Codimerization of Ethylene and Styrene Catalyzed by Bis(triphenylphosphine)σ-aryl Nickel(II) Halide - Trifluoroboron Etherate

Noboru Kawata, Ken-ichi Maruya, Tsutomu Mizoroki, and Atsumu Ozaki
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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Bis(triphenylphosphine)σ-aryl nickel(II) halide (RNi($P\phi_3)_2X$, R=*o*-tolyl, 1-naphthyl, mesityl; X=halide ion; $\phi=C_6H_5$) has been reported to dimerize ethylene selectively, when trifluoroboron etherate coexists with the nickel complex.[1] It has been found that this catalyst system has also a high catalytic activity for the selective codimerization of ethylene and styrene. Rhodium(III) chloride[2] and palladium(II) chloride[3] have been reported to catalyze the codimerization of ethylene and styrene. The former gives 2-phenyl-2-butenes under a high pressure of ethylene and the latter 1-phenyl-butenes. The present catalyst system, however, gives 3-phenyl-1-butene selectively without accompanying 1-phenyl-butenes as is shown in the table. No activity for the codimerization was observed in the absence of trifluoroboron etherate, nor when bis(triphenylphosphine)nickel(II) dibromide was used in place of the σ-aryl nickel complex. The selectivity of codimerization into 3-phenyl-1-butene depends considerably on the σ-aryl ligand of the nickel complex, although catalytic activity seems to be independent of it. When most of styrene was consumed, 3-phenyl-1-butene initially formed was gradually isomerized into *cis*- and *trans*-2-phenyl-2-butenes, and they further reacted with ethylene to form 3-methyl-3-phenyl-1-pentene, causing decrease in the selectivity of the codimerization, while only trace amounts of the isomerized products of 3-phenyl-1-butene were observed in the products obtained under the reaction conditions given in Table 1. The results can be understood by assuming the formation of a nickel hydride, with which π-coordinated styrene is transformed into α-ethylbenzene-nickel intermediate followed by insertion of ethylene to give 3-phenyl-1-butene. The hydrogen source of the nickel hydride was elucidated by means of the dimerization of deutero ethylene.[4]

Table 1. Codimerization of ethylene and styrene

R-Ni($P\phi_3)_2$Br	Styrene consumed (mmol)	3-Phenyl-1-butene obtained (mmol)	Selectivity[a] (%)
R=*o*-Tolyl	12.7	7.2	58
R=1-Naphthyl	12.9	10.3	80
R=Mesityl	12.7	11.6	91

Nickel complex, 1.0 mmol; $BF_3\cdot O(C_2H_5)_2$, 1.0 mmol; Styrene, 17.4 mmol; CH_2Cl_2, 30 m*l*; temp. 0°C; React. time, 15 min.

a) Based on the styrene consumed. The other products were styrene dimers, *etc.*

The experimental procedure is illustrated by the following ethylene-styrene codimerization. To a solution of bis(triphenylphosphine)-1-naphthyl nickel(II) bromide (1 mmol) in dry methylene chloride (30 m*l*) under nitrogen in a 50 m*l* flask were added trifluoroboron etherate (1 mmol) and styrene (17.4 mmol). The nitrogen gas in the flask had been evacuated at the temperature of liquid nitrogen before ethylene gas (700 mmHg) was introduced at 0°C with vigorous stirring. The temperature of the flask was kept at 0°C for 15 min with continuous supply of ethylene. The reaction was then terminated by adding aqueous sodium hydroxide solution (5 m*l*). Most of the volatile substances such as ethylene, butenes and the solvent were transferred into another flask by means of a liquid nitrogen trap before non-volatile materials were extracted with *n*-hexane. The amounts of non-volatile materials were quantitatively determined by gas chromatography. The results are shown in the table. 3-phenyl-1-butene (phenyl, 2.75 τ(m); CH_2=CH–, 4.0 τ (m), 4.97 τ(d); $-\underset{|}{C}H-$, 6.67 τ(m); $-CH_3$, 8.7 τ(d)) and its isomers isolated by a fractional gas chromatography were identified by NMR spectroscopy, and were also checked by hydrogenation into 2-phenyl-butane with Raney nickel catalyst.

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