

The Codimerization of Styrene and Butadiene with Three-Component Catalysts Consisting of Palladium Salt, Lewis Acid, and Tertiary Phosphine

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The reaction of styrene and butadiene in the presence of a three-component catalyst consisting of a palladium salt, a Lewis acid, and a tertiary phosphine was investigated. As the three-component catalyst, combinations of such palladium(II) salts as $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$, $(\text{PdCl}_2 \cdot \text{C}_6\text{H}_5\text{CH}=\text{CH}_2)_2$ and $\text{Pd}(\text{acac})_2$, such Lewis acids as BF_3 and AlCl_3 , and such tertiary phosphines as Ph_3P and Bu_3P were adopted. From the reaction, 1-phenyl-1,4-hexadiene (a straight-chain codimer) was obtained as the main product, together with small amounts of branched-chain codimers. The ratio of the 1-phenyl-1,4-hexadiene to the branched-chain codimers was varied to some extent by changing the molar ratio of styrene to butadiene. With an increase in the molar ratio the ratio of 1-phenyl-1,4-hexadiene to the branched-chain codimers decreased. A reaction mechanism for the selective formation of 1-phenyl-1,4-hexadiene which involves the addition of butadiene, in preference to styrene, to a palladium hydride is proposed.

Recently dimerizations and codimerizations of olefins catalyzed by organometallic complexes have attracted much attention because of the utility of the reaction products and the novelty of the type of reaction, and a number of studies have been reported. However, the codimerization between two olefins such as butadiene and styrene, both of which coordinate strongly to catalyst metals, is very difficult; only the cotrimerization of two moles of butadiene with one mole of styrene has been reported.¹⁾

In the course of our study of a three-component catalyst system²⁾ consisting of a palladium salt, a Lewis acid, and a tertiary phosphine, we have found that the codimerization of styrene with butadiene proceeds smoothly by the use of this catalyst system, thus affording 1-phenyl-1,4-hexadiene.³⁾ In the present paper, details of the codimerization, which is the first example of the catalytic synthesis of 1-phenyl-1,4-hexadiene, will be reported.

Experimental

Reagents. Palladium complexes and a 1:1 adduct of boron trifluoride and triphenylphosphine ($\text{BF}_3 \cdot \text{Ph}_3\text{P}$) were synthesized according to the methods described in the literature. $\text{BF}_3 \cdot \text{Ph}_3\text{P}$: mp 176 °C (lit.⁴⁾ mp 175 °C). The nitrobenzene was used after drying with diphosphorus pentoxide. The other reagents were used after drying and purification according to the usual manners.

Synthesis of 1-Phenyl-1,4-hexadiene. Into a 100-ml stainless-steel autoclave cooled in a ethanol-Dry Ice bath, 30 ml (345 mmol) of butadiene, 20 ml (170 mmol) of styrene, 10 ml of dichloromethane, and a solution of 0.6 mmol of $\text{BF}_3 \cdot \text{Ph}_3\text{P}$ and 0.3 mmol of di- μ -chlorobis(π -allyl)dipalladium ($(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$) in 10 ml of dichloromethane were introduced under a nitrogen atmosphere. The mixture was then stirred for 1 h at 100 °C. The unreacted butadiene was purged after cooling, and then a small amount of an aqueous solution of sodium carbonate was added to decompose the catalyst. After the precipitate has been removed by filtration, the reaction mixture was distilled, and a fraction with a bp of 95–100 °C/4 mmHg was collected. GLC analysis of this fraction showed that it contained 11.2 g (71 mmol) of 1-phenyl-1,4-hexadiene. From this fraction, 1-phenyl-1,

4-hexadiene (*trans,trans*-isomer 88%, *cis,trans*-isomer 12%) (bp 94 °C/5 mmHg (lit⁵), 122 °C/21 mmHg)) was easily separated by distillation using a spinning-band column (length, 50 cm).

Codimerization under Various Reaction Conditions. The codimerization reactions shown in Tables 1–4 were carried out in a manner similar to that described above. After the decomposition of the catalyst, the reaction products were analyzed in the following way.

Analysis of the Reaction Products. To the reaction mixture, biphenyl was added as an internal standard. A small amount of aliquots of the reaction mixture and its catalytic hydrogenation product with palladium-charcoal was analyzed by GLC. From the results of the GLC analysis, the yields of 1-phenyl-1,4-hexadiene, individual dimers of butadiene and styrene, and the trimer of butadiene and the composition of the skeleton isomers of the codimer were determined.

The codimers were analyzed using a Golay column after removing the nitrobenzene used as a solvent and the high-boiling products by means of a precut column. Golay column: Silicone DC 550, 45 m $\times$ 0.25 mm ϕ , 130 °C. Carrier gas: N_2 1 ml/min. Precut column: PEG 9000, 40 cm $\times$ 3 mm ϕ . The high-boiling products were analyzed by using a column (Silicone KF 45, 10% Diasolid M, 3 m $\times$ 3 mm ϕ) at 230 °C.

Structure Determination of the Reaction Products. A typical gas chromatogram of the products in the presence of $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3 \cdot \text{Ph}_3\text{P}$ catalyst is shown in Fig. 1. The main components of the reaction products were separated by a combination of fractional distillation and preparative GLC, and their structures were determined by means of IR, NMR, etc.

Peak 1: 1,3,6-Octatriene.

Peak 2: 5-Phenyl-1,3-hexadiene. IR; 1002 cm^{-1} , 898 cm^{-1} , 1648 cm^{-1} ($\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-$). Hydrogenation gave 2-phenylhexane.

Peak 3: 1-Phenyl-3-methyl-1,4-pentadiene. IR; 912 cm^{-1} , 993 cm^{-1} ($-\text{CH}=\text{CH}_2$), 965 cm^{-1} , 1635 cm^{-1} (*trans*- $\text{CH}=\text{CH}-$). Hydrogenation gave 1-phenyl-3-methylpentane.

Peak 4: From the fact that hydrogenation gave dodecane, it was presumed to be dodecatetraene (a trimer of butadiene).

Peaks 5, 6: Since hydrogenation gave 1-phenylhexane, they were presumed to be 1-phenylhexadiene.

Peak 7: *trans,trans*-1-Phenyl-1,4-hexadiene. IR; 963 cm^{-1} , 1650 cm^{-1} (*trans*- $\text{CH}=\text{CH}-$). NMR; 1.65 ppm (3H, m,

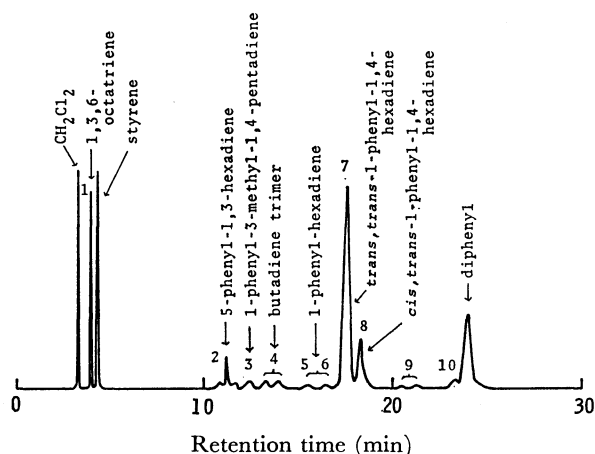


Fig. 1. Gas chromatogram of the compounds obtained by the reaction of butadiene and styrene in the presence of the catalyst consisting of $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$. ($(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ 0.15 mmol, $\text{BF}_3\cdot\text{Ph}_3\text{P}$ 0.3 mmol, $\text{CH}_2\text{-Cl}_2$ 20 ml, styrene 170 mmol, butadiene 170 mmol, reaction time 1 hr, reaction temperature 100 °C). (Column. Gelay column 45 m, temperature 120 °C)

$\text{CH}_3\text{-C=}$, 2.8 ppm (2H, m, $=\text{C-CH}_2\text{-C=}$), 5.2–6.3 ppm (4H, m, olefin proton), 7.25 ppm (5H, m, ring proton). Hydrogenation gave 1-phenylhexane.

Peak 8: *cis,trans*-1-Phenyl-1,4-hexadiene. IR; 963 cm^{-1} , 710 cm^{-1} , 1650 cm^{-1} . Hydrogenation gave 1-phenylhexane.

The constitutions of the products under the conditions adopted in Fig. 1 were approximately as follows: Peak 2, 6%; Peak 3, 2%; Peak 4, 4%; Peak 5+Peak 6, less than 1%; Peak 7, 77%; Peak 8, 11%; Peak 9+Peak 10, less than 1%. The constitutions of the alkylbenzene obtained by hydrogenation of the codimers formed in the above reaction were: 1-phenylhexane 89%, 2-phenylhexane 8%, 1-phenyl-3-methylpentane 3%.

Reaction of $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$, $\text{BF}_3\cdot\text{Ph}_3\text{P}$ and Styrene. To a solution of 1.51 mmol of $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ and 3.03 mmol of $\text{BF}_3\cdot\text{Ph}_3\text{P}$ in 7 ml of nitrobenzene, 33.4 mmol of styrene and 1.586 mmol of decane (as an internal standard) were added under a nitrogen atmosphere, after which the mixture was stirred for 15 min at 40 °C. The resulting mixture was hydrogenated under hydrogen pressure, using palladium-charcoal

in ethanol. From the GLC analysis of the hydrogenation product, the formation of 1.32 mmol of 1-phenylpentane and 0.16 mmol of 2-phenylpentane was detected.

Results and Discussion

Reaction Catalyzed by $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$.

As the catalyst systems consisting of a palladium salt, a Lewis acid, and a tertiary phosphine, various combinations are possible. In the previous papers²⁾ we have reported on various combinations which are active for the codimerization of butadiene with a monoolefin such as ethylene and propylene or for the codimerization of styrene with a monoolefin. In the present study, a catalyst system consisting of a combination of $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ and $\text{BF}_3\cdot\text{Ph}_3\text{P}$ has been mainly used because this catalyst system is comparatively soluble in many solvents.

Composition and Structure of Reaction Products. A gas chromatogram of the products of the reaction of styrene and butadiene in the presence of a typical catalyst system, $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$ (molar ratio=1:2), is shown in Fig. 1. 1-Phenyl-1,4-hexadiene was obtained as the main product; the sum of its *trans,trans*-isomer and *cis,trans*-isomer reached about 88 mol % of the C_{12} -compounds consisting of a codimer of butadiene with styrene and a butadiene trimer, showing the high selectivity of 1-phenyl-1,4-hexadiene. As reaction products, the respective dimers and trimers of butadiene and styrene were also obtained along with the codimer. However, 1-phenyldecatriene, which is known to be the main product of the reaction of styrene and butadiene catalyzed by nickel-containing catalysts,¹⁾ was scarcely obtained at all. This is of interest as a difference resulting from the metal species of the catalysts.

Effect of the Molar Ratio of Styrene to Butadiene: In the present reaction, 1-phenyl-1,4-hexadiene, which has a straight-chain structure, is obtained as the main product. As one of the factors which dominate the structure of the reaction products, the coordination strength of the olefins used can be considered. In a reaction of ethylene and styrene using the same catalyst, as in the present

TABLE 1. EFFECT OF THE MOLAR RATIO OF STYRENE TO BUTADIENE ON THE CODIMERIZATION OF STYRENE AND BUTADIENE WITH THE $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$ CATALYST (Nitrobenzene, 20 ml; $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$, 0.15 mmol; $\text{BF}_3\cdot\text{Ph}_3\text{P}$, 0.3 mmol; 100 °C, 1 h)

Run No.	Butadiene mmol	Styrene mmol	1-Phenyl-1,4-hexadiene		Styrene dimer mmol	Styrene recovd. mmol	Butadiene dimer mmol	Butadiene trimer mmol	Oligomer ^{b)} g	Composition of hydrogenated codimer ^{c)}		
			mmol	(<i>trans</i> %) ^{a)}						1-Ph-Hex ^{d)} %	2-Ph-Hex ^{e)} %	1-Ph-3-Me-Pent ^{f)} %
1	170	540	77	(88)	42	288	8	1	14	86	11	2.6
2	170	350	55	(87)	16	231	10	1	7	88	9	2.7
3	170	170	36	(87)	4	116	15	2	3	90	7	3.0
4	350	170	31	(87)	2	114	25	3	2	91	6	3.1
5	510	170	25	(89)	1	140	36	3	5	92	5	3.1
6	230	150 ^{g)}	35	(87)	3	80	22	6	3	92	5	3.0

a) Amount (%) of the *trans,trans*-isomer in the total 1-phenyl-1,4-hexadiene. b) Amount of the distillation residue obtained by the distillation of the reaction products at 180 °C (bath temp)/4 mmHg. c) Composition of the product obtained by the hydrogenation of the with codimer the palladium-charcoal catalyst. d) 1-Phenylhexane. e) 2-Phenylhexane. f) 1-Phenyl-3-methylpentane. g) Styrene was introduced into the reaction mixture at the rate of 0.2 ml/min throughout the reaction.

study, we have previously reported that no dimerization of ethylene occurs and that the codimers derived from the addition of ethylene to the α -position of styrene are obtained, because styrene coordinates to the catalyst in preference to ethylene.^{2c)} In the present reaction, both styrene and butadiene have a strong coordination ability, so it is of interest which olefin coordinates preferentially to the catalyst and, consequently, how the reaction proceeds. Therefore, the effects of the molar ratio of styrene to butadiene on the reaction were investigated. The results are shown in Table 1.

When the molar ratio was varied from 3/1 to 1/3, the yield of 1-phenyl-1,4-hexadiene decreased with the decrease in the amount of styrene or with the increase in the amount of butadiene. However, the effect of the variation in the amount of butadiene was less than that of the amount of styrene. This appears to show that butadiene coordinates to the catalyst in preference to styrene and that, hence, the effect of the concentration of butadiene is smaller than that of styrene. With the decrease in the amount of styrene relative to butadiene, the formation of the styrene dimer was greatly reduced. This also shows the preferential coordination of butadiene. When distilled, the amount of the residue increased with an increase in the amount of styrene used, and the residue is thought to be composed mainly of an oligomer of styrene.

As for the composition of the alkylbenzene obtained by the hydrogenation of the codimer, with the variation in the molar ratio of butadiene to styrene from 1/3 to 3/1 1-phenylhexane increased from 86 to 92%, and 1-phenyl-3-methylpentane slightly increased from 2.6 to 3.1%, whereas 2-phenylhexane decreased from 11 to 5%. These facts suggest that 1-phenylhexane and 1-phenyl-3-methylpentane are formed by analogous mechanisms, but 2-phenylhexane is formed by a different mechanism. It can be said that the influence of the competitive coordination of styrene and butadiene is revealed as a variation of the composition of the hydrogenation products.

The ratio of the *trans,trans* isomer to *cis,trans*-1-phenyl-

1,4-hexadiene is thought to be in equilibrium, and the ratio was approximately constant, not depending upon the butadiene/styrene ratio.

Effects of Reaction Conditions: The effects of the solvent, the reaction time, the reaction temperature, and the catalyst composition upon the reaction were investigated. The results of the experiments using nitrobenzene as a solvent are shown in Table 2, while those of the experiments using dichloromethane are shown in Table 3. As is clear from the comparison of the results of Run 7 and Run 17, or the results of Run 4 and Run 18, both the yield and the composition of the codimer are little affected by the type of solvent used. However, the separation of nitrobenzene from the reaction products is troublesome because its boiling point is close to those of the products. Therefore, the use of dichloromethane is preferable, and its separation from the products is much easier than that of nitrobenzene.

A greatly increased yield of 1-phenyl-1,4-hexadiene was obtained by the elongation of the reaction time from 1 to 2 h at 100 °C (Runs 7, 8), but by the elongation from 2 to 4 h the yield of 1-phenyl-1,4-hexadiene, the amount of styrene recovered, and the amount of the distillation residue were little affected (Run 9). On the other hand, when the reaction using double amounts of styrene and butadiene was carried out for 4 h, approximately double amounts of 1-phenyl-1,4-hexadiene were obtained (Run 10). Therefore, the results of Run 9 seem to suggest the existence of some coordination equilibrium between the reaction products and monomers and that, because of the equilibrium, the reaction does not proceed.

The codimerization occurred at 70 °C and proceeded smoothly above 100 °C. The reaction between styrene and ethylene, as we have reported in a previous paper,^{2-c)} proceeds easily at 30 °C; on the contrary, the present codimerization does not proceed at 40 °C, showing the influence of the strong coordination of butadiene.

As for the effect of the molar ratio of $\text{BF}_3 \cdot \text{Ph}_3\text{P} / (\pi\text{-C}_3\text{H}_5\text{PdCl})_2$, when the ratio is below 2 (*i.e.*, P/Pd atomic ratio < 1) the yield of 1-phenyl-1,4-hexadiene decreases

TABLE 2. CODIMERIZATION OF STYRENE AND BUTADIENE WITH THE $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3 \cdot \text{Ph}_3\text{P}$ CATALYST UNDER VARIOUS REACTION CONDITIONS
(Nitrobenzene, 20 ml; $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$, 0.15 mmol; styrene, 170 mmol; butadiene, 170 mmol)

Run No.	React. temp °C	React. time h	$\text{BF}_3 \cdot \text{Ph}_3\text{P} : \text{Pd}$ ratio ^{g)}	1-Phenyl-1,4-hexadiene		Styrene dimer mmol	Butadiene dimer mmol	Butadiene trimer mmol	Oligomer ^{b)} g	Composition of hydrogenated codimer ^{c)}		
				mmol	(<i>trans</i> %) ^{a)}					1-Ph-Hex ^{d)} %	2-Ph-Hex ^{e)} %	1-Ph-3-Me-Pent ^{f)} %
7	100	1	1	36	(87)	4	15	2	3	90	7	3
8	100	2	1	52	(86)	8	12	3	7	91	6	3
9	100	4	1	57	(86)	7	11	3	7	91	6	3
10 ^{b)}	100	4	1	108	(88)	10	33	6	5	90	7	3
11	40	1	1	0.5	—	—	—	—	1	—	—	—
12	70	1	1	7	(88)	1	5	—	1	87	10	3
13	120	1	1	52	(85)	7	10	3	7	91	6	3
14	100	1	0.75	33	(87)	4	12	2	3	90	7	3
15	100	1	0.5	21	(87)	2	9	2	2	90	7	3

a)–f) The same as in Table 1. g) The ratio of $\text{BF}_3 \cdot \text{Ph}_3\text{P}$ to monomeric $(\pi\text{-C}_3\text{H}_5\text{PdCl})$ (=P/Pd atomic ratio).

h) Three hundred and fifty millimoles of styrene and 350 mmol of butadiene were used.

TABLE 3. CODIMERIZATION OF STYRENE AND BUTADIENE WITH THE $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$ CATALYST IN DICHLOROMETHANE
(Dichloromethane, 20 ml; $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$, 0.15 mmol; $\text{BF}_3\cdot\text{Ph}_3\text{P}$, 0.3 mmol; reaction temp, 100 °C)

Run No.	Butadiene mmol	Styrene mmol	React. time h	1-Phenyl-1,4-hexadiene		Styrene dimer mmol	Styrene recovd. mmol	Butadiene dimer mmol	Butadiene trimer mmol	Oligomer ^{b)} g	Composition of hydrogenated codimer ^{c)}		
				mmol	(<i>trans</i> %) ^{a)}						1-Ph-Hex ^{d)} %	2-Ph-Hex ^{e)} %	1-Ph-3-Me-Pent ^{f)} %
16	170	350	1	61	(87)	25	175	7	1	7	88	9	3
17	170	170	1	37	(87)	4	99	16	2	4	90	7	3
18	350	170	1	32	(88)	2	124	22	2	2	91	6	3
19	170	170	2	49	(87)	5	80	14	3	5	90	6	3
20 ^{g)}	170	170	2	34	(89)	4	104	8	1	4	91	7	2
21 ^{h)}	170	170	2	33	(88)	4	113	10	2	3	88	9	3
22 ⁱ⁾	170	170	2	44	(88)	11	42	7	2	11	89	9	2
23 ^{j)}	170	170	2	0.1		—	134	0.5	—	1	—	—	—
24 ^{k)}	170	170	2	0.5 ^{l)}		—	161	0.3	—	0.5	—	—	—

a)–f) The same as in Table 1. g) $(\text{PdCl}_2\cdot\text{PhCH=CH}_2)_2$ 0.15 mmol + $\text{BF}_3\cdot\text{Ph}_3\text{P}$ 0.3 mmol was used as a catalyst. h) $(\text{Pd}(\text{acac})_2$ 0.3 mmol + $\text{BF}_3\cdot\text{Ph}_3\text{P}$ 0.3 mmol) was used as a catalyst. i) A double amount of $\text{BF}_3\cdot\text{Ph}_3\text{P}$ (0.6 mmol) was used. j) $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ 0.15 mmol + $\text{BF}_3\cdot\text{Ph}_3\text{P}$ 0.3 mmol + Ph_3P 0.3 mmol was used as a catalyst. k) $(\text{PdCl}_2\cdot\text{PhCH=CH}_2)_2$ (0.3 mmol) was used alone as a catalyst. l) Scarcely no formation of 1-phenyl-1,4-hexadiene was observed, but a compound which seemed to be phenylcyclohexene was formed just as the case in the absence of a catalyst.

with the decrease in $\text{BF}_3\cdot\text{Ph}_3\text{P}$ (Table 2), but even if 2 mol of $\text{BF}_3\cdot\text{Ph}_3\text{P}$ per atom of Pd are used, the yield does not increase (Table 3, Run 22). These results indicate that $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ is activated by 1 mol of $\text{BF}_3\cdot\text{Ph}_3\text{P}$ per atom of Pd. When triphenylphosphine is added to a $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$ catalyst system with an atomic ratio of Pd: P: B = 1: 1: 1, the resulting catalyst system (Pd: P: B = 1: 2: 1) has no activity (Run 23). It can be considered that excess phosphine coordinates strongly to palladium and inhibits the coordination of olefins.

Palladium compounds other than $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ can be used as catalyst components. The results obtained by using the $(\text{PdCl}_2\cdot\text{C}_6\text{H}_5\text{CH=CH}_2)_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$ and $\text{Pd}(\text{acac})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$ catalyst systems are given in Table 3 (Runs 20, 21). $(\text{PdCl}_2\cdot\text{C}_6\text{H}_5\text{CH=CH}_2)_2$ alone is ineffective as a catalyst, yielding only a small amount of a codimer (Run 24).⁶⁾ This is believed to be due to the

formation of a stable complex of the palladium salt with butadiene.

Reaction with a Catalyst Consisting of Palladium Salt, Aluminum Chloride, and Tertiary Phosphine. As a Lewis acid, aluminum chloride can be used instead of boron trifluoride. The results obtained by using a $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-AlCl}_3\text{-R}_3\text{P}$ catalyst system are shown in Table 4. Both the activity of the catalyst and the composition of the reaction products are not very different from those obtained by a $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$ catalyst system, though it is preferable, when aluminum chloride is used, to employ nitrobenzene as the solvent in order to carry out the reaction in a homogeneous state.

When the atomic ratio of Al/P or Al/Pd was increased from 1 to 2 by changing the quantities of palladium salt and phosphine and by using approximately constant amounts of aluminum chloride, the amounts of the

TABLE 4. CODIMERIZATION OF STYRENE AND BUTADIENE WITH THE $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-AlCl}_3\text{-R}_3\text{P}$ CATALYST
(Nitrobenzene, 20 ml; reaction temp, 100 °C; 1 h)

Run No.	Butadiene mmol	Styrene mmol	Catalyst			1-Phenyl-1,4-hexadiene		Styrene dimer mmol	Butadiene dimer mmol	Butadiene trimer mmol	Oligomer ^{b)} g	Composition of hydrogenated codimer ^{c)}		
			Pd:AlCl ₃ : R ₃ P ratio ^{e)}	R ₃ P (mmol)	R	mmol	(<i>trans</i> %) ^{a)}					1-Ph-Hex ^{d)} %	2-Ph-Hex ^{e)} %	1-Ph-3-Me-Pent ^{f)} %
25	170	170	1:1:1	(0.52)	Ph- ^{h)}	51	(85)	5	15	4	4	90	7	3
26	170	170	1:1.5:1	(0.30)	Ph-	36	(86)	4	12	2	3	90	7	3
27	170	170	1:2:1	(0.21)	Ph-	25	(86)	1	10	2	5	91	6	3
28	350	170	1:1:1	(0.47)	Ph-	39	(86)	2	23	3	1	91	6	3
29	170	350	1:1:1	(0.51)	Ph-	58	(86)	15	9	1	4	89	8	3
30 ^{j)}	170	170	1:1:1	(0.48)	Ph-	34	(85)	4	13	2	2	90	7	3
31	170	170	1:1:1	(0.44)	Bu- ⁱ⁾	16	(89)	1	6	0	1	90	5	5
32	170	350	1:1:1	(0.50)	Bu-	27	(89)	4	5	0	1	90	5	5

a)–f) The same as in Table 1. g) Pd means monomeric $(\pi\text{-C}_3\text{H}_5\text{PdCl})$. The ratio is equal to the atomic ratio of Pd: Al: P. h) Triphenylphosphine. i) Tributylphosphine. j) Reaction time, 1/2 h.

distillation residue (oligomer) per palladium atom were increased, but the yields of 1-phenyl-1,4-hexadiene per palladium atom were not increased very much (Runs 25—27). Therefore, it seems to be appropriate to use an approximately equal mole of aluminum chloride to phosphine.

The effects of the molar ratio of styrene to butadiene were similar to those of the case using a $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2\text{-BF}_3\cdot\text{Ph}_3\text{P}$ catalyst system. By increasing the molar ratio, the yield of 1-phenyl-1,4-hexadiene was increased and the proportion of 2-phenylhexane was also increased.

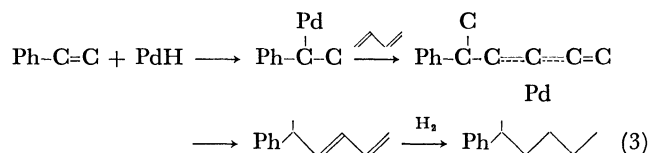
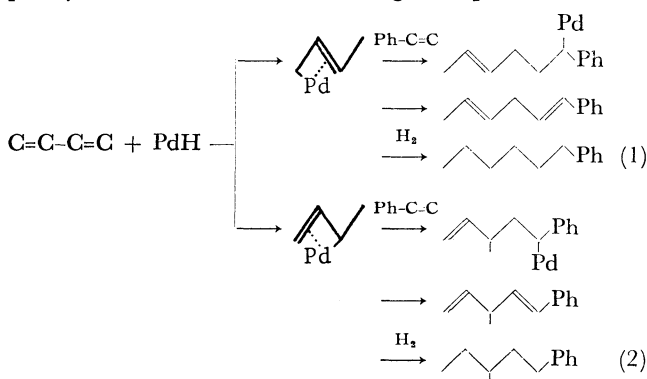
When tributylphosphine was used instead of triphenylphosphine, the yield of 1-phenyl-1,4-hexadiene decreased and the proportion of 1-phenyl-3-methylpentane to the total hydrogenated codimers increased, suggesting that butadiene tends somewhat to react in the form of



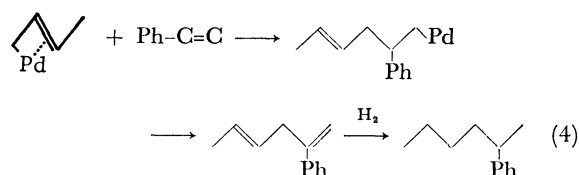
under the influence of tributylphosphine.⁷⁾

Reaction Path. For the codimerization of styrene and ethylene using the same catalyst system as in the present codimerization, we have proposed a reaction mechanism which involves the formation of a palladium hydride as an active species of the catalyst system.^{2c)} In the present codimerization, the active species of the catalyst system is believed to be essentially the same as that described above. As has already been mentioned with regard to the composition of the alkylbenzene obtained by the hydrogenation of codimers, 1-phenylhexane and 1-phenyl-3-methylpentane increased with an increase in the amount of butadiene employed, while 2-phenylhexane and styrene dimer increased with an increase in the amount of styrene (Table 1). In Fig. 1, as a compound which gives 2-phenylhexane by hydrogenation, only 5-phenyl-1,3-hexadiene has a structure capable of giving 2-phenylhexane.

From these facts, it can be considered that 1-phenylhexane and 1-phenyl-3-methylpentane are formed according to Eqs. 1 and 2 respectively, and that 2-phenylhexane is formed according to Eq. 3.



However, when the reaction of styrene with allyl groups coordinating to palladium was carried out by adding excess amounts of styrene to a solution of $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ and $\text{BF}_3\cdot\text{Ph}_3\text{P}$ in a molar ratio of 1:2, and when the resulting reaction mixture was hydrogenated, phenylpentanes (ca. 50 mol % based on the $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ used) were obtained; GLC analysis showed that the phenylpentanes consisted of 1-phenylpentane (89%) and 2-phenylpentane (11%). Therefore, it seems necessary to consider the participation of the following pathway (Eq. 4) for the formation of 2-phenylhexane:



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- 6) In the case of the reaction of styrene and ethylene, $(\text{Pd-Cl}_2\cdot\text{C}_6\text{H}_5\text{CH=CH}_2)_2$ is effective as a catalyst by itself.^{2e)}
- 7) In the oligomerization of olefins with complex catalysts containing phosphine compounds, it has been established that the structure of the oligomer formed often varies with the difference in the type of phosphine employed; B. Bogdanovic, B. Henc, H. G. Karman, H. G. Nüssel, and G. Wilke, *Ind. Eng. Chem.*, **62**, No. 12, 34 (1970).