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Codimerization of Ethylene and Styrene Catalyzed by Bis(triphenylphosphine)-σ-Arylnickel(II) Halide–Trifluoroboron Etherate

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The codimerization of styrene with ethylene was studied using the catalyst system composed of bis(triphenylphosphine)σ- aryl(bromo)nickel(II) and trifluoroboron etherate in methylene dichloride. The codimerization takes place readily at 0 °C under atmospheric pressure to give 3-phenyl-1-butene selectively. The reaction scheme was discussed on the basis of the product distribution during the course of reaction and its kinetics.

Many catalyst systems have been reported for dimerization of olefins and dienes since transition metal complexes, especially the VIII subgroup, were found to have a significant effect on selective dimerization. Attention has been paid to the active species of the catalyst, which is accepted to be a hydro metal complex. Its activity and selectivity, however, depend considerably on its metal and ligands (including solvent) as well as the olefin specified. During the course of our study on the activity and selectivity of the catalyst composed of nickel(II) compound and a Lewis acid for the ethylene dimerization, it was found that the bis(triphenylphosphine)σ-arylnickel(II) halide–trifluoroboron etherate catalyst system significantly enhanced the rate of ethylene dimerization to give butene selectively.[1)] This catalyst system is less active for the dimerization of propylene or its codimerization with ethylene, but highly active and selective for the codimerization of styrene with ethylene.[2)]

Rhodium(II) chloride[3)] and palladium(II) chloride[4,5)] catalyze the codimerization of ethylene and styrene even in the absence of Lewis acid. The former gives 2-phenyl-2-butene under a high pressure of ethylene(100 atm) and the latter 1-phenyl-butenes. Codimerization of styrene with ethylene was studied with two nickel complexes as the catalyst, one consisting of nickel diacetylacetonate, trialkylaluminium and trialkylphosphite, which gave cyclic oligomers of ethylene and styrene and only a small amount of their codimer,[6)] and the other consisting of tetrakis(trichlorophosphine)-nickel, aluminium bromide and butyl lithium, which gave a mixture of 3-phenyl-1-butene, 2-phenyl-2-butene and 2-phenyl-1-butene.[7)] The present catalyst system, however, gives 3-phenyl-1-butene selectively without being accompanied by 1-phenyl-butenes. This paper deals with the mechanism of the selective formation of 3-phenyl-1-butene.

Experimental

Materials. Dibromobis(triphenylphosphine)nickel(II)[8)] and bis(triphenylphosphine)σ-aryl(bromo)nickel(II)[9)] were prepared according to the methods given in literature. The results of elemental analysis of the carbon and hydrogen of these nickel complexes were as follows; bis(triphenylphosphine)dibromonickel(II) (Calcd: C, 58.2; H, 4.1%. Found: C, 58.2; H, 4.0%), bis(triphenylphosphine)-1-naphthyl-(bromo)nickel(II) (Calcd. C, 69.9; H, 4.7. Found: C, 69.9; H, 4.5%), bis(triphenylphosphine)-*o*-tolyl(bromo)-nickel(II) (Calcd: C, 68.5; H, 4.9%. Found: C, 67.1; H, 4.6%) and bis(triphenylphosphine)mesityl(bromo)nickel(II) (Calcd: C, 69.1; H, 5.3%. Found: C, 69.1; H, 4.7%). Commercial styrene, α- and ω-methyl styrene, ω-bromo styrene and *o*-, *m*-, and *p*-chlorostyrenes were dried under nitrogen with a molecular sieve before use. *o*-, *m*-, and *p*-Methyl styrene were prepared according to the literature[10)] and purified by vacuum distillation. Small amounts of air and water in commercial ethylene were separated by means of a liquid nitrogen trap. Benzene and diethyl ether were well dried with metallic sodium before being purified by distillation, while methylene dichloride was dried with the molecular sieve. Trifluoroboron etherate was also purified by distillating its diethyl ether solution under nitrogen.

Procedure. All experiments were operated under nitrogen atmosphere. To a well dried methylene dichloride solution of bis(triphenylphosphine)σ-aryl(bromo)nickel(II) in a two necked flask(50 ml in vol.) were added trifluoroboron 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 ethylene gas at 0 °C with vigorous stirring. The gaseous pressure inside the flask was kept constant(± 1 cmHg) during the course of reaction by adjusting the supply of ethylene with a fine needle valve. After a specified period of time, the reaction was terminated by adding an aqueous sodium hydroxide solution(1 M, 5 ml). Volatile substances such as ethylene, butenes and the solvent had been transferred to another flask by means of a liquid nitrogen trap before non-volatile materials were well extracted with *n*-hexane. They were quantitatively determined by a gaschromatography equipped with an FID detector.

Identification and Analysis. A VZ-7 column (4 mmϕ, 8 m) was used at room temperature with nitrogen as a carrier gas for the quantitative dtermination of butenes. A DC-550 column (4 mmϕ, 4 m) was used at 120 °C for the styrene-ethylene codimers. Most products were isolated by preparative gas-chromatography to be identified by NMR spectroscopy. Some of them were also checked by IR and mass spectroscopy when necessary.

3-phenyl-1-butene (CH_3– 8.70τ(d) 3H, –CH– 6.60τ(qui) 1H, CH_2=CH– 4.96τ and 4.00τ(m) 3H, and C_6H_5– 2.74τ(m) 5H): *trans*-2-phenyl-2-butene (CH_3– 8.54τ(s) 3H, CH_3–CH= 8.12τ(d) 3H, –CH= 4.48τ(m) 1H, and C_6H_5– 2.79(m) 5H): *cis*-2-phenyl-2-butene (CH_3– 8.16τ(s) 3H, CH_3–CH– 8.40τ(d) 3H, –CH= 4.23τ(m) 1H, and C_6H_5– 2.77τ(m) 5H). These phenyl butenes were all hydrogenated with Raney nickel catalyst to give 2-phenyl butane (CH_3–CH_2– 9.22τ(t) 3H, –CH_2– 8.45τ(qui) 2H, –CH– 7.50τ(m) 1H, CH_3–CH– 8.82 (d) 3H, and C_6H_5– 2.78τ(m) 5H). 3-methyl-3-phenyl-1-pentene (CH_3–CH_2– 9.30τ(t) 3H, –CH_2– 8.32τ(qua) 2H, CH_3–C– 8.75τ(s) 3H, CH_2–CH– 5.0 and 3.95τ(m) 3H, and C_6H_5–, 2.70 (m) 5H), the parent peak of its mass spectrum being 160: 3-(*p*-chlorophenyl)-1-butene (CH_3– 8.73τ(d) 3H, –CH– 6.63 (qiu) 1H, CH_2=CH– 5.00 and 4.14(m) 3H,

TABLE 1. EFFECT OF σ-ARYL LIGAND

No.	Cat.	Styrene consumed (mmol)	3-Phenyl-1-butene formed (mmol)	Select. (%)	Butenes
1	(Mesityl)NiBr$(P\phi_3)_2$	13.4	11.6	91	trace
2	(1-Naphthyl)Nibr$(P\phi_3)_2$	12.9	10.2	80	trace
3	(*o*-Tolyl)NiBr$(P\phi_3)_2$	12.7	7.2	56	trace
4	$NiBr_2(P\phi_3)_2$	3.6	0	0	no detect
5	None	1.6	0	0	no detect

(σ-aryl)NiBr$(P\phi_3)_2$, 1 mmol; $BF_3 \cdot OEt_2$, 1 mmol; styrene employed, 174 mmol (2 ml); CH_2Cl_2, 30 ml; $P_{C_2H_4}$ 45—50 cmHg; temp. 0°C; time, 15 min.

and Cl-C_6H_4- 2.92τ(m) 4H): 2,3-diphenyl-1-butene (CH_3- 8.83τ(d) 3H, -CH- 6.50τ(qua) 1H, CH_2=C- 3.65τ(s) 2H, and C_6H_5- 2.77τ(m) 10H). The other products were estimated by the relative retention time on their gas chromatograms.

Results

Effect of σ-aryl Ligand: A methylene dichloride solution (30 ml) of bis(triphenylphosphine)σ-aryl(bromo)-nickel(II) (1.0 mmol), trifluoroboron etherate (1.0 mmol) and styrene (17.4 mmol) was treated at 0 °C with ethylene under about 70 cmHg for 15 min. The results are given in Table 1. Bis(triphenylphosphine)-σ-aryl(bromo)nickel(II) (No. 1,2,3) is highly active for codimerization to give 3-phenyl-1-butene selectively. In this case, small amounts of butenes were formed, while only trace amounts of isomers of 3-phenyl-1-butene were detected. Bis(triphenylphosphine)dibromonickel(II) (No. 4) has no activity for the codimerization, where the consumption of some amount of styrene seems to be caused by its polymerization with trifluoroboron etherate. The selectivity to 3-phenyl-1-butene decreases in the order, mesityl> naphthyl>*o*-tolyl.

Figure 1 shows the variation in the amounts of products during the codimerization of styrene with ethylene under the specified conditions. The results were obtained from repeated runs of the codimerization under the same conditions. It is shown that the reaction rate is independent of the concentration of styrene and that practically no dimerization of ethylene takes place until most of the styrene is consumed. It is to be noted that the ethylene dimerization as well as isomerization of 1-butene formed is accelerated when most of the styrene is consumed, and also that 3-methyl-3-phenyl-1-pentene given by the reaction of ethylene with 2-phenyl-2-butene formed from the isomerization of 3-phenyl-1-butene, is gradually formed during the course of codimerization. The effect of ethylene pressure was examined on the amount of 3-phenyl-1-butene formed. The amount is plotted against the partial pressure of ethylene in Fig. 2, where the vapour pressure of methylene dichloride is 15 cmHg at 0 °C. The amount of 3-phenyl-1-butene increases linearly with the partial pressure of ethylene, indicating that the reaction rate is first order in ethylene

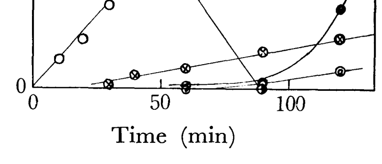


Fig. 1. Product distribution during the course of codimerization.
(1-naphthyl)NiBr$(P\phi_3)_2$, 0.5 mmol; $BF_3 \cdot OEt_2$, 0.5 mmol; styrene 19.1 mmol; CH_2Cl_2, 30 ml; $P_{C_2H_5}$, 50 cmHg; temp. 0°C. ◑: styrene, ○: 3-phenyl-1-butene, ⊗: 3-methyl-3-phenyl-1-pentene, ◎: 2-phenyl-2-butene, ●: butenes.

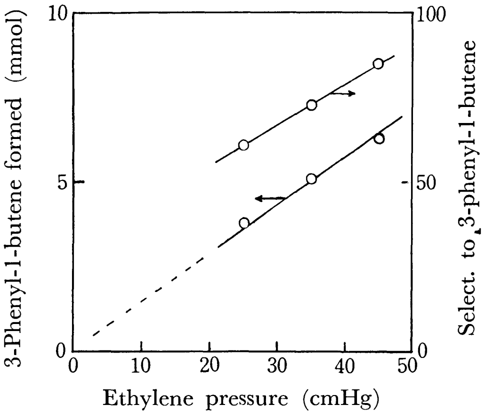


Fig. 2. Effect of ethylene pressure on the rate of codimerization; (1-naphthyl)NiBr$(P\phi_3)_2$, 0.5 mmol; $BF_3 \cdot OEt_2$, 0.5 mmol; styrene, 19.1 mmol; CH_2Cl_2, 30 ml; temp. 0°C; time. 30 min.

Effect of Concentration of Catalyst Components: The effect of trifluoroboron etherate was examined on the rate of codimerization under a constant pressure(partial pressure of ethylene, 35 mmHg), where the amount of bis(triphenylphosphine)-1-naphthyl(bromo)nickel(II) was kept constant (0.5 mmol). The rate can be shown by the amount of 3-phenyl-1-butene formed for a specific period of reaction time, since the rate is independent of the amount of styrene(Fig. 1). The amount of 3-phenyl-1-butene (mmol) formed for 15 min. is plotted against the mole ratio, trifluoroboron etherate to the nickel complex(Fig. 3). The result at the mole ratio 2.5 was estimated from the amount

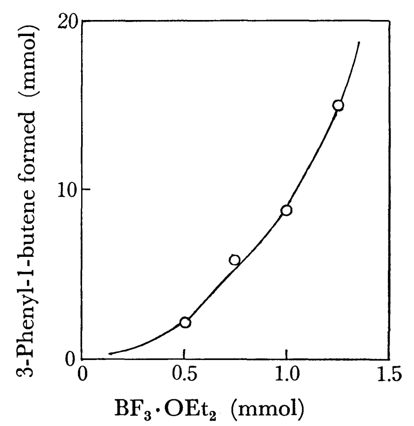


Fig. 3. Effect of the amount of $BF_3\cdot OEt_2$. (1-naphthyl)$NiBr(P\phi_3)_2$, 0.5 mmol; styrene, 19.1 mmol; CH_2Cl_2, 30 ml; $P_{C_2H_4}$, 35 cmHg; temp. 0°C; time 15 min.

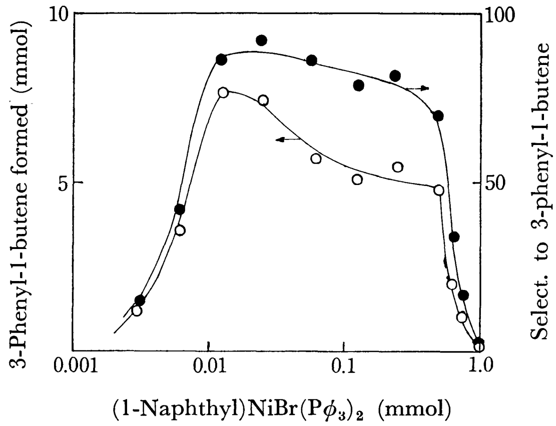


Fig. 4. Effect of the amount of (1-naphthyl)$NiBr(P\phi_3)_2$ $BF_3\cdot OEt$, 0.5 mmol; Styrene, 19.1 mmol; $P_{C_2H_4}$, 35 cmHg; CH_2Cl_2, 30 ml; temp. 0°C; time 30 min.

of 3-phenyl-1-butene formed for 10 min., since the reaction rate was too rapid. The rate seems to increase approximately in the second order with respect to the mole ratio of trifluoroboron etherate to bis(triphenylphosphine)-1-naphthyl (bromo) nickel (II). In this case, the amount of butene formed was less than 1% based on that of ethylene consumed. The effect of the amount of bis(triphenylphosphine)-1-naphthyl(bromo)nickel(II) on the codimerization rate and the selectivity to 3-phenyl-1-butene is shown in Fig. 4, where the amount of trifluoroboron etherate is kept constant (0.5 mmol). The rate increases with the amount of nickel complex and reaches maximum at about 0.0125 mmol (the mole ratio of $BF_3\cdot OEt_2$/Ni-complex=40). Above the maximum, it gradually decreases in the range 0.02~0.5 mmol, within which the selectivity of 3-phenyl-1-butene is fairly high, while the rate rapidly decreases with increasing the amount of nickel complex more than 0.5 mmol (the mole ratio, less than 1).

Codimerization with Styrene Derivatives: The codimerization of ethylene with styrene catalyzed by the present catalyst system was extended to the codimerization with styrene derivatives such as *o*-, *m*-, and *p*-methylstyrene, *o*-, *m*-, and *p*-chlorostyrene, α- and ω-methylstyrene and ω-bromostyrene. The results are summarized in Table 2. *o*-, *m*-, and *p*-Methyl styrenes are also codimerized with ethylene to give the corresponding 2-(chloro- or methyl-phenyl)butenes under the conditions given in Table 2. There is no significant difference between methylstyrene and chlorostyrene in their conversion, while the selectivity of their codimers depends considerably on the position of chloro or methyl substituted on the phenyl. The selectivity increases on the order *ortho*<*meta*<*para* in methyl styrene as well as in chlorostyrene. On the other hand, α- and ω-methyl styrene are less reactive and a considerable amount of ethylene is consumed in the formation of butene (Table 2). No codimer was detected from the reaction of vinyl chloride with ethylene in the presence of this catalyst system. ω-Bromostyrene, however, gave a small amount of its codimers with ethylene consisting of two isomers, both in nearly the same amount.

Discussion

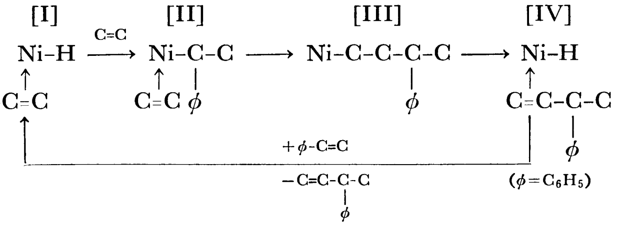
Course of Codimerization of Styrene with Ethylene. It was reported in a previous paper that the active species of the present catalyst system is a nickel hydride complex fromed from dissociative addition of ethylene to σ-aryl nickel(II) compound.[11] This has been clarified by the dimerization of deuteroethylene and its isotopic mixing with ethylene catalyzed by the present catalyst system.[12] From the product distribution of C_2H_4-C_3H_6 codimerization catalyzed by the present catalyst

Table 2. Codimerization of styrene derivatives with ethylene

Styrene derivatives (mmol)	Styrene consumed (mmol)	Codimer formed (mmol)	Select. to codimer (%)	Butenes (mmol)
p-Methylstyrene (15.2)	5.8	4.3	75	0.04
m-Methylstyrene (15.5)	6.0	4.3	72	0.05
o-Methylstyrene (15.1)	2.7	0.6	22	0.03
p-Chlorostyrene (15.1)	5.0	4.9	98	0.12
m-Chlorostyrene (15.0)	5.9	3.1	53	0.19
o-Chlorostyrene (15.0)	5.0	0.7	14	0.16
α-Methylstyrene (15.4)	1.4	0.9	67	7.3
ω-Methylstyrene (15.4)	2.4	1.7	70	2.1
ω-Bromostyrene (15.5)	1.5	0.4	26	0.31

(1-naphthyl)$NiBr(P\phi_3)_2$, 0.5 mmol; $BF_3\cdot OEt_2$, 0.5 mmol; CH_2Cl_2, 30 ml; $P_{C_2H_4}$, 35 cmHg; temp. 0° C; time, 30 min.

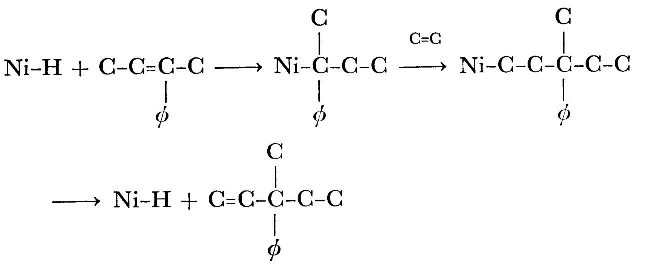
system, the nickel hydride is considered to be catalytically recycled in the course of the reaction and the reductive coupling processes of the intermediate nickel complexes can be excluded.[13] Thus selcetive formation of 3-phenyl-1-butene can also be understood in terms of the nickel hydride. Styrene reacts with the nickel hydride (Ni–H) to give σ-(1-phenylethyl)nickel intermediate(II), followed by the insertion of ethylene(III) and elimination of its β-hydrogen to give 3-phenyl-1-butene and regenerate Ni-H. It has not been clarified whether the nickel hydride is formed by dissociative addition of ethylene or styrene.



In this scheme, 3-phenyl-1-butene should be readily replaced by styrene, because the codimerization rate is independent of the concentration of styrene. This is consistent with the fact that only a trace amount of butenes and 2-phenyl-2-butene is formed before most of the styrene is consumed(Fig. 1). This might be one reason for 3-phenyl-1-butene being selectively formed. The sterically most crowded complex, [mesityl]Ni$(P\phi_3)_2$Br, gives the highest selectivity of codimerization (Table 1). This suggests that the aryl ligand remains on the nickel atom. Homodimerization of styrene and its codimerization with its derivatives are probably affected by a steric hindrance of the aryl ligand of the nickel complex. Styrene derivatives having a chloro or methyl substituent on the phenyl also give their codimers fairly selectively, except for *o*-chloro and *o*-methylstyrene (Table 2). Chloro and methyl substituents on the ortho position of phenyl seems to exhibit a sterically unfavorable effect for the reaction with ethylene. On the other hand, a considerable amount of butene is formed in the case of codimerization with α- or ω-methylstyrene. This suggests that the coordination of styrene is weakened by the methyl group.

It should be noted here that 3-phenyl-3-methyl-1-pentene is gradually accumulated during the course of codimerization of ethylene with styrene(Fig. 1). No other path can be considered for the formation of this product than the codimerization of ethylene with 2-phenyl-2-butene. This means that 2-phenyl-2-butene, once it is formed, is also readily codimerized with ethylene, though the isomerization rate of 3-phenyl-1-butene into 2-phenyl-2-butene is very small. However, the difference in their reactivities between 2-phenyl-2-butene and α-(or ω-)methylstyrene remains to be clarified(Table 2).

Role of Trifluoroboron Etherate: In the previous paper[12] dealing with ethylene dimerization catalyzed by present catalyst system, two functions of trifluoroboron etherate were discussed, its contribution as a ligand, where trifluoroboron is in contact with the nickel complex through the bromide ligand, and its removal of the triphenylphosphine coordinated to the nickel complex to offer a vacant site avairable for the coordination ethylene. It can thus be expected that the codimerization rate increases approximately in the second order with respect to the amount of trifluoroboron etherate as shown in Fig. 3. However, the result shown in Fig. 4 is not obtained only by these two functions. Side reactions of styrene should be taken into account. Preliminary experiments showed that styrene is readily oligomerized in the absence of ethylene by this catalyst system and the oligomerization is highly accelerated by increasing the amount of trifluoroboron etherate, which probably gives rise to a cationic polymerization of styrene. This might be the reason why the selectivity to 3-phenyl-1-butene based on the amount of styrene consumed decreases in the presence of a large amount of trifluoroboron etherate. On the other hand, a decrease in its amount would be more disadvantageous the coordination of ethylene than that of ethylene. This is consistent with the decrease in selectivity to 3-phenyl-1-butene with the decrease in partial pressure of ethylene(Fig. 2). Accordingly, the selectivity to the codimer becomes low again when the amount of trifluoroboron etherate added is less than that of the nickel complex. We thus see why the present catalyst system is active and selective for the codimerization of styrene with ethylene over a range of mole ratio of trifluoroboron etherate to the nickel complex (Fig. 4).



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