

Carboxylation and hydroxylation of biphenyl by the Pd/molybdovanadophosphoric acid/dioxygen system

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Abstract

Concomitant introduction of COOH and OH groups to biphenyl was achieved by allowing biphenyl to react with CO and O₂ using the Pd/molybdovanadophosphoric acid catalytic system. For instance, biphenyl reacted under a mixed gas of CO (0.5 atm) and O₂ (0.5 atm) in the presence of catalytic amounts of Pd(OAc)₂ and H₅PMo₁₀V₂O₄₀·26H₂O in acetic acid to give the corresponding hydroxybiphenylcarboxylic acids. The reaction was found to proceed through the formation of biphenylcarboxylic acid followed by hydroxylation of the resulting carboxylic acid. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

4'-Hydroxy-4-biphenylcarboxylic acid has been recognized as an attractive monomer for the production of polymer materials [1]. Several methods for preparing of this monomer have been developed so far in some patent works [2]. For example, iodation of biphenyl forming 4,4'-diiodobiphenyl followed by treatment with CO in the presence of a palladium catalyst gave 4'-iodo-4-biphenylcarboxylic acid. Then, the resulting product underwent hydrolysis affording 4'-hydroxy-4-biphenylcarboxylic acid [2c]. However, this method required three steps and the total yield of the desired product from the starting material, biphenyl, was low (37%).

The Pd-catalyzed carboxylation of an unreactive C–H bond of arenes with CO through the formation of aryl-Pd σ -complex was firstly developed by Fujiwara and coworkers [3]. Quite recently, Nozaki and coworkers reported an excellent work for the direct transformation of biphenyl into hydroxybiphenylcarboxylic acid [4]. They showed that the sequential hydroxylation–carboxylation of biphenyl efficiently occurred by allowing biphenyl to react with formic acid and K₂S₂O₈ in the presence of Pd(OCOCF₃)₂ as a catalyst in a mixture of trifluoroacetic acid and dichloromethane at 50 °C. If the reaction could be performed by the use of CO and air in place of formic acid

and K₂S₂O₈, respectively, without employment of toxic solvents like trifluoroacetic acid and dichloromethane, such a reaction would provide an alternative environmentally friendly route to hydroxybiphenylcarboxylic acid from biphenyl.

In our recent works, we have established the carboxylation of substituted arenes with CO and O₂ catalyzed by Pd(OAc)₂ combined with molybdovanadophosphoric acids (HPMoV) via the activation of C–H bond of arenes [5]. Thus, anisole was carboxylated under a mixed gas of CO (0.5 atm) and O₂ (0.5 atm) in the presence of Pd(OAc)₂ (5 mol%) and H₅PMo₁₀V₂O₄₀·*n*H₂O (2 mol%) giving an isomeric mixture of anisic acids in good yield. This work is the first example of the catalytic carboxylation of aromatic hydrocarbons using CO and air. In addition, we have reported that benzene was directly hydroxylated to phenol catalyzed by HPMoV under O₂/CO in AcOH/H₂O at 90 °C [6a]. The methyl-substituted benzenes were also hydroxylated under similar reaction system, and the reaction was considerably promoted by adding a small amount of palladium species [6b]. In this paper, we wish to disclose the application of our catalytic system to the carboxylation–hydroxylation of biphenyl under a mixed gas of CO and air.

2. Results and discussion

As a first trial, biphenyl (**1**) was allowed to react with a mixed gas of CO/O₂ (0.5/0.5 atm) in the presence of catalytic amounts of Pd(OAc)₂ and H₅PMo₁₀V₂O₄₀·26H₂O in AcOH at

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Table 1
Reaction of **1** with CO and O₂ catalyzed by Pd(OAc)₂ and various HPAs^a

Run	HPA	Conversion (%)	Selectivity (%) ^b		
			2	3	4
1	None	No reaction			
2 ^c	H ₅ PMo ₁₀ V ₂ O ₄₀ ·26H ₂ O	No reaction			
3	H ₄ PMo ₁₁ VO ₄₀ ·18H ₂ O	63	24	3	n.d.
4 ^d	H ₅ PMo ₁₀ V ₂ O ₄₀ ·26H ₂ O	61	51	3	13
5	H ₆ PMo ₉ V ₃ O ₄₀ ·22H ₂ O	62	39	5	n.d.
6	H ₅ PMo ₁₀ V ₂ O ₄₀ ·16H ₂ O	38	66	5	11
7	VO(acac) ₂	No reaction			

^a **1** (2 mmol) was allowed to react under CO/O₂ (0.5/0.5 atm) in the presence of Pd(OAc)₂ (0.05 mmol) and HPA (0.04 mmol) in AcOH (8 mL) at 110 °C for 15 h.

^b Based on **1** consumed.

^c In the absence of Pd(OAc)₂.

^d See text and Eq. (1).

110 °C for 15 h (Eq. (1) and Table 1, run 4). The reaction mainly produced 2-, 3- and 4-biphenylcarboxylic acid (**2**) (16:36:58) [7] 2- and 4-hydroxybiphenyl (**3**) (40:60), and 2', 3'- and 4'-hydroxy-4-biphenylcarboxylic acid (**4**) (34:11:55). In addition, several by-products including the regioisomeric mixtures of hydroxyl–biphenylcarboxylic acids and unidentified products were detected by LC–MS analysis:

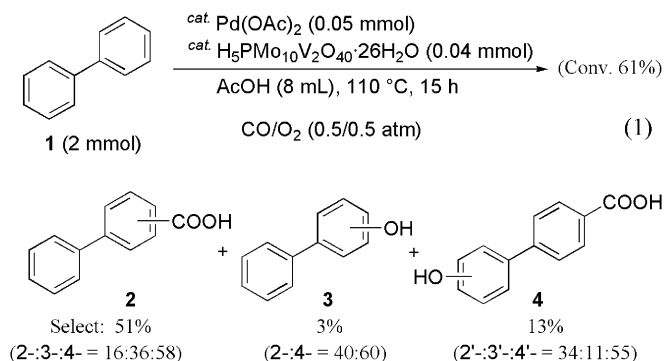


Table 1 summarizes the selected results of the reaction using various molybdovanadophosphoric acids. Needless to say, no reaction took place in the absence of HPMoV (run 1). Additionally, the reaction without employment of Pd(OAc)₂ resulted in no formation of **2** (run 2). The catalytic activity was affected by both the ratio of Mo:V and the number of hydrates in HPMoV. It was found that Pd(OAc)₂ combined with H₅PMo₁₀V₂O₄₀·26H₂O afforded the best results to lead to **2** and **3** in 51% and 13% selectivities at 61% conversion of **1** (run 4). In the case of the reactions using molybdovanadophosphoric acids other than H₅PMo₁₀V₂O₄₀·26H₂O, it was difficult to obtain the products with selectivity, and some unidentified products were produced (runs 3 and 5). H₅PMo₁₀V₂O₄₀·16H₂O did not promote the present reaction with high conversion of **1** probably due to its insolubility in AcOH (run 6). No reaction was induced by the use of VO(acac)₂ instead of HPMoV (run 7).

Thus, the Pd(OAc)₂/H₅PMo₁₀V₂O₄₀·26H₂O system was found to be effective catalytic system for the carboxylation–hydroxylation of biphenyl with CO and O₂, which was difficult to be carried out so far. However, the total material balance of the

reaction at 110 °C was not enough due to the formation of several unidentified products (Table 2, run 1). In order to improve the product selectivities, we examined the reaction under various conditions (Table 2). The longer reaction for 30 h at 110 °C resulted in decrease of the yields of the desired products although the conversion increased to 77% (run 2). When the reaction was carried out at 90 °C, the total material balance was found to be improved. The reaction of **1** with CO/O₂ in the presence of small amounts of Pd(OAc)₂ and H₅PMo₁₀V₂O₄₀·26H₂O in AcOH at 90 °C for 15 h gave **2–4** in 77%, 7% and 13% selectivities, but the conversion was low (30%) (run 3). It is interesting to note that hydroxybiphenylcarboxylic acid (**4**) was formed in 34% selectivity at 79% conversion when the reaction was prolonged to 60 h (run 5). The Pd(II)-catalyzed hydroxylation–carboxylation reaction of **1** with HCOOH and K₂S₂O₈ was reported to lead to **4** in 45% yield together with several by-products having higher molecular weights (probably functionalized biphenyl dimers) at almost 100% conversion of **1** [4a]. Therefore, the present Pd/HPMoV catalytic system using CO and O₂ provides an alternative methodology for preparing of **4** from **1**, although further improvement of the reaction is required. The ratio of a mixture of CO and O₂ gas was also important to promote the reaction at higher conversion of **1** (runs 6–8). The best result was obtained by the use of a 1:1 mixture of CO and O₂.

Fig. 1 shows the time-dependence curves for the formation of hydroxybiphenylcarboxylic acid by the present catalytic system at 90 °C. At the early stage of the reaction, **2** was produced as a major product. Then, the yield of the product **4** increased with decreasing of **2**. The yield of **3** was not considerably changed. These results suggest that **4** is produced through the hydroxylation of **2** formed during the reaction.

In order to obtain the information of the reaction pathway, the independent experiments of the reaction **2** or **3** with CO/O₂ were also performed (Eqs. (2) and (3)). When *p*-**2** reacted with CO/O₂ at 90 °C for 15 h, **4** was obtained in 86% selectivity at 7% conversion (Eq. (2)). After 48 h, the conversion of *p*-**2** was increased to 23% to give **4** in 80% selectivity.

In addition, we reported that the hydroxylation of aromatic hydrocarbons was facilitated by adding AcONa to the HPMoV under CO/O₂ atmosphere [6]. Thus, treatment of *p*-**2** with CO/O₂ (0.5/0.5 atm) in the presence of catalytic amounts of

Table 2
Reaction of **1** with CO and O₂ catalyzed by Pd(OAc)₂ and H₅PMo₁₀V₂O₄₀·26H₂O^a

Run	CO/O ₂ (atm)	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)			mb ^b
					2	3	4	
1	0.5/0.5	110	15	61	51	3	13	67
2	0.5/0.5	110	30	77	41	3	19	63
3	0.5/0.5	90	15	30	77	7	13	97
4	0.5/0.5	90	48	66	63	3	27	93
5	0.5/0.5	90	60	79	54	3	34	91
6	0.1/0.9	90	15	19	28	3	–	–
7	0.25/0.75	90	15	30	46	4	–	–
8	0.75/0.25	90	15	10	3	9	–	–

^a **1** (2 mmol) was allowed to react under CO/O₂ in the presence of H₅PMo₁₀V₂O₄₀·26H₂O (0.04 mmol) and Pd(OAc)₂ (0.05 mmol) in AcOH (8 mL).

^b mb: material balance.

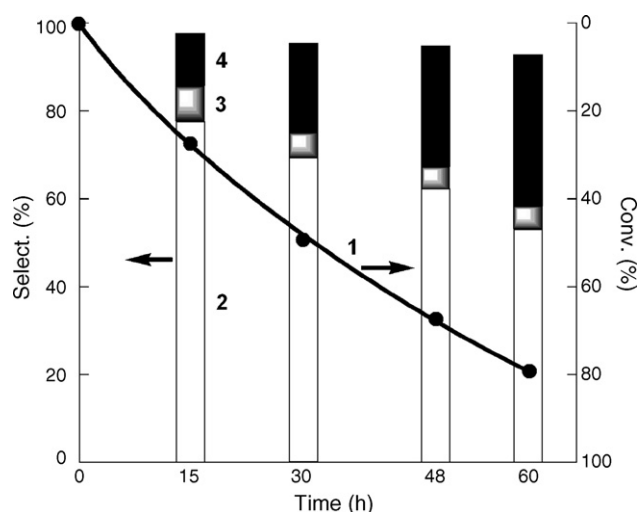
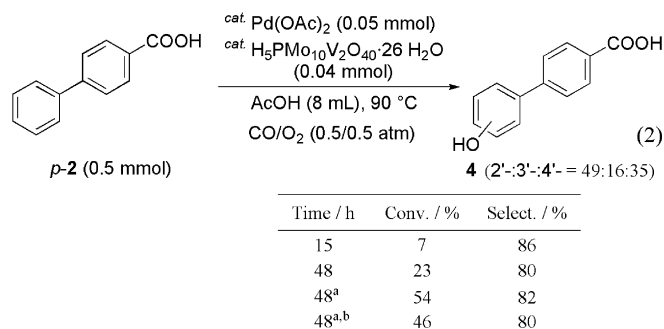


Fig. 1. Time-dependence curves for the reaction of **1**. **1** (2 mmol) was allowed to react under CO/O₂ (0.5/0.5 atm) in the presence of Pd(OAc)₂ (0.05 mmol) and H₅PMo₁₀V₂O₄₀·26H₂O (0.04 mmol) in AcOH (8 mL) at 90 °C.

Pd(OAc)₂, H₅PMo₁₀V₂O₄₀·26H₂O and AcONa at 90 °C for 48 h afforded **4** in 82% selectivity at 54% conversion (Eq. (2)). It was found that the same reaction without Pd(OAc)₂ also produced **4** with satisfactory selectivity (80% selectivity, 46% conversion).

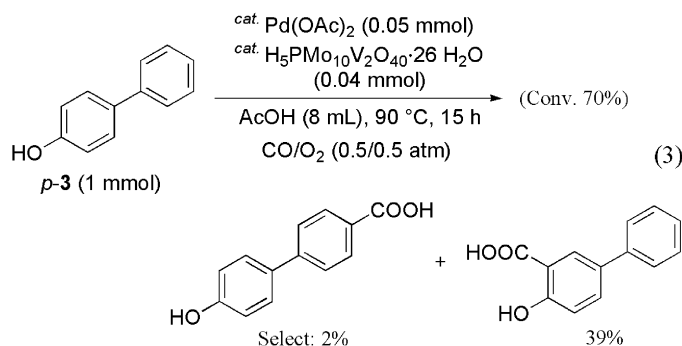


^a AcONa (0.1 mmol) was added.

^b In the absence of Pd(OAc)₂.

On the other hand, the reaction of *p-3* by the Pd/HPMoV system at 90 °C for 15 h was difficult to take place selectively, and the

4-hydroxy-3-biphenyl carboxylic acid was obtained as a major product together with several unidentified product having higher molecular weight by LC–MS analysis (Eq. (3)):



On the basis of these results, the present carboxylation–hydroxylation of **1** with CO/O₂ was reasonable to assume that the carboxylation of **1** initially occurred followed by hydroxylation of the resulting carboxylated products under the influence of Pd(OAc)₂ combined with H₅PMo₁₀V₂O₄₀·26H₂O. Nozaki and coworkers showed that **1** was oxidized to acetylated hydroxybiphenyl which subsequently carboxylated to give hydroxybiphenylcarboxylic acid [4a]. Therefore, the reaction pathway of our system was found to differ from that of the Nozaki system.

3. Conclusions

The carboxylation–hydroxylation of biphenyl (**1**) with CO and O₂ has been accomplished by using the combined catalysts system of Pd(OAc)₂/H₅PMo₁₀V₂O₄₀·26H₂O yielding hydroxybiphenylcarboxylic acid. It is reasonable to assume that the reaction of **1** produces biphenylcarboxylic acid (**2**) which is subsequently hydroxylated to form the desired hydroxybiphenylcarboxylic acid (**4**). Additionally, it was found that 4-biphenylcarboxylic acid (*p-2*) was oxidized under CO/O₂ in the presence of catalytic amounts of Pd(OAc)₂ and H₅PMo₁₀V₂O₄₀·26H₂O to give the corresponding hydroxybiphenylcarboxylic acid (**4**) and that this oxidation was facilitated by adding a small amount of NaOAc. Thus, **4** was efficiently synthesized in 82% selectivity at 54% conversion from the reaction of *p-2* with

CO/O₂ catalyzed by Pd(OAc)₂/H₅PMo₁₀V₂O₄₀·26H₂O. The present method would provide an alternative route to hydroxybiphenylcarboxylic acid from biphenyl.

4. Experimental

4.1. General

All solvents and reagents were purchased from commercial sources and used without further treatment. Heteropoly acids were obtained from Nippon Inorganic Chemical Co., Ltd. HPLC–MS spectra were recorded on HPLC–MS Waters Integrity Systems with a Thermabeam Mass Detector (EI, 70 eV), Photodiode Array detector on a cartridge column; acetonitrile–water (AcOH/AcONa buffer) mixture (gradient from 20:80 to 100:0 for 35 min; flow 0.30 mL/min) was used as the solvent. ¹H and ¹³C NMR were measured at 270 and 400 MHz, respectively, in CDCl₃ with Me₄Si as the internal standard.

4.2. General procedure for the reaction of biphenyl (**1**)

To a AcOH solution (8 mL) of Pd(OAc)₂ (0.05 mmol) and H₅PMo₁₀V₂O₄₀·26H₂O (0.04 mmol) was added **1** (2 mmol). Then, the reaction mixture was stirred at 90 °C for 15–48 h under a 1:1 mixed gas (1 atm) of CO and O₂. The conversions and yields of products were estimated from the peak areas based on the internal standard technique using HPLC. After the reaction, 3,3'-dimethylbiphenyl as an internal standard and AcOEt (2 mL) was added to the reaction mixture. Several drops of the resulting solution were added to CH₃CN (1.5 mL), and then the HPLC analysis was performed. The products were commercially available and the structures were confirmed by comparison of their ¹H and ¹³C NMR.

4.3. General procedure for the reaction of 4-biphenyl carboxylic acid (*p*-**2**)

To a AcOH solution (8 mL) of Pd(OAc)₂ (0.05 mmol), H₅PMo₁₀V₂O₄₀·26H₂O (0.04 mmol) and AcONa (0.1 mmol)

was added *p*-**2** (0.5 mmol). Then, the reaction mixture was stirred at 90 °C for 48 h under a 1:1 mixed gas (1 atm) of CO and O₂. The conversions and yields of products were determined as the same method described above.

Acknowledgements

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- [7] 9-Fluorenone (**5**) in place of 2-biphenylcarboxylic acid (*m*-**2**) was obtained in this reaction. Similar observation was reported by Nozaki et al. [4a].