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

——— CATALYTIC SYNTHESIS OF 1-PHENYL-1,4-HEXADIENE ———

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The codimerization of styrene and butadiene has not been reported, though it has been known that the cooligomerization of styrene and butadiene is catalyzed by nickel-containing complex catalysts to give 1-phenyldecatriene.[1]

In this letter, we wish to report that a catalyst system[2] consisting of palladium salt, Lewis acid, and tertiary phosphine is effective for the catalytic synthesis of 1-phenyl-1,4-hexadiene by the codimerization of styrene and butadiene.

A typical experiment was carried out as follows: Thirty milliliters (345 mmol) of butadiene, 20 ml (170 mmol) of styrene, 10 ml of dichloromethane, and a solution of 0.3 mmol of di-μ-chlorobis(π-allyl)dipalladium and 0.6 mmol of trifluoroboron triphenylphosphine complex ($BF_3 \cdot Ph_3P$) in 10 ml of dichloromethane were introduced into a 100-ml autoclave. The mixture was stirred for 1 hr at 100°C. The reaction was then terminated by adding an aqueous solution of sodium carbonate. The reaction mixture was distilled, and the fraction (A) with bp 20-82°/10 mmHg and the fraction (B, 13.1g) with bp 95-100°/4 mmHg were collected. GLC analysis showed that the fraction A contained 8.5 g (82 mmol) of unchanged styrene and 3.0 g (28 mmol) of butadiene dimer, and that the fraction B contained 11.2 g (71 mmol) of 1-phenyl-1,4-hexadiene. The fraction B was subjected to catalytic hydrogenation, and GLC analysis of the product showed that it consisted of 1-phenylhexane (86 %), 2-phenylhexane (3 %), 1-phenyl-3-methylpentane (2 %), and n-dodecane (9 %). 1-Phenyl-1,4-hexadiene fraction was separated from the fraction B by distillation on a spinning band column, and was analysed by GLC, NMR, and IR. GLC showed that the 1-phenyl-1,4-hexadiene consisted of *trans,trans*-isomer (88 %) and *cis,trans*-isomer (12 %). *trans,trans*-1-Phenyl-1,4-hexadiene: bp 94°C/5 mmHg (lit.[3] 122°C/21 mmHg); NMR CH_3-C= 1.65 ppm (3H, m), =C-CH_2-C= 2.8 ppm (2H, m), olefin proton 5.2-6.3 ppm (4H, m), ring proton 7.25 ppm (5H, m); IR *trans* -CH=CH- 965 cm^{-1}, 1640 cm^{-1}.

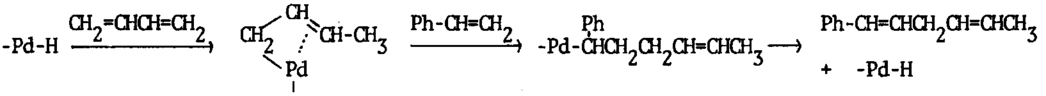
TABLE 1. CODIMERIZATION OF STYRENE AND BUTADIENE
[$(\pi\text{-}C_3H_5PdCl)_2$ 0.15 mmol, $BF_3\cdot Ph_3P$ 0.3 mmol, solvent 20 ml]

Styrene mmol	Butadiene mmol	React. time hr	React. temp. °C	Solvent	1-Phenyl-1,4-hexadiene mmol	Styrene recovered mmol
170	345	2	70	CH_2Cl_2	5	144
170	170	2	100	CH_2Cl_2	37	82
170	170	2	100	Ph-NO_2	52	61
170	345	2	100	Ph-NO_2	46	92
340	170	2	100	Ph-NO_2	75	160

Some results of the experiments using the catalyst system $(\pi\text{-}C_3H_5PdCl)_2\text{-}BF_3\cdot Ph_3P$ are summarized in Table 1. Instead of the $BF_3\cdot Ph_3P$ complex of the above catalyst system, a mixture of equimolecular amounts of $AlCl_3$ and Ph_3P can be used.

It is noteworthy that in the reaction between styrene and butadiene with the present catalyst system the formation of 1-phenyldecatriene, a main product of the corresponding reaction with nickel-containing catalyst, was hardly observed.

The reaction mechanism can be accounted for by assuming the formation of a palladium hydride species, which is proposed, though there is no direct evidence, in the isomerization or other reactions of olefins using palladium salt catalyst:[4]



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