Stereochemistry in the Hydrosilylation of Substituted Cyclohexanones Catalyzed by Chlorotris(triphenylphosphine)rhodium and the Silica-linked Rhodium(I) Complex

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(Received November 13, 1978)

The homogeneous and heterogeneous hydrosilylation of simple substituted cyclohexanones catalyzed by chlorotris(triphenylphosphine)rhodium, $RhCl(PPh_3)_3$, and the silica-linked rhodium(I) complex, ($\equiv$Si–O–$\overset{|}{\underset{|}{Si}}CH_2CH_2PPh_2)_3RhCl$, was examined. The stereoselectivity exhibited by the homogeneous catalyst was found to be nearly the same as that exhibited by the heterogeneous catalyst. The silica-linked rhodium catalyst could be re-used several times without any significant loss of the catalytic activity.

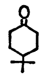
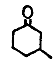
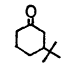
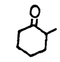
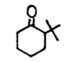
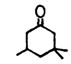
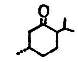
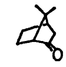
Although the homogeneous hydrosilylation of terpene ketones catalyzed by $RhCl(PPh_3)_3$ has been reported in detail by Ojima *et al.*,[1,2] that of simple cyclohexanones with alkyl substituents has not yet been studied. In order to shed further light on the reaction mechanism, we have now undertaken an investigation of the hydrosilylation of some simple substituted cyclohexanones by Et_3SiH, Ph_2SiH_2, and $PhSiH_3$ with the homogeneous rhodium(I) and the heterogeneous silica-linked rhodium(I) complexes. We have examined how the stereoselectivity is dependent on substrates, reagents, and catalysts. The stereoselectivity in the hydrosilylation effected by the recovered heterogeneous catalyst was also checked.

Results and Discussion

The results of the hydrosilylation of alkyl-substituted cyclohexanones with three kinds of hydrosilanes catalyzed by $RhCl(PPh_3)_3$ are presented in Table 1. In the reaction of 4-methyl- (**2**), 4-*t*-butyl- (**3**), 3-methyl- (**4**), and 3-*t*-butylcyclohexanone (**5**), the bulkiness of the silanes was not an important factor in controlling the stereoselectivity. However, the effects of the bulkiness of the silanes on the stereochemical course of the reduction became significant in the hydrosilylation of 2-methyl- (**6**) and 2-*t*-butylcyclohexanone (**7**). The relative amount of the more stable alcohol increased with an increase in the bulkiness of the hydrosilanes used. This trend was also realized in 3,3,5-trimethylcyclohexanone (**8**), which bears an axial methyl substituent at the 3-position. Thus, the results of **6**—**8** are in good agreement with those of menthone (**9**) and camphor (**10**).[1)]

The relative rates of the hydrosilylation for alkyl-substituted cyclohexanones catalyzed by $RhCl(PPh_3)_3$ were estimated by a comparison of conversion in competitive reactions employing a binary mixture of cyclic carbonyl compounds. The results are listed in Table 2. With each hydrosilane, the relative rates of unhindered cyclohexanones, such as **1**—**5**, were not very different from each other, while those of hindered cyclohexanones, such as **6**—**8**, were found to be smaller than those of unhindered ones. These differences in relative rates seem to be due to the steric interaction between substituents at the 2- or 3-position and hydrosilanes in the transition state. It has previously been reported that the relative rate of $PhSiH_3$ or Ph_2SiH_2 increases remarkably compared to that of Et_3SiH in the cases of terpene ketones and other acyclic carbonyl

Table 1. Stereoselectivities in hydrosilylation of substituted cyclohexanones catalyzed by $RhCl(PPh_3)_3$ (% less stable alcohol)

	 (**2**)	 (**3**)	 (**4**)	 (**5**)	 (**6**)	 (**7**)	 (**8**)	 (**9**)	 (**10**)
$PhSiH_3$	34	27	39	38	67	84	80	–(90)[b)]	–(90)[b)]
Ph_2SiH_2	39	30	38	40	64	65	79	75(85)[b)]	65(73)[b)]
Et_3SiH	40	35[a)]	42	40	35	54	63	59(64)[b)]	29(30)[b)]

a) Hexane was employed as the solvent. b) See Ref. 1.

Table 2. Comparison of conversion in competitive hydrosilylation of cyclohexanones catalyzed by $RhCl(PPh_3)_3$

	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)	(**7**)	(**8**)
$PhSiH_3$	1.00[a)]	1.06	0.94	1.16	0.95	0.38	0.06	0.63
Ph_2SiH_2	1.00[a)]	—	1.01	—	1.05	—	0.27	0.90
Et_3SiH	1.00[a)]	1.05	1.00	1.11	1.00	0.27	0.16	0.42

a) For each hydrosilane, the relative rates of hydrosilylation are normalized to 1.00 for the parent cyclohexanone (**1**).

Table 3. Stereoselectivities in hydrosilylation of substituted cyclohexanones catalyzed by $(\equiv\text{Si–O–}\overset{|}{\underset{|}{\text{Si}}}\text{CH}_2\text{CH}_2\text{PPh}_2)_3\text{RhCl}$ (% less stable alcohol)

		(2)	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**	**(8)**	**(9)**	**(10)**
$PhSiH_3$	I	46	25	43	47	67	80	82		
	II[a]		39		46		80			
	III[b]		42		44		78			
Ph_2SiH_2	I	39	38	41	52	65	69	80	69	69
	II[a]	45	44	49			71			
	III[b]	49	47	54			64			
Et_3SiH	I	35	32[c]	29	34	37	X[d]	73	26	17[c]
	II[a]	32	35[c]	27	34	X[d]	X[d]	77		
	III[b]	32	34[c]			X[d]	X[d]	85		

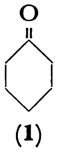
a) II shows stereoselectivities by the re-used catalyst of I. b) III shows stereoselectivities by the re-used catalyst of II. c) Hexane was employed as the solvent. d) Cyclohexanone was recovered without any hydrosilylation.

compounds.[5,6] In this study, for example, the conversion of **8** employing $PhSiH_3$ or Ph_2SiH_2 was over 90% in 15 min, but that employing Et_3SiH was 60% in 3 h. Our results also showed that the relative rate of trihydro or dihydro-silane increased compared to that of monohydro-silane in the reaction of alkyl-substituted cyclohexanones.

The hydrosilylation using $(\equiv\text{Si–O–}\overset{|}{\underset{|}{\text{Si}}}\text{CH}_2\text{CH}_2\text{PPh}_2)_3\text{RhCl}$ showed stereoselectivities similar to those using $RhCl(PPh_3)_3$. These results are summarized in Table 3. The stereoselectivity exhibited by the re-used catalyst was not significantly different from that of the original one.

The effect of repeated use on the catalytic activity of this heterogeneous catalyst was examined employing cyclohexanone (**1**) as a standard substrate (Table 4). The conversion of **1** was 70% at room temperature using the original heterogeneous catalyst, but it went up to 83% at 50 °C. As can be seen in Table 4 (Entry Nos. 1—5), the activity gradually deteriorated upon repeated use, apparently because of the repeated contact with the air. Practically speaking, however, the results of Entry Nos. 1—4 (conversion 70—44%) suggest that the silica-linked catalyst could be re-used several times. Although a closer examination is still needed of the effect of the temperature in repeated use, it should be noted that, judging from the above results, this heterogeneous rhodium complex catalyst has the advantage that the separation of the products from the catalyst is easier than in homogeneous metal complexes and that the re-use is possible.

Table 4. Change by repeated use in silica-linked catalyst[a)]

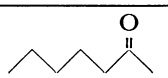
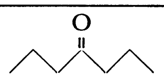
Substrate	Entry[b)] No.	Reaction time/h	Conversion /%
	1	3	70(83)[c)]
	2	3	69
	3	3	54
	4	3	44
(**1**)	5	3	13

a) Et_3SiH was employed as the hydrosilane. b) The entry number also represents the time of repeated use. c) At 50 °C.

In order to examine the regioselectivity, the competitive hydrosilylation of a binary mixture of heptanal, 2-heptanone, and 4-heptanone with Et_3SiH was performed employing the two rhodium(I) complex catalysts. The results are shown in Table 5. The rate difference between the reaction with $(\equiv\text{Si–O–}\overset{|}{\underset{|}{\text{Si}}}\text{CH}_2\text{CH}_2\text{PPh}_2)_3\text{RhCl}$ was notably greater than between those with $RhCl(PPh_3)_3$. The relative rates for 2- and 4-heptanone were 0.11 and 0.074 on respectively $RhCl(PPh_3)_3$, while the values changed to 0.02 and 0.008 with $(\equiv\text{Si–O–}\overset{|}{\underset{|}{\text{Si}}}\text{CH}_2\text{CH}_2\text{PPh}_2)_3\text{RhCl}$. These results show that the reactivity toward the internal carbonyl group in the heterogeneous catalyst is very low compared to that in the homogeneous one. The observed difference in regioselectivity between the reactions catalyzed by the two catalysts suggests that the silica support acts as a steric bulk.

Ojima *et al.* reported that the stereoselectivity in the hydrosilylation is governed only by the size of the silyl

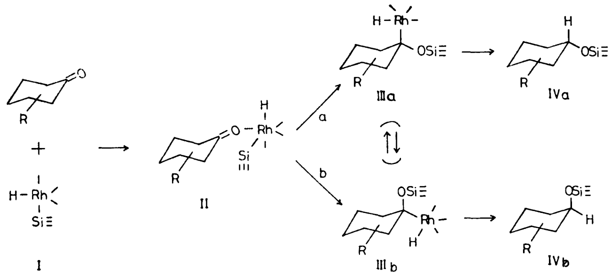
Table 5. Regioselectivities in hydrosilylation by triethylsilane–rhodium(I) complex combination

			
$RhCl(PPh_3)_3$	1[a)]	0.11	0.074
$(\equiv\text{Si–O–}\overset{|}{\underset{|}{\text{Si}}}\text{CH}_2\text{CH}_2\text{PPh}_2)_3\text{RhCl}$	1[a)]	0.02	0.008

a) For each catalyst, the relative rates of hydrosilylation are normalized to 1.00 for heptanal.

moiety. Consequently, it has been mentioned that the bulkier the substituents on silicon, the more pronounced may be the formation of the α-silyloxyalkylrhodium complex IIIa, which is a precursor of the more stable alcohol.[1,6] Although a similar change in the stereoselectivity depending on hydrosilanes was also observed in the reaction of hindered cyclohexanones (**6**—**8**), no change was found in the reaction of unhindered cyclohexanones (**2**—**5**), which gave equatorial alcohols predominantly. *A priori*, the stereoselectivity in the hydrosilylation of alkyl-substituted cyclohexanones is governed kinetically by the insertion step from II to III. Our results clearly show that, in the reaction of unhindered cyclohexanones (**2**—**5**), the axial attack of Rh predominates at the insertion step. Klein and others[7–9] have proposed a stereochemical control based on orbital-symmetry arguments. On the basis of the orbital-distortion theory, Klein[9,10] has reported that, in the absence of steric factors, an electrophilic reagent attacks the cyclohexanone from the equatorial side and a nucleophile attacks from the axial side. As is envisioned in the scheme, the transfer of Rh is supposed to be a nucleophilic reaction; hence, the predominant formation of equatorial alcohol can be accounted for in terms of Klein's criterion. On the other hand, the axial attack of Rh on hindered cyclohexanones (**6**—**8**) is restricted by the substituents at the 2- or 3-position. Consequently, the equatorial attack of Rh predominates in the reaction of hindered cyclohexanones (**6**—**8**), supporting results presented by previous workers.[1,6]

The influence of the bulkiness of silanes was thus significant only in the reaction of hindered cyclohexanones, such as **6**—**10**. These changes in the product distribution may be attributed to the equilibrium between IIIa and IIIb originating in the large interaction between the axial silyloxyl group and the substituents in the IIIb complex.[1] Therefore, the bulky silyloxyl group may occupy the less-hindered position when the silyloxyl group becomes larger than the rhodium moiety, which is kept constant in the III complex.



Experimental

A typical procedure will be described for the hydrosilylation of 4-methylcyclohexanone (**2**): To a mixture of 2 mmol of **2** and hydrosilanes, 5.2×10^{-3} mmol of $RhCl(PPh_3)_3$ or 0.1 g of $(\equiv Si\text{-}O\text{-}\overset{|}{\underset{|}{Si}}CH_2CH_2PPh_2)_3RhCl$ was added. The amount of $RhCl(PPh_3)_3$ was equalized in Rh content to that of $(\equiv Si\text{-}O\text{-}\overset{|}{\underset{|}{Si}}CH_2CH_2PPh_2)_3RhCl$, which had been found to contain 0.54 wt % of Rh. The mixture was stirred for 15 min ($PhSiH_3$), for 30 min (Ph_2SiH_2), and for 3 h (Et_3SiH) at room temperature under a nitrogen atmosphere. The silyl ether thus obtained was hydrolyzed by a MeOH–KOH–H_2O soln. to afford cyclohexanol quantitatively. The worked-up mixture was analyted by GLC.

Silica-linked Rhodium (I) Complex.[3,4] $(\equiv Si\text{-}O\text{-}\overset{|}{\underset{|}{Si}}CH_2CH_2PPh_2)_3RhCl$ was prepared from chlorotris[diphenyl[2-(triethoxysilyl)ethyl]phosphine] rhodium, $[(EtO)_3SiCH_2CH_2PPh_2]_3RhCl$, and silica gel (pore radius, 150 Å; surface area, 270 m^2/g; surface OH concentration, *ca.* 4 mmol/g) by refluxing with anhydrous benzene. The heterogeneous catalyst used was washed several times with pentane and dried under reduced pressure. This catalyst was then re-used.

Competitive Hydrosilylation. In a flask containing 5.2×10^{-3} mmol of $RhCl(PPh_3)_3$, 0.05 mmol each of two carbonyl compounds and 0.1 mmol of a hydrosilane were stirred at room temperature under a N_2 atmosphere. The composition of the mixture was checked in order to stop the reaction when half of the hydrosilane had been consumed. Water and crushed ice were added, and the resultant silyloxy compounds were hydrolyzed with a sufficient quantity of the MeOH–KOH–H_2O solution. The aqueous layer was extracted with ether, which had been washed with brine and dried over Na_2SO_4. The soln. was concentrated by removing a part of the ether, and the residual solution was subjected to GLC.

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