Straightforward and efficient synthesis of triazole derivatives catalyzed by [Cu₂ (BDC)₂ (DABCO)] in water

M.R. Naimi-Jamal, H. Tourani, M. G. Dekamin,

Research Laboratory of Green Organic Synthesis, Department of Chemistry
Iran University of Science and Technology, Tehran 16846, Iran

E-mail: tourani@chem.iust.ac.ir

Keywords:

1, 2, 3-triazoles, green chemistry, Metal–organic frameworks (MOFs)

Abstract:

1,2,3- triazoles can be prepared very fast and in excellent yields by the one pot reaction of acetylenic compound, organic halides and sodium azide by applying of [Cu₂ (BDC) ₂ (dabco)] as heterogeneous catalyst in water as a green solvent.

Introduction:

1,2,3- triazoles are 5-membered heterocyclic compounds that are used in many drugs, dyes, corrosion inhibitors and organic synthesis intermediates [1-6]. Reach to straightforward procedure for synthesis of this important compounds is an attention grabbing issue among organic synthesis researchers.

Many reported reactions have been done by employing homogeneous catalysts involving Copper [7]. Although in many case the desire products are obtained in good yield but many of these method suffer from some of the following disadvantages: Long reaction time, tedious work-up, use of homogeneous catalyst, reflux condition and use of harmful solvents.

Herein we wish to report applying of [Cu₂ (BDC)₂ (DABCO)] as a recyclable catalyst for synthesis of triazole derivatives in water as a green solvent. Low reaction time, mild and non-toxic reaction media and high yield of desire product is other aspects of mentioned procedure.

Result and Discussion

In a typical experiment a mixture of alkyne (1 mmol), halide (1 mmol), NaN3 (1.2 mmol), and 20 mg of catalyst was diluted with 2 ml deionized water as solvent in a 20 ml round-bottom flask. The reaction mixture heated up to 60 C and stirred for an appropriate time indicated in table 1. The reaction progress was monitored by TLC or GC. After reaction completion obtained colloids particle was filtered and dissolved in hot ethyl acetate. The crude was recrystallized from n-hexane:EtOH to afford the pure solid products.

Table 1: Preparation of 1,2,3- triazoles catalysed by Cu-MOF

Entry	Alkyne	Halide	Product	Time (h)	yield	Melting Point	Reference
1	ОН	Br	N N N N N N N N N N N N N N N N N N N	2.5	93	73-75	74-75 [8a]
2		Br	N N N	1.5	98	128-130	128-131 [8b]
3		CI	N N N	2.5	95	128-130	128-131 [8b]
4		Br	N N N	2	92	141-143	143-146 [8b]

Conclusion

In conclusion a mild, efficient and practical catalytic system has been developed for tree component reaction of terminal alkynes, benzyl or aryl halides and sodium azide in water as a green solvent. We found that various starting materials were able to produce exclusively 1,4-disubstituted-1,2,3-triazole regioisomers in high to excellent yield.

Acknowledgment

We acknowledge Iran University of Science and Technology (IUST) for partial financial support of this work.

Reference

- 1. (a) Banday, A. H.; Shameem, S. A.; Ganai, B. A., Antimicrobial studies of unsymmetrical bis-1,2,3-triazoles. Organic and Medicinal Chemistry Letters 2012, 2 (1), 1-7; (b) Boechat, N.; Ferreira, V. F.; Ferreira, S. B.; Ferreira, M. d. L. G.; da Silva, F. d. C.; Bastos, M. M.; Costa, M. d. S.; Lourenço, M. C. S.; Pinto, A. C.; Krettli, A. U.; Aguiar, A. C.; Teixeira, B. M.; da Silva, N. V.; Martins, P. R. C.; Bezerra, F. A. F. M.; Camilo, A. L. S.; da Silva, G. P.; Costa, C. C. P., Novel 1,2,3-Triazole Derivatives for Use against Mycobacterium tuberculosis H37Rv (ATCC 27294) Strain. Journal of Medicinal Chemistry 2011, 54 (17), 5988-5999.
- 2. Aher, N. G.; Pore, V. S.; Mishra, N. N.; Kumar, A.; Shukla, P. K.; Sharma, A.; Bhat, M. K., Synthesis and antifungal activity of 1,2,3-triazole containing fluconazole analogues. Bioorganic & Medicinal Chemistry Letters 2009, 19 (3), 759-763.
- 3. Bakunov, S. A.; Bakunova, S. M.; Wenzler, T.; Ghebru, M.; Werbovetz, K. A.; Brun, R.; Tidwell, R. R., Synthesis and Antiprotozoal Activity of Cationic 1,4-Diphenyl-1H-1,2,3-triazoles. Journal of Medicinal Chemistry 2010, 53 (1), 254-272.
- 4. Alvarez, R.; Velazquez, S.; San-Felix, A.; Aquaro, S.; Clercq, E. D.; Perno, C.-F.; Karlsson, A.; Balzarini, J.; Camarasa, M. J., 1,2,3-Triazole-[2,5-Bis-O-(tert-butyldimethylsilyl)-.beta.-Dribofuranosyl]-3'-spiro-5"-(4"-amino-1",2"-oxathiole 2",2"-dioxide) (TSAO) Analogs: Synthesis and Anti-HIV-1 Activity. Journal of Medicinal Chemistry 1994, 37 (24), 4185-4194.

- 5. Duan, T.; Fan, K.; Fu, Y.; Zhong, C.; Chen, X.; Peng, T.; Qin, J., Triphenylamine-based organic dyes containing a 1,2,3-triazole bridge for dye-sensitized solar cells via a 'Click' reaction. Dyes and Pigments 2012, 94 (1), 28-33.
- 6. González-Olvera, R.; Román-Rodríguez, V.; Negrón-Silva, G. E.; Espinoza-Vázquez, A.; Rodríguez-Gómez, F. J.; Santillan, R., Multicomponent synthesis and evaluation of new 1, 2, 3-triazole derivatives of dihydropyrimidinones as acidic corrosion inhibitors for steel. Molecules 2016, 21 (2), 250.
- 7. (a) Wang, D.; Zhao, M.; Liu, X.; Chen, Y.; Li, N.; Chen, B., Quick and highly efficient coppercatalyzed cycloaddition of organic azides with terminal alkynes. Organic & Biomolecular Chemistry 2012, 10 (2), 229-231; (b) Ji, P.; Atherton, J. H.; Page, M. I., Copper catalysed azidealkyne cycloaddition (CuAAC) in liquid ammonia. Organic & Biomolecular Chemistry 2012, 10 (39), 7965-7969.
- 8. (a) Pathigoolla A, Pola RP, and Sureshan KM. A versatile solvent-free azide—alkyne click reaction catalyzed by in situ generated copper nanoparticles. Applied Catalysis A: General 2013, 453: 151-158,. (b) Xu H, and Sun Z. General Cycloaddition Between a Trimethylsilyl-Capped Alkyne and an Azide Catalyzed by an N-Heterocyclic Carbene-Copper Complex and Pyridine-Biscarboxamide. Advanced Synthesis & Catalysis 2016, 358 (11), 1736-1740,.