

Organotitanium chemistry: substituent effects on the dimerization of isoprene catalyzed by alkenyl-substituted cyclopentadienyl titanium complexes

Li Yong, Xiaochun Tao, Fang Qian, Yanlong Qian*

*The Laboratory of Organometallic Chemistry, East China University of Science and Technology,
Meilong Road 130#, Shanghai 200237, PR China*

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Abstract

Using the catalyst system consisting of an alkenyl-substituted $\text{Cp}'_2\text{TiCl}_2$ and $i\text{-C}_3\text{H}_7\text{MgCl}$, isoprene can be dimerized to linear dimers 2,6-dimethyl-1-*trans*-3,6-octatriene and 3,6-dimethyl-1,3,6-octatriene under mild reaction condition. The substituent effects of alkenyl-substituted titanocene catalysts on both the yield and the selectivity were studied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oligomerization of isoprene; Alkenyl-substituted titanocene; Substituent effect; Catalytic activity; Selectivity

1. Introduction

How to utilize isoprene, the large quantities of by-product in petrochemicals industry, has being an urgent problem. So much research work has been done and many patents appeared in the past decades [1]. Among these works, the oligomerization of isoprene catalyzed by transition metal complexes [2–6] was fascinating because the products are very useful starting materials in the perfume industry. It was well known that isoprene can be catalyzed by transition metal complexes to give dimers and higher oligomers, and the dimers obtained were effected greatly by the transition metal and other catalyst components used. For example, the dimerization of isoprene by catalytic system [2] consisting of iron(III) acetylacetonate, 2,2'-dipyridyl, and triethylaluminum given a mix-

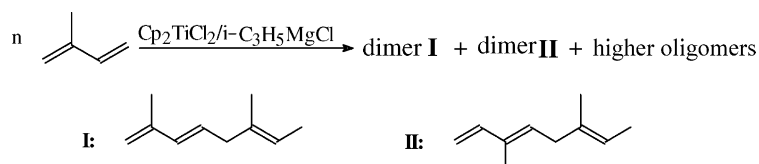
ture of cyclic dimerization of isoprene (1,5- and 2,5-dimethyl-1,5-cyclooctadiene). Using a catalyst system containing Group VI metal or chromium complex and diethylaluminum chloride, a linear dimer of isoprene (2,6-dimethyl-1-*trans*-3,6-octatriene) was obtained predominantly among the dimers of isoprene [5,6].

Considering that triethylaluminum or diethylaluminum chloride used in the reported literature is too expensive and difficult to handle, recently we investigated for the first time the dimerization of isoprene catalyzed by $\text{Cp}_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgX}$ system [7], an effective catalyst system for olefin isomerization [8] and hydrogenation [9]. It was found that isoprene did be dimerized under the appropriate reaction conditions (in THF at 65 °C), the dimers were characterized to be 2,6-dimethyl-1,3,6-octatriene (**I**) and 3,6-dimethyl-1,3,6-octatriene (**II**) by GC-MS; $^1\text{H-NMR}$; $^{13}\text{C-NMR}$ and GC-IR (Scheme 1).

In the isomerization and hydrogenation reactions of olefin catalyzed by $\text{Cp}_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgX}$, the

* Corresponding author. Fax: +86-21-64702573.

E-mail address: qianling@online.sh.cn (Y. Qian).



Scheme 1.

catalytic activities of alkenyl-substituted $\text{Cp}'_2\text{TiCl}_2$ have been proved to be higher than their corresponding alkyl-substituted $\text{Cp}'_2\text{TiCl}_2$. Therefore, after the preliminary study of various alkyl-substituted $\text{Cp}'_2\text{TiCl}_2$ catalysts in the linear dimerization of isoprene [7], we decided to investigate the catalytic activities of alkenyl-substituted $\text{Cp}'_2\text{TiCl}_2$ under our established reaction conditions (the reaction carried out at 65°C in 3 ml THF for 10 h using 1:55 molar ratio of catalyst ($\text{Cp}'_2\text{TiCl}_2$) to isoprene). Herein we wish to report the results.

2. Experimental

2.1. Reagents

Isoprene was dried over CaH_2 and deoxygenated under argon, then distilled with pumping. Tetrahydrofuran was purified with conventional methods and distilled under argon. The Grignard reagent *i*-propyl-magnesium chloride was synthesized according to the literature method [10]. All those alkenyl-substituted $\text{Cp}'_2\text{TiCl}_2$ were synthesized according to the reported literature [11] and characterized by $^1\text{H-NMR}$ (300 MHz).

2.2. Typical reaction procedure

Typical procedure for the oligomerization of isoprene: to a 50 ml Schlenk flask, 0.2 mmol of alkenyl-substituted $\text{Cp}'_2\text{TiCl}_2$, 3 ml of THF, 20 mmol of isoprene and 1.1 mmol of *i*-PrMgCl (in THF) were added under argon. The reaction mixture was heated at 65°C for 10 h with stirring. After treated with 1 ml MeOH, the reaction mixture was distilled under reduced pressure, the distillate was cooled by dry ice and then analyzed by gas chromatography to calculate

the quantity of products. The residue of the distillation was extracted by petroleum ether ($30\text{--}60^\circ\text{C}$), after the removal of the petroleum ether the oligomer was obtained.











3. Results and discussion

Under the established reaction conditions, the isoprene can also be oligomerized to dimers **I** and **II** in the alkenyl-substituted $\text{Cp}'_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgX}$ system. The results of the oligomerization of isoprene by various alkenyl-substituted cyclopentadienyl titanium dichloride are given in Table 1.

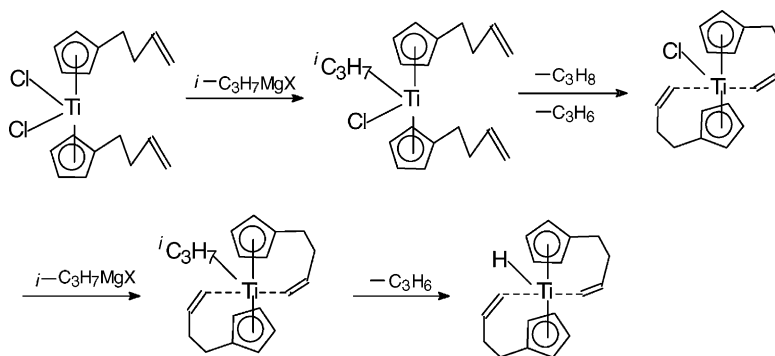
As shown in Table 1, the conversions of isoprene were more satisfactorily catalyzed by alkenyl-substituted $\text{Cp}'_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgX}$ system than their corresponding alkyl-substituted $\text{Cp}'_2\text{TiCl}_2$ (compare entries 2, 3 with 4, 5). This may be rationalized by the coordination effect between the $\text{C}=\text{C}$ bond in the side chain of Cp ring and Ti atom in the Ti(III) transition state, this coordination stabilized the Ti(III) species and subsequently increased the yield of dimers and oligomers.

It was generally accepted that $[\text{Cp}_2\text{TiH}]$ may be formed in situ as active catalytic species from the reductive system, such as $\text{Cp}'_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgCl}$ [8,12–14]. It was interesting to find that *n*-butenyl-substituted $\text{Cp}'_2\text{TiCl}_2$ (entries 5, 12, 13) show better catalytic activity than other alkenyl-substituted $\text{Cp}'_2\text{TiCl}_2$, in both the conversion of isoprene and the yield of dimers, which was consistent with the result we found in the isomerization of 1,5-hexadiene catalyzed by titanocene complexes [9]. The reason may be due to the favorite formation of the hexatomic ring in the butenyl-substituted Ti(III) transition state (Scheme 2), which should be more stable than that of other alkenyl-substituted titanocene dichlorides.

Table 1
The substituent effects of catalyst on the oligomerization of isoprene^a

Entry	Ti complex	Conversion (%)	Selectivity (%)	Distribution		Yield (%)	
				I	II	Dimer	Oligomer
1	Cp ₂ TiCl ₂	70	38	67	33	27	43
2	(C ₃ H ₇ Cp) ₂ TiCl ₂	29	10	66	34	3	26
3	(C ₄ H ₉ Cp) ₂ TiCl ₂	35	17	74	36	9	26
4	() ₂ TiCl ₂	57	23	78	22	21	36
5	() ₂ TiCl ₂	84	37	63	37	31	53
6	() ₂ TiCl ₂	68	42	72	28	29	39
7	(Cp- ) ₂ TiCl ₂	61	38	66	34	23	38
8	(Cp- ) ₂ TiCl ₂	58	37	67	33	21	37
9	(Cp- ) ₂ TiCl ₂	62	24	63	27	15	47
10	(Cp- ) ₂ TiCl ₂	44	29	65	35	13	31
11	(Cp- ) ₂ TiCl ₂	64	38	68	32	24	40
12	(Cp- ) ₂ TiCl ₂	58	36	80	20	27	41
13	(Cp- ) ₂ TiCl ₂	72	39	69	31	28	44

^a Reaction temperature: 65 °C; reaction time: 10 h; molar ratio of (Ti/isoprene) = 1:55; volume of THF: 3 ml; Cp₂TiCl₂/*i*-C₃H₇MgCl = 1:5.5.



Scheme 2.

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