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Studies on organolanthanide complexes

XLI *. Catalytic isomerization of olefins by organolanthanide complex/sodium hydride systems

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Abstract

Isomerization of several 1-alkenes catalyzed by organolanthanide complex/sodium hydride systems in THF at 45°C, affords *cis*- and *trans*-2-alkenes in excellent yields. Effects of solvent and π-ligand of complex on this isomerization are also examined. The catalytic isomerization may occur via organolanthanide hydride intermediate.

Introduction

Rare earth metal complex catalysis is one of the most active research fields of organolanthanide chemistry [1]. In recent years this field has been greatly developed and it has been found that these rare earth metal complex catalysts could: (1) activate CO [2–5] and C–H bonds [6,7]; (2) catalyze the hydrogenation [8–10] and polymerization [10–14] of alkenes and alkynes; (3) catalyze the hydrosilylation of styrene [15] and the hydroamination/cyclization of aminoolefins [16]. In the course of our studies on organolanthanide complexes, we have undertaken the study of new reducing reagents composed of a combination of sodium hydride and an organolanthanide complex. These systems have been shown to be efficient reagents for reduction and catalytic hydrogenation of olefins [17–22], catalytic dehalogenation of aryl and vinyl halides [23], deoxygenation of heteroatom oxides [24].

Although the selectivity for 1-hexene reduction by these systems is high under proper conditions, a certain quantity of isomerization product, *cis*- and *trans*-2-hexene, is also formed especially for heavy rare earth metal complexes [18]. This

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Table 1

Effect of solvents on 1-octene isomerization [a]

Entry	Solvent	Time (h)	Yield of 2-octene (%) [b]
1	THF	24	93(64/36)
2	DME	24	18(41/59)
3	Ethyl Ether	24	17(36/64)
4	Dioxane	48	7(19/81)
5	Diglyme	24	Trace
6	Toluene	48	No reaction
7	Hexane	48	No reaction

[a] Reaction conditions: $(C_5H_5)_3Y/NaH/1$-octene (0.05:7.8:1) (molar ratio), at 45°C. [b] GC yield determined using dodecane as an internal standard; the number in parentheses is the molar ratio of *Z*- to *E*-isomer.

suggests that these systems might have very interesting characteristics which has stimulated us to undertake further investigations of their reaction with olefins. Here we report the results of this reaction as well as the effects of solvent and π-ligand of the complex on the olefin isomerization.

Results and discussion

The selectivity for 1-hexene reduction by $(C_5H_5)_3Ln/NaH$ in THF is strongly affected by the molar ratio of $(C_5H_5)_3Ln$ to 1-hexene. When the ratio of $(C_5H_5)_3Ln/1$-hexene decreases to less than 0.25, only isomerization of the double bond in 1-hexene occurs, affording *cis*- and *trans*-2-hexene in excellent yield, and the two isomers are in nearly equal amounts. In the absence of $(C_5H_5)_3Ln$ no isomerization takes place. It appears clear that these complexes are necessary for this isomerization. In contrast to their reducing activity, the isomerization activity of the heavy rare earth systems is better than that of the early rare earth ones. The catalytic activities of $(C_5H_5)_3Er$ and $(C_5H_5)_3Lu/NaH$ are the highest. The radius of yttrium is close to that of erbium and $(C_5H_5)_3Y/NaH$ is also among the most reactive systems.

Isomerization of 1-octene with $(C_5H_5)_3Y/NaH$ in THF produces *cis*- and *trans*-2-octene in excellent yield. The catalytic activity of $(C_5H_5)_3Y/NaH$ for 1-octene isomerization in several other organic solvents are examined (Table 1). The results indicate that the solvent has a dramatic effect on the catalytic activity. Except in THF, the yields of 2-octene are poor in other solvents, especially in hydrocarbon solvents such as toluene and hexane when no isomerization occurs. In contrast to catalytic oligomerization of terminal alkynes by carbyls $(\eta^5\text{-}C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Y, La and Ce) [14], THF is the proper solvent for this isomerization. This might be due to the solubility of the complex and/or the hydride intermediate, or even the fact that the hydride is not formed in hydrocarbon solvents.

The catalytic activities of some other type of organoyttrium complexes for 1-octene isomerization are also investigated; the results are listed in Table 2. It can be seen that the isomerization activities of these systems also depend strongly upon π-ligands in the complexes and decrease in the following order: $(C_5H_5)_2YCl \sim (C_5H_5)_3Y > (CH_3OCH_2CH_2C_5H_4)_2Y(C_5H_5) > CH_3N(CH_2CH_2C_5H_4)_2YCl \sim$

Table 2

Effect of π-ligand on 1-octene isomerization [a]

Entry	Complex	Yield of 2-octene (%) [b]
1	$(C_5H_5)_3Y$	93(64/36)
2	$(C_5H_5)_2YCl$	98(31/69)
3	$(CH_3OCH_2CH_2C_5H_4)_2Y(C_5H_5)$	48(63/37)
4	$(CH_3OCH_2CH_2C_5H_4)_2YCl$	18(42/58)
5	$CH_3N(CH_2CH_2C_5H_4)_2YCl$	20(39/61)
6	YCl_3	8(37/63)

[a] Reaction conditions: in THF at 45°C, complex/NaH/1-octene (0.05:7.8:1). [b] GC yield after 24 h determined using dodecane as an internal standard; the number in parentheses is the molar ratio of *Z*- to *E*-isomer.

$(CH_3OCH_2CH_2C_5H_4)_2YCl > YCl_3$. For the ether-substituted and amine-bridged cyclopentadienyl yttrium complexes, the intramolecular coordination is formed from the oxygen or nitrogen atom to the central metal ion [25–27], resulting in saturated and space crowded coordination, which makes the complexes more stable and not so ready to coordinate with olefin. Therefore, these complexes are less reactive.

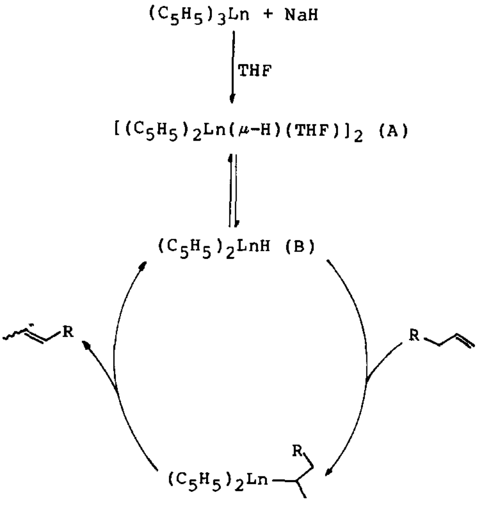
Because the catalytic activity of $(C_5H_5)_3Y/NaH$ for this isomerization is one of the highest, and its starting material, yttrium oxide, is much cheaper, we have applied the $(C_5H_5)_3Y/NaH$ system to alkenes to examine the scope and limitations of this isomerization (eq. 1).

$$RCH_2CH{=}CH_2 \xrightarrow[\text{THF, 45°C}]{\text{cat. }(C_5H_5)_3Y/NaH} RCH{=}CHCH_3 \tag{1}$$

$$R = -CH_2CH_2CH_3,\ -CH_2(CH_2)_2CH_3,\ -CH_2(CH_2)_3CH_3,$$
$$-CH_2(CH_2)_7CH_3,\ -CH(CH_3)_2,\ -Ph,\ \textit{etc.}$$

The results are summarized in Table 3. Acyclic terminal olefins such as 1-hexene and 1-dodecene are readily isomerized to internal olefins, while this catalytic system is inert to 4-vinylcyclohexene and limonene. This is probably due to the steric effect of the substrates and might provide a possible method for the chemoselective isomerization of some terminal carbon–carbon double bonds. Isomerization of 1,5-cyclooctadiene (1,5-COD) affords 1,3-COD in high yield, and during the whole procedure only a little of 1,4-COD is recorded. The possible reason may be that 1,3-COD is much more thermodynamically stable than 1,4-COD. Otherwise, the initial isomerization of 1,5-hexadiene gives 1,4-hexadiene as the major product, which is further isomerized to 2,4-hexadiene. Unfortunately, the reaction of 5-hexen-2-one with $(C_5H_5)_3Y/NaH$ is complicated, and gives a mixture of isomerization, reductive, and high boiling point products. This may be due to the reaction of sodium hydride with α-H in 5-hexen-2-one. Therefore, we protect the carbonyl group with 1,2-ethandiol to avoid this interaction. However, this ketal is inert to the $(C_5H_5)_3Y/NaH$ system and is quantitatively recovered. The reason for this might be that the coordination of the oxygen atom of the substrate with yttrium makes this system lose its catalytic activity.

As we previously reported, organolanthanide complex/sodium hydride systems possess very interesting characteristics [18,28]. Up to now, the reaction mechanism

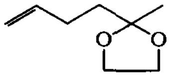


Scheme 1. Catalytic cycle.

of these systems with some organic compounds are not well understood. A proposed reaction pathway for 1-alkene isomerization is depicted in Scheme 1 [18,28]. The reaction of $(C_5H_5)_3Ln$ with NaH produces the organolanthanide hydride (**A**), which dissociates to give monomeric hydride intermediate **B**. Because of the coordinative unsaturation of **B**, the olefin then coordinates to the hydride **B**. The subsequent insertion of the C=C bond into the Ln–H σ-bond generates the compound containing a Ln–C σ-bond, which undergoes β-hydrogen elimination to

Table 3

Isomerization of olefin catalyzed by $(C_5H_5)_3Y/NaH$ [a]

Entry	Olefin	Time (h)	Yield (%) [b]
1	1-Hexene	24	86 (58/42)
2	1-Heptene	24	94 (59/41)
3	1-Octene	24	93 (64/36)
4	1-Dodecene	24	90 (57/43)
5	4-Methylpentene	28	93 (33/67)
6	3-Phenylpropene	24	99 (9/91)
7	1,5-COD	24	89 (1,3-COD)
8	1,5-Hexadiene	24	51 (1,4-hexadiene) 23 (2,4-hexadiene)
		60	8 (1,4-hexadiene) 61 (2,4-hexadiene)
9	4-Vinylcyclohexene	43	No reaction
10	Limonene	48	No reaction
11	5-Hexenone-2	24	Complicated
12		24	No reaction

[a] Reaction conditions: in THF at 45°C, $(C_5H_5)_3Y/NaH/olefin$ (0.05 : 7.8 : 1). [b] GC yield determined using dodecane or hexadecane as an internal standard, the number in the parentheses is the molar ratio of *Z*- to *E*-isomer.

give 2-alkene with regeneration of the hydride **B**. The isomerization of 1-alkenes is thus realized via this addition-elimination cycle. Every elementary reaction of this catalytic cycle is well known in organotransition-metal and organolanthanide chemistry [9,29]. Variable-temperature NMR studies of $(C_5Me_5)_2Lu(\mu\text{-}H)Lu(H)(C_5Me_5)_2$ show that, at 25°C, a 1 m*M* solution of this hydride will be greater than 10% dissociated and be in equilibrium with the terminal hydride [30]. It is reasonable to expect that the behavior of $[(C_5H_5)_2Ln(\mu\text{-}H)(THF)]_2$ will be similar. In addition, it has been found that the reactivity of organolanthanide hydride depends on the amount of steric saturation of the metal center and the type of Ln–H linkage, and the terminal Ln–H moiety is much more reactive than the bridging one [31]. An alternative organolanthanide hydride intermediate $[Na(THF)_6][(C_5H_5)_3LnHLn(C_5H_5)_3]$ [32] is also possible.

Experimental

All operations were carried out under prepurified argon by use of Schlenk techniques. All solvents were refluxed and distilled over either finely divided $LiAlH_4$ or blue sodium benzophenone under argon immediately before use. The complexes $(C_5H_5)_3Ln$ [33], $(C_5H_5)_2YCl$ [34], $CH_3N(CH_2CH_2C_5H_4)_2YCl$ [25], $(CH_3OCH_2CH_2C_5H_4)_2YCl$ [26,27], $(CH_3OCH_2CH_2C_5H_4)_2Y(C_5H_5)$ [35] and YCl_3 [36], were prepared using the reported procedures. Sodium hydride (E. Merck, with 20% paraffin oil) was washed with THF and dried in vacuum. Alkenes were dried by treatment with CaH_2 and distilled under argon.

GC–MS and GC–IR spectra were recorded on a Finnigan 4021 GC–MS and a Digilab instrument FTS-20E capillary GC–FTIR, respectively. GC analysis was performed with a Varian 3700 gas chromatographic instrument equipped with PEG-20000 capillary column.

A general procedure for the olefin isomerization was as follows (for example, entry 1 in Table 1): a 5-ml Schlenk tube equipped with a Teflon stopcock was charged with 8.1 mg (0.0285 mmol) of $(C_5H_5)_3Y$ and 107.5 mg (4.48 mmol) of NaH, cooled to −78°C, and a solution of 89.3 μl (0.57 mmol) of 1-octene in THF (2 ml) was then introduced by a syringe into the tube. The reaction mixture was allowed to warm to room temperature, and the reaction was carried out at 45°C with stirring. After the given time, the reaction was quenched with a little water, and 50.0 μl dodecane was added as internal standard. The mixture was dried with anhydrous Na_2SO_4 and then centrifuged. A solution of the products was thus obtained. The products were determined by GC–MS, GC–IR and compared with the authentic compounds. The yields and distribution of products were determined by GC analysis.

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