4} Trialkylsilyl cobalt tetracarbonyl transfers a trialkylsilyl group to the basic oxygen of the epoxide to yield an oxonium cation / $\text{Co}(\text{CO})_4^-$ ion pair.² Apparently, the oxonium cation undergoes C-O bond heterolysis to yield a benzylic cation. Hydride transfer from Et_3SiH to benzylic carbocations is a well known process in ionic hydrogenation.^{5,6} This would yield I. Nucleophilic activation of trialkylsilane by $\text{Co}(\text{CO})_4^-$ may be required in this reaction. This would result in regeneration of the trialkylsilyl cobalt tetracarbonyl and continuation of the catalytic cycle. On the other hand, the benzylic cation/ $\text{Co}(\text{CO})_4^-$ may collapse to an unstable benzyl cobalt tetracarbonyl species which undergoes β -hydride elimination to yield the silyl enol ethers (II) and $\text{HCo}(\text{CO})_4$ faster than the insertion of CO. Finally, reaction of $\text{HCo}(\text{CO})_4$ with trialkylsilane can yield hydrogen and regenerate trialkylsilyl cobalt tetracarbonyl (See Scheme).

If this proposal is correct, the difference in behavior of Et_3SiH and $t\text{-Bu}(\text{Me})_2\text{SiH}$ in these reactions results from relative differences in ease of nucleophilic attack by $\text{Co}(\text{CO})_4^-$ on the respective silyl centers. This will affect the rate of ionic hydride transfer to the benzylic carbocation. t -Butyldimethylsilyl ethers are well known to undergo hydrolysis much slower than either trimethylsilyl or triethylsilyl ethers due to steric hinderance to nucleophilic attack at the silyl center by the t -butyl group.⁷⁻⁹ Consistent with this interpretation, at higher trialkylsilane concentrations higher yields of I are obtained. (See Table)



Most of the compounds are known, their properties were in agreement with literature values: 1-phenyl-2-*t*-butyldimethylsiloxyethane,¹⁰ Z-1-phenyl-2-*t*-butyldimethylsiloxyethene,¹¹ 1-phenyl-2-triethylsiloxyethane,¹² Z- and E-1-phenyl-2-triethylsiloxyethene.¹³ E-1-Phenyl-2-*t*-butyldimethylsiloxyethene.¹⁴

Table	$\text{R}'_2\text{R}'\text{SiH}$	Total Yield	Ratio I : Z-II : E-11
	<i>t</i> -Bu(CH ₃) ₂ SiH (2.00 eq)	62%	11 : 48 : 41
	<i>t</i> -Bu(CH ₃) ₂ SiH (1.28 eq)	51%	4 : 55 : 41
	Et ₃ SiH (2.00 eq)	65%	64 : 21 : 16
	Et ₃ SiH (1.28 eq)	55%	37 : 35 : 28

Acknowledgements: This work was supported by the Air Force Office of Scientific Research Grant # 82-0333. K.T. Kang thanks the Korean Science and Engineering Foundation for their support.

References:

- K.T.K. is on sabbatical leave from the Department of Chemical Education, Pusan National University, Pusan 607, Korea.
- T. Murai, S. Kato, S. Murai, T. Toki, S. Suzuki and N. Sonoda, J. Am. Chem. Soc. **106** (1984) 6093.
- A.J. Chalk and J.F. Harrod, J. Am. Chem. Soc. **89** (1967) 1640.
- Y.L. Baay and A.G. MacDiarmid, Inorg. Chem. **8** (1969) 986.
- W.P. Weber, "Silicon Reagents for Organic Synthesis", Springer, Berlin, 1983, p. 277-288.
- F.A. Carey and H.S. Tremper, J. Org. Chem. **34** (1969) 4.
- E. Colvin, "Silicon in Organic Synthesis", Butterworths, London, 1981, p. 184-189.
- T.W. Hart, D.A. Metcalfe and F. Scheinmann, J. Chem. Soc. Chem. Comm. (1979) 156.
- E. Akerman, Acta Chem. Scand. **11** (1957) 373.
- T. Veysoglu and L.A. Mitscher, Tetrahedron Lett. **1981**, 1299.
- I. Saito, R. Nagata, H. Kotsuki and T. Matsuura, Tetrahedron Lett. **1982**, 1717.
- Y. Kita, J. Haruta, J. Segawa and Y. Tamura, Tetrahedron Lett. **1979**, 4311.
- E. Frainnet and R. Bourhis, J. Organometal. Chem. **93** (1975) 309.
- NMR: δ 0.23 (6H,s), 0.98 (9H,s), 6.05 (1H,d,J=12.2 Hz), 7.02 (1H,d,J=12.2 Hz), 7.1-7.4 (5H,m). MS m/e: 234 (29%) M⁺, 177 (100%), M-*t*-butyl⁺. Anal. Found: C, 71.54%; H, 9.48%. Calc. for C₁₄H₂₂OSi C, 71.73%; H, 9.46%.

(Received in USA 12 August 1985)