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Stereospecific Synthesis of 1,4-Dienes. IV.[1] The Catalytic Behavior of the Ethylenebis(diphenylphosphine) Complex of Iron(0)

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A zerovalent iron complex, $Fe(Ph_2P{\cdot}CH_2CH_2{\cdot}PPh_2)_2{\cdot}C_2H_4$, catalyzes addition of ethylene to butadiene to afford 1 : 1 adducts consisting of 1,*cis*-4-hexadiene, 1,3-hexadiene, 2,4-hexadiene and 1,5-hexadiene, and 2 : 1 adducts. The combination of the iron complex and a Lewis acid (triethylaluminum, diethylaluminum chloride, ethylaluminum dichloride and boron trifluoride etherate) gives 1,*cis*-4-hexadiene much more selectively. The most efficient Lewis acid component for the synthesis of 1,*cis*-4-hexadiene is diethylaluminum chloride.

There are several reports on the preparation of 1,4-dienes by addition of ethylene to 1,3-dienes using the iron-based catalysts.[2-5] The binary system consisting of iron(III) acetylacetonate and triethylaluminum[2], and the ternary system consisting of ferric chloride, ditertiaryphosphine and an organoaluminum compound[3] were reported to catalyze the reaction of ethylene with butadiene to afford 1,4-hexadiene.

In connection with investigation of the reducing property of the organoaluminum compounds in these catalyst systems, the reaction of iron(III) acetylacetonate with ethoxydiethylaluminum was carried out in the presence of ethylenebis(diphenylphosphine), and a zerovalent iron complex, $Fe(Ph_2P{\cdot}CH_2CH_2{\cdot}PPh_2)_2{\cdot}C_2H_4$, was isolated.[6] This fact suggests that one of the functions of the organoaluminum compounds in the catalyst systems is the reduction of the iron compounds to a zerovalent iron complex. It has been confirmed that this diphosphine complex catalyzed the reaction of butadiene with ethylene. This work was undertaken to study the catalytic behavior of the diphosphine complex in this reaction.

Results and Discussion

The diphosphine complex, $Fe(Ph_2P{\cdot}CH_2CH_2{\cdot}PPh_2)_2{\cdot}C_2H_4$ (hereafter the iron complex), was found to catalyze addition of ethylene to butadiene to afford 1 : 1 adducts consisting of 1,*cis*-4-hexadiene, 1,3-hexadiene, 2,4-hexadiene and 1,5-hexadiene, and 2 : 1 adducts. The 2 : 1 adducts were major products. The reaction was carried out at 85°C under ethylene pressure of 40 kg/cm^2. The result is shown in Table 1. 1,5-Hexadiene and the 2 : 1 adducts were not obtained in the iron(III) acetylacetonate-triethylaluminum catalyzed reaction.[2] The former compound was identified by comparison of its infrared spectrum and gas chromatographic retention time with those of an authentic sample. The gas chromatographic analysis of the 2 : 1 adducts using a squalane capillary column (90 m) showed that they contained four components. The molecular weights of these components were determined by mass spectroscopy to be 110 (C_8H_{14}). However, separation of these four components by preparative gas chromatography using a squalane column was unsuccessful, and hence further characterization of the adducts was not possible.

Addition of a Lewis acid to the iron complex changed remarkably the distribution of the products. The results are summarized in Tables 1

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[1] Part III. G. Hata and A. Miyake, This Bulletin, **41**, 2443 (1968).

[2] G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964); G. Hata and D. Aoki *J. Org. Chem.*, **32**, 3754 (1967).

[3] M. Iwamoto and S. Yuguchi, *ibid.*, **31**, 4290 (1966).

[4] M. Iwamoto and S. Yuguchi, This Bulletin, **39**, 2001 (1966).

[5] A. Carbonaro, A. Greco and G. Dall'Asta, *Tetrahedron Letters*, **1967**, 2037.

[6] G. Hata, H. Kondo and A. Miyake, *J. Am. Chem. Soc.*, **90**, 2278 (1968).

TABLE 1. REACTION OF BUTADIENE WITH ETHYLENE BY IRON COMPLEX CATALYST AND IRON COMPLEX-$Al(C_2H_5)_3$ CATALYST SYSTEM

$Al(C_2H_5)_3$/Fe complex molar ratio	Products (g)					
	1,5-HD	1,4-HD	1,3-HD	2,4-HD	C_8 Dienes	Residue
0	0.5	0.9	2.5	1.7	7.0	1.1
4	2.3	2.6	1.4	1.4	9.7	0.8
8	1.4	5.0	1.8	0.6	4.2	0.8
16	0.9	7.9	1.2	0.4	2.7	1.7

HD=hexadiene
Reaction conditions: $Fe(Ph_2P\cdot CH_2CH_2\cdot PPh_2)_2\cdot C_2H_4$ 0.5 mmol, toluene 30 m*l*, ethylene, 40 kg/cm^2, 85°C.

TABLE 2. REACTIONS BY IRON COMPLEX-LEWIS ACID CATALYST SYSTEM

Exp. No.	Lewis acid (mmol)		Temp °C	Time min	Products (g)	
					1,4-HD	Residue
1	$(C_2H_5)_2AlCl$	(4)	30	90	2.2	0.1
2	$(C_2H_5)_2AlCl$	(8)	50	90	19.2	0.7
3	$(C_2H_5)_2AlCl$	(4)	80	5	22.6	0.5
4	$(C_2H_5)_2AlCl$	(1)	50	90	0.4	0.3
5	$C_2H_5AlCl_2$	(1)	50	45	2.3	1.0
6	$C_2H_5AlCl_2$	(4)	50	45	1.1	2.1
7	$C_2H_5AlCl_2$	(1)	80	30	20.8	0.8
8	$BF_3\cdot O(C_2H_5)_2$	(1)	80	100	1.2	0.3

Reaction conditions: $Fe(Ph_2P\cdot CH_2CH_2CH_2\cdot PPh_2)\cdot C_2H_4$ 0.5 mmol, butadiene 0.3 mol, toluene 10 m*l*, ethylene 40 kg/cm^2.

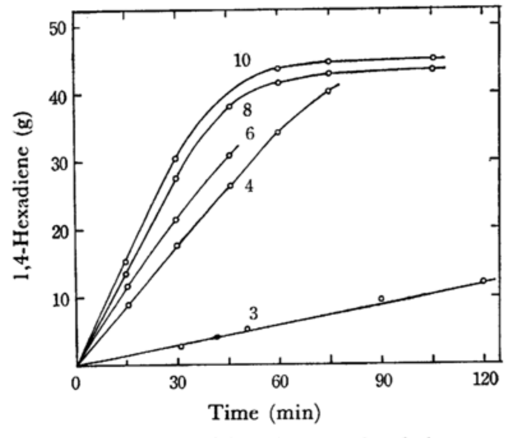

Fig. 1. Reaction of butadiene with ethylene. Reaction conditions: $Fe(Ph_2P\cdot CH_2CH_2\cdot PPh_2)_2\cdot C_2H_4$ 0.5 mmol, toluene 20 m*l*, C_4H_6 0.6 mol, C_2H_4 40 kg/cm^2, 50°C. The numbers in the table show molar ratios of $(C_2H_5)_2AlCl$ to the iron complex.

and 2. The combination of the iron complex and diethylaluminum chloride catalyzed the reaction of butadiene with ethylene to give 1,*cis*-4-hexadiene in high yield (95%). This reaction occurred at 30°C and proceeded very rapidly at 80°C (Table 2). The effect of the molar ratio of the catalyst components on the catalytic activity is shown in Fig. 1. At the molar ratios larger than 3, the reaction proceeded quickly. The catalyst system containing ethylaluminum dichloride and boron trifluoride etherate also afforded the 1,4-diene selectively. However, these Lewis acids were not so effective components, as compared with diethylaluminum chloride, because of decomposition of the catalyst during the reaction. The decomposition of the catalyst containing ethylaluminum dichloride occurs at the early stage of the reaction. When the reaction was conducted under the same conditions as listed in Run No. 7 of Table 2 except stirring for 20 min before introduction of ethylene (40 kg/cm^2), this system showed a quite low activity and only 0.2 g of 1,4-hexadiene was obtained. Almost all of the employed butadiene was recovered. This observation indicates that the catalyst decomposed during the stirring for 20 min. In contrast to these catalyst systems, the system containing triethylaluminum as a Lewis acid component gave the same products as obtained in the reaction catalyzed by the iron complex alone. However, the distribution of the products was different and the formation of 1,*cis*-4-hexadiene increased. The molar ratio of triethylaluminum to the iron complex affected the distribution of the products as shown in Table 1. At a high molar ratio, the behavior of the catalyst resembled that of the combination of the iron complex and diethylaluminum chloride, and the major product was 1,*cis*-4-hexadiene.

The function of the Lewis acids in these catalyst systems is presumably the removal of the coordinated diphosphine from the iron complex to leave a coordination site for butadiene. The stronger Lewis acid should accomplish this removal more effectively. In fact, diethylaluminum chloride is much more effective than triethylaluminum as a catalyst component for the selective synthesis of 1,*cis*-4-hexadiene. The former aluminum compound is a stronger Lewis acid than the latter. Lewis acidity of organoaluminum compounds toward a Lewis base is correlated to the complex formation between both compounds. The easiness of the complex formation of organoaluminum compounds with a Lewis base is in the following order: $C_2H_5AlCl_2 > (C_2H_5)_2AlCl > (C_2H_5)_3Al > (C_2H_5)_2AlOC_2H_5$.⁷⁾ Although ethylaluminum dichloride, the strongest Lewis acid, decomposes the catalyst during the reaction, this organoaluminum compound is more effective than diethylaluminum chloride at the low molar ratio (2 : 1) of the Lewis acid to the iron complex.

The catalyst system consisting of the iron complex and diethylaluminum chloride affords 1,4-hexadiene in a high selectivity as compared with the iron(III) acetylacetonate-triethylaluminum catalyst system.²⁾ This fact suggests the coordination of one molecule of the diphosphine in the catalyst species, which would interrupt coordination of another molecule of butadiene and suppress oligomerization of butadiene.⁸⁾

The formation of 1,4-hexadiene occurs through transfer of a hydrogen atom of ethylene to butadiene. The mechanism of the hydrogen transfer, however, is not clear.

The mixture of iron(III) acetylacetonate, ethylenebis(diphenylphosphine) and diethylaluminum chloride showed the same catalytic activity as that of the iron complex and diethylaluminum chloride, and gave 1,*cis*-4-hexadiene in 91% yield. This fact indicates that diethylaluminum chloride in the former system acts as a reducing agent as well as a Lewis acid.

The reaction of isoprene with ethylene by the ternary system gave a mixture of 4-methyl- and 5-methyl-1,4-hexadiene in 92% yield. The ratio of the former diene to the latter was 75 : 25 (at 70°C). 1,3-Pentadiene reacted with ethylene to afford 3-methyl-1,*cis*-4-hexadiene and 1,*cis*-4-heptadiene in a ratio of 85 : 15. The preferential addition of ethylene occurs at the methyl substituted side, and this is the characteristic of the reaction by the iron(III) acetylacetonate-triethylaluminum catalyst system.²⁾ In the reaction catalyzed by the latter system, the above ratios were 57 : 43 and 70 : 30 at 30°C, respectively.

Experimental

Reaction of Butadiene with Ethylene. (1) A 100 m*l* autoclave was flashed with ethylene and then charged with liquid butadiene, a toluene solution of the complex, $Fe(Ph_2PCH_2CH_2PPh_2)_2 \cdot C_2H_4$, which was prepared by the method described previously,⁶⁾ and a toluene solution of the Lewis acid. The resultant solution was stirred under ethylene pressure of 40 kg/cm². 1,*cis*-4-Hexadiene, 1,3-hexadiene and 1,5-hexadiene were separated by preparative gas chromatography and identified by comparison of their infrared spectra and gas chromatographic retention times with those of authentic samples. 2,4-Hexadiene was characterized by gas chromatographic analysis. The C_8 hydrocarbons were separated by gas chromatography on a squalane capillary column (90 m) at 40°C into four components, which were analyzed by mass spectroscopy. All of their spectra showed parent peaks at $m/e=110$ (C_8H_{14}).

(2) A mixture of 15 m*l* of toluene, 0.3 mol of butadiene, 0.177 g (0.5 mmol) of iron(III) acetylacetonate, 0.478 g (1.2 mmol) of ethylenebis(diphenylphosphine) and 8 mmol of diethylaluminum chloride was stirred at 80°C under ethylene pressure of 40 kg/cm² for 30 min. The yield of 1,*cis*-4-hexadiene was 22.5 g (91%).

Reaction of Isoprene with Ethylene. A 100 m*l* autoclave was charged with 21.0 g (0.3 mol) of isoprene, 20 m*l* of xylene, 0.177 g (0.5 mmol) of iron(III) acetylacetonate, 0.478 g (1.2 mmol) of ethylenebis(diphenylphosphine) and 8 mmol of diethylaluminum chloride. The resultant mixture was stirred at 70°C under ethylene pressure of 40 kg/cm² for 2 hr. Gas chromatographic analysis showed that the reaction mixture contained 26.6 g (92% yield) of a mixture of 4-methyl-1,*cis*-4-hexadiene and 5-methyl-1,4-hexadiene.²⁾ The ratio of the products was determined by gas chromatography using a silver nitrate-benzyl cyanide column.

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7) H. Lehmkuhl, *Angew. Chem.*, **75**, 1090 (1963).

8) M. Hidai, Y. Uchida and A. Misono, This Bulletin, **38**, 1243 (1965).