Oxidative arylation of ethylene with benzene catalyzed by $Pd(OAc)_2$/heteropoly acid/O_2 system

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Received (in Gainesville, FL, USA) 24th October 2007, Accepted 11th January 2008
First published as an Advance Article on the web 28th January 2008
DOI: 10.1039/b716425d

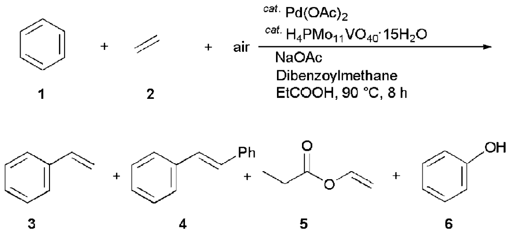
Oxidative arylation of ethylene with benzene was examined by using a $Pd(OAc)_2$/heteropoly acid/O_2 system under mild conditions. The reaction of benzene with ethylene in the presence of catalytic amounts of $Pd(OAc)_2$ combined with $H_4PMo_{11}VO_{40}\cdot 15H_2O$ (or $H_3PMo_{12}O_{40}\cdot 30H_2O$), AcONa, and dibenzoylmethane under air at 90–120 °C produced oxidative coupling products, styrene and stilbene, in fair yields (up to 167 total turnovers). From the examination of the catalyst performance of $Pd(OAc)_2$ combined with various heteropoly acids, it was found that the employment of heteropoly acids including molybdenum ion in their structure is very important to obtain high turnover numbers of Pd.

Introduction

C–C bond formation through the direct C–H bond activation of arenes is a very important methodology in organic synthesis.[1] On the other hand, the arylation of olefins, namely the well-known Heck–Mizoroki reaction involving the coupling of aryl halides with olefins, is one of the most useful coupling reactions.[2] The reaction, however, does not avoid the formation of undesired waste salts arising from the use of aryl halides and bases. Therefore, the direct oxidative coupling of arenes with simple alkenes to give alkenyl arenes without formation of any salts is an attractive methodology, particularly in industrial chemistry. Although the catalytic arylation of olefins by using Pd,[3] Ru[4] or Rh complexes[5] has been reported, most of these coupling reactions employed electron-deficient alkenes like acrylates and cinnamates as alkenes. There have been only a few reports on the coupling reaction of benzene with simple alkenes like ethylene.[5–8] Fujiwara *et al.* have reported the stoichiometric and catalytic oxidative arylations of ethylene for the production of styrene and stilbene using $Pd(OAc)_2$.[6] The Pd(II)-catalyzed arylation of ethylene in the presence of a stoichiometric amount of molybdovanadophosphoric acids was carried out by Kozhevnikov, but the turnover number (TON) of the Pd catalyst was low.[7] Hong and Yamazaki have reported the reaction of benzene with ethylene catalyzed by a rhodium carbonyl complex under CO (20–25 atm) at 200–250 °C to form styrene, but this method results in simultaneous formation of 3-pentanone as a byproduct.[8] Recently, two catalytic systems in which O_2 is used as an oxidant have been reported. The Rh-catalyzed oxidative arylation of ethylene in benzene–acetic acid solution under oxygen (20 atm) at 180 °C gave styrene in TON of 23.[9] The other one is the reaction of benzene with ethylene catalyzed by $RuCl_3\cdot 3H_2O$ under CO (6.1 atm) and O_2 (2 atm) at 180 °C to produce styrene (TON = 19).[4] The oxidative coupling of benzene with olefins reported so far has called for the reaction to be carried out at higher pressures of CO and O_2 and at elevated temperatures. Therefore, the catalytic oxidative coupling of benzene with ethylene under mild conditions is considered to be an attractive topic in organic synthesis. Recently, we reported the catalytic oxidative coupling of benzene with electron-deficient olefins such as acrylate and α,β-unsaturated aldehydes by $Pd(OAc)_2$ combined with $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPMoV) under atmospheric O_2.[10] Herein, we would like to report the oxidative coupling of benzene with ethylene by a $Pd(OAc)_2$/heteropoly acids/air system under mild conditions.

Results and discussion

The oxidative coupling reaction of benzene (**1**) with ethylene (**2**) to give styrene (**3**) was carried out by using a $Pd(OAc)_2/H_4PMo_{11}VO_{40}\cdot 15H_2O/O_2$ catalytic system under various reaction conditions (eqn (1) and Table 1).



(1)

A typical reaction was carried out as follows: in a 50 mL autoclave, benzene **1** (30 mmol) was allowed to react under ethylene **2** (0.9 atm, *ca.* 2.0 mmol) and air (1.6 atm) in the presence of $Pd(OAc)_2$ (10 μmol, *ca.* 0.5 mol% based on **2**), $H_4PMo_{11}VO_{40}\cdot 15H_2O$ (10.3 mg, *ca.* 5 μmol), AcONa (25 μmol) and dibenzoylmethane (dbm) (30 μmol) in propionic

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Table 1 Oxidative coupling of benzene (**1**) with ethylene (**2**) by $Pd(OAc)_2/H_4PMo_{11}VO_{40}\cdot 15H_2O$/air system under various conditions[a]

				TON[b] (μmol)			
Run	Base (μmol)	Ligand (μmol)	Solvent	**3**	**4**	**5**	**6**
1	AcONa (25)	dbm (30)	EtCOOH	20 (202)	5.2 (25)	5.0 (50)	3.0 (30)
2	AcONa (25)	—	EtCOOH	4.6 (46)	0	8.3 (82)	4.5 (45)
3	AcONa (25)	dbm (10)	EtCOOH	7.5(75)	0.9 (4)	6.0 (59)	3.9 (39)
4	AcONa (25)	acacH (30)	EtCOOH	14 (138)	4.8 (24)	3.8 (38)	4.9 (49)
5[c]	AcONa (25)	—	EtCOOH	12 (125)	3.1 (16)	4.4 (44)	3.7 (37)
6	AcONa (25)	dbm (30)	AcOH	No reaction			
7	—	dbm (30)	EtCOOH	1.6 (16)	0	2.0 (20)	0
8	AcOLi (25)	dbm (30)	EtCOOH	9.1 (90)	2.6 (13)	2.9 (29)	2.9 (29)
9	AcOK (25)	dbm (30)	EtCOOH	5.9 (59)	0.8 (4)	1.7 (17)	1.4 (14)
10	Na_2CO_3 (13)	dbm (30)	EtCOOH	19 (188)	9.7 (48)	5.2 (52)	7.1 (71)
11[d]	AcONa (8)	dbm (30)	EtCOOH	21 (213)	8.7 (43)	3.8 (38)	3.0 (30)
12[de]	AcONa (8)	dbm (15)	EtCOOH	30 (149)	9.1 (23)	4.4 (22)	3.6 (18)
13[df]	AcONa (8)	dbm (30)	EtCOOH	2.6 (26)	0	0	0

[a] Benzene (**1**) (30 mmol) was reacted with 0.9 atm of ethylene (**2**) in the presence of $Pd(OAc)_2$ (10 μmol), $H_4PMo_{11}VO_{40}\cdot 15H_2O$ (10.3 mg, *ca.* 5 μmol), AcONa (25 μmol) and dibenzoylmethane (dbm) (30 μmol) in propionic acid (2 mL) under 1.6 atm of air at 90 °C for 8 h. [b] Turnover number (TON) was based on $Pd(OAc)_2$. [c] $Pd(acac)_2$ was used instead of $Pd(OAc)_2$. [d] 1.7 μmol of $H_4PMo_{11}VO_{40}\cdot 15H_2O$ was used. [e] $Pd(OAc)_2$ (5 μmol) was used. [f] Under N_2 (1.6 atm) instead of air.

acid (2 mL) at 90 °C for 8 h. To depress the preferential formation of vinyl propionate (**5**), excess **1** was employed with respect to **2**. The reaction produced 202 μmol styrene (**3**) corresponding to 20 turnover numbers of Pd (TON = 20), 25 μmol *trans*-stilbene (**4**) (TON = 5.2), and 50 μmol **5** (TON = 5.0) along with 30 μmol phenol (**6**) (TON = 3.0) (run 1). Removing the dbm ligand from the catalytic system resulted in a considerable decrease of **3** (run 2).

In the absence of dbm ligand, a precipitate of Pd black was found to be formed. This shows that dbm is required to depress the formation of the Pd black during the reaction course. When the amount of dbm was reduced from 3 to 1 equiv., the yield of **3** deteriorated considerably (run 3).

Using acetylacetone (acacH) as a ligand caused a slight decrease in the yield of **3** (run 4). When $Pd(acac)_2$ was employed in place of $Pd(OAc)_2$, the reaction proceeded to some extent even in the absence of a ligand (run 5). No reaction took place in acetic acid (run 6). It was found that a reaction solution of acetic acid does not make a homogeneous solution, in contrast to the reaction solution using propionic acid which gives a uniform solution. The reaction was found to take place only with difficulty in the absence of AcONa (run 7). The use of AcOLi or AcOK instead of AcONa resulted in the formation of **3** at lower TON (runs 8 and 9). However, Na_2CO_3 was found to be an efficient base and the result was almost the same as that for AcONa (run 10). Even though the amount of $H_4PMo_{11}VO_{40}\cdot 15H_2O$ was reduced to 1.7 μmol, the result was almost the same as that obtained with 5 μmol of $H_4PMo_{11}VO_{40}\cdot 15H_2O$ (run 11). When the quantity of the $Pd(OAc)_2$ catalyst was reduced from 10 μmol to 5 μmol, the TON of **3** reached 30 (run 12). Needless to say, no reaction took place catalytically without air (O_2) (run 13). These results suggest that the $H_4PMo_{11}VO_{40}$/air system works well as a system for reoxidation of the reduced Pd(0) to Pd(II). In order to obtain information on the effect of ethylene and air concentrations on the oxidative coupling of **1** with **2**, the coupling was conducted under several varying pressures of ethylene **2** and air (Fig. 1). Under the conditions of ethylene/air = 0.9 atm/1.6 atm, the TON of Pd for **3** attained a maximum (TON = 20). The amount of vinyl propionate **5** increased with increasing ethylene pressure.

Next, the effect of varying air pressures toward 0.9 atm of ethylene **2** was investigated (Fig. 2). To avoid the explosion of **2** under air, the reaction ranging in pressures from 1.6 to 29.1 atm of air with respect to **2** (0.9 atm) was excluded. The TON of the reaction increased with increasing air pressures, but decreased at 29.1 atm of air.

In order to confirm an optimum system for reoxidation of the reduced Pd(0) catalyst, the reaction was conducted with the use of various heteropoly acids (HPA) under air (Table 2).

The reaction did not proceed catalytically in the absence of HPA (run 2). On the other hand, reactions employing $H_5PMo_{10}V_2O_{40}\cdot 28H_2O$, $H_6PMo_9V_3O_{40}\cdot 30H_2O$ and $H_7PMo_8V_4O_{40}\cdot 28H_2O$ as catalysts for reoxidation of the reduced Pd(0) afforded **3** in slightly lower yields compared with that for $H_4PMo_{11}VO_{40}\cdot 15H_2O$ (runs 3–5). $H_3PMo_{12}O_{40}\cdot 30H_2O$ not including V ion was found to serve as a good reoxidation catalyst (runs 6–8) and the highest total TON of Pd for the formation of **3** and **4** was reached at 100 and 67, respectively, under the optimum reaction conditions (run 8).

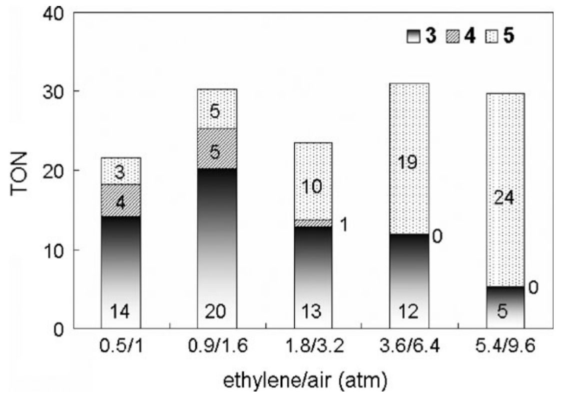

Fig. 1 Reactions of **1** with **2** under varying pressures of **2** and air. Reaction conditions were the same as for run 1 in Table 1.

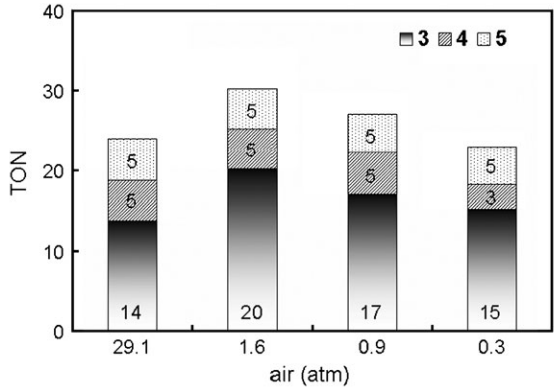

Fig. 2 Effect of air pressure toward 0.9 atm of **2** on the oxidative coupling of **1** with **2**. Reaction conditions were the same as for run 1 in Table 1.

The reactions in the presence of $H_4PMo_{11}WO_{40}\cdot 27H_2O$ and $H_5PMo_{10}W_2O_{40}\cdot 29H_2O$ were almost the same as those in the presence of $H_3PMo_{12}O_{40}\cdot 30H_2O$ (runs 9 and 10). $H_4SiMo_{12}O_{40}\cdot 27H_2O$ showed activity similar to that of $H_3PMo_{12}O_{40}\cdot 30H_2O$, while $H_5PW_{10}V_2O_{40}\cdot 27H_2O$ was found to be inactive for the present reaction (runs 11 and 12). It is interesting to note that **6** was not produced in the reaction using heteropoly acids not including V ion. Previously, we reported that heteropoly acids containing V ion like $H_7PMo_8V_4O_{40}\cdot n H_2O$ serve as good catalysts for the direct synthesis of phenol from benzene under the influence of air and CO.[11] $MoO_2(acac)_2$ did not promote the coupling reaction (run 13). From these results, it seems likely that molybdenum ion in the heteropoly acids is an essential component to promote the reoxidation of the reduced Pd(0) to Pd(II).

Since the $Pd(OAc)_2/H_3PMo_{12}O_{40}\cdot 30H_2O$/air system for the coupling reaction of **1** with **2** indicated high catalytic activity, the time-dependence curves of products obtained using this catalytic system were compared with those of the $Pd(OAc)_2/H_4PMo_{11}VO_{40}\cdot 15H_2O$/air system (Fig. 3).

The time-dependence curves of **3** and **4** using both catalytic systems were similar to each other and the yield of **3** attained a maximum for 8–10 h. The amount of vinyl propionate **5** was held almost constant during the reaction course.

It is thought that the reaction is initiated by the substitution of hydrogen on the benzene ring by $Pd(OAc)_2$ to form σ-aryl–Pd(II) complex.[10] Subsequently, ethylene insertion into the Pd(II) intermediate followed by β-hydride elimination gives styrene and PdH(OAc) or Pd(0). The Pd(0) is reoxidized with O_2 to Pd(II) by the action of heteropoly acids.

Conclusions

We have reported the direct oxidative coupling of benzene **1** with ethylene **2** to give styrene **3** using a $Pd(OAc)_2$/heteropoly acids (HPA)/air catalytic system. The coupling was achieved under mild conditions and low concentration of ethylene **2** (0.9 atm). The total TON of Pd toward the formation of **3** and stilbene **4** reached 167 with the use of a $Pd(OAc)_2/H_3PMo_{12}O_{40}\cdot 30H_2O$/air system.

Experimental section

General

All solvents and reagents were purchased from commercial sources. Heteropoly acids except for $H_4PMo_{11}VO_{40}\cdot 15H_2O$ were gifts from Nippon Inorganic Colour & Chemical Co. Ltd. GC analysis was performed on a GC instrument equipped with a flame ionization detector using a 0.22 mm × 25 m capillary column. Mass spectra were determined at an ionization energy of 70 eV on a GC-MS instrument. ^1H and ^{13}C NMR spectra were measured at 270/400 MHz and 67.5/100 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. Thin layer chromatography was performed on TLC plastic sheets F254 silica gel 60, using UV light and I_2. Infrared (IR) spectra were measured for thin films on a NaCl plate.

Table 2 Reactions of **1** with **2** in the presence of various heteropoly acids (HPA)[a]

		TON[b] (μmol)			
Run	HPA	**3**	**4**	**5**	**6**
1	$H_4PMo_{11}VO_{40}\cdot 15H_2O$	20 (202)	5.2 (25)	5.0 (50)	3.0 (30)
2	—	0.7 (7)	Trace	0	0
3	$H_5PMo_{10}V_2O_{40}\cdot 28H_2O$	16 (154)	4.2 (21)	4.4 (44)	3.8 (38)
4	$H_6PMo_9V_3O_{40}\cdot 30H_2O$	17 (166)	7.7 (38)	2.9 (29)	4.0 (40)
5	$H_7PMo_8V_4O_{40}\cdot 28H_2O$	19 (192)	4.9 (24)	6.4 (64)	3.6 (36)
6	$H_3PMo_{12}O_{40}\cdot 30H_2O$	22 (223)	11 (53)	2.9 (29)	0.3 (3)
7[c]	$H_3PMo_{12}O_{40}\cdot 30H_2O$	42 (420)	4.4(22)	3.5 (35)	0
8[cd]	$H_3PMo_{12}O_{40}\cdot 30H_2O$	100 (1003)	67 (335)	3.9 (39)	0
9	$H_3PMo_{11}WO_{40}\cdot 27H_2O$	24 (239)	12 (60)	3.0 (30)	0
10	$H_3PMo_{10}W_2O_{40}\cdot 29H_2O$	23 (228)	7.8 (39)	2.8 (28)	0
11	$H_5PW_{10}V_2O_{40}\cdot 27H_2O$	1.5 (15)	Trace	0	0
12	$H_4SiMo_{12}O_{40}\cdot 27H_2O$	22 (218)	7.8 (39)	2.9 (29)	0
13[e]	$MoO_2(acac)_2$	1.8 (18)	0.9 (9)	0	0

[a] **1** (30 mmol) was reacted with 0.9 atm of **2** in the presence of $Pd(OAc)_2$ (10 μmol), HPA (5 μmol), AcONa (25 μmol), and dibenzoylmethane (dbm) (30 μmol) in propionic acid (2 mL) under 1.6 atm of air at 90 °C for 8 h. [b] TON was based on $Pd(OAc)_2$. [c] **1** (120 mmol) was reacted with 0.9 atm of **2** in the presence of $Pd(OAc)_2$ (10 μmol), HPA (6.8 μmol), AcONa (32 μmol), and dbm (120 μmol) in propionic acid (8 mL) under 1.6 atm of air using a 120 mL autoclave. [d] The reaction was carried out at 120 °C. [e] $MoO_2(acac)_2$ (60 μmol) was used instead of HPA.

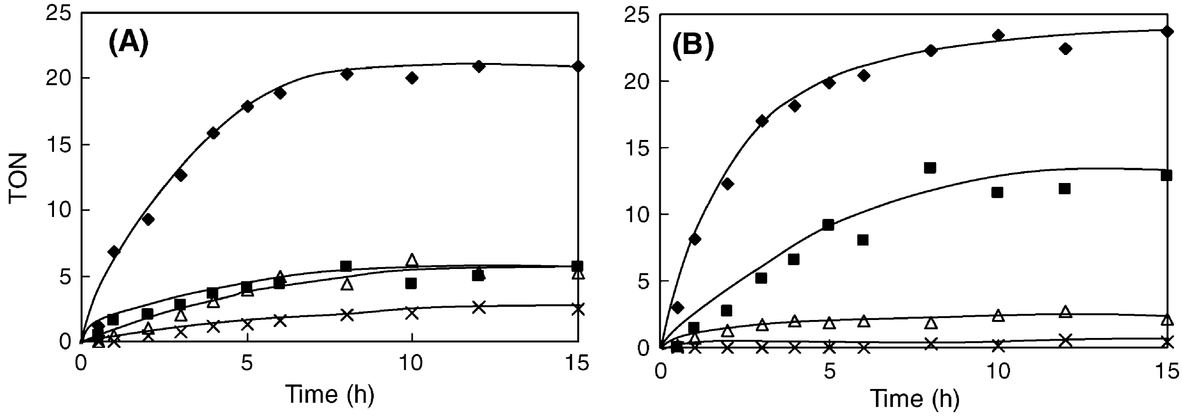

Fig. 3 Time-dependence curves of the oxidative coupling of **1** with **2** using a $Pd(OAc)_2/H_4PMo_{11}VO_{40}\cdot 15H_2O$/air system (**A**) and a $Pd(OAc)_2/H_3PMo_{12}O_{40}\cdot 30H_2O$/air system (**B**) [**3** (◆), **4** (■), **5** (△), **6** (×)].

The product yields were estimated from the peak areas on the basis of the internal standard technique by using GC.

Preparation of $H_4PMo_{11}VO_{40}\cdot 15H_2O$

$H_4PMo_{11}VO_{40}\cdot nH_2O$ was prepared by a known method.[12] $Na_2HPO_4\cdot 26H_2O$ (0.61 g, 5 mmol) was dissolved in 10 mL of water and mixed with $NaVO_3$ (1.79 g, 5 mmol) which had been dissolved by boiling in 10 mL of water. The mixture was cooled and acidified to a red color with 0.5 mL of concentrated sulfuric acid. To this mixture was added a solution of $Na_2MoO_4\cdot 2H_2O$ (13.31 g, 55 mmol) dissolved in 20 mL of water. Finally, 8.5 mL of concentrated sulfuric acid were added slowly with vigorous stirring of the solution. With this addition the dark red color changed to a lighter red. The molybdovanadophosphoric acid was then extracted with 100 mL of diethyl ether after the aqueous solution was cooled. In this extraction, the molybdovanadophosphoric acid etherate was present as a middle layer; the bottom layer (water) was yellow and probably contained vanadyl species. After separation, the middle layer was concentrated by using a rotary vacuum evaporator. The orange solid that remained was allowed to crystallize in water. The orange crystals that formed were filtered and washed with cold water. After drying under vacuum for 2 h, $H_4PMo_{11}VO_{40}\cdot 15H_2O$ was obtained. The number of crystal waters was measured by thermogravimetric analysis.

General procedure for oxidative coupling of benzene (1) with ethylene (2) using $Pd(OAc)_2/HPA/O_2$ catalytic system (run 1 in Table 1)

CAUTION: In order to avoid explosion of a mixture of ethylene and air, the reaction was carried out at an ethylene concentration outside the explosion limits ranging from 3.1 to 32%. Into a 50 mL stainless steel autoclave equipped with a magnetic stirrer bar were placed $Pd(OAc)_2$ (10 μmol), $H_4PMo_{11}VO_{40}\cdot 15H_2O$ (10.4 mg, *ca.* 5 μmol), NaOAc (25 μmol), dibenzoylmethane (30 μmol), **1** (30 mmol) and propionic acid (2 mL). Into the autoclave were introduced 0.9 atm of **2** and 1.6 atm of air, and the mixture was stirred at 90 °C for 8 h. After the reaction, the reacted mixture was transferred to a flask (50 mL) and *ca.* 25 mg of dodecane as internal standard were added to the reaction mixture. Then the GC and GC-MS analyses were performed. The products were identified through a comparison of these analytical data with those of authentic samples.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformation of Carbon Resources" from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and "High-Tech Research Center" Project for Private Universities: matching fund subsidy from the Ministry of Education, Culture, Sports, Science and Technology, 2005–2009. We also thank Nippon Inorganic Colour & Chemical Co. Ltd. for a gift of heteropoly acids.

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