

Substituent effect on oligomerization of isoprene catalyzed by ring-substituted $(\text{RCp})_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgCl}$ system

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Abstract

Using the catalyst system composed of Cp_2TiCl_2 and $i\text{-C}_3\text{H}_7\text{MgCl}$, isoprene can be oligomerized to a mixture of dimers and higher oligomers. The two dimers 2,6-dimethyl-1, *trans*-3,6-octatriene and 3,6-dimethyl-1,3,6-octatriene were characterized by GC-MS; $^1\text{H-NMR}$; $^{13}\text{C-NMR}$ and GC-IR. The effects of reaction time, molar ratio of catalyst to isoprene, temperature and solvent on the reaction were discussed. After established the appropriate reaction condition, the substituent effect of a series of alkyl ring-substituted cyclopentadienyl titanium dichlorides on catalytic activity were investigated. A mechanism of the reaction was also proposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Substituent effect; Oligomerization of isoprene; Catalysis; Ring-substituted titanocene

1. Introduction

During the past three decades, the oligomerization of isoprene has aroused the interest of many organic chemists, for its academic importance and substantial technical use [1–4]. Yoshida reported that using $\text{Hf}(\text{OBU}^n)_4/\text{Et}_2\text{AlCl}$ or $\text{Zr}(\text{OBU}^n)_4/\text{Et}_2\text{AlCl}$ catalytic system, isoprene can be oligomerized to a mixture of dimers and higher oligomers, among the dimers 2,6-dimethyl-1, *trans*-3,6-octatriene was the main product [1–3]. Later De young [4] found that adopting $\text{CpTiCl}_3/\text{Et}_3\text{Al}$ as catalyst system, the dimers obtained were composed of 2,6-dimethyl-1,6-octadiene, 2,6-dimethyl-4,7-

octadiene and 1-methyl-4-isopropylcyclohexene-1. In our previous work, $\text{Cp}_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgX}$ system was found to be an effective catalyst for isomerization [5–7] and hydrogenation [8] of olefin under mild condition. Herein we wish to report our results on oligomerization of isoprene catalyzed by $(\text{RCp})_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgCl}$ ($\text{R} = \text{H}$ or alkyl groups) system.

2. Experimental

2.1. Reagents

Isoprene was distilled under argon with pumping. Tetrahydrofuran was purified by con-

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Table 1
Effect of the solvent^a

Solvent	Conversion (%)	Yield (%)		Selectivity of dimers (%)	Distribution of I, II	
		Dimers	Oligomers		I	II
Ether	2	trace	2	/	/	/
Dioxane	4	2	2	50	55	45
THF	70	27	43	39	67	33

^aReaction temperature: 65°C; reaction time: 10 h; molar ratio of (Ti/isoprene) = 1:55; volume of THF: 3 ml; volume of ether: 3 ml; volume of dioxane: 6 ml; Cp₂TiCl₂/*i*-C₃H₇MgCl = 1:5.5.

ventional method and distilled under argon. The Grignard reagent, iso-propyl-magnesium chloride, was synthesized according to the ordinary method. Cp₂TiCl₂ and (RCp)₂TiCl₂ were synthesized in our laboratory.

2.2. Reaction procedure

Typical procedure for the oligomerization of isoprene: To a schlenk flask, 0.2 mmol of Cp₂TiCl₂, 1.5–4.5 ml of solvent, 5–20 mmol of isoprene and 1.1 mmol of *i*-PrMgCl (in THF) were added under argon. According to the mechanism, the molar ratio of Cp₂TiCl₂/*i*-C₃H₇MgCl = 1:2 is all right for catalytic reaction. But in our case Cp₂TiCl₂/*i*-C₃H₇MgCl = 1:5.5 was used to ensure the complete reduction of catalyst to form active species [Cp₂TiH] [7]. The reaction mixture was heated at 40–75°C for 5–15 h with stirring. After treated with 1 ml MeOH, it was distilled under reduced pressure, the distillation was cooled by dry ice and then analyzed by gas chromatography to calculate

the quantity of products. The rest of the distillation was washed by petroleum ether (30–60°C) and separated by centrifugation. The higher oligomer was obtained by decanting solvent in clean solution.

2.3. Analysis

The dimers were characterized by GC-MS, ¹H-NMR, ¹³C-NMR and GC-IR. The quantity of dimers was calculated on GC by using *n*-butylbenzene as internal standard. The types of quantitative analysis instruments are shown below.

GC: Shimadzu: GC-14B; GC-MS: QP-5000; GC-IR: BioRad FTS-185; ¹³C-NMR/¹H-NMR: Bruker DRX-400, DRX-300.

3. Results and discussion

Compared with other catalysts in the literature, the oligomerization of isoprene in our case

Table 2
Solvent's quantity effect^a

Volume of THF (ml)	Conversion (%)	Yield (%)		Selectivity of dimers (%)	Distribution of I, II	
		Dimers	Oligomers		I	II
1.5	71	23	48	32	65	35
3	70	27	43	39	67	33
4.5	58	23	35	40	63	37

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

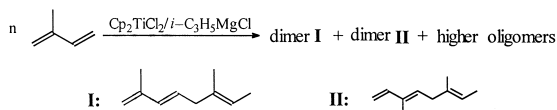
Table 3
Effect of the molar ratio of catalyst to isoprene^a

Catalyst/isoprene	Conversion (%)	Yield (%)		Selectivity (%)	Distribution of I , II	
		Dimer	Oligomer		I	II
1:40	72	5	67	7	86	14
1:55	70	27	43	39	67	33
1:80	61	22	39	36	68	32
1:100	63	24	39	43	61	39
1:120	37	20	17	54	59	41
1:150	10	5	5	50	57	43

^aReaction time: 10 h; reaction temperature: 65°C; volume of THF: 3 ml; Cp₂TiCl₂/*i*-C₃H₇MgCl = 1:5.5.

was carried out under very mild condition: 65°C, at normal atmosphere.

The products obtained were mixture of higher oligomers and two dimers. The higher oligomer was not studied in detail. The two dimers **I** and **II** have been characterized by GC-MS, ¹H-NMR, ¹³C-NMR and GC-IR, and their structures shown as follows:



We studied the effects of solvent, reaction time, molar ratio of catalyst to isoprene and temperature on the reaction to establish the appropriate reaction conditions.

3.1. The effect of solvent

Considering that the solvent used and the quantity of solvent may affect the reaction greatly, we decided to explore these two effects

firstly. The results were given in Table 1 and Table 2, respectively.

It can be seen from Table 1, that using ether or dioxane as solvent the result was disappointed, it can be explained by the bad solubility of the catalyst system in these two solvents. While using THF as solvent, the yield and selectivity of the dimer were appropriate.

From Table 2, it was observed that changing the quantity of the solvent did not affect the yield of the dimers. However, the selectivity rose when the increasing addition of the solvent. On the contrary, the conversion decreased at the same time. We conjectured that the reaction to higher oligomers is unfavorable with the dilution of the solvent.

3.2. The effect of the molar ratio of catalyst to isoprene

The experimental results for the effect of the molar ratio of catalyst to isoprene were displayed in Table 3. When the molar ratio of catalyst to isoprene was 1:55, both the yield and

Table 4
Effect of temperature^a

Reaction temperature (°C)	Yield (%)		Selectivity (%)	Distribution of I , II	
	Dimer	Oligomer		I	II
40	trace	trace	/	/	/
55	trace	trace	/	/	/
60	24	43	36	61	39
65	27	43	39	67	33
75	23	34	40	69	31

^aReaction time: 10 h; molar ratio of (Ti/isoprene) = 1:55; volume of THF: 3 ml; Cp₂TiCl₂/*i*-C₃H₇MgCl = 1:5.5.

Table 5
The effect of reaction time^a

Time (h)	Conversion (%)	Yield (%)		Selectivity of dimer (%)	Distribution of I, II	
		Dimer	Oligomer		I	II
5	57	8	49	14	68	32
10	70	27	43	39	67	33
15	57	3	54	5	89	11

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

selectivity increased to the maximum, 27% and 39% respectively.

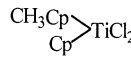
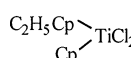
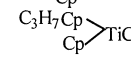
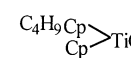
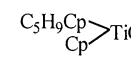
3.3. The effect of reaction temperature

After explored the effects of solvent and the molar ratio of catalyst to isoprene. The effect of

reaction temperature was studied, the results are shown in Table 4. If the reaction carried out below 55°C, the reaction did not take place. But when the temperature range from 60°C to 75°C, the effect of reaction temperature on the reaction was not obviously. The best result (both the yield and selectivity of dimers) was obtained

Table 6
The effect of alkyl-substituted Cp titanocene catalyst^a

^aReaction 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.

Entry	Cat.	Conv. (%)	Selc. of dimers (%)	Distribution of I, II (%)		Cat. Act. (g·dimer/mol·Ti)	Yield(%)	
				I	II		dimer	oligo.
1	Cp ₂ TiCl ₂	70	39	67	33	15×10 ²	27	43
2	(CH ₃ Cp) ₂ TiCl ₂	54	36	69	31	6.6×10 ²	20	34
3	(C ₂ H ₅ Cp) ₂ TiCl ₂	38	23	86	14	2.9×10 ²	9	29
4	(C ₃ H ₇ Cp) ₂ TiCl ₂	29	10	66	34	0.9×10 ²	3	26
5	(C ₄ H ₉ Cp) ₂ TiCl ₂	35	17	74	36	1.5×10 ²	9	26
6	(C ₅ H ₁₁ Cp) ₂ TiCl ₂	43	26	73	27	3.9×10 ²	11	32
7	(C ₅ H ₉ Cp) ₂ TiCl ₂	41	32	74	26	3.7×10 ²	11	30
8	(C ₆ H ₁₁ Cp) ₂ TiCl ₂	36	16	79	21	2.1×10 ²	6	30
9		59	44	65	35	8.3×10 ²	25	34
10		46	33	75	25	5.9×10 ²	15	31
11		30	16	64	36	1.7×10 ²	5	25
12		35	65	56	44	2.3×10 ²	7	28
13		45	36	64	36	6.4×10 ²	16	39

when the reaction was carried out at 65°C. The higher temperature preferred to the formation of higher oligomer, which hampered the yield of dimers.

3.4. The effect of reaction time

The effect of reaction time was shown in Table 5. With the reaction time increasing, the yield; the conversion; and the selectivity rose apparently. But if the reaction time exceeded 10 h, the yield and selectivity of dimers decreased dramatically. For the longer reaction time favoured the formation of the higher oligomers.

So the best catalyzed reaction condition of linear dimerization of isoprene by $\text{Cp}_2\text{TiCl}_2/i\text{-C}_3\text{H}_7\text{MgCl}$ system was that: molar ratio of catalyst to isoprene was 1:55; and the reaction carried out at 65°C in 3 ml THF for 10 h. After the best reaction condition was established, we investigated the catalytic activity of a series of alkyl ring-substituted cyclopentadienyl titanium dichlorides.

3.5. The effect of alkyl-substituted Cp catalyst

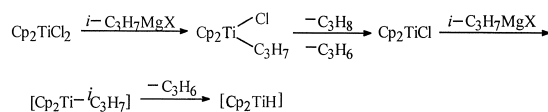
The results of the oligomerization of isoprene by various alkyl ring-substituted cyclopentadienyl titanium dichloride are given in Table 6.

It can be seen from Table 6 that the substituent on Cp-ring affected both the yield and selectivity of dimers (dimer I and dimer II) greatly. It is interesting that neither single-substituted nor double-substituted cyclopentadienyl titanium dichlorides affected dimers with the same tendency: both yield and selectivity of dimers decreased from CH_3 -substituted to C_3H_7 -substituted cyclopentadienyl titanium dichlorides, however, when the substituent comes to C_4H_9 , both the yield and selectivity of dimers increased again.

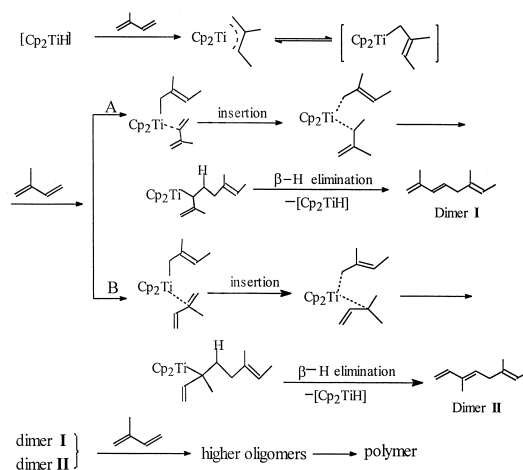
3.6. Mechanism

It was generally accepted that $[\text{Cp}_2\text{TiH}]$ may be formed in situ from the system $\text{Cp}_2\text{TiCl}_2/i\text{-}$

$\text{C}_3\text{H}_7\text{MgCl}$ as follows [7,9,10]:



Therefore, a mechanism of the reaction was proposed:



Due to the steric factor, the intramolecular coordination in the way A occurs easier than that of the way B. It is the explanation for the fact that amount of dimer I in the reaction mixture was always more than dimer II. Both dimer I and dimer II may be converted into higher oligomer or polymer in the same way.

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