

New Activators for the Coupling Reaction of Terminal Alkynes with Organic Halides

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Cross-coupling reactions of terminal alkynes with organic halides catalyzed by palladium(0) or palladium(0)/Cu(I) take place in the presence of several activators, such as silver(I) oxide, tetrabutylammonium fluoride (TBAF), and tetrabutylammonium hydroxide (TBAOH), to give the corresponding coupling products in good-to-excellent yields.

Carbon–carbon bond-forming reactions with terminal alkynes and organic electrophiles have attracted considerable attention in organic synthesis, because compounds containing the alkynyl moiety have appeared in a wide range of biologically important molecules and their synthetic intermediates.¹ Sonogashira–Hagihara coupling, which is a palladium/copper-catalyzed coupling reaction of terminal alkynes with organic halides, has been recognized as a highly practical method for introducing alkynyl moiety into organic molecules.² However, the major drawback of the reaction is the use of amine as a solvent or co-solvent, which sometimes causes difficulties in the removal of excess amine and the formed ammonium salt. Decreasing the amount of amine, in general, lowers the reactivity. Efforts to overcome such problems have been devoted to the ligand design of a palladium catalyst, which would enable the reaction using a reduced amount of amine. Indeed, the use of bulky trialkylphosphines or heteroaromatic carbenes as a ligand for the palladium catalyst achieved the Sonogashira coupling with stoichiometric, or slightly excess, amine under mild conditions.^{3,4}

On the other hand, we envisaged that another solution to the problem of the Sonogashira coupling is to design a new class of activator of the reaction instead of (excess) amine. Herein, we report that the coupling of terminal alkynes has been achieved without amines using several additives, such as silver(I) oxide, tetrabutylammonium fluoride (TBAF), and tetrabutylammonium hydroxide (TBAOH).⁵

Results and Discussion

While studying the cross coupling of silanols, we found that silver(I) oxide serves as an activator for the reaction of organosilicon reagents.^{6,7} A palladium-catalyzed reaction of aryl- and alkenylsilanols with several organic halides took place to form a carbon–carbon bond smoothly. We learned that the cross-

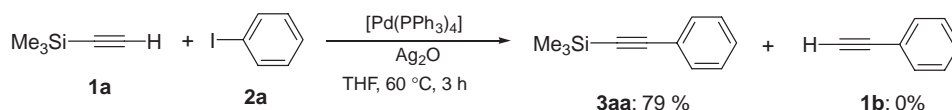
coupling of trimethylsilylalkynes with aryl halides was also promoted by silver(I) oxide.⁸ However, the reaction of trimethylsilyl ethyne (**1a**) with iodobenzene (**2a**) did not replace the trimethylsilyl group, but afforded **3aa**, which is the C–H substituted product, in 79% yield, as shown in Scheme 1.

The results show that silver(I) oxide has served as an activating agent for the coupling of terminal alkynes. Thus, we examined the reaction of several terminal alkynes with organic halides. The results are summarized in Table 1. The reaction of **1a** also proceeded smoothly with aryl iodides **2b** and **2c** bearing an electron-donating or electron-withdrawing substituent on the aromatic ring. In addition to **1a**, terminal alkynes with aryl and alkyl substituents coupled with aryl iodides. The reaction of terminal alkynes with a hydroxy group (**1d**) al-

Table 1. Palladium-Catalyzed Cross-Coupling Reaction of Terminal Alkynes with Aryl Halides in the Presence of Ag₂O

| $R^1\text{—}\equiv\text{H}$ 1 | $X\text{—}R^2$ 2 | $\xrightarrow[\text{THF, 60 } ^\circ\text{C}]{[\text{Pd}(\text{PPh}_3)_4], \text{Ag}_2\text{O}}$ | $R^1\text{—}\equiv\text{R}^2$ 3 |
|---|--|--|---|
| R^1 | $X\text{—}R^2$ | Time/h | 3 , Yield/% |
| Me ₃ Si (1a) | I–C ₆ H ₅ (2a) | 3 | 3aa , 79 |
| 1a | 4-I–C ₆ H ₄ –OCH ₃ (2b) | 8 | 3ab , 72 |
| 1a | 4-I–C ₆ H ₄ –COCH ₃ (2c) | 3 | 3ac , 99 |
| Ph (1b) | 2a | 8 | 3ba , 60 |
| 1b | Br–C ₆ H ₅ (4a) | 6 | 3ba , 0 |
| 1b | TfO–C ₆ H ₅ (5a) | 6 | 3ba , 0 |
| ⁿ C ₆ H ₁₃ (1c) | 2a | 8 | 3ca , 90 |
| HO(CH ₂) ₂ C (1d) | 2a | 6 | 3da , 73 |

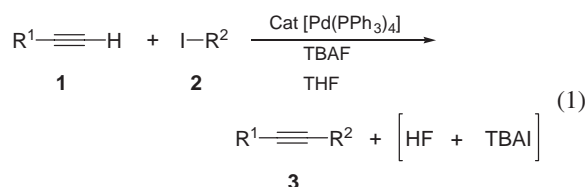
The reaction was carried out with terminal alkyne (**1**) (1.1 molar amount), **2**, **4**, or **5**, 0.05 mol. amt. of [Pd(PPh₃)₄] and Ag₂O (1.0 mol. amt.) in THF at 60 °C.



Scheme 1.

so took place without protection. The coupling promoted by Ag_2O proceeded specifically with aryl iodides. The results are consistent with the related reaction of aryl- and alkenylsilanols using Ag_2O , probably due to the interaction of silver and iodine atoms. Indeed, the reaction with bromide **4a** and triflate **5a** did not afford the coupling product at all. It was also confirmed by X-ray diffraction analysis (XRD) that silver(I) oxide is transformed into silver(I) iodide.^{6c} Hence, another by-product would be water. Worthy of note concerning the Ag_2O -promoted reaction of terminal alkynes is the ease of isolation and purification for the coupling product. Since both Ag_2O and AgI were insoluble in organic solvents, removal of the silver residue by filtration after the reaction, followed by chromatography or recrystallization, easily produced analytically pure arylated alkynes.

It was also found that the coupling of terminal alkynes was promoted by tetrabutylammonium fluoride (TBAF) in spite of the fact that stoichiometry of the reaction suggests the formation of hydrogen fluoride. The reaction was found to proceed with a smaller amount of palladium catalyst (0.005 molar amount) (Eq. 1).



When phenylethyne (**1b**) was treated with **2b** in the presence of $[\text{Pd}_2(\text{dba})_3]$ (0.005 molar amount)– PPh_3 (0.02 molar amount) in THF at 60 °C for 6 h, the corresponding coupling product **3bb** was obtained in 83% yield. As summarized in Table 2, the reaction proceeded with various terminal alkynes and aryl halides. In contrast to the case of Ag_2O , bromides also

reacted smoothly. Although TBAF is a well-known activator for the coupling of aryl- and alkenylsilanes, as well as trimethylsilylated alkynes, the C–H bond of the terminal alkyne was surprisingly activated by TBAF, and a coupling reaction with organic halides took place. Other fluoride ions and inorganic bases, such as KF (0%), CsF (0%), AgF (11%), and K_2CO_3 (0%), were examined concerning the coupling reaction; however, such additives showed little, or no, effect as competent activators.

It should be pointed out that the addition of a catalytic amount of CuI to the reaction system allowed it to undergo the coupling reaction at room temperature, although the reaction without CuI did not proceed at all under similar conditions. The reaction with several alkynes and organic halides took place similarly. It is also remarkable that isolation and purification procedures are quite simple to obtain the desired product by simple silica-gel chromatography or recrystallization after the usual workup.

In addition to TBAF, tetrabutylammonium hydroxide (TBAOH) was also found to serve as an efficient activator for the coupling reaction. Table 3 summarizes the results. The reaction with TBAOH was generally faster than that with TBAF. The reaction of phenylethyne (**1b**) with 4-iodoanisole (**2b**) in the presence of a 0.01 molar amount of $[\text{PdCl}_2(\text{PPh}_3)_2]$, a 0.02 molar amount of CuI, and a 2 molar amount of TBAOH resulted in giving the coupling product **3bb** in quantitative yield after stirring for 5 h in THF at room temperature. 1-alkynes, such as 1-octyne, also underwent the reaction smoothly. Several alkynes bearing a hydroxy substituent also reacted to afford the coupling products. The reaction of **1d** with **2b** gave the corresponding coupling product **3db** in 95% as isolated yield after stirring for 5 h at room temperature. The use of **1f** and **1g** also resulted in giving **3fb** and **3gb** in 83% and 89% isolated yields, respectively.

Table 2. Coupling of Terminal Alkynes in the Presence of TBAF^{a)}

| $\text{R}^1\text{—}\equiv\text{H}$ 1 | X—R^2 2 | Catalyst TBAF (2 mol. amt.) THF | $\text{R}^1\text{—}\equiv\text{R}^2$ 3 | | |
|---|---|---|---|--------|-------------------------------|
| R^1 | X—R^2 | Catalyst (10 ^{−2} mol. amt.) | Temp | Time/h | 3, Yield/% |
| Ph (1b) | 4-I-C ₆ H ₄ -OCH ₃ (2b) | $[\text{Pd}_2(\text{dba})_3]$ (0.5), PPh_3 (2.0) | 60 °C | 6 | 3bb , 83 |
| 1b | 4-I-C ₆ H ₄ -CN (2d) | $[\text{Pd}_2(\text{dba})_3]$ (0.5), PPh_3 (2.0) | 60 °C | 5 | 3bd , 86 |
| 1b | 4-Br-C ₆ H ₄ -COCH ₃ (4c) | $[\text{Pd}_2(\text{dba})_3]$ (0.5), PPh_3 (2.0) | 60 °C | 48 | 3bc , 54 |
| ⁿ C ₆ H ₁₃ (1c) | 2b | $[\text{Pd}_2(\text{dba})_3]$ (0.5), PPh_3 (2.0) | 60 °C | 24 | 3cb , 81 |
| 1c | 4c | $[\text{Pd}_2(\text{dba})_3]$ (0.5), PPh_3 (2.0) | 60 °C | 24 | 3cc , 75 |
| HO(CH ₂) ₂ C (1d) | I-C ₆ H ₅ (2a) | $[\text{Pd}_2(\text{dba})_3]$ (0.5), PPh_3 (2.0) | 60 °C | 24 | 3da , 64 |
| HOCH ₂ (1e) | 2a | $[\text{Pd}_2(\text{dba})_3]$ (0.5), PPh_3 (2.0) | 60 °C | 24 | 3ea , 59 |
| HO(CH ₂) ₂ (1f) | 2a | $[\text{Pd}_2(\text{dba})_3]$ (0.5), PPh_3 (2.0) | 60 °C | 5 | 3fa , 64 |
| 1b | 2a | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (3.0), CuI (2.0) | rt | 42 | 3ba , 93 ^{b)} |
| 1b | 2b | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1.0), CuI (2.0) | rt | 36 | 3bb , 99 |
| 1b | 2d | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1.0), CuI (2.0) | rt | 24 | 3bd , 99 ^{b)} |
| 1b | 2c | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1.0), CuI (2.0) | rt | 24 | 3bc , 84 |
| 1b | (<i>E</i>)-PhCH=CHBr (4e) | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1.0), CuI (2.0) | rt | 5 | 3be , 89 |
| 1c | 2a | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1.0), CuI (2.0) | rt | 3 | 3ca , 93 |
| 1c | 2b | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1.0), CuI (2.0) | rt | 6 | 3cb , 98 |
| 1c | 2d | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (1.0), CuI (2.0) | rt | 6 | 3cd , 96 ^{b)} |
| 1c | 4c | $[\text{PdCl}_2(\text{PPh}_3)_2]$ (3.0), CuI (2.0) | rt | 24 | 3cc , 87 |

a) Unless noted the reaction was carried out using 0.5 mmol aryl halide **2** or **4** and 0.6 mmol terminal alkyne **1** in the presence of 2 mol. amt. of TBAF. b) 1.2 mol. amt. of TBAF was loaded.

Table 3. Coupling of Terminal Alkynes in the Presence of TBAOH at Room Temperature^{a)}

| R ¹ | X-R ² | Time/h | 3, Yield/% |
|---|---|--------|-------------------------------|
| Ph (1b) | 4-I-C ₆ H ₄ -OCH ₃ (2b) | 5 | 3bb , 99 |
| 1b | 4-Br-C ₆ H ₄ -OCH ₃ (4b) | 24 | 3bb , 30 ^{b)} |
| 1b | 4-Br-C ₆ H ₄ -COCH ₃ (4c) | 7 | 3bc , 94 ^{c)} |
| ⁿ C ₆ H ₁₃ (1c) | 2b | 1 | 3cb , 90 |
| 1c | 2b | 6 | 3cb , 98 ^{d)} |
| HO(CH ₃) ₂ C (1d) | 2b | 5 | 3db , 95 |
| HO(CH ₂) ₂ (1f) | 2b | 3 | 3fb , 83 |
| HO(CH ₃)CH (1g) | 2b | 3 | 3gb , 89 |

a) Unless noted the reaction was carried out using 0.01 mol. amt. of [PdCl₂(PPh₃)₂], 0.02 mol. amt. of CuI and 2 mol. amt. of TBAOH at room temperature in THF. b) [PdCl₂(P(*o*-tol)₃)₂] (0.03 mol. amt.) was loaded. c) [PdCl₂(PPh₃)₂] (0.03 mol. amt.) was loaded. d) 1.2 mol. amt. of TBAOH was employed.

In summary, since we have several new activators for the coupling of terminal alkynes, described herein as Ag₂O, tetrabutylammonium fluoride (TBAF), and tetrabutylammonium hydroxide (TBAOH) in hand, the method would be a powerful tool for the synthesis of a variety of organic molecules bearing alkynyl moieties, leading to biologically active compounds and functional organic materials.

Experimental

All reactions were performed under an atmosphere of argon using standard Schlenk tubes. Commercially purchased terminal alkynes and aryl halides were used as received without further treatment. Tetrabutylammonium fluoride (TBAF) was purchased as a 1 M (= 1 mol dm⁻³) solution in THF, and tetrabutylammonium hydroxide (TBAOH) was purchased as a 40% (w/w) aqueous solution.

Trimethylsilylethynylbenzene (3aa).⁹ To a Schlenk tube were added [Pd(PPh₃)₄] (11.6 mg, 0.01 mmol), Ag₂O (46.3 mg, 0.2 mmol), and THF (2 mL). Then, **2a** (0.2 mmol), and **1a** (0.24 mmol) were successively added to the mixture. The resulting mixture was heated at 60 °C and stirring was continued for 3 h. After cooling to an ambient temperature, the mixture was diluted with diethyl ether and then passed through a Celite pad to remove the silver residue, which was washed with diethyl ether. The combined filtrate was concentrated under reduced pressure to leave a crude oil, which was subjected to column chromatography on silica gel (hexane–ethyl acetate 100:1) to give **3aa** in 79% (28 mg).

The following coupling products were obtained in the manner described above: 4-(Trimethylsilylethynyl)anisole (**3ab**),¹⁰ 1-[4-(trimethylsilylethynyl)phenyl]-1-ethanone (**3ac**),¹¹ diphenylethyne (**3ba**),¹² 1-phenyl-1-octyne (**3ca**),¹³ 2-methyl-4-phenyl-3-buten-2-ol (**3da**).¹⁴

4-(Phenylethynyl)benzonitrile (3bd).¹⁵ To a Schlenk tube were added [Pd₂(dba)₃]·CHCl₃ (2.6 mg, 0.0025 mmol), PPh₃ (2.6 mg, 0.01 mmol), and **1b** (66 μL, 0.6 mmol). The mixture was dissolved in 2 mL of THF under an argon atmosphere. To the solution were successively added **2d** (114.5 mg, 0.5 mmol) and TBAF (1.0 mL, 1.0 mmol; 1 M THF solution, water content 5 wt %: available from Aldrich). The resulting mixture was then heated at 60 °C for 5 h. After the reaction was completed, the mixture was cooled to room temperature and the solvent was removed under reduced pressure to leave a crude sample, which was sub-

jected to column chromatography on silica gel (hexane–ethyl acetate 30:1) to give **3bd** in 86% (87.4 mg).

The following coupling products were obtained in a manner described above: 4-(Phenylethynyl)anisole (**3bb**),¹⁶ 1-[4-(phenylethynyl)phenyl]-1-ethanone (**3bc**),¹⁷ 1-[4-(1-octynyl)phenyl]-1-ethanone (**3cc**),^{6c} 3-phenyl-2-propyn-1-ol (**3ea**),^{2a} 4-phenyl-3-buten-1-ol (**3fa**).^{2c}

4-(1-Octynyl)anisole (3cb).^{3c} To a solution of [PdCl₂(PPh₃)₂] (3.5 mg, 0.005 mmol) and CuI (1.9 mg, 0.01 mmol) in 3 mL of THF were added successively **2b** (117 mg, 0.5 mmol), **1c** (89 μL, 0.6 mmol), and TBAF (1 mL, as 1 M THF solution, 1.0 mmol) under argon atmosphere. Stirring was continued at room temperature for 6 h, and the resulting mixture was passed through a Celite pad. The filtrate was concentrated and subjected to column chromatography on silica gel (hexane–ethyl acetate 50:1) to afford **3cb** in 98% (106 mg).

The following coupling products were obtained in the manner described above: 1,4-Diphenyl-1-buten-3-yne (**3be**),¹⁸ 4-(1-octynyl)benzonitrile (**3cd**).¹⁹

4-(Phenylethynyl)anisole (3bb).¹⁶ To a solution of PdCl₂(PPh₃)₂ (3.5 mg, 0.005 mmol) and CuI (1.9 mg, 0.01 mmol) in 3 mL of THF were added successively **2b** (117 mg, 0.5 mmol), **1b** (66 μL, 0.6 mmol), and TBAOH (0.655 mL, 1.0 mmol) under an argon atmosphere. Stirring was continued at room temperature for 5 h, and the resulting mixture was passed through a Celite pad. The filtrate was concentrated and subjected to column chromatography on silica gel (hexane–ethyl acetate 30:1) to afford **3bb** in 99% (103 mg).

The following coupling products were obtained in the manner described above: 4-(4-Methoxyphenyl)-2-methyl-3-buten-2-ol (**3db**),²⁰ 4-(4-methoxyphenyl)-3-buten-1-ol (**3fb**),²¹ 4-(4-methoxyphenyl)-3-buten-2-ol (**3gb**).²²

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