Catalysis Letters (2020) 150:2068–2075
https://doi.org/10.1007/s10562-020-03109-y

Cu-Catalyzed Oxidative-Reaction of Tosylmethylisocyanide and Benzyl Alcohols: Efficient Synthesis of 4-(*tert*-butylperoxy)-5-aryloxazol-2(3*H*)-ones and 5-Aryloxazol-2(5*H*)-ones

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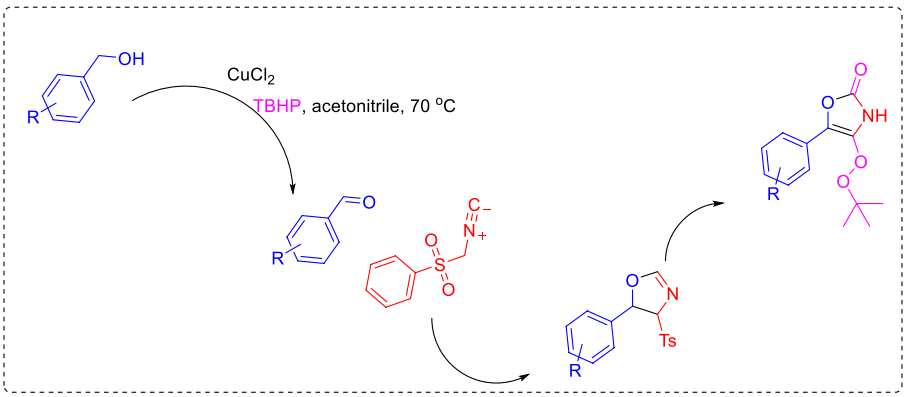
Received: 13 November 2019 / Accepted: 11 January 2020 / Published online: 20 January 2020

Abstract
Herein, a novel copper-catalyzed reaction of tosylmethylisocyanide (TosMIC) with benzyl alcohols has been developed using *tert*-butyl hydroperoxide (TBHP) for the first time. The reaction involves the in-situ oxidation of benzyl alcohol to corresponding benzaldehyde, followed by sequential formal [3+2] cycloaddition/radical addition/ring oxidation reactions, and provides an efficient method for the construction of 4-(*tert*-butylperoxy)-5-aryloxazol-2(3*H*)-ones from readily available starting materials. Replacement of TBHP with H_2O_2 led to the production of 5-aryloxazol-2(5*H*)-ones in good yields.

Graphic Abstract
Tandem oxidative Van Leusen reaction: efficient three-component approach for the synthesis of 4-(tert-butylperoxy)-5-aryloxazol-2(3H)-ones and 5-phenyloxazol-2(5H)-one for the first time.



Keywords Tosylmethylisocyanide · Benzyl alcohols · Copper-catalyzed · *tert*-Butyl hydroperoxide · 4-(*tert*-Butylperoxy)-5-aryloxazol-2(3*H*)-ones

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-020-03109-y) contains supplementary material, which is available to authorized users.

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1 Introduction

The construction of distinct types of complex molecular structures efficiently and economically is an important goal in organic synthesis and chemical biology [1]. Multi-component reactions (MCRs) have proven to be the most useful strategy to reach this goal [2–4]. Along these lines, isocyanide-based reactions, such as Passerini and Ugi reactions,

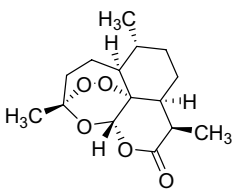
[5, 6] Groebke-Blackburn-Bienymé (GBB), and Van Leusen reactions [7–12] are exciting methods for the synthesis of amino acids, peptides, and peptide-like molecules, as well as diverse sets of heterocyclic species such as oxazoles and imidazoles [13–16]. With the patterning of the GBB and Van Leusen reactions, numerous examples of isocyanides formal [1+4] and [3+2] reactions have been developed [17–21]. In these isocyanides based cycloaddition reactions, isocyanides act as a C1 or 1,3-dipole source.

Five and six-membered heterocyclic compounds like oxazolones have occupied enormous significance in the field of medicinal chemistry [22–24] and usefulbuilding block in manywellestablishedmarketeddrugs such asfurazolidone, rilmenidine, oxaprozin, nitrofurantoin, andespeciallylinezolid, whichisactiveagainstmethicillin-resistant *Staphylococcusaureus*. Oxazolones have not only played an essential role in the synthesis of several organic molecules, including amino acids [25], amino alcohols [26], thiamine, amides, peptides, and polyfunctional compounds [27–29], but the oxazolone nucleus has various pharmacological activities as clinical and therapeutic agents [30, 31].

Some biologically interesting natural products possessing peroxide structure motifs is substantial and still growing [32]. Many peroxy natural products display antitumor, anticancer, and antiparasite activities, which are attributed to the propensity of the peroxide to initiate radical reactions in an iron-rich environment [33]. Furthermore, natural products containing peroxide moiety such as artemisinin are clinically relevant to antimalarial drugs (Fig. 1) [34]. In recent decades, various methods for the direct C–H bond peroxidation of amides of α, β-unsaturated substrate have been reported [35–37].

Recently, various reactions have been reported using oxazoles, such as direct C–H amination or arylation under oxidation conditions [38-42]. On the basis of these publishedworks and in continuation of our interest in the oxidation of organic substrate [43, 44], and design the isocyanide-based multi-component reactions [45, 46], herein, we aimed to redesign the synthesis of 5-phenyl-4-tosyl-4,5-dihydrooxazole via the tandem oxidative cycloaddition reaction of TosMIC with benzyl alcohols through a one-pot procedure in the presence of copper as catalyst and *TBHP* as an oxidant, in spite of the 1,3-dipolar reaction of TosMIC with aldehydes have been extensively studied.

Fig. 1 Artemisinin structure



2 Experimental Section

2.1 Materials and Methods

The melting point of the products has been measured using the 9100 electrothermal device and not corrected. The IR spectra of products were recorded by Thermo Nicolet Nexus 470 FT-IR spectrophotometer. ^{1}H NMR, ^{13}C NMR spectra were recorded with the AVUCE BRUK-ERDRX-300. MS spectra were recorded by Agilent Technology 5973 Network Mass Selective Detector (EI) 70 eV. Elemental analyses were performed using a Heraeus CHN–O–Rapid analyzer. The materials required and the solvents used in the reactions were purchased from Merck, Fluka and Acrose companies, and were used without purification.

2.2 Typical Procedure for the Synthesis of 4-(*tert*-butylperoxy)-5-(4-methoxyphenyl) oxazol-2(3*H*)-one3a

4-methoxybenzyl alcohol **1** (0.27 g, 2.00 mmol) and TBHP (0.40 g, 4.00 mmol) were added to mixture of acetonitrile (3.00 mL) and $CuCl_2$ (0.007 g, 0.05 mmol). The reaction mixture was stirred for 6 h at 70 °C. Next, TosMIC (0.20 g, 1.00 mmol) and piperidine (0.09 g, 1 mmol) were poured into the reaction flask and stirred for 15 min, and then acetic acid (0.06 g, 1 mmol) was added. After that, this mixture was heated to 70 °C for more 6 h. At the end of reaction, monitored by thin layer chromatography (TLC), the reaction mixture was diluted with water (5.00 mL) and extracted with ethyl acetate (3 × 2 mL), the resulting solution was purified by flash chromatography (ethyl acetate: *n*-hexane, 1:10).

***3a*:** Colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 1.63 (9H, s, $C(CH_3)_3$), 3.90 (3H, s, OCH_3), 6.93–7.00 (2H, m, Ar), 7.93–7.98 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 28.1, 55.5, 55.6, 84.4, 114.2, 131.2, 132.4, 164.1, 164.8, 185.5. MS for $C_{14}H_{17}NO_5^+$: calcd.$[M]^+$ 279.1, found 279.1. Elemental Analysis: calcd. C, 60.21, H, 6.14, N, 5.02, found C, 60.21, H, 6.15, N, 5.03.

***3b*:** Colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 1.63 (9H, s, $C(CH_3)_3$), 3.96 (2H, s, OCH_2Ph), 7.28–7.44 (3H, m, Ar), 7.54–7.57 (2H, m, Ar), 7.67–7.70 (1H, m, Ar), 8.14–8.16 (1H, m, Ar), 8.22–8.24 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 28.9, 55.2, 56.3, 85.1, 115.1, 123.3, 126.4, 131.6, 133.3, 141.8, 162.7, 165.0, 185.7. MS for $C_{20}H_{21}NO_5^+$: calcd.$[M]^+$ 355.1, found 355.1. Elemental Analysis: calcd. C, 67.59, H, 5.96, N, 3.94, found C, 67.59, H, 5.97, N, 3.95.

***3c*:** Colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 1.63 (9H, s, $C(CH_3)_3$), 7.51 (2H, d, $J = 15$ Hz,

Ar), 7.94–7.97 (2H, d, $J = 15$ Hz, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 28.4, 55.1, 85.5, 127.7, 129.5, 130.6, 133.8, 150.2, 164.9, 184.7. MS for $C_{13}H_{14}ClNO_4^+$: calcd. $[M]^+$ 283.1, found 283.1. Elemental Analysis: calcd. C, 55.04, H, 4.97, N, 4.94, found C, 55.04, H, 4.96, N, 4.95.

***3d*:** Colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 1.63 (9H, s, $C(CH_3)_3$), 6.98 (2H, dd, $J_o = 15$ Hz, $J_p = 5$ Hz,Ar), 7.96 (2H, dd, $J_o = 15$ Hz, $J_p = 5$ Hz, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 28.7, 55.7, 85.1, 123.5, 127.7, 129.5, 163.7, 169.0(d, $J = 40$ Hz), 184.9. MS for $C_{13}H_{14}FNO_4^+$: calcd.$[M]^+$ 267.1, found 267.1. Elemental Analysis: calcd. C, 58.42, H, 5.28, N, 5.24, found C, 58.42, H, 5.30, N, 5.26.

***3e*:** Colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 1.60 (9H, s, $C(CH_3)_3$), 3.87 (6H, s, $2OCH_3$), 6.43–6.62 (2H, m, Ar), 7.90–7.94 (1H, m, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 28.1, 55.6, 55.6, 55.7, 84.4, 98.6, 104.4, 110.3, 132.4, 164.1, 164.8, 166.0, 185.8. MS for $C_{15}H_{19}NO_6^+$: calcd.$[M]^+$ 309.1, found 309.1. Elemental Analysis: calcd. C, 58.25, H, 6.19, N, 4.53, found C, 58.25, H, 6.20, N, 4.53.

***3f*:** Colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 1.58 (9H, s, $C(CH_3)_3$), 2.28 (6H, s, $2CH_3$), 2.31 (3H, s, CH_3), 6.88 (1H, s, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 28.3, 29.9, 31.7, 55.46, 85.44, 127.3, 130.3, 133.1, 137.9, 164.6, 184.5. MS for $C_{16}H_{21}NO_4^+$: calcd.$[M]^+$ 291.1, found 291.1. Elemental Analysis: calcd. C, 65.96, H, 7.27, N, 4.81, found C, 65.96, H, 7.28, N, 4.81.

***B*:** Orange powder. 202–204 °C.^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm): H 2.43 (3H, s, CH_3), 5.62 (1H, d *J* 4.8 Hz, CH), 6.15 (1H, d *J* 4.8 Hz, CH), 7.47–7.56 (4H, m, arom), 7.78 (1H, s, NCHO), 7.83 (2H, d, *J* 7.5 Hz, arom), 8.28 (2H, d, *J* 7.5 Hz, arom); ^{13}C NMR (DMSO-d_6, 75 MHz, δ, ppm): C 21.6, 78.1, 91.3, 124.5, 127.5, 129.2, 129.9, 130.3, 145.2, 145.9, 148.2, 160.4.

***C*:** Yellow solid. 184–187 °C.^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm):H 7.99 (2H, d, *J* 8.7 Hz, arom), 8.02 (1H, s, CCHN), 8.33 (2H, d, *J* 8.7 Hz, arom), 8.62 (1H, s, NCHO); ^{13}C NMR (DMSO-d_6, 75 MHz, δ, ppm): C 125.0, 125.4, 126.1, 133.7, 147.3, 153.9, 156.4.

***4a*:** Colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 3.90 (3H, s, OCH_3), 5.32 (1H, s, OCH), 6.97 (2H, br, Ar), 7.28 (1H, s, CH=N), 7.90 (2H, br, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 55.6, 90.4, 114.2, 125.6, 131.2, 164.0, 164.1, 164.8. MS for $C_{10}H_9NO_3^+$: calcd.$[M]^+$ 191.1, found 191.2. Elemental Analysis: calcd. C, 62.82, H, 4.75, N, 7.33 found C, 62.82, H, 4.76, N, 7.34.

4b: Colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 3.70 (3H, s 2 OCH_3), 6.13 (1H, s, OCH), 6.72 (1H, d, $J = 9$ Hz, Ar), 7.03 (1H, s, Ar), 7.35 (1H, d, $J = 9$ Hz, Ar), 8.85 (1H, s, NCH); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 56.7, 57.4, 92.5, 101.0, 111.0, 118.1, 128.4, 157.3, 161.3, 163.9, 166.6.

4c: Pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): H 3.66 (3H, s, NCH_3), 3.69 (3H, s, NCH_3), 6.12 (1H, s, OCH), 7.35 (2H, d, $J = 9$ Hz, Ar), 7.76 (1H, d, $J = 9$ Hz, Ar),8.87 (1H, s, NCH); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): C 42.3, 91.3, 115.8, 128.8, 131.0, 154.3, 164.5, 165.7.

3 Results and Discussion

The reaction of TosMIC**1** and 4-methoxybenzyl alcohol **2a** was chosen as a model reaction to optimize the reaction conditions. Initially, TosMIC and 4-methoxybenzyl alcohol were added to the acetonitrile in the presence of TBHP and piperidine and heated at 70 °C in the presence of $CuCl_2$ for 6 h. After the formation of 5-(4-methoxyphenyl)-4-tosyloxazolidin-2-one **A** as the first intermediate, acetic acid was added to the reaction mixture. To our surprise, after 6 h, the product 4-(*tert*-butylperoxy)-5-(4-methoxyphenyl)oxazol-2(3*H*)-one **3a** was produced (Scheme 1).

The structure of product **3a** was assigned from its elemental analyses as well as ^{1}H NMR, ^{13}C NMR, and mass spectral data. The ^{1}H NMR spectrum of **3a** exhibited two singles signals at 1.63 and 3.90 ppm corresponding to *t*-butyl and methoxy groups and two multiple peaks for four aromatic hydrogens at 6.93–7.00 and 7.91–7.98 ppm. In addition, ^{1}H-decoupled ^{13}C NMR spectrum of **3a** showed 10 distinct resonances in agreement with the proposed structure. The mass spectrum, as expected, confirms its molecular weight.

The model reaction was carried out in dichloromethane, toluene, *p*-xylene, and under solvent-free conditions to evaluate the effect of solvents. As Table 1 indicates, toluene and *p*-xylene were found to be suitable solvents. The reaction yield was low under solvent-free conditions, and in dichloromethane, no reaction took place. Also, the catalytic activity of various copper salts, nickel, and cobalt chlorides was

Scheme 1 Synthesis of4-(*tert*-butylperoxy)-oxazolone**3a**

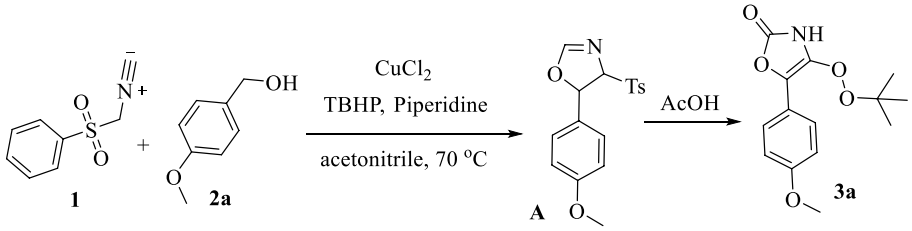


Table 1 Optimized the reaction conditions

Entry	Catalyst	Solvent	Yield (%)
1	$CuCl_2$	Acetonitrile	71
2	$CuCl_2$	Dichloromethane	0
3	$CuCl_2$	Toluene	62
4	$CuCl_2$	p-Xylene	68
5	$CuCl_2$	Solvent-free	40
6	$Cu(OAc)_2$	Acetonitrile	58
7	CuI	Acetonitrile	67
8	CuBr	Acetonitrile	25
9	$NiCl_2$	Acetonitrile	36
10	$CoCl_2$	Acetonitrile	68

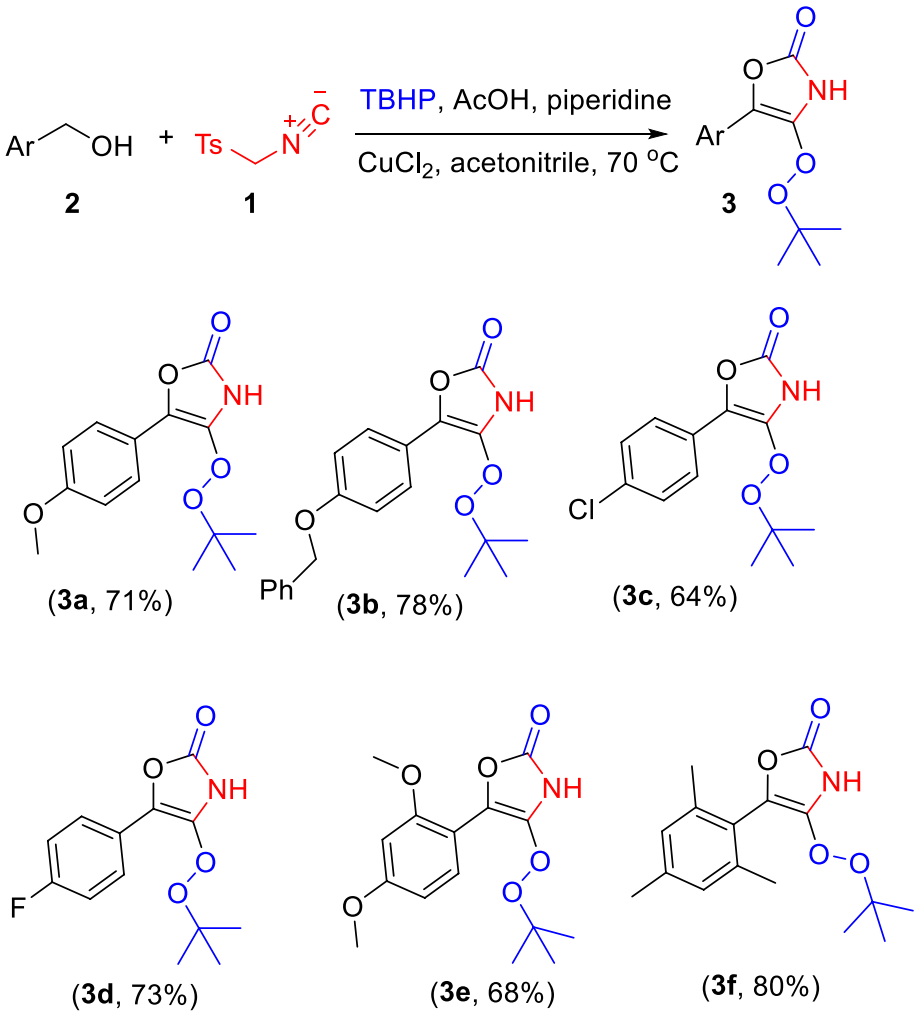
TosMIC (1 mmol), 4-methoxybenzyl alcohol (2 mmol), TBHP (4 mmol), cat. (5 mol%), piperidine (1 mmol) at 70 °C for 12 h

investigated. As shown in Table 1, the optimum conditions for the reaction were obtained using $CuCl_2$ in acetonitrile as a solvent at 70 °C.

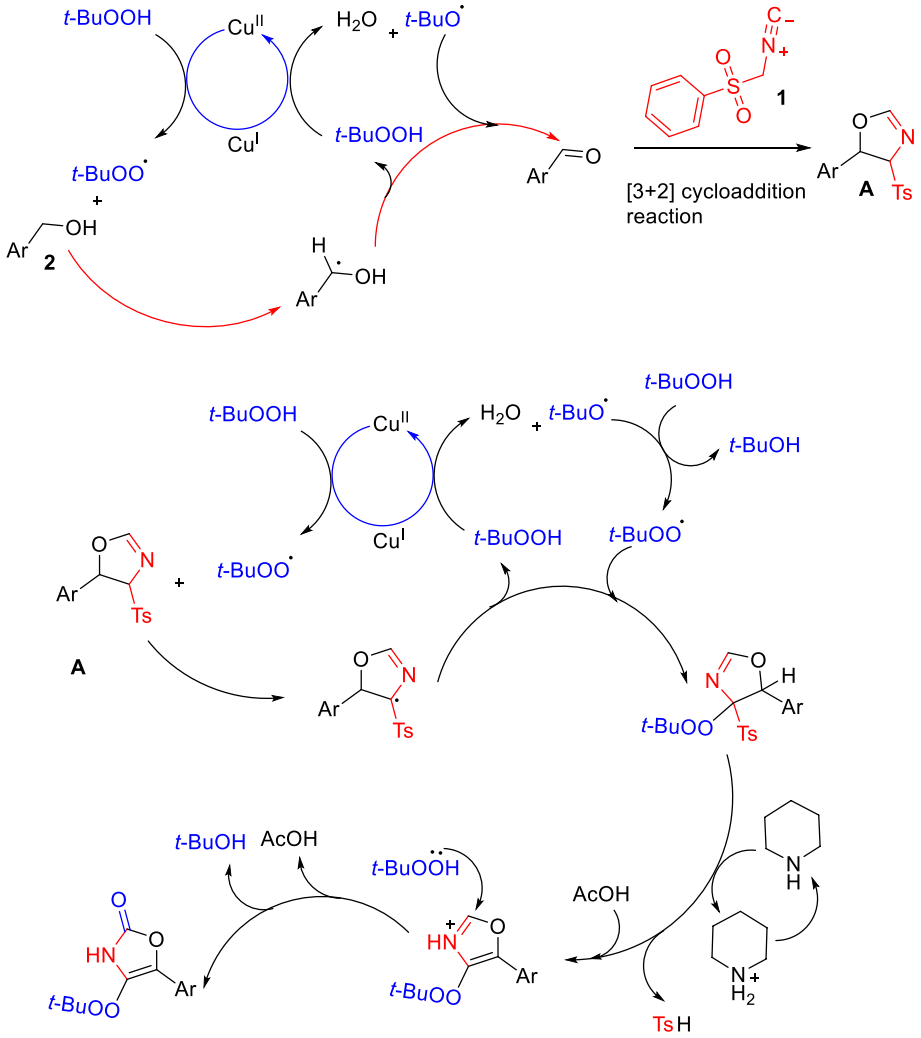
Some benzyl alcohols were examined under the same reaction conditions to investigate the comprehensiveness and limitation of the reaction. In the case of the electron releasing groups and halogens such as 4-benzyloxy, 1,4-dimethoxy, 2,4,6-trimethyl, 4-Cl, and 4-F, the reaction has resulted in good yields (Table 2). The structure of the products was deduced from their mass, ^1H, and ^{13}C NMR spectral data and as well as elemental analysis. In addition, the existence of active O_2 in the structure of the compounds **3a** was confirmed by iodometric titration [47].

According to related works for the oxidation of alcohols by TBHP in the presence of Cu(II), [48, 49] the possible mechanism for the oxidation of 4-methoxybenzyl alcohol is presented in Scheme 2. In the second step of the tandem oxidative reaction, compound **A** formed through the Van Leusen reaction. Then, intermediate **A** undergoes a radical addition of TBHP [50] and oxidizes to product **3a**. It is prominent to note, the elimination of TsH maybe takes place immediately after production of **A**, but there is no report for radical addition of TBHP radical on sp^2 carbons.

Table 2 Synthesis of 4-(*tert*-butylperoxy)-oxazolones**3**



Scheme 2 Proposed mechanism

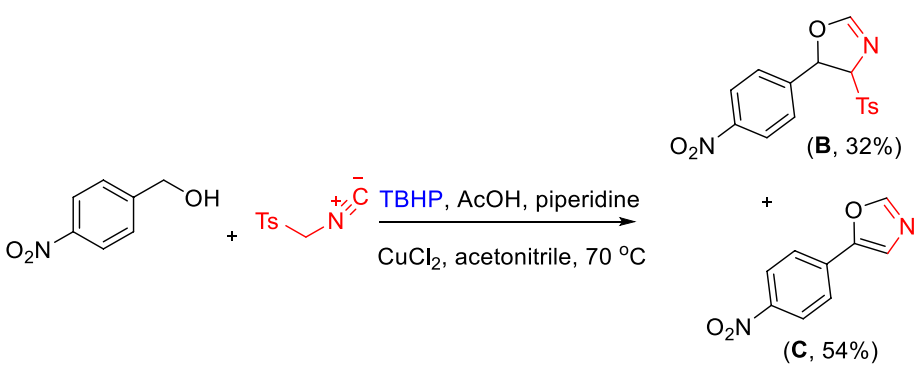


Accordingly, the elimination of TsH has occurred after addition of radical TBHP.

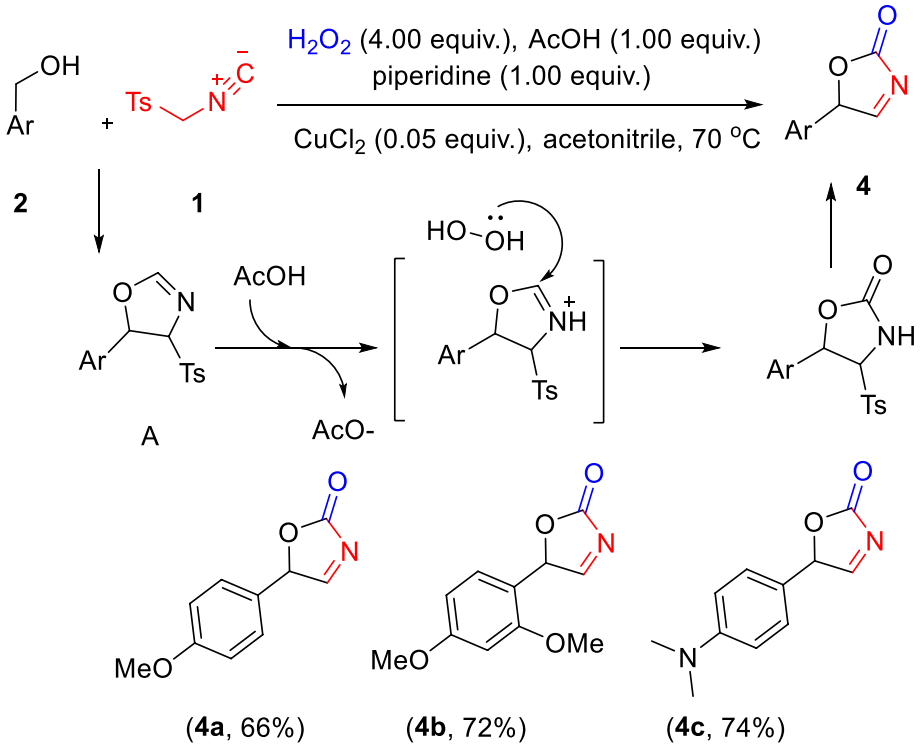
To clarify the proposed mechanism, the intermediate **A** was synthesized and reacted with the same amounts of TBHP, $CuCl_2$, piperidine and acetic acid in acetonitrile at 70 °C. Interestingly, this reaction provided **3a** in 74% yield after 6 h.

In the case of 4-nitrobenzyl alcohol with an electron-withdrawing group, a mixture of 5-(4-nitrophenyl)-4-tosyl-4,5-dihydrooxazole **B** and 5-(4-nitrophenyl)oxazole **C** was obtained (Scheme 3). The formation of a radical center at the vicinity of Ts group may be difficult by the induction effect of the nitro group, which causes radical production of the carbon that is connected to oxygen (see

Scheme 3 The reaction of 4-nitrobenzyl alcohol with TosMIC



Scheme 4 Effect of hydrogen peroxide on the reaction



the last step in Scheme 2), or formation of a complex of the nitro group with Cu and TBHP [51].

The effect of other oxidants such as molecular oxygen and hydrogen peroxide in the reaction was studied, too. The reaction did not precede using molecular oxygen as an oxidant. However, hydrogen peroxide affected on the reaction and provided 5-aryl-oxazol-2(5*H*)-one **4** as a new compound (Scheme 4). Formation of compound **4** may be realized by the generation of an intermediate like **A**, which the imine bond in the structure was oxidized to amide group by the effect of acetic acid and hydrogen peroxide. Subsequently, TsH was removed by the influence of piperidine or reaction temperature (Scheme 4). The structure of the products was deduced by spectral data and a previous report for the synthesis of the same compounds [52]. The elucidation of the product structure is discussed here for **4a** as a representative example. The mass spectrum of 4a shows the expected molecular-ion peak at m/z 191. The ^{1}H NMR spectrum of **4a** consists of a signal for the OMe (3.90 ppm) and one singlet for the benzylic CH group (5.32 ppm) which not exchange with D_2O. The aromatic hydrogen atoms give rise to characteristic signals in the aromatic region of the spectrum. The ^{1}H-decoupled ^{13}C NMR spectrum of **4a** showed 8 distinct signals, in agreement with the proposed structure.In the ^{13}C NMR spectrum, the OMe group appeared in 55.6 ppm. A signal at 90.4 ppm is related to benzylic CH group.

4 Conclusions

In conclusion, we have investigated the oxidative Van Leusen reaction in the presence of Cu(II) using TBHP and developed an efficient three-component approach for the synthesis of 4-(*tert*-butylperoxy)-5-phenyloxazol-2(3*H*)-ones and 5-aryl-oxazol-2(5*H*)-one for the first time. This reaction led to the construction of one carbon–carbon bonds and three carbon–oxygen bonds in a one-pot procedure. The potential uses of this approach in the synthesis of bioactive compounds may be remarkable since the products share structural of the biologically active molecules. Further studies and synthetic applications of this chemistry are in progress in our laboratory.

Acknowledgements We gratefully acknowledge financial support from the Research Council of Shahid Beheshti University.

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