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Palladium(0)-Catalyzed Intramolecular Decarboxylative Allylation of Ortho Nitrobenzoic Esters

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Supporting Information

ABSTRACT: A Pd/Ag bimetallic system has been developed for the decarboxylative allylation of *ortho*-nitrobenzoic esters in an intramolecular fashion. In contrast to the typical sp^2-sp^3 cross-coupling approach which requires air and moisture sensitive preformed organometallic reagents, we provide an alternative route to the synthesis of *ortho*-allyl nitroarenes from the corresponding *ortho*-nitrobenzoic acid derivatives. The reaction proceeds through a mechanistically distinct decarboxylative metalation pathway. A cooperative reactivity of palladium and silver is crucial for the reaction outcome.

Aromatic nitro compounds are useful intermediates for the synthesis of agrochemicals, pharmaceuticals, dyes, photoreactive compounds, high energetic materials, radiopharmaceutical tracers, etc.[1] A facile reduction of the aromatic nitro groups to their corresponding anilines provides common starting materials for the syntheses of a plethora of *N*-heterocycles and natural products.[2] Despite their interesting properties, access to *ortho*-substituted nitroarenes is limited due to inherent incompatibility with some organometallic reagents.[3] To overcome this problem the Knochel group introduced an elegant approach for the generation of nitro-containing organometallics via I−Mg exchange.[4] However, this protocol suffers from serious limitations such as the use of air and moisture sensitive preformed organometallic reagents, highly toxic copper(I)cyanide, and expensive organohalides. Therefore, alternative routes to the synthesis of *ortho*-functionalized nitroarenes using inexpensive, air and moisture stable starting materials are in high demand.

Recently, increasing use of nitrobenzoic acid derivatives in palladium-catalyzed decarboxylative cross-coupling reactions[5] has also motivated us to explore the *ortho*-allylation reaction. Although palladium-catalyzed decarboxylative sp^3-sp^3 allylic alkylation has been widely explored,[6] decarboxylative sp^2-sp^3 allylation is less studied.[7] In this vein, an activated coumarin moiety furnished moderate to good yields of allylation product and preferred sp^3-sp^3 allylation[6i] over the sp^2-sp^3 allylation.[7a] Decarboxylative allylation of electron-rich arenes also provided poor yields of the desired products.[7b] Decarboxylative allylation of α-oxocarboxylates resulted in α,β-unsaturated ketones through alkene isomerization.[7c] The difficulty in decarboxylative sp^2-sp^3 allylation arises due to the fact that, in sp^3-sp^3 allylation, the incipient anion after decarboxylation is stabilized by the proximal electron-withdrawing groups such as keto,[8] ester,[9] nitro,[10] cyano,[11] sulfone,[12] etc. Whereas, in the case of sp^2-sp^3 allylation, the anion on the sp^2-carbon is highly unstable and exhibits a high propensity toward protonation. Therefore, selective sp^2-sp^3 decarboxylative allylation in high yields is an extremely challenging task to achieve. To our surprise, decarboxylative sp^2-sp^3 allylation of electron-deficient arenes especially nitroarenes is not known. We hypothesized that the nitro group at the *ortho* position could be beneficial in decarboxylative allylation as it can stabilize the aryl anion which is formed after decarboxylation.

We started optimization of the reaction conditions by heating a mixture of *ortho*-nitrobenzoic acid and allyl bromide and a catalytic amount of Pd(0) at 160 °C, but no allylation product was formed. Switching to allyl acetate from allyl bromide resulted in a trace amount of allylation product along with nitrobenzene as a major product. We realized that the carboxylic acid proton could be detrimental for the allylation product formation and may lead to the undesired protonation product. Therefore, the potassium salt of the corresponding nitrobenzoic acid was employed, but unfortunately, no allylation product was observed. Next, an allyl ester of the corresponding acid was prepared and subjected to the intramolecular decarboxylative allylation (Table 1). Interestingly, all starting material was consumed and a mixture of corresponding allyl and styrenyl products was isolated in slightly improved yield (entry 18, Table 1). Still, the undesired *ortho*-nitrobenzoic acid and nitrobenzene were formed predominantly. The poor mass balance toward the allylation product can be attributed due to decomposition of the π-allyl-Pd species[13] and double bond isomerization at elevated temperature to generate the undesired styrenyl product. Therefore, we decided to use the silver(I) salt as an additive since it is known to promote decarboxylation at lower temperature[14] and decreases double bond isomerization.[15] Gratifyingly, yield was improved to 55% with the addition of only 10 mol % of the silver carbonate (entry 5, Table 1). After a rigorous study varying the catalyst, ligand, solvent, and the

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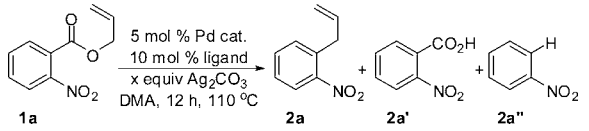
Table 1. Optimization of the Reaction Conditions[a]



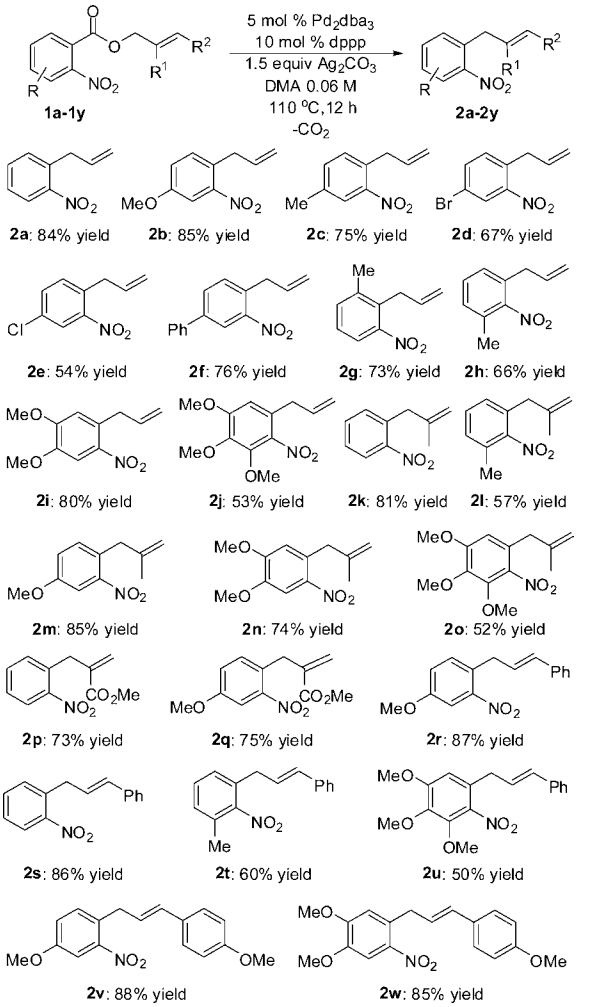
entry	Pd cat.	ligand	x	yield (%)[b]	2a:2a′:2a″[b]
1[c]	$Pd(PPh_3)_4$	–	0	0	–
2[c]	$Pd(PPh_3)_4$	–	0.2	30	70:10:20
3[c]	$Pd(OAc)_2$	–	0.2	0	–
4[c]	$Pd(tfa)_2$	–	1.5	0	–
5	Pd_2dba_3	xantphos	0.1	55	80:7:13
6	Pd_2dba_3	dppf	0.1	50	75:10:15
7	Pd_2dba_3	rac-BINAP	0.1	63	73:7:20
8	Pd_2dba_3	dppp	0.1	68	82:10:8
9	Pd_2dba_3	dppp	0.5	72	85:6:9
10	Pd_2dba_3	dppp	1.0	80	85:5:10
11	**Pd_2dba_3**	**dppp**	**1.5**	**90**	**94:0:6**
12	Pd_2dba_3	dppp	2.0	88	92:0:8
13	Pd_2dba_3	dppe	1.5	40	78:13:9
14	Pd_2dba_3	dppb	1.5	50	80:12:8
15	Pd_2dba_3	PCy_3	1.5	45	82:10:8
16	Pd_2dba_3	xphos	1.5	60	77:13:10
17[d]	Pd_2dba_3	dppp	0	0	–
18[e]	Pd_2dba_3	dppp	0	55	30:43:27
19	$Pd(tfa)_2$	dppp	1.5	48	63:27:10
20[f]	$Pd(tfa)_2$	–	3.0	7	–

[a]All reactions were carried out in 0.1 mmol scale, in DMA 0.06 M. [b]Yields refered to here are overall isolated yields, and product distributions were determined by ^{1}H NMR of the crude product. [c]10 mol % of the Pd cat. was used. [d]100 mol % of the Pd_2dba_3 and 200 mol % of the dppp were used. [e]The reaction was heated at 160 °C; a mixture of allyl and styrenyl product was isolated. [f]20 mol % of $Pd(tfa)_2$, DMF/DMSO (19:1), 120 °C.

amount of additive, the allylation product was isolated in excellent yields using a combination of 5 mol % Pd_2dba_3, 10 mol % dppp with 1.5 equiv of Ag_2CO_3 in DMA at 110 °C.

Under the optimized reaction conditions, we explored the substrate scope for the decarboxylative allylation reaction (Scheme 1). A variety of substituted nitroarenes allow the formation of allylation products in good to excellent yields. A careful study revealed that electron-donating substituents such as *p*-OMe on *o*-nitrobenzoate favor allylation product formation (**2b**, **2m**, **2q**, **2r**, **2v**, Scheme 1) and two *m*-OMe groups which are electron-withdrawing in nature lower the yields to some extent (**2i**, **2n**, **2w**, Scheme 1). However, yields of the allylation products are decreased drastically with a substitution of three adjacent −OMe groups due to low conversion, substantial amounts of protonation product, and carboxylic acid formation (**2j**, **2o**, **2u**, Scheme 1). Substrates with an electron-deficient substituent, e.g. 2,4-dinitro benzoic ester, resulted in a decarboxylative protonation product only. Therefore, electron-withdrawing substituents on the *o*-nitro-benzoate facilitate decarboxylation but they decrease the ability of the aryl anion to serve as a σ-donor for the Pd(II)allyl cation. Halogen substituents, such as Br, Cl, are compatible with the reaction conditions (**2d**, **2e**, Scheme 1) which may undergo further cross-coupling reactions. In addition to the cross-couplings of unsubstituted allyl esters, a variety of substituted and functionalized allyl esters also underwent couplings to provide allylation products (**2k**−**2q**, Scheme 1). Allyl esters from the corresponding cinnamyl alcohols and its derivatives produced

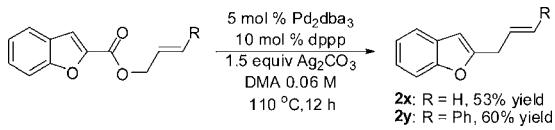
Scheme 1. Substrate Scope of Decarboxylative Allylation[a,b]



[a]All reactions were carried out in 0.3 mmol scale. [b] Yields refer to the average of isolated yields of at least two experiments.

the linear product selectively (**2r**−**2w**, Scheme 1). However, allyl esters that possess β-hydrogens such as crotyl, prenyl, 2-cyclohexenyl esters preferentially formed conjugated dienes via β-hydrogen elimination and a protonation product[6g] (see Supporting Information, Scheme 1). A selective reduction of the nitro group afforded *o*-allyl aniline in excellent yields (Supporting Information, Scheme 2).

Scheme 2. Decarboxylative Allylations of Benzofuran-2-Carboxylates



Subsequently, several heteroaromatic carboxylic esters were tested under the reaction conditions. Unfortunately, nitrogen-containing heterocycles such as indole and pyridine-2-carboxylic esters did not furnish any desired product. However, benzofuran-2-carboxylic esters furnished an allylation product in good to moderate yields (Scheme 2).

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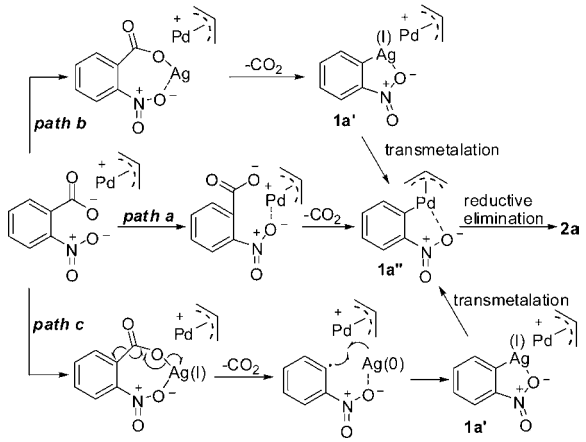
Next, we turned our attention toward gaining insight into the reaction mechanism. After oxidative addition of palladium(0) to the allyl ester **1a** the reaction may proceed in three distinct pathways. In ***path a***, the solvent-separated ion pair may undergo decarboxylation via a two-electron process[16] followed by carbopalladation to generate **1a**″ which is converted to the desired product after reductive elimination. Whereas, in ***path b***, a silver-assisted decarboxylation via an anionic route can generate the arylsilver species **1a**′ which can undergo transmetalation with palladium followed by reductive elimination to furnish an allylation product. Alternatively, this silver-assisted decarboxylation may proceed via a Hunsdiecker-type free radical pathway as depicted in ***path c*** (Scheme 3). The *ortho*-nitro group can stabilize to either the organosilver(I) or organopalladium(II) prior to and after decarboxylation through coordination.

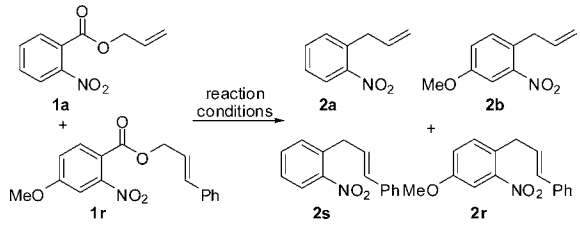
Scheme 3. Possible Mechanistic Pathways



To elucidate, several control experiments were performed. Heating the reaction mixture at 110 °C without any silver salt resulted in only nitrobenzoic acid. Even a stoichiometric amount of palladium also failed to promote decarboxylation at this temperature (entry 17, Table 1), whereas heating the reaction mixture at 160 °C with a catalytic amount of palladium afforded the desired product albeit in low yield (entry 18, Table 1). On the other hand, when *ortho*-nitro benzoic acid was heated at 110 °C only with the silver carbonate the nitrobenzene was formed indicating silver-assisted decarboxylation. To elucidate further, the reaction was carried out under the standard reaction conditions in the presence of 1.0 equiv of TEMPO, a radical scavenger. Almost the same yield of **2a** as under the standard conditions (84%) was obtained, which rules out the radical mechanism as shown in ***path c***. When Pd(II)/Ag(I) was used in lieu of Pd(0)/Ag(I), only starting material was recovered which indicates that Pd(0) is essential to initiate the reaction (entry 20, Table 1). An extensive crossover was also observed between two structurally disparate allyl esters, which is supportive evidence that the solvent-separated ion pairs are formed and undergo all possible combinations to provide the crossover products (Scheme 4).

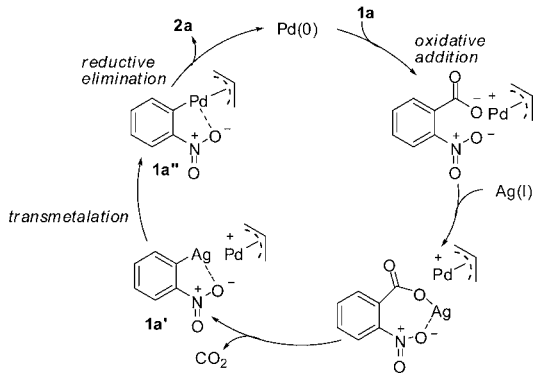
Based on these observations, we presumed that the reaction may proceed through ***path a*** at an elevated temperature vs ***path b*** under a Pd/Ag bimetallic system at a lower temperature. Initially, palladium(0) undergoes an oxidative addition to the allyl ester **1a** to form a π-allyl-Pd complex and an *ortho*-nitrobenzoate anion. Subsequently, a silver salt of the

Scheme 4. Crossover Experiment



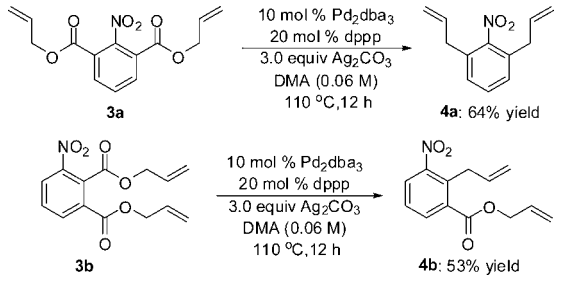
corresponding *ortho*-nitrobenzoic acid may form and undergo Ag(I)-assisted decarboxylation to afford the corresponding aryl-Ag species **1a**′. A transmetalation between an aryl-Ag and π-allyl-Pd complex generates an aryl-Pd species **1a**″. Finally, reductive elimination yields the desired allylation product and the Pd(0) to complete the catalytic cycle (Scheme 5).

Scheme 5. Plausible Catalytic Cycle for the Decarboxylative Allylation



Finally, to demonstrate the role of the nitro group in decarboxylative allylation, we synthesized diallyl ester **3a** where both ester groups are *ortho* to the nitro group and its corresponding regioisomer **3b** where one allyl ester group is at the *ortho* position and the other one is at the *meta* position. Under slightly modified reaction conditions, **3a** afforded a diallylation product in good yield via double decarboxylative allylations, whereas **3b** afforded the monoallylation along with the decarboxylative protonation product at the *ortho* position leaving the *meta* allyl ester intact (Scheme 6). Similarly, *para*-nitro benzoic ester was inactive under the reaction conditions. Presumably, the nitro group at the *ortho* position has a dual role in decarboxylation. First, it can coordinate to either the Ag(I) or Pd(II) prior to and after decarboxylation. This is particularly important for "post-decarboxylation" acting as a C/O bidentate

Scheme 6. Selective Decarboxylative Allylation of Nitro Benzoic Esters



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ligand to form a relatively stable 5-membered palladacycle. Second, it imparts a strong inductive effect that stabilizes the incipient anion which leads to rapid decarboxylation followed by allylation.

In conclusion, we have developed a Pd/Ag bimetallic system for the decarboxylative sp^2–sp^3 allylation of *ortho*-nitrobenzoic esters in an intramolecular fashion. A synergistic effect of palladium and silver was observed in this decarboxylative allylation. Mechanistic studies suggest that silver-assisted decarboxylation occurs in an anionic pathway at the presented reaction conditions which lead to an allylation product via transmetalation and reductive elimination.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectroscopic data, ^1H and ^{13}C NMR spectra for all synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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