

Ti-Catalyzed Selective Isomerization of Terminal Mono-substituted Olefins

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Transition metal complexes have been utilized in the homogeneous catalysis because of selectivity and catalytic activity under mild conditions.¹ The isomerization of olefins catalyzed by transition metal complexes constitutes one of important type of reaction in organometallic chemistry.² The isomerization of olefins occurs either by a metal hydride addition-elimination or by a π -allyl metal hydride intermediate.^{2b} HCo(CO)₄, [(C₂H₄)₂RhCl]₂, Ni[P(OEt)₃]₄, and PtCl₂(PPh₃)₂-SnCl₂ are effective catalysts for isomerization of olefins *via* a metal hydride addition-elimination mechanism,^{3,4} and Fe₃(CO)₁₂ catalyzed isomerization of 3-ethyl-1-pentene and isomerization of 1-heptene catalyzed by (PhCN)₂PdCl₂ occur *via* a π -allyl metal hydride mechanism.^{4,5} The *cis/trans* ratio of 2-butene obtained from isomerization of 1-butene by RhH(CO)(PPh₃)₃ has also been investigated.⁶ The skeletal isomerization of olefins catalyzed by (R₃P)₂NiCl₂ is developed such as conversion of *cis*-1,4-hexadiene to *trans*-2-methyl-1,3-pentadiene.⁷ Titanium complexes serve as an effective catalysts for a variety of reactions such as hydroalumination,^{8,9} hydroboration,¹⁰ and hydrogenation¹¹ of unsaturated hydrocarbons. We have been interested in the selective reactions of unsaturated hydrocarbons by using titanium and zirconium compounds.⁹⁻¹² The reagent system composed of LiAlH₄/Cp₂TiCl₂ ≤ 2 in the molar ratio promotes the isomerization of 1-octene,^{8b,d} but the detailed reaction for isomerization of olefins has not been reported. We report here a selective isomerization of olefins with low valent titanium complex generated from Cp₂TiCl₂ (Cp=cyclopentadienyl) and LiAlH₄.

Experimental Section

All glassware used was predried in an oven, assembled hot and cooled with a stream of argon in glove box. All reactions were carried out under an argon atmosphere. All solvents were distilled and stored over an appropriate drying agent. Cp₂TiCl₂, *Cp₂TiCl₂ (*Cp=pentamethylcyclopentadienyl), and LiAlH₄ were purchased from Strem Co., and used without further purification. All olefins were purified before use. ¹H NMR spectra were recorded in CDCl₃ on Varian Gemini-200 spectrometer with tetramethylsilane as an internal standard. Infrared spectra were measured in a KBr pellet with a Matterson Genesis II FT-IR spectrophotometer. GC analyses were carried out with a Younglin GC-600D gas chromatograph equipped with HP-5 (Hewlett Packard, 0.32 mm, 30 m) or BP-5 (SGE, 0.32 mm, 60 m) capillary columns.

Mass spectra were obtained using a Shimadzu GC/MS QP-5050.

Typical procedure for isomerization. The mixture of (C₅H₅)₂TiCl₂ (0.251 g, 1.01 mmol), LiAlH₄ (0.079 g, 2.08 mmol), and THF (15 mL) was placed in a vessel under an argon atmosphere. After stirring for 1 h, allylbenzene (2.508 g, 21.2 mmol) was slowly introduced to the mixture at 0 °C. The complete reaction was confirmed by GC, and the mixture was treated with dilute hydrochloric acid (10 mL) and extracted with *n*-pentane. The organic layer was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on alumina with *n*-pentane as an eluent, and *n*-pentane was removed to yield *trans*-1-phenyl-1-propene (1.728 g, 69%). ¹H NMR (CDCl₃): δ 7.11-7.36 (m, 5H, C₆H₅), 6.34 (d, 1H, CH), 6.16 (m, 1H, CH), 1.87 (d, 3H, CH₃). IR (cm⁻¹): 3059, 3024, 2914, 2853, 1704, 1601, 1495, 1443, 962, 735, 693.

Preparation of 2,3-dibromo-2-methylbutane. To a solution of LiAlH₄ (0.078 g, 2.06 mmol) and (C₅H₅)₂TiCl₂ (0.256 g, 1.03 mmol) in THF (15 mL) was added 3-methyl-1-butene (1.410 g, 20.1 mmol). The reaction mixture was stirred at 0 for 1 h. Excess bromine (5.114 g, 32.0 mmol) in diethyl ether (40 mL) was added dropwise at 0 °C. After completion of bromine addition, the reaction mixture was allowed to remain 0.5 h at room temperature. Then the mixture was washed with 10% sodium thiosulfate solution, and saturated sodium chloride solution. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane) to give 2,3-dibromo-2-methylbutane (3.060 g, 66%). ¹H NMR: δ 4.43 (q, 1H CH), 1.92 (s, 6H, CH₃), 1.85 (d, 3H, CH₃). IR (cm⁻¹): 2978, 2926, 2864, 1375, 1202, 839, 719, 532. Mass m/e 228 (M⁺), 230 (M⁺+2), 232 (M⁺+4).

The products were characterized by comparison with authentic samples using GC and spectral data.

Results and Discussion

We have studied the isomerization of representative olefins under the reaction conditions outlined in Table 1. As shown in Table 1, the isomerization of aliphatic terminal olefins such as 1-butene, 3-methyl-1-butene, and 1-octene occurred to give the desired compounds by bromination (entries 1 and 2) and hydrolysis (entry 4) at 0 °C in THF

Table 1. Selective isomerization of olefins^a

Entry	Olefin	Time (h)	Product	Yield (%) ^b
1	CH ₃ CH ₂ CH=CH ₂	1	$\begin{array}{c} \text{CH}_3\text{CH}-\text{CHCH}_3 \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$	96
2	(CH ₃) ₂ CHCH=CH ₂	1	$\begin{array}{c} (\text{CH}_3)_2\text{CH}-\text{CHCH}_3 \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$	96(66)
3	CH ₃ (CH ₂) ₂ C(CH ₃)=CH ₂	3		0
4	C ₅ H ₁₁ CH ₂ CH=CH ₂	1	C ₅ H ₁₁ CH=CHCH ₃	98 ^c
5 ^d	C ₅ H ₁₁ CH ₂ CH=CH ₂	3	C ₅ H ₁₁ CH=CHCH ₃	42 ^e
6 ^d	C ₅ H ₁₁ CH=CHCH ₃	5		0
7	PhCH ₂ CH=CH ₂	1	PhCH=CHCH ₃	98 ^f (69)
8		1		97 ^g
9		1		98 ^h
10	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 \\ \\ \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 \end{array}$	1	$\begin{array}{c} \text{CH}_2\text{CH}=\text{CHCH}_3 \\ \\ \text{CH}_2\text{CH}=\text{CHCH}_3 \end{array}$	96
11		1		95

^aCp₂TiCl₂:LiAlH₄:Olefin = 1:2:20. Reaction performed at 0 °C. ^bGC yields and numbers in parenthesis indicate isolated yields. ^ctrans/cis = 85/15. ^dCp₂TiCl₂-LiAlH₄ was used. ^etrans/cis = 97/3. ^ftrans/cis = 96/4. ^gtrans/cis = 95/5. ^htrans/cis = 97/3.

under an argon atmosphere in an excellent yields. The reactivity of *Cp₂TiCl₂-LiAlH₄ system was compared with that of Cp₂TiCl₂-LiAlH₄ system in the isomerization of 1-octene and 2-octene, respectively. When using *Cp₂TiCl₂ as the catalyst in the reaction of 1-octene, 2-octene (*trans/cis* = 97/3) was only obtained in low yield for 3 h (entry 5), but 2-octene was not isomerized even after 5 h (entry 6). As a detailed study, 1-octene and *cis*- and *trans*-2-octenes were isomerized in the presence of Cp₂TiCl₂-LiAlH₄ under the same conditions, respectively. In the reaction of 1-octene, 2-octene (*trans/cis* = 85/15) as major product was obtained for 1 h, but 3- and 4-octenes were detected in the product mixture for 3 h. 2-Octene was gradually isomerized to 3- and 4-octenes as time progresses. Production of 3- and 4-octenes could be attributed the reaction of the 2-octene with the catalyst to afford the more isomerization product. In case of *cis*-2-octene, *trans*-2-octene was obtained (36%) with 3- and 4-octenes (9%) for 5 h, but reaction of *trans*-2-octene to *cis*-2-octene hardly occurred. The results indicate that *trans*-2-octene is produced from 1-octene as a major product in preference to the *cis*-2-octene in the initial stage of the reaction, and *cis*-2-octene gradually isomerizes to *trans*-2-octene during the reaction. We examined the isomerization of 2,2-disubstituted olefin such as 2-methyl-1-pentene (entry 3), but this olefin was not isomerized at 0 °C even after 3 h. Aromatic olefins such as allylbenzene, allyl anisole, and safrole were smoothly isomerized to the corresponding

internal olefins in excellent yields (entries 7, 8, and 9). When the reaction of 1-octene, allylbenzene, and safrole was investigated at 0 °C to examine the selectivity for this system (entries 4, 7, and 9), the *trans*-isomers were predominantly obtained. This system shows very good selectivity toward mono-substituted terminal olefins. The reagent system was applied to dienes such as 1,7-octadiene and 1,5-cyclooctadiene to produce 2,6-octadiene and 1,3-cyclooctadiene, respectively (entries 10 and 11). Thermal treatment of organoboranes converts internal olefins into terminal olefins *via* the contrathermodynamic isomerization of olefins.¹³ Therefore, the isomerization of 2-octene and β -methylstyrene was tried to convert internal olefins into terminal olefins by heating, but these reactions were not achieved. The isomerization of olefins catalyzed by Cp₂TiCl₂-LiAlH₄ system is presumed to proceed *via* the thermodynamic stability. The scope of the catalytic reaction and applicability for organic syntheses are now under study.

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