

Transformation of organic compounds in the presence of metal complexes

IV *. Hydrosilylation of 2- and 4-alkylcyclohexanones on rhodium(I) complexes

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Abstract

The hydrosilylation of 2- and 4-alkylcyclohexanones with Ph_2SiH_2 was studied under various conditions. The isomeric distribution of the resulting alcohols, i.e. the stereochemistry of the hydrosilylation, is influenced by the position and size of the alkyl groups, the catalyst concentration, the reaction temperature, and the types of ligand attached.

Introduction

Since the Si–H bond in silanes can be much more readily activated than the H–H bond in the hydrogen molecule, Si–H addition to unsaturated bonds can be catalysed by a large number of transition metal complexes [1]. This is particularly important in the case of carbonyl compounds, for the O–Si bond formed as a result of the addition can readily be hydrolysed, and hydrosilylation is thus a suitable procedure for the preparation of alcohols. Various authors have studied the enantioselective variant of the addition in the case of open-chain ketones and α -keto-esters [2–6]. In particular, Rh-containing complexes are appropriate as catalysts of the process [7,8]. Relatively few data are available on the hydrosilylation of cyclic ketones. In connection with terpenoid ketones, it has been established that the bulky trialkylsilanes give the more stable isomeric alcohol, while the mono- and di-alkylsilanes give the less stable one [7]. In the hydrosilylation of some alkyl-substituted cyclohexanones, the stereoselectivity has been studied as a function of silane size

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and the type of alkyl substituents [9–11]. The enantioselective hydrosilylation of some steroid ketones has also been investigated [12].

Data on the hydrosilylation of 4-*t*-butylcyclohexanone with Ph_2SiH_2 have been published [9,10].

Although the reaction conditions were nearly the same, different stereoselectivities were observed: the *cis*/*trans* isomer ratio was 30/70 [10] and 57/43 [9]. Since the authors of the two publications used different substrate-catalyst ratios, we thought it necessary to carry out detailed studies to examine the extent to which the stereoselectivity is influenced by the quantity of catalyst, the position and size of the alkyl group, the reaction temperature, and nature of the ligand. We therefore investigated the hydrosilylation of the 2- and 4-alkylcyclohexanones with Ph_2SiH_2 , in benzene solvent, in the presence of $\text{RhCl}(\text{PPh}_3)_3$ or other, similar catalyst prepared in situ.

Results

It can be seen from the data in Tables 1 and 2 that the less stable, *cis* isomer is formed in greater amounts from the 2-alkylcyclohexanones, whereas the 4-alkylcyclohexanones yield larger quantities of the more stable, *trans* isomer. A change in the reaction conditions usually has a much smaller effect on the 2-alkylcyclohexanones in terms of stereoselectivity; this demonstrates that the determining factor in this case is the closeness of the alkyl group. A considerable difference is observed when hydrosilylations are carried out under similar conditions; the 4-alkylcyclohexanones show conversions of 95–100%, whereas those undergone by the 2-alkylcyclohexanones show conversions of only 60–70%. A large change is seen with the 4-alkylcyclohexanones insofar as the increase in the quantity of catalyst is accompanied by a considerable rise in the amount of the less-stable alcohol. Further investigations are required to explain this, although a further increase in the quantity of catalyst leads to solubility problems. The 4-alkylcyclohexanones show a similar change in stereoselectivity when the temperature is raised. The data in Table 3 reveal that a bulkier ligand favours the formation of the more stable alcohol isomer. However, neither this effect, nor variation of the size of the alkyl sub-

Table 1

Relative amount (%) of *cis*-2- and *cis*-4-alkylcyclohexanols produced during the hydrosilylation of cyclohexanones by $\text{RhCl}(\text{PPh}_3)_3$ ^a

Cyclohexanone	Catalyst (mol%)				
	0.05 ^b	0.1	0.25	1	10
2-Me	–	70	65	63	62
2- <i>i</i> -Pr	75	70	74	76.5	75
2- <i>t</i> -Bu	82	84	81	78	75
2-Ph	–	–	71	67	–
4-Me	–	32	39	41	51
4- <i>i</i> -Pr	25	32.5	–	46	58
4- <i>t</i> -Bu	31	36.5	–	46	57.5
4-Ph	–	–	31	42	–

^a Reaction time 0.5 h. ^b Reaction time 1 h.

Table 2

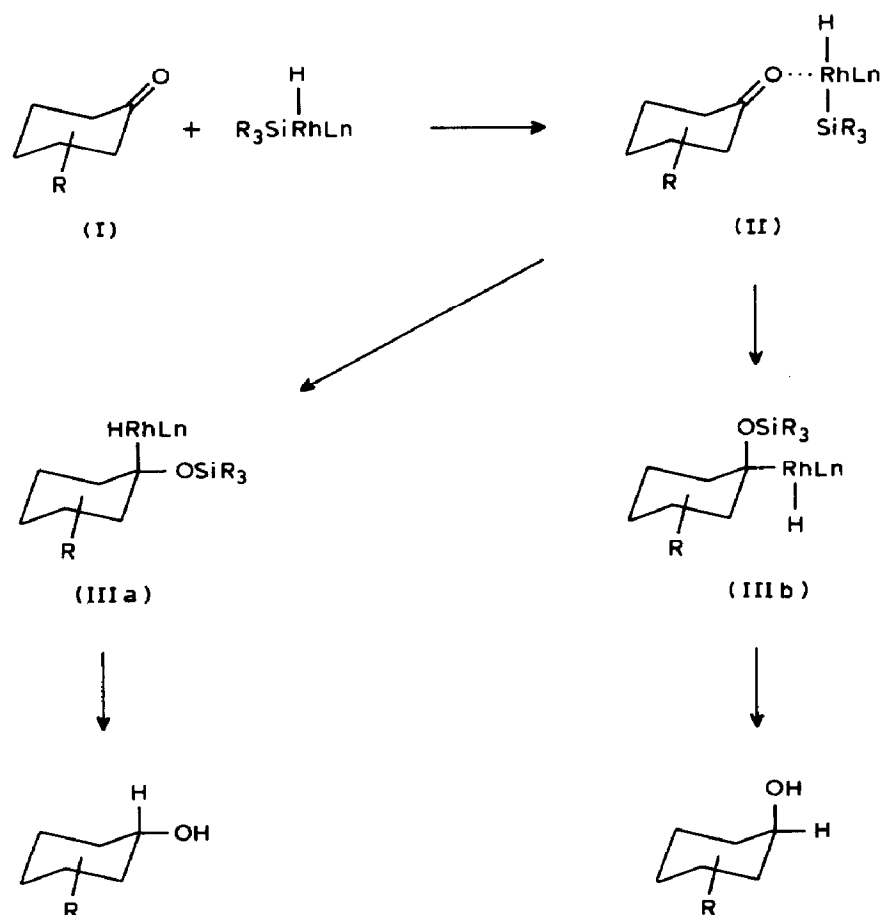
Dependence of the amount *cis*-isomer (%) on temperature in the hydrosilylation of 2- and 4-alkylcyclohexanones by $\text{RhCl}(\text{PPh}_3)_3$ ^a

Cyclohexanone	Temperature (°C)			
	-10 ^b	0	25	50
2-Me	—	70	63	63
2-i-Pr	77	74	76.5	74
2-t-Bu	—	77	78	80
4-Me	21	30	41	—
4-t-Bu	33	35	46	—

^a Reaction time 0.5 h, 1 mol% of catalyst. ^b In benzene/ether 1/1.

stituent, causes such a large change in the stereoselectivity as that reportedly due to a change in the size of the silane [7,9].

Our most recent observations can be explained on the basis of the orbital distortion theory of Klein [10,13] (see Scheme 1), in which the transition $\text{II} \rightarrow \text{III}$ Rh transfer from the axial direction is enhanced when steric factors are absent: so that



Scheme 1

Table 3

Effect of the ligand on the stereoselectivity in the hydrosilylation of 4-*t*-butylcyclohexanone by a Rh catalyst ^a prepared in situ

Ligand	<i>cis</i> -4- <i>t</i> -Bu-cyclohexanol (%)
PPh ₃	59
PBu ₃	61.5
DPE	56.5
DPB	51
Diphenylphosphinoferrocene	49.5
Diphenylenephényl phosphine	44.5

^a 10 mol% catalyst; [P]/[Rh] = 2, temp. 25 °C, conversion 95–100%, reaction time 0.5 h.

for 4-*R*, equatorial attachment of the hydroxy group results, but for 2-*R*, the axial binding of Rh is hindered, and so equatorial binding becomes more favoured, which leads to axial attachment of the hydroxy group.

Our results relating to an increase of the catalyst concentration also lend support to the above picture: elevation of this concentration, affected the *cis* to *trans* isomer ratio in the case of the 4-alkylcyclohexanones. (The proximity of the alkyl group is the determining factor in terms of the stereoselectivity in the hydrosilylation of the 2-alkylcyclohexanones.)

Experimental

The ketones used were either Fluka products or were prepared from Fluka alcohols by standard methods. The RhCl(PPh₃)₃ and the ligands were purchased from Aldrich Chemie, while the [Rh(COD)Cl]₂ was prepared by a published procedure [14].

To a measured amount of catalyst in a reaction vessel, which was constantly being flushed out with a stream of nitrogen, was added a solution of the ketone and the diphenylsilane in benzene (ketone/diphenylsilane ratio 1/1.2).

The reaction mixture was then diluted to 3 ml with benzene, the vessel was transferred to a thermostatted bath, and the contents were stirred for 30 min. After the benzene had been evaporated off, the residue was boiled for 30 min in a solvent mixture of *p*-TsOH/H₂O/MeOH. In the case of the catalysts prepared in situ, the [Rh(COD)Cl]₂ and the ligand were first mixed for 5 min in 1 ml benzene, and then the solution of the ketone and the diphenylsilane was added.

Gas chromatographic studies were performed with a Chrom 4 instrument (Czechoslovakia): on a 2.4 m 5% Carbowax 20M/Chromosorb P column equipped with a flame ionization detector, and nitrogen as the carrier gas. The calculations were carried out with a Digint 34 μ integrator (Chinoin, Budapest).

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