CHEMISTRY LETTERS, pp. 1047-1048, 1972. Published by the Chemical Society of Japan

CODIMERIZATION OF ETHYLENE AND BUTADIENE BY THREE-COMPONENT CATALYSTS CONSISTING OF PALLADIUM SALT, LEWIS ACID, AND TERTIARY PHOSPHINE

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A novel catalyst system consisting of palladium salt, Lewis acid, and tertiary phosphine was found to be effective for the codimerization of ethylene and butadiene in a solvent containing nitrobenzene. This catalyst system is characterised by the fact that any reducing agent is not included.

Many catalyst systems have been developed for the codimerization of ethylene and butadiene. Typical catalyst systems for this reaction contain iron, cobalt, nickel or rhodium1), and most of them, except a few*), also contain reducing agents such as aluminum alkyls. On the other hand, palladium-containing catalysts are known to promote the dimerization of ethylene or butadiene. For example, palladium chloride was used for the dimerization of ethylene2), and low-valent palladium complexes were used for the dimerization of butadiene3). However, palladium-containing catalysts useful for the codimerization of ethylene and butadiene have scarcely been reported, and the catalyst patented by Goodrich Company4) is the only codimerization catalyst containing palladium. This latter catalyst also contains a reducing agent such as diethylaluminum chloride.

Now we wish to report a novel catalyst system which comprises a palladium salt and is characterised by the fact that any reducing agent is not included. This catalyst system consists of palladium salts, tertiary phosphines and Lewis acids, and promotes the codimerization of ethylene with butadiene in a solvent containing nitrobenzene to afford 1,4-hexadiene and 2,4-hexadiene. A typical example of the experiment with this catalyst system will be described below.

Fifteen ml of nitrobenzene, 15 ml of decalin, 0.15 mmol of di-μ-chlorodi-π-allyldipalladium, 0.3 mmol of triphenyl phosphine, 0.6 mmol of aluminum chloride, and 115 mmol of butadiene were introduced into a stainless steel autoclave (100 ml) filled with an inert gas. The mixture was stirred for 1 hr at 60°C under constant ethylene pressure (13 kg/cm^2), and the reaction product was then separated from the catalyst by distillation. The distillate contained 30 mmol of 1,4-hexadiene (cis/trans = 1/19.5), 12 mmol of 2,4-hexadiene (trans,trans/cis,trans = 4.8/1), 1 mmol of butadiene linear dimer, and unreacted butadiene. Their yields were determined by a gas-chromatographic procedure, and the structures were determined unambiguously by their IR and NMR spectra.

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*) A few catalysts containing no reducing agent, such as $Fe(Ph_2P\cdot CH_2CH_2\cdot PPh_2)_2\cdot C_2H_4$-$BF_3\cdot O(C_2H_5)_2$, $CoH(Ph_2P\cdot CH_2CH_2\cdot PPh_2)_2$-phenols or aluminum trichloride, and $RhCl_3$, have been reported to promote the reaction of ethylene and butadiene1-i,h,j,g).

The principal products obtained by the use of the catalyst system were the same as those obtained by the use of $RhCl_3$ catalyst1g).

Table 1 summarizes the results obtained by conducting similar experiments.

TABLE 1 Codimerization of Ethylene and Butadiene by Palladium Salt-Lewis Acid-Tertiary Phosphine Catalyst

(Butadiene 115 mmol, Ethylene 13 kg/cm^2, Nitrobenzene 15 ml, Decalin 15 ml)

Palladium compound (0.15 mmol)	Lewis acid (0.6 mmol)	Phosphine (0.3 mmol)	React. temp. °C	React. time hr	Hexadiene* yield %	1,4-hexadiene / (1,4- + 2,4-hexadienes) mole ratio
$(\pi\text{-}C_3H_5PdCl)_2$**	$AlCl_3$	Ph_3P	60	1	37	0.73
$(\pi\text{-}C_3H_5PdCl)_2$	$AlCl_3$	Ph_3P	80	1	58***	0.43
$(\pi\text{-}C_3H_5PdCl)_2$	$AlCl_3$	Ph_3P	80	3	53****	0.16
$(\pi\text{-}C_3H_5PdCl)_2$	$BF_3\cdot OEt_2$*****	Ph_3P	60	1	11	0.92
$(Ph_3P)_2PdCl_2$******	$AlCl_3$	-	80	1	32	0.73
$(Bu_3P)_2PdCl_2$******	$AlCl_3$	-	80	1	46	0.72

*) Hexadiene fraction was composed of 1,4-hexadiene and 2,4-hexadiene. Yield is expressed in mole per cent based on the amount of butadiene employed. **) Di-μ-chlorodi-π-allyldipalladium. ***) Besides hexadiene fraction, C_8-diene fraction was obtained in a yield of 1 %. ****) Besides hexadiene fraction, C_8-diene fraction (consisting mainly of 3-methyl-1,4-heptadiene and 3-ethyl-1,4-hexadiene) was obtained in a yield of 21 %. *****) 1.2 mmol of $BF_3\cdot OEt_2$ was used. ******) 0.3 mmol of $(R_3P)_2PdCl_2$ was used.

It is considered that 1,4-hexadiene is first formed and isomerized to 2,4-hexadiene. At a somewhat higher temperature and prolonged reaction time (e.g., 80 °C, 3 hr), C_8-dienes were formed as by-products. The formation of the C_8-dienes, as indicated by Alderson1g) who worked with $RhCl_3$ catalyst, may be due to the addition of ethylene to conjugated hexadienes resulting from the isomerization of 1,4-hexadiene.

The use of nitrobenzene as a component of the solvent is very important to keep the reaction homogeneous and also to suppress the formation of oily polymer from butadiene.

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(Received August 30, 1972)