



Aryldiazonium silica sulfates as efficient reagents for Heck-type arylation reactions under mild conditions

Amin Zarei^{a,*}, Leila Khazdooz^b, Azadeh Pirisedigh^c, Abdol R. Hajipour^d, Hojjat Seyedjamali^c, Hamidreza Aghaei^e

^a Department of Science, Fasa Branch, Islamic Azad University, Post Box No 364, Fasa 7461713591, Fars, Iran

^b Department of Science, Khorasgan Branch, Islamic Azad University, Isfahan 81595-158, Iran

^c Department of Chemistry, Kazerun Branch, Islamic Azad University, Kazerun, Iran

^d Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran

^e Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza 311-86145, Isfahan, Iran

ARTICLE INFO

Article history:

Received 9 April 2011

Revised 14 June 2011

Accepted 24 June 2011

Available online 1 July 2011

Keywords:

Aryldiazonium silica sulfates

Heck-type reaction

Pd(OAc)₂

Mild conditions

ABSTRACT

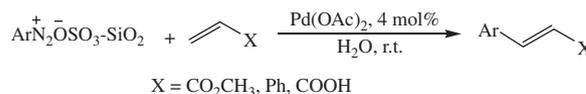
An efficient and straightforward procedure for Heck-type arylation reactions was studied using aryldiazonium silica sulfates and olefins in the presence of a catalytic amount of Pd(OAc)₂. These reactions were carried out in water at room temperature without using a base or additional ligands. The use of a non-toxic solvent, a simple and clean work-up, short reaction times, and good yields are advantages of this method.

© 2011 Elsevier Ltd. All rights reserved.

Palladium-catalyzed Heck coupling reactions using aryl halides or aryl triflates and olefins are important and valuable reactions for carbon–carbon bond formation in modern organic synthesis.^{1,2} Although some of these methods have convenient protocols and afford good to high yields of products, the majority suffer from at least one of the following disadvantages: high temperature with an additional base, the use of an appropriate ligand to accelerate the reaction, long reaction times, and the use of organic solvents. Moreover, the use of high-cost aryl iodides or aryl triflates is a drawback of these reactions. Aryldiazonium salts have several advantages over aryl halides including the availability of aryl amines as the arenediazonium salt precursors, and superior reactivity as a better leaving group than halides or aryl triflates. In comparison with conventional Heck couplings, these reactions with aryldiazonium salts are carried out under mild conditions, with shorter times and higher yields of products.^{3–17} It is notable that some of these reactions are carried out without using a base or additional ligands. In continuation of our studies on the stabilization of diazonium salts on silica sulfuric acid and their application in organic synthesis,¹⁸ we report herein an efficient and convenient procedure for Heck-type coupling reactions employing aryldiazonium silica sulfates with methyl acrylate, styrene, and acrylic acid

in the presence of a catalytic amount of Pd(OAc)₂ (Scheme 1). Unlike traditional methods, these reactions were carried out in water at room temperature without using a base or additional ligands.

Aryldiazonium salts have been prepared and studied as useful intermediates in classical and modern organic synthesis due to their ready availability and high reactivity.^{10,19} These salts, however, have a serious drawback in their intrinsic instability. They are usually synthesized at around 10 °C and, to avoid their decomposition, they are handled below 0 °C. Moreover, because of this instability, subsequent reactions with diazonium salts must be carried out under the same conditions. Thus, diazonium salts with higher stability and versatility that can be easily made and stored under solid state conditions with explosion-proof properties are desired and necessary.^{11,17,20} For example, many diazonium tetrafluoroborates are relatively stable and can be stored over extended periods of time without decomposition.¹⁷ Recently, we reported an efficient, fast, and convenient method for the preparation of aryldiazonium salts supported on the surface of silica sulfuric acid (aryldiazonium silica sulfates).¹⁸ We found that these new aryldiazonium salts, ArN₂⁺OSO₃⁻–SiO₂, could be kept at room



Scheme 1.

* Corresponding author. Tel.: +98 917 1302528; fax: +98 311 2289113.

E-mail address: aj_zarei@yahoo.com (A. Zarei).

Table 1
Pd(OAc)₂-catalyzed vinylation of aryldiazonium silica sulfates with olefins at room temperature ^a

Entry	Olefin	Diazonium salt	Product	Time (min)	Yield (%)
1	Methyl acrylate	PhN ₂ ⁺ OSO ₃ –SiO ₂		25	86
2	Methyl acrylate	4-MeC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	85
3	Methyl acrylate	2-MeC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		35	81
4	Methyl acrylate	4-MeOC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		35	80
5	Methyl acrylate	4-BrC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	87
6	Methyl acrylate	4-ClC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	85
7	Methyl acrylate	3-ClC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	83
8	Methyl acrylate	2-ClC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		35	82
9	Methyl acrylate	4-NCC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	84
11	Methyl acrylate	4-MeCOC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	83
12	Methyl acrylate	4-PhC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		35	81
13	Methyl acrylate	4-O ₂ NC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	87
14	Methyl acrylate	3-O ₂ NC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	84
15	Methyl acrylate	2-O ₂ NC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		30	83
16	Methyl acrylate	2-HOCOC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		35	81
17	Styrene	PhN ₂ ⁺ OSO ₃ –SiO ₂		45	85
18	Styrene	4-MeC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		80	88
19	Styrene	2-MeC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		90	80
20	Styrene	4-BrC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		100	87
21	Styrene	3-ClC ₆ H ₄ N ₂ ⁺ OSO ₃ –SiO ₂		90	82

(continued on next page)

temperature under anhydrous conditions. Moreover, these new aryldiazonium salts are explosion-proof and can be used under different conditions¹⁸ because of their stability. In the present work, different aryldiazonium silica sulfates, as electrophiles, were exposed to Heck-type coupling reactions using methyl acrylate, styrene, and acrylic acid as the olefins, under mild conditions. The vinylation of these diazonium salts was catalyzed using Pd(OAc)₂ at room temperature without using a base or additional ligands (Table 1). Methyl acrylate, and acrylic acid reacted with the aryldiazonium silica sulfates in water and the products were obtained in good yields and short reaction times. We studied the reaction of styrene with phenyldiazonium silica sulfate under these conditions. As styrene is not miscible with water, the product was obtained in 40% yield after a prolonged reaction time (5 h). By changing the solvent to ethanol, the corresponding stilbenes were obtained in good yields and short reaction times (Table 1, entries 17–26). Aryldiazonium silica sulfates with electron-withdrawing groups or electron-donating groups also reacted effectively. The steric effects of *ortho* substituents and the electronic effects of functional groups on the aryl rings of the aryldiazonium silica sulfates had relatively little influence on the yields and reaction times. The products were *trans*-isomers. The corresponding phenol derivatives were formed in trace amounts as by-products. We also studied the effect of temperature on these reactions and it was found that on increasing the temperature phenol formation increased. The optimum temperature for these reactions was room temperature. It was notable that a bromide or chloride on the aromatic ring of the aryldiazonium silica sulfates remained intact during the course of the reaction. Another advantage of this method was the easy work-up since the crude products were extracted with ethyl acetate and, if necessary, were purified by short column chromatography.^{21,22}

To show the merit of the present work in comparison with that reported recently, we compared our results with the results obtained from Heck-type reactions using arenediazonium tetrafluoroborates,^{5,7,8,13,16} arenediazonium *o*-benzenedisulfonimides,⁹ and arenediazonium tosylates.¹¹ The results show that the reaction yields were comparable with those reported, and in many cases, the results using the aryldiazonium silica sulfates were superior (Table 2). By supporting the aryldiazonium salt on silica sulfuric acid, the surface area of the reaction increases lowering the reaction time.^{18,23}

To summarize, we have reported an efficient, rapid, and experimentally simple method for Heck-type reactions of aryldiazonium silica sulfates with methyl acrylate, styrene, and acrylic acid to form the corresponding cinnamates, stilbenes and cinnamic acids with *trans*-configuration.

Acknowledgments

We gratefully acknowledge the funding support received for this project from the Islamic Azad University, Fasa Branch.

References and notes

- (a) Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320; (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009; (c) Whitcombe, N. J.; Hii, K. K.; Gibson, S. E. *Tetrahedron* **2001**, *57*, 7449.
- (a) Iranpoor, N.; Firouzabadi, H.; Tarassoli, A.; Fereidoonzhad, M. *Tetrahedron* **2010**, *66*, 2415; (b) Franchi, L.; Rinaldi, M.; Vignaroli, G.; Innitzer, A.; Radi, M.; Botta, M. *Synthesis* **2010**, 3927; (c) Wu, S.; Ma, H.; Jia, X.; Zhong, Y.; Lei, Z.

- Tetrahedron* **2011**, *67*, 250; (d) Mao, H.; Wan, J. P.; Pan, Y.; Sun, C. *Tetrahedron Lett.* **2010**, *51*, 1844; (e) Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Sreedhar, B. *J. Am. Chem. Soc.* **2002**, *124*, 14127; (f) Jaegli, S.; Vors, J. P.; Neuville, L.; Zhu, J. *Tetrahedron* **2010**, *66*, 8911; (g) Pan, D.; Jiao, N. *Synlett* **2010**, 1577; (h) Bararjanian, M.; Balalaie, S.; Rominger, F.; Movassagh, B.; Bijanzadeh, H. R. *J. Org. Chem.* **2010**, *75*, 2806; (i) Majumdar, K. C.; Ray, K.; Ganai, S. *Tetrahedron Lett.* **2010**, *51*, 1736; (j) Overman, L. E.; Rosen, M. D. *Tetrahedron* **2010**, *66*, 6514; (k) Nguyen, U. B.; Ung, A. T.; Pyne, S. G. *Tetrahedron* **2009**, *65*, 318.
- Sengupta, S.; Sadhukhan, S. K. *Tetrahedron Lett.* **1998**, *39*, 715.
- Carpes, M. J. S.; Correia, C. R. D. *Tetrahedron Lett.* **2002**, *43*, 741.
- Andrus, M. B.; Song, C.; Zhang, J. *Org. Lett.* **2002**, *4*, 2079.
- Severino, E. A.; Costenaro, E. R.; Garcia, A. L. L.; Correia, C. R. D. *Org. Lett.* **2003**, *5*, 305.
- Masllourens, J.; Moreno-Manas, M.; Pla-Quintana, A.; Roglans, A. *Org. Lett.* **2003**, *5*, 1559.
- Kabalka, G. W.; Dong, G.; Venkataiah, B. *Tetrahedron Lett.* **2004**, *45*, 2775.
- Artuso, E.; Barbero, M.; Degani, I.; Dughera, S.; Fochi, R. *Tetrahedron* **2006**, *62*, 3146.
- Roglans, A.; Pla-Quintana, A.; Moreno-Manas, M. *Chem. Rev.* **2006**, *106*, 4622.
- Filimonov, V. D.; Trusova, M.; Postnikov, P.; Krasnokutskaya, E. A.; Lee, Y. M.; Hwang, H. Y.; Kim, H.; Chi, K. W. *Org. Lett.* **2008**, *10*, 3961.
- Moro, A. V.; Cardoso, F. S. P.; Correia, C. R. D. *Tetrahedron Lett.* **2008**, *49*, 5668.
- Ahmed-Omer, B.; Barrow, D. A.; Wirth, T. *Tetrahedron Lett.* **2009**, *50*, 3352.
- Laudien, J.; Fouquet, E.; Zakri, C.; Felpin, F. X. *Synlett* **2010**, 1539.
- Siqueira, F. A.; Taylor, J. G.; Correia, C. R. D. *Tetrahedron Lett.* **2010**, *51*, 2102.
- Kalkhambkar, R. G.; Laali, K. K. *Tetrahedron Lett.* **2011**, *52*, 1733.
- Taylor, J. G.; Moro, A. V.; Correia, C. R. D. *Eur. J. Org. Chem.* **2011**, 1403.
- (a) Zarei, A.; Hajipour, A. R.; Khazdooz, L.; Mirjalili, B. F.; Najafichermahini, A. *Dyes Pigments* **2009**, *81*, 240; (b) Zarei, A.; Hajipour, A. R.; Khazdooz, L. *Synthesis* **2009**, 941; (c) Zarei, A.; Hajipour, A. R.; Khazdooz, L.; Aghaei, H. *Tetrahedron Lett.* **2009**, *50*, 4443; (d) Zarei, A.; Hajipour, A. R.; Khazdooz, L.; Aghaei, H. *Synlett* **2010**, 1201; (e) Zarei, A.; Khazdooz, L.; Hajipour, A. R.; Aghaei, H. *Dyes Pigments* **2011**, *91*, 44.
- (a) Zollinger, H. *Diazo Chemistry I*; VCH: Weinheim, 1994; (b) Zollinger, H. *The Chemistry of Amino, Nitroso, Nitro and Related Groups*; Wiley and Sons: New York, 1996; (c) Olah, G. A.; Laali, K. K.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, 1998; (d) Tour, J. M. *J. Org. Chem.* **2007**, *72*, 7477; (e) Barral, K.; Moorhouse, A. D.; Moses, J. E. *Org. Lett.* **2007**, *9*, 1809; (f) Hubbard, A.; Okazaki, T.; Laali, K. K. *J. Org. Chem.* **2008**, *73*, 316; (g) Fabrizi, G.; Goggiamani, A.; Sferrazza, A.; Cacchi, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4067.
- (a) Barbero, M.; Crisma, M.; Degani, I.; Fochi, R.; Perracino, P. *Synthesis* **1998**, 1171; (b) Barbero, M.; Degani, I.; Dughera, S.; Fochi, R. *Synthesis* **2004**, 2386; (c) Krasnokutskaya, E. A.; Semenischeva, N. I.; Filimonov, V. D.; Knochel, P. *Synthesis* **2007**, 81; (d) Gorusko, D. A.; Filimonov, V. D.; Krasnokutskaya, E. A.; Semenischeva, N. I.; Go, B. S.; Hwang, H. Y.; Cha, E. H.; Chi, K. W. *Tetrahedron Lett.* **2008**, *48*, 1080; (e) Lee, Y. M.; Moon, M. U.; Vajpayee, V.; Filimonov, V. D.; Chi, K. W. *Tetrahedron* **2010**, *66*, 7418.
- General procedure for Heck-type reactions of aryldiazonium silica sulfate with methyl acrylate or acrylic acid*: To a solution of Pd(OAc)₂ (0.009 g, 4 mol %) in H₂O (10 mL), methyl acrylate or acrylic acid (2 mmol) was added and the mixture was stirred for few minutes. Next, freshly prepared aryldiazonium silica sulfate (1 mmol)¹⁷ was added gradually and the mixture was stirred vigorously at room temperature for the time specified in Table 1. The reaction progress was monitored by TLC (hexane/EtOAc, 75:25). After completion of the reaction (absence of azo coupling with 2-naphthol), the mixture was diluted with EtOAc (15 mL) and filtered after vigorous stirring. The residue was extracted with EtOAc (3 × 10 mL) and the combined organic layer washed with H₂O and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to afford the corresponding product and if necessary, the crude product was purified by short column chromatography.
- General procedure for Heck-type reactions of aryldiazonium silica sulfate with styrene*: To a solution of Pd(OAc)₂ (0.009 g, 4 mol %) in 95% aqueous EtOH (10 mL), styrene (2 mmol) was added and the mixture was stirred for a few minutes. Next, freshly prepared aryldiazonium silica sulfate (1 mmol)¹⁷ was added gradually and the mixture was stirred vigorously at room temperature for the time specified in Table 1, entries 17–26). The reaction progress was monitored by TLC (hexane/EtOAc, 75:25). After completion of the reaction (absence of azo coupling with 2-naphthol), the mixture was diluted with EtOAc (15 mL) and filtered. The residue was extracted with EtOAc (3 × 10 mL) and the combined organic layer washed with H₂O and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to afford the corresponding product and if necessary, the crude product was purified by short column chromatography.
- Clark, J. H. *Catalysis of Organic Reactions by Supported Inorganic Reagents*; VCH: Weinheim, 1994.