

Tetrahedron report number 721

Palladium-catalysed reactions of alcohols. Part C: Formation of ether linkages[☆]

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[☆] See Refs. 1 and 2.

Keywords: Palladium; Alcohols; Etherification; Heterocyclisation; Oxypalladation; η^3 -Allylpalladium.

Abbreviations: atm, atmosphere; BINAP, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; cat., catalytic; COD, 1,5-cyclooctadiene; conv, conversion; Cy, cyclohexyl; dba, dibenzylidene acetone; DBU, 1,8-diazabicyclo[5.4.0]undec-7ene; de, diastereoisomeric excess; DMA, *N,N*-dimethylacetamide; dppe, 1,2-bis(diphenylphosphino)ethane; dppb, 1,4-bis(diphenylphosphino)butane; dppf, 1,1'-bis(diphenylphosphino)ferrocene; dppp, 1,3-bis(diphenylphosphino)propane; dr, diastereoisomeric ratio; ee, enantiomeric excess; equiv, equivalent; MS, molecular sieves; phenan, phenanthroline; Py, pyridine; rt, room temperature; THP, tetrahydropyranyl; tol-BINAP, 2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl; Ts, 4-methylphenylsulfonyl; TON, turnover number; TPPTS, tris(3-sulfonatophenylphosphine) trisodium.

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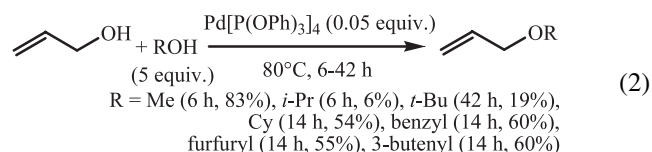
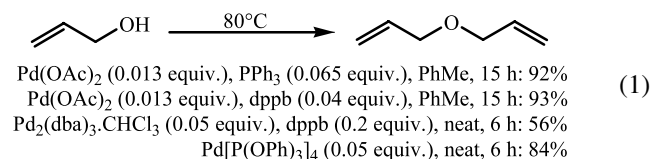
1. Introduction

The literature contains an impressive number of Pd-catalysed reactions using alcohols as substrates or reagents, and we are attempting to cover this topic with a series of reviews. The oxidation reactions of alcohols to the corresponding carbonyl compounds have been the subject of Part A,¹ while Part B has summarised the formation of C–C and C–N bonds from unsaturated alcohols.² The present review is devoted to the formation of C–O bonds, the oxygen atom coming from an alcohol, and is organised, as previously, according to, firstly, the type of reaction and, secondly, the nature of the substrate. The next review, Part D, will complete the series, with, mainly, a description of the rearrangement, cleavage, carbonylation and carbonylation reactions. As mentioned in Part B, the reports concerning phenols, and those where the hydroxy group is recovered unmodified at the end of the process, are beyond the scope of these reviews.

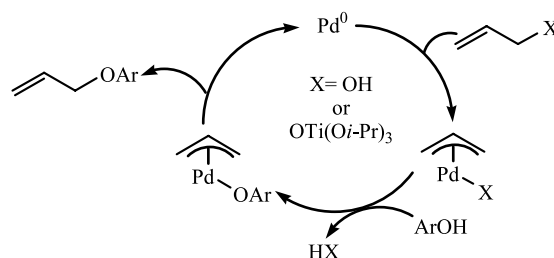
2. Addition of alcohols to η^3 -allylpalladium intermediates

2.1. η^3 -Allylpalladium intermediates from allylic alcohols

2.1.1. Intermolecular reactions. The homocoupling of allylic alcohols (Eq. 1)^{3–6} and the dehydrative allylation of primary and secondary alcohols (Eq. 2)^{4,6,7} to afford ethers are mediated by various palladium catalysts, the concomitant formation of some 1,3-butadiene from crotyl alcohol indicating an η^3 -allylpalladium intermediate.⁶



The Pd-catalysed etherification of allylic alcohols with phenols is promoted by titanium^{IV} isopropoxide (Eq. 3), and the proposal of a transient allyl titanate leading to an η^3 -allylpalladium intermediate (Scheme 1) is supported by the formation of the diallyl ether and allyl isopropyl ether in the absence of a phenol.⁸



Scheme 1.

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