JOURNAL OF CATALYSIS 39, 134–140 (1975)

Reaction Path Study of Styrene-α-Olefin Codimerization Catalyzed by σ-Arylnickel(II) Halide–Boron Trifluoride Etherate

KIYOSHI KAWAKAMI, NOBORU KAWATA, KEN-ICHI MARUYA,
TSUTOMU MIZOROKI AND ATSUMU OZAKI

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Ohokayama, Meguroku, Tokyo, Japan*

Received January 21, 1975

The codimerization of styrene with α-olefins catalyzed by bis(triphenylphosphine)σ-aryl(bromo)nickel(II) and boron trifluoride etherate was investigated for its reaction path by identification of products. The main products are 4-phenyl-1-pentene from propylene and 5-phenyl-2-hexene from 1-butene, which are characterized by the β-elimination from the side chain, not from the main chain of the alkyl-nickel intermediate. A reaction scheme via nickel-hydride intermediate is given on the basis of deuterium distribution in the codimerization products of styrene with deuteroethylene.

INTRODUCTION

It is known for the codimerization of styrene with olefin (*1*) that [$PdCl_2 \cdot$ styrene]$_2$ (*2*) catalyst gives mainly 1-phenyl-1-butene or 1-phenyl-1-pentene for ethylene or propylene, respectively, while only a trace amount of 1-phenyl-1-hexene for 1-butene. $RhCl_3 \cdot 3H_2O$ (*2*) or (π-$C_3H_5PdCl_2$)–BF_3–$P(C_6H_5)_3$ (*3*) is also known to be active for the codimerization of styrene with olefins. However the considerable extent of isomerization accompanying those codimerizations obstructs the elucidation of reaction path.

In the preceding paper (*4*), it was shown that the bis(triphenylphosphine)σ-aryl(halo)nickel(II)–boron trifluoride etherate is highly active for the codimerization of styrene with ethylene to give 3-phenyl-1-butene selectively without further isomerization. Taking advantage of this catalyst, the work has been extended to propylene and 1-butene to study the products, and the reaction path was examined using deuterium tracer for the codimerization with ethylene.

EXPERIMENTAL METHODS

Materials

Bis(triphenylphosphine)-*o*-tolyl(bromo)nickel(II) (found: C, 68.2; H, 4.7; Br, 11.6%; calcd: C, 68.1; H, 4.8; Br, 10.8%) was prepared according to the method given in the literature (*5*). Small amounts of air and water contained in commercial propylene and 1-butene were excluded by distillation. Deuteroethylene (C_2D_4, 93.5; C_2D_3H, 6.5%) was obtained by deuteration of deuteroacetylene. Methylene dichloride was dried with P_2O_5 before distillation under nitrogen. Styrene and boron trifluoride etherate were also distilled under dry nitrogen.

Procedure

All experiments were carried out under nitrogen atmosphere. To a well-dried methylene dichloride solution of bis(triphenylphosphine)-*o*-tolyl(bromo)nickel(II) in a flask (50 ml vol) were added boron trifluoride etherate, followed by adding a given amount of styrene. The nitrogen gas in the flask was evacuated at the temperature of liquid nitrogen, and the flask was kept in an ice water bath before introducing olefin gas at 0°C with vigorous stirring. The pressure inside the flask was kept constant (±1 cm Hg) during the course of reaction by adjusting the supply of olefin with a gas burette, while 1-butene was absorbed so fast that the pressure fluctuated within ±3 cm Hg. After a specified period of time, the reaction was terminated by adding an aqueous sodium hydroxide solution (10 *N*, 3 ml). Volatile substances such as C_2D_4, propylene, butenes and methylene dichloride were transferred to another flask using a liquid nitrogen bath before nonvolatile materials were well extracted with *n*-hexane. Codimers and styrene were quantitatively determined by a gas chromatography equipped with a FID detector.

Identification and Analysis

A VZ-7 column (4 mmϕ, 8 m) was used at room temperature for C_2D_4, propylene and butenes. A PEG-6000 column (4 mmϕ, 6 m) was used at 120–140°C with nitrogen as carrier gas for the quantitative determination of codimers. A SE-30 column (4 mmϕ, 3 m) was used at 150–250°C with hydrogen as carrier gas for the detection of styrene oligomers. Most products were isolated by preparative gas chromatography to be identified by NMR spectroscopy. Some of them were also checked by ir and MS when necessary.

2-Methyl-3-phenyl-1-butene. NMR: CH_3—, 8.63 (d) 3H; CH_3—C=, 8.40 (s) 3H; —CH—, 6.67 (qua)1H; CH_2=, 5.18 (d) 2H; C_6H_5—, 2.91 5H; ir: CH_2=C—, 892 cm^{-1}.

4-Phenyl-1-pentene. NMR: CH_3—, 8.76 (d) 3H; —CH_2—, 7.68 (m) 2H; —CH—, 7.25 (sex)1H; $\mathrm{H{-}\underset{|}{C}{=}\overset{|}{C}{-}C}$, 5.20 (s) 1H; $\mathrm{H{-}\underset{|}{C}{=}\underset{|}{C}{-}C}$, 5.08 (split d)1H; C=CH—C, 4.48 (m) 1H; C_6H_5—, 3.00 5H; ir: CH_2=CH—, 995, 912 cm^{-1}.

4-Phenyl-2-pentene. NMR: CH_3—, 8.69 (d) 3H; CH_3—C=, 8.33 (d) 3H: —CH—, 6.65 (qui) 1H; —CH=CH—, 4.65 (m) 2H; C_6H_5—, 2.92 5H; ir: —CH=CH—, 965 cm^{-1}; the parent peak of MS, 146.

2-Ethyl-3-phenyl-1-butene. NMR: CH_3—, 9.05 (t) 3H; CH_3—, 8.67 (d) 3H; —CH_2—, 8.15 (qua)2H; —CH—, 6.68 (qua)1H; CH_2=, 5.18 (d) 2H; C_6H_5—, 2.93 5H; ir: CH_2=C—, 893 cm^{-1}.

trans-5-Phenyl-2-hexene. NMR: CH_3—, 8.82 (d) 3H; CH_3—C=, 8.45 (d) 3H; —CH_2—, 7.84 (t) 2H; —CH—, 7.37 (sex) 1H; —CH=CH—, 4.75 (m) 2H; C_6H_5—, 2.94 5H; ir: $\mathrm{H{-}\underset{|}{C}{=}\overset{|}{C}{-}H}$, 967 cm^{-1}; the parent peak of MS, 160.

cis-5-Phenyl-2-hexene. NMR: CH_2—, 8.77 (d) 3H; CH_3—C=, 8.49 (d) 3H; —CH_2—, 7.80 (t) 2H; —CH—, 7.32 (sex) 1H; —CH=CH—, 4.72 (m) 2H; C_6H_5—, 2.92 5H; ir: $\mathrm{H{-}\underset{|}{C}{=}\underset{|}{C}{-}H}$, 1405 cm^{-1}.

RESULTS

1. Codimerization of styrene with propylene. A methylene dichloride solution (15 ml) of bis(triphenylphosphine)-*o*-tolyl(bromo)nickel(II) (0.5 mmol), boron trifluoride etherate (0.5–1.5 mmol) and styrene (20.0 mmol) was treated at 0°C with propylene under about 37 cm Hg. The representative results are given in Table 1. Codimerization products are 2-methyl-3-phenyl-1-butene, 4-phenyl-1-pentene and 4-phenyl-2-pentene. In the absence of a catalytic amount of water, no codimerization product was obtained. Thus it was reconfirmed that water en-

TABLE 1

CODIMERIZATION OF STYRENE WITH PROPYLENE[a]

H_2O (mmol)	BF_3OEt_2 (mmol)	Reaction time (min)	Residual styrene (mmol)	Products (mmol) 2-m-3-p-1-b	4-p-1-p	4-p-2-p
0.0	0.5	80	Much	0.00	0.00	0.00
0.1	1.5	80	0.97	0.16	0.36	0.11
0.1	1.5	210	Much	0.18	0.53	0.13
0.1	1.5	25	0	0.81	Tr	2.19

[a] Condition: (o-tolyl)Ni($P\phi_3$)$_2$Br, 0.5 mmol; styrene employed, 20.0 mmol; CH_2Cl_2, 10 ml; temp, 0°C; $P_{C_3'}$, 37 cm Hg. 2-m-3-p-1-b = 2-methyl-3-phenyl-1-butene; 4-p-1-p = 4-phenyl-1-pentene; 4-p-2-p = 4-phenyl-2-pentene.

hances significantly the rate of codimerization as noted in the preceding papers (*6*). Figure 1 shows the variation in the amounts of products during the codimerization of styrene with propylene. 4-Phenyl-1-pentene and 2-methyl-3-phenyl-1-butene are the initial codimers. It is shown that when styrene is completely consumed, 4-phenyl-1-pentene is rapidly isomerized to 4-phenyl-2-pentene and a rapid homodimerization of propylene takes place. No further isomerization product of 4-phenyl-2-pentene and 2-methyl-3-phenyl-1-butene was detected. The rate of propylene homodimerization was faster than that of the codimerization with styrene. The selectivity to codimers on styrene basis was poor, because of homo-oligomerization of styrene in the presence of boron trifluoride etherate. All attempts to suppress the oligomerization were unsuccessful. On the other hand, the amount of codimers was almost quantitative as to the absorbed propylene.

2. *Codimerization of styrene with 1-butene.* The representative results are shown in Fig. 2. The codimerization products are 2-ethyl-3-phenyl-1-butene, *cis-* and *trans-*5-phenyl-2-hexene with the last one being main product. A significant amount of styrene was found unreacted at 15 min but no styrene was found at 65 min period. The product distribution during the course of codimerization shows that the amounts of these codimers proportionally increases with time, and that no isomerization of products takes place even after the disappearance of styrene in 65 min period, while 1-butene was found to isomerize rapidly to the equilibrium distribution (1-B, 3.3%; t-2-B, 70.1%, c-2-B, 26.6%) after the consumption of styrene.

3. *Codimerization of styrene with C_2D_4.* The codimerization of styrene with C_2D_4

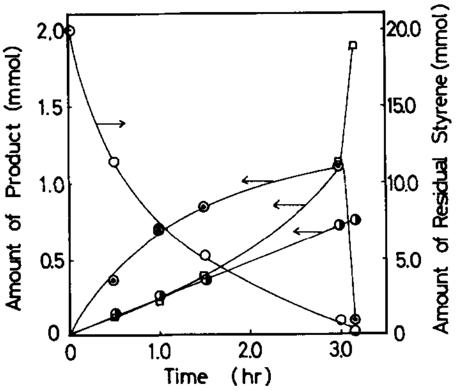

FIG. 1. Products distribution during the codimerization of styrene with propylene. (o-tolyl)Ni($P\phi_3$)$_2$Br, 0.5 mmol; BF_3OEt_2, 1.5 mmol; H_2O, 0.1 mmol; styrene, 20.0 mmol; CH_2Cl_2, 10 ml; temp, 0°C; $P_{C_3'}$ 50 cm Hg. (◐) 2-Methyl-3-phenyl-1-butene; (◉) 4-phenyl-1-pentene; (□) 4-phenyl-2-pentene; (○) residual styrene.

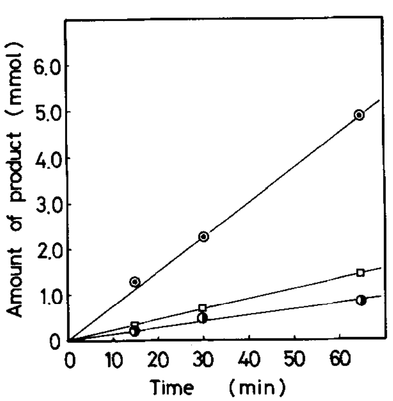

FIG. 2. Products distribution during the codimerization of styrene with 1-butene. (o-tolyl)Ni($P\phi_3$)$_2$Br, 0.5 mmol; BF_3OEt_2, 0.5 mmol; styrene, 20.0 mmol; CH_2Cl_2, 10 ml; temp, 0°C; $P_{C_4'}$, 37 cm Hg. (◐) 2-Ethyl-3-phenyl-1-butene; (◉) *trans*-5-phenyl-2-hexene; (□) *cis*-5-phenyl-2-hexene.

TABLE 2
ISOTOPIC EXCHANGE DURING THE CODIMERIZATION[a]

Run	Ethylene	Deuterium distribution (%)					
		d_4	d_3	d_2	d_1	d_0	f_D
1	Before reaction	41.0	10.9	1.6	0.8	45.7	50.1
	After reaction	30.3	13.8	10.3	6.8	38.8	47.5
2	Before reaction	93.5	6.5	—	—	—	98.4
	After reaction	89.8	10.2	—	—	—	97.4

[a] f_D is the atomic fraction of deuterium in the total ethylene. Condition: (*o*-tolyl)Ni(Pϕ_3)$_2$Br, 0.5 mmol; BF_3OEt_2, 0.5 mmol; styrene, 20.0 mmol; CH_2Cl_2, 15 ml; temp, 0°C; $P_{C_2'}$, 37 cm Hg; time, 25 min.

was carried out to study the reaction path. The codimerization was terminated before stryene was completely consumed to avoid the isomerization. Run 1 of Table 2 indicates that the isotopic mixing of C_2H_4-C_2D_4 is inhibited during the codimerization presumably due to the presence of styrene, although the mixing is known to be rapid with this catalyst (*7*). Run 2 indicates that the atomic fraction of deuterium in the total ethylene remains unchanged during the codimerization with C_2D_4. This was also checked by no detection of ^{2}D-[^{1}H] NMR of the recovered styrene. From these results it is concluded that the hydrogen exchange between styrene and ethylene is negligible. Codimerization products were 3-phenyl-1-butene (6.96 mmol), 2-phenyl-2-butene (0.19 mmol) and 3-phenyl-3-methyl-1-pentene (0.81 mmol). The last one is the codimer of 2-phenyl-2-butene with ethylene. They were identified by use of ^{1}H and ^{2}D-[^{1}H] NMR spectroscopy[1] (Fig. 3). Their structural formulas are $CD_2{=}CD{-}CH(C_6H_5){-}CH_2D$, $CD_2H{-}CD{=}C(C_6H_5){-}CH_2D$ and $CD_2{=}CD{-}(CH_2D)C(C_6H_5){-}CD_2{-}CHD_2$, respectively. It is remarkable that the methyl group of 3-phenyl-1-butene contains two hydrogen atoms and one deuterium atom.

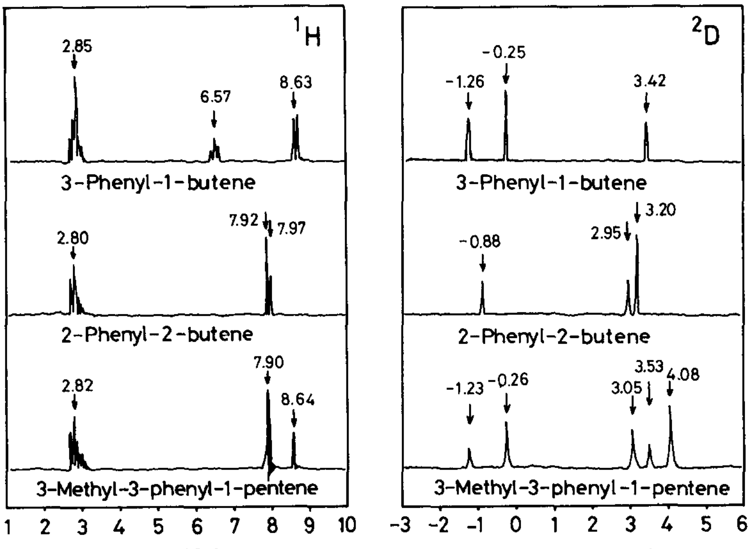

FIG. 3. ^{1}H and ^{2}D-[^{1}H] NMR spectra of the codimers of styrene with deuteroethylene.

---

[1] The nuclear over Hauser effect was negligibly small, since the peak area of ^{2}D NMR spectra without H-decoupling was almost equal to that of ^{2}D-[^{1}H] NMR spectra.

DISCUSSION

1. Codimerization of styrene with propylene or 1-butene. In the previous paper (*4*), the reaction path of codimerization by the present catalyst system was explained in terms of a nickel-hydride, which was proposed to be supplied from dissociative addition of olefin to σ-arylnickel(II) compound (*7*). The codimerization products of styrene with propylene or 1-butene (Table 1 and Fig. 2) also can be explained by the nickel-hydride intermediate (Fig. 4). Namely, styrene first interacts with the nickel-hydride to give an α-phenylethylnickel intermediate, followed by insertion of propylene or 1-butene and elimination of the β-hydrogen to give the corresponding codimers. In case of the codimerization with propylene, it is noteworthy that 4-phenyl-1-pentene is the initial main product as shown in Fig. 1. The most plausible explanation is that the β-elimination takes place preferably from the methyl group rather than from the methylene group of the intermediate, $Ni\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_3$. This specific phenomenon is also observed in the codimerization with 1-butene as shown in Fig. 2. 5-Phenyl-2-hexene, which is the main product in this case, is given by the β-elimination from the side chain of the

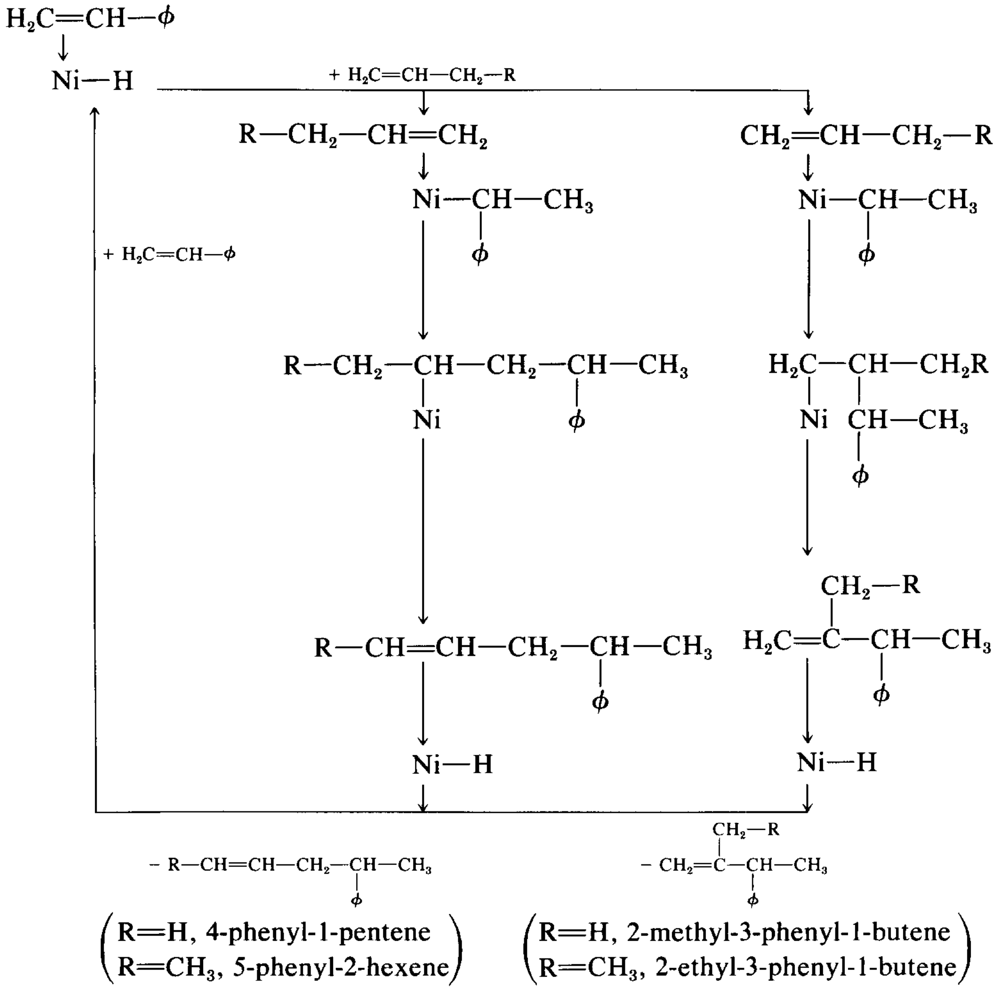

FIG. 4. Codimerization of $CH_2{=}CH{-}CH_2{-}R$ with styrene.

intermediate, Ni-$CH(CH_2CH_3)$-CH_2-$CH(C_6H_5)$-CH_3 (Fig. 4). The methylene group on the main chain which is adjacent to the phenyl group may be sterically unfavorable for the elimination, although we admit the lack of further informations.

Another point of notice is that 4-phenyl-1-pentene is rapidly isomerized to 4-phenyl-2-pentene when styrene is exhausted (Fig. 1), while 5-phenyl-2-hexene seems not to be isomerized appreciably even after all of styrene is consumed. This suggests that the present catalyst system is much more reactive and attractive for terminal olefin, in particular for styrene, than for inner olefin. In fact, practically no isomerization of 1-butene takes place during the codimerization with styrene, while after styrene is consumed, 1-butene isomerizes rapidly to 2-butene without accompanying appreciable isomerization of its codimers. Similarly, in the codimerization with ethylene reported previously (*4*), 3-phenyl-1-butene, the main codimer in this case, is rapidly isomerized to 2-phenyl-2-butene after most of styrene is consumed. These results are in conformity with coordination control of olefin reactions. Accordingly the coordination sequence of olefin in this catalyst system may be assessed as styrene $\gg$ the other terminal olefin (C_2', C_3', $1-C_4'$, 3-phenyl-1-butene, 4-phenyl-1-pentene) $>$ inner olefin ($2-C_4'$, 4-phenyl-2-pentene, 5-phenyl-2-hexene). Although 2-methyl-3-phenyl-1-butene and 2-ethyl-3-phenyl-1-butene are terminal olefins, they hardly undergo isomerization as shown in Figs. 1 and 2, presumably because of its high bulkiness.

2. Codimerization of styrene with C_2D_4. The deuterium distribution in 3-phenyl-1-butene can also be fully explained by a scheme via the nickel-hydride intermediate (Fig. 5), although it remains still unknown whether the initial hydrogen of the nickel-hydride comes from ethylene or styrene. Anyway, in the steady state, styrene is expected to react with Ni–D to give α-phenylethylnickel, followed by insertion of C_2D_4 and elimination of β-hydrogen to give 3-phenyl-1-butene, which has one deuterium at its methyl position and three at its vinyl position. This prediction is borne out in the products as shown in Fig. 3. Table 2 shows that the isotopic exchange between olefins during the codimerization is almost negligible, because both deuterium distribution and atomic fraction of deuterium in the residual ethylene are almost the same as those of the starting ethylene. This seems to be caused by the same reason as for the inhibition of olefin isomerization in the presence of styrene.

No detection of deuterium at the

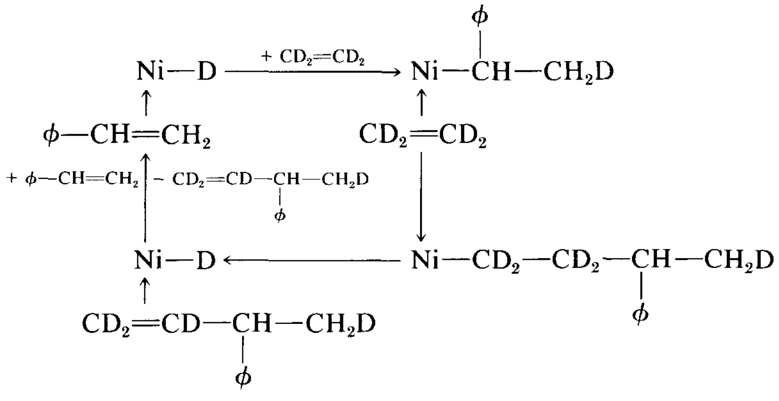

FIG. 5. Codimerization of C_2D_4 with styrene.

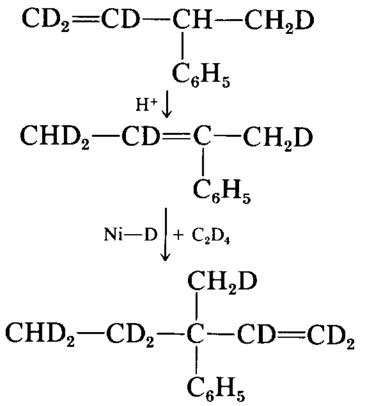

FIG. 6. Isomerization followed by codimerization with C_2D_4.

methyne position of 3-phenyl-1-butene suggests that the insertion of styrene to the Ni–D bond is almost irreversible, because if the insertion were reversible some deuterium should be found at the methyne position.

The deuterium distributions in minor products, 2-phenyl-2-butene and 3-methyl-3-phenyl-1-pentene, are also worthy of mention. If $CD_2{=}CD{-}CH(C_6H_5){-}CH_2D$ is isomerized to 2-phenyl-2-butene by Ni–D, $CD_3{-}CD{=}C(C_6H_5){-}CH_2D$ would be formed. ^1H and ^2D-[^1H] NMR spectra shown in Fig. 3, however, indicate that 2-phenyl-2-butene observed is $CD_2H{-}CD{=}C(C_6H_5){-}CH_2D$. This suggests that the nickel-hydride is not responsible for the isomerization to 2-phenyl-2-butene, because nickel-hydride should be in the form of Ni–D under the steady state. An alternative species would be a Brönsted acid originated from $BF_3 \cdot OEt_2$ and a trace amount of water:

$$BF_3 \cdot OEt_2 + H_2O \rightarrow H^+ + [BF_3 \cdot OH]^- + Et_2O.$$

On the other hand, 3-methyl-3-phenyl-1-pentene seems to be formed also via the nickel-hydride from 2-phenyl-2-butene and ethylene, since 3-methyl-3-phenyl-1-pentene obtained is $CHD_2{-}CD_2{-}(CH_2D)C(C_6H_5){-}CD{=}CD_2$ as evidenced in Fig. 3. The overall process of the isomerization of initial product, 3-phenyl-1-butene, followed by further codimerization with C_2D_4 is illustrated by Fig. 6.

In this way the results obtained are as a whole in conformity with the nickel-hydride intermediate.

REFERENCES

1. Alderson, T., Jenner, E. L., and Lindsey, R. V., Jr., *J. Amer. Chem. Soc.* **87**, 5638 (1965); Barlow, M. G., Beyant, M. J., Hasezeldine, R. N., and Mackie, A. G., *J. Organometal. Chem.* **21**, 215 (1970).
2. Kawamoto, K., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Jap.* **43**, 2512 (1970); Kawamoto, K., Tatani, A., and Teranishi, S., *Bull. Chem. Soc. Jap.* **44**, 1239 (1971).
3. Ito, T., Takahashi, K., and Takami, Y., *Nippon Kagaku Kaishi* **1974**, 1097.
4. Kawata, N., Maruya, K., Mizoroki, T., and Ozaki, A., *Bull. Chem. Soc. Jap.* **47**, 413 (1974).
5. Hidai, M., Kashiwagi, T., Ikeuchi, T., and Uchida, Y., *J. Organometal. Chem.* **30**, 279 (1971).
6. Nozima, H., Kawata, N., Nakamura, Y., Maruya, K., Mizoroki, T., and Ozaki, A., *Chem. Lett.* **1973**, 1163; Kawata, N., Maruya, K., Mizoroki, T., and Ozaki, A., *Bull. Chem. Soc. Jap.* **47**, 2003 (1974).
7. Maruya, K., Mizoroki, T., and Ozaki, A., *Bull. Chem. Soc.* **45**, 2255 (1972).