

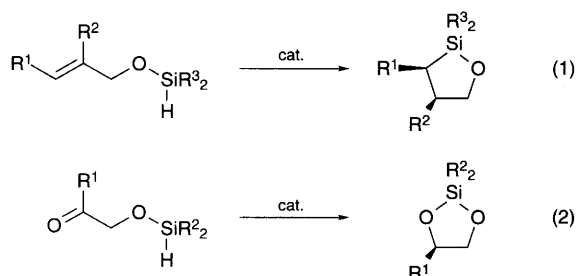
Sequential homogenous catalysis. Catalytic formation of allylic and β -keto silyl ethers from dihydrosilanes and the corresponding alcohols followed by intramolecular hydrosilylation

Xianqi Wang, William W. Ellis and B. Bosnich

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, USA

The catalyst, $[\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]^+$ engages in a consecutive catalytic sequence where allylic alcohols, β -keto alcohols and α,β -unsaturated aldehydes in the presence of dihydrosilanes are first converted to the corresponding monohydrosilyl ethers, which are then cyclized.

We¹ and others^{2,3} have employed intramolecular catalytic hydrosilylation in order to control both regio- and enantio-selection. The most common reactions are those illustrated in eqns. (1) and (2), where only 5-membered ring products are

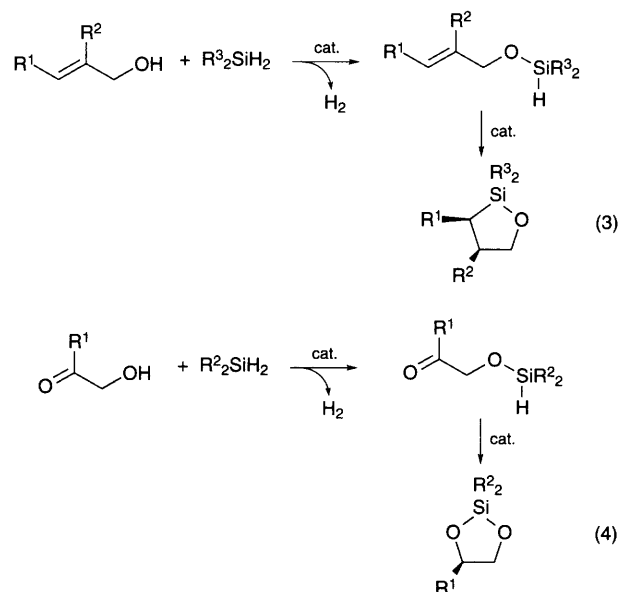


formed and, in many cases, high enantioselection is observed.^{1,3} The enhanced regio- and enantio-selection is believed to arise from the formation of cyclic transition states. The potential practicality of these reactions is diminished by the generally lengthy, low yield procedures required to isolate the pure substrates. The necessity of isolating the substrates might be circumvented if the catalyst were capable of successively generating the substrates as well as the product. Various reports^{4–8} suggest that the sequences illustrated in eqns. (3) and (4) may be possible with certain rhodium(I) catalysts. The process involves dehydrogenative coupling of allylic or β -keto alcohols followed by cyclization.

Successful asymmetric catalysts^{1,3} for intramolecular hydrosilylation are of the type $[\text{Rh}(\text{chiral diphosphine})(\text{solvent})_2]^+$ which are usually prepared *in situ* by hydrogenation of the norbornadiene precursor.¹ As a representative of this class of catalysts, we chose $[\text{Rh}(\text{diphos})(\text{solvent})_2]\text{ClO}_4$ (diphos = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) for evaluating these consecutive catalytic sequences. All reactions were performed at 25 °C using 2–4% catalyst loadings, generally in CH_2Cl_2 solutions containing 0.4 M concentrations of both the alcohol and the silane. The reactions were followed by ^1H NMR spectroscopy and in some cases the products were isolated.

Table 1 lists a representative collection of results obtained with a variety of substrates. In all cases, the substrates are completely consumed to give the indicated products during the times listed. The yields of the listed products are >95% in all catalytic reactions. The allylic alcohols 1–5 all give varying amounts of the hydrogenated allylic silyl ether, but no reduced allylic alcohol was detected. The amount of the desired cyclic product can be increased by up to 10% by passing argon through the catalytic solution, but the addition of 1 equiv. of a sacrificial alkene such as styrene or cyclohexene does not significantly

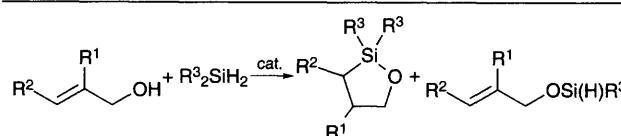
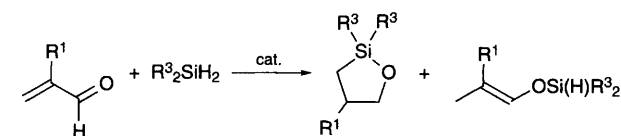
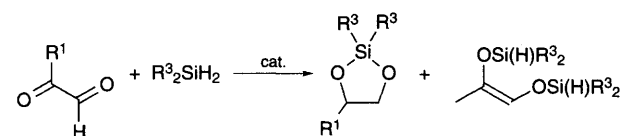
reduce the amount of allylic alkene hydrogenation. In CH_2Cl_2 solutions catalysis is complete in < 10 min for 1 and 2, but the phenylated substrates 3–5 react slowly, presumably because π -aryl complexes are formed with the catalyst. Addition of an equal volume of acetone increases the rate of catalysis for these phenylated substrates. For these slower reacting allylic alcohols, ^1H NMR spectroscopy showed that >90% of allylic silyl ether intermediate [eqn. (3)] formed before any cyclic product was detected. This observation indicates that dehydrogenative coupling is a much faster process than either intra- or possible inter-molecular hydrosilylation. Despite the rapid dehydrogenative coupling, no silyl diethers were detected with any of the alcohols, suggesting that the intermediate ethers [eqns. (3) and (4)] are deactivated to catalytic dehydrogenative coupling.

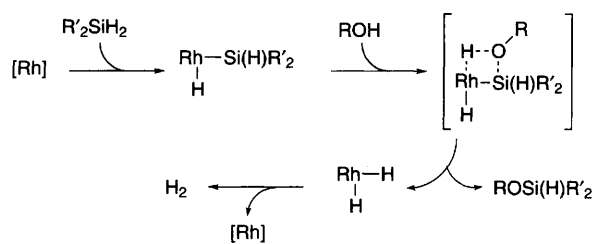


One possible method of preserving the consecutive catalytic sequence but avoiding the alkene hydrogenation is to start with α,β -unsaturated aldehydes. Entries 6 to 9 show that, in addition to the desired 1,2-addition products, 1,4-addition can also occur to give the vinyl silyl ethers. The ratio of these two addition modes depends on the substrate (Table 1). Using monohydrosilanes, other catalysts have been reported to give varying amounts of 1,2- and 1,4-additions to α,β -unsaturated aldehydes.^{5,6}

Although dehydrogenative coupling occurs with β -keto alcohols (entries 10 to 12), no ketone hydrogenation is observed. Using equivalent amounts of the silane and β -keto alcohol gives, in addition to the expected product, 5–10% of the disilylated diol (Table 1). If, however, the amount of the silane is reduced to 90% of the equivalent amount, negligible amounts of the disilylated diols are observed. As for the case of the allylic alcohols, dehydrogenative coupling to give the intermediate is a

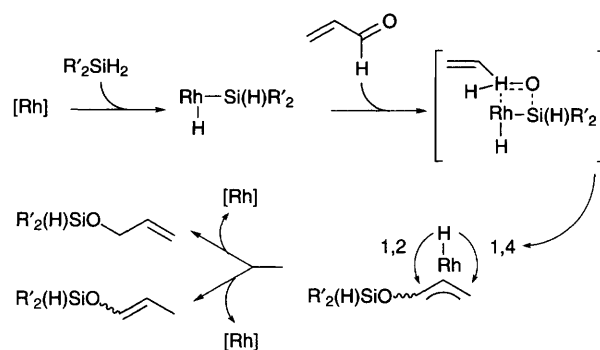
Table 1 Catalytic hydrosilations of allylic alcohols, β -keto alcohols and α,β -unsaturated aldehydes using the $[\text{Rh}(\text{diphos})]\text{ClO}_4$ catalyst

Substrate		Silane		Time	Product ratio
R ¹	R ²	R ³			
					
1	Me	H	Ph	< 10 min	95 : 5
2	Me	H	Et	< 10 min	95 : 5
3	Ph	H	Ph	5 h	85 : 15
4	Ph	H	Et	10 h	80 : 20
5	H	Ph	Ph	24 h	70 : 30
					
6	Me	—	Ph	3 h	75 : 25
7	Me	—	Et	10 h	20 : 80
8	Et	—	Ph	5 h	94 : 6 (<i>E</i> : <i>Z</i> = 2 : 1)
9	Bu	—	Ph	12 h	100 : 0
					
10	Me	—	Ph	2 h	90 : 10
11	Et	—	Ph	5 h	93 : 7
12	Ph	—	Ph	18 h	95 : 5

**Scheme 1**

much faster process than intramolecular hydrosilation of the ketone. During catalysis, >90% of the keto silyl ether intermediate [eqn. (4)] is observed before any cyclization or any other product is detected. Presumably, therefore, the disilylated diol side products are formed by intermolecular hydrosilation of the ketone of the intermediate rather than by intermolecular hydrosilation of the keto group of the β -keto alcohol.

The proposed mechanism of catalytic dehydrogenative coupling of alcohols to silanes is outlined in Scheme 1, where

**Scheme 2**

σ -bond metathesis is invoked to produce the product and the dihydride. For the hydrosilation of α,β -unsaturated aldehydes^{6–10} the mechanism outlined in Scheme 2 is proposed where the 1,2- and 1,4-addition modes are controlled by the hydrido π -allylic intermediates, for which the *syn* and *anti* isomers control the *E* : *Z* ratio of the silyl ether products.

It is clear from the results in Table 1 that the double catalytic sequence can provide a practical alternative to the usual method of starting with the silyl ethers [eqns. (1) and (2)]. The amounts of side product vary with the substrate but in most cases the desired cyclic product predominates. Since the desired products are formed from the intermediate allylic and β -keto silyl ethers, the enantioselectivity will be governed by the cyclization of these intermediates as is the case when the intermediates are prepared conventionally.

This work was supported by grants from the National Institutes for Health.

References

- S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 2121; S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 2128; X. Wang and B. Bosnich, *Organometallics*, 1994, **13**, 4131.
- K. Tamao, T. Tanaka, T. Nakajima, R. Sumiya, H. Arai and Y. Ito, *Tetrahedron Lett.*, 1986, **27**, 3377; K. Tamao, T. Nakajima, R. Sumiya, H. Arai, N. Higuchi and Y. Ito, *J. Am. Chem. Soc.*, 1986, **108**, 6090; K. Tamao, T. Yamauchi and Y. Ito, *Chem. Lett.*, 1987, 171; K. Tamao, Y. Nakagawa, H. Arai, N. Higuchi and Y. Ito, *J. Am. Chem. Soc.*, 1988, **110**, 3712; K. Tamao, K. Maeda, T. Tanaka and Y. Ito, *Tetrahedron Lett.*, 1988, **29**, 6955; K. Tamao, Y. Nakagawa and Y. Ito, *J. Org. Chem.*, 1990, **55**, 3438; K. Tamao, T. Tohma, N. Inui, O. Nakayama and Y. Ito, *Tetrahedron Lett.*, 1990, **31**, 7333.
- M. S. Buck and J. E. Feaster, *Tetrahedron Lett.*, 1992, **33**, 2099.
- R. J. P. Corriu and J. J. E. Noreau, *J. Organomet. Chem.*, 1976, **114**, 135.
- I. Ojima and T. Kogure, *Organometallics*, 1982, **1**, 1390.
- G. Z. Zheng and T. H. Chan, *Organometallics*, 1995, **14**, 70.
- I. Ojima and M. Nihonyanani, *J. Organomet. Chem.*, 1973, **50**, C26.
- S. Xin and J. F. Harrod, *J. Organomet. Chem.*, 1995, **499**, 181.
- I. Ojima, T. Kogure and T. Kumagai, *J. Org. Chem.*, 1977, **42**, 1671.
- K. Yamamoto, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, 1973, **54**, C45.

Received, 24th July 1996; Com. 6/05169C