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Stereospecific Synthesis of 1,4-Dienes. III. The Cobalt Chloride - Phosphorus Compound - Triethylaluminum Catalyst System

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The admixture of cobalt chloride, $(RO)_nPCl_{3-n}$ $(n=0—3)$, and triethylaluminum catalyzes the codimerization of 1,3-dienes with ethylene to give exclusively *cis* isomers of 1,4-dienes, which result from the 1,4-addition of a C–H bond of ethylene to the 1,3-dienes. The addition of ethylene to methyl-substituted 1,3-dienes occurs predominantly on the substituted sides of the 1,3-dienes. The activity of the catalyst is strongly affected by the nature of the trivalent phosphorus components.

The admixture of first-row transition metal compounds of Group VIII of the periodic table and organoaluminum compounds catalyzes reactions between butadiene and ethylene. Wilke has reported the formation of *trans, cis*-1,5-cyclodecadiene by the reaction of butadiene with ethylene using the nickel acetylacetonate - ethoxydiethylaluminum catalyst system (zerovalent nickel).[1] On the other hand, the cobalt acetylacetonate - triethylaluminum system[2] and the iron acetylacetonate - triethylaluminum system[3] have afforded linear codimers, 1,3-hexadiene and 1, *cis*-4-hexadiene respectively. It has recently been found that admixtures of ditertiary phosphine complexes of cobalt or tertiary phosphine complexes of nickel and organoaluminum compounds also catalyze the formation of 1, 4-hexadiene.[4,5] We have investigated an effective catalyst system for this reaction. This paper will report the results of the 1,4-diene synthesis by means of a ternary catalyst system, cobalt chloride - $(RO)_nPCl_{3-n}$ triethylaluminum $(n=0—3)$, and the effect of the nature of the phosphorus compounds upon the catalytic activity.

Results

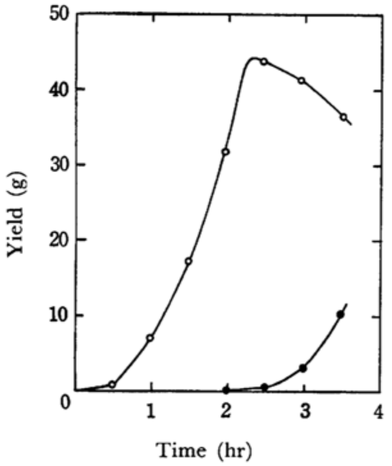

Fig. 1. Yield of 1,4- and 2,4-hexadiene *vs.* reaction time.
Reaction conditions: $CoCl_2$ 0.5 mmol, $(C_6H_5O)_3P$ 2.0 mmol, Et_3Al 12 mmol, butadiene 0.6 mol, ethylene 40 kg/cm², 80°C
○ 1,*cis*-4-hexadiene, ● 2,4-hexadiene

The catalyst was prepared by mixing cobalt chloride, $(RO)_nPCl_{3-n}$ $(n=0—3$, R=ethyl, *n*-butyl, phenyl, chlorophenyl and tolyl) and triethylaluminum in the presence of butadiene. The addition of ethylene (40 kg/cm²) to the resultant mixture at 60—80°C led to the formation of 1,*cis*-4-hexadiene. The preparation of the catalyst in the absence of butadiene showed a poor activity. When the molar ratio of a phosphorus component to cobalt chloride was higher than one, the catalyst showed an excellent activity and a high selectivity (95%). After the complete consumption of the butadiene, the isomerization of 1,*cis*-4-hexadiene to 2,4-hexadiene took place, as may be seen in Fig. 1. The stereospecific formation of 1,*cis*-4-hexadiene has also been observed in $Fe(acac)_3$ - Et_3Al catalyst system[3] and the $CoCl_2(Ph_2PCH_2CH_2PPh_2)_2$-$Et_3Al$ catalyst system.[4] However, the $NiCl_2(PR_3)_2$-R_2AlCl catalyst system[5] and the

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3) a) G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964). b) G. Hata and D. Aoki, *J. Org. Chem.*, **32**, 3754 (1967).
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TABLE 1. REACTION OF BUTADIENE WITH ETHYLENE (80°C, ethylene 40 kg/cm²)

Run No.	Catalyst component				BD^a) ml	Time min	Product (g)		
	$CoCl_2$ mmol	Phosphorus compound	mmol	Et_3Al mmol			1,4-HD^b)	2,4-HD	Residue
1	0.5	$(C_6H_5O)_3P$	2	10	26	120	21.7	0.8	0.5
2	0.5	$(C_6H_5O)_3P$	0.5	10	26	120	15.6	1.7	3.2
3	0.5	$(o\text{-}CH_3C_6H_4O)_3P$	2	10	26	130	15.7	0.3	0.8
4	0.5	$(m\text{-}CH_3C_6H_4O)_3P$	2	10	26	130	22.6	0.2	0.6
5	0.5	$(p\text{-}ClC_6H_4O)_3P$	2	10	26	85	20.1	2.9	1.0
6	0.25	$(C_6H_5O)PCl_2$	0.5	3	52	25	41.9	3.5	0.4
7^c)	0.25	$(C_6H_5O)PCl_2$	0.5	3	52	100	42.3	0.7	0.2
8	0.5	$(C_2H_5O)_3P$	2	10	26	120	0.5	0	0.2
9	0.25	$(n\text{-}C_4H_9O)_3P$	0.5	6	52	300	0.6	0	0.2
10	0.25	$(n\text{-}C_4H_9O)PCl_2$	0.5	3	52	75	42.5	1.2	0.4

a) Liquefied butadiene (0°C) b) HD=hexadiene c) Reaction at 60°C

TABLE 2. REACTION OF ISOPRENE WITH ETHYLENE (80°C, ethylene 40 kg/cm²)

Run No.	Catalyst component				Isoprene mol	Time min	Product (g)		
	$CoCl_2$ mmol	$(RO)_nPCl_{3-n}$	mmol	Et_3Al mmol			Me-1,4-HD	Conjugated C_7-diene	Residue
11	1	$(C_6H_5O)_3P$	2	10	0.3	140	21.9	2.6	1.3
12	1	$(C_6H_5O)_3P$	1	10	0.3	140	15.5	0.3	2.8
13	0.5	$(C_6H_5O)PCl_2$	1	4	0.6	120	51.5	0.9	1.7
14	0.5	PCl_3	1	4	0.6	90	48.2	0.4	1.7

TABLE 3. EFFECT OF PHOSPHORUS COMPONENT UPON THE CATALYTIC ACTIVITY

$(C_6H_5O)_nPCl_{3-n}$	$Et_3Al/CoCl_2$ molar ratio	Time min	Product (g)		
			1,4-HD	2,4-HD	Residue
$(C_6H_5O)_3P$	20	50	4.6	trace	0.5
	10	50	1.3	0	0.2
$(C_6H_5O)_2PCl$	20	50	7.9	trace	0.5
	10	50	17.5	0	0.6
	6	50	0.1	0	0.1
$(C_6H_5O)PCl_2$	20	50	4.1	0.2	0.3
	10	50	41.7	1.2	0.5
	6	50	27.1	0.5	1.3
PCl_3	20	50	7.9	trace	0.3
	10	50	38.2	1.0	0.9
	6	30	39.8	0.6	0.7

Reaction conditions: $CoCl_2$ 0.5 mmol, $(C_6H_5O)_nPCl_{3-n}$ 1 mmol, toluene 5 m*l*, butadiene 0.6 mol, ethylene 40 kg/cm², 60°C

$RhCl_3$ catalyst[6] have been reported to afford a mixture of the geometrical isomers of 1,4-hexadiene.

The product corresponds to the 1,4-addition of a C-H bond of ethylene to butadiene. In unsymmetrical 1,3-dienes, there are two possible modes of the addition of ethylene. Isoprene reacted with ethylene to afford 4-methyl-1, *cis*-4-hexadiene and 5-methyl-1,4-hexadiene (in a ratio of 84 : 16) in about a 90% yield (Table 2). This reaction proceeded more slowly than that of butadiene with ethylene (Fig. 2). 1,3-Pentadiene reacted with ethylene to give 3-methyl-1,*cis*-4-hexadiene and 1,*cis*-4-heptadiene in a ratio of 91 : 9. The *trans* isomer of 1,3-pentadiene was found to be consumed faster than the *cis* isomer. These ratios of the products show that a vinyl moiety of ethylene attaches to the terminal carbon atom of the substituted double bond of a 1,3-diene system rather than to that of the non-substituted one.

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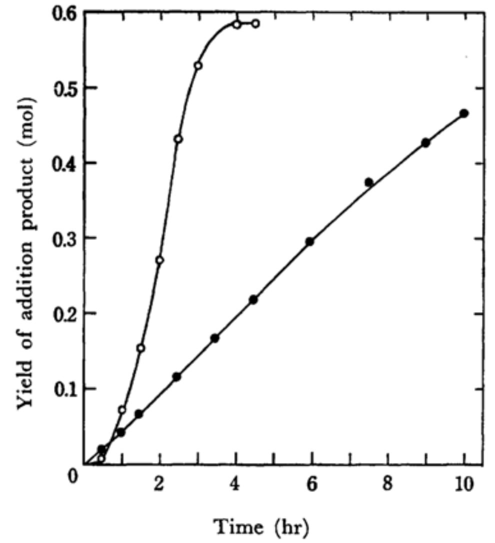


Fig. 2. Reaction of butadiene and isoprene with ethylene.
The same reaction conditions as shown in Fig. 1
○ butadiene, ● isoprene

The activity of the catalyst has been found to be strongly influenced by the nature of the trivalent phosphorus components. The results obtained by using different kinds of phosphorus components are listed in Tables 1, 3, and 4. Although the activity of the catalyst containing trialkyl phosphite was low, the catalyst containing triphenyl phosphite showed quite a high activity. The replacement of the butoxyl groups of tri-*n*-butyl phosphite or the phenoxyl groups of triphenyl phosphite by chlorine atoms increased the catalytic activity remarkably. The effect of the number of chlorine atoms in $(C_6H_5O)_nPCl_{3-n}$ upon the catalytic activity is summarized in Table 3. The results show that the phosphorus compound with more chlorine atoms directly bonded to the phosphorus atom is the more effective component of the catalyst. The effectiveness of the phosphorus components increases in the following order: $(C_6H_5O)_3P < (C_6H_5O)_2PCl < (C_6H_5O)PCl_2 < PCl_3$. In the catalyst system containing triphenyl phosphite, the higher molar ratio of triethylaluminum to cobalt chloride shows a higher activity. However, the catalyst systems of which phosphorus components have at least one P-Cl bond show a maximum activity at an appropriate molar ratio, as is shown in Table 3.

The results of the reaction using methyl or chlorine-substituted triphenyl phosphite as a catalyst component are summarized in Table 4. Tris(chlorophenyl)phosphites were more effective components than tritolyl phosphites. The effect of the *ortho*-substituents on the catalytic activity was quite large compared with that of the *para*-substituents. The *ortho*-substituted phenyl phosphites are arranged in the order of increasing effectiveness: $(o\text{-}CH_3C_6H_4O)_3P < (C_6H_5O)_3P < (o\text{-}ClC_6H_4O)_3P$.

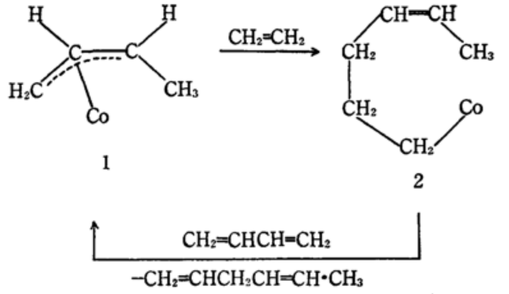
TABLE 4. EFFECT OF A SUBSTITUENT OF TRIARYL PHOSPHITE UPON THE CATALYTIC ACTIVITY

Triaryl phosphite	Yield of 1,4-HD (g)
$(o\text{-}ClC_6H_4O)_3P$	25.9
$(p\text{-}ClC_6H_4O)_3P$	18.5
$(C_6H_5O)_3P$	17.5
$(p\text{-}CH_3C_6H_4O)_3P$	15.0
$(m\text{-}CH_3C_6H_4O)_3P$	12.3
$(o\text{-}CH_3C_6H_4O)_3P$	4.8

Reaction conditions: $CoCl_2$ 0.5 mmol, triaryl phosphite 2 mmol, Et_3Al 12 mmol, toluene 20 cc, butadiene 0.6 mol, ethylene 40 kg/cm², 80°C, 1.5 hr

Discussion

An organoaluminum compound has been found to reduce a cobalt compound to yield a cobalt hydride complex.[7] It is known that a cobalt hydride complex adds to 1,3-dienes to give substituted π-allylcobalt complexes.[8] Recently, a substituted π-allylcobalt complex has been recognized as an important intermediate in the linear dimerization of butadiene by the $CoCl_2\text{-}Al(C_2H_5)_3$ catalyst system.[9] These facts suggest that the most probable intermediates in this reaction are substituted π-allylcobalt complexes coordinated with the phosphorus compounds. The reaction is believed to proceed through the following steps: the addition of ethylene to the 1-methyl-π-allylcobalt complex, **1**, and the subsequent reaction of the 4-hexenylcobalt intermediate, **2**, with butadiene. A 1-methyl-π-allylcobalt complex may exist in two isomeric forms, *syn* and *anti*. Since the 1,4-hexadiene obtained consists only of the *cis* isomer, the 1-methyl-π-allyl group must be bonded to the cobalt atom in the *anti* form, **1**.



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The investigation of the effect of the phosphorus component upon the catalytic activity indicates that a less basic phosphorus component accelerates the reaction. Triphenyl phosphite has been reported to be less basic than triethyl phosphite,10) as is to be expected from the electron-attracting property of a phenyl group. The former compound is a more effective catalyst component than the latter. The electron-attracting ability of a chlorine atom is expected to be greater than those of alkoxyl and phenoxyl groups. Therefore, the basicities of the phosphorus compounds would decrease in the following order: $(n\text{-}C_4H_9O)_3P > n\text{-}C_4H_9OPCl_2$; $(C_6H_5O)_3P > (C_6H_5O)_2PCl > (C_6H_5O)PCl_2 > PCl_3$. This order accords with the increasing order of the activities of the phosphorus components.

The introduction of a substituent on each phenyl group of triphenyl phosphite affected the catalytic activity. An electron-attracting substituent accelerated the reaction, while an electron-donating substituent retarded the reaction, as expected. The increasing order of the inductive effect of the substituents is: *para* < *meta* < *ortho*. A remarkable effect of the *ortho* substituents was observed.

The catalyst systems the phosphorus components of which has P-Cl bonds were deactivated by excess triethylaluminum (Table 3). It has been reported that a P-Cl bond has been alkylated by trialkylaluminum.11,12) This deactivation of the catalyst would be due to the alkylation of the P-Cl bond of the phosphorus components by triethylaluminum. The alkylation is accompanied by an increase in the basicity of the phosphorus components, which results in a decrease in the catalytic activity.

Trivalent phosphorus compounds can participate in both σ- and π-bonding in transition metal complexes. A decrease in the electron density on the phosphorus atom is believed to increase the π-bonding ability of the phosphorus ligand. The above results indicate that the π-bonding character of the Co-P bond of the catalyst species greatly affects the activity of the catalyst.

Experimental

Butadiene was purified by vaporization from a mixture of the liquefied diene and triethylaluminum. Isoprene and 1,3-pentadiene were distilled over calcium hydride. The solvents were refluxed over a K-Na alloy prior to distillation.

Triethyl phosphite, tri-*n*-butyl phosphite, triphenyl phosphite, and phosphorus trichloride were purified by distillation. Tris(*o*-chlorophenyl) phosphite, tris(*p*-chlorophenyl) phosphite, tri-*o*-tolyl phosphite, tri-*m*-tolyl phosphite, and tri-*p*-tolyl phosphite were each prepared by the addition of phosphorus trichloride to a *n*-hexane solution of the corresponding phenol and pyridine. *n*-Butyl phosphorodichloridite13) and diphenyl phosphorochloridite14) were prepared by the previously-reported methods. Phenyl phosphorodichloridite was synthesized by the following method. In a 1 *l* flask, 411 g (3 mol) of phosphorus trichloride were gently refluxed, and then 188 g (2 mol) of phenol were added. A vigorous evolution of hydrogen chloride occurred. After the addition, the unreacted phosphorus trichloride was removed under reduced pressure. Phenyl phosphorodichloridite distilled at 71°C/3 mmHg; 195 g (50% yield based on phenol). All of the above phosphorus compounds were distilled under a vacuum. Anhydrous cobalt chloride was prepared by the reaction of cobalt acetate with acetyl chloride.15)

Addition of Ethylene to Butadiene. A 100 m*l* autoclave was charged with 20 m*l* of toluene, 5.0 m*l* of *n*-heptane (as an internal standard for gas chromatographic analysis), 0.065 g (0.5 mmol) of cobalt chloride, and 0.620 g (2 mmol) of triphenyl phosphite. After the gas within the autoclave has been replaced by ethylene, 52 m*l* (0.6 mol) of liquefied butadiene and a toluene solution of triethylaluminum (12 mmol) were added. The resultant mixture was stirred under ethylene pressure (40 kg/cm^2) at 80°C. The results are shown in Fig. 1.

Addition of Ethylene to Isoprene. A 100 m*l* autoclave was charged with 20 m*l* of xylene, 0.130 g (1 mmol) of cobalt chloride, 1.240 g (4 mmol) of triphenyl phosphite, 21.0 g (0.3 mol) of isoprene, and a xylene solution of triethylaluminum (20 mmol). The resultant mixture was stirred under ethylene pressure (40 kg/cm^2) at 80°C for 2 hr. The reaction product was decomposed with methanol and dilute hydrochloric acid. The oily layer was analyzed by gas chromatography using a squalane column. It contained 25.3 g (88% yield) of a mixture of 4-methyl-1,*cis*-4-hexadiene and 5-methyl-1,4-hexadiene and 2.6 g of C_7-conjugated dienes. The ratio of 4-methyl-1,4-hexadiene to 5-methyl-1,4-hexadiene was determined to be 84 : 16 by gas chromatography using a silver nitrate-benzyl cyanide column.

Addition of Ethylene to 1,3-Pentadiene. A 100-m*l* autoclave was charged with 10 m*l* of toluene, 0.065 g (0.5 mmol) of cobalt chloride, 0.620 g (2 mmol) of triphenyl phosphite, 20.4 g of 1,3-pentadiene (*trans-cis* ratio 66 : 34, purity 89%), and a toluene solution of triethylaluminum (12 mmol). The resultant mixture was stirred under ethylene pressure (40 kg/cm^2) at 80°C for 2 hr, yielding 13.8 g of 3-methyl-1,*cis*-4-hexadiene and 1.4 g of 1,*cis*-4-heptadiene in a 91% yield based on the 1,3-pentadiene consumed. The recovered 1,3-pentadiene consisted of 38% *trans* isomer and 62% *cis* isomer.

The addition products were identified by a comparison of their infrared spectra and gas chromatographic retention times with those of authentic samples.3)

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