Preparation of 3-Methyl-1,4-heptadiene, 3-Ethyl-1,4-hexadiene, and Methyl-1,4-hexadienes[1,2]

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We have found that the catalyst consisting of cobaltous chloride–1,2-bis(diphenylphosphino)ethane complex and triethylaluminum was very effective for a selective synthesis of 1,4-hexadiene from a reaction of butadiene with ethylene.[3] In the course of the investigation of the reaction conditions, it was found that higher oligomers were obtained as main products besides 1,4-hexadiene and its rearranged product, namely, 2,4-hexadiene, when a vigorous reaction took place at the initial stage. The oligomers were found to be C_8-dienes and the same C_8-dienes were formed in a reaction of 1,4-hexadiene with ethylene and that of 2,4-hexadiene with ethylene. As shown in Table I, the reaction of 1,4-hexadiene with ethylene in the presence of the catalyst described above yielded a mixture of 2,4-hexadiene and C_8-dienes.

TABLE I

TEMPERATURE DEPENDENCE OF THE REACTION OF 1,4-HEXADIENE WITH ETHYLENE[a]

	Amount, g				
Products	100°	120°	130°	140°	150°
1,4-Hexadiene	12	3.6	1.0	0.6	0.1
1,3-Hexadiene		0.2	0.3	0.3	0.3
2,4-Hexadiene	11.7	24.9	31.4	31.8	36.3
3-Methyl-1,4-heptadiene	25.3	12.4	9.1	7.8	5.2
3-Ethyl-1,4-hexadiene	7.7	15.8	12.9	13.3	9.7
Residue	0.9	1.6	2.2	3.3	4.8

[a] Reaction conditions: 1,4-hexadiene (56 g), the cobalt complex (0.24 g), triethylaluminum (1.5 g), ethylene (40 kg/cm^2), and 2 hr.

Conversion of 1,4-hexadiene increased with the reaction temperature, but at higher reaction temperature the formation of the C_8-dienes decreased. The formation of 1,4-hexadiene was carried out selectively in a temperature range 80–100°,[2] but at temperatures higher than 100° the initial product, namely 1,4-hexadiene, isomerized to the conjugated dienes to a considerable extent. A reaction temperature higher than 100° is not favorable for oligomer formation. Composition of the C_8-dienes depended upon the reaction temperature. After purification by preparative vpc they were identified as 3-methyl-1,4-heptadiene and 3-ethyl-1,4-hexadiene by analysis of nmr, infrared, and mass spectra.

Rearrangement of 1,4-hexadiene to 2,4-hexadiene proceeded almost quantitatively in the presence of the cobalt complex catalyst. In the isomerized product, a very small quantity of 1,3-hexadiene was always detected by vpc. Treatment of the 2,4-isomer with the cobalt complex catalyst at 80° for 21 hr gave a slight increase in the amount of the 1,3- and 1,4-isomers. 1,3-Hexadiene prepared separately and purified by distillation, contained 3.7% of the 2,4-isomer and about 1% of the 1,4-isomer. The 1,3-hexadiene was contacted with the cobalt complex catalyst at 80° for 20 hr and analysis of the reaction mixture by vpc showed an increase in the proportions of the 2,4- and 1,4-isomers.

Reaction of 2,4-hexadiene with ethylene also yielded two C_8-dienes. It was found that a few per cent of the 1,4-isomer was contained in the reaction mixture but the 1,3-isomer was not detected. The content of 3-ethyl-1,4-hexadiene in the C_8-dienes obtained from 2,4-hexadiene was lower than that in the C_8-dienes obtained from the 1,4-isomer. Pure 1,3-hexadiene reacted rapidly with ethylene to give the C_8-dienes composed of almost 3-ethyl-1,4-hexadiene. As in the reaction of butadiene with ethylene, if an exclusive 1,4 addition of ethylene to a conjugated diene in the presence of the cobalt complex catalyst is assumed to proceed in the above reactions, it is considered that 3-ethyl-1,4-hexadiene and 3-methyl-1,4-heptadiene are derived from 1,3-hexadiene and the 2,4-isomer, respectively. Although the mixtures obtained by reactions of isomerization and oligomer formation contained only a trace quantity of 1,3-hexadiene, the formation of the two C_8-dienes may occur by an intermediate formation of the 1,3-isomer and its rapid reaction with ethylene. Similar results were reported by Alderson and co-workers for the rhodium chloride catalyzed reaction of butadiene with ethylene.[4]

Butadiene reacted readily with propylene to give a mixture of *cis*-2-methyl-1,4-hexadiene and small quantities of two by-products detected by vpc. A selectivity for the formation of the 1,4-addition product, namely *cis*-2-methyl-1,4-hexadiene, based on the reacted butadiene, was found to be over 60%. As in the case of 1,4-hexadiene formation, reaction of isoprene with ethylene was characterized by rapidity and high selectivity (Table II). Methyl-1,4-hexadiene thus obtained contained a 4-methyl isomer as a major component (80–100%) with the 5-methyl isomer. Also in

TABLE II

RESULTS OF SYNTHESIS OF METHYL-1,4-HEXADIENES[a]

	No.		
	1	2	3
Toluene, ml	50	50	0
Water content of isoprene,[b] ppm	28.5	28.5	22.4
Isoprene, g	34	34	68
Triethylaluminum, g	0.42	0.29	0.42
Al/Co molar ratio	42.3	29.6	42.3
Temp, °C	80–95	80–96	80–98
Products, g			
1,4-Dienes	45.0	39.8	51.2
Conjugated dienes	0.43	0.15	0.76
Residue	0.3	0.2	0.75
Conversion, %	95.8	83.8	55.5
Selectivity,[c] %	98.5	99.0	97.2

[a] Reaction conditions: the cobalt complex (0.08 g), ethylene (40 kg/cm^2), and 1 hr. [b] Karl-Fischer method. [c] 1,4-Dienes (moles)/isoprene converted (moles) × 100.

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[1] This work is part V of "Reaction of Butadiene with Ethylene."

[2] Part IV: M. Iwamoto and S. Yuguchi, *Bull. Chem. Soc. Japan*, in press.

[3] A. Miyake, G. Hata, M. Iwamoto, and S. Yuguchi, The Seventh World Petroleum Conference, Panel Discussion, 22nd Section, No. 3, Mexico City, April 1967.

[4] T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1965).

this reaction, isomerization of the 1,4-dienes to 2,4-isomers proceeded at a higher reaction temperature, and the second molecule of ethylene added to the conjugated dienes to yield C_9-dienes. As the isomerization increased, more of the 4-methyl isomer was found in the product. It indicated that the 5-methyl isomer was apt to isomerize to the conjugated isomer more easily than the 4-methyl isomer did. Careful control of the reaction temperature is desirable to obtain methyl-1,4-hexadienes selectively.

Experimental Section

Reaction of Butadiene with Ethylene.—A 200-ml pressure vessel equipped with a magnetic stirrer was charged with 50 ml of 1,2-dichloroethane, 33.5 g of liquefied butadiene, 0.09 g of cobaltous chloride–1,2-bis(diphenylphosphino)ethane complex, and 0.456 g of pure triethylaluminum and then was tightly closed. After the temperature was raised to 80°, ethylene was injected directly from a cylinder to a pressure of 40 kg/cm^2 and the pressure was held constant for 2 hr. A remarkable absorption of ethylene was observed during the first 0.5 hr. After cooling to room temperature, unreacted ethylene was vented and the catalyst was deactivated by adding a small quantity of methanol, and then the reaction mixture was washed with water containing a small amount of hydrochloric acid. A distillation of the organic phase was performed at atmospheric pressure. The distillate taken up to a bath temperature of 200° was assayed by vpc (relative peak areas) with toluene as an internal standard (Apiezon Grease L packing column 3 m, 100°), and 0.22 g of 1,4-hexadiene, 2.8 g of 2,4-hexadiene, and 38.3 g of a major product were found. Further, analysis by vpc using a 5-m, paraffin wax coated column showed that the main product consisted of two components. Each of the two components was purified by preparative vpc. Since both components showed the same molecular peak at m/e 110 in the mass spectra, they should be C_8-dienes. The characteristic absorptions of the terminal double bond, *cis* unsaturation, methyl group, and nonconjugated system were shown in the infrared spectra. Hydrogenation of the components gave a mixture of 3-methylheptane and 3-ethylhexane, which were identified by their mass spectral cracking patterns. From these data it was concluded that two kinds of C_8-diene were 3-methyl-1,4-heptadiene and 3-ethyl-1,4-hexadiene. Proton nmr spectra were consistent with these structures.

Reaction of 1,4-Hexadiene with Ethylene.—Reactions of 1-*cis*-4-hexadiene with ethylene were carried out in a manner similar to that described above. A mixture of 56 g of 1,4-hexadiene, 0.24 g of the cobalt complex, and 1.5 g of triethylaluminum was charged into the vessel. At various reaction temperatures, a series of reactions was carried out for 2 hr under a constant ethylene pressure of 40 kg/cm^2. The results are shown in Table I.

Isomerization of 1,4-Hexadiene.—A 2-l. pressure vessel was charged with 1 kg of 1-*cis*-4-hexadiene, 2 g of the cobalt complex, and 12.5 g of triethylaluminum. The temperature was raised to 150° during 3.5 hr and was kept there for an additional 4 hr. The product consisted of 0.7% of 1,4-hexadiene, 2.1% of 1,3-isomer, and 97.2% of the 2,4-isomer which was fractionally distilled under atmospheric pressure to give the 2,4-isomer of 99.8% purity. The 2,4-isomer thus obtained contained three structural isomers and their proportion was slightly varied with the reaction conditions. In order to determine the proportion, analysis by vpc using a column packed with benzylcyanide-silver nitrate coated on Celite 545 was carried out at 35°.

Reaction of 2,4-Hexadiene with Ethylene.—A mixture of 56 g of 2,4-hexadiene, 0.24 g of the cobalt complex, and 1.5 g of triethylaluminum was charged into the vessel and then ethylene was injected at a pressure of 40 kg/cm^2. The reaction was carried out at 100° for 19 hr. After a work-up similar to that already described, 48.6 g of a distillate, bp 80–130°, was obtained. The distillate gave 28.1 g of the C_8-dienes, which consisted of 84.2% of 3-methyl-1,4-heptadiene and 15.8% of 3-ethyl-1,4-hexadiene.

Preparation of 1,3-Hexadiene.—To dried ethanol, deoxygenated and saturated with butadiene in the 2-l. autoclave, 6.4 g of cobaltous nitrate hexahydrate and 3.8 g of sodium borohydride were added and dissolved. About 400 g of butadiene was condensed into the autoclave. Under 60 kg/cm^2 of ethylene pressure at 60°, reaction was carried out for 17.5 hr. The reaction mixture consisted of C_6-dienes and linear dimers of butadiene. 1,3-Hexadiene of 96.5% purity was obtained by a rectification through 1.5-m packed column.

Reaction of 1,3-Hexadiene with Ethylene.—The reaction mixture consisted of 50 ml of toluene, 15 g of the 1,3-hexadiene, 0.24 g of the cobalt complex, and 1.5 g of triethylaluminum which were charged into the vessel. The reaction was carried out under 40 kg/cm^2 of ethylene pressure at 80° for 18.5 hr. The C_8-dienes thus obtained consisted of 3.3% of 3-methyl-1,4-heptadiene and 96.7% of 3-ethyl-1,4-hexadiene.

Reaction of Butadiene with Propylene.—The reaction vessel was charged with 20 ml of 1,2-dichloroethane, 0.08 g of the cobalt complex, 0.83 g of triethylaluminum, 22.8 g of butadiene, and 28 g of propylene. The temperature was raised to 80° and was held there for 5 hr. After the similar work-up, the diene fraction obtained by 1,1 addition was composed of three components. They were separated by preparative vpc, and a major product which was 84.7% of the fraction, was identified by infrared and mass spectra as 2-methyl-1,4-hexadiene. Two minor components were identified, by means of infrared and mass spectra and hydrogenation over a palladium catalyst, as *n*-heptadiene (10.8%) and 2-methyl-1,3-hexadiene (4.8%).

Reaction of Isoprene with Ethylene.—In a similar manner described above, a mixture of 20 ml of 1,2-dichloroethane, 102 g of isoprene, 0.08 g of the cobalt complex, and 0.83 g of triethylaluminum was treated under 40 kg/cm^2 of ethylene pressure at 100°. Immediately, a reaction was started and a vigorous absorption of ethylene and a rapid rise of the reaction temperature were occurred. A good control of the reaction temperature is needed in order to obtain a selective formation of methyl-1,4-hexadiene. After the work-up, a fraction containing 67.9 g of methyl-1,4-hexadienes and 5.6 g of conjugated dienes was separated. A conversion based on the charged isoprene was 51%. Analysis of the isomer content of methyl-1,4-hexadienes by vpc using a column packed with benzylcyanide-silver nitrate on Celite 545 at 45° showed that 4-methyl-1,4-hexadiene in this example was 81.3%. The results are shown in Table II.

The Reaction of Di-*n*-butylcadmium with Derivatives of Ketal Acids[1]

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Perhaps no other method of ketone preparation has the scope of the method utilizing organocadmium reagents in their reaction with acid chlorides[2] or mixed carboxylic–carbonic anhydrides.[3] However, treatment of either the acid chloride or the mixed carboxylic–carbonic anhydride I from 2-methyl-2-(3-carboxyethyl)-1,3-dioxolane[4] with di-*n*-butylcadmium gave only the dioxocane derivative II and none of the expected ketone I ($R = n\text{-}C_4H_9$). The structure of II is based on the infrared spectrum (5.75 μ), the nmr spectrum (a two-hydrogen multiplet centered at τ 5.64 for $-CH_2O\overset{|}{C}{=}O$ and a two-hydrogen multiplet centered at τ 6.38 for $-OCH_2-$), and the elemental analysis. Basic hydrolysis of II followed by esterification with diazomethane gave the hydroxy ester III while hydrolysis with 3 *N*

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[2] J. Cason, *Chem. Rev.*, **40**, 15 (1947).

[3] D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **22**, 245 (1957).

[4] C. K. Warren and B. C. L. Weedon, *J. Chem. Soc.*, 3979 (1958).