Asymmetric Catalysis. Comparison of the Enantioselection of Rhodium-Catalyzed Intramolecular Hydrosilation and Hydroacylation

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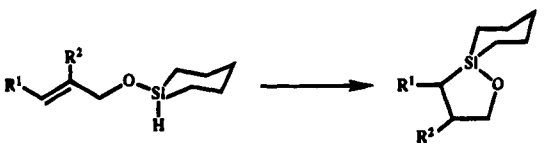
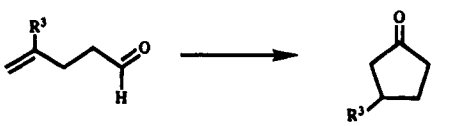
Summary: The previously reported observation that 4-pentenals bearing either a tertiary group or acyl or ester substituents at the 4-position gave very high ee's for hydroacylation using the [Rh(S-binap)(solvent)$_2$]$^+$ catalyst suggested that the same catalyst might give high ee's for intramolecular hydrosilation of similarly substituted allylic alkoxides bound to diaryl- or dialkylsilanes. Although the chemical yields and ee's are dependent on the solvent used and on the olefin and silicon substituents, there are combinations of these parameters which lead to high ee's for hydrosilation of substrates bearing these substituents.

Complexes of the type [Rh(diphosphine)(S)$_2$]$^+$ (S is a weakly coordinating solvent) are efficient catalysts for intramolecular hydrosilation[1,2] (eq 1) and for intramolecular hydroacylation[3–5] (eq 2). When the chiral

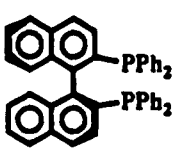


(1)



(2)

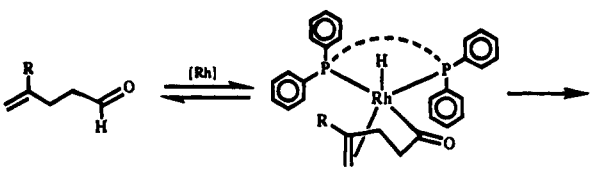
diphosphine binap (**1**) is incorporated, very high enantioselectivity is observed for both reactions for certain types of substrates. For hydrosilation we found that the



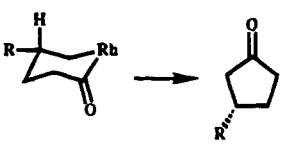
S-binap

1

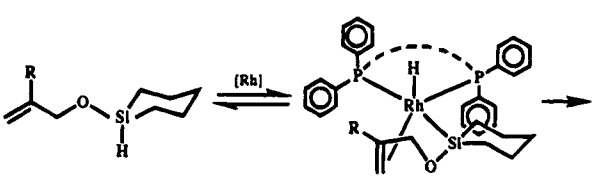
use of the silacyclohexane group gave efficient turnover, and in combination with an aryl R^1 group, very high ee's were observed.[1,2] These ee's were essentially insensitive to R^2 substituents such as H, CH$_3$, and Ph, which is consistent with the observation[1] that when R^1 = H the substrates bearing R^2 = CH$_3$, Ph gave low ee's. For hydroacylation the binap catalyst gave almost quantitative ee's when the substrate (eq 2) bore an R^3 group which was a tertiary group,[5,6] an acyl substituent,[5] or an ester group.[5] As in the case of hydrosilation modest ee's were observed for hydroacylation when the R^3 group was an alkyl substituent equal to or less bulky than isopropyl.[5] We postulated that for hydroacylation the enantioselection might be controlled by the putative diastereomeric intermediate **3**, where only the (chiral)



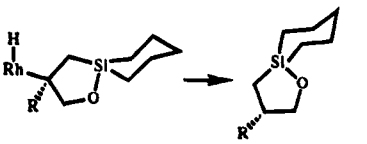
2 **3**



orientations of the phenyl groups of the *S*-binap ligand are illustrated. The diastereomer **3** with the illustrated olefin face selection leads to the observed prevailing chirality of the cyclopentanone product. This chirality connection between intermediate **3** and the chirality of the hydroacylation product led us to entertain the possibility that a similar connection might exist for hydrosilation. Thus, we sought to determine whether hydrosilation by the binap catalyst of substrates of the type **4**, where R = a tertiary group, acyl substituent, or



4 **5**



ester function, would lead to high enantioselectivity as was observed for analogous hydroacylation substrates. If such an analogy were to exist, then the diastereomeric

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(1) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121.
(2) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128.
(3) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 946.
(4) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936.
(5) Barnhart, R. W.; Wang, X.; Noheda, P.; Bergens, S. H.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1994**, *116*, 1821.
(6) Wu, X.; Funakoshi, K.; Sakai, K. *Tetrahedron Lett.* **1992**, *33*, 6331.

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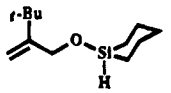
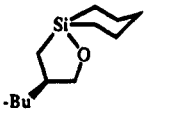
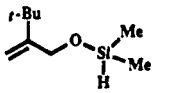
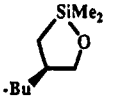
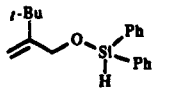
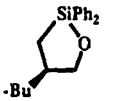
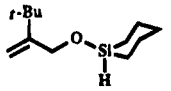
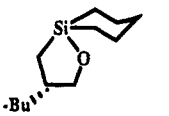
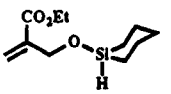
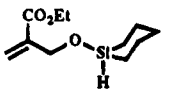
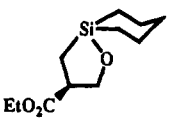
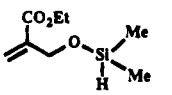
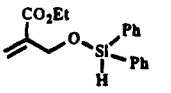
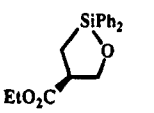
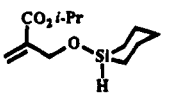
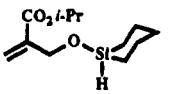
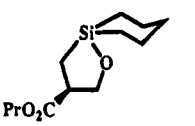
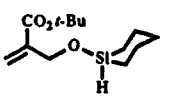
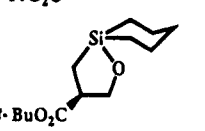
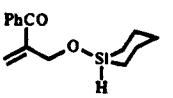
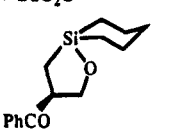
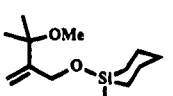
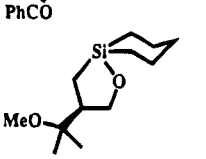
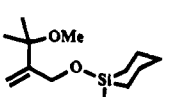
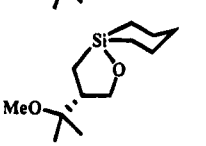
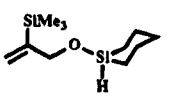
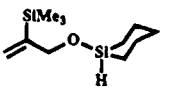
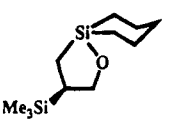
Table 1. Asymmetric Catalytic Hydrosilation of Allylic Silyl Ethers Using 1 mol % [Rh(*S*-binap)(solvent)$_2$]ClO$_4$ Catalyst at 25 °C

entry no.	substrate	solvent	time, min	yield, % NMR	yield, % prep	(confign) ee, %	product
1		acetone	<5	100	98	(*R*) 96	
2		acetone	<5	100	100	(*R*) 69	
3		acetone	<10	100	93	(*R*) 51	
4		CH_2Cl_2	60	98	87	(*S*) 32	
5		acetone	90	<45			
6		CH_2Cl_2	<5	95	90	(*S*) 69	
7		CH_2Cl_2	4	60			
8		CH_2Cl_2	35	96	70	(*S*) 68	
9		acetone	<4	0			
10		CH_2Cl_2	5	100	83	(*S*) 87	
11		CH_2Cl_2	5	100	93	(*S*) 81	
12		CH_2Cl_2	<5	100	100	(*S*) 96	
13		acetone	5	100	98	(*S*) 95	
14		CH_2Cl_2	35	95	91	(*R*) 20	
15		acetone	4	0			
16		CH_2Cl_2	15	25	15	(*R*) 78	

intermediate **5** would produce the shown prevailing enantiomer of the hydrosilation product. It should be recognized that this analogy embodies a number of assumptions which are related to the differences in the substrate structures and the mechanisms of hydroacylation and hydrosilation. Although the hydrosilation and hydroacylation substrates **2** and **4** are structurally similar in their allylic portions, the other parts of these substrates are distinctly different. The mechanisms of the two reactions are also different, hydrosilation proceeds by silyl–olefin insertion,[2] whereas hydroacylation involves alkyl–acyl reductive elimination.[4,5] Despite these structural and mechanistic differences, the analogy is superficially appealing and we report a test of its validity here.

Catalytic hydrosilation was generally carried out in CH_2Cl_2 and acetone solutions at 25 °C using 1 mol % of the *S*-binap catalyst. The results are collected in Table 1. The supplementary material contains procedures for the preparation of the substrates and for determining the ee's of the products. The ee's were determined by reacting the products with PhLi to cleave the silicon–oxygen bond followed by an analysis of the ^{19}F and ^{1}H NMR spectra of the Mosher esters[7] of the resultant alcohols. There are a variety of methods[8] of converting the hydrosilation products to the (silicon-free) half-esters of 1,3-diols if these are required. On the assumption that analogous Mosher diastereomers will give the same relative chemical shift independent of the R group of the product, we correlated the absolute configurations by using both ^{19}F and ^{1}H NMR shifts of the diastereomers. The resonances of the two nuclei gave the same correlation. The absolute configurations were then referenced to the product bearing the methyl substituent, for which the absolute configuration is known.[1,9]

The data in Table 1 show that, although very high ee's are obtained for many of the substrates, no simple conclusions can be drawn about the origins of the enantioselection. The first indication of the problem is illustrated by entries 1–4. Varying the silicon substituents of the same allylic substituent leads to varying ee values when the catalysis is performed in acetone solution (entries 1–3). In these cases the ee appears to be controlled by both the *tert*-butyl group and the groups on the silicon although the former group appears dominant. That steric effects emanating from the substrate are not the sole contributors to the enantioselection is demonstrated by the ee observed in CH_2Cl_2 solutions (entry 4), where the ee is low and the sense of induction is reversed compared to entry 1. This solvent effect on ee was also observed for hydroacylation.[5] As well as being an influence on the energies of the diastereomeric transition states, the solvent also affects the catalytic chemical yield of the product as is exemplified by the ester substrates (entries 5–11). The ethyl ester with the silacyclohexyl group (entry 5) is converted in poor chemical yield in acetone solution. Although in CH_2Cl_2 solution (entry 6) rapid conversion to product occurs, the product is decomposed to unidentified products at a rate comparable to that of the initial catalytic product formation. With the diphenyl silicon substrate the ethyl ester gives a high chemical yield (entry 8) and the ee is the same as for the silacyclohexyl analogue (entry 6). In an attempt to increase the ee for esters, we investigated the isopropyl and *tert*-butyl esters and found that the ee increased, the isopropyl ester giving the highest ee, 87%. Substrate decomposition was observed for the isopropyl ester in acetone solution (entry 9), but in CH_2Cl_2 solutions excellent conversion to the product occurred, as was the case for the *tert*-butyl ester (entry 11). In CH_2Cl_2 solution the phenacyl substrate (entry 12) gave excellent chemical and optical yield, as did the dimethylmethoxy substrate (entry 13) in acetone. In CH_2Cl_2 solutions, however, the latter gave good chemical yield but the ee was low and of the opposite sense (entry 14). The trimethylsilyl bearing substrate was converted poorly (entry 16) or not at all (entry 15), depending on the solvent. Although extensive substrate decomposition occurred, the ee was good in CH_2Cl_2 (entry 16).

It is clear from these results that the chemical yields and ees depend on both the substrate structure and the solvent employed. When the right combination of substrate, catalyst, and solvent is found, extremely fast and efficient conversion can be achieved and excellent ees can be obtained. Returning to the possible chirality connection between the putative intermediates **3** and **5** and the absolute configurations of the prevailing enantiomers of the hydroacylation and hydrosilation products, respectively, the present results indicate that no clear analogy exists despite the fact that the analogy provided a guide for selecting substrates which gave high ee's. In fact, the high ee results in Table 1 refer to products which have an absolute configuration opposite to that predicted by intermediate **5**. These results serve to illustrate how subtle mechanistic, structural, and solvent effects can influence the outcome of asymmetric catalytic reactions and how appealing models for enantioselection can be as fanciful as they are successful.

Acknowledgment. This work was supported by grants from the NIH.

Supplementary Material Available: Text giving the preparative procedures for the substrates, derivatization of the products to their Mosher esters, and methods used for performing the catalysis and tables giving the ^{1}H NMR data for the allylic alcohol precursors (Table II), the ^{1}H NMR data for the allylic silyl ether substrates (Table III), the ^{1}H NMR data for the hydrosilation products (Table IV), the ^{1}H NMR data for the alcohols formed from reaction of the hydrosilation products with PhLi (Table V) and the ^{19}F NMR data for the diastereomeric Mosher esters (Table VI) (12 pages). Ordering information is given on any current masthead page.

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(7) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(8) Tamao, K.; Yamauchi, T.; Ito, Y. *Chem. Lett.* **1987**, 171. Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712. Tamao, K.; Tanaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 3377. Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29. Fleming, I.; Kilburn, J. D. *J. Chem. Soc., Chem. Commun.* **1986**, 305. Fleming, I.; Sanderson, E. J. *Tetrahedron Lett.* **1987**, *28*, 4229.

(9) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873. Meyers, A. I.; Hudspeth, J. P. *Tetrahedron Lett.* **1981**, *22*, 3925.