BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2001—2004 (1966)

The Reaction of Butadiene with Ethylene. I.* A New Synthesis of 3-Methyl-1, 4-pentadiene

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(Received January 20, 1966)

3-Methyl-1, 4-pentadiene, 1, 4-hexadiene, and 1, 3-hexadiene were obtained, in the weight ratio of 2 : 1 : 2, by the use of a ternary catalyst consisting of a combination of ferric chloride and triethylaluminum, with triphenylphosphine as the third component. The products were identified by means of gas chromatography, infrared spectroscopy, mass spectroscopy, NMR, and hydrogenation. The effects of the catalyst compositions and the reaction conditions on the yield and the product composition were also studied. In order to obtain the C_6-dienes in the weight ratio described above, the following conditions are desirable; temperature 20—30°C, P/Fe mole ratio 1—2, Al/Fe mole ratio 3—5, and a high ethylene pressure. Although the use of several phosphorus compounds as the third component in the catalyst instead of triphenyl phosphine was investigated, these compounds were ineffective in the selective formation of C_6-dienes. It was suggested that the compound which serves as the third component in the catalyst plays an important role.

A linear dimerization of butadiene has been made by means of catalytic actions of cobalt complex catalysts$^{1-4)}$ and a ternary catalyst consisting of a combination of ferric chloride and alkylaluminum compounds, with triphenyl phosphine as the third component.$^{5)}$

In the course of our study of the preparation of 1, 4-hexadiene from butadiene and ethylene, we have found that the ternary catalyst mentioned above catalyzed the formation of a mixture of C_6-dienes, i. e., 3-methyl-1, 4-pentadiene, 1, 4-hexadiene, and 1, 3-hexadiene. This paper will describe the identification of the reaction products and will study the factors affecting the reaction.

3-Methyl-1, 4-pentadiene was recently obtained by the thermally-initiated reaction of acetylene with 2-butene.$^{6)}$ The preparation procedure described in this paper is also a convenient method to obtain the compound.

Experimental

Reagents.—Butadiene (purity: 98%) was purified by passing it through a series of columns filled with a ethyleneglycol-metallic sodium solution, potassium hydroxide pellets, activated alumina, and a triethylaluminum-liquid paraffin solution (about 10%) successively; it was then condensed in a measuring vessel kept in a dry ice - methanol bath. Ethylene (Nihon Petrochemical Co.) was used without further purification. Toluene (Udex grade) was purified by distillation under nitrogen. Anhydrous ferric chloride was sublimated in vacuo before use. The triphenyl phosphine and other compounds used as the third component in the catalysts were obtained commercially. Triethylaluminum (Ethyl Corp.) was uesd without purification.

Reaction Procedure.—A 200 ml. stainless steel autoclave equipped with a magnetic stirrer was used as the reactor. Calculated amounts of anhydrous ferric chloride, toluene, triphenyl phoshine, butadiene, and triethylaluminum were introduced, in that order, into the reactor, which had been flushed with nitrogen in advance. During the procedure, the reactor was kept at below −20°C to prevent the evaporation of butadiene. Then the reactor was closed and kept at reaction temperatures. The reaction was carried out under a constant ethylene pressure while the mixture was continuously being stirred. After a proper reaction time the catalyst was quenched by adding a small amount of methanol, and then the reaction mixture was washed with water containing a small amount of dilute hydrochloric acid.

The organic layer was thoroughly washed with water, dried with anhydrous sodium sulfate, and disitlled. A fraction which was distilled at bath temperature of up to 200°C was collected and analyzed by gas chromatography. The compositions of the products were calculated by the area ratios of the gas chromatogram. Higher boiling materials were recorded as a residue.

Analysis.—For the gas chromatographic analysis of the reaction products, copper tubing (4 mm. in diameter and 3 m. long) packed with Apiezon Grease L was used. For the hydrogenated product, a Golay column (45 m. long) coated with Apiezon Grease L was used. The purifications of 3-methyl-1, 4-pentadiene

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* Presented at the 14th Symposium on Polymer Science, Kyoto, October, 1965.

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and 1, 3-hexadiene in order to identify them were carried out after a preparative gas chromatography (Yanagimoto model GCS-1003). All analyses were carried out at 100°C, using helium as the carrier gas.

The infrared spectra of samples were determined by a Hitachi infrared spectrometer, model EPI-S. The NMR spectrum of 3-methyl-1, 4-pentadiene was obtained by a Varian A60 apparatus at 60Mc. Mass spectra were taken, in order to determine the molecular weight and in order to identify the skeletal structures of the hydrogenated products, by a Hitachi mass spectrometer, RMU-6.

Results and Discussion

The Identification of the Reaction Products. —The gas chromatogram (Fig. 1) of the reaction mixture indicates that it includes several components. The peaks 1, 2, 4, 6, 7, 8, and 9 in Fig. 1 were identified as air, unreacted butadiene, 1, 4-hexadiene, cyclohexene, 3-methyl-1, 4, 6-heptatriene, toluene, and 1, 3, 6-octatriene respectively by comparing their retention times with those of authentic samples. For the identification of the unknown products, each of the components of peaks 3 and 5 was collected by preparative gas chromatography. The infrared spectrum of the component of peak 3 showed the presence of a terminal double bond (910 and 992 cm^{-1}) and a methyl group (1377 cm^{-1}). The spectrum of the component of peak 5 showed the presence of a conjugated double bond (1600 and 1640 cm^{-1}), a trans-double bond (960 cm^{-1}), a terminal double bond (898 and 1002 cm^{-1}), and a methyl group (1374 cm^{-1}). Since both components had the same molecular peak, at *m/e* 82, in their mass spectra, these compounds must be hydrocarbons with the same six carbon atoms. The distillate, b. p. 45—60°C, was collected by distillation at atmospheric pressure and was hydrogenated at room temperature with hydrogen, using palladium black as the catalyst. Before the hydrogenation, the distillate contained three components and peaks 1′, 2′, and 3′ in Fig. 2A corresponded to the peaks 3, 4, and 5 respectively in Fig. 1. However, the hydrogenated product contained only two components (Fig. 2B). The area ratio of the peak 1′ to the two other peaks combined in Fig. 2A was about 1 to 2, and the ratio of the two peaks in Fig. 2B was about 1 to 1.8. It may be considered, therefore, that the components of the peaks 2′ and 3′ were hydrogenated to the same saturated hydrocarbon. Both components in the hydrogenated product had the same molecular peak, at m/e 86. This suggests that each of the components of peaks 3 and 5 in Fig. 1 has two double bonds, those of the component of peak 3 being of the vinyl type and those of the component of peak 5 being conjugated. The pattern coefficients of 3-methylpentane and *n*-hexane in API data agreed entirely with the mass spectral data of the two components of the hydrogenated product. In the NMR spectrum of the component of peak 3, the doublet at 8.9 τ indicates the presence of a secondary methyl group, while the multiplet at 7.14 τ indicates the presence of the following partial structure: $=CH-CH(CH_3)-CH=$.

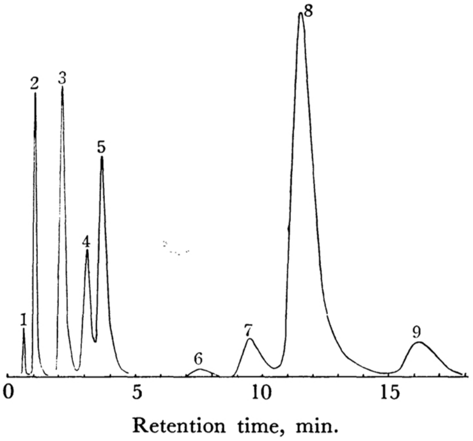

Fig. 1. Gas chromatogram of the reaction mixture of Exp. 5 in Table II.

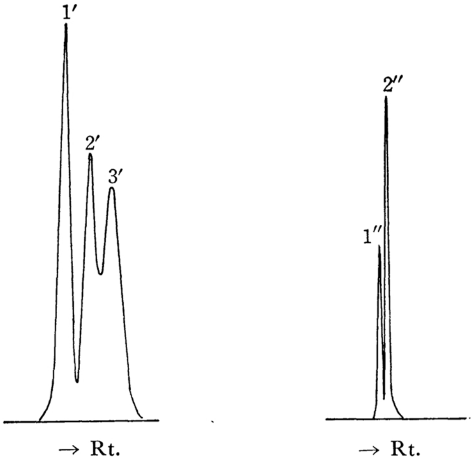

Fig. 2. Gas chromatograms, A: Before hydrogenation, B: After hydrogenation.

It is quite reasonable to conclude, from the evidence described above, that the component of peak 3 is 3-methyl-1, 4-pentadiene and that the component of peak 5 is 1, 3-hexadiene.

The Reaction of Butadiene with Ethylene. —The reaction of butadiene with ethylene can form the following four compounds as a 1 : 1 addition product; 3-methyl-1, 4-pentadiene, 1, 4-hexadiene, 1, 3-hexadiene, and cyclohexene.

The reaction conditions were examined using a catalyst consisting of a combination ferric chloride, triphenyl phosphine, and triethylaluminum. The catalyst containing no triphenyl phosphine was inactive in the reaction of butadiene with

Table I. Effect of the catalyst composition in $FeCl_3$-$P(C_6H_5)_3$-$(C_2H_5)_3Al$ system*[1]

Exp. No.	P/Fe mole ratio	Al/Fe mole ratio	Yield of product, g.			C_6-dienes composition, %*[3]		
			C_6-dienes	BD dimer*[2]	Residue	MPD	1,4-HD	1,3-HD
1	1	3.6	6.1	6.7	2.9	31	31	28
2	1.5	3.6	9.1	3.0	0.6	33.7	24.4	41.9
3	2	3.6	9.2	5.4	1.5	29.5	29.9	40.6
4	1.5	1	0.9	0.3	0.1	29.4	24.8	45.8
5	1.5	1.8	3.2	0.5	0.9	30.1	27.6	42.3
6	1.5	5	5.1	4.9	1.1	28.1	34.3	37.6
7	1.5	7.3	2.5	4.3	1.5	21.5	45	33.5

*[1] Toluene 50 g., Butadiene 13.4 g., $FeCl_3$ 0.35 g., Ethylene pressure 40 kg./cm², 50°C, 3 hr.

*[2] Butadiene linear dimers.

*[3] MPD = 3-methyl-1,4-pentadiene, 1,4-HD = 1,4-hexadiene, 1,3-HD = 1,3-hexadiene.

Table II. Effects of the reaction temperature

Exp. No.	1	2	3	4	5	6
$FeCl_3$ (g.)	0.32	0.32	0.32	0.32	0.52	0.35
$P(C_6H_5)_3$ (g.)	0.78	0.78	0.78	0.78	1.2	0.8
$(C_2H_5)_3Al$ (g.)	0.83	0.83	0.83	0.83	1.5	0.9
Toluene (g.)	50	50	50	66	16	50
Butadiene (g.)	13.4	13.4	13.4	27	46.9	30.1
Ethylene (kg./cm²)	40	40	40	100	100	100
Temperature (°C)	20	50	70	20	30	30
Reaction time (hr.)	3	3	3	5	17.5	16.5
Product (g.)						
MPD	3.3	3.1	1.4	9.7	14.1	9.5
1,4-HD	1.7	2.2	1.6	4.9	7.8	5
1,3-HD	3.4	3.8	1.9	9.8	15	10.8
The others combined*[1]	6	4.8	6.8	8.6	18	10.2

*[1] Cyclohexene, butadiene dimers, and residue are included.

Table III. Variation of the third component*[1]

Exp. No.	The third component	Mole ratio*[2]	Butadiene g.	Products, g.		
				C_6-dienes	BD dimers	Residue
1	$As(C_6H_5)_3$	1.5	30.1	0.25	0.5	1.8
2	$Sb(C_6H_5)_3$	1.5	24.1	0.22	trace	1.4
3	PCl_3	1.5	26.8	0.5	0.2	1.2
4	$POCl_3$	1.5	26.8	1.7	7.8	1.9
5	$P(OC_4H_9)_3$	1.5	26.8	0.3	20	5.1
6	$PO(C_6H_4)_3$	1.5	26.8	3.0	7.3	2.2
7	$P(OC_2H_5)_3$	1.5	13.4	0.8	8.9	4.5
8	$P(OC_6H_5)_3$	1	13.4	0.3	0.6	1.0
9	$P(OC_6H_5)_2$ $(OC_6H_4CH_3)$	1	13.4	3.4	1.2	1.9
10	$P(C_4H_9)_3$	1	13.4	3.5	3.3	2.1

*[1] $FeCl_3$ 0.32 g., $(C_2H_5)_3Al$ 0.83 g., Toluene 60 g.
Exp. No. 1—6 Ethylene pressure 60 kg./cm², 20°C, 5 hr.
Exp. No. 7—10 Ethylene pressure 100 kg./cm², 30°C, 16 hr.

*[2] The third component/$FeCl_3$ mole ratio.

ethylene. The effects of the catalyst composition are shown in Table I. In all the runs, considerable side reactions of butadiene (the dienylation of butadiene) occurred, giving linear dimers as a by-product. The dienylation of ethylene gave 1,3-hexadiene, which amounted to about 40 wt.% of the C_6-dienes obtained. The formation rate of 1,3-hexadiene decreased slightly at higher Al/Fe mole ratios. A proper Al/Fe mole ratio of high activity probably exists in the range from two to five. The reaction temperature affected the yield of C_6-dienes and their composition (Table II). The reactions proceeded smoothly even at 20°C. More 3-methyl-1,4-pentadiene than 1,4-hexadiene was formed at lower reaction temperatures. The weight ratio of three C_6-dienes, i. e., 3-methyl-1, 4-pentadiene, 1, 4-hexadiene, and 1, 3-hexadiene, in the products obtained at 20—30°C was about 2 : 1 : 2. The average formation ratio of C_6-dienes to butadiene dimers in ten runs under the same conditions was 4.5 to 1. Therefore, the average yield of 3-methyl-1, 4-pentadiene was about 25—30%. The condition of high ethylene pressure was advantageous to the formation of C_6-dienes. As the butadiene initially-charged increased, the yield of C_6-dienes decreased because more butadiene dimers and higher boiling materials were formed. As is shown in Table III, the butadiene dimers were predominantly formed by the catalysts containing phosphorus oxychloride, triphenyl phoshine oxide, tributyl phosphite or triethyl phosphite rather than triphenyl phoshine. Both triphenyl arsine and triphenyl stibine were ineffective. It may be considered that phosphorus compounds as the third component in the catalyst played an important role, one which might characterize the nature of the active site. These experimental results suggest that the variations in the reaction conditions affect the composition of the reaction products only slightly but that the third component affects it intensely. According to this suggestion, a search for the proper third component has been carried out and a new catalyst for the exclusive formation of 1, 4-hexadiene has been found. The details will be reported shortly.

In order to form the linear 1 : 1 addition products, a hydrogen atom transfer from either butadiene or ethylene is indispensable. The catalyst, consisting of cobalt compound and metal alkyl, studied by Wittenberg⁴⁾ promoted exclusively the hydrogen transfer from butadinene to give 1, 3-hexadiene; however, the catalyst, consisting of $Fe(C_5H_7O_2)_3$ and triethylaluminum, studied by Hata⁷⁾ promoted the transfer from ethylene to give 1, 4-hexadiene. In contrast, the ternary catalyst in this study can promote both reactions; further, the hydrogen which is transferred from ethylene adds to butadiene in two ways, that is, by 1, 2-addition to give 3-methyl-1, 4-pentadiene and by 1, 4-addition to give 1, 4-hexadiene. These ways are analogous to the linear dimerization of butadiene to give 3-methyl-1, 4, 6-heptatriene and 1, 3, 6-octatriene. The direction of the addition of hydrogen in all cases obeyed Markownikov's rule. Which monomers release a hydrogen atom is probably governed by the nature of the active site that is characterized by the combined effects of the catalyst components. Hydrogen transfer may occur in the same way as in the dimerzation of butadiene, through an intermediate with a hydrogen-metal bond.⁸⁾ However, it is not clear whether the hydrogen in the intermediate is a protonic or a hydride ion. Since a more detailed study of the mechanism of the hydrogen transfer reaction is required, this will be the subject of a future report.

The authors wish to express their thanks to Dr. H. Kobayashi for permission to publish this work. They wish also to thank Mr. I. Shionoya for his kindness in measuring the mass spectra.

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