

HETEROGENEOUS CODIMERIZATION OF ACETYLENES AND ALLYL HALIDES
WITH POLYMER-SUPPORTED PdCl_2 CATALYST

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The reaction of acetylenes and allyl halides using polymer-supported PdCl_2 complex was carried out at room temperature for 48 hr. Codimerization products, 1,4-pentadiene derivatives, could be obtained in high yields. The catalytic behavior of the heterogeneous polymer Pd complex was compared with that of the homogeneous complex.

Much attention has been given to insoluble polymer-supported metal complexes for catalysts useful in organic synthesis in view of problem of separation of catalyst from reaction mixture. Little is known about oligomerization of olefins or acetylenes with the polymer complexes,¹⁾ while hydrogenation and carbonylation have been extensively studied.²⁾ We recently reported on a facile and unique synthesis of 1,4-pentadiene and 1,3,6-heptatriene derivatives from the reaction of acetylenes and allyl halides with homogeneous palladium catalysts.³⁾

In this communication, we wish to report on the codimerization using a polymer-supported palladium chloride complex. This is the first example of oligomerization using palladium polymer complex. This polymer catalyst, compared with the homogeneous catalysts, has three major advantages: i) easy separation of catalyst from reaction mixture, ii) reuse of catalyst, and iii) prevention against polymerization of acetylene compounds.

The following experiment provides a typical procedure of the codimerization. To a suspension of the Pd-polymer catalyst (0.10 g, 0.18 mmol as Pd), prepared from polymeric diphenylbenzylphosphine and PdCl_2 ,²⁾ in allyl chloride (13.8 g, 0.18 mol) was added phenylacetylene (1.80 g, 18 mmol)⁴⁾ and it kept stirring for 48 hr. Then the reaction mixture was filtered to remove the polymer catalyst.

After usual work-up, the codimer products were analyzed and isolated by gas chromatography (Apiezon grease L).

Experimental data obtained in the codimerization of various acetylenes and allyl halides, with those of a homogeneous palladium complex, $\text{PdCl}_2(\text{NPh})_2$, are summarized in Table I. This polymer catalyst has the activity of the

Table I. the Reaction of Acetylenes and Allyl Halides

Acetylene	Codimerization products ^{a)}	
	Heterogeneous reaction ^{b)} (yield%)	Homogeneous reaction ^{c)} (yield%)
Ph-C \equiv CH	CH ₂ =CHCH ₂ CH=C(Ph)Cl (61) CH ₂ =CHCH ₂ C(Ph)=CHCl (23)	CH ₂ =CHCH ₂ CH=C(Ph)Cl (95)
Ph-C \equiv CH ^{d)}	CH ₂ =CHCH ₂ CH=C(Ph)Br (79) CH ₂ =CHCH ₂ C(Ph)=CHBr (13)	CH ₂ =CHCH ₂ CH=C(Ph)Br (95)
Ph-C \equiv CCH ₃	CH ₂ =CHCH ₂ C(CH ₃)=C(Ph)Cl (29) ^{e)} CH ₂ =CHCH ₂ C(Ph)=C(CH ₃)Cl (13) ^{e)}	CH ₂ =CHCH ₂ C(CH ₃)=C(Ph)Cl (97)
HC \equiv CH ^{f)}	CH ₂ =CHCH ₂ CH=CHCl (75) ^{g)}	CH ₂ =CHCH ₂ CH=CHCl (2330) ^{g)}
n-Pr-C \equiv CH	CH ₂ =CHCH ₂ CH=C(n-Pr)Cl (78)	CH ₂ =CHCH ₂ CH=C(n-Pr)Cl (90)
n-Bu-C \equiv CH	CH ₂ =CHCH ₂ CH=C(n-Bu)Cl (82)	CH ₂ =CHCH ₂ CH=C(n-Bu)Cl (90)
Et-C \equiv C-Et	CH ₂ =CHCH ₂ C(Et)=C(Et)Cl (54)	CH ₂ =CHCH ₂ C(Et)=C(Et)Cl (95)
Ph-C \equiv C-Ph	no reaction	CH ₂ =CHCH ₂ C(Ph)=C(Ph)Cl (95)

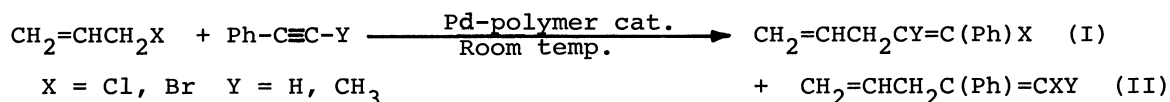
a) All new compounds exhibited correct NMR, IR and elemental analysis data.

b) Unless otherwise noted, acetylene : allyl chloride : catalyst $\approx 10^2 : 10^3 : 1$, for 48 hr, at 20°C. c) Conditions were the same as in ref.3a). d) Allyl bromide was used. e) For 700 hr. f) In acetylene atmosphere. g) Based on Pd and others are based on reactant acetylene.

codimerization for various acetylene compounds except for diphenylacetylene, though the rate of dimer formation is slower than in the homogeneous palladium catalyst. Remarkable differences between the heterogeneous polymer catalyst and homogeneous catalyst in the codimerization reaction are as follows. 1) By using the polymer catalyst, the rate of codimerization is strongly affected by the molecular size of acetylene compounds. The steric bulk of the substituents on acetylenic carbons controls the rate; $\text{C}_6\text{H}_5\text{-C}\equiv\text{CH} > \text{C}_6\text{H}_5\text{-C}\equiv\text{C-CH}_3 \gg \text{C}_6\text{H}_5\text{-C}\equiv\text{C-C}_6\text{H}_5$. Similar phenomena have been observed also in the case of olefin hydrogenation.²⁾

2) In the case of phenyl substituted acetylenes, e.g., phenylacetylene and

methyl phenylacetylene, internal phenyl substituted codimers can be obtained by only using the polymer catalyst. The product ratio of external phenyl substituted



codimer(I) vs. internal phenyl substituted codimer(II) was found to be affected by the solvents used. The results are shown in Table II. In ethyl ether,

Table II. Solvent Effect of the Codimerization of Phenylacetylene and Allyl Chloride^{a)}

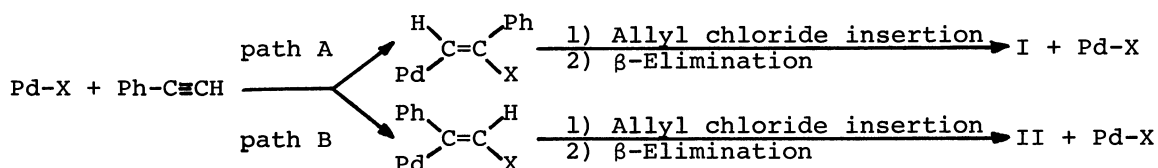
Solvent	I ^{b)} (%)	II ^{c)} (%)	I/II	Solvent	I	II	I/II
DMF	39.8	41.5	0.96	EtOAc	18.9	22.5	0.81
EtOH	33.7	23.1	1.44	CHCl ₃	22.6	18.5	1.22
CCl ₄	38.2	14.9	2.56	Benzene	24.8	10.0	2.44
THF	33.4	17.4	1.92	Acetone	17.3	15.3	1.14
n-PrOH	31.3	15.8	1.96	Cyclohexane	21.9	6.8	3.23
MeOH	36.0	10.0	3.60	Ethyl ether	23.5	4.8	4.76
CH ₃ NO ₂	17.8	23.7	0.75	CH ₂ Cl ₂	12.7	14.9	0.87

a) Reaction time 48 hr, temperature 20°C, Pd-catalyst 0.18 mmol, phenylacetylene 3.6 mmol, allyl chloride 36 mmol.

b) External phenyl compound, CH₂=CHCH₂CH=C(Ph)Cl.

c) Internal phenyl compound, CH₂=CHCH₂C(Ph)=CHCl.

methanol, and cyclohexane solvents, the formation of I codimer predominates, but the proportion of II increases in nitromethane, ethyl acetate, and dichloromethane, while the best yield of the codimer is obtained in DMF solvent. The ratio I/II is also sensitive to the conditions of polymer ligand preparation. For example, using the polymer ligand containing fewer phosphine moieties, the proportion of II increases. Although we can not give a good answer to the above phenomena at present, it can be said that the origin of both I and II is derived by the direction of Pd-X addition to the acetylenic triple bond (path A and path B).



The resulting solution separated from the catalyst had no catalytic activity. This fact shows that the codimerization is catalyzed by the palladium supported on polymer. The polymer catalyst can be reused without any appreciable loss in activity. The improvement of catalytic activity and the application of this polymer complex to other catalytic reactions are under investigation.

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- 4) In the case of homogeneous palladium catalyst, acetylene compound should be added dropwise carefully to the mixture of palladium complex and allyl chloride, holding the reaction temperature below 30°C. If acetylene is added instantly to the palladium solution, the reaction becomes strongly exothermic and acetylene polymerizes.

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