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Isomerization of 1,5-Hexadiene Catalyzed by Bis-(Cyclopentadienyl) Lanthanide Schiff Base/NaH Systems; Ln = Sm, Dy, Y, Er

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Abstract. Catalytic isomerization of 1,5-hexadiene by Cp_2Ln Schiff base/NaH (Schiff base = $C_{14}H_{14}NO_2$, Ln = Sm, Dy, Y, and Er) systems was studied. The isomerization resulted in a mixture of 1,4-hexadiene, 2,4-hexadiene, 1,3-hexadiene, methylene-cyclopentane, and methylcyclopentene. 1,4-Hexadiene and methylenecyclopentane were the intermediate products, while 2,4-hexadiene and methylcyclopentene were the end-products. The effects of the nature of catalyst, temperature, amount of the catalyst, time and solvent, on the isomerization rate and product composition were also studied. The ratio of the linear to the cyclic product in the reaction depended on the amount of catalyst used.

Keywords: isomerization, 1,5-hexadiene, 2,4-hexadiene, lanthanocene complexes, Schiff base/NaH systems, methylcyclopentene

Introduction

The recent growth in organolanthanide chemistry has primarily focused on complexes stabilized by tridentate Schiff base ligand system. Further interest in exploring the metal ion complexes with Schiff base ligands has continually increased, since it has been recognized that many of such complexes may serve as biologically important, naturally occuring ionophores. On the other hand, metal hydride complexes are fundamental components in a wide range of stoichiometric and catalytic organometallic reactions (Teller and Bau, 1981). However, the hydrides of the lanthanide metals have been previously described only for interstitial metallic compounds. The simple binary hydrides, LnH_x, have been known for many years (Mueller *et al.*, 1968). The literature survey verifies that hydride complexes of lanthanide metals are important factors for the rapid advancement of the developing organolanthanide chemistry. The investigations concerning lanthanide complexes with Schiff bases have been devoted to their synthesis, structural studies, and biological application of metal enzymes or protein bondings. A large number of Schiff bases and their complexes have been studied for their interesting and important properties, such as, their ability to reversibly bind oxygen (Jones *et al.*, 1979) catalytic activity in hydrogenation of olefins (Henrici-Olie and Olive, 1984), transfer of amino group (Dugas and Penny, 1981), photochromic properties (Margerrum and Miller, 1971), complexing ability towards some toxic metals (Sawodny and Reiderer, 1977), catalytic synthesis of polymethylmethacrylate (Yousaf *et al.*, 2000 a; b), and so on. Untill now, such type of complexes have not been attempted for isomerization of olefins. Earlier works indicate that the catalytic isomerization of 1,5-hexadiene by Cp_2TiCl_2/i-C_3H_7MgBr system results in a mixture of 1,4-hexadiene, 1,3-hexadiene, 2,4-hexadiene, methylenecyclopentane, and methylcyclopentene (Akita *et al.*, 1983; Lehmkuhi and Qian, 1983). Later on, it was verified that isomerization of 1,5-hexadiene with cyclopen-tadienyl titanium complexes resulted into a mixture of simi-lar isomeric products as reported above (Qian *et al.*, 2000). Thus, there was an interest in the synthesis of monomeric lanthanocene complexes with tridentate Schiff base [N-I-(ortho-methoxyphenyl)] as a ligand, which is the electronic equivalent to cycloentadienyl ligand, and then catalytic isomerization of 1,5 hexadiene.

Materials and Methods

All the operations were carried out under prepurified argon by use of schlenk techniques. All the solvents were refluxed and distilled over blue sodium benzophenone under argon immediately before use. All the complexes were newely synthesized by using the reported procedures (Yousaf *et al.*, 2000c; d; Liu and Ding, 1998) and were characterized by MS, EA, and IR. Sodium hydride was washed with THF and dried under vacuum. 1,5-hexadiene was dried by treating with CaH_2 and distilled under argon. A general procedure was as follows (refer to entry 1 in Table 1): a 25 ml schlenk tube, equipped with a teflon stopcock, was charged under argon with 0.052 g (0.10 mmole) of $(C_5H_5)_2Sm(OC_{14}H_{13}NO)$ and 0.12 g of NaH,

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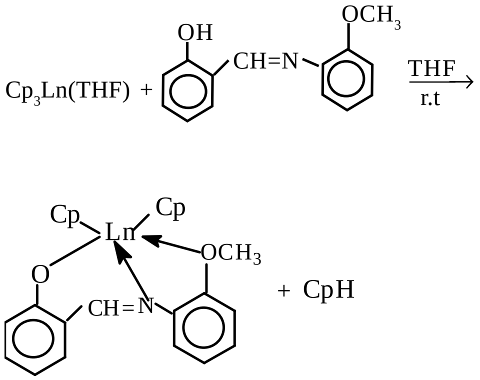
then 3 ml THF was poured along with stirring, cooled to -78°C, and 0.164 g (0.24 ml) of 1, 5-hexadiene was introduced by a syringe. The reaction mixture was allowed to warm to room temperature, and then was continued at 60°C. After the given time, the reaction was quenched with 1 ml of methanol. The reaction mixture was then distilled out under reduced pressure and the distillate was collected in schlenk tube at -78°C. The solution of the products thus obtained was injected into the GC, and products were identified by comparing with authentic compounds.

Results and Discussion

The Cp_2Ln Schiff base complexes were synthesized as follows:



Ln = Sm, Dy, Y, Er

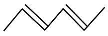
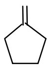
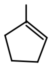
The results of isomerization of 1,5-hexadiene catalyzed by different Cp_2LnSb catalysts are shown in Table 1.

It was observed that neither these novel lanthanocene complexes, nor NaH alone, did show any encouraging activity. When the complexes were, however, embedded with NaH (1:50), then they exhibited reasonable efficiency.

As is explained by the observations listed in Table 1, the catalytic efficiency of $(C_5H_5)_2Sm(OC_{14}H_{13}NO)$ was more than any other attempted complexes. Further, the synthetic yield of this complex was much more than others. So, this complex was used as a representative of all the samples tested to study the effect of catalyst, tempareture, catalyst/substrate ratio, time, and solvent on the isomerization of 1,5-hexadiene. At 60 °C, the $(C_5H_5)_2Sm(OC_{14}H_{13}NO)$ favours the conversion of 1,5-hexadiene into linear products, especially 1,4-hexadiene (80.6%), whereas $(C_5H_5)_2Er(OC_{14}H_{13}NO)$ conveys 1,5-hexadiene into cyclic ones, preferably methylenecyclopentane (25.2%). There was no significant difference between the convertion efficiency of $(C_5H_5)_2Er(OC_{14}H_{13}NO)$ and $(C_5H_5)_2ErCl\ (OC_{14}H_{13}NO).THF$. This suggests that both complexes may offer the same kind of hydride system. Generally, the catalytic efficiency of $(C_5H_5)_2Sm(OC_{14}H_{13}NO)$ was better (28.7%) than any other complex used, which may be because of the ionic radius of samarium being larger than any other metal used. It means that greater the ionic radius, the greater will be the coordination sphere of the metal. Hence, easier the active species, such as CpLnH will be produced, and also easier the monomeric unit will make attachment with the metal during the isomerization process. Moreover, it should be kept in mind that the role of Schiff base ligand in such type of the complexes is to facilitate the generation of active species, like CpLnH, because Schiff base, being polar, can react with NaH easily to produce such active species. Further, there was found no catalytic activity with $ErCl_3$/NaH system.

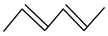
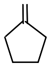
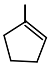
The effect of temperature, as shown in Table 2, indicates that at high temperature, 1,4-hexadiene was the prominent product, whereas at the lower temperature, methylenecyclopentane was the major one. Conclusively at 60 °C, as is clear from Fig. 1, the catalytic efficiency was appreciable.

Table 1. Effect of catalysts on the isomerization of 1,5-hexadiene*

Catalyst	Conversion (%)	Selectivity (%)				Linear/cyclic
			 cc,ct,tt			
$(C_5H_5)_2Sm(OC_{14}H_{13}NO)$	28.7	80.6	2.4	12.4	4.6	83.0/17.0
$(C_5H_5)_2Dy(OC_{14}H_{13}NO)$	25.8	81.3	2.7	11.7	4.2	84.0/16.0
$(C_5H_5)_2Y(OC_{14}H_{13}NO)$	25.7	75.0	7.1	13.1	4.8	82.1/17.9
$(C_5H_5)_2Er(OC_{14}H_{13}NO)$	20.6	55.8	9.1	25.2	9.9	64.9/35.1
$(C_5H_5)_2ErCl(OC_{14}H_{13}NO)$. THF	20.0	62.1	7.0	23.3	7.6	69.1/30.9
$ErCl_3$	1.1	100	trace	trace	trace	

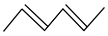
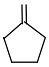
*reaction conditions: catalyst/hexadiene = 1:20; catalyst/NaH = 1:50; time 24 h; temperature = 60 °C ; solvent: THF

Table 2. Effect of temperature on the isomerization of 1,5-hexadiene*

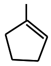
Temperature (°C)	Conversion (%)	Selectivity (%)				Linear/cyclic
			 cc,ct,tt			
30	7.9	28.8	5.2	49.0	17.0	36.7/63.3
45	21.3	75.3	3.5	15.6	5.6	78.8/21.2
60	28.7	80.6	2.4	12.4	4.6	30.0/17.0

*reaction conditions: catalyst/hexadiene = 1:20; catalyst/NaH = 1:50; solvent = THF; time = 24 h

Table 3. Effect of mole ratio on the isomerization of 1,5-hexadiene*

Temperature (°C)	Conversion (%)	Selectivity (%)				Linear/cyclic
		 cc,ct,tt				
1:10	31.3	84.0	3.0	9.5	3.5	87.0/13.0
1:20	28.7	80.6	2.4	12.4	4.6	83.0/17.0
1:40	14.4	46.1	10.9	32.4	10.5	51.0/43.0

*reaction conditions: catalyst/NaH 1:50; time = 24 h; temperature = 60 °C; solvent = THF



In the case of catalyst/substrate, as shown in Table 3, for 1:10 to 1:20, there was no significant difference in the conversion of 1,5-hexadiene into either linear (87.0% and 83%) products, or the cyclic ones (13% and 17%). However, at 1:40, a remarkable difference was observed. The linear products were smaller but cyclic were higher than the above ones. This indicates that the more the catalyst, the more linear the products, which is in accordance with the results reported earlier (Liu *et al.*, 1998). The results listed in Table 3 were further verified by Fig. 2.

The results listed in Table 4 show that untill 10 h, the catalytic efficiency of the catalyst was very rapid, being 25.6%. Then, during the further period of 10 h, it was comparatively slower, 27.4%, and after this there was no significant increase, being only 1.3% in the next 10 h. It means that after 10 h the isomerization equilibrium had been reached. It was possible perhaps to initiate further isomerization of the remaining 75% material on the removal of the product. Conclusively, isomerization of 1,5-hexadiene can be completed during 20 h by using such type of a catalytic system. The whole discussion was verified through Fig. 3, which shows that the conversion of isomerization flattens after 10 h.

The results as presented in Table 5 prove justifiably that THF was the best solvent for this study, showing (7.9%) maximum conversion, whereas toluene had shown the least activity

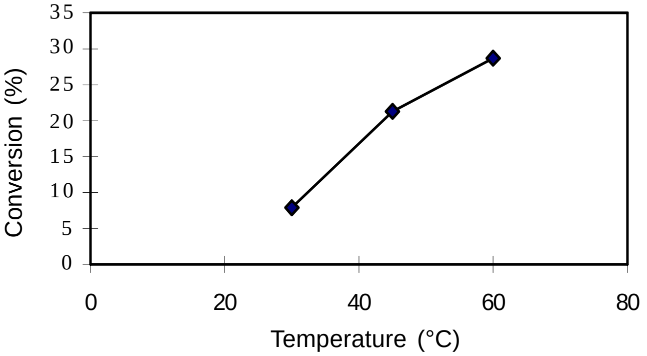


Fig. 1. Effect of temperature on the conversion of 1, 5-hexadiene.

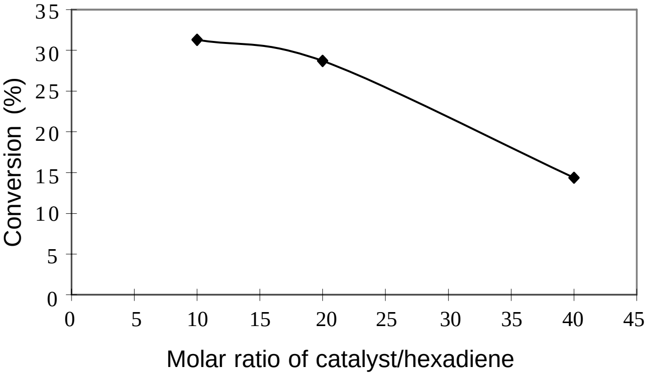


Fig. 2. Effect of catalyst/hexadiene molar ratio on the isomerization of 1, 5-hexadiene.

(0.5%). From these results it was concluded that polarity of the solvent played a vital role for the isomerization of 1,5-hexadine. In other words, solubility of the catalyst was more in THF than any other solvents used (Et_2O and toluene). Moreover, in the case of THF, 1,3-hexadiene and methylene-cyclopantane were the main components.

The proposed mechanism is presented in the reaction scheme as shown in Fig. 4 (Qian *et al.*, 2000; Akita *et al.*, 1983; Lehmkuhi and Qian, 1983).

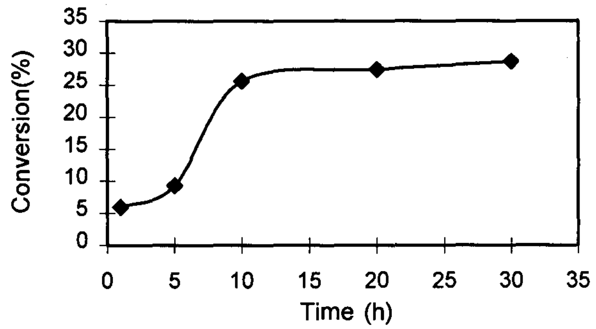


Fig. 3. Effect of time on the isomerization of 1, 5-hexadiene.

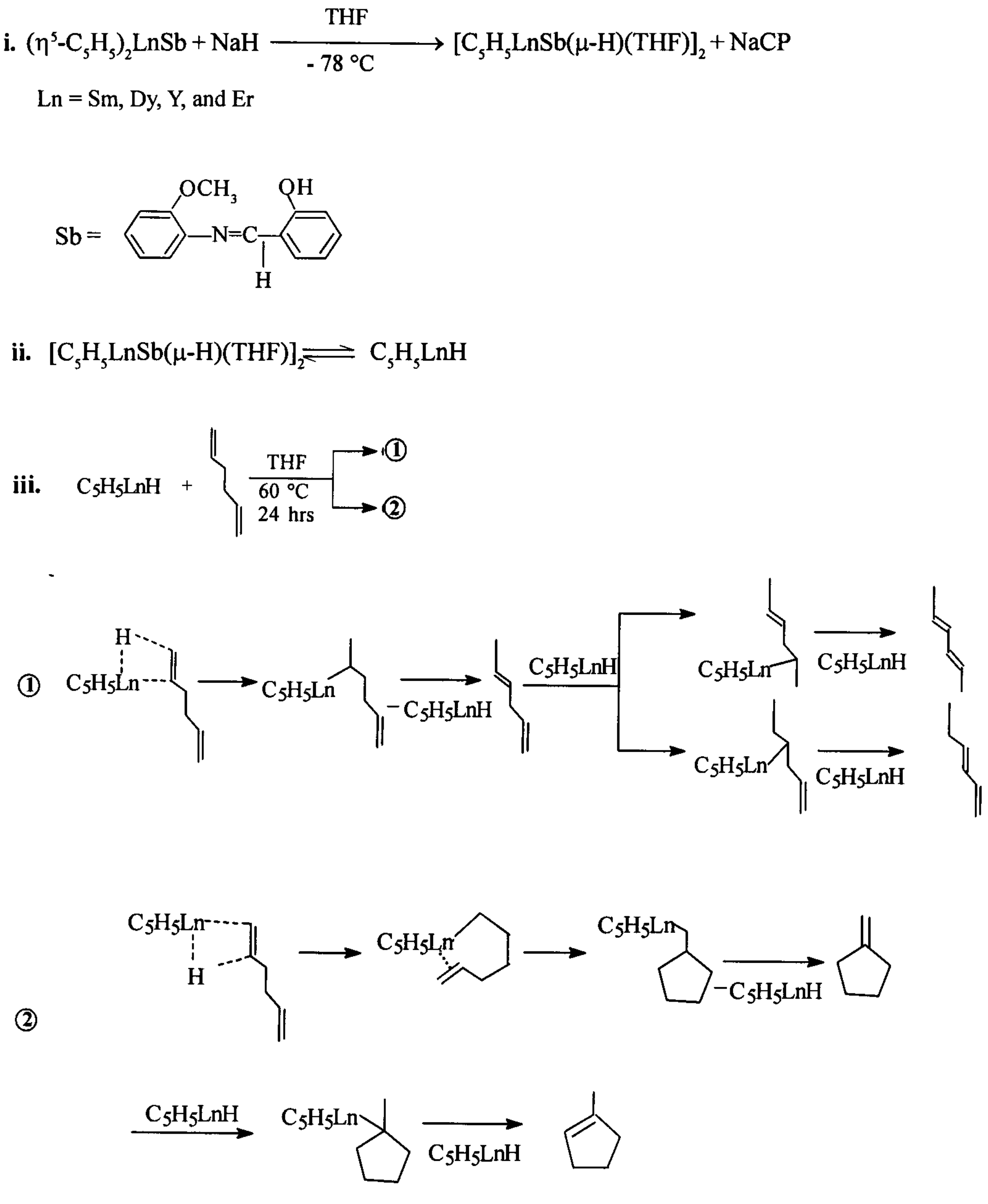
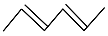
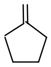
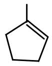


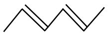
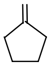
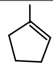
Fig. 4. Proposed mechanism of the isomerization of 1,5-hexadiene.

Table 4. Effect of time on the isomerization of 1,5-hexadiene*

Temperature (℃)	Conversion (%)	Selectivity (%)				Linear/cyclic
			 cc,ct,tt			
1	5.9	8.2	18.4	53.7	19.7	26.6/73.4
5	9.3	5.5	33.2	41.9	19.4	38.7/61.3
10	25.6	81.7	3.2	11.2	9.0	84.8/15.2
20	27.4	82.4	2.3	11.1	4.2	84.7/15.3
30	28.7	80.6	2.4	12.4	4.6	83.0/17.0

*reaction conditions: catalyst/hexadiene = 1:20; catalyst/NaH = 1:50; temperature = 60 °C ; solution = THF

Table 5. Effect of solvent on the isomerization of 1,5- hexadiene*

Solvent	Conversion (%)	Selectivity (%)				Linear/cyclic
			 cc,ct,tt			
THF	7.9	28.8	5.2	49.0	17	34/ 66
Et$_2$O	3.5	100	trace	trace	trace	
Toluene	0.5	100	nil	nil	nil	

*reaction conditions: catalyst/hexadiene = 1: 20; catalyst/NaH = 1:50; time = 24 h; temperature = 60 °C

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