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One-pot, efficient, and regioselective syntheses of 1,4-disubstituted 1,2,3-triazoles using aryldiazonium silica sulfates in water

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ABSTRACT

A one-pot, efficient, and straightforward procedure for the copper-catalyzed synthesis of 1,4-disubstituted 1,2,3-triazoles is studied by in situ generation of aryl azides via the reaction of aryldiazonium silica sulfates and sodium azide, followed by coupling with a terminal alkyne. These reactions are carried out in water at room temperature without using any additional ligands.

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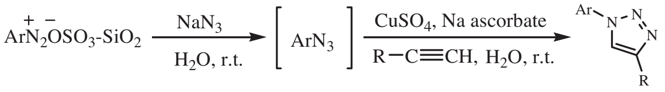
An important example of click chemistry[1] is the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes (CuAAC)[2] for the regioselective synthesis of 1,4-disubstituted 1,2,3-triazole derivatives. These compounds have received significant attention because of their wide applications in chemical, material, and biological sciences.[3] For example, some of these compounds show a variety of properties including anti-HIV,[4] antiallergic,[5] antidiabetic,[6] antifungal,[7] and antibacterial.[8] Moreover, 1,2,3-triazoles are stable and tolerant to many functional groups and conditions. Therefore, they have been widely used in organic synthesis, industrial applications, bioconjugation, and drug discovery.[9] Different methods have been reported to develop the 1,3-dipolar cycloaddition of alkynes with organic azides. For example, using Cu(II) in the presence of reductants,[2e,10] Cu(I) directly,[11] a variety of ligands to stabilize the Cu(I) oxidation state,[12] copper-containing nanoparticles,[13] copper(I) immobilized on various supports,[14] the in situ generation of organic azides that not only simplifies the experimental procedure, but also minimizes the risk of handling hazardous azides,[15] and the use of microwave or ultrasound irradiation to reduce reaction times.[16] 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.

Aromatic azides are versatile intermediates with various applications in organic and bioorganic chemistry. They are very useful starting materials for the click reaction and are commonly prepared by the reaction of diazonium salts with azides. Although organic azides are often stable under most reaction conditions, derivatives with low molecular weight can sometimes be explosive. Moreover, high temperatures lead to decomposition of the aryl azides. Therefore, the in situ generation of organic azides followed by their immediate reactions, is a desirable and attractive method to minimize the potential explosive risks. In continuation of our studies on the stabilization of diazonium salts on silica sulfuric acid and their application in organic synthesis,[17] we report herein an efficient, convenient, and one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles by the in situ generation of aryl azides via reaction of aryldiazonium silica sulfates and sodium azide followed by coupling with a terminal alkyne (Scheme 1). Unlike traditional methods, these reactions were carried out in water at room temperature without using any additional ligand.

Aryldiazonium salts are useful intermediates in organic synthesis due to their ready availability and high reactivity.[18] These compounds, however, have a serious drawback in their intrinsic instability and hence they are usually synthesized at around 10 °C and, to avoid their decomposition, they are handled at temperatures 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



Scheme 1. One-pot synthesis of 1,4-disubstituted 1,2,3-triazoles

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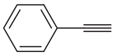
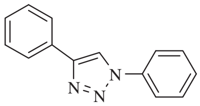
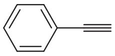
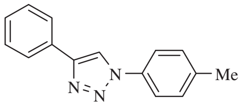
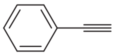
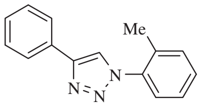
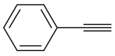
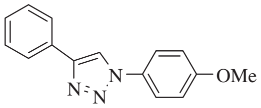
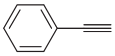
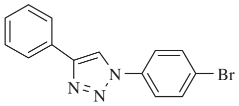
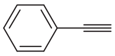
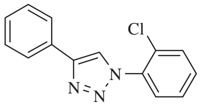
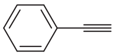
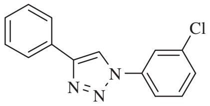
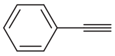
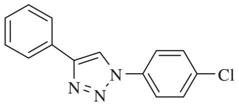
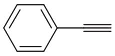
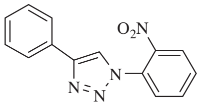
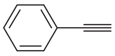
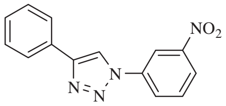
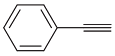
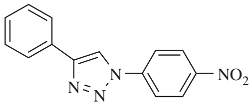
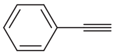
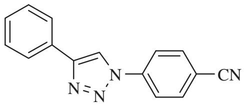
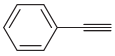
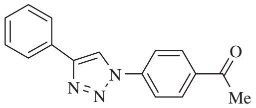
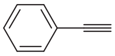
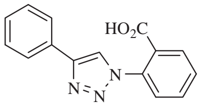
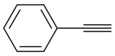
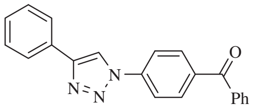
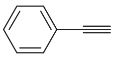
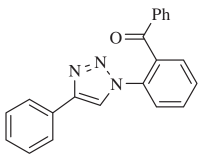
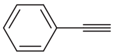
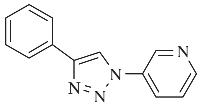
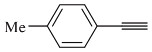
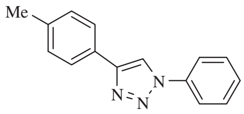
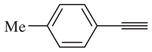
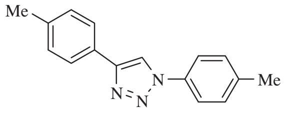
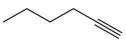
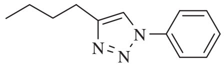
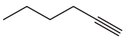
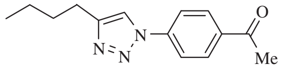
Table 1
One-pot synthesis of 1,4-disubstituted 1,2,3-triazoles using aryldiazonium silica sulfates

Entry	Diazonium salt	Alkyne	Product	Time (h)	Yield[a] (%)
1	$C_6H_5N_2{}^{+-}OSO_3\text{-}SiO_2$			5	87
2	$4\text{-}MeC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	81
3	$2\text{-}MeC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			7	73
4	$4\text{-}MeOC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	78
5	$4\text{-}BrC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	80
6	$2\text{-}ClC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	79
7	$3\text{-}ClC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			5	86
8	$4\text{-}ClC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	82
9	$2\text{-}NO_2C_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	65
10	$3\text{-}NO_2C_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			5	90
11	$4\text{-}NO_2C_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	81
12	$4\text{-}NCC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	78
13	$4\text{-}MeCOC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	72
14	$2\text{-}HO_2CC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			6	60
15	$4\text{-}PhCOC_6H_4N_2{}^{+-}OSO_3\text{-}SiO_2$			7	79

(*continued on next page*)

Table 1 (*continued*)

Entry	Diazonium salt	Alkyne	Product	Time (h)	Yield[a] (%)
16	2-$PhCOC_6H_4N_2{}^{+-}OSO_3$-$SiO_2$			7	76
17	3-$PyridylN_2{}^{+-}OSO_3$-SiO_2			5	75
18	$C_6H_5N_2{}^{+-}OSO_3$-SiO_2			7	80
19	4-$MeC_6H_4N_2{}^{+-}OSO_3$-SiO_2			7	77
20	$C_6H_5N_2{}^{+-}OSO_3$-SiO_2			5	83
21	4-$MeCOC_6H_4N_2{}^{+-}OSO_3$-$SiO_2$			6	78

[a] The yield refers to isolated pure products which were characterized from their spectral data and by comparison with those reported in the literature. [10b,c,11b,12f,13a,d,15]

and versatility, and that can be easily made and stored under solid-state conditions with explosion-proof properties are desirable.[19,20] For example, many diazonium tetrafluoroborates are relatively stable and can be stored over extended periods of time without decomposition.[21] 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). [17a] We found that these new aryldiazonium salts ($ArN_2{}^{+-}OSO_3$-SiO_2) were stable and could be stored at room temperature under anhydrous conditions and used under different reaction conditions.[17]

Initially, to minimize the potential explosive risk, in situ generation of aryl azides was studied by the reaction of aryldiazonium silica sulfates with sodium azide in water. These reactions were carried out at room temperature in a few minutes. [17c] After completion of azide formation, an aqueous solution of sodium ascorbate and a catalytic amount of $CuSO_4$ were added to generate the Cu(I) catalyst in situ, followed by addition of the corresponding terminal alkyne. To examine the generality of the process, the reactions of a variety of aryldiazonium silica sulfates and alkynes were studied in water at room temperature.[22,23]

As shown in Table 1, the reactions were carried out under mild heterogeneous conditions and the corresponding 1,4-disubstituted 1,2,3-triazoles were obtained in relatively short reaction times and in good yields. Aryldiazonium silica sulfates with electron-withdrawing or electron-donating groups also reacted effectively. The steric effects of *ortho* substituents on the aryl rings of the aryldiazonium silica sulfates had relatively little influence on the yields and reaction times (Table 1, entries 3, 6, 9, 14 and 16).

Although most CuAAC reactions proceed either in organic solvents or in mixtures with water (i.e. water/MeCN or water/*t*-BuOH), only a few reactions have been reported in water alone.[24] However, in all of these, it was necessary to use an appropriate ligand to accelerate the reaction rate. Moreover, in most of these methods, raised temperatures were required to allow the reaction to progress. Recently, Alonso and coworkers[13c] developed a one-pot method for the CuAAC reaction using $ArN_2{}^{+}BF_4{}^{-}$, NaN_3, and terminal alkynes in water catalyzed by copper nanoparticles on activated carbon. These reactions were carried out at 70 °C in 2–8 h without using any ligand. However, it was necessary to use an organic solvent and relatively expensive materials for the synthesis of the copper nanoparticles.[13c]

By using aryldiazonium silica sulfates as heterogeneous systems with high surface areas, contamination of the desired products with residual copper decreased due to the reduction of Cu(I) leaching from the surface. Furthermore, by supporting the aryldiazonium salt on silica sulfuric acid, the surface area of the reaction increased thereby lowering the reaction time.[17,25] 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.

To summarize, we have reported an efficient, one-pot, safe, and experimentally simple method for the synthesis of 1,4-disubstituted 1,2,3-triazoles in good yields. These reactions were carried out using aryldiazonium silica sulfates, sodium azide, terminal alkynes, and a catalytic amount of $CuSO_4$ in the presence of sodium ascorbate. It was notable that all the reactions took place in pure water at room temperature without using any additional ligand.

Acknowledgement

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22. *Typical procedure for the synthesis of 1,4-diphenyl-1H-1,2,3-triazole* (Table 1, *entry 1)*: To a stirred solution of NaN_3 (0.15 g, 2.3 mmol) in H2O (5 mL), freshly prepared phenyldiazonium silica sulfate[17] (1 mmol) was gradually added and the mixture was stirred at room temperature for 5 min. Next, a mixture of CuSO4·5H2O (0.04 g, 15 mol %), sodium ascorbate (0.18 g, 0.9 mmol), and phenylacetylene (0.25 mL, 2.3 mmol) in H_2O (5 mL) was added and the mixture stirred for 5 h at room temperature. The mixture was diluted with EtOAc (15 mL) and filtered after vigorous stirring. The filtrate was extracted with EtOAc (3 × 12 mL) and the combined organic layer washed with H_2O (15 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The residue was washed with *n*-hexane (5 mL) to afford the pure product (0.19 g, 87%). Column chromatography was used for some cases to obtain the pure product.
23. *Spectral data of new compounds: phenyl [4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl]ketone (*Table 1, *entry 15)*: Pale yellow solid; mp 206–208 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 9.45 (1 H, s), 8.17 (2 H, d, $J = 8.6$ Hz), 8.00–7.96 (4 H, m), 7.79 (2 H, d, $J = 7.6$ Hz), 7.72 (1 H, t, $J = 7.4$ Hz), 7.60 (2 H, t, $J = 7.6$ Hz), 7.52 (2 H, t, $J = 7.6$ Hz), 7.40 (1 H, t, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ 195.82, 148.52, 140.13, 137.61, 137.58, 133.84, 132.41, 130.86, 130.55, 129.93, 129.58, 129.32, 126.29, 120.59, 120.55; IR (KBr): 3130, 3055, 1647, 1604, 1411, 1319, 1281, 1230, 1041, 927, 852, 771, 703 cm^{-1}; Anal. Calcd for $C_{21}H_{15}N_3O$: C, 77.52; H, 4.65; N, 12.91%; Found: C, 77.39; H, 4.69; N, 12.81. *Phenyl [2-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl]ketone (*Table 1, *entry 16)*: Yellow solid; mp 108–110 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 9.06 (1 H, s), 7.89–7.84 (2 H, m), 7.77 (2 H, d, $J = 7.8$ Hz), 7.76–7.71 (2 H, m), 7.61 (2 H, d, $J = 7.7$ Hz), 7.52 (1 H, t, $J = 7.3$ Hz), 7.45–7.39 (4 H, m), 7.33 (1 H, t, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ 194.83, 147.90, 136.91, 135.24, 134.74, 134.22, 132.77, 130.85, 130.62, 130.44, 129.80, 129.41, 129.09, 126.15, 125.05, 122.91; IR (KBr): 3136, 3103, 3061, 1663, 1600, 1579, 1501, 1483, 1449, 1316, 1288, 1262, 1226, 929, 767, 749, 691 cm^{-1}; Anal. Calcd for $C_{21}H_{15}N_3O$: C, 77.52; H, 4.65; N, 12.91%; Found: C, 77.43; H, 4.76; N, 12.83.
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