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Suzuki–Miyaura cross-coupling of aryldiazonium silica sulfates under mild and heterogeneous conditions

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The palladium-catalyzed Suzuki-Miyaura cross-coupling reaction is an attractive method for C-C bond formation, especially for the synthesis of biaryl derivatives, which are used as the building blocks for a wide range of natural products, pharmaceuticals, and advanced materials.¹ Coupling of organoboron compounds with an aryl halide in the presence of a base provides a simple and straightforward method to synthesize various biaryl compounds.² Recently, many modifications have been reported including the use of different catalysts, bases, ligands, solvents, and reaction conditions.³⁻¹⁴ Although some of these methods have convenient protocols with good to high yields, the majority suffers from at least one of the following disadvantages: high temperature, 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 some 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 triflates. However, only a few publications report on Suzuki-Miyaura cross-coupling reactions using arenediazonium salts as the electrophilic precursors.¹⁵ In comparison with conventional Suzuki-Miyaura reactions, these reactions are carried out under mild reaction conditions and in

ABSTRACT

An efficient and straightforward procedure for the Suzuki–Miyaura cross-coupling reaction was studied by using aryldiazonium silica sulfates and sodium tetraphenylborate in the presence of a catalytic amount of Pd(OAc)₂. These reactions were carried out in water at room temperature without using additional ligands.

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short reaction times. In view of environmental and economic reasons, the development of catalytic systems without employing an additional ligand and using water instead of organic solvents are attractive fields in this area of research. In continuation of our studies on the stabilization of diazonium salts on silica sulfuric acid and their application in organic synthesis,¹⁶ we report herein an efficient and convenient procedure for Suzuki–Miyaura cross-coupling reactions employing aryldiazonium silica sulfates with sodium tetraphenyl borate 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 an additional ligand.

Aryldiazonium salts are useful intermediates in organic synthesis due to their ready availability and high reactivity.¹⁷ These compounds, however, have a serious drawback in their intrinsic instability. Therefore, these salts 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

$$\operatorname{ArN}_{2}^{+} \overline{OSO_{3}}\text{-}\operatorname{SiO}_{2} + \operatorname{NaBPh}_{4} \xrightarrow{Pd(OAc)_{2}, 1.5 \text{ mol}\%} \operatorname{Ar} \xrightarrow{} \operatorname{Ar} \xrightarrow{}$$

Scheme 1. Suzuki-Miyaura cross-coupling of aryldiazonium silica sulfates.





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Table 1

Suzuki-Miyaura cross-coupling of aryldiazonium silica sulfates with so	odium tetraphenylborate in water at room	temperature ^a
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Entry	Diazonium salt	Product	Time (min)	Yield (%)
1	PhN ₂ ⁺⁻ OSO ₃ -SiO ₂		20	88
2	$4\text{-MePhN}_2{}^{+-}\text{OSO}_3\text{SiO}_2$	Me	45	72
3	$4\text{-MeOPhN}_2^{+-}\text{OSO}_3\text{SiO}_2$	MeO	120	10
4	2-MeOPhN2 ⁺⁻ OSO3-SiO2	OMe	120	Trace
5	4-MeOPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	MeO	10	60 ^b
6	4-MeOPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	MeO-	1	70 ^c
7	2-MeOPhN2 ⁺⁻ OSO3-SiO2	OMe	1	65 ^c
8	4-BrPhN2 ⁺⁻ OSO3-SiO2	Br	15	74
9	4-CIPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	Cl-	15	78
10	3-ClPhN ₂ ⁺⁻ OSO ₃ -SiO ₂		15	80
11	$2\text{-ClPhN}_2^{+-}\text{OSO}_3\text{SiO}_2$		15	75
12	$4\text{-NCPhN}_2{^{+-}}\text{OSO}_3\text{SiO}_2$	NC	10	79
13	4-MeCOPhN ₂ ⁺⁻ OSO ₃ -SiO ₂	Me-Ë	15	82
14	$4\text{-PhCOPhN}_2{}^{+-}\text{OSO}_3\text{SiO}_2$	O C C Ph	20	72
15	2-PhCOPhN2 ⁺⁻ OSO3-SiO2	Ph O C C C	25	68
16	1-NaphthN2 ⁺⁻ OSO3-SiO2		20	83
17	4-PhPhN ₂ ⁺⁻ OSO ₃ -SiO ₂		20	76
18	$4-NO_2PhN_2^{+-}OSO_3-SiO_2$	O ₂ N	10	80
19	3-NO ₂ PhN ₂ ⁺⁻ OSO ₃ -SiO ₂	O ₂ N	10	81
20	2-NO ₂ PhN ₂ ⁺⁻ OSO ₃ -SiO ₂		10	77
21	$2\text{-HO}_2\text{CPhN}_2^{+-}\text{OSO}_3\text{SiO}_2$		20	75
22	$4\text{-HO}_2\text{CPhN}_2^{+-}\text{OSO}_3\text{SiO}_2$	HO ₂ C-	20	78

^a The yield refers to isolated pure product characterized from spectral data by comparison with authentic samples.

^b The reaction was carried out at 60 °C.

^c The reaction was irradiated at 60 °C using a microwave (Milestone, Microsynth model, 1024) at a power level of 400 W.

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 desirable.^{18–20} For example, many diazonium tetrafluoroborates are relatively stable and can be stored over extended periods of time without decomposition. 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).¹⁶ We found that these new aryldiazonium salts, $ArN_2^{+-}OSO_3 - SiO_2$, could be stored at room temperature under anhydrous conditions. These aryldiazonium salts are stable and can be used under different reaction conditions.¹⁶ In the present work, various aryldiazonium silica sulfates, as electrophiles, were employed in Suzuki-Miyaura cross-coupling reactions using sodium tetraphenylborate and Na₂CO₃ under mild and heterogeneous conditions.²¹ These reactions were catalyzed using Pd(OAc)₂ at room temperature without using additional ligands (Table 1). The corresponding phenol derivatives were formed in trace amounts as by-products. We also studied the effect of temperature on these reactions and found that by increasing the reaction temperature, phenol formation increased. Aryldiazonium silica sulfates with electron-withdrawing groups or electron-donating groups also reacted effectively. The steric effects of ortho substituents had relatively little influence on the yields and reaction times. We also observed electronic effects due to functional groups on the aryl rings of the aryldiazonium silica sulfates. In comparison with electron-withdrawing groups, aryldiazonium silica sulfates with electron-donating groups decreased the rates of the reactions at room temperature (Table 1, entries 2-4). Thus, to accelerate the reaction rate, these reactions were carried out under conventional heating and under microwave irradiation at 60 °C. The corresponding products were obtained in good yields (Table 1, entries 5-7). It was notable that a halogen group (Br or Cl) on the aromatic ring of the aryldiazonium silica sulfate remained intact during the course of the reaction

Traditionally, Suzuki–Miyaura coupling reactions have been carried out using homogeneous palladium catalysts in the presence of either a ligand or an additive to stabilize the Pd species during the reaction, otherwise Pd⁰ tends to aggregate and precipitate before completion of the reaction. Furthermore, the cross-coupling products are frequently contaminated by the remaining palladium black and ligands, which can be difficult to separate from the final products. Thus, using heterogeneous Pd catalysts could represent an attractive method to overcome this problem because the heterogeneous catalysts can be easily separated from the reaction mixture.^{6,8} In the present procedure, by using aryldiazonium silica sulfate as a heterogeneous system with high surface area, contamination of the desired product with residual palladium decreased due to reduction of the metal leaching from the surface.

To summarize, we have reported an efficient, rapid, and experimentally simple method for the Suzuki–Miyaura cross-coupling of aryldiazonium silica sulfates with sodium tetraphenylborate to form the corresponding biaryl derivatives in good yields.

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References and notes

- (a) Phakhodee, W.; Toyoda, M.; Chou, C. M.; Khunnawutmanotham, N.; Isobe, M. Tetrahedron 2011, 67, 1150; (b) Afonso, A.; Feliu, L.; Planas, M. Tetrahedron 2011, 67, 2238; (c) Yin, L.; Liebscher, J. Chem. Rev. 2007, 107, 133; (d) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. J. Am. Chem. Soc. 2007, 129, 7236; (e) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. Adv. Synth. Catal. 2006, 348, 609; (f) De Meijere, A.; Diederich, F. Metal-Catalyzed Cross-Coupling Reactions; Wiley: Weinheim, 2004; (g) Hargreaves, S. L.; Pilkington, B. L.; Russell, S. E.; Worthington, P. A. Tetrahedron Lett. 2000, 41, 1653; (h) Nicolaou, K. C.; Ramanjulu, J. M.; Natarajan, S.; Bräase, S.; Rübsam, F. Chem. Commun. 1997, 1899.
- 2. Miyaura, N.; Suzuki, A. Chem. Rev. 1995, 95, 2457.
- 3. Molnar, A. Chem. Rev. 2011, 111, 2251.
- Jana, R.; Pathak, T. P.; Sigman, M. S. Chem. Rev. 2011, 111, 1417.
 Rossi, R.: Bellina, F.: Lessi, M. Tetrahedron 2011, 67, 6969.
- 5. Rossi, R.; Bellina, F.; Lessi, M. *Tetrahedron* **2011** 6. Yang J.: Li P.: Wang J. Synthesis **2011** 1295
- 6. Yang, J.; Li, P.; Wang, L. Synthesis **2011**, 1295.
- Zhou, W. J.; Wang, K. H.; Wang, J. X.; Gao, Z. R. Tetrahedron 2010, 66, 7633.
 Chen, W.; Li, P.; Wang, L. Tetrahedron 2011, 67, 318.
- 9. Du, Z.; Zhou, W.; Wang, F.; Wang, J. X. *Tetrahedron* **2011**, 67, 4914.
- 10. Zhang, P. P.; Zhang, X. X.; Sun, H. X.; Liu, R. H.; Wang, B.; Lin, Y. H. Tetrahedron Lett 2009 50 4455
- 11. Alonso, D. A.; Civicos, J. F.; Najera, C. Synlett 2009, 3011.
- 12. Fujihara, T.; Yoshida, S.; Ohta, H.; Tsuji, Y. Angew. Chem., Int. Ed. 2008, 47, 8310.
- 13. Alonso, F.; Beletskaya, I. P.; Yus, M. Tetrahedron 2008, 64, 3047.
- 14. Lu, G.; Franzen, R.; Zhang, Q.; Xu, Y. Tetrahedron Lett. 2005, 46, 4255.
- (a) Taylor, R. H.; Felpin, F. X. Org. Lett. 2007, 9, 2911; (b) Qin, Y.; Wei, W.; Luo, M. Synlett 2007, 2410; (c) Roglans, A.; Pla-Quintana, A.; Moreno-Manas, M. Chem. Rev. 2006, 106, 4622; (d) Andrus, M. B.; Song, C. Org. Lett. 2001, 3, 3761; (e) Sengupta, S.; Sadhukhan, S. K. Tetrahedron Lett. 1998, 39, 715; (f) Sengupta, S.; Bhattacharyya, S. J. Org. Chem. 1997, 62, 3405.
- (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; (f) Zarei, A.; Khazdooz, L.; Pirisedigh, A.; Hajipour, A. R.; Seyedjamali, H.; Aghaei, H. Tetrahedron Lett. 2011, 52, 4554.
- (a) Zollinger, H. Diazo Chemistry I; VCH: Weinheim, 1994; (b) Zollinger, H. The Chemistry of Amino, Nitroso; Nitro and Related Groups; John 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; (h) Felpin, F. X.; Nassar-Hardy, L.; Callonnec, F. L.; Fouquet, E. Tetrahedron 2011, 67, 2815.
- 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.
- 19. Taylor, J. G.; Moro, A. V.; Correia, C. R. D. Eur. J. Org. Chem. 2011, 1403.
- (a) Barbero, M.; Degani, I.; Dughera, S.; Fochi, R. Synthesis 2004, 2386; (b) Krasnokutskaya, E. A.; Semenischeva, N. I.; Filimonov, V. D.; Knochel, P. Synthesis 2007, 81; (c) Gorlushko, 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; (d) Lee, Y. M.; Moon, M. U.; Vajpayee, V.; Filimonov, V. D.; Chi, K. W. Tetrahedron 2010, 66, 7418.
- 21. General procedure for Suzuki-Miyaura cross-coupling of aryldiazonium silica sulfates NaBPh₄: To a solution of Pd(OAc)₂ (0.003 g, 1.5 mol %) and Na₂CO₃ (0.11 g, 1 mmol) in H₂O (10 mL), NaBPh₄ (0.11 g, 0.3 mmol) and freshly prepared aryldiazonium silica sulfate (0.5 mmol)¹⁶ were added. The mixture was stirred 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 (2 × 10 mL) and the combined organic layer was washed with H₂O (2 × 10 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was purified by short column chromatography.