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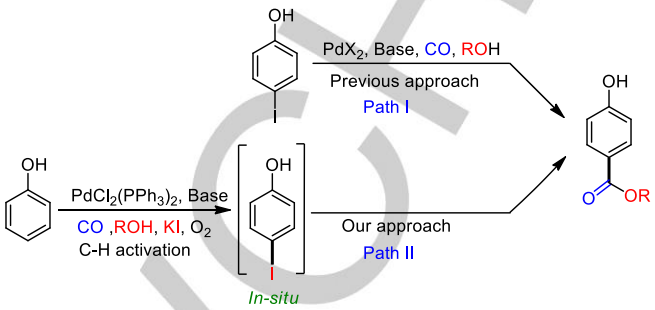
Palladium-Catalyzed Aerobic Oxidative Carbonylation of C-H Bond of Phenol for the Synthesis *p*-hydroxybenzoate

Vinayak V. Gaikwad[a] and Bhalchandra M. Bhanage*[a]

Abstract: This work reports the synthesis of *p*-hydroxybenzoate directly from phenol by oxidative carbonylation. In this work aryl C-H bond of phenol was carbonylated via oxidative iodination, leading to the synthesis of *p*-hydroxybenzoate. The developed methodology is efficient and economically attractive because phenols are cheap and easily available starting material. This novel one-pot strategy has been expediently applied for the synthesis of variety *p*-hydroxybenzoate utilizing simple primary and secondary alcohols with phenols under mild reaction condition. Advantageously, this reaction proceeded without the need of co-catalyst, co-solvent and external ligand. Utilization of molecular oxygen as a terminal oxidant for oxidation of C-H bond is an additional benefit of this strategy.



Scheme 1.. Synthesis of *p*-hydroxybenzoate by Carbonylation method.

Introduction

Transition metal catalyzed carbonylation of aryl halides or pseudohalides has been a most potent methodology for the synthesis of carboxylic acid and its derivatives and this method was established in 1974 by Heck and co-workers.[1–8] On the other hand, activation of the inert C-H bond is very attractive and difficult task in synthetic chemistry, however with a precise selection of catalyst and substrate the task can be achieved.[9–12] Even so, carbonylation of C-H bond has a great challenge and attractive field. Synthesized benzoic acid by carbonylation of aryl C-H bond was pioneered by Fujiwara and co-workers in 1980.[13] In past two decades, the significant efforts have been made towards broadening the scope of carbonylation reaction *via* C-H bond activation. These reactions are environmentally benign and greener, as it avoids multiple steps for functionalization of such substrates. Palladium-catalyzed carbonylation of C-H functionalization of arenes and heteroarenes are shown for the synthesis of carboxylic acids and their derivatives.[14–19] Nowadays, Directing group-assisted carbonylation of the simple C-H bond has been emerged as an ideal strategy by introducing of carbon monoxide to construct variety carbonylative compounds. Numerous, directing groups such as amide, amines, heteroatoms and hydroxy groups have been used for carbonylation of C-H bond.[20–27] However, most of this progress is practiced by molecules containing directing groups, utilizing hazardous metals and oxidant such as copper, silver salt or peroxide which are undesirable from a green chemistry point of view. Molecular oxygen as an ideal and readily available, nonhazardous oxidant in oxidative carbonylation reactions. [28–30]

p-hydroxybenzoate is a major chemical feedstock in the research field of natural products, pharmaceuticals, agrochemicals and functional materials.[31–36] In the past decade, significant attention has been made towards the synthesis of these carbonylative compounds by the traditional approach.[37–41] Among these, palladium catalyzed carbonylation of *p*-iodophenol was followed by nucleophilic attack of alcohols leads to the synthesis of *p*-hydroxybenzoate is one of the dominant route used in the laboratory as well as an industrial scale (**Path I**).[42–45] Recently, Elango and co-workers have successfully synthesized *p*-hydroxybenzoate by activation of bromophenol using carbonylation method.[46] However, those methodologies have some limitations such as the use of expensive starting materials, longer reaction time, harsh reaction conditions, uses of traditional solvents, co-catalyst and lewis acids. Thus, to overcome these limitations we report here the synthesis of *p*-hydroxybenzoate directly from phenol.

Herein, we communicate a palladium catalyzed carbonylation of aryl C-H bond of phenol for the synthesis of *p*-hydroxybenzoate as an efficient approach (**path II**). In this context, carbonylation occurs selectively at the para position of phenol by activation of aryl C-H bond via oxidative iodination. Additionally, the advantage of this methodology is a single step process, utilizing molecular oxygen as an ideal and environmentally benign oxidant.

Results and Discussion

The carbonylative coupling between phenol and methanol for the synthesis of methyl 4-hydroxybenzoate was selected as a model reaction. Various reactions parameters have been screened on this model reaction (**Table1**). Initially, we investigate various palladium precursors for the carbonylative

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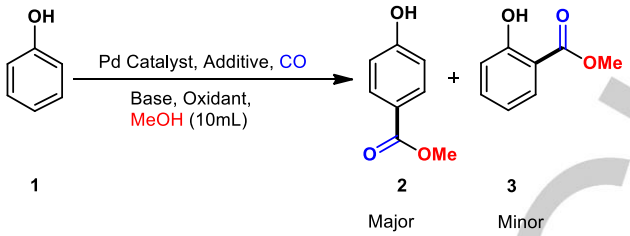
† Electronic supplementary information (ESI) available; (Study of time, temp.and press, copies of ^{1}H and ^{13}C NMR)

Table 1: Screening of optimal reaction condition[a]



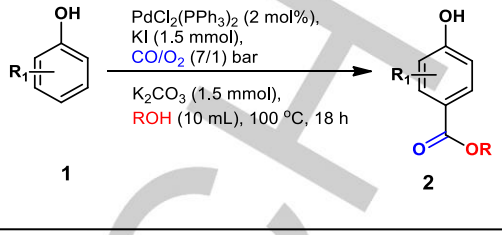
1 2 Major 3 Minor

Entry	Pd precursor	Oxidant	Additive	Base	Solvent	Conversion[b] (%)	Selectivity[b] p:o (%)
1	$Pd(OAc)_2$	O_2	KI	K_2CO_3	MeOH	80	85:15
2	$PdCl_2$	O_2	KI	K_2CO_3	MeOH	79	80:20
3	$Pd(PPh_3)_4$	O_2	KI	K_2CO_3	MeOH	80	68:32
4	$PdCl_2(PPh_3)_2$	O_2	KI	K_2CO_3	MeOH	98	93:7
5	$PdCl_2(PPh_3)_2$	Ag_2O	KI	K_2CO_3	MeOH	--	--
6	$PdCl_2(PPh_3)_2$	Cu $(OAc)_2$	KI	K_2CO_3	MeOH	--	--
7	$PdCl_2(PPh_3)_2$	Oxone	KI	K_2CO_3	MeOH	--	--
8	$PdCl_2(PPh_3)_2$	$K_2S_2O_8$	KI	K_2CO_3	MeOH	--	--
9	$PdCl_2(PPh_3)_2$	O_2	TBAI	K_2CO_3	MeOH	80	85:15
10	$PdCl_2(PPh_3)_2$	O_2	NaI	K_2CO_3	MeOH	70	65:35
11	$PdCl_2(PPh_3)_2$	O_2	NH_4I	K_2CO_3	MeOH	55	60:40
12	$PdCl_2(PPh_3)_2$	O_2	I_2	K_2CO_3	MeOH	30	63:37
13[c]	$PdCl_2(PPh_3)_2$	O_2	KI	K_2CO_3	CH_3CN	30	70:30
14[c]	$PdCl_2(PPh_3)_2$	O_2	KI	K_2CO_3	DMF	25	65:35
15[c]	$PdCl_2(PPh_3)_2$	O_2	KI	K_2CO_3	THF	17	60:40
16[c]	$PdCl_2(PPh_3)_2$	O_2	KI	K_2CO_3	Toluene	--	--
17	$PdCl_2(PPh_3)_2$	O_2	KI	Na_2CO_3	MeOH	78	80:20
18	$PdCl_2(PPh_3)_2$	O_2	KI	Cs_2CO_3	MeOH	80	83:17
19	$PdCl_2(PPh_3)_2$	O_2	KI	NaOH	MeOH	75	65:35
20	$PdCl_2(PPh_3)_2$	O_2	KI	KOH	MeOH	72	62:37
21	$PdCl_2(PPh_3)_2$	O_2	KI	NEt_3	MeOH	60	60:40
22	$PdCl_2(PPh_3)_2$	O_2	KI	DBU	MeOH	50	55:45
23[d]	$PdCl_2(PPh_3)_2$	O_2	KI	K_2CO_3	MeOH	60	75:25
24[e]	$PdCl_2(PPh_3)_2$	O_2	KI	K_2CO_3	MeOH	55	69:31

[a]**Reaction conditions**: Phenol (1 mmol), base (1.5 mmol), MeOH (10 mL), additive (1.5 mmol), catalyst (2 mol %), $CO:O_2$ (7:1), 8 bar, 100 °C, 18 h [b]Conversion and selectivity determined by GC &GC-MS. [c]MeOH (5 mL) and solvent (5 mL).[d] PPh_3 (5 mol %) [e] Xantphose (5 mol %)

coupling between phenol with methanol in presence of $CO:O_2$ (7+1=8 bar) mixture. We used molecular oxygen as a terminal oxidant along with KI for 18 h at 100°C. Initially, we used $Pd(OAc)_2$ as a catalyst precursor and observed carbonylative product of methyl 4-hydroxybenzoate (***p***) and methyl 2-hydroxybenzoate (***o***) with 80% conversion of **1** and showing 85:15% selectivity. (Table 1 **entry 1**). However, the selectivity of ***p*:*o*** was decreased to 80:20% and 68:32% at 80% conversion by using $PdCl_2$ and $Pd(PPh_3)_4$ as a catalyst respectively (Table 1 entry **2** and **3**). Next, we obtained 93:7% selectivity of ***p*:*o*** with 98% conversion by using $PdCl_2(PPh_3)_2$ as an effective catalyst. Since, this catalyst furnished higher conversion, we used this catalyst for further studies. (Table 1, **entry 4**). Further, we screened various commercial oxidants such as Ag_2O, $Cu(OAc)_2$, Oxone and $K_2S_2O_8$ to see the effect on conversion and selectivity. Molecular oxygen was the only oxidant which gave a better conversion of **1** (Table 1, **entries 5-8**) and was used for the next optimization study. Furthermore, we investigated $PdCl_2(PPh_3)_2$ catalyst along with different additives to increase the selectivity of the desired ester of **2**. We have carried out the reaction by using various additives such as TBAI, NaI, NH_4I and I_2 and it gave ***p*:*o*** selectivity of 85:15%, 65:35%, 60:40 % and 63:37% respectively (Table 1, entries **9-12**). The highest conversion as well as selectivity was obtained by using of KI as an additive and further reactions were carried out with it. Subsequently, the effect of various solvents was investigated. We observed 98% conversion of **1** by using methanol as a solvent. However, methanol is good solvent and it also acts as an effective nucleophile and hence considered for the next optimization studies (Table 1 entry **13-16**). The conversion of **1** was significantly increased by using of K_2CO_3 as a base and it furnished good selectivity ratio of ***p*:*o*** product, while other inorganic bases such as Na_2CO_3, Cs_2CO_3, NaOH and KOH reduces conversion and selectivity (Table 1 entries **17-20**). Organic bases such as NEt_3 and DBU provides 60% and 50% conversion of **1** with poor selectivity (Table 1 entries **21** and **22**). Further, we extended this work for the study of various phosphorous containing ligands along with $PdCl_2(PPh_3)_2$ as a catalyst, and we have detected 60% conversion of **1** with PPh_3 as a ligand. Next, the conversion was declined to 55%, when the reaction was carried along Xantphos as a ligand with good selectivity i.e. the negligible effect of ligands on the conversion and selectivity of carbonylation reaction. The used of additional ligands was not observed in the carbonylative reaction. (Table 1 **entries 23** and **24**). Further, we studied the effect of CO pressure on the reaction. We observed the superior conversion of **1** by applying $CO:O_2$ (7:1 bar) pressure with showing good selectivity ratio (93:7%). However, a decrease in $CO:O_2$ pressure (5:1 bar), led to decrease in conversion (80%) and selectivity (see ESI, Table 1, **entry 1-3**). Further, we study the effect of temperature on conversion as well as selectivity. The increase in the temperature from 100 °C to 120 °C has not a significant effect on conversion and selectivity. Next, we observed 95% conversion, when the reaction was carried out 80 °C for 18h. (see ESI Table 1, **entry 4-6**). Time study

Table 2. Substrate scope of Phenol[a]



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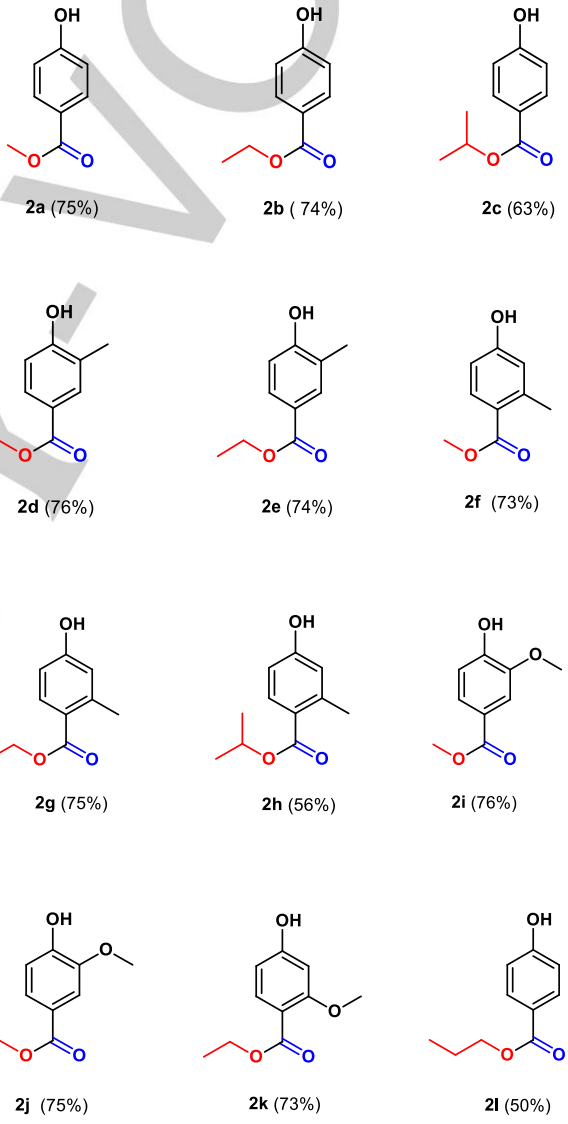
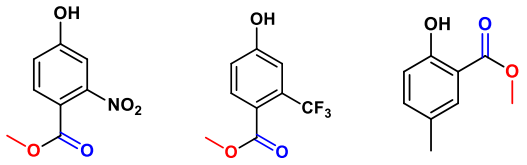




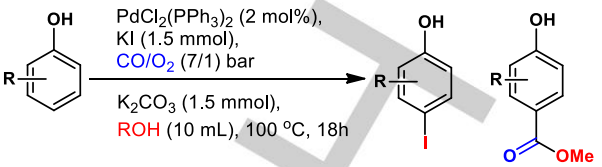
2m (0%) **2n** (0%) **2l** (0%)

[a]**Reaction conditions**: Phenol (1 mmol), base (1.5 mmol), MeOH (10 mL), additive (1.5 mmol), catalyst (2 mol %), CO:O_2 (7:1 bar), 18 h. [b] Isolated Yield.

revealed that 18h was enough for good conversion (98%) and selectivity of the desired ester (see ESI Table 1, **entry 7-9**).

After optimization of reaction conditions, we further investigated the synthesis of the various ester from a range of substituted phenols with alcohols. Methylparaben and ethylparaben are major backbones of pharmaceutically active drug molecules and it is considered as very important in medicinal chemistry. We have successfully synthesized those compounds by carbonylative reaction between phenol with methanol and ethanol underdeveloped condition, providing 75% (2a) and 74% (2b) yield and a trace amount of ortho product respectively. However, secondary alcohol such as isopropanol (IPA) reacted with phenol and generated 63% yield of **2c** and very negligible ortho product**.** Next, we proceeded reaction between ortho-cresol with methanol and ethanol which led to the synthesis of **2d** and **2e** in 76% and 74% yield respectively. Furthermore, we were successfully able to synthesize methyl 4-hydroxy-2-methyl benzoate (**2f**) and ethyl 4-hydroxy-2-methyl benzoate (**2g**) by carbonylative coupling between m-cresol with methanol and ethanol offered in excellent yield. When IPA reacted with meta-cresol, the steric crowing between methyl groups of alcohols and m-cresol led to decrease in yield of desired ester **2h**. Further, the phenol bearing the strong electron donating group (-OMe), carbonylative coupling with methanol and ethanol offered the corresponding ester **2i** and **2j, 2k** with excellent yield. Next, we proceeded reaction with propanol and moderate yields of respected ester (**2l**) were observed. Next, we carried out the reaction of methanol with electron withdrawing substituents, meta-nitro, meta- fluoro on phenol, but no little product of **2m** and **2n** was observed. Next, we proceed reaction of *p*-cresol with methanol, unfortunately, reaction failed to the product of **2l** in 0 % yield. To gain inside the mechanism we have carried out the controlled experiments by carbonylative coupling between phenol and methanol under different conditions**.** Without the use of an active catalyst, the reaction proceeded with no ester product **3** observed showing that active catalyst have a major role in the reaction (Scheme 2 entry **1**). Next, we got 4-iodophenol in 90% yield, without applying of carbon monoxide pressure, this result clearly indicates that formation of 4-iodophenol as an intermediary in carbonylative transformation (Scheme 2 entry **2**). Further, we remove KI from standard condition and reaction proceeded with 0% yield of **2** and **3**. These results indicate that molecular oxygen has a very crucial role for activation of C-H bond, as the yield of product **3** drastically reduced to 10%

Scheme 2: Controlling experiment[a]

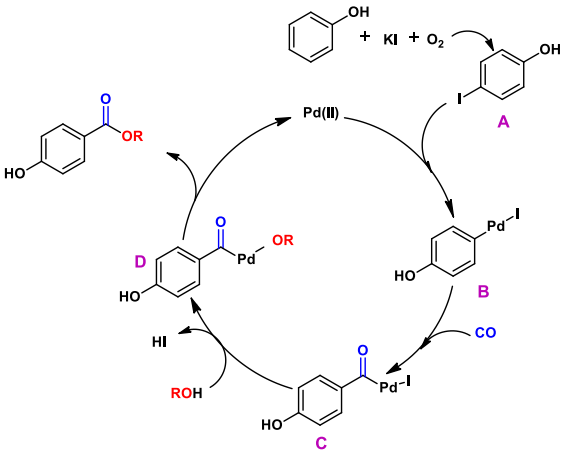


1 **2** **3**

Entry No	Variation from std condition	Yield [b] (%)
1	No $PdCl_2(PPh_3)_2$	2 (95), 3 (0)
2	No CO	2 (90), 3 (0)
3	No KI	2 (0), 3 (0)
4	Without O_2	2 (15), 3 (10)

[a]**Reaction conditions**: Phenol (1 mmol), base (1.5 mmol), MeOH (10 mL), additive (1.5 mmol), catalyst (2 mol %), CO:O_2 (7:1, bar). [b] Isolated Yield

when reaction proceeded without oxidant (Scheme 2 entries **3** and **4**). On the basis of obtained results and previous literature survey [47], we have proposed the plausible reaction mechanism in **Scheme 3**. In the first step, molecular oxygen oxidizes the KI and release iodine, subsequently, iodination occurs at the para position of phenol by aryl C-H bond activation to form of species A (^{1}H NMR spectrum of Isolated intermediate shown in ESI). Next, Pd (II) insert between RX bond and formation of aryl palladium species B take place. Next, CO coordinates with aryl palladium species to the



Scheme 3: Plausible reaction mechanism of esterification of Phenol.

formation of species C. Then the nucleophilic attack of alcohol on species C to offered *p*-hydroxybenzoate *via* reductive elimination of palladium metal.

Conclusion

In summary, we have developed a simple and effective protocol for the synthesis of valuable *p*-hydroxy benzoate directly from phenol. Developed methodology received a lot of attention as highly enviable and attractive access for inserting carbonyl moiety on account of its high atom and step economy. In this context carbonylation of aryl C-H bond *via* oxidative iodination followed by nucleophilic attack of alcohols leading to the synthesis of *p*-hydroxybenzoate. Compared to previous reports, this methodology demonstrates one spot synthesis and good selectivity towards the para C-H bond activation. This methodology does not require external ligands, co-catalysts and co-solvents. Molecular oxygen as an ideal and cheap as well as green oxidant. The new strategy generates 4-iodophenol intermediate and it opens the access for the synthesis of a variety of compounds directly from phenol.

Experimental Section

All chemicals purchased from Sigma Aldrich, Alfa Asear, Wako chemicals, S.D. fine and used without further purification. All dehydrated solvents were purchased advent chemical Mumbai. The CO gas cylinder purchased from Rakhangi gas services, Mumbai.

General procedure for synthesis of ester from Phenol

Phenol (1 mmol), alcohol (10 mL), $PdCl_2(PPh_3)_2$ catalyst (2 mol %), and K_2CO_3 (1.5 mmol) were added to 100 mL stainless steel autoclave. The reactor was closed and flushed with CO gas for three times. Then autoclave pressurized with $CO:O_2$ (7:1, bar) at 100°C. The reaction mixture stirred with a mechanical stirrer (450 rpm) for 18h. After completion of the reaction, the autoclave was cooled to room temperature and the pressure was carefully released and the reactor opened. The crude organic product was extracted with ethyl acetate two times (20 mL each) and it evaporates under vacuum. The obtained crude product was confirmed by GC-MS and thin layer chromatography using Merck silica gel 60 F254 plates and it detect using 254 nm UV lamp. The product was purified by use of column chromatography on a silica gel 100-200 mesh (Flow rate 2 mL/min). The yield of product calculates by using a Perkin Elmer Clarus 400 Gas Chromatography with Flame ionization detector (FID) and capillary column (30 m × 0.25 mm × 0.25 µm). ^1H spectra were recorded on 400 MHz and 500 MHz spectrometer and product dissolved in $CDCl_3$ with TMS as an internal standard. ^{13}C were recorded on 101 MHz and 126 MHz spectrometer using $CDCl_3$ solvent. The chemical shift was recorded in part per million (ppm) with respect to TMS and coupling constant measured in Hertz. The splitting patterns were described as s (singlet), d (doublet), dd (doublet of doublet), t (triplet) and m (multiplate).

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Keywords: Aerobic Oxidation; Carbonylation; C-H Activation; Phenol; *p*-Hydroxybenzoate

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Layout 1:

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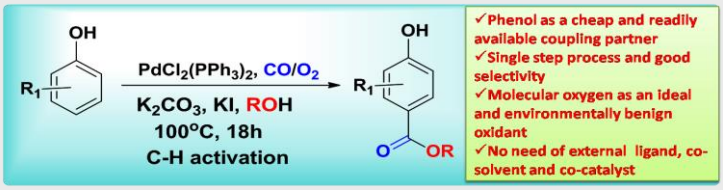

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Oxidative Carbonylation, C-H bond activation

Key Topic*

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Title: Palladium-Catalyzed Aerobic Oxidative Carbonylation of C-H Bond of Phenol for the Synthesis of p-hydroxybenzoate