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Easy One-Pot Synthesis of 1-Monosubstituted Aliphatic 1,2,3-Triazoles from Aliphatic Halides, Sodium Azide and Propiolic Acid by a Click Cycloaddition/Decarboxylation Process

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1-Monosubstituted aliphatic 1,2,3-triazoles were synthesized by a one-pot reaction from aliphatic halides (Cl and Br), sodium azide and propiolic acid. The yields ranged from moderate to good. The reaction was easily carried out in DMF with Cs_2CO_3 at 100 ℃ by copper-catalyzed click cycloaddition/decarboxylation.

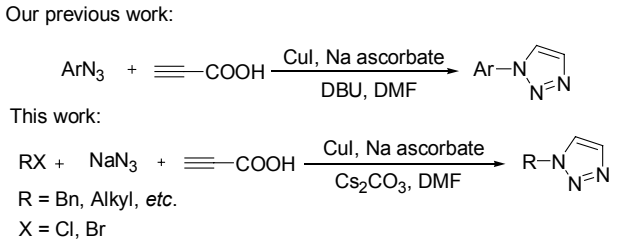
Keywords click chemistry, copper-catalyzed, decarboxylation, 1-monosubstitued aliphatic 1,2,3-triazole

Introduction

1,2,3-Triazole is an important structural unit of numerous pharmaceuticals, agrochemicals, and chemical reagents. Various 1,2,3-triazole derivatives also have wide-ranging applications in the fields of materials science and molecular structure design.[1] The Cu-catalyzed "click chemistry" reaction between azide and terminal alkyne is extensively used for the practical and efficient preparation of 1,4-disubstituted 1,2,3-triazoles since the robust Huisgen 1,3-dipolar cycloaddition was established.[2] However, reports on the synthesis methods of 1-monosubstituted 1,2,3-triazoles are limited. One strategy is the decarboxylation of triazoles bearing a carboxylic acid substituent, but the reactions require long reaction times and extreme temperatures.[3] Another protocol is the cycloaddition of azides to acetylene[4] and its analogs such as acetylides[5] as well as the cycloaddition of vinyl compounds.[6] A method has also been developed for the synthesis of monosubstitued 1-aryl-1*H*-1,2,3-triazoles from arylboronic acids and prop-2-ynoic acid or CaC_2.[7]

In a preliminary paper,[8] we reported a novel and useful protocol for the synthesis of 1-monosubstitued 1,2,3-triazoles by click reaction/decarboxylation[9] under mild conditions. In the present study, we developed an easy one-pot synthesis of 1-monosubstituted aliphatic 1,2,3-triazoles from aliphatic halides (Cl and Br), sodium azide and propiolic acid by a click cycloaddition/decarboxylation process. These previous and present methods are compared in Scheme 1.

Scheme 1



Experimental

Melting points were recorded using a Krüss Optronic GmbH KSPII melting-point apparatus and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker ARX400 spectrometer on $CDCl_3$ solutions with $SiMe_4$ as an internal standard. IR spectra were obtained on a Thermo FT-IR spectrophotometer. MS data were measured with a Varian-310 mass spectrometer. High resolution mass spectra were determined using a Finnigan-MAT GC/MS/DS 8430 spectrometer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with a Huanghai GF 254 system and silica gel coated plates. Column chromatography was carried out using 300—400 mesh silica gel at medium pressure.

Preparation of compound 2

A solution of aliphatic halides (Cl and Br; 0.2 mmol), NaN_3 (16 mg, 0.24 mmol), propiolic acid (17 mg, 0.24 mmol), CuI (8 mg, 0.04 mmol), Na ascorbate (16 mg, 0.08 mmol), and Cs_2CO_3 (33 mg, 0.1 mmol) in DMF (2

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mL) in a sealed tube was stirred under nitrogen. The reaction mixture was heated to a certain temperature until the starting aliphatic halides were completely consumed (monitored by TLC). The reaction solution was diluted with water and extracted three times with EtOAc. The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford a crude product. This product was subjected to column chromatography (silica gel and EtOAc-petroleum ether) to afford 1-monosubstituted 1,2,3-triazoles **2**.

Spectral data of all synthesized compounds 2a－2j

1-Benzyl-1*H*-1,2,3-triazole (2a)[10] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.70 (s, 1H, TrH), 7.49 (s, 1H, TrH), 7.25－7.37 (m, 5H, ArH) , 5.56 (s, 2H, CH_2).

1-(4-Methylbenzyl)-1*H*-1,2,3-triazole (2b) Light yellow solid. m.p. 55.7－56.6 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.68 (s, 1H, TrH), 7.47 (s, 1H, TrH), 7.17 (s, 4H, ArH) , 5.51 (s, 2H, CH_2), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.15, 53.75, 123.26, 128.07, 129.75, 131.71, 134.15, 138.63; IR (KBr) v: 3132, 2914, 1605, 1254, 1213, 1176, 1068, 1048 cm^{-1}. HRMS m/z caled for $C_{10}H_{11}N_3$: 173.0953 $[M]^+$; found 173.0954.

1-(3-Methylbenzyl)-1*H*-1,2,3-triazole (2c)[11] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.71 (s, 1H, TrH), 7.50 (s, 1H, TrH), 7.27 (t, J=7.2 Hz, 1H, ArH), 7.17 (d, J=7.2 Hz, 1H, ArH), 7.08 (s, 1H, ArH), 7.07 (d, J=7.2 Hz, 1H, ArH), 5.53 (s, 2H, CH_2), 2.34 (s, 3H, CH_3).

1-(2-Methylbenzyl)-1*H*-1,2,3-triazole (2d)[10] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.68 (s, 1H, TrH), 7.38 (s, 1H, TrH), 7.27－7.31 (m, 1H, ArH), 7.20－7.23 (m, 2H, ArH), 7.13－7.17 (m, 1H, ArH), 5.56 (s, 2H, CH_2), 2.27 (s, 3H, CH_3).

1-Phenethyl-1*H*-1,2,3-triazole (2e)[12] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.61 (s, 1H, TrH), 7.30 (s, 1H, TrH), 7.08－7.28 (m, 5H, ArH), 4.62 (t, J=7.2 Hz, 2H, $ArCH_2$), 3.20 (t, J=7.2 Hz, 2H, $TrCH_2$).

1-(2-Phenoxyethyl)-1*H*-1,2,3-triazole (2f) White solid. m.p. 91.8－92.4 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.78 (s, 1H, TrH), 7.70 (s, 1H, TrH), 7.28 (t, J=8.0 Hz, 2H, ArH), 6.98 (t, J=7.2 Hz, 1H, ArH), 6.86 (d, J=8.0 Hz, 2H, ArH), 4.79 (t, J=4.8 Hz, 2H, $ArOCH_2$), 4.34 (t, J=4.8 Hz, 2H, $TrCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 49.63, 66.37, 114.55, 121.72, 124.64, 129.69, 133.93, 157.83; IR (KBr) v: 3147, 3113, 2926, 1603, 1489, 1252, 1219, 1171, 1085, 1043 cm^{-1}. HRMS m/z caled for $C_{10}H_{11}N_3O$: 189.0902 $[M]^+$; found 189.0904.

1-(4-Fluorobenzyl)-1*H*-1,2,3-triazole (2g) Light yellow solid. m.p. 51.3－52.2 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.71 (s, 1H, TrH), 7.51 (s, 1H, TrH), 7.25－7.29 (m, 2H, ArH), 7.05 (t, J=8.8 Hz, 2H, ArH), 5.54 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 53.17, 116.18, 123.31, 129.84, 134.29, 161.57, 164.04; IR (KBr) v: 3103, 1609, 1514, 1266, 1238, 1211, 1082 cm^{-1}. HRMS m/z caled for $C_9H_8FN_3$: 177.0702 $[M]^+$; found 177.0705.

1-(2,6-Difluorobenzyl)-1*H*-1,2,3-triazole (2h) Light yellow solid. m.p. 114.0－115.0 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.69 (s, 1H, TrH), 7.63 (s, 1H, TrH), 7.33－7.41 (m, 2H, ArH), 6.95－7.00 (m, 2H, ArH), 5.66 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 41.15, 111.69, 123.47, 131.42, 134.07, 160.10, 162.67; IR (KBr) v: 3142, 3122, 1629, 1594, 1472, 1213, 1165, 1078, 1024 cm^{-1}. HRMS m/z caled for $C_9H_7F_2N_3$: 195.0608 $[M]^+$; found 195.0610.

1-(4-Nitrobenzyl)-1*H*-1,2,3-triazole (2i)[13] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.24 (d, J=8.8 Hz, 2H, ArH), 7.79 (s, 1H, TrH), 7.58 (s, 1H, TrH), 7.40 (d, J=8.4 Hz, 2H, ArH), 5.70 (s, 2H, CH_2).

1-(1-Phenylethyl)-1*H*-1,2,3-triazole (2j)[13] ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.68 (s, 1H, TrH), 7.47 (s, 1H, TrH), 7.25－7.38 (m, 5H, ArH), 5.85 (q, J=7.2 Hz, 1H, CH), 1.99 (d, J=7.2 Hz, 3H, CH_3).

Results and Discussion

The optimum reaction conditions were preliminarily screened using benzyl chloride (0.3 mmol), NaN_3 (1.2 equiv.), and propiolic acid (1.2 equiv.) as the model substrates (Table 1). We first investigated the effects of different bases (none, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), Et_3N, K_2CO_3, and Cs_2CO_3) on the formation of 1-benzyl-1*H*-1,2,3-triazole (**2a**) (Table 1, Entries 1－5). Among the bases we tested, Cs_2CO_3 (0.5 equiv.) gave the highest yield of 90% in DMF at 100 ℃ for 0.5 h (Table 1, Entry 5). The reason may be that cesium propiolate is more soluble in DMF than potassium propiolate, and the solubility drives faster reaction. However, the organic bases often cause more side reactions in the transition metal catalyzed reactions. On the other hand, the solvent system significantly affected the reaction outcome, and DMF was much more effective than other single solvents or mixed solvents (Table 1, Entries 5－8). Moreover, product **2a** was not obtained when water was used as a solvent. The reason may be the decrease in the reactant solubility in this reaction system. We also studied the effects of various amounts of CuI and sodium ascorbate on the formation of the triazole **2a** (Table 1, Entries 9－13). As expected, CuI (0.2 equiv.) and sodium ascorbate (0.4 equiv.) were necessary. Eventually, the optimum reaction conditions were concluded to be CuI (0.2 equiv.), Cs_2CO_3 (0.5 equiv.), and sodium ascorbate (0.4 equiv.) in DMF solvent at 100 ℃ for 0.5 h (Table 1, Entry 5).

Under the optimized conditions, the substrate scope of this one-pot synthesis of 1-monosubstituted aliphatic 1,2,3-triazoles from aliphatic halides (Cl and Br), sodium azide and propiolic acid by a click cycloaddition/decarboxylation process was investigated.

The newly established conditions appeared to be general for most aliphatic halides (Cl and Br) and afforded 1-momosubstitued 1,2,3-triazoles in moderate to good yields (Table 2). Nevertheless, 1-(2-methylbenzyl)-1*H*-1,2,3-triazole (**2d**) suffered from a low re-

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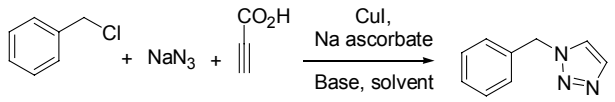
Table 1 Reaction optimization



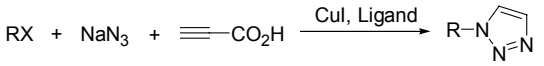
Entry	CuI/ equiv.	Na ascorbate/ equiv.	Base	Solvent	T/℃	Time/h	Yield[a]/% of 2**a**
1	0.2	0.40	0	DMF	100	0.5	30
2	0.2	0.40	DBU	DMF	100	0.5	82
3	0.2	0.40	Et_3N	DMF	100	0.5	68
4	0.2	0.40	K_2CO_3	DMF	100	0.5	55
5	0.2	0.40	Cs_2CO_3	DMF	100	0.5	90
6	0.2	0.40	Cs_2CO_3	CH_3CN/ H_2O(9/1)	100	0.5	12
7	0.2	0.40	Cs_2CO_3	DMSO	100	0.5	75
8	0.2	0.40	Cs_2CO_3	H_2O	100	0.5	0
9	0.1	0.20	Cs_2CO_3	DMF	100	0.5	61
10	0.5	1.00	Cs_2CO_3	DMF	100	0.5	91
11	0.2	0.30	Cs_2CO_3	DMF	100	0.5	83
12	0.2	0	Cs_2CO_3	DMF	100	0.5	10
13	0.2	0.40	Cs_2CO_3	DMF	100	2	90

[a] Isolated yields.

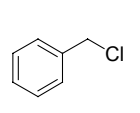
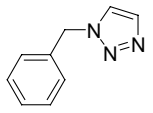
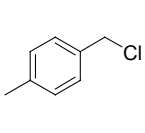
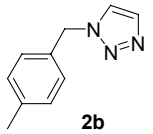
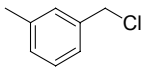
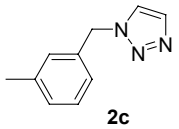
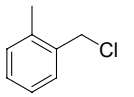
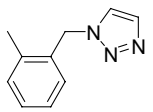
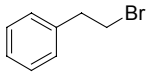
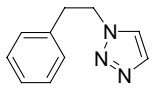
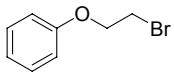
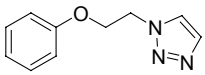
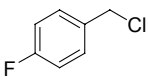
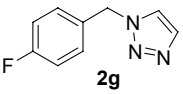
action rate because of the steric hindrance effect with 70% yield at 120 ℃ for 1 h (Table 2, Entry 4).

To elucidate this novel and useful protocol, we proposed a mechanism as shown in Scheme 2. The azide **B** is obtained from aliphatic halides (Cl and Br) (**1**) with iodine anion catalysis in cycle I. Simultaneously, at the initial stage of catalytic cycle II, the dehydrogenation of propiolic acid with Cs_2CO_3 and CuLn produces the copper acetylide carbonate ion **A**. Afterwards, the intermediate **C** is readily formed by the [3＋2] cycloaddition reaction between **A** and **B**. Immediately, intermediate **D** is obtained by electronic transition with CO_2 re-

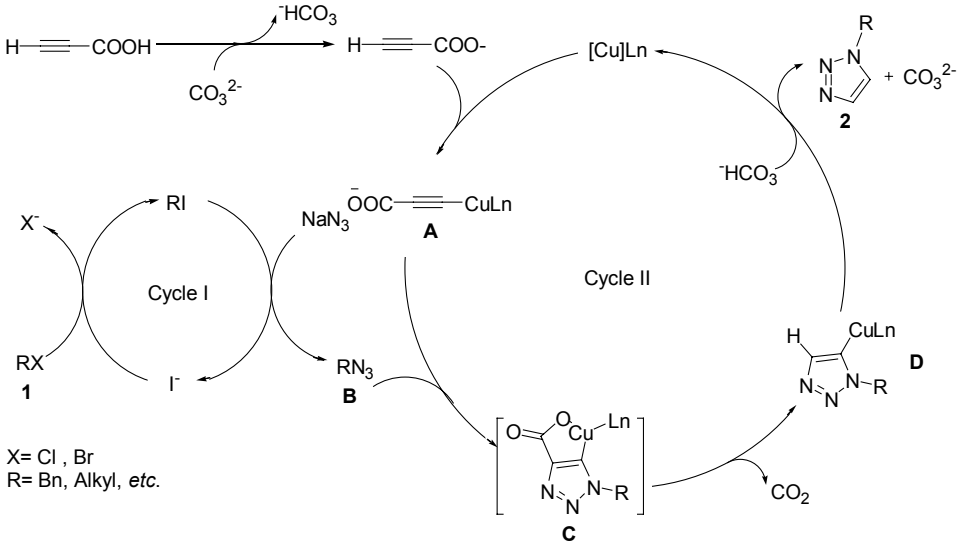
Table 2 Synthesis of 1-monosubstituted aliphatic 1,2,3-triazoles (**2**) from aliphatic halides (Cl and Br) (**1**)



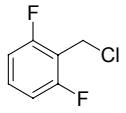
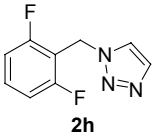
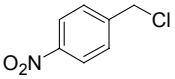
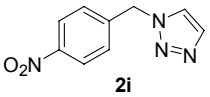
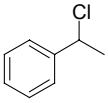
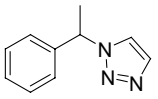
1 **2**

Entry	**1**	**2**	(T/℃)/ (t/h)	Yield of **2**[a]/%
1		 **2a**	100/0.5	90
2		 **2b**	100/0.5	82
3		 **2c**	100/0.5	80
4		 **2d**	120/1	70
5		 **2e**	100/0.5	86
6		 **2f**	100/0.5	85
7		 **2g**	100/0.5	78

Scheme 2 Possible mechanism of the reaction



Continued

Entry	1	2	(T/℃)/(t/h)	Yield of 2[a]/%
8		 **2h**	100/0.5	85
9		 **2i**	100/0.5	75
10		 **2j**	100/0.5	81

[a] Isolated yields.

lease. Eventually, the stable 1-monosubstituted 1,2,3-triazole **2** is formed through protonation.

Conclusions

We developed an easy and useful protocol for the synthesis of 1-monosubstitued 1,2,3-triazoles by click reaction/decarboxylation under mild conditions. Propiolic acid was found to be equivalent to gaseous acetylene and its analogs in the click cycloaddition and provided mild access to 1-monosubstitued aliphatic 1,2,3-triazoles, which are important heterocyclic compounds in medicinal chemistry and materials science.

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