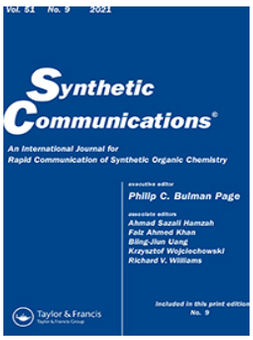

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TBHP/Cu(OAc)$_2$ mediated oxidation of pyrazolines: A convenient method for the preparation of pyrazoles

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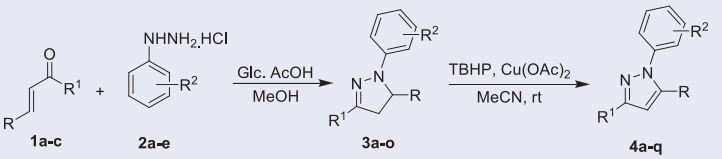
ABSTRACT

An efficient and simple oxidative protocol has been developed for the preparation of pyrazoles from pyrazolines mediated by TBHP/Cu(OAc)$_2$ at room temperature. The present protocol has been successfully applied for the preparation of various pyrazole compounds from heterocyclic pyrazolines.

GRAPHICAL ABSTRACT



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KEYWORDS
Pyrazolines; pyrazoles; Cu(OAc)2; TBHP

Introduction

Pyrazolines[1,2] and pyrazoles[3,4] are important heterocyclic compounds plays an important role in the pharmaceutical and agrochemical industries. Pyrazole scaffold is present in drug molecules such as celecoxib, lonazolac and Viagra. Ruxolitinib, Ipazilide and Fezolamine are furthermore important pyrazole drug molecules are well documented in the literature.[5] Further, pyrazoles act as ligands in coordination chemistry; serve as optical brighteners and UV stabilizers.[6] The most common method for the preparation of pyrazoles involves the condensation of hydrazine derivatives with 1,3-dicarbonyl compounds.[7–9] 1,3-Dipolar addition reactions of diazo compounds with olefins or alkynes and transition-metal catalyzed cross-coupling reactions are other approaches are available for the preparation of pyrazoles.[10,11] Recently, Togo et al. reported the 3-arylpyrazoles by the reaction of arenes with β-bromopropionyl chloride and hydrazines.[12]

Conversely, pyrazolines are important heterocycles have shown a wide range of pharmacological properties such as anticancer, antibacterial, antidepressant activity and anti-WN virus activities.[13–16] Due to the attractive medicinal properties of the pyrazolines various efficient approaches have been developed for the preparation of these

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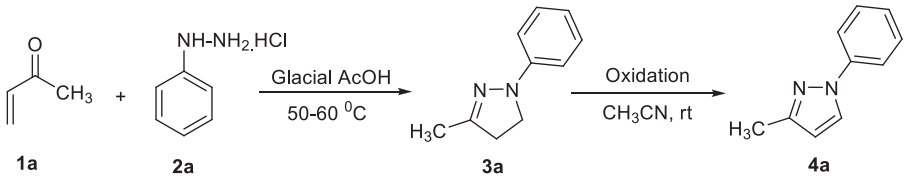
compounds. Matthias Beller et al. reported regioselective synthesis of pyrazolines from phenylhydrazines with 3-butynol in the presence of $Zn(OTf)_2$.[17] Ohno et al. reported poly substituted pyrazolines by three-component, one-pot reaction between aldehydes, hydrazines and alkynes promoted by gold catalyst.[18] Wang et al. achieved pyrazolines by three-component annulations reaction of aldehydes, hydrazines and alkenes catalyzed by $Cu(OTf)_2$.[19] Heng-shan Wang et al. reported series of pyrazolines starting from propargyl alcohols and hydrazines using *t*-BuOK as a catalyst.[20]

The oxidation of pyrazolines to pyrazoles is one of the quite simple method due to its simplicity and versatility. To the best of our knowledge, there is only one oxidative method which is available in the literature for the preparation of 3-methyl-1-phenyl-1*H*-pyrazole from 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazole has been reported by Kost et al. with sulfur at 180–200 °C.[21] Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$) has been used as a mild, efficient and inexpensive oxidant for the aromatization of several 1,3,5-trisubstituted 2-pyrazolines to pyrazoles in acetic acid under microwave irradiation.[22] The oxidation of pyrazolines has been achieved by Liu et al. by the treatment of catalytic amount of HIO_3 or I_2O_5 in water.[23] Yu et al. reported 1,3,5-trisubstituted pyrazolines were oxidized to the corresponding pyrazoles in high yields by molecular oxygen in the presence of catalytic amount of *N*-hydroxyphthalimide (NHPI) and $Co(OAc)_2$ in acetonitrile at room temperature.[24] A simple and high yielding method for the synthesis of tri-substituted pyrazoles via Fe (III) catalyzed aerobic oxidative aromatization of pyrazolines has been reported by Balakrishna and coworkers[25] Off late, Hayashi et al. has reported the catalytic oxidation of pyrazolines by Pd/C under aerobic condition.[26]

However, most of these reagents occupied with several disadvantages such as time consuming, unavailability of the reagents and toxicity due to the presence of certain toxic elements with unsatisfactory yields of the products. Thus, in view of these drawbacks, there is a need to search for better reagents which gives high yields, environmentally safe and commercially available reagents for the conversion of pyrazolines to pyrazoles. As part of our ongoing research, we have reported the synthesis of pyrazoles, triazolyl pyrazoles and chromenopyrazoles.[27–29] Herein, we report the oxidation of pyrazolines to pyrazoles mediated by TBHP/$Cu(OAc)_2$.[30] Further, we have prepared heterocyclic pyrazolines and converted them into pyrazoles conveniently and the results are depicted below.

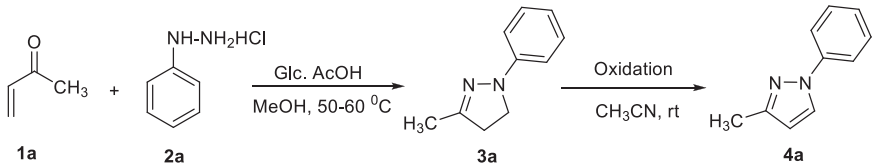
Results and discussion

In an initial experiments, the 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazole **3a** has been chosen as a substrate to establish the reaction conditions. The required substrate **3a** was prepared by the reaction of but-3-en-2-one (**1a**, 1.0 equiv.) with phenylhydrazine hydrochloride (**2a**, 1.0 equiv.) in the presence of glacial AcOH at room temperature (Scheme 1, 50–60 °C).[31] Thus obtained pyrazoline (**3a**, 1.0 equiv.) was subjected for oxidation with catalysts such as NBS, DDQ, CAN and Oxone (1.0 equiv., Scheme 1). The pyrazole compound **4a** procures 50% yield at room temperature and 90% yield under reflux conditions with NBS (Table 1, entries 2–5). The pyrazole compound **4a** was obtained in 80% yield with Oxone but it is a time consuming process. The compound **4a** was



Scheme 1. Preparation of 3-methyl-1-phenyl-1*H*-pyrazole **4a**.

Table 1. Optimization of reaction conditions for the preparation of **4a**.



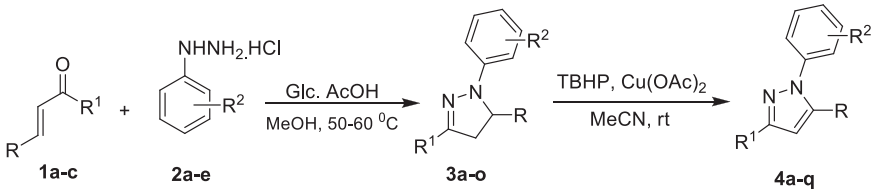
Entry	Catalyst (equiv.)	Peroxide (equiv.)	Solvent	Time (h)	Yield (%)[a,b]
01	AcOH (1.0)	–	MeCN	48	15
02	NBS (1.0)	–	MeCN	24	50
03	DDQ (1.0)	–	MeCN	48	20
04	CAN (1.0)	–	MeCN	48	60
05	Oxone (1.0)	–	MeCN	24	80
06	CuI (1.0)	–	MeCN	24	20
07	$CuCl_2$ (1.0)	–	MeCN	24	82
08	$Cu(OAc)_2$ (1.0)	–	DCM	24	Trace
09	$Cu(OAc)_2$ (1.0)	–	EtOH	24	10
10	$Cu(OAc)_2$ (1.0)	–	MeCN	48	60
11	$Cu(OAc)_2$ (0.3)	–	MeCN	48	40
12	–	TBHP (1.0)	MeCN	24	60
13	–	TBHP (5.0)	MeCN	18	80
14	$Cu(OAc)_2$ (0.3)	TBHP (1.0)	MeCN	24	60
15	**$Cu(OAc)_2$ (0.3)**	**TBHP (5.0)**	**MeCN**	**0.1**	**95**
16	$Cu(OAc)_2$ (0.3)	TBHP (3.0)	MeCN	02	92
17	$Cu(OAc)_2$ (0.15)	TBHP (3.0)	MeCN	04	90
18	$Cu(OAc)_2$ (0.1)	TBHP (2.0)	MeCN	09	90
19	$Cu(OAc)_2$ (0.1)	TBHP (5.0)	MeCN	1.5	92

[a]Room temperature.
[b]Isolated yields.
The bold values indicating the better condition.

characterized by spectral data and compared with literature (see Supporting Information).[21]

Next, the reaction **3a** has been tested with copper catalysts such as CuI, $CuCl_2$ and $Cu(OAc)_2$ (1.0 equiv.) in solvents such as DCM, CH_3CN and C_2H_5OH (Table 1, entry 6–11). The pyrazole **4a** was obtained in very good yields with $CuCl_2$ and $Cu(OAc)_2$ in acetonitrile. The product yield was reduced drastically (40%), when the reaction conducted with 30 mol% equivalent of copper catalyst and the reaction takes long time (Table 1, entry 11). The reaction also conducted with peroxide *tert*-butyl hydroperoxide (TBHP, 70 wt% in water, 1.0 & 5.0 equiv.) in acetonitrile at room temperature (Table 1, entries 12–13). The reaction required 5.0 equivalents of TBHP to complete the reaction which gives **4a**. Then, we have planned the reaction with the combination of $Cu(OAc)_2$ and TBHP. Accordingly, pyrazoline **3a** (1.0 equiv.) was stirred in acetonitrile with catalytic amount of $Cu(OAc)_2$ (30 mol%) in the presence of TBHP (*tert*-butyl hydroperoxide

Table 2. Synthesis of pyrazoles **4a–4q**.



Entry	Compound	R	R^1	R^2	Yield (%)[a]
1	**4a**	H	CH_3	H	91
2	**4b**	H	CH_3	CH_3	78
3	**4c**	H	CH_3	OCH_3	87
4	**4d**	H	CH_3	Cl	92
5	**4e**	H	CH_3	Br	80
6	**4f**	Ph	CH_3	H	80
7	**4g**	Ph	CH_3	CH_3	83
8	**4h**	Ph	CH_3	OCH_3	95
9	**4i**	Ph	CH_3	Cl	92
10	**4j**	Ph	CH_3	Br	85
11	**4k**	Ph	Ph	H	86
12	**4l**	Ph	Ph	CH_3	95
13	**4m**	Ph	Ph	OCH_3	94
14	**4n**	Ph	Ph	Cl	96
15	**4o**	Ph	Ph	Br	95
16	**4p**	Ph	Ph	*m*-CH_3	71
17	**4q**	Ph	*p*-Cl Ph	H	68
18[b]	**4r**	Ph	*p*-OMe Ph	H	–

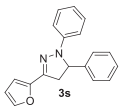
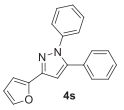
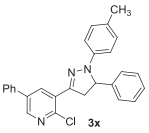
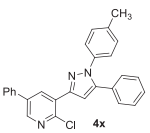
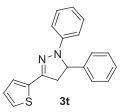
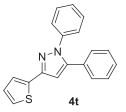
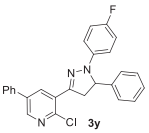
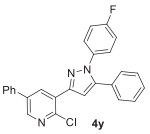
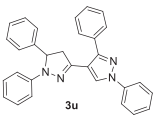
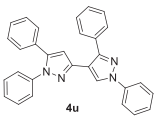
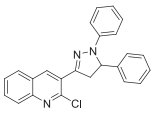
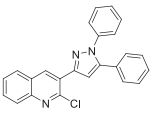
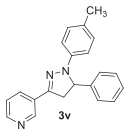
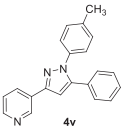
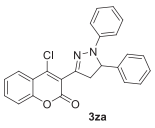
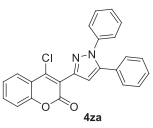
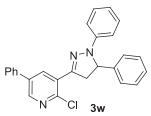
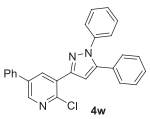
[a]Isolated yields of pyrazoles **4a–q**.
[b]No reaction.

(–70 wt% in water, 1.0 & 5.0 equiv.) at room temperature. Interestingly, the combination of these catalysts worked well and produced pyrazole **4a** obtained 95% yield in 10 min (Table 1, entries 14–15). Further, we have reduced the mole ratio of reagents and the couple of reactions have been conducted with $Cu(OAc)_2$ (10–30 mol%) and TBHP (2.0–5.0 equiv, Table 1, entries 16–19) provided the compound **4a** but this modifications took longer hours (1.5–9 h).

Hence, $Cu(OAc)_2$ (30 mol%) in the presence of TBHP (5.0 equiv.) with acetonitrile at room temperature was found to be better condition to get the compound **4a** with very good yield. This, interesting result prompted us to explore the methodology with several of pyrazolines to pyrazoles and the results are depicted in Table 2. The required pyrazolines **3b–q** were prepared from (*E*)-pent-3-en-2-one **1a**, (*E*)-4-phenylbut-3-en-2-one **1b** and chalcones **1c** with phenylhydrazine hydrochlorides **2a–e** in the presence of glacial acetic acid at 50–60 °C in methanol. The pyrazolines **3b–q** are known compounds and compared with literature.[17,32–34] Thus, obtained pyrazolines **3b–q** were subjected for oxidation with $Cu(OAc)_2$ (30 mol%) in presence of TBHP (5.0 equiv.) in acetonitrile at room temperature. These reactions were undergone facilely and provided the pyrazoles **4a–q** (Table 2). These pyrazoles **4a–q** are known compounds and compared with literature. [17,21,32,35–39]

Having achieved the preparation of pyrazoles **4a–q**, the method has been applied to another set of pyrazoline compounds to show the diversity of present protocol. The

Table 3. Oxidation of pyrazolines **3s–3za** to pyrazoles **4s–4za**.

Entry	Substrate	Product	Time	Yield (%)[a]	Entry	Substrate	Product	Time	Yield (%)[a]
1	 **3s**	 **4s**	2 h	94	6	 **3x**	 **4x**	18 h	27
2	 **3t**	 **4t**	3 h	93	7	 **3y**	 **4y**	20 h	77
3	 **3u**	 **4u**	24 h	94	8	 **3z**	 **4z**	3 h	40
4	 **3v**	 **4v**	5 h	45	9	 **3za**	 **4za**	1 h	63
5	 **3w**	 **4w**	4 h	52					

[a]Isolated yields of pyrazoles **4s–za.**

pyrazolines such as furan (**3s**), thiophene (**3t**), pyrazole (**3u**), pyridyl (**3v**), 2-chloropyridyl (**3w–y**), quinoline (**3z**), coumarin (**3za**) have been prepared from corresponding carboxaldehydes with phenylhydrazine hydrochlorides **2a–c** as per the established experimental procedure (see Supporting Information). The pyrazoles **3s–t**, **3v–y** are known compounds and compared with literature.[40–43] The pyrazolines **3u**, **3z** and **3za** are unknown and characterized by spectral data (see Supporting Information). Thus obtained pyrazoline compounds **3s–za** were subjected for the oxidation under the optimized conditions which are provided series of corresponding pyrazoles **4s–za**. The pyrazoles **4s–t**, **4v** are known compounds and compared with literature.[41,43–45] The compounds **4u, 4w–za** are unknown and characterized by spectral data and incorporated in Supporting Information (Table 3).

Conclusion

In conclusion, an efficient and inexpensive method has been developed for the oxidative aromatization of pyrazolines to pyrazoles in the presence of catalytic amount of $Cu(OAc)_2$ with TBHP (70 wt% in water) at room temperature. The procedure offers several advantages such as simple experimental procedures, utilization of commercially available catalyst with good yields which make this an attractive alternate approach for the preparation of pyrazoles.

Experimental section

Procedure for the preparation of 3-methyl-1-phenyl-1H-pyrazole (4a)

$Cu(OAc)_2$ (10 mol%) was added to a stirred solution of 4,5-dihydro-1*H*-pyrazole (**3a**, 1.0 mmol) in acetonitrile at room temperature and followed by TBHP (*tert*-butyl hydroperoxide (70 wt% in water, 5.0 mmol). The reaction mixture was stirred at the same temperature and the reaction was monitored by TLC. After completion of the reaction (10 min), the solvent was removed under reduced pressure and subjected for the column chromatography purification using silica gel (60:120, ethyl acetate/hexane 2:98) afforded 1*H*-pyrazole (**4a**) as colorless solid. The pyrazoles **4b–za** were prepared from corresponding pyrazolines **3b–za** under optimized reaction conditions.

Supporting Information (copies of ^{1}H, ^{13}C NMR and HRMS spectra of all the prepared compounds) associated with this article can be found through the "Supplementary Content" section of this article's webpage.

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