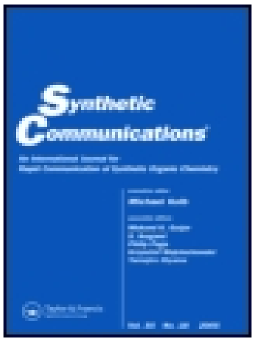

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Oxidation of 1,4-disubstituted-1,2,3-triazoles with H_2O_2–CF_3CO_2H: efficient synthesis of 1,2,3-triazole 3-oxides

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Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Universidad Autónoma del Estado de México, Toluca, Estado de México, Mexico

ABSTRACT
A collection of 1,2,3-triazole-3-oxides was obtained from oxidation of the corresponding 1,4-disubstituted-1,2,3-triazoles mediated by a $H_2O_2–CF_3CO_2H$ system through a simple protocol in good yields showing high efficiency.

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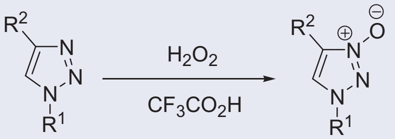
KEYWORDS
Hydrogen peroxide; oxidation; trifluoroacetic acid; 1,2,3-triazole 3-oxides

GRAPHICAL ABSTRACT



Introduction

A new synthetic challenge has emerged as a result of the development of new applications in coupling and cycloaddition reactions for 1,2,3-triazole *N*-oxides used as departure materials,[1–7] which requires more synthetic procedures for these last compounds. Nowadays, the available methods to prepare 1,2,3-triazole *N*-oxides involve the cyclization of α-azoxyoximes,[8] hydrazonoximes,[9–14] and nitroso azoxy compounds.[15] In addition, an alternative approach to obtain 1,2,3-triazole *N*-oxides is based on direct oxidation of 1,2,3-triazole moiety. Described first by Begtrup and Jonsson,[16] this method has the outstanding characteristic that takes a previously synthesized heterocyclic ring as starting material, similar to other heterocyclic systems such as pyridines.[17] However, the reaction times are slow, affording the corresponding product in poor yields, besides only 1-methyl- or unsubstituted 1,2,3-triazoles have been used in this process.

These facts motivated us to investigate thoroughly the oxidation on 1,4-disubstituted-1,2,3-triazoles which are easily available from Copper-catalyzed Azide–Alkyne cycloaddition (CuAAC), the most important click reaction. Initially developed by the Meldal[18]

CONTACT Erick Cuevas-Yañez ecuevasy@uaemex.mx Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Universidad Autónoma del Estado de México, Carretera Toluca-Atlacomulco Km 14.5, Toluca, Estado de México 50200, Mexico.

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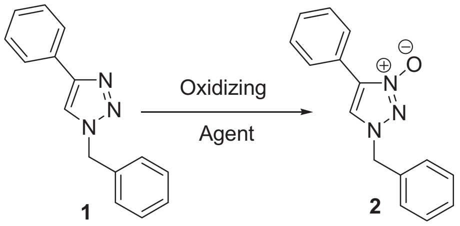


Scheme 1. Synthesis of triazole 3-oxide **2** from 1,2,3-triazole **1**.

Table 1. Synthesis of triazole **2** using oxidzing agents.

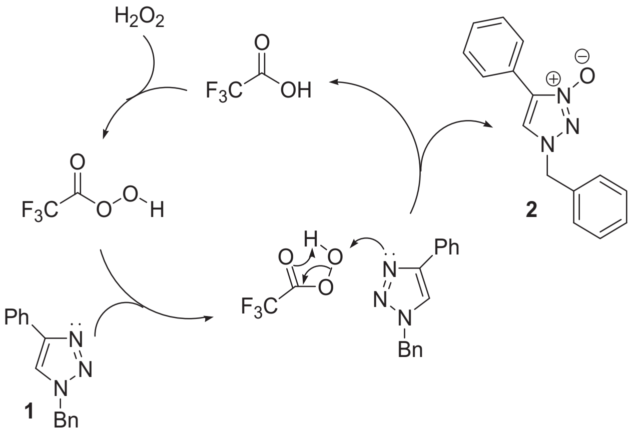
Entry	Oxidzing agent	Solvent	Oxidzing agent ratio	Temperature, °C	Reaction time, h	% Yield
1	mCPBA	AcOEt	1.25 molar equiv.	R.T.	96	5
2	mCPBA	AcOEt	2.5 molar equiv.	R.T.	96	7
3	mCPBA	AcOEt	5.0 molar equiv.	R.T.	96	10
4	mCPBA	AcOEt	1.25 molar equiv.	45	72	10
5	mCPBA	AcOEt	2.5 molar equiv.	45	72	12
6	mCPBA	AcOEt	5.0 molar equiv.	45	72	15
7	mCPBA	AcOEt	1.25 molar equiv.	reflux	72	20
8	mCPBA	AcOEt	2.5 molar equiv.	reflux	72	20
9	mCPBA	AcOEt	5.0 molar equiv.	reflux	72	25
10	H_2O_2	AcOH	1 ml/mmol	reflux	72	25
11	H_2O_2	AcOH	5 ml/mmol	reflux	48	30
12	H_2O_2	AcOH	10 ml/mmol	reflux	48	30
13	H_2O_2-Urea	CF_3CO_2H	5 ml/mmol	40	48	30
14	H_2O_2-Urea	CF_3CO_2H	10 ml/mmol	40	48	35
15	H_2O_2-Urea	CF_3CO_2H	5 ml/mmol	reflux	48	35
16	H_2O_2-Urea	CF_3CO_2H	10 ml/mmol	reflux	48	38
15	H_2O_2	CF_3CO_2H	1 ml/mmol	40	12	60
16	H_2O_2	CF_3CO_2H	5 ml/mmol	40	10	75
17	H_2O_2	CF_3CO_2H	10 ml/mmol	40	5	89
18	H_2O_2	CF_3CO_2H	1 ml/mmol	reflux	5	60
19	H_2O_2	CF_3CO_2H	5 ml/mmol	Reflux	5	65
20	H_2O_2	CF_3CO_2H	10 ml/mmol	Reflux	5	80
21	H_2O_2	No solvent	5 ml/mmol	40	24	0
22	H_2O_2	No solvent	10 ml/mmol	40	24	0
23	H_2O_2	No solvent	5 ml/mmol	reflux	24	0
24	H_2O_2	No solvent	10 ml/mmol	reflux	24	0

and Sharpless–Fokin[19] groups, CuAAC reaction is the biggest source of 1,2,3-triazoles and also the molecular assembly method par excellence.[20–22]

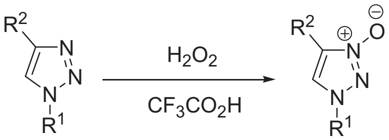
This report summarizes our most recent findings of the oxidation on 1,2,3-triazoles derived from CuAAC reaction aiming to develop a new, mild and efficient procedure to prepare triazole *N*-oxides.

Results and discussion

In order to reproduce and extend initial triazole oxidation conditions described by Begtrup and Jonsson[16] to 1,4-disubstituted-1,2,3-triazoles, 1.25 molar equivalents of *m*-chloroperoxybenzoic acid were added to an AcOEt solution of 1-benzyl-4-phenyl-1,2,3-triazole **1** at room temperature as a model reaction. After 96 h, a compound that was identified as 1-benzyl-4-phenyl-1,2,3-triazole 3-oxide **2** was obtained under these conditions in only 5% yield (Scheme 1). Experiments with different amounts of mCPBA were made in combination with various reaction times and temperatures, the results



Scheme 2. Mechanism of formation of triazole 3-oxide **2** from 1,2,3-triazole **1**.



Scheme 3. Synthesis of 1,2,3-triazole 3-oxides from 1,2,3-triazoles.

summarized in Table 1 show an improvement of reaction yields to 25%. In a sequential series of experiments, other oxidizing agents were compared with mCPBA such as H_2O_2–AcOH,[23,24] H_2O_2–urea–$(CF_3CO)_2O$,[25] and H_2O_2–CF_3CO_2H,[26] which have been used previously in the preparation of pyridine N-oxides. Results in Table 1 state that optimal conditions (entry 17, Table 1) are achieved using a H_2O_2–CF_3CO_2H oxidizing system affording triazole 3-oxide **2** in 88.8% yield, requiring only 5 h to complete the reaction at 40 °C, in contrast to traditional conditions to prepare pyridine *N*-oxides.[23–26]

The use of additives like urea did not increase reaction yields, however, the presence of acidic organic solvent together with the use of H_2O_2 as an oxidizing agent is fundamental in this process. As results in Table 1 indicate (entries 21–24), direct treatment of triazole **1** with H_2O_2 in the absence of an organic acid did not give triazole 3-oxide **2**, recovering only starting material. This feature suggests that organic acid plays a role, not only in solubilizing the triazole but also in the *in situ* generation of a peroxy acid, in our case, trifluoroperoxyacetic acid presumably formed from CF_3CO_2H and H_2O_2.[27] Subsequent trifluoroperoxyacetic acid interaction with the N3 of 1,2,3-triazole provides triazole 3-oxide **2** according to the mechanism proposed in Scheme 2.

The success of this process prompted us to extrapolate the procedure to other 1,2,3-triazoles, which were prepared from adaptations of methodologies described by the groups of Meldal[18] and Cuevas-Yañez.[28,29] From these 1,2,3-triazoles used as starting materials, a simple synthetic protocol was developed and a series of 1,2,3-triazole 3-oxides were synthesized with high efficiency (Scheme 3, Table 2).

All compounds were characterized by the conventional spectroscopic techniques and compound **2** was a crystalline solid which was studied by X-ray crystallography,

Table 2. Synthesis of N-unsubstituted triazoles.Table Layout

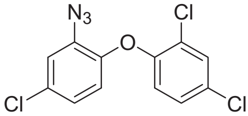
Compound	R^1	R^2	% Yield
2	$PhCH_2$	Ph	88.8
3	Ph	Ph	63.7
4	$4\text{-}CH_3C_6H_4$	Ph	57.7
5	$4\text{-}CH_3OC_6H_4$	Ph	87.5
6	$4\text{-}NO_2C_6H_4$	Ph	49.5
7	$4\text{-}ClC_6H_4$	Ph	72.0
8	$4\text{-}BrC_6H_4$	Ph	75.5
9	$PhCH_2$	$CH_2O(4\text{-}NO_2)C_6H_4$	90.0
10	$PhCH_2$	$CH_2O(2\text{-}Cl)C_6H_4$	84.9
11	Ph	$CH_2O(4\text{-}Cl)C_6H_4$	58.7
12	$4\text{-}CH_3C_6H_4CH_2$	Ph	56.4
13	$2\text{-}BrC_6H_4CH_2$	Ph	85.0
14		$CH_2O(4\text{-}CO_2CH_3)C_6H_4$	67.6

Table 3. Crystal data and structure refinement of X-ray diffraction for compound **2**.

Crystal data	2
Empirical formula	$C_{15}H_{13}N_3O$
Formula weight	251.28
Temperature (K)	100(2)
Wavelength Å	0.71073
Crystal system	Monoclinic
Space group	P 21/c
Unitcell dimensions (Å, °)	–
a	9.2438(3)
b	6.2011(2)
c	21.7126(7)
a	90
β	91.5434(7)
γ	90
Volume ($Å^3$)	1244.15(7)
Z	4
Calculated densityD (mgm^{-3})	1.342
F(000)	528
Absorption coefficient μ (mm^{-1})	2.552
Crystal size (mm^3)	0.440 x 0.171 x 0.080
θ_{max}(°)	25.349
θ_{min}(°)	1.877
h	$-11 \rightarrow 11$
k	$-7 \rightarrow 7$
l	$-26 \rightarrow 26$
Reflections collected	15819
Independent reflection	2282 [R(int) = 0.0163]
Data/restraints/parameters	2282 / 0 / 172
Goodness-of-fit on F^2	1.036
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0327, wR2 = 0.0822$
R indices (all data)	$R1 = 0.0352, wR2 = 0.0842$

confirming the proposed structure for this compound; crystallographic data and structural refinement parameters of **2** are summarized in Table 3. From single-crystal X-ray diffraction analysis, crystal structure of **2** displays a distance between nitrogen and oxygen atoms in N-oxide, N3–O1 = 1.2815 Å and angles O1–N3–N2 (120.0°), O1–N3–C2 (127.31°) and N2–N3–C2 (112.68°), which demonstrate not only the N-oxide formation

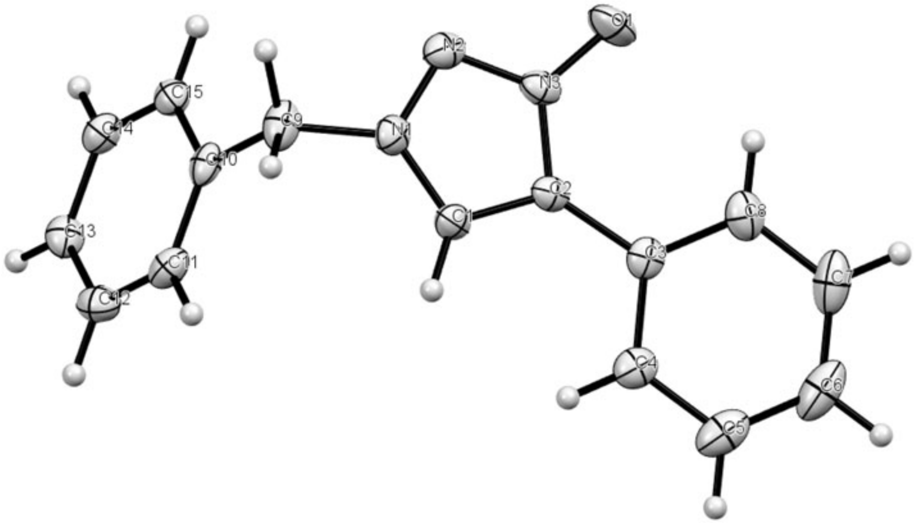
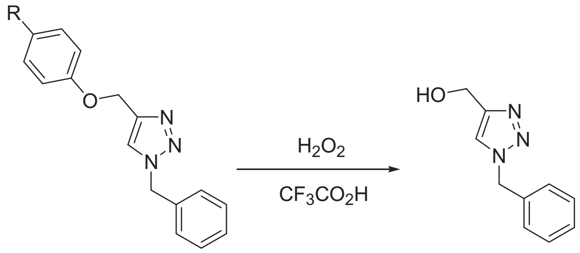


Figure 1. ORTEP diagram and atom labeling system for compound **2**.



15 R=Me
16 R=*i*Pr

17

Scheme 4. Generation of 1-benzyl-1,2,3-triazol-4-yl methanol **17** from compounds **15** and **16**.

in 1,2,3-triazole moiety but also the selectivity of this process in the N3-position of 1,2,3-triazole ring (Figure 1).

On the other hand, this synthesis of 1,2,3-triazole 3-oxides has one important limitation. Some (4-alkyl)phenoxymethyl-1,2,3-triazoles, in our case compound **15** (R = methyl) and compound **16** (R = isopropyl) are converted to 1-benzyl-1,2,3-triazol-4-yl methanol **17** (Scheme 4), probably derived from an oxidative ether cleavage which is described for propargyl and homoallyl ethers using a $Hg(OCOCF_3)_2/HCl/CF_3CO_2H/OsO_4$ oxidizing system,[30] as well as Ag_2O,[31] $RuH_2(CO)(PPh_3)_3$,[32] and IBX,[33] used in oxidative dealkylation of methyl aryl ethers.

The examples described above demonstrate that oxidation of 1,2,3-triazoles with H_2O_2–CF_3CO_2H represents a useful method to synthesize 1,2,3-triazole 3-oxides. In addition, a novel small library of 1,4-disubstituted-1,2,3-triazoles *N*-oxides was easily obtained in good yields and purity levels. As a consequence, a mild methodology was developed with promising applications in synthetic organic chemistry.

Conclusions

In summary, 1,2,3-triazole 3-oxides are easily prepared from 1,4-disubstituted-1,2,3-triazoles which in turn are obtained from CuAAC reaction. This simple synthetic protocol allows a fast access to this kind of compounds, which will increase the research in this area. The simplicity of the method suggests that this route to 1,2,3-triazole 3-oxides will enjoy the widespread application.

Experimental

General remarks

The starting materials were purchased from Aldrich Chemical Co. and were used without further purification. Solvents were distilled before use. Silica plates of 0.20 mm thickness were used for thin layer chromatography. Melting points were determined with a Krüss Optronic melting point apparatus and they are uncorrected. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 300 MHz (Bruker, MA, USA), and a Varian 500 MHz (Varian, CA, USA); the chemical shifts (δ) are given in ppm relative to TMS as internal standard (0.00). For analytical purposes, the mass spectra were recorded on a Shimadzu GCMS-QP2010 Plus (Shimadzu, Kyoto, Japan) in the EI mode, 70 eV, 200 °C through a direct inlet probe. Only the molecular and parent ions (m/z) are reported. IR spectra were recorded on a Bruker TENSOR 27 FT instrument. 1,2,3-triazoles were prepared according to the literature.[18,27,28]

For the X-ray diffraction studies, crystals of compounds **5** and **8** were obtained by slow evaporation of a dilute MeOH solution, and the reflections were acquired with a Bruker APEX DUO diffractometer equipped with an Apex II CCD detector. Three standard reflections every 97 reflections were used to monitor the crystal stability. The structures were solved by direct methods; missing atoms were found by difference-Fourier synthesis, and refined on F2 by a full-matrix least-squares procedure using anisotropic displacement parameters using SHELX-97. Crystallographic data for the structures reported herein have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 1873609 for compound **2**). Copies of available materials can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (facsimile: (44) 01223 336033); e-mail: deposit@ccdc.ac.uk.

Synthesis of 1,2,3-triazole 3-oxides

Typical procedure

A 30% aqueous solution of H_2O_2 (5 mL) was added to a pre-cooled solution of the appropriate 1,2,3-triazole (300 mg) in CF_3CO_2H (4 mL) at 0 °C. The resulting reaction mixture was stirred at room temperature during 1 h and an additional aliquot of 30% H_2O_2 solution (5 mL) was added. The resulting mixture was heated at 40 °C for 2 h. If necessary, 30% H_2O_2 solution (2 mL) was added every hour (maximum 5 h) to total disappearance of starting material monitored by TLC. The mixture was cooled to room temperature and A saturated solution of $NaHCO_3$ (10 mL) was added and the organic layer was extracted with AcOEt (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the final product was purified by column chromatography (SiO_2, hexane/AcOEt 7:3). **1-benzyl-4-phenyl-1,2,3-triazole 3-oxide (2)**. White solid, m. p. 193–195 °C (88.8%). IR (ATR, cm^{-1}): 3056, 2958, 1496, 1466, 1394 (N–O), 1164, 760. ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, 2H), 7.55 (s, 1H), 7.39–7.28 (m, 8H), 5.22 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.8, 129.4, 127.4, 127.0, 127.2, 126.7, 126.7, 124.4, 123.4, 119.8, 53.6. MS [EI+] m/z(%):251 $[M]^+$ (32), 234 $[M–O]^+$ (5), 116 $[M–C_7H_7N_2O]^+$ (23), 102 $[M–C_8H_9N_2O]^+$ (30), 91 $[C_6H_5–CH_2]^+$ (100), 65 $[C_5H_5]+$ (25). HRMS (EI+): for $C_{15}H_{13}N_3O$ calcd. 251.1059, found 251.1063.

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ORCID

Erick Cuevas-Yañez http://orcid.org/0000-0002-9437-637X

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