Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron 61 (2005) 5955–6008

Tetrahedron

Tetrahedron report number 721

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

Jacques Muzart*

Unité Mixte de Recherche 'Réactions Sélectives et Applications', CNRS, Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France

Received 17 March 2005

Contents

☆ 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-sulfanatophenylphosphine) trisodium.

* Tel.: +33 3 2691 3237; fax: +33 3 2691 3166; e-mail: jacques.muzart@univ-reims.fr

0040–4020/$ - see front matter
doi:10.1016/j.tet.2005.04.002

---

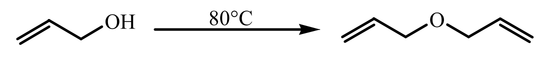
1. Introduction

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 carboxylation 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.

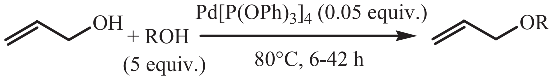
2. Addition of alcohols to η^3-allylpalladium intermediates

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]

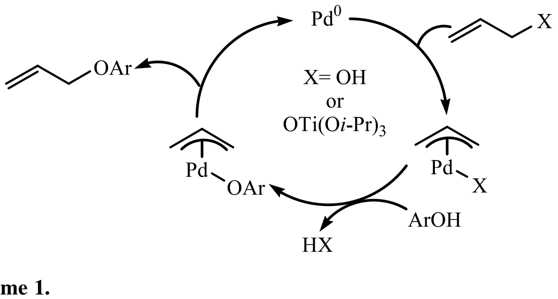


$Pd(OAc)_2$ (0.013 equiv.), PPh_3 (0.065 equiv.), PhMe, 15 h: 92%
$Pd(OAc)_2$ (0.013 equiv.), dppb (0.04 equiv.), PhMe, 15 h: 93%
$Pd_2(dba)_3.CHCl_3$ (0.05 equiv.), dppb (0.2 equiv.), neat, 6 h: 56%
$Pd[P(OPh)_3]_4$ (0.05 equiv.), neat, 6 h: 84% (1)



R = Me (6 h, 83%), *i*-Pr (6 h, 6%), *t*-Bu (42 h, 19%), Cy (14 h, 54%), benzyl (14 h, 60%), furfuryl (14 h, 55%), 3-butenyl (14 h, 60%) (2)

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.