

EFFECTS OF AMINES ON THE DIMERIZATION OF ISOPRENE CATALYZED  
BY BIS(TRIPHENYLPHOSPHINE)NICKEL DICHLORIDE REDUCED  
BY SODIUM BOROHYDRIDE

Isao MOCHIDA\*, Shigeki YUASA, and Tetsuro SEIYAMA  
Research Institute of Industrial Science\*, and Department of  
Applied Chemistry, Faculty of Engineering, Kyushu University,  
Fukuoka, 812

Amines introduced into the dimerization of isoprene catalyzed by  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2\text{-NaBH}_4$  gave significant effects on the catalytic activity and selectivity. Yield of linear dimers was 60% by n-propylamine, whereas it was only 3% by tert-butylamine. The formation of cyclo dimers was increased by pyridine and its derivatives.

Conjugated dienes have been dimerized by a wide variety of transition metal complexes.<sup>1</sup> The complexes containing zero-valent nickel have been reported to yield cyclic dimers from dienes in aprotic solvents, and linear oligomers in protonic solvents,<sup>2</sup> although  $\text{Ni}(\text{PPh}_3)_2\text{X}_2$  (X; halide) reduced by Grignard reagent gave a linear isoprene dimer in tetrahydrofuran.<sup>3</sup> In the present study, we will report a significant effect of amine on the catalytic activity of  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  reduced by  $\text{NaBH}_4$  for the dimerization of isoprene.

$\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  was prepared according to the method described in the literature.<sup>4</sup> Isoprene and amines were distilled and dried under nitrogen. Reactions were carried out in a sealed tube. In a typical experiment, after being filled with nitrogen, the tube was charged with 0.5mmole  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ , 1.5mmole of  $\text{NaBH}_4$ , 1 ml isoprene, 1 ml amine and 1 ml pentane, then sealed and shaken in a water bath of a constant temperature for 24 hr. After the reaction mixture was treated with HCl to eliminate the amine from products, a mixture of isoprene oligomers was extracted with  $\text{CCl}_4$  and then analyzed by a gas-chromatograph using a column packed with Apiezon L. Major components of the products were isolated with a gas-chromatograph for the identification by means of NMR, IR, and Mass spectroscopy.

Addition of n-propylamine resulted in the preferential formation of 2,6-dimethyl-1,3,6-octatriene (DMOT) and dimethyloctadiene (DMOD), such as 2,6-dimethyl-1,6-octadiene and 2,6-dimethyl-2,6-octadiene, 2,7-dimethyl-2,6-octadiene in addition to some trimers and cyclodimers of 1,5-dimethylcyclooctadiene, 2,7-dimethylcyclooctadiene (DMCOD) and dipentene (DP). Amines were not found in the products under the present conditions as Baker et al.<sup>5</sup> and Furukawa et al.<sup>6</sup> reported their formation, using less reducing reagent against nickel catalyst. Cyclodimers were only products in the case without the amine (Table) as reported before.<sup>2</sup> It

Table.  
Effects of Amine on the Product Distribution of Isoprene  
Dimerization Catalyzed by  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2\text{-NaBH}_4$   
 $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ ; 0.5mmole,  $\text{NaBH}_4$ ; 1.5mmole, Amine; 1ml  
Isoprene; 1ml, pentane; 1ml,  
Reaction temperature and period; 80°, 24 hr

| product<br>Amine       | selectivity and yield (in parenthesis), % |                |                |                |  | %**  |
|------------------------|---|----------------|----------------|----------------|--|------|
|                        | DMOD                                      | DMOT           | DP             | DMCOD          | trimers and un-<br>identified products |      |
| n-PrNH <sub>2</sub>    | 16.2<br>(15.9)                            | 45.0<br>(44.1) | 5.5<br>( 5.4)  | 12.5<br>(12.3) | 20.9*<br>(20.6)                        | 98   |
| tert-BuNH <sub>2</sub> | 44.3<br>( 2.8)                            | 0              | 31.0<br>( 2.6) | 14.4<br>( 1.2) | 10.3<br>( 8.6)                         | 8.3  |
| Pyridine               | 24.7<br>(20.6)                            | 23.8<br>(19.9) | 14.1<br>(11.8) | 26.5<br>(22.2) | 10.6*<br>( 8.9)                        | 84   |
| γ-Picoline             | 11.3<br>( 9.9)                            | trace<br>( - ) | 22.8<br>(20.0) | 34.6<br>(30.3) | 31.2*<br>(27.2)                        | 87.5 |
| α-Picoline             | 12.8<br>( 2.5)                            | trace          | 13.8<br>( 2.7) | 73.8<br>(14.1) | 22.9*<br>( 4.4)                        | 19.1 |
| None                   | --  | --             | 79<br>( 4.2)   | 4.1<br>( 0.2)  | 16.9                                   | 5.3  |

\*Trimers contained are more than 60% of the value.

\*\*Conversion.

should be noted that DMOT was derived from a head-to-tail dimerization, although DMOD was not necessary from a head-to-tail. A profile of yields of oligomers vs. reaction time is shown in Figure, where the formation of DMOD was saturated at the early stage of reaction, whereas the formation of DMOT was increased with the reaction time, denying the consecutive hydrogenation of DMOT into DMOD. The selectivity for DMOT may be improved by the increased ratio of isoprene/catalyst.

Largest activities for dimerization were observed where the ratio of amine/ $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  was between 25 and 50. The formation of DMOT was most affected by this ratio, indicating that the amine may play an important role in the hydrogen shift step of the linear dimerization as concluded by Heimbach.<sup>2d</sup> Excess amine may occupy the coordination sites of the catalyst to decrease the activity.

Table shows the effect of some amines on the activity and product distribution of the catalyst at 80°. Catalytic activity was lowered very much by the addition of

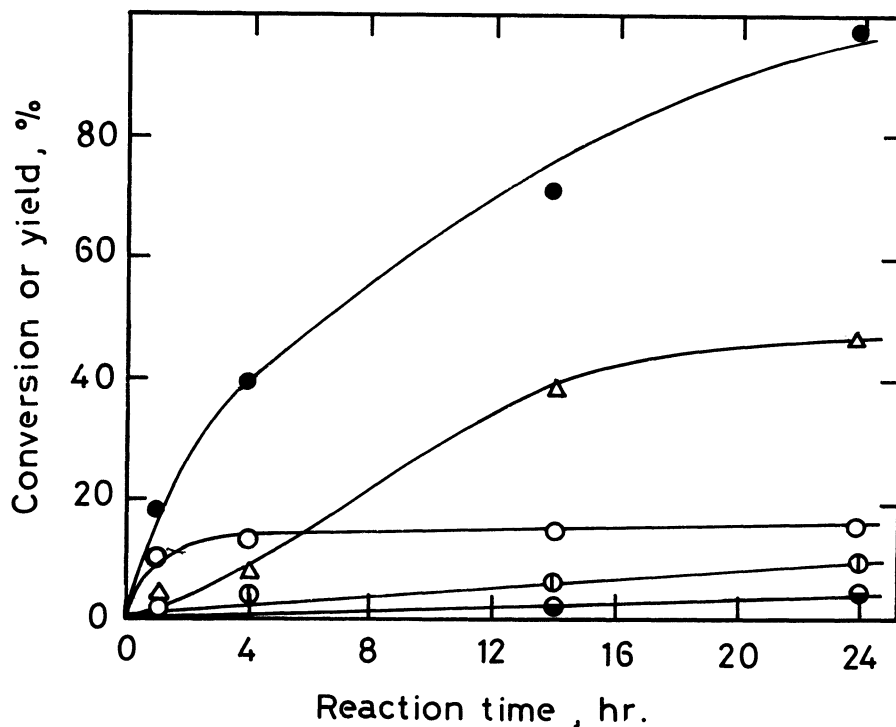


Figure. Yields of oligomers vs. reaction time.

- : Conversion of isoprene, %
- △ : Yield of DMOT, %
- : Yield of DMOD, %
- ⊙ : Yield of DMCOD, %
- : Yield of DP, %

Reaction temp.; 80°C, isoprene/ $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  mole ratio; 20,  
 $\text{NaBH}_4/\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  mole ratio; 3,  
 $\text{N-PrNH}_2/\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  mole ratio; 3

tert-butylamine compared with n-propylamine. Pyridine, which has no active hydrogen, provided such a high activity as n-propylamine did, however, the selectivity was quite different from the case of the latter amine. The formation of cyclooligomers was promoted whereas the formation of DMOT was limited. Such a tendency was enhanced by  $\gamma$ -picoline without any decrease in activity, although  $\alpha$ -picoline lowered the activity very much. These results imply that steric as well as electronic properties of the amine may provide significant effects on catalytic activities of the nickel catalyst for the dimerization reaction. A quantitative explanation is now tried to be offered.

Effects of amines on the dimerization of butadiene are now under investigation.

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