

CODIMERIZATION OF PROPYLENE AND BUTADIENE BY PALLADIUM COMPLEX CATALYST:  
CONTROL OF THE STRUCTURE OF THE CODIMER BY PHOSPHORUS LIGANDS

Takehiko Ito, Tsunehisa Kawai, and Yasuo Takami

National Chemical Laboratory for Industry, Shibuya-ku, Tokyo, Japan

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In recent years, various transition metal catalysts for the codimerization of monoolefin and conjugated diolefin have been developed<sup>1)</sup>. In the case of the codimerization of propylene with butadiene by these catalysts, it has been reported that 2-methylhexadiene-1,4 (branched-chain C<sub>7</sub>-diene) is obtained as a codimer product<sup>2-4)</sup>, whereas the formation of heptadiene of straight-chain structure has scarcely been reported in the literature<sup>5)</sup>.

Previously we have reported that a novel catalyst system<sup>6)</sup> consisting of di- $\mu$ -chlorodi- $\pi$ -allyldipalladium, aluminum chloride, and tertiary phosphine can effectively catalyze the codimerization of ethylene with butadiene in a solvent containing nitrobenzene. In this communication, we wish to report that the codimerization of propylene with butadiene by the use of this catalyst system affords heptadienes (straight-chain C<sub>7</sub>-dienes) along with 2-methylhexadienes as codimer products, and also that the ratio of the heptadienes to the methylhexadienes (ratio of straight-chain codimer to branched-chain codimer) in the products can be varied by changing the structure of phosphorus ligand employed as a component of the catalyst system.

A typical codimerization experiment was carried out as follows: Fifteen milliliters of nitrobenzene, 15 ml of decalin, 0.15 mmol of di- $\mu$ -chlorodi- $\pi$ -allyl-dipalladium, 0.3 mmol of triphenylphosphine, 0.6 mmol of aluminum chloride, 10 ml (115 mmol) of butadiene and 10 ml (140 mmol) of propylene were introduced into a 100 ml stainless steel autoclave filled with an inert gas. The mixture was stirred for 2 hrs at 100°C. After unreacted propylene and butadiene were

recovered, the reaction product was separated from the catalyst by distillation at reduced pressure. The distillate was qualitatively and quantitatively analyzed by VPC, IR, and NMR.

The distillate contained 33 mmol of  $C_7$ -dienes (29 % yield based upon the mole of butadiene introduced) and 9.1 mmol of butadiene dimers, and the distillation residue contained 0.4 g of nonvolatile oily polymer. The composition of the  $C_7$ -dienes was as follows:

*trans*-2-Methylhexadiene-1,4 (9.6 mmol): bp. 94-95°C; IR 1647, 890  $cm^{-1}$  ( $CH_2=C<$ ), 969  $cm^{-1}$  (*trans*, -CH=CH-); NMR 4.55  $\tau$  (2H, m), 5.32  $\tau$  (2H, s), 7.33  $\tau$  (2H, m), 8.30  $\tau$  (3H, s), 8.35  $\tau$  (3H, m). *trans,trans*-Heptadiene-2,5 (8.9 mmol): bp. 104°C; IR 965  $cm^{-1}$  (*trans*, -CH=CH-); NMR 4.7  $\tau$  (4H, m), 7.45  $\tau$  (2H, m), 8.45  $\tau$  (6H, m). *trans,cis*-Heptadiene-2,5 (3.6 mmol): IR 710  $cm^{-1}$  (*cis*, -CH=CH-), 965  $cm^{-1}$  (*trans*, -CH=CH-). *trans*-Heptadiene-1,5 (3.6 mmol): bp. 97-98°C; IR 910, 990, 1640  $cm^{-1}$  ( $CH_2=CH-$ ), 964  $cm^{-1}$  (*trans*, -CH=CH-); oxidation with potassium permanganate gave succinic acid. Besides these dienes, some other  $C_7$ -dienes, not further characterized, were present. The carbon skeletons of all the  $C_7$ -dienes described above were determined by catalytic hydrogenation to the appropriate alkanes (*n*-heptane and 2-methylhexane) and the number of double bonds was determined by the amount of hydrogen absorbed.

Some results of the codimerization of propylene and butadiene with the catalyst consisting of a combination of di- $\mu$ -chlorodi- $\pi$ -allyldipalladium and aluminum chloride with various kinds of tertiary phosphines or phosphites, are shown in Table 1.

The Table indicates that the extent of the formation of straight-chain  $C_7$ -dienes is dependent upon the nature of the phosphorus ligands. In the series  $(C_6H_{11})_3P$  to  $(C_6H_5O)_3P$  the ratio of straight-chain  $C_7$ -dienes to total  $C_7$ -dienes increases gradually from 0.22 to 0.80. The dependence of the structure of the codimer products upon the nature of the phosphorus ligands is of considerable interest in respect to the catalysis mechanism. Catalytic activity is influenced by both Al/Pd and P/Pd ratios. The catalytic activity is low when the Al/Pd ratio is below 1, but increases with ratios from 1 to 2. The activity does not change greatly with ratios higher than 2. On the other hand, the

activity increases with the rise in the P/Pd ratio from 0 to 1, but does not change at ratios from 1 to 2. At higher ratios the activity decreases. The variations of the Al/Pd and P/Pd ratios have little effect on the extent of the formation of the straight-chain C<sub>7</sub>-dienes.

TABLE 1. Influence of Phosphine or Phosphite on the Structure of Codimer Products of the Codimerization of propylene with Butadiene by  $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-AlCl}_3\text{-R}_3\text{P}$  Catalyst

[  $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2^*$  0.15 mmol, AlCl<sub>3</sub> 0.6 mmol, R<sub>3</sub>P 0.3 mmol, butadiene 115 mmol, propylene 140 mmol, nitrobenzene 15 ml\*\*, decalin 15 ml, 100°C, 2hrs. ]

| R <sub>3</sub> P                                  | Conversion of butadiene to C <sub>7</sub> -dienes mol %*** | Ratio of straight-chain C <sub>7</sub> -dienes to total C <sub>7</sub> -dienes**** |
|---|--|--|
| (C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> P  | 28   | 0.22   |
| (n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> P | 33   | 0.44   |
| (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P   | 29   | 0.64   |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P  | 14   | 0.68   |
| (C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> P  | 22   | 0.80   |

\*) Di- $\mu$ -chlorodi- $\pi$ -allyldipalladium.

\*\*\*) The use of nitrobenzene as a component of solvent is very important for keeping the reaction homogeneous and to suppress the formation of oily polymer from butadiene.

\*\*\*\*) Based on the amount of butadiene introduced.

\*\*\*\*\*) This ratio was determined from the ratio of n-heptane to the sum of 2-methylhexane and n-heptane which were formed by catalytic hydrogenation of C<sub>7</sub>-diene fraction.

Recently, several studies have been made on the dimerization of propylene with nickel catalysts modified with tertiary phosphines<sup>7-10</sup>). It has been found that the structure of the propylene dimers is greatly influenced by the nature of the phosphines employed as ligands. This influence of the phosphine ligands

has been discussed in term of the electronic and steric effects of the phosphines by Wilke and coworkers<sup>7)</sup>. Their discussions appear to be of much use in the consideration of the results in Table 1, but a more detailed experimental research is required to elucidate the role of the phosphorus ligands in the present codimerization of propylene and butadiene.

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