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Oligomerization of Isoprene by Zirconium Catalysts

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The oligomerization of isoprene by catalyst systems consisting of a zirconium compound and an organoaluminum compound was studied. Isoprene was dimerized to 2,6-dimethyl-1,*trans*-3,6-octatriene by a catalyst system consisting of zirconium(IV) *n*-butoxide and diethylaluminum chloride. The selectivity for this dimer was increased to more than 90% by adding triphenylphosphine or tetrahydrofuran to this catalyst system. The effects of the molar ratio of the catalyst components and those of catalyst species were studied.

It is well known that the oligomerizations of olefins are catalyzed by transition metal complexes. The structures of the oligomers are affected by the transition metal and other catalyst components. We reported previously the cyclic dimerization of isoprene to a mixture of 1,5- and 2,5-dimethyl-1,5-cyclooctadiene with a catalyst system consisting of iron(III) acetylacetonate, 2,2′-dipyridyl, and triethylaluminum.[1]

Some catalyst systems containing titanium or chromium have been reported to give a linear dimer of isoprene, 2,6-dimethyl-1,3,6-octatriene along with other oligomers.[2,3]

We now wish to report on the selective linear dimerization of isoprene by catalyst systems consisting of zirconium(IV) *n*-butoxide, diethylaluminum chloride, and an additive, such as triphenylphosphine or tetrahydrofuran. The dimer was 2,6-dimethyl-1, *trans*-3,6-octatriene. The effects of the molar ratios of the catalyst components on the selectivity for the dimer were studied.

Experimental

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

Allyl chloride was dried over calcium sulfate and distilled under an atmosphere of nitrogen.

Organoaluminum compounds were distilled at reduced pressures and dissolved in benzene.

Benzene, toluene, tetrahydrofuran, and ethyl ether were purified by conventional procedures.

Zirconium(IV) *n*-butoxide was prepared according to the reported method.[4]

Zirconium(IV) acetylacetonate was prepared by the reaction of pyridinium hexachlorozirconate and excess acetylacetone in benzene, to which mixture triethylamine was added, drop by drop, over a 30-min period, and was then purified by recrystallization from acetylacetone.

Tetra-π-allylzirconium was synthesized according to the method reported by Wilke.[5]

Triphenylphosphine and 2,2′-dipyridyl were commercial reagents.

Reactors. The reaction was carried out in a 30 m*l* glass tube, a 200 m*l* glass autoclave, or a 100 m*l* stainless steel autoclave.

Reaction Procedure. In a typical reaction, 5.4 mmol of triphenylphosphine were put into a stainless steel autoclave; the autoclave was swept several times with dry nitrogen, and then 6.28 g of benzene, 50 mmol of isoprene, 0.5 mmol of zirconium(IV) *n*-butoxide (16.7 wt% benzene solution), and 5.0 mmol of diethylaluminum chloride (19.9 wt% benzene solution) were added, in this order, under a dry nitrogen stream. The total amount of benzene was controlled so as to be 8.3—8.5 g. Then the autoclave was closed and kept at 100°C for 2 hr.

Analysis. For the separation of the products, the reaction solution was washed with diluted hydrochloric acid and with water, and then dried over anhydrous sodium sulfate and fractionally distilled. For the determination of the products, gas chromatography, infrared spectrography and nuclear magnetic resonance spectrography were applied, together with elementary analysis and molecular weight measurement. The gas chromatography was also used in calculating the conversion percent of isoprene and the yields of the products. A 2 m stainless steel column, 4-mm in diameter and 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 temperature, 300°C;

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

[2] a) L. I. Zakharkin, *Dokl. 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] D. C. Bradley, F. M. Abd-El Halim, E. A. Sadek and W. Wardlaw, *J. Chem. Soc.*, **1952**, 2032.

[5] G. Wilke, B. Bogdanovic, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter and H. Zimmermann, *Angew. Chem.*, **78**, 157 (1965).

carrier gas (helium) speed, 30 ml/min. Benzene was used as the internal standard.

Infrared spectra of the products were taken with 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

Structures of the Products. The reaction mixtures were analyzed by gas chromatography (Table 1).

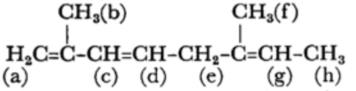
TABLE 1. GAS CHROMATOGRAPHIC RESULTS OF DIMERS AND TRIMERS OF ISOPRENE

Column temp., °C	Relative retention time of product based on benzene					
	Dimer		Trimer			
112	2.8	3.4				
180			2.9	4.9	6.8	9.9

TABLE 2. NMR SPECTRA ASSIGNMENT OF 2,6-DIMETHYL-1,*trans*-3,6-OCTATRIENE

NMR (τ-value)		Assignment*
8.45	doublet	h
8.40	singlet	f
8.25	singlet	b
7.25	doublet	e
5.12	singlet	a
4.67	quartet	g
4.42	sextet	d
3.75	doublet	c

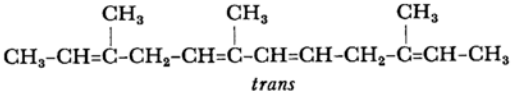
* The protons of 2,6-dimethyl-1,*trans*-3,6-octatriene are represented as follows.



$$\underset{(a)}{H_2C}=\overset{CH_3(b)}{C}-\underset{(c)}{CH}=\underset{(d)}{CH}-\underset{(e)}{CH_2}-\overset{CH_3(f)}{C}=\underset{(g)}{CH}-\underset{(h)}{CH_3}$$

The coupling constants are $J_{c-d}=15$ cps, $J_{d-e}=6$ cps, and $J_{g-h}=6$ cps.

A product with the relative retention time of 2.8 (112°C) was the main product. For analysis, it was isolated by distillation. The structure of the product was identified as 2,6-dimethyl-1,*trans*-3,6-octatriene by means of its nuclear magnetic resonance spectra, shown in Table 2; this structure was supported by the infrared spectra, which showed absorptions due to methyl and methylene groups (2960, 2905, 2840, 1455, 1440, and 1375 cm^{-1}), conjugated and isolated double bonds (1655, 1645, and 1610 cm^{-1}), a *trans* double bond (965 cm^{-1}), a terminal methylene group (885 cm^{-1}), and a tri-substituted double bond (815 cm^{-1}). A mixture of the products whose relative retention times were 4.9, 6.8, and 9.9 (180°C) was also separated by distillation. These compounds were confirmed to be trimers by molecular weight measurements (Found: 200, Calcd for $C_{15}H_{24}$: 204). The products whose relative retention times were 4.9 and 9.9 (180°C) were obtained in a relatively highly pure state by the fractional distillation. The infrared spectra of the product whose relative retention time was 9.9 showed absorptions due to methyl and methylene groups (2960, 2910, 2840, 1440, and 1375 cm^{-1}), a *trans* di-substituted double bond (965 cm^{-1}), and a tri-substituted double bond (810 cm^{-1}). No absorption was observed due to a terminal methylene or a vinyl group. The structure of this trimer has not yet been confirmed, but we assume it to be as shown below:



$$CH_3-CH=\overset{CH_3}{C}-CH_2-CH=\overset{CH_3}{C}-\underset{trans}{CH=CH}-CH_2-\overset{CH_3}{C}=CH-CH_3$$

The absorption characteristic of a conjugated double bond was not observed, but this can be explained by the fact that this compound has a nearly symmetric structure. The nuclear magnetic resonance spectra of this compound showed absorptions at about τ=8.4 due to a methyl group which was attached to an unsaturated carbon atom, at τ=7.3 (doublet) due to methylene protons between double bonds, and at τ=4—5 (multiplet) due to olefinic protons; these absorptions do not contradict the structure shown above. This compound might be formed by the addition of isoprene to the 1-position of the dimer, 2,6-dimethyl-1,*trans*-3,6-octatriene. The infrared spectra of the trimer whose relative retention time was 4.9 showed absorptions due to methyl and methylene groups (2960,

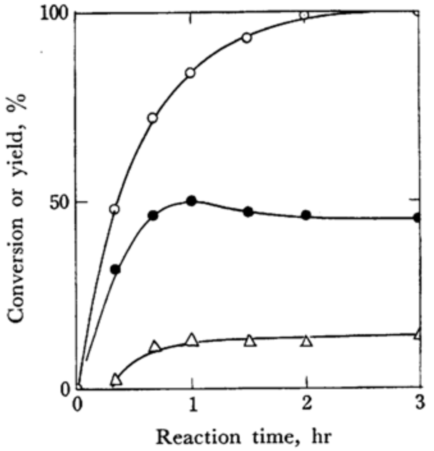


Fig. 1. Time dependence of the reaction.

○: Conversion of isoprene, %

●: Yield of 2,6-dimethyl-1,*trans*-3,6-octatriene, %

△: Yield of trimers, %

Reaction temp.: 100°C

Isoprene/Zr($O^nC_4H_9$)$_4$ mol ratio: 100

AlEt$_2$Cl/Zr($O^nC_4H_9$)$_4$ mol ratio: 10

2910, 2840, 1455, 1440, and 1380 cm^{-1}), *trans* di-substituted, tri-substituted, and conjugated double bonds (1660, 1645, 1610, 965, and 815 cm^{-1}), and a terminal methylene group (885 cm^{-1}). This trimer can be considered to be linear, but its structure has not yet been confirmed. The trimer with a relative retention time of 6.8 could not be isolated in sufficient purity for its structure to be studied in detail.

The Time Dependence of the Reaction. The time dependence of the reaction of isoprene by the catalyst system consisting of zirconium(IV) *n*-butoxide, and diethylaluminum chloride was studied (Fig. 1). The conversion of isoprene became almost 100% in 2 hr. The yield of 2,6-dimethyl-1,*trans*-3,6-octatriene reached a maximum at about 1 hr, and then it decreased slightly. It is probable that the dimer was consumed in the successive reaction to higher oligomers.

The Effects of the Molar Ratio of the Catalyst Components. The effects of the molar ratio of the components of the catalyst consisting of zirconium(IV) *n*-butoxide and diethylaluminum chloride or triethylaluminum are shown in Figs. 2 and 3 respectively.

In the case of diethylaluminum chloride, the conversion of isoprene increased with the increase in the molar ratio. The yield of 2,6-dimethyl-1,*trans*-3,6-octatriene reached a maximum at the molar ratio of 10. The yield of trimers was almost constant when the molar ratio exceeded 10 , and the polymer yield was increased as the molar ratio was increased. On the other hand, in the case of triethylaluminum the maximum conversion of isoprene appeared at the molar ratio of 18. By this catalyst system, isoprene was consumed mainly by high polymerization, and the yield of 2,6-dimethyl-1,*trans*-3,6-octatriene was small (0—7%) at the molar ratios between 7 and 22.

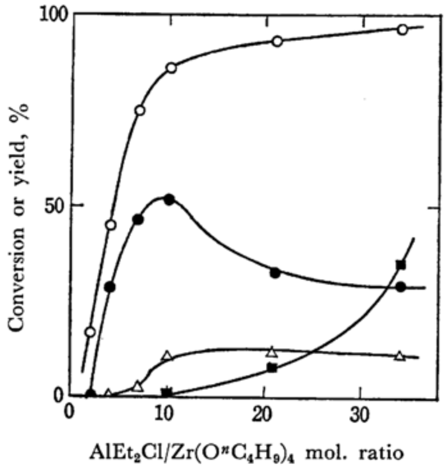


Fig. 2. Effect of the molar ratio of diethylaluminum chloride to zirconium(IV) *n*-butoxide.
○: Conversion of isoprene, %
●: Yield of 2,6-dimethyl-1,*trans*-3,6-octatriene, %
△: Yields of trimers, %
■: Yield of polymer, %
Reaction temp.: 100°C, Reaction time: 2 hr
Isoprene/Zr(O^{n}C$_4$H$_9$)$_4$ mol ratio: 100

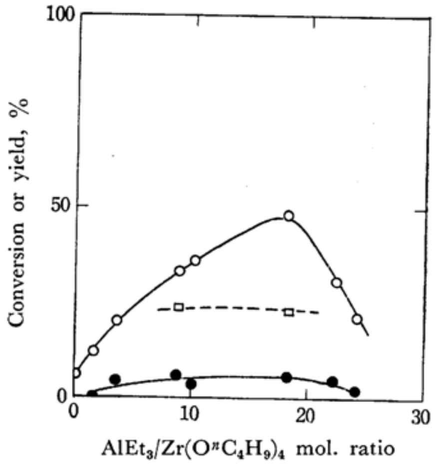


Fig. 3. Effect of the molar ratio of triethylaluminum to zirconium(IV) *n*-butoxide.
○: Conversion of isoprene, %
●: Yield of 2,6-dimethyl-1, *trans*-3,6-octatriene, %
□: Yield of polymer, %
Reaction temp.: 100°C, Reaction time: 2 hr
Isoprene/Zr(O^{n}C$_4$H$_9$)$_4$ mol ratio: 100

As other organoaluminum compounds, diethylaluminum ethoxide and ethylaluminum dichloride were used. In the case of diethylaluminum ethoxide, however, the reaction of isoprene did not take place. The binary system of zirconium(IV) *n*-butoxide and ethylaluminum dichloride polymerized isoprene immediately. The infrared spectrum of the polymer obtained by this binary catalyst system showed only methyl and methylene absorptions and did not show any absorption due to carbon-carbon double bonds. This spectrum was identical with that of the polymer obtained by ethylaluminum dichloride only. Ethylaluminum dichloride was reported to cause the cationic polymerization of isoprene to a ladder polymer.[6]

The best organoaluminum compound as a catalyst component was thus found to be diethylaluminum chloride, and the best yield of the dimer of isoprene was accomplished when the molar ratio of diethylaluminum chloride to zirconium(IV) *n*-butoxide was about 10.

The Effects of Additives. In the oligomerization of olefins, the addition of an electron donor to the reaction system strongly affects the reaction

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[6] B. A. Dolgoplosh, G. P. Belonovskaja, I. I. Boldgreva, E. N. Kropacheva, K. V. Nelson, Ja. M. Rosinoer and J. D. Chernova, *J. Polymer Sci.*, **53**, 209 (1961).

products, *e.g.*, in the oligomerization of butadiene with iron complex catalysts.[7] In the present study some electron donors were added to the catalyst system consisting of zirconium(IV) *n*-butoxide and diethylaluminum chloride (Al/Zr; 10). The results are shown in Fig. 4.

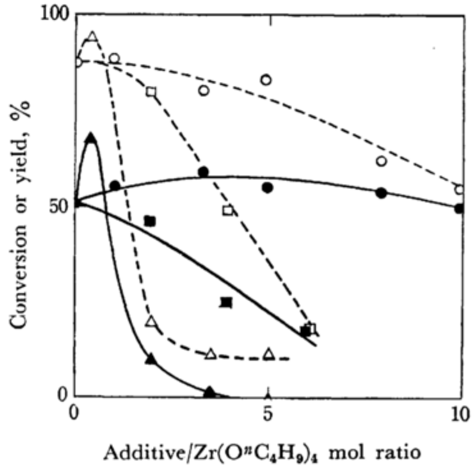

Fig. 4. Effects of additives.
----: Conversion of isoprene, %
——: Yield of 2,6-dimethyl-1,*trans*-3,6-octatriene, %
Additives are represented by
○●: PPh_3, □■: THF, △▲: 2,2′-dipyridyl.
Reaction temp.: 100°C, Reaction time: 2 hr
Isoprene/Zr($O^nC_4H_9$)$_4$ mol ratio: 100
$AlEt_2Cl$/Zr($O^nC_4H_9$)$_4$ mol ratio: 10

The addition of triphenylphosphine lowered only the conversion of isoprene, while the yield of 2,6-dimethyl-1,*trans*-3,6-octatriene was slightly increased. In the case of tetrahydrofuran, both the conversion and the yield were decreased. The formation of higher oligomers was strongly suppressed in both cases, and the selectivity for the dimer increased to more than 90%. The addition of 2,2′-dipyridyl suppressed the reaction of isoprene.

The Reaction with Catalyst Systems Consisting of Other Zirconium Compounds. Zirconium(IV) acetylacetonate, zirconium(IV) chloride, and tetra-π-allylzirconium were used in place of zirconium(IV) *n*-butoxide in the reaction of isoprene.

When zirconium(IV) acetylacetonate and diethylaluminum chloride were used as catalysts, no oligomerization of isoprene took place, but polymerization did occur. The polymer obtained was a white powder melting at 123°C; the infrared spectrum of the polymer showed methyl and methylene absorptions and two absorptions at 890 cm^{-1} and 980 cm^{-1}.

In the case of the catalyst system consisting of zirconium(IV) chloride and triethylaluminum or diethylaluminum chloride, the reaction solution was not homogeneous and only a small amount of polymer was formed at the surface of zirconium(IV) chloride.

In tetra-π-allylzirconium, the π-allyl ligand is supposed to be replaced with isoprene. In the reaction of isoprene by tetra-π-allylzirconium alone, the dimerization of isoprene to 2,6-dimethyl-1,*trans*-3,6-octatriene was observed along with the polymerization reaction. When diethylaluminum chloride was employed as a catalyst component, the conversion of isoprene and the yield of the dimer increased as the molar ratio of diethylaluminum chloride to tetra-π-allylzirconium increased. However, the formation of the dimer became constant at the higher molar ratio. The effect of the molar ratio of diethylaluminum chloride to tetra-π-allylzirconium is shown in Fig. 5. From this result, the addition of diethylaluminum chloride seemed to be necessary to produce an effective catalyst for the dimerization.

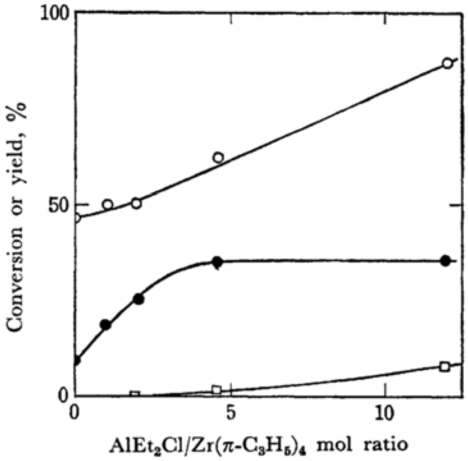

Fig. 5. Effect of the molar ratio of diethylaluminum to tetra-π-allylzirconium.
○: Conversion of isoprene, %
●: Yield of 2,6-dimethyl-1,*trans*-3,6-octatriene, %
□: Yields of trimers, %
Reaction temp.: 100°C, Reaction time: 2 hr
Isoprene/Zr(π-C_3H_5)$_4$ mol ratio: 100

In the oligomerization of dienes with the catalyst system consisting of a transition metal and an alkylaluminum, the alkylaluminum is considered to act as an alkylating reagent of the transition metal. A low-valent transition metal species is then formed by the homolytic splitting of the carbon-metal bond. The catalyst systems consisting of zirconium(IV) *n*-butoxide and diethylaluminum chloride, with or without a stoichiometric amount of isoprene, were diamagnetic at room temperature and after having been heated at 100°C for 30 min.

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[7] M. Hidai, K. Tamai, Y. Uchida and A. Misono, This Bulletin, **39**, 1357 (1966).

From these results, we assume that zirconium is in its four-valent state during the dimerization reaction.

The small difference between triphenylphosphine and tetrahydrofuran in the effects on the dimerization of isoprene by the catalyst system consisting of zirconium(IV) *n*-butoxide and diethylaluminum chloride can be explained on the assumption presented above. If zirconium is in its four-valent state (d^0), the back donation to ligands does not play an important part in the catalytic reaction.