

Synthesis of Aromatic Esters Catalyzed by Palladium on Charcoal: An Efficient Heterogeneous Catalyst for Alkoxy carbonylation of Aryl Iodides

Chinnasamy Ramesh, Ryo Nakamura, Yoshihiro Kubota, Minoru Miwa, Yoshihiro Sugi*

Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan

E-mail: sugi@apchem.gifu-u.ac.jp

Received 12 November 2002; revised 16 January 2003

Abstract: Palladium on charcoal was found to catalyze the carbonylation of aryl iodides with various aliphatic alcohols as well as less reactive phenols to give the corresponding esters in high yield at 140 °C and in the presence of carbon monoxide (1.0 MPa). The carbonylation-polycondensation of 2,7-diiodo-9,10-dihydrophenanthrene with bisphenol-A afforded high molecular weight polyarylate, poly [oxy-1,4-phenylene (1-methylethylidene)-1,4-phenyleneoxycarbonyl (9,10-dihydro-2,7-phenanthrenediyl) carbonyl].

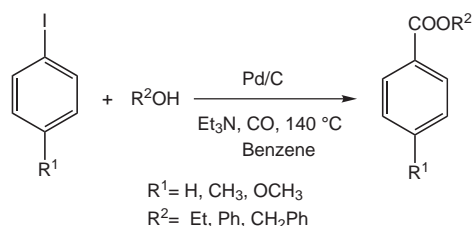
Key words: palladium on charcoal, carbonylation, aryl iodide, aromatic ester, polyarylate

The synthesis of aromatic carbonyl compounds such as esters, amides, anhydrides and carboxylic acids is of fundamental importance in organic chemistry. Transition metal catalyzed carbonylation reactions such as alcohol carbonylation,¹ ester carbonylation,² oxidative carbonylation,³ Reppe carbonylation of alkenes, alkynes, and dienes,⁴ and carbonylation of aryl halides⁵ provides an efficient gateway into such carbonyl compounds. The carbonylation of aryl halides with alcohols and amines catalyzed by palladium complexes is the convergent and direct route to the synthesis of aromatic esters as well as aromatic amides. Such a palladium-catalyzed carbonylation also finds an important application in the synthesis of various aromatic carbonyl compounds, especially of key intermediates in organic synthesis^{5–7} and conductive polymers *viz* polyesters and polyamides in polymer chemistry.^{8,9} In all the above carbonylation reactions, palladium salts with triphenylphosphine ligand were employed as the catalysts. Even though palladium catalysts with triphenylphosphine as a ligand are widely employed as the best catalytic system in the carbonylation of aryl halides, those catalysts are difficult to separate and reuse for the reaction without further processing. The major drawbacks of palladium catalyst with triphenylphosphine ligand are, oxidation of triphenylphosphine to phosphine oxide, reduction of palladium complex to metal and termination of catalytic cycle.

Improvements in efficiency and recycling of the catalyst are essential in view of practical and industrial applications and environment concerns. To overcome these problems, recently a few research groups have reported the

phosphine free and active palladium catalysts for catalytic C–C bond forming reactions.¹⁰ However, these catalysts suffer from drawbacks such as (i) preparation involves many steps and expensive ligands and (ii) recycling the catalyst. Considering the importance and applications of palladium catalyzed carbonylation reactions from industrial as well as academic point of view, it is essential and challenging to focus on the quest to find efficient, inexpensive and recyclable catalysts.

Our interest has been in the development of novel and efficient palladium based catalytic system for the carbonylation of aryl halides with alcohols and amines. We recently studied a palladacycle complex for phosphine free palladium catalyst for the carbonylation.¹¹ However, it finds disadvantages such as recycling and activating aryl bromides and chlorides. In the present work, we describe palladium catalyst on charcoal or alumina for the carbonylation of aryl iodides with various aliphatic alcohols as well as phenols in high yields (Scheme 1).



Scheme 1 Carbonylation of aryl iodides to aromatic esters

A brief study was carried out on the reaction parameters such as base, temperature, pressure and solvent. The phenoxycarbonylation of 4-iodoanisole was studied in the presence of various bases (Table 1). It was observed that triethylamine is the best base under our condition. The pressure of carbon monoxide was also an important parameter. The reactions proceeded well and gave high conversion under 1.0 MPa of carbon monoxide. However, the reactions under lower pressure lead to lower yields; the carbonylations of 4-iodoanisole and of 4-iodotoluene with benzyl alcohol under 0.5 MPa of carbon monoxide afforded 57% and 54%, respectively. The phenoxycarbonylation of 4-iodoanisole was found to give the target esters at the temperature range of 80–150 °C, yield of the product increased with temperature of up to 140 °C. It is to be noted that the best reaction temperature is 140–150 °C.


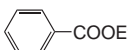

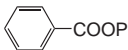

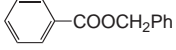
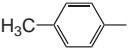
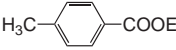
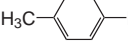
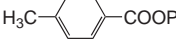
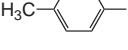
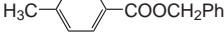
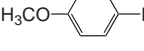
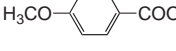
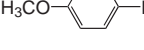
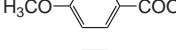
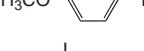
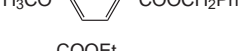






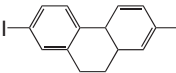
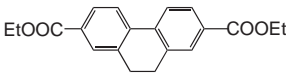
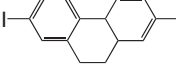
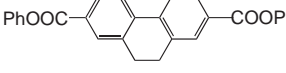
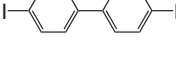
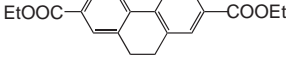
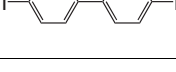
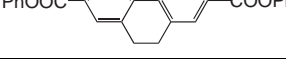
Table 1 Effects of Bases on the Phenoxy carbonylation of 4-Iodoanisole

Entry	Base	Yield (%)
1	Et ₃ N	92
2	DBU	78
3	Pyridine	22
4	NaHCO ₃	28
5	K ₂ CO ₃	75

It is a key point to note that amount of palladium catalyst plays an important role in the product yields, the carbonylation of 4-iodoanisole (2.5 mmol) with phenol was studied with amount of catalyst ranging from 20–300 mg. It was found that lower catalyst level (below 50 mg) led to incomplete reaction and higher catalyst level (above 50mg) resulted in the formation of unexpected product, hence the yields were lowered.

Table 2 shows the carbonylation of various aryl iodides with ethanol, benzylalcohol, and phenol catalyzed by palladium on charcoal in the presence of triethylamine. Most of the reactions proceeded well and led to expected carbonylated product in high yields; especially the carbonyla-

Table 2 The Carbonylation of Aryl Iodides Catalyzed by Palladium on Charcoal

Entry	Aryl iodide	Alcohol	Product	Yield (%)
1		EtOH		80
2		PhOH		92
3		PhCH ₂ OH		70
4		EtOH		75
5		PhOH		87
6		PhCH ₂ OH		73
7		EtOH		77
8		PhOH		92
9		PhCH ₂ OH		76
10		EtOH		74
11		PhOH		97
12		PhCH ₂ OH		83
13		EtOH		81
14		PhOH		85
15		EtOH		80
16		PhOH		82

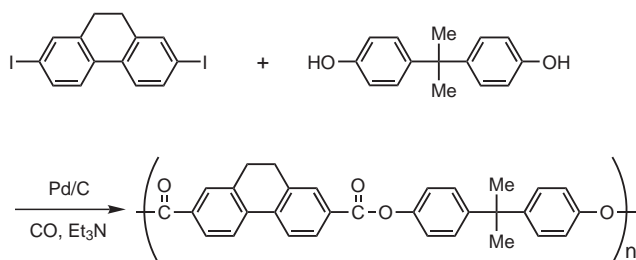
tion of aryl iodides using phenol gave higher yields than aliphatic alcohols. However, the reaction of bromoaromatics failed to give the expected product. The carbonylation of 4-iodoanisole with phenol catalyzed by 5% palladium on alumina under the same reaction also led successfully to carbonylated product with yield of 96%.

To elucidate the active species, the carbonylation of iodobenzene was examined in the filtrate after the carbonylation of 4-iodobenzene with phenol. No further catalytic activity was observed without palladium on charcoal under our conditions. It is concluded that the active catalytic species is palladium metal supported on charcoal and not palladium species resolved under the reaction conditions.

The palladium on charcoal can be recovered and recycled for the further reaction. The catalyst was recovered by the filtration using membrane filter after the carbonylation of 4-iodoanisole with phenol. Recovered catalyst was used for the reaction under the same condition; the yields of phenyl 4-methoxybenzoate were 92% (1st time), 90% (2nd time), and 84% (3rd time).

The carbonylation of 2,7-diiodo-9,10-dihydrophenanthrene with ethanol and phenol was examined over palladium on charcoal under the conditions described above. Diethyl and diphenyl 9,10-dihydrophenanthrene-2,7-dicarbonylates were obtained in excellent yield as shown in Table 2.

We have carried out the carbonylation-polycondensation of diiodide with diol and carbon monoxide over palladium charcoal to yield polyesters in a one-pot synthesis using chlorobenzene as a solvent and triethylamine as a base. The combination of 2,7-diiodo-9,10-dihydrophenanthrene and bisphenol-A with carbon monoxide yielded high molecular weight polyarylate, poly[oxy-1,4-phenylene (1-methylethylidene)-1,4-phenyleneoxycarbonyl (9,10-dihydro-2,7-phenanthrenediyl)carbonyl] in excellent yield (Scheme 2, Table 3); the weight averaged molecular weight (M_w) was in the range of 5,000–7,000, and M_w/M_n in the range of 1.5–12.



Scheme 2 Carbonylation-polycondensation of diiodide with diol

High temperature such as 150 °C gave lower molecular weight polyarylate compared at lower temperatures. The detailed study of the carbonylation-polycondensation is in progress towards higher molecular weight polyarylate and aramides catalyzed by palladium on charcoal and on alumina.

Table 3 The Carbonylation-Polycondensation Catalyzed by Palladium on Charcoal

Entry	Temperature (°C)	M_w	M_w/M_n
1	140	6866	1.578
2	145	7090	2.114
3	150	2095	12.164

This is a first report of such a heterogeneous catalytic system for the carbonylation where the reaction occurs on metal surface. The palladium on charcoal can be recovered after the reaction, and reused for further reaction. We believe that palladium on charcoal is an excellent and versatile heterogeneous catalyst for the carbonylation of aromatic halides in organic synthesis.

Pd/C was obtained from Wako Pure Chem. Ind. Ltd., Tokyo, Japan.

Carbonylation; General Procedure

In a typical procedure, aryl iodide (2.5 mmol), alcohol (2.5–3.0 mmol), Et_3N (3 mmol) and 5% Pd/C (50 mg) in freshly distilled benzene (5 mL) were taken in autoclave (50 mL), flushed with nitrogen (3 times) and pressurized with carbon monoxide (1 MPa). The autoclave was placed in oil bath pre-heated at 140 °C, and the reaction mixture was stirred for 6 h. After stopping the reaction, the autoclave was cooled, excess carbon monoxide was purged, and benzene was evaporated. The product was isolated by silica gel column chromatography (hexane–benzene). All the products were characterized by IR and ^1H NMR. IR and ^1H NMR data of representative examples are given.

7

IR: 2981, 1730 cm^{-1} .

^1H NMR: δ = 8.02 (d, 2 H, J = 18 Hz, Ar-H), 6.90 (d, 2 H, J = 18 Hz, Ar-H), 4.2 (q, 2 H, J = 8.2 Hz, OCH_2), 3.84 (s, 3 H, OCH_3), 1.3 (t, 3 H, J = 8.2 Hz, CH_3).

11

IR: 1730 cm^{-1} .

^1H NMR: δ = 9.02 (d, 1 H, J = 8.4 Hz, Ar-H), 8.44 (d, 1 H, J = 8.0 Hz, Ar-H), 8.1 (d, 1 H, J = 8.0 Hz, Ar-H), 7.92 (d, 1 H, J = 8.0 Hz, Ar-H), 7.66–7.62 (m, 1 H, Ar-H), 7.60–7.54 (m, 2 H, Ar-H), 7.32–7.25 (m, 2 H, Ar-H), 7.48–7.44 (m, 2 H, Ar-H), 7.32–7.25 (m, 3 H, Ar-H).

12

IR: 2989, 1730 cm^{-1} .

^1H NMR: δ = 8.7 (d, J = 8 Hz, 1 H), 8.02–7.97 (m, 1 H), 7.8 (d, J = 9.4 Hz, 1 H), 7.65–7.62 (m, 1 H), 7.42–7.10 (m, 7 H), 7.01 (d, J = 8 Hz, 1 H), 5.22 (s, 2 H).

13

IR: 2991, 1730 cm^{-1} .

^1H NMR: δ = 7.8–7.5 (m, 4 H, Ar-H), 7.20–7.0 (m, 2 H, Ar-H), 4.2 (q, 4 H, J = 8.0 Hz, OCH_2), 2.6 (s, 4 H, Ar- CH_2), 1.21 (t, 6 H, J = 8.0 Hz, CH_3).

15IR: 2991, 1730 cm⁻¹.¹H NMR: δ = 8.16 (d, 4 H, *J* = 17.2 Hz, Ar-H), 7.71 (d, 4 H, *J* = 17.2 Hz, Ar-H), 4.2 (q, 4 H, *J* = 8.2 Hz, OCH₂), 1.3 (t, 6 H, *J* = 8.2 Hz, CH₃).**16**IR: 1730 cm⁻¹.¹H NMR: δ = 8.33 (d, 4 H, *J* = 18 Hz, Ar-H), 7.8 (d, 4 H, *J* = 18 Hz, Ar-H), 7.48–7.42 (m, 4 H), 7.32–7.20 (m, 6 H).**Carbonylation-Polycondensation; General Procedure**

In a typical procedure, 2,7-diiodo-9,10-dihydrophenanthrene (2.5 mmol), bisphenol-A (2.5 mmol), Et₃N (5.5 mmol) and 5% Pd/C (50 mg) in chlorobenzene (5 mL) were taken in autoclave (50 mL), flushed 3 times with nitrogen, and pressurized with carbon monoxide (1.0 MPa). The autoclave was placed in oil bath pre-heated at 140–150 °C, and the whole reaction mixture was stirred for 6 h. After the reaction, the autoclave was cooled, excess carbon monoxide was purged, and the reaction mixture was filtered. The filtrate was poured into MeOH (200 mL). Pale-yellow solid was filtered and dried to afford poly [oxy-1,4-phenylene (1-methylethylidene)-1,4-phenyleneoxycarbonyl (9,10-dihydro-2,7-phenanthrenediyl) carbonyl]. All the products were characterized by IR and NMR. Molecular weight was determined by gel permeation chromatography using polystyrene as a standard. Typical results are shown in Table 3.

¹H NMR: δ = 8.17–8.05 (m, 4 H, Ar-H), 7.94–7.82 (m, 2 H, Ar-H), 7.20–7.0 (m, 8 H, Ar-H), 3.0 (s, 4 H, CH₂), 1.73 (s, 6 H, CH₃).**Acknowledgment**

C. Ramesh thanks the Ministry of Education, Culture, Sports, Science, and Technology, Japan for the fellowship.

References

- (1) Riemenschneider, W. In *Ullmanns Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A5; VCH: Weinheim, **1986**, 235.
- (2) Gauss, M.; Seidel, A.; Torrence, P.; Heymanns, P. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1; VCH: New York, **1996**, 104.
- (3) (a) Klausener, A.; Jentsch, J. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1; VCH: New York, **1996**, 169. (b) Hayashi, M.; Takezaki, H.; Hashimoto, Y.; Takaoki, K.; Saigo, K. *Tetrahedron Lett.* **1998**, 39, 7529.
- (4) (a) Tsuji, J. In *Palladium Reagents and Catalysts*; Wiley: New York, **1999**. (b) Hohn, A. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1; VCH: New York, **1996**, 137. (c) Beller, M.; Tafesh, A. M. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1; VCH: New York, **1996**, 187.
- (5) (a) Schoenberg, A.; Bartoletti, I.; Heck, R. F. *J. Org. Chem.* **1974**, 39, 3318. (b) Schoenberg, A.; Heck, R. F. *J. Org. Chem.* **1974**, 39, 3327. (c) Hidai, M.; Hikita, T.; Wada, Y.; Fujikura, Y.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1975**, 48, 2075. (d) Ito, T.; Mori Mizoroki, T.; Osaki, A. *Bull. Chem. Soc. Jpn.* **1975**, 48, 2091. (e) Stille, J. K.; Wong, P. K. *J. Org. Chem.* **1975**, 40, 532.
- (6) (a) Tsuji, J. In *Palladium Reagents and Catalysts*; John Wiley & Sons: Tokyo, **1995**, 188–209. (b) Sugihara, T.; Coperet, C.; Owczarczy, Z.; Haring, L. S.; Negishi, E. *J. Am. Chem. Soc.* **1994**, 116, 7923. (c) Grigg, R.; Sridharan, V. *Tetrahedron Lett.* **1993**, 34, 7471. (d) Harris, G. D.; Herr, R. J.; Weinreb, S. *J. Org. Chem.* **1992**, 2528. (e) Harris, G. D.; Herr, R. J.; Weinreb, S. *J. Org. Chem.* **1993**, 58, 5452.
- (7) (a) Sugi, Y.; Takeuchi, K.; Hanaoka, T.; Matsuzaki, T.; Takagi, S.; Doi, Y. *J. Jpn. Pet. Inst.* **1994**, 37, 70. (b) Kubota, Y.; Hanaoka, T.; Takeuchi, K.; Sugi, Y. *Synlett* **1994**, 515–517. (c) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1988**, 21, 1908.
- (8) (a) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1989**, 22, 2593. (b) Perry, R. J.; Tuner, S. R.; Blevins, R. W. *Macromolecules* **1993**, 26, 1509.
- (9) (a) Kubota, Y.; Takeuchi, K.; Hanaoka, T.; Sugi, Y. *Bull. Chem. Soc. Jpn.* **1994**, 67, 563. (b) Kubota, Y.; Takeuchi, K.; Hanaoka, T.; Sugi, Y. *Catal. Today* **1996**, 31, 27. (c) Kubota, Y.; Nakada, S.; Sugi, Y. *Mat. Trans., JIM* **2002**, 43, 326.
- (10) (a) Albisso, D. A.; Bedford, R. B.; Staley, E. A. *Chem. Commun.* **1998**, 2095. (b) Ohff, M.; Ohff, A.; Milstein, D. *Chem. Commun.* **1999**, 357. (c) Iyer, S.; Ramesh, C. *Tetrahedron Lett.* **2000**, 41, 8981. (d) Ohff, M.; Ohff, A.; Vander Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, 119, 11687.
- (11) Ramesh, C.; Kubota, Y.; Miwa, M.; Sugi, Y. *Synthesis* **2002**, 2171.