



Polymer-bound Palladium-catalyzed Coupling of Allylic Alcohols with Hypervalent Iodonium Salts

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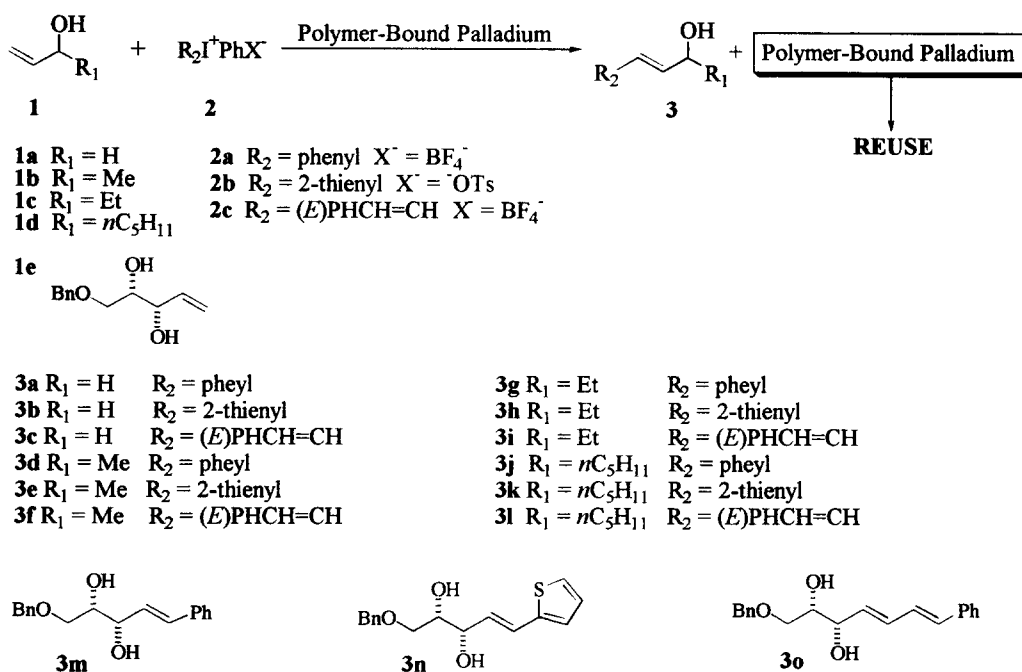
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Abstract: The polymer-bound palladium-catalyzed cross-coupling reaction of allylic alcohols with hypervalent iodonium salts to form carbon-carbon bonds was achieved at room temperature under extremely mild and aqueous conditions even in the absence of base with very high activity in the Stille coupling reaction. The polymeric catalyst can be easily separated from a reaction mixture and reused more than 10 times with no decrease in activity © 1997 Elsevier Science Ltd.

The formation of a carbon-carbon bond by palladium-catalyzed coupling of aryl or vinyl halides with olefins, known as the Heck reaction, has become a powerful tool in organic chemistry.¹ In the case of allylic alcohols, palladium-catalyzed reaction of organic halides usually affords β -substituted ketons or aldehydes rather than the β -substituted allylic alcohols.²

Jeffery³ reported that in the presence of a stoichiometric amount of silver acetate or silver carbonate, a highly selective formation of the substituted allylic alcohols can be achieved. Cacchi⁴ reported that Pd(0)-catalyzed reaction of allylic alcohols with triflates in the presence of Et₃N provided two isomeric substituted allylic alcohols. Tamaru⁵ utilized *O*-substituted allylic alcohols to direct the Pd(0)-catalyzed coupling without elimination of proton adjacent to the oxygen-bearing carbon. Finally, I have found that the coupling reaction of hypervalent iodonium salts⁶ with allylic alcohols in the presence of polymer-bound palladium catalyst affords the substituted allylic alcohols as the sole products under mild conditions with high catalytic efficiency. Recently, I reported that palladium-catalyzed cross-coupling reactions using polymer-bound palladium catalyst.⁷ In connection with my programs to utilize polymer-bound palladium catalyst in palladium-catalyzed cross-coupling reactions, I have investigated the coupling of allylic alcohols with hypervalent iodonium salts. Hybrid catalysts combining the attributes of conventional homogeneous catalysts with the experimental simpli-

city of heterogeneous catalysts have been proven to be fruitful subjects for research by both academic and industrial chemists⁸ and polystyrene-supported palladium catalysts have been successfully used for a variety of organic reactions.⁹ However, there is no specific papers containing about using polymer-bound palladium catalyst for Heck reactions, I first have tried useful Heck reactions of allylic alcohols with hypervalent iodonium salts using our reusable polymer-bound palladium complex.¹⁰ I describe herein the characteristic features of the polymer-bound palladium catalyst for various kinds of Heck reactions which are shown in Scheme 1.



Scheme 1

The results of polymer-bound palladium-catalyzed coupling of allylic alcohols with hypervalent iodonium salts are summarized in Table 1. We first coupled allylic alcohol(**1a**) with diphenyliodonium tetrafluoroborate(**2a**) in the presence of polymer-bound Pd(1 mol %) in $\text{CH}_2\text{CN}/\text{H}_2\text{O}$ (4 : 1) at room temperature to afford cinnamyl alcohol(**3a**) in 92% yield with high catalytic efficiency(entry 1). It is notable that even in the absence of base, 91% yield with high catalytic efficiency(entry 1). Treatment of allylic alcohol(**1a**) with 2-thienyl(phenyl)iodonium tosylate(**2b**) under the same conditions afforded 2-thienyl-substituted allylic alcohol(**3b**) in 92% yield(entry 2). Treatment of allylic alcohol(**1a**) with alkenyl(phenyl)iodonium tetrafluoroborate(**2c**) in the same conditions afforded alkenyl-substituted allylic

alcohol(**3c**) in 89% yield(entry 3). Finally, treatment of allylic diol(**1e**) with diphenyliodonium tetrafluoroborate(**2a**) in the same conditions afforded phenyl-substituted allylic diol(**3m**) in 88% yield(entry 13).

Table 1. Polymer-bound Palladium-catalyzed Coupling of Allylic Alcohols with Hypervalent Iodonium Salts

Entry	Allylic Alcohol	Iodonium salt	Product	Yield(%) ^b	Yield(%) ^c
1	1a	2a	3a	92(91)	89
2	1a	2b	3b	92(90)	86
3	1a	2c	3c	89(87)	83
4	1b	2a	3d	91(90)	88
5	1b	2b	3e	90(90)	85
6	1b	2c	3f	88(86)	81
7	1c	2a	3g	91(88)	87
8	1c	2b	3h	90(87)	83
9	1c	2c	3i	87(84)	80
10	1d	2a	3j	90(89)	84
11	1d	2b	3k	89(86)	81
12	1d	2c	3l	85(82)	79
13	1e	2a	3m	88(82)	78
14	1e	2b	3n	86(81)	76
15	1e	2c	3o	80(80)	72

^aTypical Procedure: To a mixture of diphenyliodonium tetrafluoroborate(1 equiv) and polymer-bound Pd(1 mol %) was added NaHCO₃(1 equiv) or no NaHCO₃ under air atmosphere followed by allylic alcohol(1 equiv) in MeCN/water (4 : 1, 10 mL) at room temperature. The reaction mixture was stirred at room temperature for 10 min and then filtered. The reaction mixture was extracted with ether(20 mL x 2) and the organic layer was dried over anhydrous magnesium sulfate and then evaporated in vacuo. The crude product was separated by SiO₂ column chromatography to afford the substituted allylic alcohol. ^bThe yields were isolated yields and the yields in parentheses are those obtained in the absence of the base. ^cThe isolated yields obtained by the use of the polymer bound palladium catalyst prepared from palladium acetate, in place of palladium chloride (see Notes 11).

Typically, as in the reactions described above Table 1, recycling the palladium catalyst was quite successful here. We recycled the polymer-bound palladium catalyst at least 7 times. However, in most cases, the catalyst was used more than 10 times with no decrease in activity. In these experiments, the catalyst was recycled more than 10 times with maintaining the yield which was given in first catalytic cycle(Total turnover number of > 600 mmol product / mmol of catalyst).

In summary, the selected formation of the substituted allylic alcohols without formation of β -substituted carbonyl compounds was achieved by reacting allylic alcohols with hypervalent iodonium salts in the presence of the polymer-bound palladium as the catalyst at room temperature under extremely mild and aqueous conditions even in the absence of base, and catalytic activity is comparable to that of a close homogeneous analogue palladium catalysts Pd(OAc)₂.

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- Preparation of polymer-bound Pd(0) Complex: The polystyrene resin with a 100% chloromethylated aromatic ring was treated with LiPPh₂ at 25 °C for 48 h. The reaction of the phosphinated resin(5 g) with PdCl₂(0.75 g) in a molar ratio of P/Pd of 3 was carried out to give a yellow polymeric Pd(II) complex. The Pd(II) complex(5 g, 3.71 mmol of Pd) was added to ethanol(50 mL) containing PPh₃(2.09 g, 7.42 mmol). The mixture was stirred at rt for 3 h. Then hydrazine hydrate(1.87 g, 3.71 mmol) was added to the mixture, and stirring was continued for 2 h. The resulting polymer was filtered, washed with ethanol and ether, and dried under vacuum to give a dark green polymer complex. All above procedures were carried out under a nitrogen atmosphere. The analysis showed the following: C, 74.51%; H, 5.67%; Cl, 2.76%; P, 9.15%. This corresponds to a ratio of P/Pd of 3.9, here the palladium content was calculated by difference.

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