ORGANIC
LETTERS

2004
Vol. 6, No. 24
4623−4625

Oxidative Cross-Coupling of Acrylates with Vinyl Carboxylates Catalyzed by a $Pd(OAc)_2$/HPMoV/O_2 System

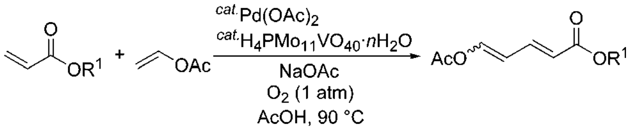
Yuji Hatamoto, Satoshi Sakaguchi, and Yasutaka Ishii*

Department of Applied Chemistry, Faculty of Engineering, Kansai University,
Suita, Osaka 564-8680, Japan

ishii@ipcku.kansai-u.ac.jp

Received October 4, 2004

ABSTRACT



Oxidative cross-coupling of acrylates with vinyl carboxylates was first successfully achieved by the use of a $Pd(OAc)_2$/HPMoV/O_2 system in fair to good yields. For instance, the reaction of *n*-butyl acrylate with vinyl acetate in the presence of catalytic amounts of $Pd(OAc)_2$ and $H_4PMo_{11}VO_{40}\cdot nH_2O$ under O_2 in acetic acid at 70 °C for 12 h afforded the corresponding cross-coupling product, *n*-butyl 5-(acetoxy)-2,4-pentadienoate, in 70% yield.

The cross-coupling reaction of organometallic reagents with electrophiles such as organic halides provides a straightforward method for carbon−carbon bond formation.[1] However, direct cross-coupling through the C−H bond activation of two different alkenes is very difficult to carry out because of the difficulty in activating the alkenyl C−H bond. The homodimerization of functional alkenes such as acrylates and acryronitrile leading to dicarboxylates and dinitriles, respectively, can be achieved by various transition metal compounds such as Co,[2] Ni,[3] Ru,[4] Rh,[5] and Pd.[6] However, the oxidative coupling reaction of alkenes such as acrylates to muconates is difficult to carry out by these catalysts. Dimethyl muconate is reported to be formed as a minor product in the dimerization of methyl acrylate by a Pd complex.[7] Oxidative coupling of vinyl acetate with $Pd(OAc)_2$ produced 1,4-diacetoxy-1,3-butadiene.[8] To our knowledge, there has been little study on the catalytic oxidative cross-coupling reaction between different functional alkenes. In the course of our study, we have investigated the direct Heck-type coupling reaction of benzene with acrylates by $Pd(OAc)_2$ combined with vanadomolybdophospholic acids under O_2.[9] Recently, our attention has been focused on the $Pd(OAc)_2$-catalyzed oxidative coupling reaction of acrylates with vinyl carboxylates under the influence of $Pd(OAc)_2/H_4PMo_{11}VO_{40}/O_2$ in acetic acid (eq 1).

The reaction of *n*-butyl acrylate (**1c**) with vinyl acetate (**2a**) was chosen as a model reaction and was carried out in

---

(1) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds; Wiley-VCH: New York, 1998.

(2) Kanai, H.; Okada, M. *Chem. Lett.* **1975**, 167. Kanai, H.; Ishii, K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1015.

(3) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185.

(4) McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080. McKinney, R. J. *Organometallics* **1986**, *5*, 1752. Bennet, M. A. *Organometallics* **1995**, *14*, 2565.

(5) Alderson, T.; Jenner, E. T.; Lindsey, R. V. J. *J. Am. Chem. Soc.* **1965**, *87*, 5638. Nikishin, G. I.; Kovalev, I. P.; Ignatenko, A. V. *Tetrahedron Lett.* **1991**, *132*, 1077. Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777. Brookhart, M.; Hauptman, E. *J. Am. Chem. Soc.* **1992**, *114*, 4437. Hauptman, E.; Etienne, S. S.; White, P. S.; Brookhart, M.; Garner, J. M.; Fagan, P. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 8038.

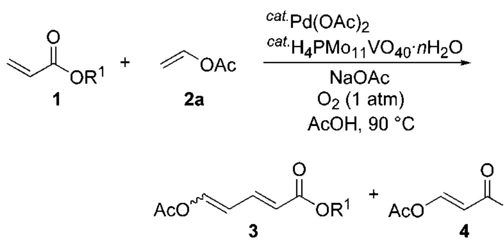
(6) Oehme, G.; Pracejus, H.; *Tetrahedron Lett.* **1979**, 3434. Nugent, W. A.; Hobbs, F. W. J. *J. Org. Chem.* **1983**, *48*, 5364. Tkatchenko, I.; Neibecker, D.; Grenouillet, P. *Organometallics* **1984**, *3*, 1130. Guibert, I.; Neibecker, D.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1989**, 1850.

(7) Oenme, G.; Pracejus, H. *J. Prakt. Chem.* **1980**, *322*, 798. Guibert, I.; Neibecker, D.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1989**, 1850.

(8) Kohll, C. F.; Van Helden, R. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1930 [CAN 66:104490].

(9) Yokota, T.; Tani, M.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2003,** *125*, 1476.

10.1021/ol047971u CCC: $27.50



(1)

the presence of $Pd(OAc)_2$, $H_4PMo_{11}VO_{40}$, and O_2 in acetic acid under various conditions (Table 1).

Table 1. Oxidative Cross-Coupling of *n*-Butyl Acrylate (**1c**) with Vinyl Acetate (**2a**) by a $Pd(OAc)_2$/HPMoV/O_2 System[a]

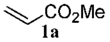
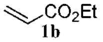
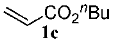
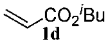
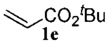
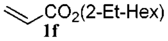
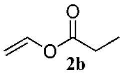
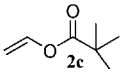
run	**2a** (mmol)	temp (°C)	time (h)	conversion[b] (%)	% yield[b] (*E*/*Z*)[c]
1	5	90	5	78	62 (60/40)
2	3	90	5	86	31 (55/45)
3	9	90	5	67	60 (58/42)
4	5	90	6	83	58 (59/41)
5	5	70	10	63	56 (66/34)
6	5	70	12	73	70 (65/35)
7	5	70	18	80	66 (62/38)
8[d]	5	70	12	54	36 (56/44)
9[e]	5	70	12	73	65 (60/40)
10[f]	5	70	12	12	6 (50/50)
11[g]	5	70	12	62	32 (63/37)

[a] **1c** (1 mmol) was reacted with **2a** in the presence of $Pd(OAc)_2$ (0.1 mmol), $H_4PMo_{11}VO_{40}$ (0.02 mmol), and NaOAc (0.1 mmol) under O_2 (1 atm). [b] Based on **1c** used. **4c** was formed in 4−6% yield in every entry. [c] *E*/*Z* ratio of coupling products. [d] In the absence of NaOAc. [e] Under air (1 atm). [f] Under N_2 (1 atm). [g] In the absence of $H_4PMo_{11}VO_{40}$.

The reaction of **1c** (1 mmol) with **2a** (5 mmol) under the influence of $Pd(OAc)_2$ (0.1 mmol), $H_4PMo_{11}VO_{40}$ (0.02 mmol), NaOAc (0.1 mmol), and O_2 (1 atm) in acetic acid at 90 °C for 5 h gave a mixture of *E*- and *Z*- cross-coupling products, *n*-butyl 5-(acetoxy)-2,4-pentadienoate (*E*- and *Z*-**3ca**) in 62% yield along with *n*-butyl 3-acetoxy acrylate (**4c**) (5%) and oligomers of **2a** (run 1). This is the first successful oxidative cross-coupling reaction of **1c** with **2a**. When the quantity of **2a** used was reduced from 5 to 3 mmol, the yield of **3ca** was lowered to 31% (run 2). The best yield of **3ca** (70%) was obtained by the reaction at 70 °C for 12 h (run 6). The reaction in the absence of NaOAc resulted in considerable decrease of **3ca** (run 8). It is well-known that NaOAc prevents the deposition of Pd(0) generated in the course of the reaction. The cross-coupling was also influenced by the concentration of O_2. The reaction proceeded slowly under air (1 atm) to form **3ca** (65%), but the reaction under N_2 produced **3ca** corresponding to a stoichiometric amount of $Pd(OAc)_2$ used (run 10). The reaction by $Pd(OAc)_2$ under O_2 in the absence of $H_4PMo_{11}VO_{40}$ resulted in **3ca** in low yield even for 12 h. These results show that O_2 and $H_4PMo_{11}VO_{40}$ are essential components that serve as oxidants of the reduced Pd(0) to Pd(II) during the reaction course.

On the basis of these results, several acrylates (**1a**−**f**) were reacted with **2a** under selected conditions (Table 2).

Table 2. Oxidative Cross-Coupling of Several Acrylates with Vinyl Carboxylates by a $Pd(OAc)_2$/HPMoV/O_2 System[a]

run	acrylate	vinyl carboxylates	conv.[b] / %	product	yield[b] (*E*/*Z*)[c] / %
1	 **1a**	**2a**	80	**3aa**	45 (56/44)
2	 **1b**	**2a**	79	**3ba**	50 (56/44)
3	 **1c**	**2a**	78	**3ca**	62 (60/40)
4	 **1d**	**2a**	83	**3da**	67 (60/40)
5	 **1e**	**2a**	90	Complex mixture	
6	 **1f**	**2a**	84	**3fa**	76 (58/42)
7	**1f**	 **2b**	65	**3fa**	53 (66/34)
8	**1f**	 **2c**	65	**3fa**	51 (65/35)

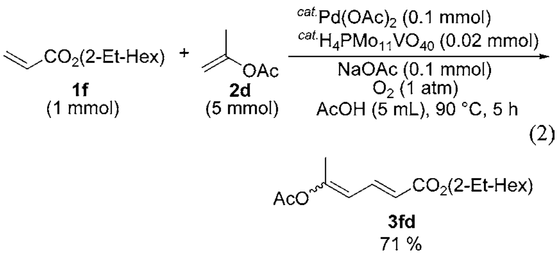
[a] Acrylate (1 mmol) was reacted with vinyl carboxylate (5 mmol) in the presence of $Pd(OAc)_2$ (0.1 mmol), $H_4PMo_{11}VO_{40}$ (0.02 mmol), and NaOAc (0.1 mmol) in acetic acid (5 mL) under O_2 (1 atm) at 90 °C for 5 h. [b] Based on acrylate used. [c] *E*/*Z* ratio of coupling products.

It is interesting that the selectivity of the cross-coupling reaction was considerably affected by the alkoxy moiety in acrylates (**1a**−**f**). Yields of coupling products, **3aa**−**fa**, increased with increasing the carbon length of the alkoxy moiety in acrylates except for *t*-butyl acrylate (**1e**), which led to a complex mixture of products (runs 1−6). The best result was obtained by the reaction of 2-ethylhexyl acrylate (**1f**) with **2a** to give the corresponding coupling product, 2-ethylhexyl 5-(acetoxy)-2,4-pentadienoate (**3fa**) (*E*:*Z* = 58:42), in 76% yield (run 6).

It is interesting to note that the reaction of **1f** with vinyl propionate (**2b**) or vinyl pivalate (**2c**) afforded the same coupling product **3fa** in fair yields (runs 7 and 8). Since the alkoxy moiety of **2b** and **2c** easily underwent acetolysis with acetic acid used as the solvent, the same coupling product **3fa** is formed in both reactions. The formation of acetolysis product **3fa** from **1f** and **2b** or **2c** is rationally explained by considering transvinylation between acetic acid with the vinyl carboxylate under the influence of Pd catalyst.[10]

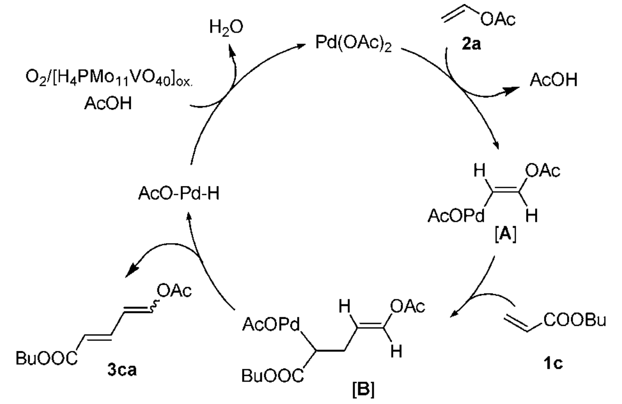
We next examined the reaction of **1f** with isopropyl acetate (**2d**) under these conditions. The coupling proceeded in the same manner as **2a** to form a coupling product **3fd** in 71% yield (eq 2).

Scheme 1 shows a plausible reaction path for the present



(2)

Scheme 1. Plausible Reaction Path for Cross-Coupling



oxidative cross-coupling of *n*-butyl acrylate (**1c**) with vinyl acetate (**2a**).

The reaction may be initiated by the formation of a vinyl palladium species [**A**] from vinyl acetate **2a** and $Pd(OAc)_2$. In fact, a dimerization product such as 1,4-diacetoxy-1,3-butadiene was detected in the reaction of **2a** alone by the present reaction system, although conversion of **2a** and yield of the product were very low (ca. 5%). Additionally, no formation of the dimerization product was observed in the reaction of **1c** alone. These results suggest that **2a**, not **1c**, reacts with Pd(II) species in the first step. Coordination of acrylate to [**A**] followed by insertion into the Pd−vinyl bond leads to a σ−Pd complex [**B**], and after β-hydride elimination, coupling product **3ca** is formed. The resulting Pd hydride complex is oxidized by $H_4PMo_{11}VO_{40}$ to regenerate Pd(II), and the reduced $H_4PMo_{11}VO_{40}$ is oxidized with O_2 to the original $H_4PMo_{11}VO_{40}$.

In conclusion, the first oxidative cross-coupling reaction between acrylates and vinyl carboxylates was achieved by the use of a $Pd(OAc)_2/H_4PMo_{11}V_1/O_2$ system in acetic acid.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (S) from the Ministry of Education, Culture, Sports and Technology (MEXT), Japan.

Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL047971U

---

(10) Henry, P. M. *Acc. Chem. Res.* **1973**, *6*, 16.