

Pd-Catalyzed Nucleophilic Allylation of Carbonyls with 1,3-Dienes

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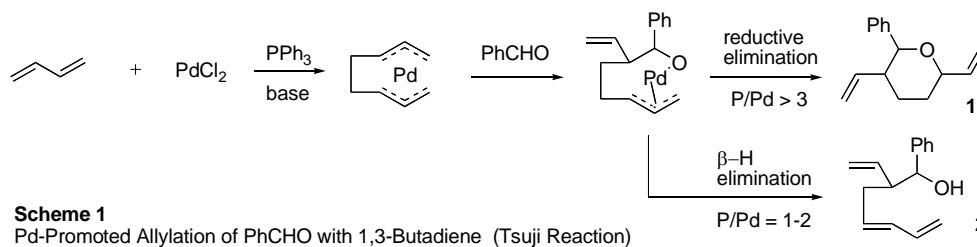
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Abstract

In the presence of Pd catalyst and triethylborane, aldehyde undergoes nucleophilic allylation with butadiene to provide dienyl homoallyl alcohols *via* bis- π -allylpalladium. The reaction feature depends on the kind of ligands; *n*-Bu₃P promotes two molecules of aldehydes to react with bis- π -allylpalladium and produces symmetrical dienyl diols, whereas bidentate ligands, dppf and dppe, provide dienyl homoallyl alcohols.

Introduction

Palladium salt serves as an active catalyst for the dimerization of conjugated dienes, and readily forms bis- π -allylpalladium. Amphiphilic allylation of aldehydes involving bis- π -allylpalladium has been developed by J. Tsuji et al. (Scheme 1).¹ In this case, the nucleophilic allylation at one of the π -allylpalladium moieties occurs to provide an oxa- π -allylpalladium intermediate, which undergoes reductive elimination to afford tetrahydropyran **1** or β -H elimination to provide trienyl alcohol **2**. The reaction feature extremely depends on the ratio of phosphine ligand and palladium catalyst.

**Results and Discussions**

The nucleophilic allylation of PhCHO with 1,3-butadiene was undertaken in the presence of triethylborane and Pd(OAc)₂ catalyst with a variety of phosphine ligands under nitrogen atmosphere (eq 1). The results with various kinds of ligands

are summarized in Table 1. In the absence of ligand, PhCHO underwent the nucleophilic allylation with two equivalents of 1,3-butadiene to afford dienyl homoallyl alcohol **4** in high yield (run 1, Table 1). In the presence of trialkylphosphines, 1,3-butadiene serves as an octadienyl dicarbanion equivalent *via* bis- π -allylpalladium, which reacts with two molecules of PhCHO to exert symmetrical diol **3** as the major product (runs 2 and 3, Table 1). Using PPh₃ as a ligand, Tsuji reaction predominated over the formations of diol **3** and dienyl alcohol **4** (runs 4 and 5, Table 1). Tris(*o*-tolyl)phosphine accelerated the mono allylation to give dienyl alcohol **4** in quantitative yield (run 6, Table 1).

The reaction has a great influence on the nature of aldehydes as well as ligands. Contrasting selectivities of *n*-Bu₃P and dppf ligands for the result of various aldehydes with 1,3-butadiene are listed in Table 2. In the presence of *n*-Bu₃P, active aldehydes, such as aromatic aldehydes, cinnamaldehyde, and paraformaldehyde, underwent the nucleophilic allylations to provide diols **3** (runs 1-5, Table 2), whereas alkylaldehydes provided the dienyl alcohols **4** as a sole product (runs 6 and 7, Table 2). Dppf ligand produced the dienyl alcohols **4** exclusively, irrespective of the kinds of aldehydes.

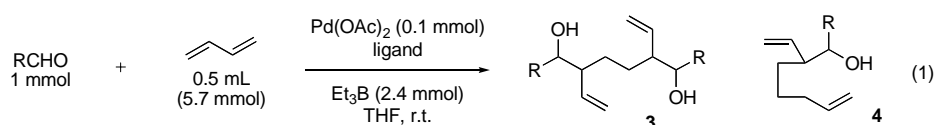


Table 1. Allylation of PhCHO (R = Ph) with 1,3-Butadiene

run	ligand (mmol)	time (h)	isolated yield (%)			
			1	2	3	4
1	none	72	0	0	trace	84
2	<i>n</i> -Bu ₃ P (0.2)	24	0	0	80	14
3	Me ₃ P (0.2)	24	0	0	71	28
4	PPh ₃ (0.2)	2	54	45	0	0
5 ^{a)}	Pd(PPh ₃) ₄ (0.1)	6	18	84	0	0
6	(<i>o</i> -tolyl) ₃ P (0.2)	2	0	0	0	99
7	dppe (0.1)	3	0	0	0	99
8	dppf (0.1)	4	0	0	0	99

a) Pd(PPh₃)₄ was used in place of Pd(OAc)₂ as a catalyst.

Table 2. Pd/Et₃B Promoted Allylation of Various Aldehydes

run	Aldehyde R	<i>n</i> -Bu ₃ P		dppf	
		3	4	3	4
1	<i>p</i> -F-C ₆ H ₄	84	15	---	67
2	<i>p</i> -MeC ₆ H ₄	69	8	---	91
3	<i>p</i> -MeOC ₆ H ₄	78	21	---	99
4	(<i>E</i>)-PhCH=CH	61	25	---	89
5	H	41	18	---	48
6		---	48	---	92
7	<i>n</i> -Pentyl	---	37	---	54

The reaction was undertaken in the presence of Pd(OAc)₂ (0.1 mmol), *n*-Bu₃P (0.2 mmol) or dppf (0.1 mmol), aldehydes (1 mmol), and butadiene (5.7 mmol) at room temperature under N₂.

Conclusions

The catalytic system of Pd catalyst and triethylborane promotes aldehydes to undergo the nucleophilic allylation with 1,3-butadiene. The reaction feature depends on the kind of ligands; *n*-Bu₃P promotes bis- π -allylpalladium to react with two molecules of aldehydes to provide symmetrical dienyl diols, whereas dppf ligand accelerates the monoallylation to give dienyl homoallyl alcohols.

Reference

1. J. Tsuji et al., *Tetrahedron Lett.*, 3687 (1970).