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Codimerization of Butadiene and Ethylene Catalyzed by σ-Arylnickel(II) Compound in the Presence of Boron Trifluoride Etherate

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The codimerization of butadiene with ethylene was studied with use of the catalyst system consisting of bis(triphenylphosphine)σ-arylnickel(II) halide and boron trifluoride etherate in methylene dichloride. The codimerization took place readily at 15 °C under 20 kg/cm^2 to give *trans*- and *cis*-1,4-hexadiene and 3-methyl-1,4-pentadiene. A catalytic amount of water significantly enhanced the catalytic activity. The reaction path to form the codimers is discussed in terms of the variation in product distribution with time and the reaction kinetics.

During the course of studies on the dimerization of ethylene catalyzed by nickel(II) compound, it was found that the bis(triphenylphosphine)σ-arylnickel(II) halide-boron trifluoride etherate system significantly enhances the rate of dimerization to give butene selectively.[1] This catalyst system was found to be less efficient for the dimerization of propylene or its codimerization with ethylene,[2] but highly active for the dimerization of styrene with ethylene.[3] This suggests that it is particularly efficient for the codimerization of ethylene with conjugated olefins. For confirmation the codimerization of ethylene with butadiene was examined, the reaction conditions to give a selective formation of the codimers with high yield being investigated.

A number of homogenous catalyst systems have been reported for the codimerization of butadiene with ethylene. They frequently consist of a transition metal compound and an alkylaluminium compound as a reducing agent.[4~7] The present catalyst system is characterized by the absence of such reducing agent, exhibiting a considerably high activity in the presence of boron trifluoride etherate. Hata and Miyake employed boron trifluoride etherate for the codimerization catalyzed by a zerovalent iron complex $Fe(\phi_2PCH_2CH_2P\phi_2)_2 \cdot C_2H_4$,[7] although the catalytic activity was not very high.

Experimental

Materials. Bis(triphenylphosphine)σ-arylnickel(II) halide was prepared according to the methods in the literature.[8,9] The results of elemental analysis of the nickel complex were as follows:

Complex		Calcd.		Found		Ref.
		C(%)	H(%)	C(%)	H(%)	
1-naphthyl-Ni$(P\phi_3)_2$Br	(A)	69.9	4.7	69.9	4.5	8
phenyl-Ni$(P\phi_3)_2$Br	(B)	68.2	4.7	68.4	4.6	9
o-tolyl-Ni$(P\phi_3)_2$Br	(C)	68.5	4.9	67.1	4.6	9
mesityl-Ni$(P\phi_3)_2$Br	(D)	69.1	5.3	69.1	4.7	8
o-tolyl-Ni$(P\phi_3)_2$Cl	(E)	72.8	5.2	73.5	5.4	9
o-tolyl-Ni$(P\phi_3)_2$I	(F)	64.5	4.6	65.7	4.7	9
o-tolyl-Ni$[P\phi(C_2H_5)_2]_2$Br	(G)	57.7	8.3	57.6	8.1	9

$(\phi = C_6H_5)$

Butadiene was dried by passing through a molecular sieve column at room temperature. 1,4-Hexadiene was dried with anhydrous potassium carbonate and distilled under nitrogen. Cylinder ethylene was used without purification. Methylene dichloride was dried with a molecular sieve and distilled under nitrogen. Boron trifluoride etherate was also purified by distillation under nitrogen.

Procedure. All the operations were carried out under nitrogen atmosphere. Codimerization was performed in a Hasteloi autoclave(100 ml) equipped with a magnetic stirrer. The autoclave was first evacuated and flashed with ethylene, then cooled to −20 °C, at which temperature a methylene dichloride solution of a nickel complex and butadiene, separately prepared and kept at dry ice temperature, was introduced into the autoclave, followed by the addition of boron trifluoride etherate with or without water through a syringe. The autoclave was then warmed up to 15 °C, and ethylene was introduced to initiate codimerization. The pressure was kept constant during the course of reaction by supplying ethylene. Saturated aqueous solution of sodium hydroxide (*ca.* 15 ml) was added to terminate the reaction.

Analysis. The liquid product was separated by distillation at 110 °C into two parts, volatile(below C_8) and non-volatile (above C_{10}). The volatile part was analyzed by gas chromatography(PEG-6000 column), using benzene as an internal standard. The non-volatile part was well extracted with diethyl ether and the weight of extracted material was measured.

Identification. Most products were isolated by fractional distillation and identified by NMR, IR and/or Mass spectroscopy. 1,4-Hexadiene fraction(bp 65—67 °C) consisted of two components whose gas chromatographic retention times corresponded to those of authentic samples of *trans*- and *cis*-1,4-hexadiene. They were further confirmed by IR absorption (1653(C=C), 995 and 913 (vinyl), 967 (*trans* –CH=CH–), and 707 (*cis*–CH=CH–) cm^{-1}), and by NMR (an array of peaks from 6.10 to 4.80 ppm (CH_2=CH– and –CH=CH– 5H), and complex multiplets centered at 2.27 ppm (–CH_2– 2H) and 1.68 ppm (CH_3– 3H). 3-Methyl-1,4-pentadiene was estimated by means of the gas chromatographic retention time and mass spectroscopy, since its amount was too small to be isolated. 2,4-Hexadiene fraction (bp 81.5—82.5 °C) consisted of two components whose gas chromatographic retention times corresponded to those of authentic samples of *trans-trans* and *cis-trans* isomers. NMR spectra of the mixture showed an array of peaks from 6.50 to 4.8 ppm (–CH=CH–CH=CH– 4H) and a doublet centered at 1.65 ppm (2CH_3– 6H). IR absorption bands were observed at 1666(w), 1653(w), 987(s), 948(m), 926(m), 820(m), 735 (w), 707(m), and 675(m) cm^{-1}. The C_8-diene fraction (bp 108.6—110 °C) consisted of two major components, although they could not be isolated. Both components had the same molecular weight(110), which was determined by mass spectroscopy connected with gas chromatography. IR absorption bands of the fraction were observed at 1653, 991, and 917 cm^{-1} characterized by 1,4-diene. The NMR showed that the peak area ratio of aliphatic to olefinic protons was 9/5, which was also in conformity with 1,4-C_8-dienes.

Results

Effect of Water. The codimerization of butadiene and ethylene takes place fairly rapidly at room temperature, but the reproducibility of yield and the selectivity of codimerization is poor. The purer the materials used in the reaction, the greater the decrease in yield. It was found that a catalytic amount of water present in the solution promotes catalytic activity. Such an effect was also found for the codimerization of styrene with ethylene by σ-phenylpalladium(II) complex catalyst.[10]

The effect of water added, when *o*-tolyl-bromo-nickel was used, is shown in Fig. 1. The products obtained were 1,4-hexadiene in *trans*/*cis* ratio 2.0—2.5 and 3-methyl-1,4-pentadiene in a 1/10—1/20 ratio to 1,4-hexadiene. The C_6+C_8 diene yield increases with the amount of water added and reaches a maximum at around 0.83 mmol (molar ratio, $H_2O/BF_3OEt_2=0.1$), the higher oligomers monotonically increasing with the amount of water added. Although the C_6+C_8 diene yield depends on the amount of water, the selectivity of C_6-diene to C_6+C_8 dienes and that of 1,4-hexadiene to C_6-dienes is constant (Fig. 1-b). The effect of methanol and phenol instead of water were similarly tested. They also showed a promoting effect but less efficient than water. The effect of water was examined for ethylene dimerization and its codimerization with styrene, using the phenyl-bromo-nickel complex(B) at 0 °C under 1 atm. The results are summarized in Table 1. In both dimerization (Nos. 1 and 2) and codimerization (Nos. 3 and 4), the yield of butene or 3-phenyl-1-butene per min increases about 3 times with the addition of water ($H_2O/BF_3OEt_2=0.4$). Formation of small amounts of styrene, phenylbutenes, and 3-methyl-3-phenyl-1-pentene was observed in the dimerization of ethylene, indicating that the ligand in the complex reacted with ethylene.

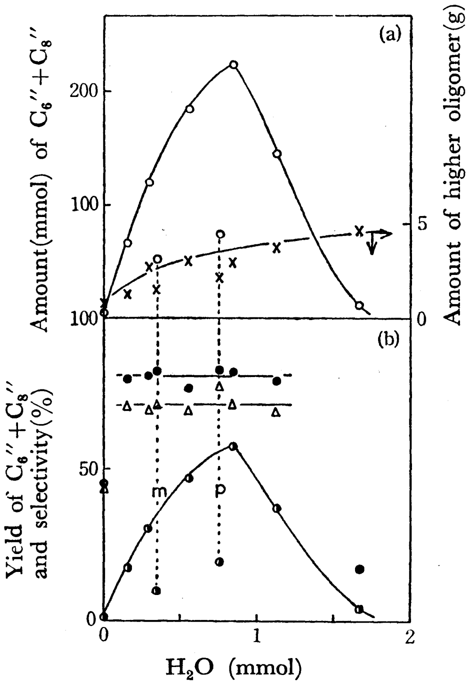


Fig. 1. Effect of added water.
Ni-complex(C), 0.5 mmol; BF_3OEt_2, 8 mmol; Butadiene, 0.39 mol; CH_2Cl_2, 20 ml; C_2H_4, 40 kg/cm^2; 15 °C; 1 hr.
○, $C_6''+C_8''$; ×, higher oligomer; ●, $C_6''/(C_6''+C_8'')$; △, 1,4-hexadiene/C_6''; ◑, yield of $C_6''+C_8''$ in butadiene basis.
Methanol(m) and phenol(p) were added in place of water.

Effect of Ethylene Pressure. The effect of ethylene pressure under fixed conditions using the *o*-tolyl-bromo-

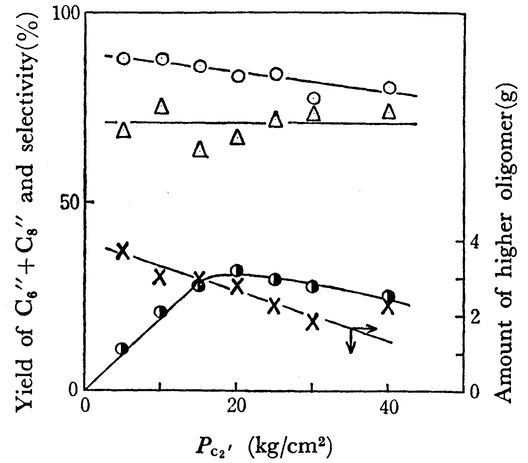


Fig. 2. Effect of ethylene pressure.
Ni-complex(C), 0.5 mmol; BF_3OEt_2, 8 mmol; H_2O, 0.83 mmol; Butadiene, 0.39 mol; CH_2Cl_2, 20 ml; 15 °C; 30 min.
◑, yield of $C_6''+C_8''$; ×, higher oligomer; ○, $C_6''/(C_6''+C_8'')$; △, 1,4-hexadiene/C_6''.

TABLE 1. DIMERIZATION OF ETHYLENE AND ITS CODIMERIZATION WITH STYRENE

No.	H_2O/BF_3OEt_2	Time (min)	Amounts (mmol) in product				
			Sty.1)	3-p-1-b2)	2-p-2-b3)	3-m-3-p-1-p4)	C_4'5)
1	0	30	tr.	0.17	tr.	0.01	1.0
2	0.4	10	tr.	0.14	tr.	0.02	1.0
3	0	30	10.0	2.0	tr.	tr.	tr.
4	0.4	20	5.6	5.1	0.07	0.33	tr.

Phenyl-Ni$(P\phi_3)_2$Br, 0.5 mmol; BF_3OEt_2, 0.5 mmol; Styrene (No. 3, 4), 17.4 mmol; CH_2Cl_2, 30 ml; 0 °C, 1 atm. 1) styrene, 2) 3-phenyl-1-butene, 3) 2-phenyl-2-butene, 4) 3-methyl-3-phenyl-1-pentene, and 5) butenes.

nickel complex(C) is illustrated in Fig. 2. The yield of C_6+C_8 diene increases linearly with ethylene pressure and reaches a maximum at around 20 kg/cm^2. The amount of butenes formed also increases, whereas the higher oligomers decrease with ethylene pressure. The higher oligomers obtained at 5 kg/cm^2 and above 10 kg/cm^2 were separately hydrogenated with Raney nickel catalyst. The amounts of absorbed hydrogen were 19.2 and 13.0 mmol/g respectively, suggesting that the oligomers formed under low pressure were more unsaturated and involved more butadiene than those under high pressure. The results are reasonable since the increase in ethylene concentration should be more favorable for cooligomerization than homooligomerization of butadiene.

Variation in Product Distribution with Time. In order to study the reaction path, variation in product distribution with time was examined using *o*-tolylbromo-nickel complex(C) as a catalyst component. The results are given in Fig. 3, where the amount of butadiene consumed for higher oligomers was estimated to be 40% at 100% conversion of butadiene. The rate of reaction, as given by the rate of increase in the amount of C_6+C_8 diene or 1,4-hexadiene, is rather insensitive to the decrease in butadiene concentration, suggesting a zero order reaction with respect to butadiene while 1,4-hexadiene rapidly disappears after butadiene is mostly consumed, being accompanied by an increase in C_8-dienes, higher oligomer and 2,4-hexadiene. Probably 1,4-hexadiene is first isomerized into its conjugated form 2,4-hexadiene, which, like butadiene, reacts readily with ethylene. The increase in higher oligomers in the later stage would be due to both homodimerization of hexadiene and codimerization of C_8-dienes with ethylene.

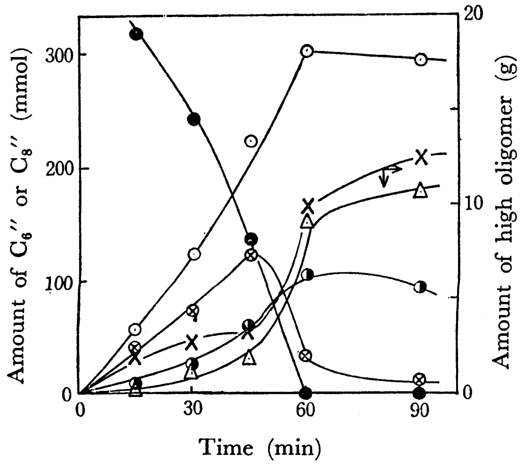
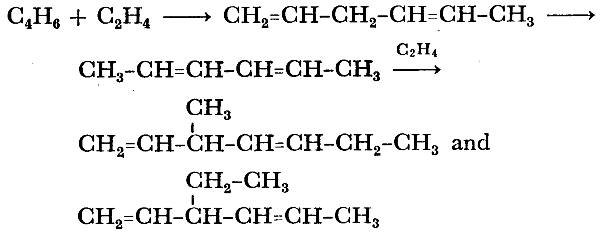


Fig. 3. Products distribution during the codimerization.
Ni-complex(C), 0.5 mmol; BF_3OEt_2, 8 mmol; H_2O, 0.83 mmol; Butadiene, 0.39 mol; C_2H_4, 20 kg/cm^2; CH_2Cl_2, 20 ml; 15 °C.
○, $C_6''+C_8''$; ⊗, 1,4-hexadiene; ◑, 2,4-hexadiene; △, C_8''; ●, butadiene(calculated); ×, higher oligomer.

In order to confirm the above interpretation, the codimerization of 1,4-hexadiene with ethylene was examined using the same catalyst. The results are given in Fig. 4. 1,4-Hexadiene is rapidly isomerized to 2,4-hexadiene, followed by the reaction with ethylene to give 1,4-C_8-dienes. Thus the reaction path might be deduced to be as follows:



$$C_4H_6 + C_2H_4 \longrightarrow CH_2{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3 \longrightarrow$$

$$CH_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_3 \xrightarrow{C_2H_4}$$

$$CH_2{=}CH\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3 \text{ and}$$

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

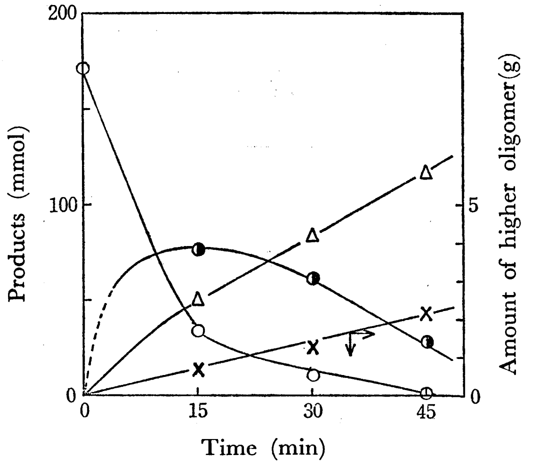


Fig. 4. Products distribution during the codimerization of ethylene with 1,4-hexadiene.
Ni-complex(C), 0.25 mmol; BF_3OEt_2, 4 mmol; H_2O, 0.41 mmol; 1,4-hexadiene(*trans*/*cis*=10), 0.172 mol; C_2H_4, 20 kg/cm^2; 15 °C.
○, 1,4-hexadiene; ◑, 2,4-hexadiene; △, C_8''; ×, higher oligomer.

Effect of BF_3OEt_2 Concentration. The codimerization was carried out by varying the amount of BF_3OEt_2 using *o*-tolyl-bromo-nickel complex(C), the amount of the complex(0.5 mmol) and the molar ratio H_2O/BF_3OEt_2 being fixed. The rate of reaction can

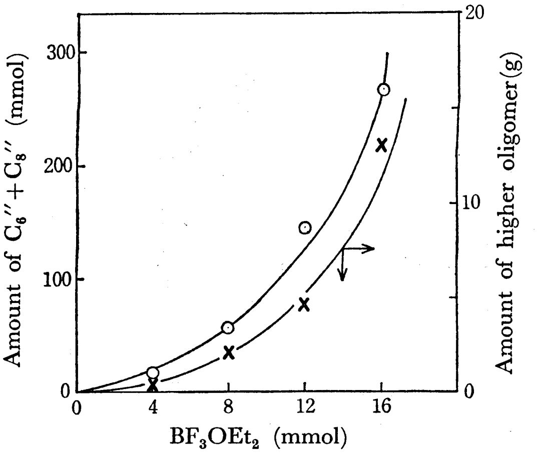


Fig. 5. Effect of amount of BF_3OEt_2.
Ni-complex(C), 0.5 mmol; $BF_3OEt_2/H_2O=10$; butadiene, 0.39 mol; C_2H_4, 20 kg/cm^2; CH_2Cl_2, 20 ml; 15 °C; 15 min.
○, $C_6''+C_8''$; ×, higher oligomer.

TABLE 2. EFFECT OF LIGANDS

No.	Ni-Complex	Product					Yield and Selectivity		
		3-m-1,4-PD[a] (mmol)	1,4-HD[b] (mmol)	2,4-HD[c] (mmol)	C_8'' (mmol)	Olig[e] (g)	$C_6''+C_8''$ (%)	$(C_6''/C_6''+C_8'')$ (%)	(1,4-HD/C_6'') (%)
1	D	7.3	83.3	32.0	27.2	4.0	38.4	81.9	67.9
2	C	5.6	70.8	28.0	20.4	2.9	32.0	83.6	67.8
3	B	6.0	72.9	21.6	15.9	2.6	29.8	86.3	72.5
4	A	2.7	39.5	9.5	6.9	1.7	15.0	88.2	76.4
5	E	6.8	81.2	23.0	14.0	2.4	32.1	88.8	73.1
6	F	5.0	66.6	18.8	15.3	2.9	27.1	85.5	73.7
7	G	4.7	56.5	24.7	14.1	3.4	25.6	85.9	65.8

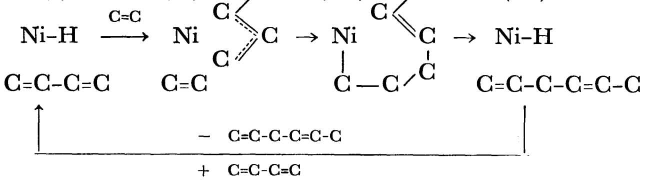
Ni-Complex, 0.5 mmol; BF_3OEt_2, 8 mmol; H_2O, 0.83 mmol; butadiene, 0.39 mol; CH_2Cl_2, 20 ml; C_2H_4, 20 kg/cm^2; 15 °C; 30 min. a) 3-methyl-1,4-pentadiene, b) 1,4-hexadiene, c) 2,4-hexadiene, d) C_8-diene, and e) higher oligomers.

be estimated from the amount of C_6+C_8 dienes or higher oligomers formed in 15 min. (Fig. 5). It appears that the reaction rate obeys approximately the second order kinetics with respect to BF_3OEt_2, as in the codimerization of styrene with ethylene by the same catalyst system.

Effect of Ligands. Seven complexes with different ligands were prepared and tested for the effect of ligand on the selectivity and activity in codimerization. The results are summarized in Table 2. The difference in the selectivity of C_6-dienes or 1,4-hexadiene seems too small to estimate a ligand effect. The catalytic activity, as given by the yield of C_6-dienes or C_6+C_8 dienes, is affected by the σ-aryl ligand (Nos. 1—4), but to a smaller extent by the halide or phosphine ligand (Nos. 2, 5, 6, and 7), *viz.* the activity decreases in the order, mesityl>*o*-tolyl>phenyl>naphthyl.

Discussion

Reaction Path for Butadiene and Ethylene Codimerization. It was postulated that the active species of the present catalyst system is a nickel hydride complex formed from dissociative addition of olefin to σ-arylnickel(II) compound, with the σ-aryl ligand remaining on the nickel atom during the course of catalytic reaction.[2] The formation of 1,4-hexadiene can also be understood in terms of the nickel hydride intermediate as follows. Butadiene reacts with the nickel hydride(I) to give 1-methyl-π-allyl nickel(II), followed by an insertion of ethylene to form 4-hexenyl nickel(III) and elimination of β-hydrogen to give 1,4-hexadiene.



In this scheme, 1,4-hexadiene should be readily replaced by butadiene, since the codimerization rate is of nearly zero order in butadiene concentration. This would be reasonable if the conjugated diene preferentially occupies the coordination site of the nickel. An abrupt change in the distribution of 1,4-hexadiene and C_8-dienes was observed when butadiene is mostly consumed (Fig. 3). Although the isomerization of 1,4-hexadiene to 2,4-hexadiene is very fast in the absence of butadiene (Fig. 4), the formation of 2,4-hexadiene during the butadiene and ethylene codimerization was not so high in spite of very high concentration of 1,4-hexadiene. This suggests that the isomerization of 1,4-hexadiene is greatly retarded by the presence of butadiene. The nickel hydride is likely to be utilized for the isomerization. Thus after the consumption of butadiene, the nickel hydride becomes available for isomerization, resulting in the rapid decrease in 1,4-hexadiene. Since 2,4-hexadiene thus formed is conjugated, it is readily attacked by ethylene to give the C_8-dienes, resulting in the rapid increase in their amounts. In this way the variation in product distribution with time is explained in terms of preferential occupation of coordination site by conjugated dienes.

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