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Oligomerization of Isoprene by Hafnium Catalysts

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Oligomerization of isoprene by the catalyst system consisting of hafnium(IV) *n*-butoxide and diethylaluminum chloride was studied. Isoprene was oligomerized to a mixture of dimers, trimers and higher oligomers. The compound, 2,6-dimethyl-1-*trans*-3,6-octatriene, was the main dimer of isoprene in this reaction. The maximum yield of this dimer in the reaction at 130°C for 2 hr was accomplished when the molar ratio of diethylaluminum chloride to hafnium(IV) *n*-butoxide was 4.7. The addition of tetrahydrofuran or triphenylphosphine kept the selectivity for the dimer nearly constant. These results were compared with those obtained by the catalyst system consisting of titanium(IV) *n*-butoxide or zirconium(IV) *n*-butoxide and diethylaluminum chloride.

Many catalyst systems containing transition metals are known to oligomerize olefins. In the course of our studies on the catalytic oligomerization of conjugated dienes, we found the cyclic dimerization of isoprene into a mixture of 1,5- and 2,5-dimethyl-1,5-cyclooctadiene by iron complex catalysts.[1] Some catalyst systems containing titanium[2] or chromium[3] are reported to give a linear dimer of isoprene along with other oligomers.

In the preceding paper,[4] we reported the linear dimerization of isoprene to 2,6-dimethyl-1,*trans*-3,6-octatriene by the catalyst system consisting of zirconium(IV) *n*-butoxide, diethylaluminum chloride and with or without electron donors.

In this paper, we report on the oligomerization of isoprene by the catalyst system consisting of hafnium(IV) *n*-butoxide and diethylaluminum chloride. This catalyst system gave a mixture of oligomers of isoprene, and 2,6-dimethyl-1,*trans*-3,6-octatriene was formed predominantly among dimers of isoprene. The selectivity for this compound in the reaction at 130°C for 2 hr was 43% when the molar ratio of diethylaluminum chloride to hafnium(IV) *n*-butoxide was 4.7. The addition of triphenylphosphine or tetrahydrofuran did not raise the selectivity for the dimer. The reaction of isoprene by the catalyst system consisting of titanium(IV) *n*-butoxide and diethylaluminum chloride was also studied, but our results were different from those reported by Takahashi and Yamaguchi.[2b] These results were compared with those obtained by the catalyst system consisting of zirconium(IV) *n*-butoxide and diethylaluminum chloride.

Experimental

Reactors. A 100 m*l* stainless steel autoclave was used.

Reagents. Isoprene was dried over Drierite, distilled and was deoxygenated by the freeze-thaw method with pumping.

Benzene and tetrahydrofuran were purified by conventional methods and were distilled under a nitrogen stream.

Diethylaluminum chloride and titanium(IV) *n*-butoxide were purified by distillation and were diluted in benzene.

Hafnium(IV) *n*-butoxide was made according to the analogous method for zirconium(IV) *n*-butoxide[5] and was diluted in benzene.

Commercial triphenylphosphine was used without further purification.

Reaction Procedure. In a typical reaction, to an autoclave filled with nitrogen, 5.70 g of benzen, 50 mmol of isoprene, 0.5 mmol of hafnium (IV) *n*-butoxide (16.3 wt% benzene solution) and 2.0 mmol of diethylaluminum chloride (17.6 wt % benzene solution) were charged with injectors under a nitrogen stream. The total amount of benzene was controlled to be 8.3—8.5 g. The autoclave was then heated at 130°C for 2 hr with stirring.

Analysis. The gas chromatography was used for calculating the conversion percent of isoprene and for the quantitative analysis of products. A 2 m stainless steel column, 4 mm in diameter, packed with polydiethylene glycol succinate on Shimalite was used. Operation conditions: column temperature, 112°C and 180°C for dimers and trimers, respectively; flash evaporator, 300°C; carrier gas (helium) speed, 30 m*l*/min. Benzene

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1) A. Misono, Y. Uchida, M. Hidai and Y. Ohsawa, This Bulletin, **39**, 2425 (1966).

2) a) L. I. Zakharkin, *Doklady Akad. Nauk, S.S.S.R.*, **131**, 1069 (1960); *b*) H. Takahashi and M. Yamaguchi, *Osaka Kogyo Gijutsu Shikensho Kiho*, **15**, 271 (1964).

3) G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959).

4) A. Misono, Y. Uchida, K. Furuhata and S. Yoshida, This Bulletin, in press.

5) D. C. Bradley, F. M. Abd-El Halim, E. A. Sadek and W. Wardlaw, *J. Chem. Soc.*, **1952**, 2032.

was used as an internal standard.

Infrared spectra were taken using a Nihon Bunko Model DS-301.

Nuclear magnetic resonance spectra were recorded on a Nihon Denshi Model C-60.

Molecular weights were measured by the cryoscopic method in benzene.

Results and Discussion

Products obtained in the reaction of isoprene by the catalyst system consisting of hafnium(IV) *n*-butoxide and diethylaluminum chloride were dimers, trimers and higher oligomers. Two dimers were found on gas chromatography and the structure of the dimer with the relative retention time 2.8 was determined to be 2,6-dimethyl-1,*trans*-3,6-octatriene by comparing the retention time with the pure sample obtained by the zirconium catalyst.[4] A small amount of another dimer with the relative retention time 3.4 was found on gas chromatography, but this compound was not studied in detail.

The Effect of the Molar Ratio of Catalyst Components. The effect of the molar ratio of diethylaluminum chloride to hafnium(IV) *n*-butoxide on the reaction of isoprene is shown in Fig. 1. The reaction was carried out at 130°C for 2 hr and the maximum yield of dimers was accomplished when the molar ratio of diethylaluminum chloride to hafnium(IV) *n*-butoxide was 4.7. At this temperature only traces of trimers were formed and the rest were higher oligomers. The infrared spectra of the mixture of these higher oligomers showed absorption bands due to a methyl group (2975, 1450 and 1375 cm^{-1}), a methylene group (2925 and 1450 cm^{-1}), a *trans* double bond (1650 and 965 cm^{-1}), a conjugated double bond (1610 cm^{-1}) and a terminal methylene group (1780 and 885 cm^{-1}). The mean polymerization degrees of liquid oligomers obtained were 6.5, 8.1 and 9.3 when the molar ratios of diethylaluminum chloride to hafnium(IV) *n*-butoxide were 4.0, 6.0 and 15.6, respectively. These data indicate that the excess of diethylaluminum chloride promoted the oligomerization of isoprene to higher oligomers. A similar result was reported in the case of oligomerization of butadiene by iron catalysts.[6,7]

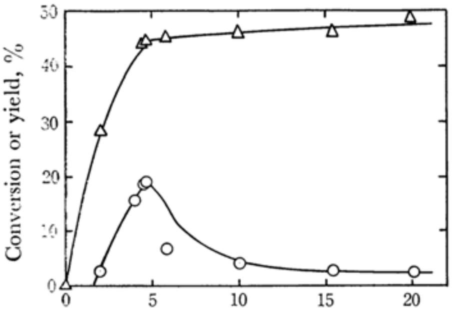

Fig. 1. Effect of the molar ratio of Et_2AlCl to $Hf(OBu)_4$.
—△—: Conversion of isoprene, %
—○—: Yield of 2,6-dimethyl-1, *trans*-3,6-octatriene, %
Reaction temp.: 130°C; reaction time: 2 hr;
Isoprene/$Hf(OBu)_4$: 100

The Effect of the Reaction Temperature. The effect of the reaction temperature on the formation of oligomers of isoprene was examined keeping the molar ratio of diethylaluminum chloride to hafnium(IV) *n*-butoxide constant at 4.0 and the reaction time 2 hr (Fig. 2). The maximum yield of the dimer was accomplished at about 160°C. The formation of trimers was observed significantly at the temperature higher than 150°C. Four trimers were detected on gas chromatography, and one isomer was predominantly formed. Solid polymers of isoprene were precipitated from the reaction solution at higher temperature when an excess amount of methanol was added, but the higher oligomers formed in the reaction at 130°C remained in the benzene layer.

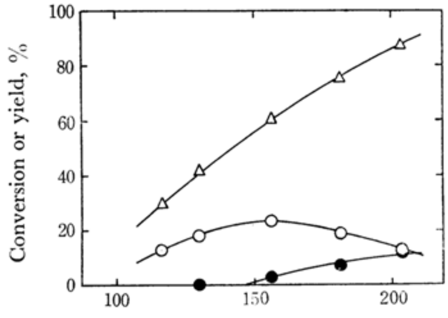

Fig. 2. Effect of the reaction temperature.
—△—: Conversion of isoprene, %
—○—: Yield of 2,6-dimethyl-1, *trans*-3,6-octatriene, %
—●—: Yield of a trimer, %
Reaction time: 2 hr; Isoprene/$Hf(OBu)_4$: 100;
$Et_2AlCl/Hf(OBu)_4$: 4.0

The Effect of Electron Donors. The effect of electron donors on the oligomerization of isoprene was examined using triphenylphosphine and tetrahydrofuran (Fig. 3). The reactions were carried out at 156°C for 2 hr.

The addition of triphenylphosphine to the catalyst system did not change the selectivity for 2,6-dimethyl-1,*trans*-3,6-octatriene. The same result was observed in the selectivity for the trimer.

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[6] M. Hidai, Y. Uchida and A. Misono, This Bulletin, **38**, 1243 (1965).

[7] A. Carbonaro, A. Greco and G. Dall'Asta, *Tetrahedron Letters*, **1967**, 2037.

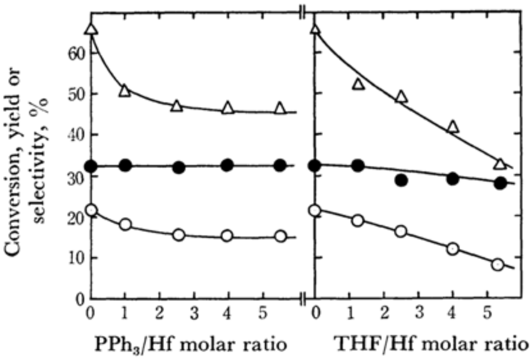

Fig. 3. Effect of electron donors.
—△—: Conversion of isoprene, %
—○—: Yield of 2,6-dimethyl-1, *trans*-3,6-octatriene, %
—●—: Selectivity for 2,6-dimethyl-1, *trans*-3,6-octatriene, %
Reaction temp.: 156°C; reaction time: 2 hr; Isoprene/$Hf(OBu)_4$: 100; $Et_2AlCl/Hf(OBu)_4$: 4.0

In the case of tetrahydrofuran, the selectivity for the dimer decreased slowly as the molar ratio of added tetrahydrofuran to hafnium(IV) *n*-butoxide increased. In this case, no trimer was found when the molar ratio exceeded five.

There was little difference between triphenylphosphine and tetrahydrofuran regarding the influence on the oligomerization of isoprene by the catalyst system consisting of hafnium(IV) *n*-butoxide and diethylaluminum chloride. These electron donors suppressed the conversion of isoprene, but the selectivity for the dimer was nearly constant in both cases, and they did not change the nature of the reaction.

In the oligomerization of olefins catalyzed by transition metals, an alkylaluminum compound acts as an alkylating reagent and the resulting alkyltransition metal is usually reduced to a low valent state by a homolytic splitting of the transition metal-carbon bond.

In order to examine the reaction of catalyst components in the oligomerization of isoprene by this catalyst system, the nuclear magnetic resonance spectra of catalyst components were studied. Hafnium(IV) *n*-butoxide showed an absorption centered at $\tau=5.5$ ppm (triplet) due to methylene protons next to oxygen in the Hf–O–C linkage. On the other hand, ethylaluminum *n*-butoxide chloride formed by the reaction of equal amounts of diethylaluminum chloride and *n*-butanol showed an absorption centered at $\tau=6.3$ ppm (triplet), which can be assigned to methylene protons next to oxygen in Al–O–C linkage. A mixture of hafnium(IV) *n*-butoxide and diethylaluminum chloride (molar ratio: about 1:4) showed absorptions centered at $\tau=5.7$ (triplet) and 6.4 ppm (triplet) which can be assigned to methylene protons next to oxygen in the linkage of Hf–O–C and Al–O–C, respectively. From this result, it can be said that a ligand exchange reaction between hafnium(IV) *n*-butoxide and diethylaluminum chloride occurred. No significant change was observed after heating this solution at 100°C for 2.5 hr. The solution remained diamagnetic after heating at the reaction temperature and the valency of hafnium was probably four. The ligand exchange reaction could also be observed in the infrared spectra.

Brown precipitates were separated from the benzene solution of hafnium(IV) *n*-butoxide and diethylaluminum chloride after heating at 110°C for 2.5 hr, but when the solution contained a stoichiometric amount of isoprene along with hafnium(IV) *n*-butoxide and diethylaluminum chloride, it remained homogeneous for a long time after the heating. This solution was also diamagnetic before and after the heating.

From these results, it can be said that hafnium is in its four valent state in the oligomerization of isoprene by hafnium(IV) *n*-butoxide and diethylaluminum chloride, and the little difference in the effect of triphenylphosphine and tetrahydrofuran on the catalysis can be explained by the fact that there is no *d*-electron in the four-valent hafnium and thus the back donation can be of little significance in the reaction.

The Oligomerization of Isoprene by Titanium Catalysts. The oligomerization of isoprene by the catalyst system consisting of titanium(IV) *n*-butoxide and diethylaluminum chloride was studied and the results were compared with those mentioned above.

The Effect of the Molar Ratio of Catalyst Components. The effect of the molar ratio of diethylaluminum chloride to titanium(IV) *n*-butoxide is shown in Fig. 4. The reactions were carried out at 35°C for 2 hr. Takahashi and Yamaguchi reported that

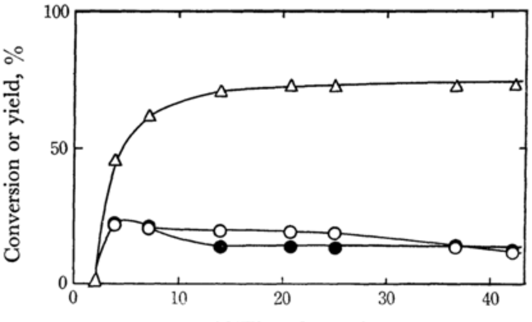

Fig. 4. Effect of the molar ratio of Et_2AlCl to $Ti(OBu)_4$.
—△—: Conversion of isoprene, %
—○—: Yield of 2,6-dimethyl-1, *trans*-3,6-octatriene, %
—●—: Yield of dimethylvinylcyclohexene, %
Reaction temp.: 35°C; reaction time: 2 hr; Isoprene/$Ti(OBu)_4$: 100

this catalyst system gave only 2,6-dimethyl-1,*trans*-3,6-octatriene as the dimer of isoprene,[2b] but in our experiment another dimer was found. This dimer was purified by preparative gas chromatography and analyzed. From the infrared and nuclear magnetic resonance spectra, this compound had two methyl groups (IR: 2975, 1450 and 1375 cm^{-1}; NMR: τ=8.37 and 9.02 ppm, 6H), three methylene groups (IR: 2925, 2850, 1440 and 1415 cm^{-1}; NMR: τ=8.02—8.63 ppm, 6H), one vinyl group (IR: 1830, 1645, 1000 and 910 cm^{-1}; NMR: τ=4.17, 4.92 and 5.22 ppm, 3H) and one three-substituted double bond (IR: 1645 and 805 cm^{-1}; NMR: τ=4.69 ppm, 1H). Therefore, this compound was 1,4- and/or 2,4-dimethyl-4-vinylcyclohexene. The boiling point (bp 48—49°C/14 mmHg) and the refractive index (n_D^{26} 1.4638) were very colse to 2,4-dimethyl-4-vinylcyclohexene reported by Zakharkin[2a] (bp 48—48.5 C/14 mmHg; n_D^{20} 1.4646).

Dimers were formed selectively when the molar ratio of diethylaluminum chloride to titanium(IV) *n*-butoxide was 3.6, and at higher molar ratio, reactions to higher oligomers were favored. The yield of dimethylvinylcyclohexene was constant at the higher molar ratio, but that of 2,6-dimethyl-1,*trans*-3,6-octatriene decreased.

The effect of electron donors on this catalyst system was shortly examined keeping the molar ratio of diethylaluminum chloride to titanium(IV) *n*-butoxide at 20. At this molar ratio, the selectivities for 2,6-dimethyl-1,*trans*-3,6-octatriene and dimethylvinylcyclohexene were 24 and 17%, respectively. When triphenylphosphine was added (molar ratio to titanium(IV) *n*-butoxide: 8.2), the selectivities for two dimers lowered to 19 and 16%, respectively. In the case of tetrahydrofuran (molar ratio to titanium(IV) *n*-butoxide: 6.7), the selectivities were 9 and 8%, respectively. An increase in the selectivity for dimers was not observed and the addition of tetrahydrofuran favored the reaction of isoprene to higher oligomers.

In the oligomerization of isoprene by the catalyst system consisting of zirconium(IV) *n*-butoxide and diethylaluminum chloride, the addition of triphenylphosphine or tetrahydrofuran raised the selectivity for 2,6-dimethyl-1,*trans*-3,6-octatriene to more than 90%.[4] The addition of these electron donors to the catalyst system consisting of titanium(IV) *n*-butoxide or hafnium(IV) *n*-butoxide and diethylaluminum chloride suppressed the conversion of isoprene but the increase of the selectivity for the linear dimer was not observed. The adidtion of triphenylphosphine kept the selectivity for the dimer nearly constant in both cases. The addition of tetrahydrofuran to the hafnium catalyst caused a faint decrease in the selectivity for the dimer. In the case of the reaction of isoprene by the catalyst system consisting of titanium(IV) *n*-butoxide and diethylaluminum chloride, the addition of tetrahydrofuran favored the reaction of isoprene to higher oligomers.