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Oligomerization of Isoprene by the Catalyst Systems Consisting of Tetraallylzirconium and Aluminum Compounds

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Recently, we have reported on the oligomerization of isoprene by zirconium bases catalysts.[1] In this paper, we report on the oligomerization of isoprene by the catalyst systems consisting of tetraallylzirconium and aluminum compounds.

Tetraallylzirconium itself was not a good catalyst for the oligomerization of isoprene and 12% of isoprene was converted into 2,6-dimethyl-1, *trans*-3,6-octatriene (selectivity, 36%) in the reaction at 100°C for 2 hr. Ethylaluminium sesquichloride was found to be a particularly good co-catalyst and 66% of isoprene was converted into the dimer (selectivity, 78%; Al/Zr molar ratio, 2) under the same conditions.

Results and Discussion

We examined five aluminum compounds, triethylaluminum, diethylaluminum chloride, ethylaluminum sesquichloride, ethylaluminum dichloride, and aluminum trichloride as co-catalyst.

Effect of Et_3Al. When triethylauminum was used as a co-catalyst, the dimer yield was less than 3% in the region of the Al/Zr molar ratio between 1 and 11. The conversion of isoprene decreased at lower molar ratios and reached a minimum at 4.2. The conversion increased at Al/Zr molar ratios higher than 4.2.

Effect of Et_2AlCl. The effect of diethylaluminum chloride on the oligomerization of isoprene by tetraallylzirconium has been reported.[1] The dimer yield was about 40% in the region of the Al/Zr molar ratio between 4.5 and 10. The yield of trimers was less than 10%.

Effect of $Et_{1.5}AlCl_{1.5}$. The effect of the molar ratio of ethylaluminum sesquichloride on the oligomerization of isoprene is shown in Fig. 1. The maximum yield of the dimer was attained at the Al/Zr molar ratio

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[1] A. Misono, Y. Uchida, K. Furuhata, and S. Yoshida, This Bulletin, **42** 2330 (1969).

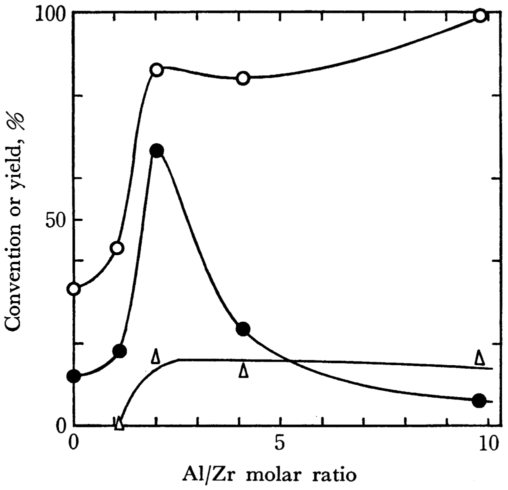

Fig. 1. Effect of $Et_{1.5}AlCl_{1.5}/Zr(C_3H_5)_4$ molar ratio.
—○—: Conversion of isoprene, %
—●—: Yield of the dimer, %
—△—: Yield of trimers, %
100°C, 2 hr, isoprene/$Zr(C_3H_5)_4$=100

of 2.

Effect of $EtAlCl_2$. Ethylaluminum dichloride showed a similar effect to that of ethyaluminum sesquichloride on the oligomerization of isoprene and the maximum yield of the dimer was attained at the Al/Zr molar ratio of 1. The conversion of isoprene was 66% and the dimer yield was 51% at this molar ratio. In contrast, isoprene was cyclopolymerized at room temperature by the catalyst system consisting of zirconium (IV) *n*-butoxide and ethylaluminum dichloride.[1]

Effect of $AlCl_3$. The conversion of isoprene and the dimer yield increased by the addition of aluminum trichloride to tetraallylzirconium. The maximum yield was observed at the Al/Zr molar ratio of 0.46 but both the conversion and the yield decreased at higher molar ratios. The maximum conversion was 48% and the maximum yield was 17%.

The results are summarized in Table 1. The acidity of aluminum compounds increases in the order $Et_3Al < Et_2AlCl < EtAlCl_2$.[2]

Absorption peaks of tetraallylzirconium in the nuclear magnetic resonance spectrum were shifted to lower field in the presence of diethylaluminum chloride. The difference of chemical shifts between methyl and methylene protons of diethylaluminum chloride in the mixed system was −1.0 ppm, while that of free diethylaluminum chloride was −0.9 ppm. This suggests that diethylaluminum chloride receives electrons from tetraallylzirconium.[3]

The presence of a second component with adequate acidity seems to be necessary for the dimerization of isoprene by tetraallylzirconium.

Table 1. Dimerization of isoprene by $Zr(C_3H_5)_4$ and aluminum compounds

Aluminum compound	Best Al/Zr$^{a)}$ mol. ratio	Best yield of the dimer
$Et_3Al^{b)}$	×	×
Et_2AlCl	4.5—10	40%
$Et_{1.5}AlCl_{1.5}$	2	66%
$EtAlCl_2$	1	51%
$AlCl_3$	0.46	17%
none	—	12%

a) Al/Zr molar ratio where the yield of the dimer reached a miximum.
b) Yield of the dimer was less than 3%.
Reaction conditions: 100°C, 2 hr; Isoprene/$Zr(C_3H_5)_4$ molar ratio, 100.

Experimental

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

Tetraallylzirconium was synthesized according to the reported method[4] and was stored at −78°C as an isoprene solution (3.29 wt% or 1.0 mole%). Isoprene hardly reacted at all under this condition.

Alkylaluminum compounds were diluted in dry benzene before use.

Aluminum trichloride was purified by sublimation.

Reaction Procedure. In a typical reaction, to a glass ampule filled with dry nitrogen, 2.36 g of benzene, 0.66 mmol of tetraalllylzirconium, 66 mmol of isoprene and 2.91 mmol of diethylaluminum choride (19.9 wt% benzene solution) were charged with syringes under a nitrogen stream. The ampule was then sealed and kept at 100°C for 2 hr.

Analysis. The dimer was determined to be 2,6-dimethyl-1,*trans*-3,6-octatriene by comparing its infrared spectrum with that of the authentic sample.[1]

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

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

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[3] R. T. Narashimhan and M. T. Rogers, *J. Amer. Chem. Soc.*, **82**, 5983 (1960).

[4] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmermann, *Angew. Chem.*, **78**, 157 (1966).