



Pd-catalyzed Suzuki–Miyaura cross-coupling of $[\text{Ph}_2\text{SR}][\text{OTf}]$ with arylboronic acids



Xiao-Yan Wang, Hai-Xia Song, Shi-Meng Wang, Jing Yang, Hua-Li Qin, Xin Jiang, Cheng-Pan Zhang*

School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, 205 Luoshi Road, Wuhan, 430070, China

ARTICLE INFO

Article history:

Received 19 August 2016

Received in revised form 6 October 2016

Accepted 9 October 2016

Available online 11 October 2016

Keywords:

Palladium

Fluorine

Sulfonium salts

Arylboronic acids

ABSTRACT

The Pd-catalyzed Suzuki–Miyaura cross-coupling of alkyl- and fluoroalkyl(diphenyl)sulfonium triflates with arylboronic acids was compared. The fluorine substitution on the alkyl groups of $[\text{Ph}_2\text{SR}][\text{OTf}]$ had a big influence on the reaction. Perfluoroalkyl(diphenyl)sulfonium triflates (**2b–d**) were unsuccessful participants in the Pd-catalyzed phenylation of arylboronic acid under the standard conditions because of the strong electronegativity of the long-chain perfluoroalkyl groups, which underwent S–R_m bond cleavage instead. Polyfluoroalkyl(diphenyl)sulfonium triflates (**2f–h**) reacted with arylboronic acid to afford the phenylation product in very low yields due to the tendency of deprotonation and β-F elimination of the sulfonium salts. Eventually, (2,2,2-trifluoroethyl)diphenylsulfonium triflate (**2e**), methyl- or ethyl(diphenyl)sulfonium triflate (**2i** or **2j**), and triphenylsulfonium triflate (**2m**) were found to be more effective reagents than other tested phenylsulfonium salts for Pd-catalyzed phenylation, which provided much higher yields of the desired products under mild conditions.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Arylsulfonium salts have gained great interest in areas of chemistry and materials science in the past several decades.¹ They can be readily reduced by pulse radiolytic, chemical, photochemical, and electrochemical methods via single electron transfer processes.² This intriguing property has led to triarylsulfonium salts as important photoinitiators in cationic polymerization reactions and as excellent photoacid generators capable of releasing protons under irradiation, which have been widely used in the fields of coatings, adhesives, photoresists, microfabrication, and patterning.³ The aryl radicals derived from triarylsulfonium salts under photocatalytic conditions have accomplished the carbon–carbon bond formation with allyl sulfones and activated olefins.⁴ The conjugate addition of nucleophiles to vinyl(diphenyl)sulfonium salts in situ forms sulfur ylides, which have been successfully utilized in a variety of cyclization reactions.^{5,6}

It has been well known that the introduction of fluorine atoms into organic compounds can dramatically change their physical, chemical, and biological properties.⁷ The incorporation of perfluoroalkyl groups into diphenylsulfoniums at the sulfur center has

yielded (perfluoroalkyl)diphenylsulfonium salts, which are effective electrophilic perfluoroalkylation reagents (e.g., Yagupolskii–Umamoto reagents) to perfluoroalkylate various nucleophiles under mild reaction conditions, showing much different reactivities from the non-fluorinated (alkyl)diphenylsulfonium analogs.⁸ (Trifluoromethyl)diphenylsulfoniums, the fluorinated version of (methyl)diphenylsulfoniums, are also effective CF₃ transfer sources in the reductive trifluoromethylation reactions towards a wide range of substrates, initiated by copper, photoredox catalysts, and other reductants.⁹ Moreover, (2,2,2-trifluoroethyl)diphenylsulfonium triflate, a partially fluorinated version of (ethyl)diphenylsulfonium triflate, is an efficient ylide reagent and trifluoromethylcarbene source to successfully afford a large number of trifluoromethyl cyclopropanes and their derivatives.¹⁰

Recently, we found that (trifluoromethyl)diarylsulfonium triflates could be used as cross-coupling partners in Pd-catalyzed Suzuki–Miyaura reaction with arylboronic acids.¹¹ The use of 1-aryl(tetrahydro)thiophenium salts as cross-coupling agents in the similar reaction was also reported.¹² Since the fluorine substitution often significantly alters the properties of molecules, we speculated that phenylsulfonium salts bearing fluoroalkyl groups might have distinctive reaction profiles compared to the non-fluorinated analogs in the Pd-catalyzed Suzuki–Miyaura cross-couplings. To understand the ‘fluorine effects’ and to determine the efficient cross-coupling partners in this type of transformation, we further studied

* Corresponding author. E-mail addresses: cpzhang@whut.edu.cn, zhangchengpan1982@hotmail.com (C.-P. Zhang).

the reactions of arylboronic acids with a family of phenylsulfonium salts bearing either fluoroalkyl or alkyl moieties on the sulfur atoms.

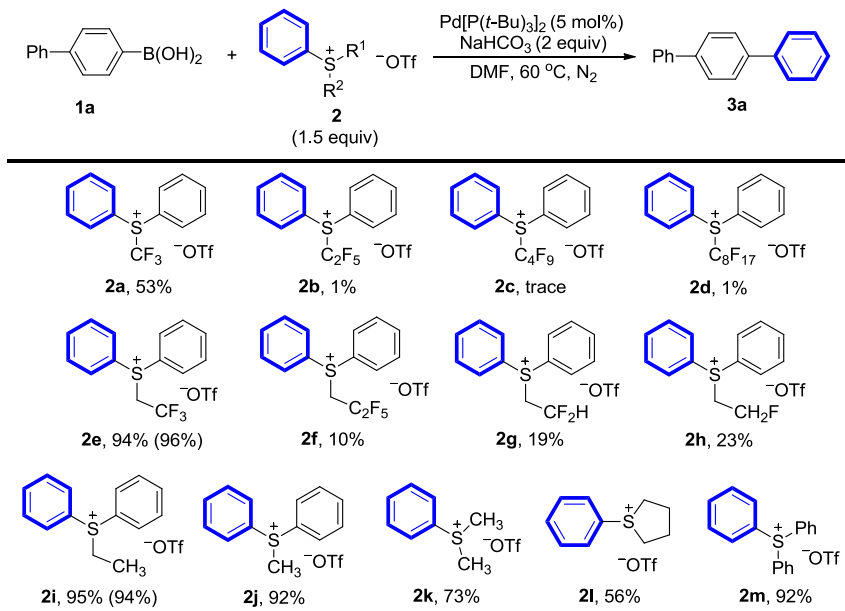
2. Results and discussion

Initially, the reaction of (trifluoromethyl)diphenylsulfonium triflate (**2a**, 1.5 equiv) with [1,1'-biphenyl]-4-ylboronic acid (**1a**) in DMF in the presence of Pd[P(*t*-Bu)₃]₂ (5 mol %) and NaHCO₃ (2 equiv) at 60 °C for 6 h provided 1,1':4',1''-terphenyl (**3a**) in 53% yield (Table 1) (For reaction condition optimization see [Electronic Supplementary Information \(ESI\)](#)). When (perfluoroethyl)diphenylsulfonium (**2b**), (perfluorobutyl)diphenylsulfonium (**2c**), or (perfluorooctyl)diphenylsulfonium triflate (**2d**) was used instead of **2a** in the same reaction, **3a** was obtained in trace amount (Table 1). This phenomenon may be attributed to the stronger electronegativity of the long-chain perfluoroalkyl groups of [Ph₂SR_{fn}][OTf] than the CF₃ moiety, which preferentially underwent the S–R_{fn} bond cleavage of [Ph₂SR_{fn}] cations in the reaction (see ESI). Interestingly, if (2,2,2-trifluoroethyl)diphenylsulfonium triflate (**2e**) was treated with **1a** under the standard conditions, **3a** was formed in 94% yield (Table 1). Nevertheless, treatment of (2,2,3,3,3-pentafluoropropyl)diphenylsulfonium triflate (**2f**) with **1a**, **3a** was prepared in 10% yield. Similarly, the reaction of (2,2-difluoroethyl)diphenylsulfonium triflate (**2g**) or (2-fluoroethyl)diphenylsulfonium triflate (**2h**) with **1a** gave **3a** in 19% or 23% yield, respectively. The ¹⁹F NMR analysis of the reaction mixtures indicated that **2f–h** decomposed in the reaction, which might cause the poor yields of **3a**.

triflate (**2l**) with **1a** provided **3a** in 56% yield, which was approximate to those using other aryl(tetrahydro)thiopheniums as the cross-coupling partners in Suzuki–Miyaura reactions with organoboron reagents.¹² These results implied that the non-fluorinated alkyl diphenylsulfonium triflates were more effective participants than the non-fluorinated dialkyl phenylsulfonium compounds in the Pd-catalyzed Suzuki–Miyaura cross-couplings. In addition, the reaction of **1a** with triphenylsulfonium triflate (**2m**), a well-known photoacid generator, could give **3a** in 92% yield under the standard reaction conditions, the yield of which was nearly equal to those using **2e**, **2i**, and **2j** (Table 1).

To shed more light on this transformation, we monitored the reactions of several representative phenylsulfonium triflates by HPLC (Fig. 1). It was found that the Pd-catalyzed reactions of **1a** with **2e**, **2i**, and **2j** exhibited similar reactivity profiles, which were almost completed in 3 h and gave comparable yields of **3a** after 6 h. Furthermore, the cross-coupling of **2a** with **1a** proceeded fast at the beginning of the reaction and 1 h later it slowed down, which finally provided **3a** in moderate yield. Likewise, a fast formation of **3a** was observed in the cases of **2g** and **2h** during the first 40–60 min of the reactions and later the transformation shut down. We suggested that the cleavage of the S–R_{fn} bonds of [Ph₂SR_{fn}][OTf] and the β-F elimination of the CH₂R_{fn} groups of [Ph₂SCH₂R_{fn}][OTf] might happen in these reactions (according to ¹⁹F NMR analysis of the reaction mixtures, see ESI),¹³ which ceased the Suzuki–Miyaura cross-coupling once the sulfonium salts were completely consumed. This trend could be strengthened with the elongation of perfluoroalkyl chains of [Ph₂SR_{fn}][OTf] (e.g., **2b–d**), which led to the

Table 1
Pd-catalyzed Suzuki–Miyaura cross-coupling of [Ph₂SR_{fn}][OTf] with [1,1'-biphenyl]-4-ylboronic acid (**1a**)^a



^a Reaction conditions: **1a** (0.1 mmol)/**2** (0.15 mmol)/Pd[P(*t*-Bu)₃]₂ (0.005 mmol, 5 mol %)/NaHCO₃ (0.2 mmol)/DMF (2 mL)/N₂/60 °C/6 h. Yields of **3a** were determined by HPLC using 1,1':4',1''-terphenyl as the external standard (*t*_R=6.145 min, λ_{max}=278.3 nm, CH₃OH/H₂O=90:10 (v/v)). Isolated yield is depicted in the parentheses.

The non-fluorinated phenylsulfonium salts were also investigated in the reaction (Table 1). (Ethyl)diphenylsulfonium triflate (**2i**) and (methyl)diphenylsulfonium triflate (**2j**) reacted with **1a** under the standard reaction conditions to supply **3a** in 95% and 92% yield, respectively. These yields were comparable to that of **2e** and higher than that of **2a**. Moreover, reaction of (dimethyl)phenylsulfonium triflate (**2k**) with **1a** under the standard conditions gave **3a** in 73% yield. Treatment of phenyl(tetrahydro)thiophenium

triflate (**2l**) with **1a** provided **3a** in 56% yield, which was approximate to those using other aryl(tetrahydro)thiopheniums as the cross-coupling partners in Suzuki–Miyaura reactions with organoboron reagents.¹² These results implied that the non-fluorinated alkyl diphenylsulfonium triflates were more effective participants than the non-fluorinated dialkyl phenylsulfonium compounds in the Pd-catalyzed Suzuki–Miyaura cross-couplings. In addition, the reaction of **1a** with triphenylsulfonium triflate (**2m**), a well-known photoacid generator, could give **3a** in 92% yield under the standard reaction conditions, the yield of which was nearly equal to those using **2e**, **2i**, and **2j** (Table 1).

failure of the conversions. Since **2e** has more steric hindrance than **2g** and **2h** (because of the shielding of β-fluorine atoms), the deprotonation of **2e** followed by β-F elimination is to some extent prohibited (see ESI). Increasing the length of perfluoroalkyl groups of [Ph₂SCH₂R_{fn}][OTf], however, the deprotonation and β-F elimination became predominant due to the strong electron-withdrawing power of R_{fn} moiety, which counteracted the steric effects, thus leading to serious inhibition of the phenylation (e.g., **2f**).

Download English Version:

<https://daneshyari.com/en/article/5213089>

Download Persian Version:

<https://daneshyari.com/article/5213089>

[Daneshyari.com](https://daneshyari.com)