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Reaction of Butadiene with Ethylene. IV.[*1] Synthesis of 1,4-Hexadiene by a Cobaltous Chloride-Ditertiary Phosphine Complex and an Organoaluminum Compound Catalyst

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A new catalyst consisting of a cobaltous chloride-ditertiary phosphine complex and an organoaluminum compound was found to be effective for the selective preparation of 1,4-hexadiene by the reaction of butadiene with ethylene. The effects of the reaction variables on the activity and on the selectivity in 1,4-hexadiene formation were studied. It is considered that a coordination of the ditertiary phosphine on the catalytically activated intermediate is essential for the selective catalysis. A reaction mechanism is proposed which involves an activated hydrido-cobalt complex as intermediate.

This investigation has been undertaken in order to find catalysts suitable for the highly-selective synthesis of 1,4-hexadiene from butadiene and ethylene. The catalytic preparation of the diene has been reported by Hata(1) and by Alderson *et al.*(2) In Hata's process, the maximum selectivity(3) in 1,4-hexadiene formation was, at most, 50%, and a fairly large amount of the charged butadiene was consumed in forming higher oligomers and polymeric substances. Binary catalysts containing various iron compounds gave similar results. In a previous paper,(4) however, we reported that a new catalyst consisting of an iron halide, an organoaluminum compound, and a ditertiary phosphine exerted an excellent selectivity (more than 80%) is the formation of the diene.

Since Wilke has opened a new field of cyclic butadiene oligomer formation, involving such substances as cyclododecatriene and cyclooctadiene, numerous patents and reports have been published in this field.(5) The formation of 1,4-hexadiene is formally a 1,4-addition of ethylene to butadiene; this type of oligomerization is found in the linear dimerization of butadiene catalyzed by cobalt-containing compounds.(6-9) A transfer of one hydrogen atom is involved in these reactions.

Table 1 summarizes the characteristic catalytic activities of iron, cobalt, and nickel compounds in the addition reactions of butadiene and butadiene-ethylene. It seems likely that the cobalt complex is one of the most suitable catalysts for the oligomerization of butadiene involving hydrogen transfer. The reaction of butadiene with ethylene catalyzed by a cobalt compound metal alkyl catalyst gave 1,3-hexadiene as a 1 : 1 addition product.(9) A ternary iron catalyst consisting of ferric chloride, triphenylphosphine, and triethylaluminum acted similarly to the cobalt catalyst in the reaction of butadiene, while a different behavior was observed in the reaction of butadiene with ethylene.(10) By adding triphenylphosphine to a binary cobalt catalyst, *e.g.*, a cobalt tris(acetylacetonate) and triethylaluminum catalyst, the activity with regard to the dimerization of butadiene disappeared.(8) In the reaction of butadiene with ethylene, however, no ternary cobalt catalyst containing a phosphorus compound has been investigated.

In this paper the results of our studies of the addition reaction of butadiene with ethylene catalyzed by a cobaltous halide-ditertiary phosphine complex and an organoaluminum compound will be described.

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1) G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964).

2) T. Alderson, E. L. Jenner and R. V. Lindsey, Jr., *ibid.*, **87**, 5638 (1964).

3) Defined as moles of 1,4-hexadiene obtained divided by moles of butadiene converted ×100.

4) M. Iwamoto and S. Yuguchi, *J. Org. Chem.*, **31**, 4290 (1966).

5) H. Müller, D. Wittenberg, H. Seibt and E. Scharf, *Angew. Chem.*, **77**, 318 (1965).

6) S. Otsuka, T. Kikuchi and T. Taketomi, *J. Am. Chem. Soc.*, **85**, 3709 (1963).

7) T. Saito, T. Ohno, Y. Uchida and A. Misono, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1099 (1963).

8) S. Tanaka, K. Mabuchi and N. Shimazaki, *J. Org. Chem.*, **29**, 1926 (1964).

9) D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963).

10) M. Iwamoto and S. Yuguchi, This Bulletin, **39**, 2001 (1966).

TABLE 1. CATALYTIC ACTIVITIES OF IRON, COBALT, AND NICKEL COMPLEXES

System[a]	Reactant	Iron	Cobalt	Nickel
$M(acac)_n$-R_3Al	Butadiene	Linear trimer[b]	Linear dimers[c]	Cyclic trimer[d]
$M(acac)_n$-$P(C_6H_5)_3$-R_3Al	Butadiene	Linear dimers[e]	No reaction[c]	Cyclic dimer[d]
$M(acac)_n$-R_3Al	Butadiene and Ethylene	1,4-Hexadiene[f]	1,3-Hexadiene[g]	Cyclic C_{10}-diene[d]
MCl_n-$P(C_6H_5)_3$-R_3Al	Butadiene and Ethylene	C_6-Dienes[h]		Cyclic C_{10}-diene[d]

a) M=Iron, cobalt, or nickel, acac=acetylacetonate, *n*=2 or 3.
b) M. Hidai, Y. Uchida and A. Misono, This Bulletin, **38**, 1243 (1965).
c) Ref. 7. d) Ref. 5. e) H. Takahashi, S. Tai and M. Yamaguchi, *J. Org. Chem.*, **30**, 166 (1965).
f) Ref. 1. g) Ref. 9. h) Ref. 10.

Results

As shown in Table 2, the dienylation reaction to yield 1, 3-hexadiene and linear dimers of butadiene was predominant, although the formation of 1, 4-hexadiene was slightly promoted by the cobaltous halide-triphenylphosphine complex catalyst. The results also suggest the possibility of modifying the catalytic properties of the cobalt compound by the addition of a proper ligand. It has been reported before that a ditertiary phosphine had an excellent effect in making the ternary iron catalyst highly selective for the preparation of 1, 4-hexadiene.[4]

The cobaltous chloride-1, 2-bis(diphenylphosphino)ethane complex, in which the ditertiary phosphine was coordinated as a chelate ligand to the cobaltous ion, was used as one component of the catalyst. The results are summarized in Table 3. At a relatively high concentration of the catalyst, a rapid exothermic reaction proceeded and the absorption of ethylene stopped in a short time. An almost exclusive formation of one product was found by gas chromatographic analysis; this product was identified by its boiling point, its retention volume in a gas chromatogram, the results of a mass analysis, and its infrared absorption spectrum, as 1, *cis*-4-hexadiene.

The effects of reaction temperatures ranging from 30 to 140°C are shown in Fig. 1. It seems likely that the optimum reaction temperature is

TABLE 2. CATALYTIC ACTION OF $CoX_2(P(C_6H_5)_3)_2$-$(C_2H_5)_3Al$ SYSTEM IN THE REACTION OF BUTADIENE WITH ETHYLENE

(Toluene 20 m*l*, Butadiene 33.5 g (0.62 mol), Cobalt complex, 2 mmol, $(C_2H_5)_3Al$ 7.3 mmol, Ethylene 40 kg/cm², 80°C, 16 hr)

Cobalt Complex	Product (g)
$CoCl_2$	1,3-Hexadiene (2.5) Butadiene dimers (4.5) Tacky soild polymer
$CoCl_2(P(C_6H_5)_3)_2$	1,4-Hexadiene (2.2) 1,3-Hexadiene (a small quantity) Butadiene dimers (4.6)
$CoBr_2(P(C_6H_5)_3)_2$	1,4-Hexadiene (2.1) 1,3-Hexadiene (9.6) Butadiene dimers (8.1)

TABLE 3. SYNTHESIS OF 1,4-HEXADIENE: $CoCl_2[(C_6H_5)_2PCH_2$-$CH_2P(C_6H_5)_2]_2$-$(C_6H_5)_3Al$ SYSTEM

No.	1	2	3	4
Co Complex, g	0.167	0.09	0.09	0.09
Al, g	0.92	0.47	0.92	0.5
Solvent,[a] m*l*	CB 50	T 20	T 20	T 20
Butadiene, g	33.5	53.6	80.4	80.4
Ethylene, kg/cm²	20	25	50	50
Temp., °C	70—80	80	90	80
Time, hr	1.25	2	5	17.3
Product, g				
1,4-Hexadiene	45.4	48.1	48.3	66.5
Others	6	1.3	5.3	3.2
Conversion,[b] %	100	61.6	44.5	57
Selectivity,[c] %	89.6	97	90.5	97

a) CB=Monochlorobenzene, T=Toluene
b) Based on the charged butadiene
c) 1,4-Hexadiene (mol)/Butadiene reacted (mol) ×100

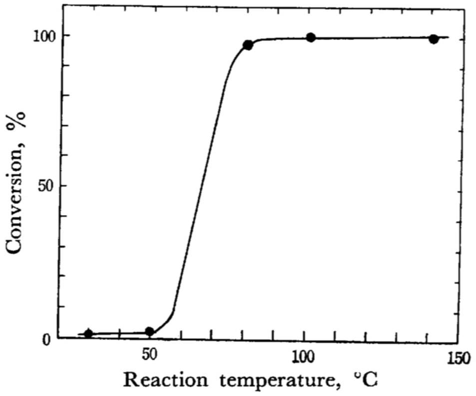

Fig. 1. Reaction temperature *vs.* conversion of the butadiene charged.

in the range from 80 to 100°C. At temperatures higher than 100°C, a considerable isomerization of 1, 4-hexadiene to conjugated dienes, mainly to 2, 4-hexadiene, was observed. The product obtained at 140°C contained 71.6% of the 2, 4-isomer in the C_6-fraction. When the reaction was carried out at 150°C or above, only the 2, 4-isomer appeared. The effect of the molar ratio of Al/Co on the reaction was also studied; the results are shown in Tables 4 and 5. The selectivity of 1, 4-hexadiene was not influenced by the molar ratio. In using this catalyst, a large amount of triethylaluminum was required for the activation, in particular at a low concentration of the cobalt complex, it is considered that the purity of the reactions and solvents also affects the molar ratio of Al/Co.

Table 4. Effect of Al/Co molar ratio (I)
(Toluene 50 m*l*, $(C_2H_5)_3Al$ 0.46 g (4 mmol), Butadiene 33.5 g, Ethylene 50 kg/cm², 90—100°C, 2 hr)

Al/Co Molar ratio	Product, g			Conversion %
	1,4-Hexadiene	2,4-Hexadiene	Residue	
8	46.3	3.3	0.4	96.2
16	49.7	3.8	0.4	100
25	45.7	3.2	1.0	100

Table 5. Effect of Al/Co molar ratio (II)
(Toluene 50 m*l*, Cobalt complex 0.09 g (0.097 mmol), Butadiene 33.5 g, Ethylene 55 kg/cm², 80—90°C, 2 hr)

Al/Co Molar ratio	Product, g			Conversion %
	1,4-Hexadiene	2,4-Hexadiene	Residue	
10.5	2.5	0.2	0.34	6.9
29.9	6.5	0.2	0.27	14.8
49.5	35.3	2.0	0.6	77.4
71.9	45.6	4.4	0.4	99.4

Although the cobalt complex is insoluble in common organic solvents, a homogeneous catalyst solution can be obtained by mixing the two components of the catalyst. The solution can be stored at room temperature without a decline in catalytic activity (Table 6). The cobalt complex is soluble in 1, 2-dichloroethane to give a dark green solution. A more rapid reaction occurred in the initial stage when 1, 2-dichloroethane was used as the solvent. In this case the control of the reaction temperature was impossible and side reactions occurred to a considerable extent to give the 2, 4-isomer and C_8-dienes. In Table 7 the results obtained by using a variety of solvents are shown. Although the reaction could be carried out smoothly without any solvent, a higher conversion was attained when a proper solvent was used. 1, 4-Hexadiene itself can also be used as a solvent.

In all the reactions described above, triethylaluminum was used as a reducing component. In addition, some other organometallic compounds were also used as reducing agents; the results are summarized in Table 8. It was found that triisobutylaluminum, diisobutylaluminum hydride, and diethylzinc were highly effective in making

Table 6. Activity of the catalyst solution after storage

Period of ftorage, day	Butadiene g	Product, g			Conversion %
		1,4-Hexadiene	2,4-Hexadiene	Residue	
2	33.5	36.4	1.05	0.3	75.7
12	36.5	38.3	0.9	0.4	74.8

Table 7. Effect of solvent

Solvent m*l*	None	$C_6H_5CH_3$ 50	C_6H_5Cl 50	n-C_7H_{16} 50	$Cl_2C{=}CCl_2$ 50	$(CH_2Cl)_2$ 4	$(CH_2Cl)_2+C_6H_5CH_3$ 4+50
Co complex, g	0.09	0.09	0.169	0.169	0.09	0.09	0.09
$(C_2H_5)_3Al$, g	0.46	0.92	0.92	0.46	0.83	0.83	0.83
Butadiene, g	67	68.4	67	33.5	33.5	67	33.5
Ethylene, kg/cm²	40	20	20	40	40	50	50
Temp., °C	80	70	70	80	95	90	90
Time, hr	2	1	2	2	2	2	2
Product, g							
1,4-HD	53.4	80	74.6	39.8	57.3	59.6	38.6
2,4-HD	1.4	1.8	11	9.1	3.1	16.5	2.2
Others	1.1	0.2	1.8	1.0	1.2	18.9[a]	1.2
Conversion, %	56.2	80	86.5	100	100	90.1	85

a) C_8-dienes were contained.

TABLE 8. EFFECT OF VARIOUS ORGANOMETALLICS[a]

Organo-metallics	g	Time hr	Product, g 1,4-Hexadiene	2,4-Hexadiene	Residue	Conversion %
$(i\text{-}C_4H_9)_3Al$	1.5	2	15.3	0.5	0.4	32.6
$(i\text{-}C_4H_9)_2AlH$	1.5	3	15.8	1.1	0.6	35.3
$(C_2H_5)_2AlCl$	1.0	2	19.7		10.6	73.5
$(C_2H_5)_3Al_2Cl_3$	1.0	2	0	0	22	65.6
$(C_2H_5)_2Al(OC_2H_5)$	1.3	16	0	0	0	0
$(C_2H_5)_2Zn$	1.18	16	11.4	1.02	0.77	26.8
$(C_2H_5)_2Mg$	0.65	16	trace			

a) $CoCl_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ 0.08 g, Toluene, 20 *ml*, Butadiene, 33.5 g, 40 kg/cm², 80°C.

the cobalt catalysts selective for 1, 4-hexadiene formation. Although the activity of the catalyst containing diethylaluminum chloride or ethylaluminum sesquichloride was fairly high, the selectivity of 1, 4-hexadiene was low and a considerable amount of polymeric substance was formed. Diethylaluminum ethoxide reacted with the cobalt complex to give a dark brown solution, but no catalytic activity was observed.

It was confirmed that butadiene did not react with isobutene and *n*-butene under the reaction conditions. Therefore, it is possible to use the B-B fraction as a source of butadiene instead of pure butadiene.

Discussion

In a previous paper,⁽⁴⁾ the effect of the ditertiary phosphine in the iron ternary catalyst on the selective formation of 1, 4-hexadiene was discussed. It is expected that the ditertiary phosphine will occupy one or more coordination sites around the catalytically active metal atom and that, hence, the coordination of reactants will be suppressed. The ditertiary phosphine, having an apt structure for chelate coordination, was effective. In the preparation of a catalyst for the linear oligomerization of butadiene, the catalyst components should be mixed in the presence of butadiene in order to obtain a highly-active catalyst; otherwise, a black precipitate is separated and no active catalyst is obtained. On the other hand, the cobaltous chloride-ditertiary phosphine complex catalyst can be prepared in the absence of the reactants and kept without a decline in catalytic activity. This fact indicates that low-valent cobalt, formed by a reaction of the cobalt complex with triethylaluminum, is stabilized by the coordination of the ditertiary phosphine. The function of the phosphine in stabilizing a low-valent state of a metal atom is generally accepted.⁽¹¹⁾ It is known that a reaction of cobaltous chloride-1, 2-bis(diphenylphosphino)-ethane complex with lithium aluminum hydride or sodium borohydride gives a hydride-cobalt complex, $CoH((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2$.⁽¹²⁾ A reaction of cobalt tris(acetylacetonate) with diethylaluminum ethoxide in the presence of the ditertiary phosphine also gives the hydride-cobalt complex.⁽¹³⁾ However, these combinations of the cobalt complex with lithium aluminum hydride and diethylaluminum ethoxide are catalytically inactive; these facts suggest that the hydrido-cobalt complex itself is not an active species, because the hydrido-cobalt complex is coordinately saturated. It is considered that an organoaluminum compound in the catalyst acts in two ways, that is, as a reducing agent to form the hydrido-cobalt complex, and as an activating agent to place the hydrido-cobalt complex in a coordinately-unsaturated state.

It was found that 1, 2-bis(diphenylphosphino)-ethane formed a 2 : 1 complex with cobaltous chloride, whereas 1, 3-bis(diphenylphosphino)propane formed a 1 : 1 complex. The 1 : 1 complex combined with triethylaluminum revealed a selective activity for the preparation of 1, 4-dienes.⁽¹⁴⁾ On the basis of these findings, it seems that a complete inhibition of the dienylation reaction can be realized by blocking one or two coordination sites around the catalytically active cobalt atom. The coordination of nitrogen-containing ligands to cobalt chloride was, however, ineffective in preparing the diene selectively (Table 9).

From these experimental results, the following mechanism may be proposed; first, the hydrido-cobalt complex is formed as a transient intermediate by the reaction of the cobaltous chloride-1, 2-bis(diphenylphosphino)ethane complex with triethylaluminum, and then the hydrido-cobalt complex is activated to a coordinately unsaturated state by the action of the organoaluminum compound. Butadiene reacts with the activated complex to

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11) J. Chatt, *J. Inorg. Nucl. Chem.*, **8**, 515(1958).

12) F. Zingales, F. Canziani and A. Chiesa, *Inorg. Chem.*, **2**, 1303 (1963).

13) Toyo Rayon, Japanese Patent Publication No. 42-2426 (Feb. 2, 1967).

14) M. Iwamoto, Unpublished work.

Table 9. Effect of nitrogen containing chelate ligands[a)]

Cobalt Complex[b)] mmol	$(Co(Dipy)_3)Cl_2 \cdot 6H_2O$ 1	$(Co(en)_2Cl_2)Cl$ 0.5	$(Co(en)_3)Cl$ 1
$(C_2H_5)_3Al$, mmol	16	8	8
Temperature, °C	80	80	70
Product, g	36.9	31	25.2
Composition, wt%			
1,4-Hexadiene	2.4	1.1	0.6
2,4-Hexadiene	1.9	1.0	0
1,3-Hexadiene	16.0	17.8	15.9
MHT[c)]	34.2	48.7	54.5
n-OT[d)]	7.8	10.3	7.9
High Boilers	37.6	21.0	21.1
Conversion, %	86.5	68.0	56.7

a) Butadiene 33.5 g, Toluene 50 m*l*, Ethylene pressure 50 kg/cm², Reaction time 2 hr.
b) Dipy=α, α'-Dipyridyl, en=Ethylenediamine.
c) MHT=3-Methyl-1,4,6-heptatriene.
d) *n*-OT=*n*-1,3,6-Octatriene.

give a π-butenyl complex such as that derived from butadiene and cobalt hydrocarbonyl.[15)] An ethylene molecule coordinated to the activated cobalt complex attacks the π-allyl part of the butenyl group to give a 4-hexenyl complex. This intermediate finally yields 1, *cis*-4-hexadiene, which is set free, while, at the same time, the hydrido-complex is regenerated for further reaction. The exclusive formation of the *cis*-isomer and the facile and selective reaction of butadiene with ethylene constitute strong evidence for the coordination mechanism.

Experimental

Reagents. The solvents were purified by conventional methods. The butadiene (Japan Synthetic Rubber Co.) was dried by passing it through columns of a sodium glycolate-ethylene glycol solution, potassium hydroxide, activated alumina, and a molecular sieve, and then condensed in a measuring vessel kept in a dry ice-acetone bath. The ethylene (Nihon Petrochemical Co.) was used without further purification. The organoaluminum compounds (Ethyl Corp.) were obtained commercially. The triphenylphosphine (Techno Chemie G. m. b. H.) was used without purification. The ditertiary phosphines were prepared according to the method described by Hewertson and Watson.[16)] Commercially available ethylenediamine and α, α'-dipyridyl were used. The cobalt halide-triphenylphosphine complex was prepared according to the method of Venanzi.[17)]

The cobalt halide-ditertiary phosphine complex was obtained by the reaction of anhydrous cobaltous halide with the ditertiary phosphine in ethanol. The hydrido-cobalt complex was prepared according to the method of Zingales.[12)] The cobalt complexes with chelate ligands containing nitrogen atoms were prepared according to the method described in the literature.[18),19)]

Reaction Procedure. The reaction was usually carried out in a 200-m*l* pressure vessel equipped with a magnetic stirrer. Under a nitrogen atmosphere, calculated amounts of the solvent, the cobalt complex, liquified butadiene, and the organoaluminum compound were charged in this order into the vessel. After the vessel had then been tightly closed, ethylene was injected directly from the cylinder until a given pressure was reached at a reaction temperature. The mixture was heated with agitation for a given time, cooled to room temperature, and vented to remove any unreacted ethylene. The catalyst was then deactivated by the addition of a small amount of methanol containing dilute hydrochloric acid. The reaction mixture was repeatedly washed with water, after which the organic layer was separated and dried with anhydrous sodium sulfate overnight. A distillate obtained at atmospheric pressure was analyzed by gas chromatography using a copper tube (3 mm in diameter and 3 m long) packed with Apiezon Grease L at 100°C. The yield was calculated by comparing the peak area with that of a substance added as an internal standard. The validity was confirmed by the analysis of a known mixture.

Effect of the Storage of the Catalyst Solution on the Activity. The catalyst solution was prepared by mixing 0.74 g (0.8 mmol) of the cobalt-ditertiary phosphine complex and 3.65 g (32 mmol) of triethylaluminum in 100 m*l* of toluene. The solution was then stored in a 300-m*l* Erlenmeyer flask equipped with a glass stopper under a nitrogen atmosphere at room temperature. After 2 days and 12 days, 20-m*l* portions of the solution were used as catalysts for the reaction of butadiene with ethylene, carried out at 80°C for 2 hr; the results are shown in Table 6.

B-B Fraction as a Source of Butadiene. A B-B fraction purchased from the Mitsubishi Petrochemical Co. was vaporized from a cylinder and condensed in a glass pressure vessel. The B-B fraction was purified by

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15) H. B. Jonassen, R. I. Stearns, J. Kenttamaa, D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, **80**, 2586 (1958).
16) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.
17) L. M. Venanzi, *ibid.*, **1958**, 719.
18) J. B. Work, "Inorganic Syntheses," Vol. II, p. 221 (1946).
19) J. C. Bailar, Jr., *ibid.*, Vol. II, p. 222.

passing it through the column system for butadiene purification described above. It was then again condensed in a measuring vessel. The content of butadiene in the purified B-B fraction was 42.4% while the remainder consisted of C_4-olefins and lower homologues. A 200-m*l* pressure vessle was charged with 10 m*l* of 1, 2-dichloroethane, 100 m*l* of the liquefied B-B fraction, 0.09 g of the cobalt complex, and 0.944 g of triethylaluminum. Under an ethylene pressure of 50 kg/cm^2, the reaction was then carried out for 2 hr at 100°C. Gas chromatographic analysis of the reaction mixture showed that 58.5 g of 1, 4-hexadiene and 2.2 g of 2, 4-hexadiene were produced.

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