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Facile and Selective Deallylation of Allyl Ethers Using Diphosphinidenecyclobutene-Coordinated Palladium Catalysts

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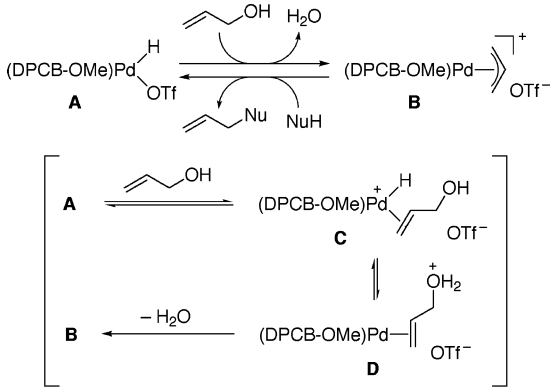
(π-Allyl)palladium triflate bearing a 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-*tert*-butylphenylphosphinidene)cyclobutene ligand (DPCB-OMe), [Pd(η^3-C_3H_5)(DPCB-OMe)]OTf, efficiently catalyzes deallylation of a variety of allyl ethers in aniline to give corresponding alcohols in high yields under mild conditions. The reactions can be performed in air without loss of a variety of functionalities including vinyl, alkynyl, hydroxy, acetoxy, silyloxy, and acetal groups. Allyl 2-allyloxybenzoate selectively undergoes deallylation of the allyloxy group to give allyl salicylate in quantitative yield.

Introduction

The palladium-catalyzed allylation is a useful means of constructing C−C, C−N, and C−O bonds in organic synthesis.[1] This reaction generally employs allylic esters derived from allylic alcohols as allylation agents. On the other hand, there have been considerable efforts to develop the catalysts that enable direct conversion of allylic alcohols into allylation products. This is mainly because such a reaction forms water as the only coproduct and possibly serves as an environmentally benign process with high atom efficiency.[2] However, due to the poor leaving ability of the OH group, most of the catalysts so far examined required rather severe conditions; otherwise, the reactions were conducted with in situ activation of allylic alcohols using considerable amounts of additives such as Lewis acids.[3−5]

SCHEME 1



We recently found that (π-allyl)palladium complex **1** bearing 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-*tert*-butylphenylphosphinidene)cyclobutene (DPCB-OMe) efficiently catalyzes direct conversion of allylic alcohols into *N*- and *C*-allylation products under mild conditions (eq 1).[6] We proposed a novel catalytic process given in Scheme 1. Thus, unlike common allylation reactions involving oxidative addition of a C−O bond to a Pd(0) species, it was considered that the C−O bond of allylic alcohols is cleaved by the action of hydridopalladium complex **A**. Proton-transfer from the Pd to the OH group in **C**, followed by elimination of water from **D**, forms π-allyl complex **B**. We reasoned that strong π-accepting ability of DPCB−OMe ligand as an sp^2-hybridized phosphorus compound[7] efficiently stabilizes **D** as a Pd(0)

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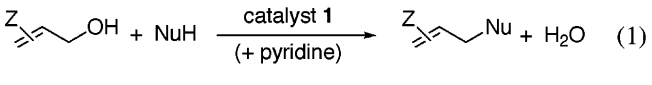
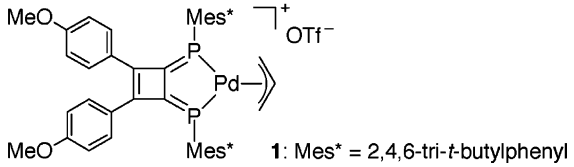
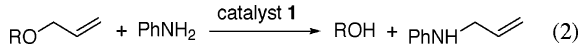
species by π-back-donation to facilitate the proton-transfer in **C**.



(1)



In this paper, we report application of this novel catalysis. A particular interest is focused on catalytic deallylation of allylic ethers (eq 2). Thus, the protection and deprotection of alcohols are central subjects in organic synthesis, especially in carbohydrate synthesis.[8] The allyl group is utilized as a versatile protecting group, owing to the easy introduction as well as the high stability of the resulting ethers under a wide range of reaction conditions. The deprotection was originally achieved by two-steps procedures, consisting of transition metal-catalyzed isomerization of allyl group and hydrolysis or oxidative cleavage of the resulting enol ethers.[9] More recently, one-step procedures have been investigated as more convenient methods (e.g., DDQ,[10] $NaBH_4/I_2$,[11] $TiCl_3$/Li/THF,[12] $Yb(OTf)_3$,[13] electrochemically generated Ni,[14] $ZrCl_4/NaBH_4$,[15] TMSCl/NaI,[16] $CeCl_3 \cdot 7H_2O$/NaI,[17] $TiCl_4/Bu_4NI$,[18] *t*-BuLi,[19] I_2,[20] *p*-TSA,[21] and SmI_2[22]). The palladium-catalyzed allylation has been examined as a simple approach to catalytic deprotection.[8a,23−28]



(2)

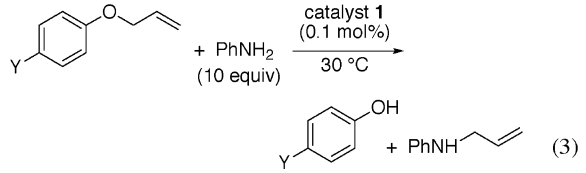
As described below, complex **1** exhibits high catalytic performance for deallylation of a variety of allylic ethers in aniline. The reactions can be conducted in air without loss of various functionalities.

Results and Discussion

First of all, the catalytic reactions were examined with aliphatic ethers as substrates. The results are summarized in Table 1. As a representative example, allyl hexyl ether (**2**; 71 mg, 0.50 mmol) was treated with 2 mol % of **1** in aniline (0.46 mL, 5.0 mmol) at 50 °C. The reaction was completed in 2 h as confirmed by GLC. The reaction mixture was poured into a 6 N HCl solution and extracted with Et_2O. Purification of the ethereal extract by silica gel column chromatography gave a 95% yield of *n*-hexanol. The deallylation could be performed also in toluene (0.8 mL) as a solvent using 2 equiv of aniline (1.0 mmol), while the reaction became somewhat slower (6 h) at the same temperature.

A variety of aliphatic ethers (**3**−**14**) were similarly deallylated. The present catalysis could be successfully applied to the substrates having vinyl (**3**), alkynyl (**5**), hydroxy (**5**), acetoxy (**7**, **8**), silyloxy (**9**, **10**), and acetal (**11**−**14**) groups. In particular, TBDMS (**9**, **10**), THP (**11**), and MOM (**12**) as typical protecting groups for alcohols remained unchanged in the catalytic reactions. Thus, the allylic deprotection catalyzed by **1** is compatible with other protection methods of alcohols. All reactions proceeded quantitatively as confirmed by GLC. 4-Pentenol derived from **3** was significantly volatile, and its isolated yield was somewhat lowered (84%). Since the products having acetal units were unstable under acidic conditions, their isolation was carried out directly by column chromatography without acid extraction.

Deallylation of aromatic ethers could be performed much more easily with 0.1 mol % of **1** at 30 °C (eq 3). Table 2 lists the results for allyl phenyl ethers having a variety of para-substituents. The reactions were completed within 30 min, except for **21** and **22** having the acetyl and bromo substituents, giving almost quantitative yields of phenols after chromatographic purification. The reaction of **15** was accomplished in a few minutes, when the amount of catalyst was increased to 0.5 mol %.



(3)

We next examined deprotection of allyloxycarbonyl (Alloc), which is known to be a useful protecting group for the hydroxy groups in carbohydrates and amino and imido groups in nucleoside bases and peptides. Very recently, deprotection of this group from several carbamates has been examined with $Pd(PPh_3)_4$ (1 mol %) and K_2CO_3 (3 equiv) in MeOH, where the reactions take hours

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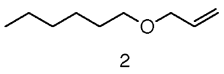
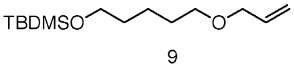
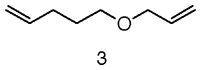
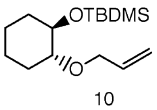
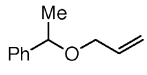
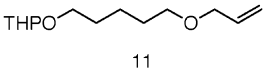
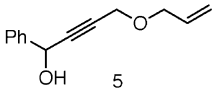
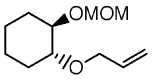
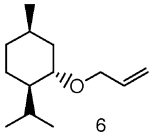
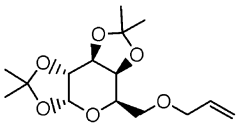
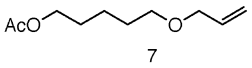
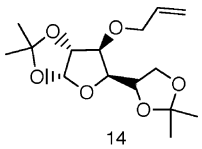
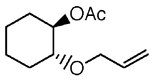
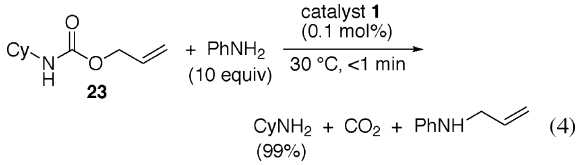
TABLE 1. Deallylation of Allyl Alkyl Ethers Catalyzed by 1 in Aniline[a]

substrate	time (h), yield (%)	substrate	time (h), yield (%)
 2	2 h, 94%	 9	4 h, 95%
 3	3 h, 84%	 10	3 h, 99%
 4	8 h, 92%	 11	24 h, 88%
 5	24 h, 82%	 12	5 h, 85%
 6	2 h, 99%	 13	2 h, 98%
 7	5 h, >99%	 14	24 h, 97%
 8	7 h, 95%		

[a] All reactions were run at 50 °C using 0.5 mmol of allyl ethers and 2 mol % of **1** in aniline (0.46 mL, 10 equiv).

for completion at room temperature.[27] On the other hand, in the presence of 1 mol % of **1** in aniline, the deprotection from cyclohexylcarbamate **23** was completed within 1 min at 30 °C (eq 4).[29]



(4)

Highly selective deallylation was observed for 2-, 3-, and 4-hydroxybenzoic acid derivatives having allyl ether and allyl ester moieties (**24**−**26**) (eqs 5−7). The reaction site was dramatically changed with substitution patterns. Thus, the ortho isomer **24** exclusively underwent deallylation from the allyl ether part, even in the presence of an excess of aniline, to give a quantitative yield of allyl salicylate **27** (eq 5).[30] On the other hand, treatment of the meta and para isomers **25** and **26** with 1 equiv of aniline in toluene caused deallylation from the allyl ester part in 93 and 92% selectivities, respectively (eqs 6 and 7), while both allyl groups were eliminated when the reactions were conducted with more than 2 equiv of aniline.

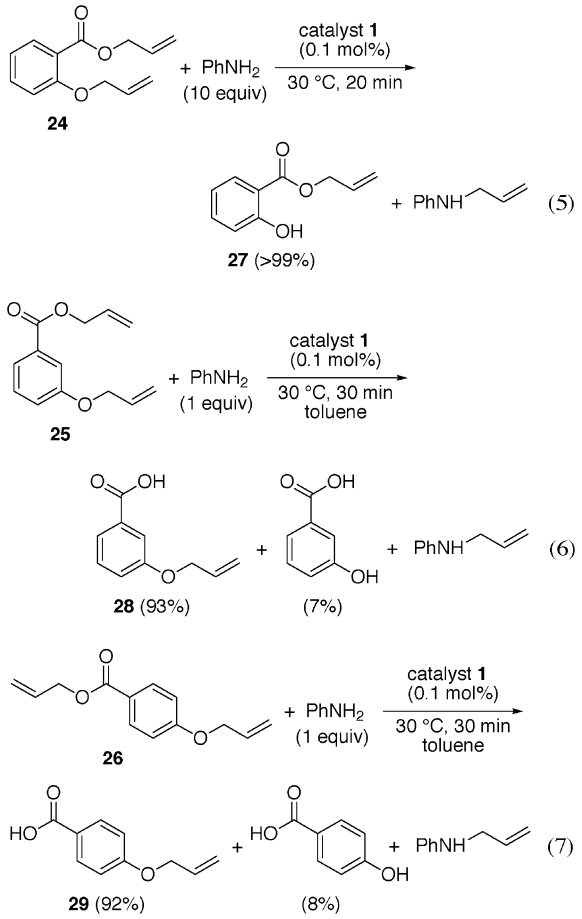
TABLE 2. Deallylation of Para-Substituted Allyl Phenyl Ethers (eq 3)[a]

compd	Y	time (min)	yield (%)
15	H	20	98
16	CN	20	99
17	CHO	20	99
18	CO_2Me	20	99
19	CH_2OH	20	99
20	CH(OH)Me	30	99
21	COMe	60	99
22	Br	180	>99

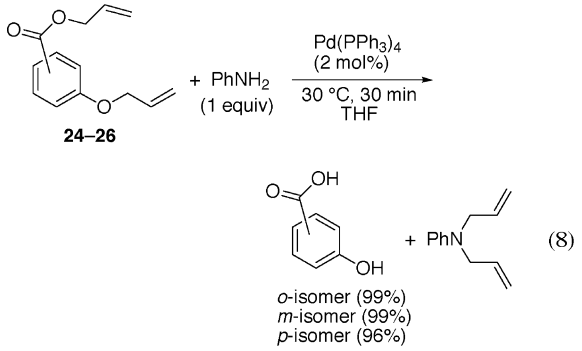
[a] All reactions were run at 30 °C using 0.5 mmol of allyl ethers and 0.1 mol % of **1** in aniline (0.46 mL, 10 equiv).

In contrast to the above reactions using catalyst **1**, no selective deallylation proceeded with $Pd(PPh_3)_4$ as a catalyst (eq 8). For example, treatment of **24** with 1 equiv of aniline in THF[31] in the presence of 2 mol % of $Pd(PPh_3)_4$ caused simultaneous elimination of the two allyl groups to give a quantitative yield of salicylic acid,

(29) The reaction was finished in 10 min with 0.1 mol % of **1**.
(30) Product **27** remained unchanged for 24 h at 30 °C in the reaction solution, but converted to salicylic acid at 50 °C.



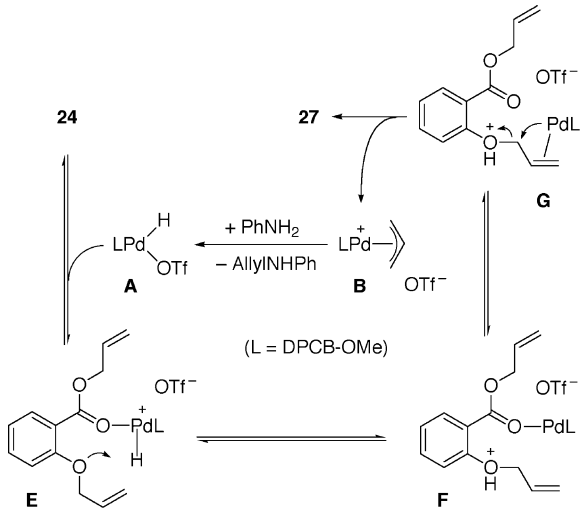
along with byproduction of *N*,*N*-diallylaniline. This reaction pattern was preserved when a smaller amount of aniline was employed. Thus, the reaction with 0.5 equiv of aniline afforded 50% yield of salicylic acid; i.e., 50% of **24** remained unreacted. Similarly, **25** and **26** reacted with aniline (1 equiv) in THF in the presence of $Pd(PPh_3)_4$ (2 mol %) to give 3- and 4-hydroxybenzoic acids.



Summary

We demonstrated that complex **1** bearing a DPCB-OMe ligand serves as a highly efficient catalyst for deallylation of allylic compounds. The reactions could be conducted simply by mixing allylic substrates with aniline as the scavenger of allyl group. The observed reactivity was comparable or higher than that of the palladium-catalyzed systems recently reported.[23−28] Furthermore, it was noted that only one of the allyl groups in allyl allyloxybenzoates **24**−**26** can be deprotected, whereas the $Pd(PPh_3)_4$ catalyst shows no notable selectivity. Selective deallylation from the allyl ether part in **24** is of particular interest, because allyl ethers are generally less reactive than allyl esters toward palladium-catalyzed allylations. Since the meta and para isomers **25** and **26** underwent deallylation from the allyl ester part, the unusual selectivity observed for **24** should be related to a neighboring group effect. Scheme 2 illustrates a possible reaction process. First, the substrate **24** is coordinated to **A**. Proton-transfer from the Pd to the ether oxygen in **E**, followed by transfer of the Pd(DPCB-OMe) moiety from the carbonyl group to the allyl group in **F**, forms **G**. It was considered that the protonation takes place at the ether oxygen with higher electron density, rather than the ester oxygen. Elimination of **27** from **G** affords **B**, which subsequently reacts with aniline to reproduce **A**. Further applications of this highly selective catalysis will be reported in due course.

SCHEME 2



Experimental Section

Allylic substrates were prepared by allylation of the corresponding alcohols. Catalyst **1** was synthesized as previously reported.[6b,32]

Catalytic Deallylation. Complex **1** (11.1 mg, 0.010 mmol) and biphenyl (15.4 mg, 0.10 mmol, GLC standard) were placed in a 10 mL Schlenk tube and dissolved in allyl alkyl ether (0.50 mmol) and aniline (0.46 mL, 5.0 mmol). The solution was stirred at 50 °C until the starting ether disappeared in GLC. The mixture was extracted with a 6 N HCl solution and Et_2O and subsequently subjected to silica gel column chromatography to afford deallylation products as listed in Table 1. Deallylation products derived from **11**−**14** were isolated without acid extraction. The reactions listed in Table 2 and eqs 5−7 were similarly conducted using 0.1 mol % of **1** (0.56 mg, 0.50 μmol) at 30 °C. The ^{1}H NMR spectra of reaction products (except for **27**−**29**) were identical with those of the starting alcohols.

Since **27**−**29** were known compounds, they were characterized by ^{1}H NMR and IR spectroscopy. The site of deallylation was clearly confirmed by ^{1}H NMR spectroscopy. Thus, the

(31) THF was used as a solvent because the $Pd(PPh_3)_4$-catalyzed reaction was significantly slow in toluene.

(32) Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4501.

starting compounds **24**−**26** exhibited two sets of methylene proton signals at δ 4.6 and 4.8, which were assignable to the allyl ether and allyl ester groups, respectively. The former signal disappeared in the spectrum of **27**, whereas the latter disappeared in the spectra of **28** and **29**.

Allyl Salicylate (27).[33] White solid. ^{1}H NMR ($CDCl_3$, 20 °C): δ 4.81 (ddd, J = 5.7, 1.2, 1.2 Hz, 2H), 5.45 (ddt, J = 10.1, 1.2, 1.2 Hz, 1H), 5.50 (ddt, J = 17.1, 1.2, 1.2 Hz, 1H), 6.10 (ddd, J = 17.1, 10.1, 5.7 Hz, 1H), 7.05 (dd, J = 8.4, 0.9 Hz, 1H), 7.15 (ddd, J = 7.8, 7.2, 0.9 Hz, 1H), 7.56 (ddd, J = 8.4, 7.2, 1.8 Hz, 1H), 8.20 (dd, J = 7.8, 1.8 Hz, 1H). IR (KBr): 3239, 3063, 3011, 2925, 2856, 1660, 1612, 1249, 995 cm^{-1}.

3-Allyoxybenzoic Acid (28).[34] White solid. ^{1}H NMR ($CDCl_3$, 20 °C): δ 4.61 (ddd, J = 5.1, 1.5, 1.5 Hz, 2H), 5.32 (ddt, J = 10.8, 1.5, 1.5 Hz, 1H), 5.45 (ddt, J = 17.4, 1.5, 1.5 Hz, 1H), 6.07 (ddd, J = 17.4, 10.8, 5.1 Hz, 1H), 7.18 (ddd, J = 7.8, 2.4, 0.6 Hz, 1H), 7.38 (dd, J = 7.8, 7.7 Hz, 1H), 7.63 (dd, J = 2.4, 1.5 Hz, 1H), 7.72 (ddd, J = 7.7, 1.5, 0.6 Hz, 1H). IR (KBr): 3286, 3074, 2830, 1716, 1604, 1263, 999 cm^{-1}.

4-Allyoxybenzoic Acid (29).[35] White solid. ^{1}H NMR ($CDCl_3$, 20 °C): δ 4.62 (ddd, J = 5.1, 1.5, 1.5 Hz, 2H), 5.33 (ddt, J = 10.8, 1.5, 1.5 Hz, 1H), 5.43 (ddt, J = 17.1, 1.5, 1.5 Hz, 1H), 6.06 (ddd, J = 17.1, 10.8, 5.1 Hz, 1H), 6.96 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.7 Hz, 2H). IR (KBr): 3080, 3025, 2982, 2942, 2875, 2253, 1677, 1605, 1428, 1253, 907, 733 cm^{-1}.

Deallylation of 24−26 Catalyzed by $Pd(PPh_3)_4$ (eq 8). As an example, **25** (218.3 mg, 1.0 mmol), $PhNH_2$ (94.6 mg, 1.01 mmol), and $Pd(PPh_3)_4$ (23.1 mg, 0.020 mmol) were placed in a 10 mL Schlenk tube and dissolved in THF (1 mL) at room temperature. The solution was stirred for 30 min. GLC analysis of the solution revealed complete conversion of aniline to diallylaniline.[6a] The product was extracted with AcOEt and a 6 N HCl solution. Organic extract was dried over $MgSO_4$ and concentrated to dryness to give 3-hydroxybenzoic acid as a white solid (139.0 mg, 99%).

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Supporting Information Available: Experimental details and ^{1}H NMR spectra of all new compounds and **27**−**29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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