ORGANIC LETTERS

2011
Vol. 13, No. 22
5980–5983

Palladium-Catalyzed Carbonylative Reaction of 1-(2,2-Dibromovinyl)-2-alkenylbenzene and Carbon Monoxide, with Phenol or Alcohol

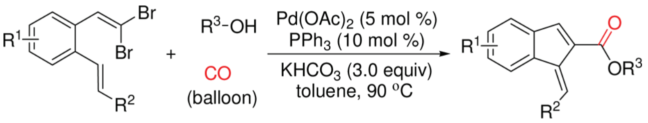
Shengqing Ye[†] and Jie Wu*[,†,‡]

Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China

jie_wu@fudan.edu.cn

Received September 7, 2011

ABSTRACT



A palladium-catalyzed carbonylative reaction of 1-(2,2-dibromovinyl)-2-alkenylbenzene and carbon monoxide, with phenol or alcohol, is reported, which affords 1-methylene-1*H*-indene-2-carboxylates in moderate to good yields. This cascade process, which includes carbonylation and Heck reaction, proceeds smoothly with good functional group tolerance and high selectivity.

Currently, palladium-catalyzed carbonylation reactions have become a powerful device in synthetic organic chemistry, which provide straightforward access to (hetero)-aromatic carboxylic acid derivatives.[1] The synthesis of acids, amides, esters, ketones, and aldehydes has been well established by using this method, starting from easily available aryl halides.[2] Recently, *gem*-dihaloolefins have found broad applications in organic synthesis with good stereoselectivity.[3−5] For example, Lautens and co-workers reported efficient pathways for the construction of carbo- and heterocycles starting from *gem*-dihaloolefins.[5] We also

---

[†] Fudan University.

[‡] Chinese Academy of Sciences.

(1) For reviews on palladium-catalyzed carbonylations, see: (a) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114. (b) Brennführer, A.; Neumann, H.; Beller, M. *ChemCatChem* **2009**, *1*, 28. (c) Barnard, C. F. J. *Organometallics* **2008**, *27*, 5402. (d) Beller, M. Carbonylation of Benzyl- and Aryl-X Compounds. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002; pp 145−156. (e) Skoda-Földes, R.; Kollár, L. *Curr. Org. Chem.* **2002**, *6*, 1097. (f) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley: Chichester, 1995. (g) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation, Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991.

(2) For selected examples of palladium-catalyzed carbonylations of aryl halides, see: (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) Schoenberg, A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 7761. (d) Klaus, S.; Neumann, H.; Zapf, A.; Strübing, D.; Hübner, S.; Almena, J.; Riermeier, T.; Gross, P.; Sarich, M.; Krahnert, W.-R.; Rossen, K.; Beller, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 154. (e) Martinelli, J. R.; Clark, T. P.; Watson, D. A.; Munday, R. H.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 8460. (f) Liu, J.; Peng, X.; Sun, W.; Zhao, Y.; Xia, C. *Org. Lett.* **2008**, *18*, 3933. (g) Neumann, H.; Brennführer, A.; Beller, M. *Chem.—Eur. J.* **2008**, *14*, 3645. (h) Zhang, Z.; Liu, Y.; Gong, M.; Zhao, X.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 1139. (i) Wu, X.-F.; Neumann, H.; Spannenberg, A.; Schulz, T.; Jiao, H.; Beller, M. *J. Am. Chem. Soc.* **2010**, *132*, 14596. (j) Zhang, H.; Liu, D.; Chen, C.; Liu, C.; Lei, A. *Chem.—Eur. J.* **2011**, *17*, 9581 and references cited therein.

(3) For reviews of *gem*-dihaloolefins, see: (a) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; p 650. (b) Xu, B.; Ma, S. *Chin. J. Org. Chem.* **2001**, *21*, 252.

(4) For selected examples, see: (a) Zeng, X.; Qian, M.; Hu, Q.; Negishi, E. *Angew. Chem., Int. Ed.* **2004**, *43*, 2259. (b) Molander, G. A.; Yokoyama, Y. *J. Org. Chem.* **2006**, *71*, 2493. (c) Knorr, R.; Pires, C.; Freudenreich, J. *J. Org. Chem.* **2007**, *72*, 6084. (d) Sun, C.; Xu, B. *J. Org. Chem.* **2008**, *73*, 7361. (e) Fukudome, Y.; Naito, H.; Hata, T.; Urabe, H. *J. Am. Chem. Soc.* **2008**, *130*, 1820. (f) Ma, S.; Xu, B. *J. Org. Chem.* **1998**, *63*, 9156. (g) Ma, S.; Xu, B.; Ni, B. *J. Org. Chem.* **2000**, *65*, 8532. (h) Ye, W.; Mo, J.; Zhao, T.; Xu, B. *Chem. Commun.* **2009**, 3246. (i) Bandyopadhyay, A.; Varghese, B.; Hopf, H.; Sankararaman, S. *Chem.—Eur. J.* **2007**, *13*, 3813. (j) Gholami, M.; Melin, F.; McDonald, R.; Ferguson, M. J.; Echegoyen, L.; Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 9081. (k) Ye, S.; Ren, H.; Wu, J. *J. Comb. Chem.* **2010**, *12*, 670. (l) Ye, S.; Yang, X.; Wu, J. *Chem. Commun.* **2010**, *46*, 2950. (m) Zeng, F.; Alper, H. *Org. Lett.* **2011**, *13*, 2868. (n) Vieira, T. O.; Meaney, L. A.; Shi, Y.-L.; Alper, H. *Org. Lett.* **2008**, *10*, 4899. (o) Arthuis, M.; Pontikis, R.; Florent, J. C. *Org. Lett.* **2009**, *11*, 4608.

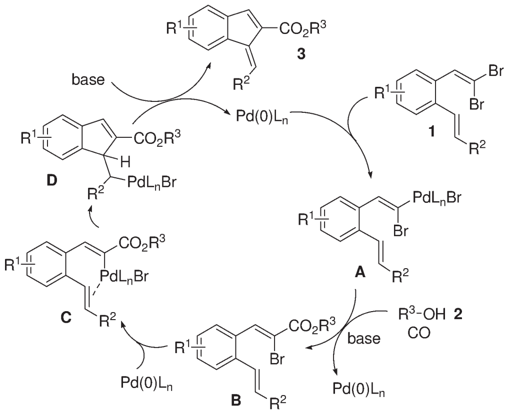
10.1021/ol202420j

used *gem*-dibromoolefins as substrates for the synthesis of 1-methyleneindenes through palladium-catalyzed tandem reactions[6] with arylboronic acids.[4k,l]

Indene has been recognized as a privileged fragment, which can be found in many natural products and drug candidates.[7] Additionally, applications of indenes in materials science have been discovered.[8] So far, synthetic methodologies to this carbacycle (including 1-methyleneindene) have been developed.[9,10] Due to its importance, it is still of high interest and great demand to develop novel approaches for efficient generation of functionalized indenes, especially in the field of chemical biology. Prompted by the achievement of palladium-catalyzed carbonylation reactions and the versatility of *gem*-dihaloolefins, we conceived that the combination of 1-(2,2-dibromovinyl)-2-alkenylbenzene and carbon monoxide would provide a novel and efficient pathway for the formation of indene derivatives. Herein, we report a palladium-catalyzed carbonylation tandem reaction of 1-(2,2-dibromovinyl)-2-alkenylbenzene, carbon monoxide, and phenol or alcohol, which affords 1-methylene-1*H*-indene-2-carboxylates. Although several routes to the 1-methylene-1*H*-indene-2-carboxylates were reported,[9g−i] they usually suffered from multiple steps, low yields, and high temperature. Additionally, the functional group tolerance is not satisfactory, which limits its diversity-oriented synthesis.

Our proposed synthetic route is shown in Scheme 1, which includes a cascade carbonylation and Heck reaction. 1-(2,2-Dibromovinyl)-2-alkenylbenzene **1** could be easily accessed using a well-known method.[4k] We hypothesized that, in this reaction process, an oxidative addition would occur in the presence of Pd(0) to produce intermediate **A**. Subsequently, a nucleophile (phenol or alcohol) and carbon monoxide were involved through a palladium-catalyzed carbonylation reaction to afford compound **B**. Concurrently the Pd(0) was released, which then underwent oxidative addition of vinyl bromide **B** again to furnish intermediate **C**. After intramolecular insertion and β-hydrogen elimination, (Z)-1-methylene-1H-indene-2-carboxylate **3** would be generated according to the Heck reaction mechanism.[11] In the meantime, the Pd(0) would re-enter the catalytic cycle. We believed that this hypothesis was feasible, although several competitive reactions seemed inevitable.

Scheme 1. Proposed Route for the Palladium-Catalyzed Carbonylative Reaction of 1-(2,2-Dibromovinyl)-2-alkenylbenzene, Alcohol or Phenol, and Carbon Monoxide



In an initial attempt, 1-(2,2-dibromovinyl)-2-alkenylbenzene **1a** and *n*-butyl alcohol **2a** were used as model substrates for reaction development. At the outset, the reaction was catalyzed by Pd(OAc)$_2$ (5 mol %) and PPh$_3$ (10 mol %) in the presence of K$_2$CO$_3$ (3.0 equiv) as a base in toluene at 100 °C with a balloon of carbon monoxide (Table 1, entry 1). However, only a trace amount of product was observed. To our delight, the expected product **3aa** (50% yield) was formed when KHCO$_3$ was employed as a replacement of base in the reaction (Table 1, entry 2).

---

(5) (a) Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2005**, *7*, 3549. (b) Yuen, J.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2006**, *8*, 653. (c) Fayol, A.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2006**, *8*, 4203. (d) Fang, Y.-Q.; Karisch, R.; Lautens, M. *J. Org. Chem.* **2007**, *72*, 1341. (e) Nagamochi, M.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2007**, *9*, 2955. (f) Fang, Y.-Q.; Lautens, M. *J. Org. Chem.* **2008**, *73*, 538. (g) Bryan, C. S.; Lautens, M. *Org. Lett.* **2008**, *10*, 4633. (h) Bryan, C. S.; Lautens, M. *Org. Lett.* **2010**, *12*, 2754. (i) Bryan, C. S.; Braunger, J. A.; Lautens, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7064. (j) Newman, S. G.; Aureggi, V.; Bryan, C. S.; Lautens, M. *Chem. Commun.* **2009**, 5236. (k) Chai, D. I.; Lautens, M. *J. Org. Chem.* **2009**, *74*, 3054.

(6) For selected examples, see: (a) Montgomery, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3890. (b) Negishi, E.; Coperet, C.; Ma, S.; Liou, S. Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365. (c) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115. (d) Grigg, R.; Sridharan, V. *J. Organomet. Chem.* **1999**, *576*, 65. (e) Miura, T.; Murakami, M. *Chem. Commun.* **2007**, 217. (f) Malacria, M. *Chem. Rev.* **1996**, *96*, 289. (g) Nicolaou, K. C.; Montagnon, T.; Snyder, S. A. *Chem. Commun.* **2003**, 551. (h) Nicolaou, K. C.; Edmonds, D. J.; Bulger, P. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7134. (i) Enders, D.; Grondal, C.; Hüttl, M. R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1570. (j) Tietze, L. F.; Brasche, G.; Gericke, K. *Domino Reactions in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2006.

(7) For selected examples, see: (a) Clegg, N. J.; Paruthiyil, S.; Leitman, D. C.; Scanlan, T. S. *J. Med. Chem.* **2005**, *48*, 5989. (b) Lautens, M.; Marquardt, T. *J. Org. Chem.* **2004**, *69*, 4607. (c) Gao, H.; Katzenellenbogen, J. A.; Garg, R.; Hansch, C. *Chem. Rev.* **1999**, *99*, 723.

(8) For selected examples, see: (a) Yang, J.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **2000**, *65*, 6739. (b) Barbera, J.; Rakitin, O. A.; Ros, M. B.; Torroba, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 296. (c) Akbulut, U.; Khurshid, A.; Hacioglu, B.; Toppare, L. *Polymer* **1990**, *31*, 1343.

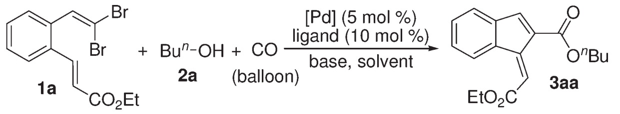
(9) For selected examples, see: (a) Zhang, D.; Liu, Z.; Yum, E. K.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 251. (b) Xi, Z.; Guo, R.; Mito, S.; Yan, H.; Kanno, K.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2003**, *68*, 1252. (c) Kuninobu, Y.; Tokunaga, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 202. (d) Romines, K. R.; Lovasz, K. D.; Mizsak, S. A.; Morris, J. K.; Seest, E. P.; Han, F.; Tulinsky, J.; Judge, T. M.; Gammill, R. B. *J. Org. Chem.* **1999**, *64*, 1733. (e) Zhou, F.; Yang, M.; Lu, X. *Org. Lett.* **2009**, *11*, 1405. (f) Lu, J.-M.; Zhu, Z.-B.; Shi, M. *Chem.—Eur. J.* **2009**, *15*, 963. (g) Kim, K. H.; Kim, S. H.; Park, B. R.; Kim, J. N. *Tetrahedron Lett.* **2010**, *51*, 3368. (h) Watanabe, M.; Shiine, K.; Ideta, K.; Matsumoto, T.; Thiemann, T. *J. Chem. Res.* **2008**, 669. (i) Haddad, N.; Abu-Shqara, E. *J. Org. Chem.* **1994**, *59*, 6090.

(10) For recent examples, see: (a) Bucher, G.; Mahajan, A. A.; Schmittel, M. *J. Org. Chem.* **2008**, *73*, 8815. (b) Furuta, T.; Asakawa, T.; Iinuma, M.; Fujii, S.; Tanaka, K.; Kan, T. *Chem. Commun.* **2006**, 3648. (c) Rahman, S. M. A.; Sonoda, M.; Ono, M.; Miki, K.; Tobe, Y. *Org. Lett.* **2006**, *8*, 1197. (d) Basurto, S.; Garcia, S.; Neo, A. G.; Torroba, T.; Marcos, C. F.; Miguel, D.; Barbera, J.; Ros, M. B.; de la Fuente, M. R. *Chem.—Eur. J.* **2005**, *11*, 5362. (e) Bekele, T.; Christian, C. F.; Lipton, M. A.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 9216. (f) Schmittel, M.; Vavilala, C. *J. Org. Chem.* **2005**, *70*, 4865. (g) Schreiner, P. R.; Prall, M.; Lutz, V. *Angew. Chem., Int. Ed.* **2003**, *42*, 5757. (h) Ye, S.; Gao, K.; Zhou, H.; Yang, X.; Wu, J. *Chem. Commun.* **2009**, 5406. (i) Gao, K.; Wu, J. *Org. Lett.* **2008**, *10*, 2251. (j) Qiu, G.; Ding, Q.; Gao, K.; Peng, Y.; Wu, J. *ACS Comb. Sci.* **2011**, *13*, 13.

(11) Jutand, A. In *The Mizoroki−Heck Reaction*; Oestreich, M., Ed.; John Wiley and Sons: Hoboken, NJ, 2009; p 1.

Other bases such as KOAc, K_3PO_4, and $^iPr_2NEt$ were not effective in the transformation (Table 1, entries 3−5). The yields could not be improved when other ligands were screened (Table 1, entries 6−9). The palladium source was examined subsequently, which showed that the acetate anion was crucial for the successful conversion (Table 1, entries 10−15). Solvent effect was then explored, and no better results were obtained (Table 1, entries 16−18). The same outcome was obtained when the reaction was performed at 90 °C (Table 1, entry 19). The yield was decreased when the reaction occurred at 70 °C (12% yield, Table 1, entry 20). The reaction was retarded when a catalytic amount of palladium acetate was reduced to 2.5 mol % (Table 1, entry 21). No improvement was observed when the amount of palladium catalyst was increased to 10 mol % (Table 1, entry 22).

Table 1. Initial Studies for the Palladium-Catalyzed Reaction of 1-(2,2-Dibromovinyl)-2-alkenylbenzene **1a**, *n*-Butyl Alcohol **2a**, and Carbon Monoxide

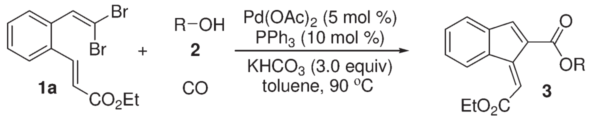


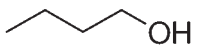
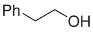
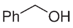
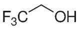
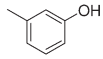
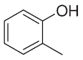
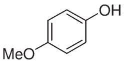
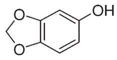
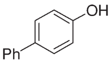
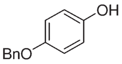
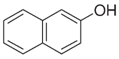
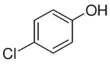
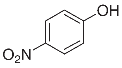
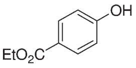
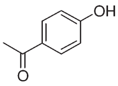
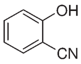
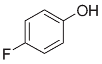
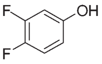
entry	[Pd]	ligand	base	solvent	yield (%)[a]
1	$Pd(OAc)_2$	PPh_3	K_2CO_3	toluene	trace
2	$Pd(OAc)_2$	PPh_3	$KHCO_3$	toluene	50
3	$Pd(OAc)_2$	PPh_3	KOAc	toluene	trace
4	$Pd(OAc)_2$	PPh_3	K_3PO_4	toluene	trace
5	$Pd(OAc)_2$	PPh_3	$^iPr_2NEt$	toluene	nr
6	$Pd(OAc)_2$	PCy_3	$KHCO_3$	toluene	30
7	$Pd(OAc)_2$	DPPF	$KHCO_3$	toluene	26
8	$Pd(OAc)_2$	DPPP	$KHCO_3$	toluene	24
9	$Pd(OAc)_2$	S-Phos	$KHCO_3$	toluene	20
10	$Pd(PPh_3)_2Cl_2$	PPh_3	$KHCO_3$	toluene	nr
11[b]	$Pd(PPh_3)_2Cl_2$	PPh_3	$KHCO_3$	toluene	24
12	$Pd(PhCN)_2Cl_2$	PPh_3	$KHCO_3$	toluene	nr
13[b]	$Pd(PhCN)_2Cl_2$	PPh_3	$KHCO_3$	toluene	33
14	$Pd_2(dba)_3$	PPh_3	$KHCO_3$	toluene	nr
15[b]	$Pd_2(dba)_3$	PPh_3	$KHCO_3$	toluene	33
16	$Pd(OAc)_2$	PPh_3	$KHCO_3$	dioxane	trace
17	$Pd(OAc)_2$	PPh_3	$KHCO_3$	DMF	nr
18	$Pd(OAc)_2$	PPh_3	$KHCO_3$	DMSO	nr
19[c]	$Pd(OAc)_2$	PPh_3	$KHCO_3$	toluene	50
20[d]	$Pd(OAc)_2$	PPh_3	$KHCO_3$	toluene	12
21[c,e]	$Pd(OAc)_2$	PPh_3	$KHCO_3$	toluene	trace
22[c,f]	$Pd(OAc)_2$	PPh_3	$KHCO_3$	toluene	40

[a] Isolated yield based on 1-(2,2-dibromovinyl)-2-alkenylbenzene **1a**. [b] In the presence of 10 mol % of AgOAc. [c] The reaction was performed at 90 °C. [d] The reaction was performed at 70 °C. [e] In the presence of 2.5 mol % of $Pd(OAc)_2$ and 5 mol % of PPh_3. [f] In the presence of 10 mol % of $Pd(OAc)_2$ and 20 mol % of PPh_3.

Under the optimized conditions [$Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), $KHCO_3$ (3.0 equiv), toluene, 90 °C], we investigated the scope of this palladium-catalyzed carbonylation tandem reaction. The results are summarized in Tables 2 and 3. Various alcohols and phenols were examined for the reaction of 1-(2,2-dibromovinyl)-2-alkenylbenzene **1a** with carbon monoxide. All reactions worked well to give the desired product **3** in moderate to good yields. For instance, when 2-phenylethanol **2b** was used as a nucleophile, the corresponding indene **3ab** was afforded in 46% yield (Table 2, entry 2). The conditions could be

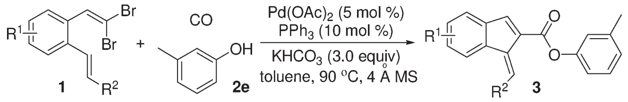
Table 2. Palladium-Catalyzed Carbonylative Reaction of 1-(2,2-Dibromovinyl)-2-alkenylbenzene **1a**, Alcohol or Phenol **2**, and Carbon Monoxide

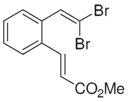
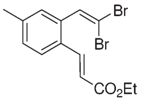
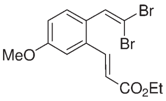
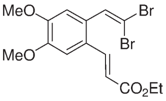
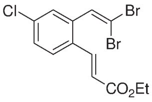
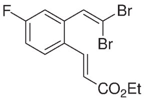
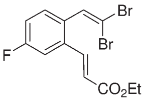
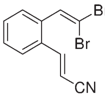
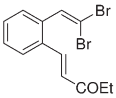
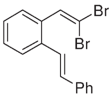
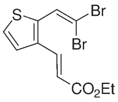


entry	ROH	product	yield (%)[a]
1	 **2a**	**3aa**	50
2	 **2b**	**3ab**	46
3	 **2c**	**3ac**	50
4	 **2d**	**3ad**	40
5	 **2e**	**3ae**	67
6	 **2f**	**3af**	64
7	 **2g**	**3ag**	75
8	 **2h**	**3ah**	55
9	 **2i**	**3ai**	61
10	 **2j**	**3aj**	70
11	 **2k**	**3ak**	45
12	 **2l**	**3al**	76
13	 **2m**	**3am**	48
14	 **2n**	**3an**	58
15	 **2o**	**3ao**	52
16	 **2p**	**3ap**	60
17	 **2q**	**3aq**	70
18	 **2r**	**3ar**	64

[a] Isolated yield based on 1-(2,2-dibromovinyl)-2-alkenylbenzene **1a**. Molecular sieves (4 Å) were added for the reactions of phenols.

Table 3. Palladium-Catalyzed Carbonylative Reaction of 1-(2,2-Dibromovinyl)-2-alkenylbenzene **1**, Phenol **2e**, and Carbon Monoxide



entry	substrate **1**	product	yield (%)[a]
1	 **1b**	**3be**	80
2	 **1c**	**3ce**	82
3	 **1d**	**3de**	50
4	 **1e**	**3ee**	44
5	 **1f**	**3fe**	72
6	 **1g**	**3ge**	68
7	 **1h**	**3he**	57
8	 **1i**	**3ie**	40
9	 **1j**	**3je**	trace
10	 **1k**	**3ke**	trace
11	 **1l**	**3le**	30

[a] Isolated yield based on 1-(2,2-dibromovinyl)-2-alkenylbenzene **1**.

applicable to the reaction of benzyl alcohol **2c** or 2,2,2-trifluoroethanol **2d** as well, which gave rise to the expected product **3ac** or **3ad** in 50% and 40% yield, respectively (Table 2, entries 3 and 4). Further investigations with various phenols were conducted under the standard conditions. However, the yields were very low. We finally realized that the results could be improved after adding 4 Å molecular sieves, which was not effective for the reaction of alcohols. Thus, reaction of 1-(2,2-dibromovinyl)-2-alkenylbenzene **1a**, 3- methylphenol **2e**, and carbon monoxide led to the desired product **3ae** in 67% yield (Table 2, entry 5). Reaction of 2-methylphenol **2f** showed similar reactivity (64% yield, Table 2, entry 6). 1-(2,2-Dibromovinyl)-2-alkenylbenzene **1a** reacted with 4-methoxyphenol **2g** in the presence of carbon monoxide, leading to the corresponding product **3ag** in 75% yield (Table 2, entry 7). Lower yields were generated when benzo[*d*][1,3]dioxol-5-ol **2h**, 4-phenylphenol **2i**, 4-benzoxyphenol **2j**, or 2-naphthalenol **2k** was employed in the reaction (Table 2, entries 8–11). Noticeably, phenols with chloro, nitro, ester, ketone, cyano, and fluoro groups attached on the aromatic ring were all compatible under the standard conditions (Table 2, entries 12–18).

Next, investigations with various 1-(2,2-dibromovinyl)-2-alkenylbenzenes **1** were conducted in the reaction of 3-methylphenol **2e** with carbon monoxide under the optimized conditions (Table 3). Compound **1b** displayed good reactivity during the transformation (Table 3, entry 1). Different functional groups in the aromatic ring of 1-(2,2-dibromovinyl)-2-alkenylbenzenes **1** were all tolerated when an ester group was located at the R^2 position (Table 3, entries 3–7). When R^2 is a cyano group, the corresponding product **3ie** was generated in 40% yield (Table 3, entry 8). However, only a trace amount of product was observed when the R^2 position was replaced by a ketone or phenyl group (Table 3, entries 9 and 10). It is noteworthy that thiophenyl incorporated substrate **1l** was a good reactant as well in this palladium-catalyzed carbonylation cascade reaction, although the yield is low (30% yield, Table 3, entry 11).

In conclusion, we have described a novel and efficient approach for the synthesis of 1-methylene-1*H*-indene-2-carboxylates via a palladium-catalyzed carbonylation cascade reaction of 1-(2,2-dibromovinyl)-2-alkenylbenzene, carbon monoxide, and phenol or alcohol. This cascade process, which includes carbonylation and a Heck reaction, proceeds smoothly with good functional group tolerance and high selectivity. Currently, application of *gem*-dihaloolefins in other tandem processes is under investigation in our laboratory, and the results will be reported in due course.

Acknowledgment. Financial support from National Natural Science Foundation of China (Nos. 21032007 and 21172038) is gratefully acknowledged.

Supporting Information Available. Experimental procedure, characterization data, ^1H and ^{13}C NMR spectra of compounds **3**. This material is available free of charge via the Internet at http://pubs.acs.org.