Direct oxidative coupling of benzenes with acrylonitriles to cinnamonitriles catalyzed by $Pd(OAc)_2/HPMoV/O_2$ system†

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A facile direct synthesis of cinnamonitriles from acrylonitriles and benzenes is successfully achieved by using $Pd(OAc)_2/HPMoV/O_2$ catalyst system *via* the direct C–H bond activation of benzenes using molecular oxygen as a terminal oxidant.

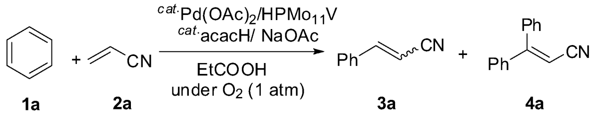
α,β-Unsaturated nitriles are important compounds as a building block in organic synthesis, because the nitrile group is a key functionality in natural products, agricultural chemicals, and biologically active compounds.[1] In particular, cinnamonitriles are important starting materials possessing both the aromatic group and the reactive α,β-unsaturated nitrile group in synthetic chemistry.[2] Therefore, various methods for preparing the cinnamonitriles have been reported.[3–5] The most widely used method to synthesize cinnamonitriles is dehydration of cinnamamides or cinnamaldoximes,[4,5] which generally required hazardous, toxic, or expensive dehydration agents including strong acids and bases.[6] The unsaturated nitriles can also be prepared by the Wittig-type reactions using cyanoalkylphosphates, which produce a large amount of inorganic salts as wastes.[7] Another approach to cinnamonitrile is the reaction of alcohols with ammonia.[8] However, this reaction calls for the use of a stoichiometric amount of oxidants such as *tert*-BuOOH and I_2.[8] Quite recently, Mizuno and coworkers reported that the $Ru(OH)_x/Al_2O_3$-catalyzed catalytic oxidative reaction of cinmamalcohol (or cinnamaldehyde) and ammonia using air (6 atm) leading to cinnamonitrile in 82% yield.[9]

Alternatively, the Pd-catalyzed Mizoroki–Heck reaction of acrylonitrile with aryl halides is also employed as a useful synthetic tool for cinnamonitriles.[10] However, this method does not avoid the formation of undesired waste salts arising from the use of aryl halides and bases. Therefore, the direct oxidative coupling of benzene with acrylonitrile leading to cinnamonitrile is highly desirable from the standpoint of green chemistry.

To date, the oxidative coupling of arenes with olefins through the direct activation of the C–H bond of arenes is a topic of current investigation.[10–11] Therefore, considerable research works have been performed by ours and other groups.[12–13] As for the most successful example of this protocol, we have found that the combination of molybdovanadophosphoric acid (HPMoV) with O_2 serves as an efficient reoxidation system of Pd(0) to Pd(II)[14] and the oxidative coupling reaction of benzene with olefins such as acrylate, acrolein, and ethylene was achieved by using the $Pd(II)/HPMoV/O_2$ system.[12] But the reaction of benzene with acrylonitrile has not yet been successful under previously reported conditions, giving cinnamonitrile only in low yield (9%).[12b] However, it is very important to develop the direct catalytic method for the activation of the C–H bond of benzene from the synthetic and mechanistic point of view.

In this communication, we wish to report a facile synthetic method of cinnamonitriles through the coupling of excess amount of benzene and acrylonitrile by $Pd(II)/HPMoV/O_2$ catalytic system. This reaction provides a clean method to cinnamonitriles from easily accessible mass feedstocks such as benzene and acrylonitrile using molecular oxygen as terminal oxidant.

The results of the reaction of benzene (**1a**) with acrylonitrile (**2a**) are shown in Table 1 (eqn (1)).



(1)

The reaction of **1a** (60 mmol) with **2a** (1.5 mmol) catalyzed by $Pd(OAc)_2$ (0.1 mmol) combined with $H_4PMo_{11}VO_{40}{\cdot}22H_2O$ ($HPMo_{11}V$) (0.02 mmol) proceeded smoothly in the presence of small amounts of acetylacetone (0.1 mmol), and NaOAc (0.1 mmol) under 1 atm of O_2 in propionic acid at 90 °C for 5 h to give cinnamonitrile (**3a**) in 66% yield as a mixture of streoisomers ($E:Z$ = 75 : 25) along with a trace amount of β-phenylcinnamonitrile (**4a**) (entry 1). The yields of the coupling products (**3a** and **4a**) were markedly affected by the amount of **1a** used. Thus, when 90 mmol of **1a** was used toward **2a** (1.5 mmol), the total yield of the oxidative coupling products was reached to 89% as a mixture of **3a** (78%) and **4a** (11%) (entry 2). Fortunately, most of the unreacted benzene using in excess was easily recovered by simple distillation from a reaction mixture. On the other hand, the yield of **3a** was considerably decreased to 12% when 30 mmol of **1a** was used (entry 3). However, the yield of **3a** was high (68%) when the reaction of **1a** (30 mmol) and **2a** (0.75 mmol) was carried out (entry 4). In this reaction, HPMoV under the influence of molecular oxygen using a terminal oxidant serve as efficient reoxidation catalysts of the reduced Pd(0) to Pd(II) during the reaction course. Indeed, the reaction did not proceed catalytically in the absence of HPMoV(entry 5). Furthermore, the reaction under argon was sluggish under these conditions (entry 6). It is noteworthy that the reaction under open air gave the coupling product **3a** in substantial yield (entry 7). The effect of the HPMoV was examined under the same reaction conditions as entry 1, Table 1 (entries 8–10).

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Table 1 Reaction of benzene (**1a**) with acrylonitrile (**2a**) by Pd(II)/HPMoV/O_2 system under various conditions.[a]

						Yield/%[b c]		
Entry	Pd-catalyst	**1a**/mmol	**2a**/mmol	HPMoV	Base	total (**3a**+**4a**)	**3a** (*E* : *Z*)	**4a**
1	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	68	66 [47] (75 : 25)	2
2	$Pd(OAc)_2$	90	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	89 [82]	78 [74] (69 : 31)	11 [8]
3[e]	$Pd(OAc)_2$	30	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	12	12 (72 : 28)	n.d.[d]
4[e]	$Pd(OAc)_2$	30	0.75	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	77	68 (74 : 26)	9
5	$Pd(OAc)_2$	60	1.5	None	NaOAc	7	7 (67 : 33)	n.d.[d]
6[f]	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	6	6 (69 : 31)	n.d.[d]
7[g]	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	55	54 (76 : 24)	1
8	$Pd(OAc)_2$	60	1.5	$H_5PMo_{10}V_2O_{40}\cdot 23H_2O$	NaOAc	56	55 (75 : 25)	1
9	$Pd(OAc)_2$	60	1.5	$H_6PMo_9V_3O_{40}\cdot 20H_2O$	NaOAc	35	35 (75 : 25)	Trace
10	$Pd(OAc)_2$	60	1.5	$H_7PMo_8V_4O_{40}\cdot 22H_2O$	NaOAc	32	32 (74 : 26)	n.d.[d]
11	$Pd(OAc)_2$	60	1.5	$H_3PMo_{12}O_{40}\cdot 24H_2O$	NaOAc	42	42 (74 : 26)	Trace
12	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	None	Trace	Trace	n.d.[d]
13	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	$NaHCO_3$	58	54 (72 : 28)	4
14	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	Na_2CO_3	49	49 (73 : 27)	n.d.[d]
15	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	LiOAc	20	20 (72 : 28)	n.d.[d]
16	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	CsOAc	20	20 (70 : 30)	n.d.[d]
17[h]	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	17	17 (67 : 33)	n.d.[d]
18[h]	$Pd(acac)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	62	60 (73 : 27)	2
19	$Pd(DBA)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	68	65 (74 : 26)	3
20[h]	$Pd(DBA)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	24	23 (75 : 25)	1
21	$Pd(OCOCF_3)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	12	12 (72 : 28)	n.d.[d]
22	$PdCl_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	n.d.[d]	n.d.[d]	n.d.[d]
23[i]	$Pd(OAc)_2$	60	1.5	$H_4PMo_{11}VO_{40}\cdot 22H_2O$	NaOAc	52	50 (77 : 23)	2

[a] **1a** was reacted with **2a** in the presence of Pd-catalyst (0.1 mmol), HPMoV (0.02 mmol), Base (0.1 mmol), acetylacetone (0.1 mmol) in EtCOOH (10 mL) at 90 °C for 5 h. [b] Yields are determined based on **2a** used. Numbers in the square bracket show isolated yields. [c] Cinnamamide was obtained as by-product (<9%) [d] Not detected by GC. [e] EtCOOH (5 mL) was used. [f] Reaction was performed under argon. [g] Reaction was performed under open air. [h] Reaction was performed without acetylacetone. [i] Reaction was performed in AcOH (10 mL) instead of EtCOOH.

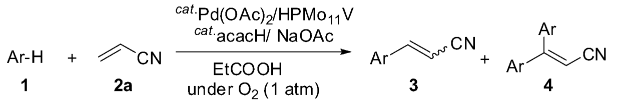
The best yield of **3a** was obtained when $H_4PMo_{11}VO_{40}\cdot 22H_2O$ was used as the reoxidation catalyst. The catalytic performance of HPMoV was affected by the vanadium content in the HPMoV and the increasing the content of V resulted in decreasing the catalytic activity (entries 8–10). The reaction by the use of 12-molybdophosphoric acid ($HPMo_{12}$) not involving V ion led to the moderate yield of **3a** (entry 11).

Addition of a small amount of a base such as NaOAc is indispensible to achieve the reaction.[12] Therefore, removing of NaOAc from the present catalytic system did not produce any coupling products at all (entry 12). The use of $NaHCO_3$ or Na_2CO_3 as a base gave the coupling products in slightly lower yields (entries 13–14), while LiOAc and CsOAc were found to be less efficient than NaOAc (entries 15–16).

The catalytic activity in the present reaction markedly enhanced by adding a small amount of acetylacetonate (acacH) as a ligand of the Pd catalyst (entry 1 *vs.* entry 17). Indeed, when $Pd(acac)_2$ was used as the catalyst, comparable catalytic activity to the $Pd(OAc)_2$/acacH system was observed (entry 1 *vs.* entry 18). $Pd(dba)_2$ also showed high catalytic activity by a combination with acetylacetone as a ligand (entries 19–20). However, other palladium catalysts such as $Pd(OCOCF_3)_2$ and $PdCl_2$, brought about low yields of the products (entries 21–22). Among various solvents examined, propionic acid was found to be the best solvent. The use of acetic acid led to the decrease of the yield of **3a** (entry 23) because a reaction in acetic acid does not make a homogeneous solution. The reaction in selected solvents such as *tert*-BuOH and benzonitrile did not give any desired coupling products.

Several substituted benzenes were reacted with **2a** under the optimized conditions and the results are shown in Table 2.

Table 2 Reaction of aromatic compounds (**1**) with acrylonitrile (**2a**) by $Pd(OAc)_2/HPMo_{11}V/O_2$ system under various conditions.[a]

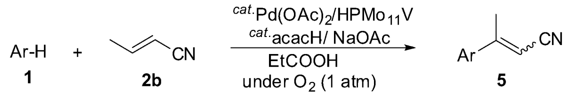


		Yield/%[b c]				
Entry	Ar–H (**1**)	Total (**3**+**4**)	**3** (*o*: *m*: *p*)[d]		**4**[e]	
1	Benzene	68 [47]	**3a**	66[47] (–)	**4a**	2
2	Toluene	58 [47]	**3b**	51[43] (23 : 29 : 48)	**4b**	7[4]
3[f]	Toluene	73	**3b**	66 (23 : 38 : 39)	**4b**	7
4[g]	Toluene	69	**3b**	59 (22 : 38 : 40)	**4b**	10
5	Anisole	80 [67]	**3c**	47[43] (22 : 15 : 63)	**4c**	33[24]
6	Chlorobenzene	29 [28]	**3d**	29[28] (36 : 27 : 37)	**4d**	n.d.[h]
7	*p*-Xylene	46 [37]	**3e**	46[37] (–)	**4e**	Trace

[a] **1** (60 mmol) was reacted with **2a** (1.5 mmol) in the presence of $Pd(OAc)_2$ (0.1 mmol), $H_4PMo_{11}VO_{40}\cdot 22H_2O$ (0.02 mmol), NaOAc (0.1 mmol), acetylacetone (0.1 mmol) in EtCOOH (10 mL) at 90 °C for 5 h. [b] Based on **2a** used. Numbers in the square bracket show isolated yields. [c] Small amount of the corresponding cinnamamides were detected by GC (<7%). [d] The products were obtained as a mixture of stereoisomers (*E*:*Z* ratios are in the range of 6 : 4 to 8 : 2). [e] Regiochemistry was not determined. [f] Toluene (120 mmol) was used. [g] Toluene (90 mmol) was used and the reaction time was 24 h. [h] Not detected by GC.

The reaction of toluene (**1b**) with **2a** afforded the corresponding coupling products in 58% total yield as an isomeric mixture (*o*-**3b** : *m*-**3b**: *p*-**3b** = 23 : 29 : 48) along with a small amount of diaryl product **4b** (entry 2). The yield of the coupling products (**3b** and **4b**) was increased to 73% when the reaction was carried out using **1b** (120 mmol) in large excess (entry 3). Prolonged reaction time

Table 3 Reaction of various arenes (**1**) with crotononitrile (**2b**) by $Pd(OAc)_2/HPMo_{11}V/O_2$ system (under selected conditions).[a]



Entry	Ar–H (**1**)	Yield/%[b] (*o*: *m*: *p*)[c]	
1	Benzene	**5a**	49 [42] (–)
2[d]	Toluene	**5b**	53 [53] (21 : 43 : 36)
3	Anisole	**5c**	63 [58] (13 : 23 : 64)
4[d]	Chlorobenzene	**5d**	51 [47] (35 : 30 : 35)
5[d]	*p*-Xylene	**5e**	49 [43] (–)

[a] **1** (60 mmol) was reacted with **2b** (1.5 mmol) in the presence of $Pd(OAc)_2$ (0.1 mmol), $H_4PMo_{11}VO_{40}\cdot 22H_2O$ (0.02 mmol), NaOAc (0.1 mmol), acetylacetone (0.1 mmol) in EtCOOH (10 mL) at 90 °C for 5 h. [b] Based on **2b** used. Numbers in the square bracket show isolated yields. [c] The products were obtained as a mixture of stereoisomers (E:Z ratios are in the range of 1 : 1 to 3 : 7). [d] Reaction time was 15 h.

was also effective to increase the yield of **3b** in the reaction of **1b** with **2a** (entry 4).

The reactivity of anisole (**1c**) in the present reaction was considerably high and the corresponding coupling products (**3c** and **4c**) were obtained in 80% total yield (entry 5). The reaction of chlorobenzene (**1d**) with **2a** gave lower yield of products (entry 6). The reaction of *p*-xylene (**1e**) gave the monoarylated product (**3e**) as a major product (entry 7).

The reaction could be successfully extended to the reaction of arenes (**1**) with crotononitrile (**2b**) and the results are shown in Table 3. The reaction of benzene with **2a** gave β-methylcinnamonitrile (**5a**) as a mixture of stereoisomer ($E:Z$ = 32 : 68). The reaction of toluene (**1b**) with **2b** under optimized conditions afforded a mixture of structural and stereoisomers (**5b**) (o: m: p = 21: 43 : 36) in 53% yield (entry 2). Similarly, the reaction of anisole (**1c**), chlorobenzene (**1d**), and *p*-xylene (**1e**) gave the corresponding oxidative coupling products (**5b–5e**) in 49–63% yields (entries 3–5).

A detailed reaction mechanism remains to be further elucidated, but the reaction course would be explained rationally by a pathway similar to that proposed by ours[12] and Kitamura/Fujiwara group (Figure S1 in ESI†).[13b] Namely, the initial electrophilic attack of a Pd(II) to arene **1** would lead to a σ-aryl-palladium(II) intermediate (**A**) followed by the insertion of acrylonitriles **2** to **A** gives σ-alkyl-palladium(II) intermediate **B**. Subsequently, *β*-hydride elimination of the **B** gives the cinnamonitriles **3** along with Pd–H intermediate. The Pd–H intermediate is reduced to Pd(0), and the resulting Pd(0) species is reoxidized by the HPMoV/O_2 system to generate Pd(II) species, as we previously reported.[12,14] In this reaction, the use of less amount of benzene may preferentially subject to coordination of acrylonitrile to Pd in prior to benzene activation by Pd.

In conclusion, we have developed the direct route to cinnamonitriles from acryronitrile and benzenes by Pd(II)/$HPMo_{11}V/O_2$ system. This method provides a clean route to various cinnamonitriles from fundamental chemicals like benzenes and acrylonitriles by using molecular oxygen as the terminal oxidant. This work was supported by a Grant-in-Aid for Scientific Research from MEXT, Japan.

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