Stereoselective Reduction of Ketones with Hydrosilane-Rhodium(I) Complex Combinations

Iwao Ojima, Mitsuru Nihonyanagi, and Yoichiro Nagai*
Sagami Chemical Research Center, Onuma, Sagamihara 229
** Department of Chemistry, Gunma University, Kiryu, Gunma 376*

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Aluminum hydrides,[1] aluminum alkoxides,[1,2] tin hydrides[3] and hydroboranes[5] can reduce ketones to alcohols stereoselectively and each reducing agent displays the respective characteristics of stereoselectivity. It is rather surprising that, in spite of the known capability of silicon hydrides to reduce ketones,[6] no attention has been so far drawn to stereochemistry in the reductions with these hydrides. Now, we wish to report here our preliminary results of the reduction of terpene ketones by hydrosilane-rhodium(I) complex combinations[4] which finds several marked differences in stereochemical selectivity from other reducing systems.

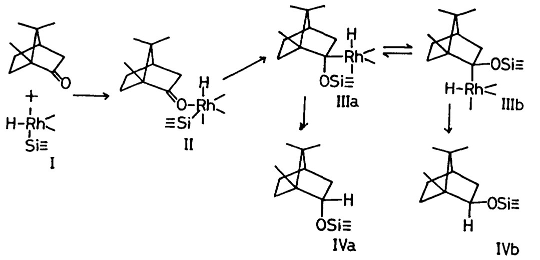
The reaction was carried out by stirring an equivalent mixture of a ketone and a hydrosilane at 0—80 °C in the presence of a catalytic amount of $(Ph_3P)_3RhCl$. Alcohols were obtained by hydrolysis of the resulting silylethers. Yields of alcohols were nearly quantitative in all cases. Results of the hydrosilane reduction of camphor and menthone, representative terpene ketones, are listed in the Table. Included also in the Table are the reported selectivities achieved by other known reducing agents.

Table. Stereoselectivities in the reduction of terpene ketones by hydrosilane-rhodium(I) complex combinations (% less stable alcohol)

Reducing agent	Camphor	Menthone
$PhSiH_3$	90[a]	90[a]
Et_2SiH_2	91[a]	83[a]
$PhMeSiH_2$	75[a]	86[a]
Ph_2SiH_2	73[a]	85[a]
Et_3SiH	30[b]	64[c]
$PhMe_2SiH$	—[d]	0[c]
$LiAlH_4$	91[e]	29[f]
$Al(OPr\text{-}i)_3$		70[g]
$NaBH_4$		51[g]
B_2H_6	52[e]	
Disiamylborane	65[e]	
Dicyclohexylborane	93[e]	
Diisopinocamphenylborane	100[e]	
Ph_2SnH_2		52[g]

a) The reaction was performed without solvent using 0.1 mol% $(Ph_3P)_3RhCl$. b) 1.0 mol% $(Ph_3P)_3RhCl$ was used and *n*-hexane was employed as a solvent. c) 1.0 mol% $(Ph_3P)_3RhCl$ was used without solvent. d) Camphor was recovered without any hydrosilation. e) See Ref. 5a. f) A. K. Macbeth and J. S. Shannon, *J. Chem. Soc.*, **1952**, 2852. g) See Ref. 3.

As shown in the Table, the bulkiness of silanes exerts large influence on the stereochemical course of the reduction and a bulky hydrosilane favors the production of the more stable alcohols. This trend is quite unusual since it has been shown by Brown and Varma that, in the reduction of monocyclic and bicyclic ketones, the more bulky hydroborane produces the larger percentage of less stable of the two possible alcohols.[5a] The peculiarity found in the hydrosilane reduction catalyzed by rhodium(I) complex suggests that the transition state for the reaction cannot be accommodated with a simple four-centered type.[7] However, a possible explanation for the observed trend can be advanced by taking into account the intermediacy of the organorhodium complex III as shown below, the formation of which is quite reasonable[10] in view of the well-documented "soft-hard conception".[9] As the steric course would be governed only by the size of the silyl moiety,[10] it can be said that the bulkier the substituents on silicon, the more pronounced may be the formation of the complex IIIa which is a precursor of the more stable alcohol. A further work on the mechanism of the rhodium(I) complex catalyzed reductions is now under investigation.



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1) For example, E. L. Eliel, and D. Nasipuri, *J. Org. Chem.*, **30**, 3809 (1965); W. Hückel, M. Maier, E. Jordan, and W. Seeger, *Ann. Chem.*, **616**, 46 (1958) and references therein.

2) J. C. Richer, *J. Org. Chem.*, **30**, 324 (1965); E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970); E. C. Ashby, J. P. Sevenair, and F. R. Dobbs, *J. Org. Chem.*, **36**, 197 (1971).

3) H. G. Kuivila, *Synthesis*, **1970**, 499; H. G. Kuivila and O. F. Beumel, Jr., *J. Amer. Chem. Soc.*, **83**, 1246 (1961).

4) I. Ojima, T. Kogure, M. Nihonyanagi, and Y. Nagai, This Bulletin, **45**, 3232 (1972).

5) a) H. C. Brown and V. Varma, *ibid.*, **88**, 2871 (1966); b) D. C. Wigfield and D. J. Phelps, *Chem. Commun.*, **1970**, 1152.

6) C. Eaborn, "Organosilicon Compounds," Butterworth, London (1960), p. 213.

7) For example, H. O. House, and J. E. Oliver, *J. Org. Chem.*, **33**, 929 (1968); H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, **87**, 5620 (1965).

8) The conversion of the complex II to III will be favored on the basis of the following two points; i) as the Rh^I complex I is a soft acid, the Rh^I-C bond may be stronger than the Rh^I-O bond. ii) the Si-O bond newly formed in the complex III is very strong.

9) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

10) The only variable steric factor is the size of silyl group, and therefore the bulky silyloxy group may occupy the less hindered site when the silyloxy group becomes larger than the rhodium moiety which is kept constant in the complex III.