BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2512—2515 (1970)

The Codimerization of Styrene with Ethylene Catalyzed by Olefin-palladium(II) Chloride Complexes

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(Received December 12, 1969)

The codimerization of styrene with ethylene catalyzed by the olefin-palladium chloride complexes was investigated in a homogeneous system under mild conditions; di-μ-chloro-dichlorobis-(styrene)dipalladium(II), $(Pd(C_6H_5CH=CH_2)Cl_2)_2$, was found to be an effective catalyst. When ethylene was bubbled into a styrene solution containing the styrene-palladium complex at 50°C for 6 hr, codimers including *trans*-1-phenyl-1-butene, *cis*-1-phenyl-1-butene, and *trans*-1-phenyl-2-butene were obtained in 1278, 57 and 170% yields respectively, based on palladium(II) used. However, the absence of ethylene resulted in the formation of a 70% yield of the dimer of styrene, *trans*-1,3-diphenyl-1-butene. The order of the solvent effect on the rate of the codimerization was as follows: nitrobenzene$>$nitromethane$>$acetic acid, phenol$>$dioxane$\gg$benzene$\gg$acetonitrile. A possible mechanism for this reaction was discussed on the basis of the present results.

Many investigations have recently been reported into the cooligomerizations of conjugated dienes with mono-olefins catalyzed by transition-metal compounds.[1] Only little is known, however, about the codimerization of styrene with ethylene catalyzed by transition-metal compounds. Müller and his co-workers have reported that the cocatalyst consisting of nickel acetylacetonate, trialkylaluminum, and phosphite catalyzes the codimerization of styrene with ethylene to give cocyclic higher oligomers and a small amount of codimer.[2] Alderson and his co-workers described how rhodium chloride and ruthenium chloride also catalyze the codimerization of styrene with ethylene under a high pressure to give 2-phenyl-2-butene.[3]

As has been reported in a preliminary communication,[4] we have found that di-μ-chloro-dichlorobis-(styrene)dipalladium (II) is an effective catalyst for the codimerization of styrene with ethylene. In this paper detailed studies of the reaction catalyzed by olefin - palladium chloride complexes will be reported.

Experimental

Codimerization of Styrene with Ethylene by a Styrene-palladium Complex Catalyst. A reaction vessel was charged with 4.5 g of styrene-palladium chloride and 150 m*l* of styrene, and then ethylene was bubbled into the mixture at 50°C for 6 hr. This solution became a reddish-yellow. The color did not vary during the reaction, indicating that the complex functions as a stable catalyst, although only a slight precipitation of metallic palladium was observed in the final stage of the reaction. The resulting solution was diluted with petroleum ether after the unreacted styrene had been removed under reduced pressure at 50°C; then it was filtered in order to remove the palladium complex and palladium metal. The distillation of the filtrate gave 27.1 g of *trans*-1-phenyl-1-butene, 1.2 g of *cis*-1-phenyl-1-butene, 3.6 g of *trans*-1-phenyl-2-butene, and 0.4 g of acetophenone, all of which were identical with authentic samples.[5]

trans-1-Phenyl-1-butene: IR spectrum: *trans*-HC=CH- 960 cm^{-1}, phenyl 740 and 690 cm^{-1}. NMR spectrum: CH_3 τ 8.80 (triplet), CH_2 τ 7.70 (quintet), -HC=CH- τ 3.70 (multiplet), phenyl τ 2.38 (multiplet). Found: C, 90.92; H, 9.13%. Calcd for $C_{10}H_{12}$: C, 90.90; H, 9.12%.

cis-1-Phenyl-1-butene: NMR spectrum: CH_3 τ 8.95 (triplet), CH_2 τ 7.63 (quintet), -HC=CH- τ 3.67 and 4.40 (multiplet), phenyl τ 2.83 (multiplet).

trans-1-Phenyl-2-butene: IR spectrum: *trans*-HC=CH- 968 cm^{-1}, phenyl 745 and 695 cm^{-1}. NMR spectrum: CH_3 τ 8.31 (doublet), CH_2 τ 6.73 (doublet), -HC=CH- τ 4.50 (multiplet), phenyl τ 2.85 (multiplet).

Reaction Kinetics. The apparatus and procedure used to measure the reaction rates were similar to those employed before.[6] The reaction rates were determined

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[1] See, for example, C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Logos Press, London (1967), p. 50.

[2] H. Müller, D. Wittenberg, H. Seibt and E. Scharf, *Angew. Chem. Intern. Ed.* **4**, 327 (1965).

[3] T. Alderson, E. L. Tenner and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **87**, 5638 (1965).

[4] K. Kawamoto, T. Imanaka and S. Teranishi, *Kogyo Kagaku Zasshi*, **72**, 1612 (1969).

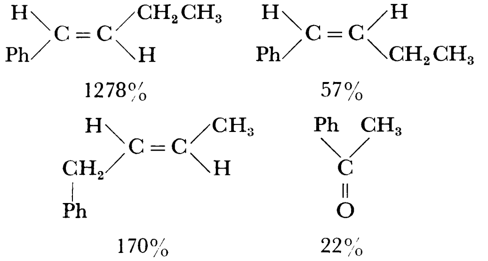
[5] a) A. Klages, *Ber.*, **37**, 2312 (1904). b) E. Erlenmeyer, *Ann.*, **135**, 122 (1865). c) F. R. Mayo, *J. Amer. Chem. Soc.*, **90**, 1289 (1968).

[6] K. Kawamoto, T. Imanaka and S. Teranishi, *Nippon Kagaku Zasshi*, **89**, 639 (1968).

by measuring the amount of *trans*-1-phenyl-1-butene formed and that of ethylene absorbed.

Results and Discussion

Products. The codimerization reaction of styrene with ethylene catalyzed by the styrene-palladium chloride was carried out at 50°C for 6 hr, ethylene being bubbled into the styrene solution containing the catalyst.[4] The following products were obtained:



(based on palladium(II))

The total amount was more than 15 mol equivvalents of the palladium complex, indicating that the styrene-palladium complex is an effective catalyst for the codimerization reaction under the mild conditions here adopted.

It is interesting that no dimers of styrene and ethylene were formed. In the absence of ethylene under the same conditions, the dimer of styrene, *trans*-1,3-diphenyl-1-butene, and acetophenone were formed in 70 and 30% yields respectively, on the basis of palladium(II). It has previously been reported[6] that the dimerization reaction of ethylene proceeded when ethylene was bubbled into a reaction mixture of dioxane and ethylene-palladium chloride. These facts indicate that the coexistence of styrene and ethylene inhibits the dimerization reactions.

The formation of acetophenone may be due to the reaction of styrene with the moisture, since a partial precipitation of metallic palladium in the course of the reaction was observed.[7]

Activity of Styrene-, Ethylene-palladium Complexes and Palladium Chloride. The codimerization reaction of styrene with ethylene was studied by using styrene- and ethylene-palladium complexes and palladium chloride. The results are shown in Fig. 1, where the amount of ethylene absorbed from the gas phase and that of the *trans*-1-phenyl-1-butene formed are plotted *vs.* the reaction time. From the gas-chromatographic analysis, it was found that the amounts of the other codimers were proportional to that of *trans*-1-phenyl-1-butene, and that the absorbed ethylene was almost completely consumed in the codimerization. As is shown in Fig. 1, the reaction has an induction period (*ca.* 30 min) which was slightly different for various solvents.

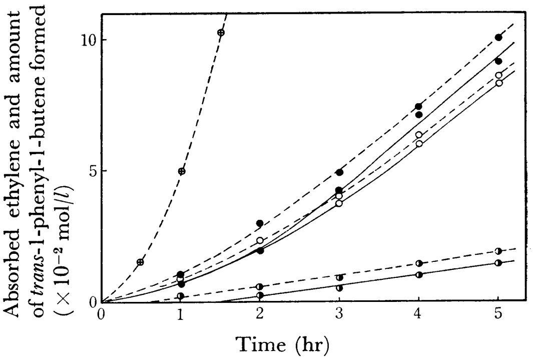


Fig. 1. The time dependences of the absorption of ethylene and the formation of *trans*-1-phenyl-1-butene.
——: amount of *trans*-1-phenyl-1-butene, ------: absorbed ethylene, ⊕: ethylene-palladium complex-dioxane system, ●: styrene-palladium complex, ○: ethylene-palladium complex, ◑: $PdCl_2$, neat(styrene at 8.72 mol/*l*), (Pd): 1.06×10^{-2} mol/*l*, concentration of ethylene: 6.36×10^{-2} mol/*l*, 50±0.2°C.

The dimerization of ethylene, which was observed in the reaction system of dioxane and ethylene-palladium complex, is also shown in Fig. 1. It is necessary to point out that the dimerization reaction of ethylene is much faster than the codimerization reaction of styrene with ethylene. However, no dimer of ethylene has been formed in the present system.

The reactivities of palladium complexes decreased in the following order: styrene complex$\gtrsim$ethylene complex$\gg$palladium chloride.

Solvent Effect. The solvent effect on the codimerization reaction of styrene with ethylene is summarized in Table 1. The dipole moments and the dielectric constants of the solvents are also shown in Table 1.

The reaction rate is subjected to restriction in both a nonpolar solvent such as benzene and a strongly polar solvent such as acetonitrile. In acetonitrile palladium complex is changed into an insoluble yellow complex. The reaction rate is particularly enhanced in a solvent containing oxygen atom. A similar effect was also observed in the dimerization reaction of ethylene.[9]

The rate decreases in the following sequence: nitrobenzene>nitromethane>acetic acid>phenol >dioxane. Table 1 shows that the sequence agrees

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[7] The formation of acetophenone from styrene and water by palladium salts is well known. For example, (i) J. Smidt, W. Hafner, R. Jira, J. Sedlmeiner, R. Sieber, R. Ruttinger and H. Kojer, *Angew. Chem.*, **71**, 176 (1959). (ii) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier and A. Sabel, *ibid.*, **74**, 93 (1962).

[9] K. Kawamoto, T. Imanaka and S. Teranishi, *Nippon Kagaku Zasshi*, **91**, 39 (1970).

TABLE 1. EFFECT OF SOLVENTS

Solvent	Concentration of ethylene ($\times 10^{-2}$mol/l)	Rate of formation for *trans*-1-phenyl-1-butene ($\times 10^{-2}$ mol/l hr)	Dipole moment[8] μ	Dielectric constant[8] ε (°C)
Nitrobenzene	4.46	6.36	4.21	34.8 (25)
Nitromethane	4.90	4.60	3.46	35.9 (30)
Acetic acid	6.36	2.25	1.73	6.15 (20)
Phenol	3.65	1.90	1.14	9.87 (60)
Dioxane	6.37	1.25	—	2.28 (0)
Benzene	6.01	0.96	0	2.44 (0)
Acetonitrile	5.41	0.22	—	37.5 (20)
Styrene	6.36	1.38	—	2.43 (25)

Styrene-palladium complex (Pd): 1.12×10^{-2} mol/l. Solvent+styrene (1:1 vol. ratio): 80 cc.
Reaction temperature: 50 ± 0.2°C.

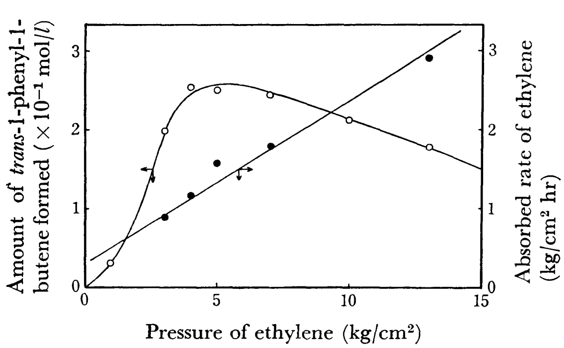

Fig. 2. The dependence of ethylene pressure on the amount of *trans*-1-phenyl-1-butene formed.
styrene - palladium complex (Pd): 2.97×10^{-2} mol/l, styrene+benzene (1 : 1 vol. ratio) : 60 cc, 100 cc glass autoclave, 50°C, 5 hr.

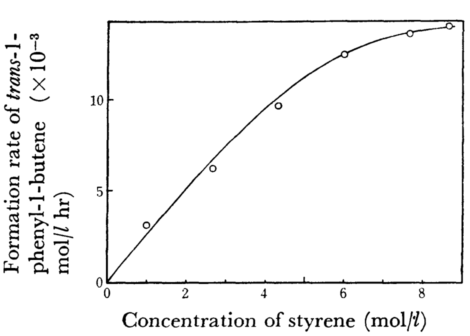

Fig. 3. The dependence of the concentration of styrene on the formation rate of *trans*-1-phenyl-1-butene.
styrene-palladium complex (Pd): 1.12×10^{-2} mol/l, concentration of ethylene: 6.01×10^{-2} mol/l, solvent: benzene, 50 ± 0.2°C.

with the decreases in the dipole moment (μ) and dielectric constant (ε).

It should be noted here that; (i) the complex is partly reduced to metallic palladium in the early stage of the reaction in phenol, and (ii) the liquid-phase concentration of ethylene is much lower in phenol than in acetic acid. These facts indicate that the corrected rate of the codimerization in phenol is faster than that in acetic acid.

Effect of Ethylene Pressure. The codimerization was examined as the ethylene pressure increased from 1 to 15 atm. The results are shown in Fig. 2. The styrene - palladium complex was used as a catalyst. The amount of *trans*-1-phenyl-1-butene formed initially increases, reaches a maximum at an ethylene pressure of 4 atm, and then gradually decreases. At a high pressure of ethylene, the rate of the formation of butene increases with an increase in the ethylene pressure.

These results indicate that the codimerization reaction is favored at low pressures of ethylene and that the dimerization reaction of ethylene predominates above an ethylene pressure of 4 atm.

Effect of Styrene Concentration. The formation rate of *trans*-1-phenyl-1-butene was measured by diluting styrene with benzene. In benzene the codimerization and dimerization reactions did not occur. The results are shown in Fig. 3. The reaction rate increased with an increase in the styrene concentration, and the order of the reaction changed from one to zero.

Reaction Mechanism. In view of the above facts, we propose the reaction mechanism of the codimerization shown in Scheme 1.

The styrene-palladium complex (1) initially dissociates into the complex (2) in the presence of a solvent. The coordination of ethylene with the complex (2) results in the complex (3). In the complex (3) the insertion between the coordinated styrene and ethylene produces the complex (4). Finally styrene rapidly displaces the coordinated dimer in the complex (4), reforming the complex (2). In the stage of changing from the complex (4) to (2), the amount of coordinated ethylene instead of styrene can be ignored, since the liquid-

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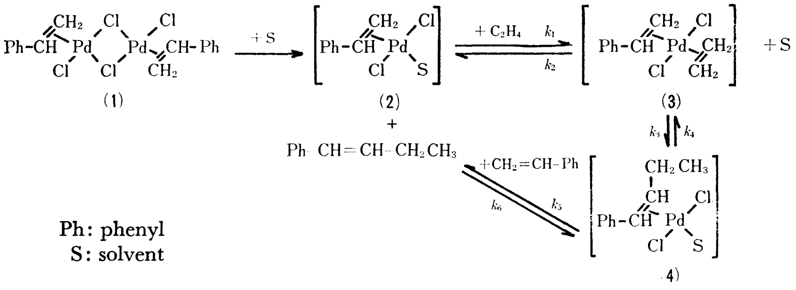
[8] The Chem. Soc. Japan, "Kagaku Binran, Kisohen I," Maruzen, Tokyo (1966), pp. 1003, 1226.



Scheme 1

phase concentration of styrene is more than 100 mol equivalents of that of ethylene at a low pressure of ethylene. However, with an increase in the pressure of ethylene, this amount can not be ignored, and another complex coordinated by ethylene and the solvent must be formed. In this case, another circulation was previously proposed for the dimerization of ethylene by the present authors.[6]

In the stage of changing from the complex (2) to (3), it is natural that the complex coordinated by two molecules of styrene is formed, since the concentration of styrene is much higher than that of ethylene. Therefore, the fact that styrene does not undergo the dimerization suggests that the insertion reaction between coordinated styrene and ethylene is much faster than that between coordinated styrenes.

When the stage of changing from the complex (3) to (4) is the rate-determining step,[6] the rate of the codimerization is given by;

$$r_c = k(\mathrm{St})(\mathrm{S})/\{(k'+k''(\mathrm{St}))(\mathrm{S})+k'''(\mathrm{St})\}$$

where $k=k_1k_3k_5/(k_2+k_3)$, $k'=k_1k_3/(k_2+k_3)+k_6(\mathrm{C})$, $k''=k_5/(\mathrm{E})$, and $k'''=k_1k_5/(k_2+k_3)$, and where (C), (E), (St), (S) represent the liquid-phase concentration of the codimer, ethylene, styrene, and the solvent respectively.

The above equation shows that the reaction order changes from one to zero with an increase in the styrene concentrations. The experimental evidence in the reaction order can, therefore, be interpreted on the basis of Scheme 1.

The fact that solvents containing oxygen atom are effective in the codimerization reaction can be reasonably understood by considering that the oxygen atom tends to have a moderate ability of coordination. The ease of the solvents in both coordination to and dissociation from the complex leads to a promotion of the reactivity of the coordination site. The same argument was previously made by the present authors for the dimerization of ethylene.[9]