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Highly Efficient Cu(I)-Catalyzed Oxidation of Alcohols to Ketones and Aldehydes with Diaziridinone

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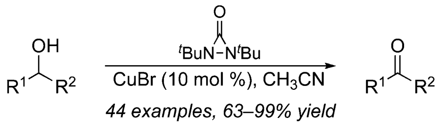
ABSTRACT



A novel and efficient Cu(I)-catalyzed oxidation of alcohols has been achieved with di-*tert*-butyldiaziridinone as the oxidant under mild conditions. A wide variety of primary and secondary alcohols with various functional groups can be oxidized to aldehydes and ketones in high yields. The reaction proceeds under neutral conditions making it compatible with acid- or base-sensitive substrates, and it is amenable to gram scale.

The oxidation of alcohols to the corresponding ketones or aldehydes is one of the most fundamental and widely utilized transformations in organic synthesis.[1] Various effective reagents and methods have been developed, including chromium reagents,[2] manganese(IV) oxide,[3] activated DMSO,[4] hypervalent iodine reagents,[5] ruthenium reagents,[6] osmium(VIII) oxide,[7] metal-[8−16] or TEMPO-catalyzed[17,18] oxidation, etc. Due to the importance of this transformation in organic synthesis, the development of

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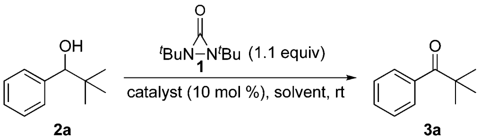
new, efficient, safe, and mild oxidation processes is still highly desirable and valuable.

We have previously reported that readily prepared di-*tert*-butyldiaziridinone (**1**)[19,20] is a highly effective nitrogen source for the Pd(0)[21] and Cu(I)[22] catalyzed diamination of olefins. In our efforts to further explore the reactivity of diaziridinone and expand its synthetic utility, we have found that alcohols can be efficiently oxidized to the corresponding carbonyl compounds with di-*tert*-butyldiaziridinone (**1**) in the presence of a Cu(I) catalyst under mild reaction conditions. Herein we wish to report our preliminary studies on this subject.

Table 1. Studies on Reaction Conditions[a]



entry	catalyst	solvent	time (h)	conv (%)[b]	yield (%)[c]
1	CuCN	$CDCl_3$	4	0	–
2	CuI	$CDCl_3$	4	47	38
3	CuCl	$CDCl_3$	4	93	78
4	CuBr	$CDCl_3$	4	97	87
5	$CuBr_2$	$CDCl_3$	4	57	49
6	CuBr-P(^{n}Bu)$_3$ (1:1)	$CDCl_3$	4	65	53
7	CuBr	CH_2Cl_2	4	99	82
8	CuBr	DCE	4	99	80
9	**CuBr**	$\mathbf{CH_3CN}$	**2**	**100**	**94**
10	CuBr	DMF	4	42	29
11	CuBr	THF	4	89	79
12[d]	none	CH_3CN	24	0	–
13[e]	CuBr	CH_3CN	24	0	–

[a] All reactions were carried out with alcohol **2a** (0.30 mmol), di-*tert*-butyldiaziridinone (**1**) (0.33 mmol), and Cu catalyst (0.030 mmol) in solvent (0.6 mL) at rt under Ar unless otherwise stated. [b] The conversion was based on alcohol **2a** and determined by the ^{1}H NMR. [c] Isolated yield. [d] The reaction was carried out at rt or 60 °C under Ar. [e] The reaction was carried out at 60 °C under air in the absence of **1**.

Our initial studies were carried out with 2,2-dimethyl-1-phenyl-1-propanol (**2a**) as a test substrate. Several copper catalysts were first screened in $CDCl_3$ at room temperature (Table 1, entries 1–5). High conversions were obtained with CuCl and CuBr (Table 1, entries 3 and 4). In the case of CuBr, ketone **3a** was isolated in 87% yield. The yield decreased to 53% when P(^{n}Bu)$_3$ was added (Table 1, entry 6). Among the solvents examined (Table 1, entries 7–11), CH_3CN gave the highest yield (94%) for ketone **3a** (Table 1, entry 9). No reaction occurred in the absence of the Cu catalyst (Table 1, entry 12) or di-*tert*-butyldiaziridinone (**1**) under air (Table 1, entry 13), suggesting that both the Cu catalyst and di-*tert*-butyldiaziridinone (**1**) are required for the reaction.

With the optimal reaction conditions in hand, the generality for the oxidation was subsequently investigated with various secondary alcohols. As shown in Table 2, high yields were obtained for a wide range of alcohols.

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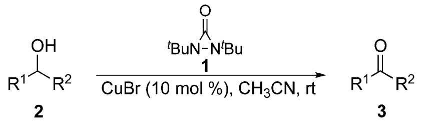
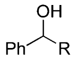
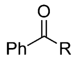
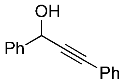
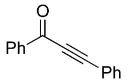
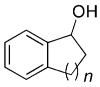
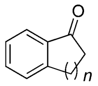
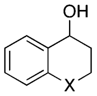
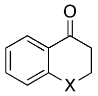
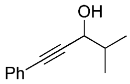
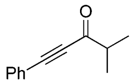
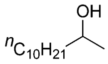
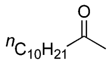
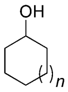
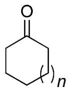
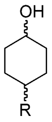
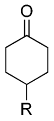
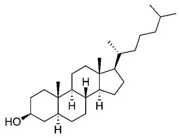
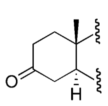
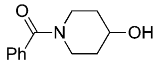
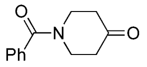
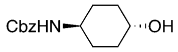
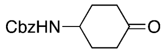
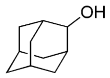
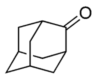
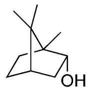
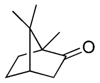
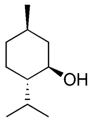
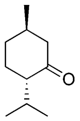
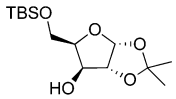
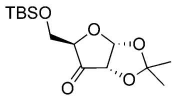
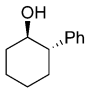
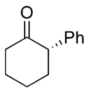
Table 2. Oxidation of Secondary Alcohols[a]

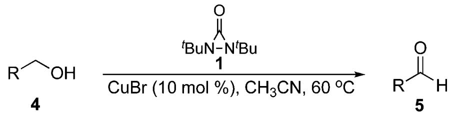


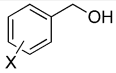
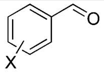
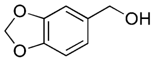
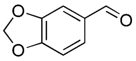
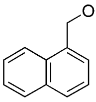
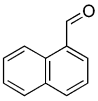
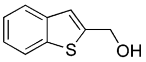
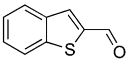
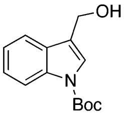
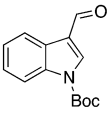
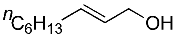
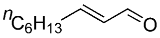
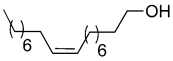
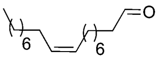
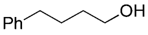
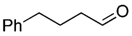
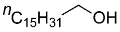
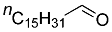
entry	substrate **2**	product **3**	time (h)	yield (%)[b]
				
1	**2a**, R = ^{t}Bu	**3a**	2	95
2	**2b**, R = Me	**3b**	10	97
3[c]	**2c**, R = Ph	**3c**	12	99
4	**2d**, R = cyclopropyl	**3d**	3	99
5	**2e**, R = 2-phenylvinyl	**3e**	0.2	99
6	**2f**, R = vinyl	**3f**	5	87
7	**2g**, R = allyl	**3g**	1.5	74
8[d]	 **2h**	 **3h**	4.5	99
				
9	**2i**, $n = 1$	**3i**	6	97
10	**2j**, $n = 2$	**3j**	3	98
11	**2k**, $n = 3$	**3k**	0.5	91
				
12	**2l**, X = O	**3l**	12	98
13[e]	**2m**, X = S	**3m**	5	73
14[d]	 **2n**	 **3n**	4.5	86
15	 **2o**	 **3o**	12	99
				
16[f]	**2p**, $n = 1$	**3p**	12	80
17	**2q**, $n = 3$	**3q**	12	85
18[g]	**2r**, $n = 7$	**3r**	6	99
				
19	**2s**, R = Ph	**3s**	10	99
20	**2t**, R = OSiEt$_3$	**3t**	12	93
21[h]	 **2u**	 **3u**	12	90
22[d]	 **2v**	 **3v**	5	91
23[i]	 **2w**	 **3w**	8	74
24[h]	 **2x**	 **3x**	8	83
25	 **2y**	 **3y**	3	90
26	 **2z**	 **3z**	8	92
27[j]	 **2aa**	 **3aa**	4	87
28	 **2bb** (>99% ee)	 **3bb** (>99% ee)	11	98

[a] All reactions were carried out with alcohol **2** (0.60 mmol), di-*tert*-butyldiaziridinone (**1**) (0.66 mmol), and CuBr (0.060 mmol) in CH$_3$CN (1.2 mL) at rt under Ar unless otherwise stated. [b] Isolated yield. [c] The reaction was carried out on 10 mmol scale of **2c** under open air. [d] The reaction was carried out at 60 °C. [e] The reaction was carried out with 0.90 mmol of **1** at 60 °C. [f] The reaction was carried out on 0.90 mmol scale of **2p**. [g] The reaction was carried out in CH$_3$CN (2.0 mL) at 60 °C. [h] The reaction was carried out in CDCl$_3$ (1.5 mL) at 60 °C. [i] The reaction was carried out with 1.14 mmol of **1** in CDCl$_3$ (1.5 mL) at 60 °C. [j] The reaction was carried out in CH$_3$CN (2.4 mL) at 60 °C.

Various acyclic and cyclic secondary benzylic alcohols with alkyl, cyclopropyl, vinyl, allyl, alkynyl, and thioether groups were effectively oxidized to ketones in 73–99% yields (Table 2, entries 1–13). As illustrated in the oxidation of benzhydrol (**2c**) (Table 2, entry 3), the method is amenable to gram scale. The oxidation can also be extended to a variety of nonbenzylic secondary alcohols, giving the corresponding ketones in 74–99% yields (Table 2, entries 14–28). Acyclic aliphatic alcohol **2o** was oxidized to ketone **3o** in 99% yield (Table 2, entry 15). Cyclic alcohols with variable ring sizes and substituents were found to be effective substrates (Table 2, entries 16–28). Acid-sensitive groups such as silyl ethers and ketal can be tolerated (Table 2, entries 20 and 27). The mildness of

Table 3. Oxidation of Primary Alcohols[a]



entry	substrate **4**	product **5**	time (h)	yield (%)[b]
				
1	**4a**, X = H	**5a**	5	83
2	**4b**, X = *o*-OMe	**5b**	3	90
3	**4c**, X = *m*-OMe	**5c**	3	89
4	**4d**, X = *p*-OMe	**5d**	3	90
5	**4e**, X = *p*-SMe	**5e**	5	63
6	**4f**, X = *p*-^{i}Pr	**5f**	3	91
7	**4g**, X = *p*-Br	**5g**	3	82
8	**4h**, X = *p*-CO_2Me	**5h**	3	94
9	 **4i**	 **5i**	2	92
10	 **4j**	 **5j**	5	96
11	 **4k**	 **5k**	4	90
12	 **4l**	 **5l**	4	80
13[c]	 **4m**	 **5m**	12	87
14[d]	 **4n**	 **5n**	4	70
15	 **4o**	 **5o**	10	83
16[d]	 **4p**	 **5p**	4	90

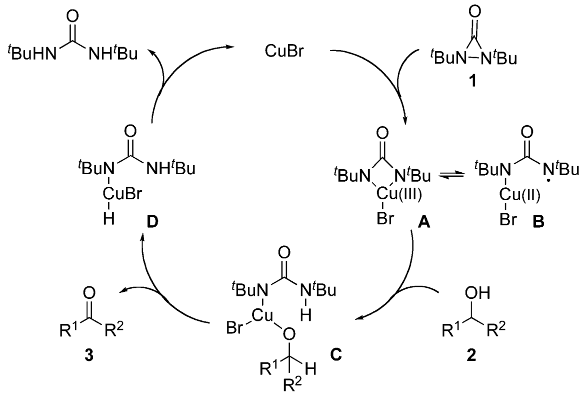
[a] All reactions were carried out with alcohol **4** (0.60 mmol), di-*tert*-butyldiaziridinone (**1**) (0.66 mmol), and CuBr (0.060 mmol) in CH_3CN (1.2 mL) at 60 °C under Ar unless otherwise stated. [b] Isolated yield. [c] The reaction was carried out with 0.72 mmol of **1**. [d] The reaction was carried out in $CDCl_3$ (1.2 mL).

the reaction conditions was further demonstrated in the oxidation of (1*R*,2*S*)-*trans*-2-phenyl-1-cyclohexanol (**2bb**) (Table 2, entry 28). Ketone **3bb** was obtained in 98% yield, and no racemization of the α-stereocenter occurred during the oxidation.

Primary alcohols were also found to be effective substrates but generally less reactive than secondary alcohols. To shorten the reaction time, the reaction temperature was raised to 60 °C. Under these reaction conditions, various benzylic alcohols with different substituents on the phenyl ring can be efficiently oxidized to the corresponding aldehydes in 63–96% yields (Table 3, entries 1–10). Heterocyclic primary alcohols were smoothly oxidized to give the aldehydes in good yields (Table 3, entries 11 and 12). In addition, allylic and aliphatic alcohols were also effective substrates, giving the corresponding aldehydes in 70–90% yields (Table 3, entries 13–16).

While a precise understanding of the reaction mechanism awaits further study, a plausible catalytic pathway is proposed in Scheme 1. The CuBr first reductively cleaves the N–N bond of di-*tert*-butyldiaziridinone (**1**) to form four-membered Cu(III) species **A** and/or Cu(II) nitrogen radical **B**,[22e,f] which reacts with alcohol **2** to generate alkoxy Cu(III) species **C**. The *β*-H elimination of intermediate **C** affords ketone **3** and Cu(III) species **D**, which undergoes reductive elimination to form urea and regenerate the CuBr catalyst.

Scheme 1. Proposed Catalytic Cycle for the Oxidation



In summary, we developed a novel oxidation of alcohols with CuBr as the catalyst and di-*tert*-butyldiaziridinone (**1**) as the oxidant. Various primary and secondary alcohols can be efficiently oxidized under mild conditions to the corresponding aldehydes and ketones in high yields. The present process exhibits the following favorable features: (1) the procedure is effective for a wide range of substrates bearing various functional groups, such as, alkenyl, alkynyl, thioether, silyl ether, amide, carbamate, ketal, ester, and heterocycles; (2) the reaction proceeds under neutral and mild conditions (no acid or base required) making it compatible with acid- or base-sensitive substrates; (3) the method is amenable to gram scale with no special precautions to exclude air or moisture. Further development of other reaction processes with diaziridinones and related compounds is currently underway.

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Supporting Information Available. Experimental procedures, characterization data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.