Reaction of *cis*-1,4-Hexadiene with Iron Pentacarbonyl

Jitsuo Kiji[*1] and Masao Iwamoto

Central Research Lab., Toyo Rayon Company, Ltd., Sonoyama, Otsu

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Nonconjugated dienes, such as 1,4-pentadiene and 1,5-hexadiene, react with iron pentacarbonyl ($Fe(CO)_5$) to give diene-iron tricarbonyl complexes, in which the ligand is an isomeric conjugated hydrocarbon.[1] Recently, *cis*-1,4-hexadiene has been easily obtainable by the reaction of butadiene with ethylene using a cobalt catalyst.[2] It is of interest now to study the migration of double bonds and to compare the structure of the ligand with that of free diene. The present paper is concerned with the reaction of *cis*-1,4-hexadiene with $Fe(CO)_5$.

The reaction of this hydrocarbon with $Fe(CO)_5$ affords the *trans*-1,3-hexadiene-iron tricarbonyl complex (I), plus a small amount of the *trans,trans*-2,4-hexadiene complex(II). The reactions were carried out in a stainless steel autoclave. The results are summarized in Table 1, in which the results obtained by the reactions of 1,3-hexadiene and 2,4-hexadiene are also included. The results of the elemental analysis of the complex obtained from 1,4-hexadiene were as follows; Found: C, 49.3; H, 4.8%. Calcd for $C_9H_{10}FeO_3$ (($(C_6H_{10})Fe(CO)_3$):

Table 1. Reactions of hexadiene with $Fe(CO)_5$

						Composition of hexadiene (%)					
						The liganded diene		The recovered diene			
No.	$Fe(CO)_5$ mol	Hexadiene isomer (mol)	Temp. °C	Time hr	Product g	1,3-	*trans,trans*-2,4-	1,3-	*cis*-1,4-	*trans,trans*-2,4-	*trans,cis*-2,4-
1	0.075	1.4—(0.13)	120	20	0.9	60	40	1.5	81.9	9.4	7.2
2	0.11	1.4—(0.13)	130	24	4.3[c]	70	30	5.2	2.0	59.0	33.8
3	0.11	2.4[a]—(0.13)	170	20	3.5[d]	n.d.		n.d.			
4	0.033	1.3[b]—(0.038)	150	24	2.7[e]	92	8	54.5	—	45.5	—

a) Prepared by isomerization of *cis*-1,4-hexadiene with $CoCl_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$-$(C_2H_5)_3Al$ catalyst; Composition of the isomers; *trans,trans*- 5%, *trans,cis*- 65%, *cis,cis*- 30%.

b) Prepared by the reaction of butadiene with ethylene using $Co(C_5H_7O_2)_3$-$(C_2H_5)_3Al$ catalyst and purified by a preparative chromatography. Purity 92%.

c) 67—70°C/6 mmHg. d) 73—74°C/7 mmHg. e) 80—82°C/8 mmHg.

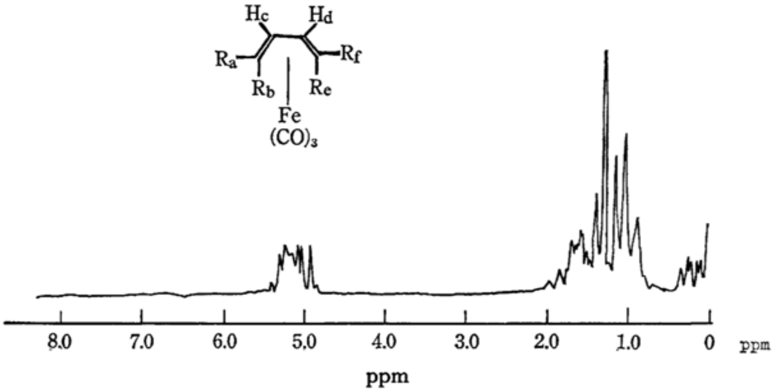


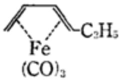
Fig. 1. NMR spectrum of the complex.
I: R_a, R_b, and R_e=H, R_f=C_2H_5. II: R_b and R_e=H, R_a and R_f=CH_3.

[*1] Present address: Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto.

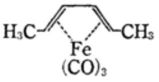
[1] R. West and F. G. A. Stone, ed., "Advances in Organometallic Chemistry." Vol. 1, Academic Press, New York (1964), p. 13.

[2] M. Iwamoto and S. Yuguchi, This Bulletin, **41**, 150 (1968).

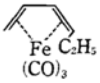
C, 48.6; H, 4.5%. The NMR spectrum is shown in Fig. 1. The multiplets centered at 5.1 and 0.2 ppm were assigned to the olefinic protons of I, and that at 5.0 ppm, to that of II.³⁾ The absence of the peaks in the 2—3 ppm range shows that the *cis*-1,3-hexadiene complex (III) and the *trans,cis*-2,4-hexadiene complex (IV) were not formed.



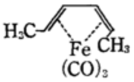
(I)



(II)



(III)



(IV)

To examine the structure of the liganded dienes, an ethereal solution of the complex was treated with an excess 10% aqueous solution of ferric chloride at 0°C for 3 hr.⁴⁾ After it had been washed with water, the ethereal solution was gas-chromatographically analyzed. (Apiezon Grease L; column, 5 m; 100°C). *trans*-1,3-Hexadiene and *trans,trans*-2,4-hexadiene were detected (Table 1), with the former predominant. The reaction of $Fe(CO)_5$ with an isomeric mixture of 2,4-hexadiene (the *cis,trans*-isomer was predominant) gave II as the sole product.[*2] The compositions of the hexadiene recovered as unreacted hydrocarbon are also shown in Table 1; it was indicative that 1,4-hexadiene was catalytically isomerized to the conjugated dienes with $Fe(CO)_5$. The fact that a considerable amount of *trans,trans*-2,4-hexadiene was found in both the unreacted dienes and the liganded dienes shows that *cis-trans* isomerization occurred during the reaction with $Fe(CO)_5$. The isomerization by $Fe(CO)_5$ proceeded so as to favor the end products lacking *cis*-substitutions, though the isomerization of *cis*-1,4-hexadiene with a carbanion (*e. g.*, $CH_3SOCH_2^-$ at 50°C) or a Ziegler catalyst (*e. g.*, $CoCl_2(DPE)_2$[*3]-Et_3Al, at 150°C) gave an isomeric mixture containing *trans, cis*-2,4-hexadiene as the main component.

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3) G. F. Emerson, J. E. Mahler, R. Kochhar and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).

4) H. W. Whitlock, Jr., and Y. N. Chuah, *Inorg. Chem.*, **4**, 424 (1965).

[*2] It has been reported (*cf.* Ref. 3) that *cis,trans*-2,4-hexadiene reacts with $Fe(CO)_5$ at 110°C to yield *cis,trans*-2,4-hexadiene-iron tricarbonyl (yield, 6%).

[*3] DPE: $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$