BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1118—1121 (1971)

Oligomerization of Isoprene by Vanadium Catalysts

Yasuzo Uchida, Ken-ichi Furuhata, and Hisayasu Ishiwatari
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

(Received November 5, 1970)

Oligomerization of isoprene by the catalyst system consisting of $VO(OEt)_3$ and organoaluminum compounds was studied. Isoprene was oligomerized to a mixture of dimers, trimers and higher oligomers by $VO(OEt)_3$–Et_2AlCl catalyst system. 2,6-Dimethyl-1,*trans*-3,6-octatriene was the main dimer of isoprene in this reaction. The addition of tetrahydrofuran, dioxane, triphenylphosphine, bis-diphenylphosphinoethane, triethylamine or tetramethylethylenediamine to this catalyst system raised the reaction rate and the selectivity for the dimer at lower donor/$VO(OEt)_3$ molar ratios but suppressed the reaction at higher molar ratios. By $VO(OEt)_3$–Et_3Al catalyst system, isoprene was converted to a liquid polymer and by $VO(OEt)_3$–$EtAlCl_2$ catalyst system, it was cyclopolymerized to an insoluble polymer. Structures of two new oligomers of isoprene were also reported.

The oligomerization of isoprene to linear oligomers of head-to-tail structures is of great interest for the synthesis of raw materials of terpenic compounds. A linear dimer of isoprene, 2,6-dimethyl-1,3,6-octatriene which is formed by the head-to-tail addition of isoprene, was formed by titanium,[1] chromium,[2] or nickel[3] based catalysts but by these catalysts cyclic dimers were also formed. Palladium based catalyst[4] gave selectively 2,7-dimethyl-1,3,7-octatriene from isoprene but this compound has a tail-to-tail structure.

We reported previously the oligomerization of isoprene by zirconium[5] and hafnium[6] based catalysts. By these catalysts, 2,6-dimethyl-1,*trans*-3,6-octatriene was formed without six- or eight-membered cyclic dimers, and in the case of zirconium based catalysts, the addition of electron donors such as triphenylphosphine to the catalyst system raised the selectivity for this dimer to over than 90%.

In this paper we report the oligomerization of isoprene by the catalyst system consisting of ethyl orthovanadate and organoaluminum compounds.

Experimental

Reagents. Isoprene, benzene, tetrahydrofuran, 1,4-dioxane, triethylamine, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine and tetrahydrothiophene were dried and distilled under a nitrogen stream.

Organoaluminum compounds were purified by distillation and were diluted in benzene.

Ethyl orthovanadate synthesized by the reported method[7] was diluted in benzene and stored in a refrigerator.

1,2-Bisdiphenylphosphinoethane was synthesized by the reported method.[8]

Commercial triphenylphosphine was used without further purification.

Reaction Procedure. In a typical reaction, to a 20 m*l* glass ampule filled with nitrogen, 3.75 g of benzene, 50 mmol of isoprene, 0.5 mmol of ethyl orthovanadate (14.3 wt% benzene solution) and 6.0 mmol of diethylaluminum chloride (14.8 wt% benzene solution) were charged in this order with syringes under a nitrogen stream. The total amount of benzene was controlled to be 8.3—8.5 g. The ampule was then sealed and kept at 70°C for 1 hr.

Analysis. The gas chromatography was used for calculating the conversion percent of isoprene and quantitative analysis of products. A 2 m stainless steel column,

---

[1] 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). c) L. I. Zakharkin and V. M. Akhmedev, *Azerb. Khim. Zh.*, **1969**, 58.

[2] G. Wilke, *J. Polym. Sci.*, **38**, 45 (1959).

[3] S. Watanabe, K. Suga, and H. Kikuchi, *Aust. J. Chem.*, **23**, 385 (1970).

[4] N. Takahashi, T. Sibano, and N. Hagihara, *Shokubai (Catalyst)*, **11**, 4 (1969).

[5] A. Misono, Y. Uchida, K. Furuhata, and S. Yoshida, This Bulletin, **42**, 2303 (1969).

[6] A. Misono, Y. Uchida, K. Furuhata, and S. Yoshida, *ibid.*, **42**, 1383 (1969).

[7] W. Prandtl and L. Hess, *Z. Anorg. Chem.*, **82**, 103 (1913).

[8] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

4 mm in diameter, packed with polydiethylene glycol succinate on Shimalite was used. Operation conditions: column temperature, 120°C and 180°C for dimers and trimers, respectively; flash evaporator, 300°C; carrier gas(helium) speed, 30 ml/min. Benzene was used as an internal standard.

Infrared spectra were taken using a Hitachi infrared spectrophotometer EPI-S2.

Nuclear magnetic resonance spectra were taken using a JMN-4H-100(Japan Electron Optics Laboratory Co.).

Results and Discussion

Oligomerization of Isoprene by $VO(OEt)_3$—Et_2AlCl Catalyst System. Isoprene was oligomerized to a mixture of dimers, trimers and higher oligomers by this catalyst system. Two dimers were found on gas chromatography and the structure of the main dimer was determined to be 2,6-dimethyl-1,*trans*-3,6-octatriene by comparing the infrared spectrum with that of the pure sample obtained by the zirconium catalyst.[5] The yield of another dimer was less than 14% of that of 2,6-dimethyl-1,*trans*-3,6-octatriene. As shown from the gas chromatographic data, the mixture of trimers was consisted of more than six isomers in which four were predominantly formed.

The Effect of the Al/V Molar Ratio: The effect of the molar ratio of diethylaluminum chloride to ethyl orthovanadate is shown in Fig. 1. Reactions were carried out at 70°C for 1hr. At the molar ratio 4, the reaction solution was very viscous and no low oligomers were formed. A yellow, wax-like polymer of isoprene obtained at this ratio contained 67% of *cis*-1,4-, 25% of *trans*-1,4-, 6% of 3,4- and 2% of 1,2-structures.[9]

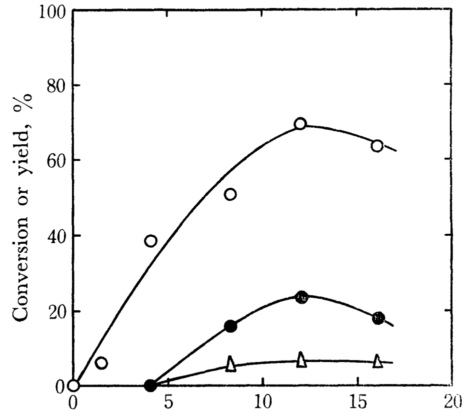


Fig. 1. Effect of the molar ratio of Et_2AlCl to $VO(OEt)_3$.
-○-: Conversion of isoprene, %
-●-: Yield of 2,6-dimethyl-1, *trans*-3,6-octatriene, %
-△-: Yield of trimers, %
Reaction temp.: 70°C; reaction time: 1 hr;
Isoprene/$VO(OEt)_3$: 100

The maximum yield of 2,6-dimethyl-1,*trans*-3,6-octatriene was accomplished when the molar ratio of diethylaluminum chloride to ethyl orthovanadate was 12. The yield and the selectivity for this dimer at this ratio were 23.3% and 33.4%, respectively. The infrared spectrum of the mixture of higher oligomers obtained at this ratio showed absorptions due to methyl and methylene groups (2960, 2920, 2850, 1450, and 1380 cm^{-1}), a three-substituted double bond (1670 and 840 cm^{-1}), a terminal methylene group (1650 and 890 cm^{-1}) and a *trans* two-substituted double bond (980 cm^{-1}, weak). At higher molar ratios, the conversion of isoprene and the yield of dimers slightly decreased.

The Effect of Electron Donors: The effect of electron donors on the oligomerization by this catalyst system was studied using monodentate and potentially bidentate compounds (Figs. 2—5). The reactions were carried out at 70°C for 1 hr keeping the molar ratio of diethylaluminum chloride to ethyl orthovanadate constant at 12.0. The addition of tetrahydrofuran, 1,4-dioxane, triethylamine, *N,N,N′,N′*-tetramethylethylenediamine,

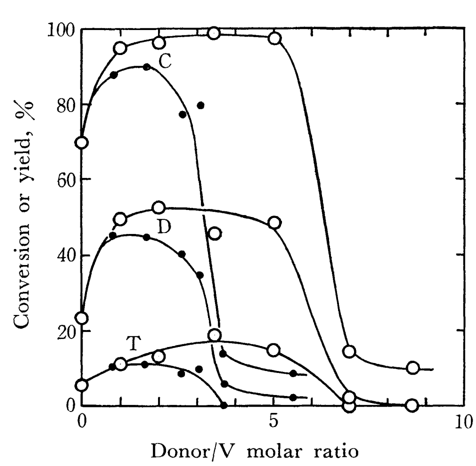


Fig. 2. Effect of tetrahydrofuran and dioxane.
-○-: Tetrahydrofuran
-●-: Dioxane
C: Conversion of isoprene, %
D: Yield of 2,6-dimethyl-1, *trans*-3, 6-octatriene, %
T: Yield of trimers, %
Reaction conditions: 70°C, 1 hr,
Isoprene/$VO(OEt)_3$: 100, $Et_2AlCl/VO(OEt)_3$: 12

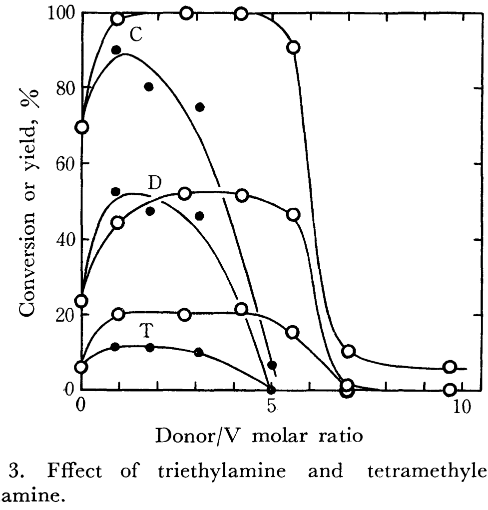


Fig. 3. Fffect of triethylamine and tetramethylethylenediamine.
-○-: Triethylamine
-●-: Tetramethylethylenediamine
C: Conversion of isoprene, %
D: Yield of 2,6-dimethyl-1, *trans*-3,6-octatriene, %
T: Yield of trimers, %
Reaction conditions: 70°C, 1 hr,
Isoprene/$VO(OEt)_3$: 100, $Et_2AlCl/VO(OEt)_3$: 12

---

[9] W. S. Richardson and A. Sacher, *J. Polym. Sci.*, **10**, 353 (1953).

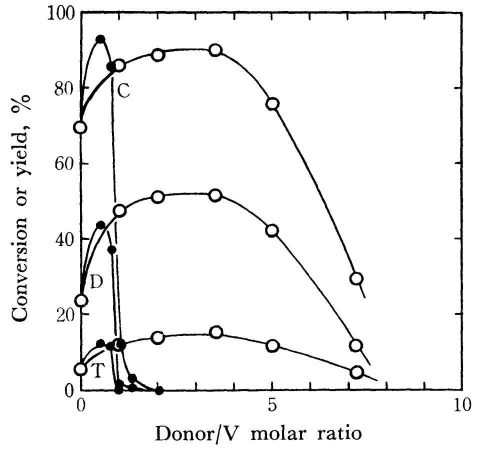


Fig. 4. Effect of triphenylphosphine and bis-diphenylphosphinoethane.
-○-: Triphenylphosphine
-●-: Bis-diphenylphosphinoethane
C: Conversion of isoprene, %
D: Yield of 2,6-dimethyl-1, *trans*-3,6-octatriene, %
T: Yield of trimers, %
Reaction conditions: 70°C, 1 hr,
Isoprene/$VO(OEt)_3$: 100, $Et_2AlCl/VO(OEt)_3$: 12

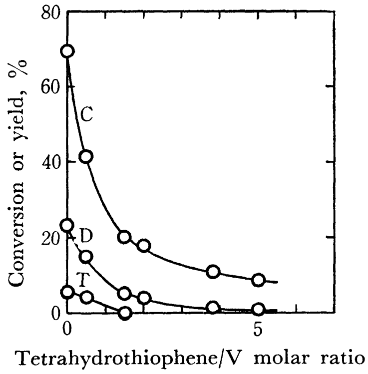


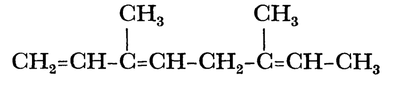
Fig. 5. Effect of tetrahydrothiophene.
C: Conversion of isoprene, %
D: Yield of 2,6-dimethyl-1, *trans*-3,6, octatriene, %
T: Yield of trimers, %
Reaction conditions: 70°C, 1 hr,
Isoprene/$VO(OEt)_3$: 100, $Et_2AlCl/VO(OEt)_3$: 12

triphenylphosphine or 1,2-bis-diphenylphosphinoethane raised the reaction rate at lower donor/$VO(OEt)_3$ molar ratios. The selectivity for 2,6-dimethyl-1,*trans*-3,6-octatriene was also raised to 50—60%. The reactions were suppressed at higher molar ratios. Tetrahydrothiophene suppressed the reaction at every molar ratio.

Reaction of Isoprene by $VO(OEt)_3$—Et_3Al or $VO(OEt)_3$—$EtAlCl_2$ Catalyst System. By the catalyst system consisting of ethyl orthovanadate and triethylaluminum, isoprene was consumed nearly completely and was converted into a liquid polymer in the reaction at 40—100°C for 1 hr. Only small amount of the dimer (less than 1.3%) was formed at 40—70°C. The infrared spectrum of the brown liquid polymer obtained in the reaction at 70°C for 1 hr and at the molar ratio of triethylaluminum to ethyl orthovanadate 5—10 showed absorptions due to methyl and methylene groups (2950, 2925, 2850, 1455, and 1380 cm^{-1}), a terminal methylene group (1790, 1650, and 890 cm^{-1}), three-substituted and *trans* double bonds (1670, 970, 840, and 810 cm^{-1}) and a vinyl group (910 cm^{-1}, sh). It contained about 55% of 1,4,-40% of 3,4- and 5% of 1,2-structures.[9]

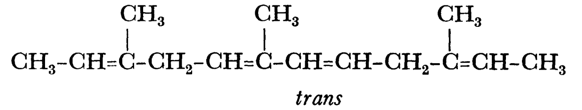
The catalyst system consisting of ethyl orthovanadate and ethylaluminum dichloride caused the vigorous polymerization of isoprene at room temperature. The infrared spectrum of the insoluble polymer obtained showed only methyl and methylene absorption (2925, 2850, 1455, and 1380 cm^{-1}) and did not show any absorption due to carbon-carbon double bonds. This spectrum was idential with that of the polymer formed by the cationic cyclopolymerization of isoprene by ethylaluminum dichloride.[10]

Structures of New Oligomers of Isoprene. The minor dimer formed by the catalyst consisting of ethyl orthovanadate and diethylaluminum chloride had the same gas chromatographic retention times as the dimer obtained in a small amount by zirconium[5] and hafnium[6] based catalysts. The mixture of dimers obtained by the zirconium catalyst was fractionated by distillation and the sample of the minor dimer (92% purity, containing 8% of 2,6-dimethyl-1,*trans*-3,6-octatriene) was analyzed with the use of infrared and nuclear magnetic resonance spectra. The infrared spectrum showed absorptions due to methyl and methylene groups (2965, 2925, 2850, 1440, and 1380 cm^{-1}), a conjugated double bond (1610 cm^{-1}), a vinyl group (1795, 1645, 990, and 895 cm^{-1}), a three-substituted double bond (1670 and 810 cm^{-1}) and a weak absorption at 960 cm^{-1} due to 2,6-dimethyl-1,*trans*-3,6-octatriene. The nuclear magnetic resonance spectrum showed the presence of three methyl groups (τ=8.41, doublet; 8.38, singlet; 8.24, singlet), one methylene group between two double bonds (τ=7.17, doublet), one vinyl group (τ=5.17—4.87, three absorptions; 3.68, double doublet) and two olefinic protons (τ=4.90—4.55, complex absorptions). Thus the structure of this compound is considered to be 3,6-dimethyl-1,3,6-octatriene.



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

Relative retention times (retention time of benzene =1) of four main trimers obtained by the catalyst system consisting of ethyl orthovanadate and diethylaluminum chloride were 4.1, 4.6, 6.8, and 9.9 (operation conditions of gas chromatography, see experimental part). Two isomers (relative retention time, 6.8 and 9.9) were gas chromatographically identical with those obtained by the zirconium based catalyst and one isomer (relative retention time, 9.9) was assumed to be 3,6,10-trimethyl-2,5,*trans*-7,10-dodecatetraene.[5]



$$CH_3{-}CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3$$

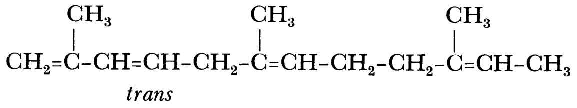
trans

The mixture of trimers obtained by the zirconium catalyst was fractionally distilled and the isomer with the relative retention time 6.8 was obtained in a pure

---

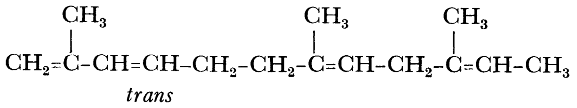
10) I. Koessler, M. Stolka, and K. Mach, *J. Polym. Sci. Pt C*, **No. 4**, 977 (1963).

state. The infrared spectrum of this isomer showed absorption due to methyl and methylene groups (2970, 2925, 2850, 1455, 1445, and 1380 cm^{-1}), a conjugated double bond (1610 cm^{-1}), a *trans* double bond (1670 and 970 cm^{-1}), a terminal methylene group (1780, 1650, and 885 cm^{-1}) and three-substituted double bonds (1670, 840, and 810cm^{-1}). Its nuclear magnetic resonance spectrum showed the presence of four methyl groups(τ= 8.45, doublet; 8.34, singlet, two methyl groups; 8.20, singlet), two adjacent methylene groups between doubl bonds (τ=7.98—7.90), one methylene group between double bonds (τ=7.20, doublet), one terminal methyl group (τ=5.16, singlet), two olefinic protons (τ=4.92—4.70, complex absorptions) and one *trans* two-substituted double bond (τ=4.48, double triplet; 3.88, doublet). Thus the structure of this isomer is considered to be 2,6,10-trimethyl-1,*trans*-3,6,10-dodecatetraene or 2,7,10-trimethyl-1,*trans*-3,7,10-dodecatetraene.



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

or



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