Tetrahedron Letters 73 (2021) 153094

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

# Rapid, chemoselective and mild oxidation protocol for alcohols and ethers with recyclable *N*-chloro-*N*-(phenylsulfonyl)benzenesulfonamide

Amey Palav [a,b], Balu Misal [a,b], Prerna Ganwir [a], Purav Badani [c], Ganesh Chaturbhuj [a,*]

[a] Institute of Chemical Technology, Matunga, Mumbai 400019, India
[b] Loba Chemie Pvt. Ltd, Research, and Development Center, Tarapur, Thane 401506, India
[c] Department of Chemistry, University of Mumbai, Kalina, Mumbai 400098, India

ARTICLE INFO

*Article history:*
Received 12 February 2021
Revised 9 April 2021
Accepted 13 April 2021
Available online 17 April 2021

*Keywords:*
*N*-chloro-N-(phenylsulfonyl) benzenesulfonamide
*N*-chloro reagents
Alcohol oxidation
Ether oxidation
PS-TEMPO

ABSTRACT

Chlorine is the 20th most abundant element on the earth compared to bromine, iodine, and fluorine, a sulfonimide reagent, *N*-chloro-*N*-(phenylsulfonyl)benzenesulfonamide (NCBSI) was identified as a mild and selective oxidant. Without activation, the reagent was proved to oxidize primary and secondary alcohols as well as their symmetrical and mixed ethers to corresponding aldehydes and ketones. With recoverable PS-TEMPO catalyst, selective oxidation over chlorination of primary and secondary alcohols and their ethers with electron-donating substituents was achieved. The reagent precursor of NCBSI was recovered quantitatively and can be reused for synthesizing NCBSI.



Aldehyde and ketones are the most important functional groups which serve as building blocks for transformation into primary and secondary amines, oximes, and acids which serve as the important intermediates to synthesize active pharmaceutical intermediates (API), agrochemicals as well as specialty chemicals. Moreover, they are the key raw materials for multicomponent reactions *viz.* Biginelli [1], Kabachnik-Fields [2], Hantzsch pyridine synthesis [3], Strecker reaction [4] as well as BODIPY [5] synthesis. The most common methodology to synthesize aldehydes and ketones is the oxidation of corresponding alcohols. To achieve this transformation, highly efficient classical systems have been reported by Parikh-Doering [6], Swern [7,8], Corey Kim [9] Jones [10] and Oppenauer [11], but had limitations due to noxious byproducts and tedious reaction condition. Hypervalent iodine reagents like Dess Martin periodinane (DMP) [12], 2-iodoxybenzoic acid (IBX) [13] were the next choice, however, due to shock sensitivity and explosive nature, restricted scale-up. Catalytic oxidations systems using complexes of precious metals like ruthenium [14], gold [15], palladium [16], platinium [17], iridium [18] and tungsten [19] with various organic ligands are also reported. But had limitations of reaction time and cost. Besides these, *N*-halo reagents like *N*-bromosuccinimide (NBS), *N*-bromoacetamide, 1,3-dibromo-5–5-dimethyl hydantoin [20], 1,3-dichloro-5–5-dimethyl hydantoin (DCDMH), *N*-chlorosuccinimide (NBS), *N*-chlorosaccharin (NCSAC), *N*-chlorophthalimide (NCPI), and trichloro isocyanuric acid (TCCA) in combination with additives like, NBS-thiourea [21], NBS-$H_2O$/-dioxane [22], NBS-1-Butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) [23], NBS/ tetrabutylammonium iodide (TBAI) [24], NBS/pyridine [25], NCS/TEMPO [26], *N*-iodosuccinimide/*hν* [27], TCCA/2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) [28]. Additives might alter the electronic structures of reagents and promote the halogen detachment, resulting in rapid oxidation but could contaminate with halogenated byproducts. Another most divergent methodology for the synthesis of aldehydes and ketones is the oxidation of corresponding primary and secondary ethers. Since the oxidation of ethers of primary and secondary alcohol are uncommon but important in organic synthesis. Most of the literature methodologies are time-consuming, harsh [29] with limited scope, and are nonselective [30], leading to the formation of esters and acids.

After successfully working on safe *N*-oxidation of pyridines and quinolines [31] we decided to explore the oxidation of alcohols and ethers using a chlorine reagent. Our prime goal was to identify an operationally convenient, bench stable, selective oxidizing *N*-Cl reagent which would generate electrophile ($Cl^+$) without additive, since chlorine being the 20th most abundant element [32] present on the earth, compared to bromine and iodine. In our recently published article [33], we reported a reagent *N*-chloro-*N*-(phenylsulfonyl)benzenesulfonamide (NCBSI), as a chlorinating agent for

* Corresponding author.
*E-mail address:* gu.chaturbhuj@gmail.com (G. Chaturbhuj).

https://doi.org/10.1016/j.tetlet.2021.153094
0040-4039/

aromatics without any activation. Due to its high electrophilicity, it may satisfy the criteria of an ideal oxidizing agent. Although the reagent is also used as a starting material for preparing *N*-trifluoro methyl thiolating reagent [34] however, its potential as an oxidizing agent is being explored for the first time.

According to the physicochemical parameters of *N*-chloro reagents and NCBSI *in-silico* by density-functional theory (DFT) theory, NCBSI exhibited the highest electrophilic nature and reactivity due to a longer *N*-Cl bond length, lower bond dissociation energy (BDE), and lower absolute charge density on chlorine [33]. Overwhelmed with these findings, we eagerly performed oxidation of benzyl alcohol using *N*-chloro reagents including NCBSI, in the absence of an additive in specially dried acetonitrile under an inert atmosphere at 20–25 °C (Table 1). No oxidation product was observed in NCS, NCPI, and TCCA. This revealed that shorter *N*-Cl bond length and higher BDE affect the oxidation. NCSAC and DCDMH showed marginal oxidation products for over 12 h. Although the values of these *N*-Cl reagents are close to NCBSI, both had comparatively shorter bond lengths. Hence, practically NCBSI is a rapid oxidant that resulted in the complete conversion of benzyl alcohol to benzaldehyde in acetonitrile (MeCN) in 5 min with 98% yield and 99.8% purity (Table 1, entry 6).

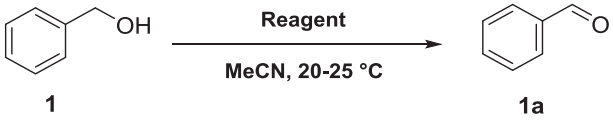
A solvent optimization study was also performed (Table 2). In chlorinated solvents, the time for the reaction was increased from dichloromethane (DCM) to carbon tetrachloride ($CCl_4$), due to decreased solubility of the reagent (Table 2, entries 2–5). In DMF, the oxidation was highly exothermic, resulted in low yield due to work-up issues (Table 2, entry 6). To study, the generality and scope, the optimized reaction condition were applied to primary and secondary alcohols with electron-withdrawing and electron-donating substitution on aromatic rings (Table 3)

We applied optimized condition to electron-deficient alcohols, in which unsubstituted and 4-halo substituted benzyl alcohols were oxidized readily with excellent yield (Table 3, entries 1, 2, 5, 8, and 12). On the other hand, 2 and 3 halo benzyl alcohols took a longer time (Table 3, entries 3, 4, 6, and 7). In the case of nitro alcohols, 4-nitrobenzyl alcohol, and 1-(4-nitrophenyl)ethanol (Table 3, entries 9 and 13) were oxidized smoothly to 4-nitrobenzaldehyde and 4-nitroacetophenone. For 1,4-phenylene dimethanol selective mono oxidation was not observed using one mole equivalent of the reagent. With 2 mole equivalents of reagent, both the alcohols were successfully oxidized to obtain terephthalaldehyde (Table 3, entry 10). The reagent was selective towards 1,2-diphenylethane-1,2-diol, resulting in mono keto product (Table 3, entry 17). Aliphatic alcohols oxidized to ketones and aldehyde in good yields under solvent-free condition (Table 3, entries 18, 19). Alicyclic alcohols (±) cyclohexanol, (±) menthol, and (±) borneol were also oxidized smoothly to cyclohexanone, menthone, and camphor (Table 3, entries 20–21).

When the same protocol was applied for the oxidation electron-rich alcohol, *viz.* 1-(4-methoxyphenyl)ethanol, the ring chlorination dominated over oxidation due to the high electrophilic nature of the reagent, and traces of oxidized product was obtained (see supplementary information Fig. 3). The foresaid optimized protocol was not suitable for the oxidation of electron-rich aromatic alcohols in a polar solvent. To achieve selective oxidation, there was a need to alter the mechanism by modifying the ionic character of the reagent by trapping-transfer of chlorine to dominate the oxidation over chlorination. Since TEMPO is widely used for oxidation of alcohol with a variety of secondary oxidant [35,36] and literature [22] encouraged us to use it in a catalytic amount. The study began with a pilot reaction with a catalytic amount of TEMPO (1.49% to 5.35 mol%) in acetonitrile, chlorinated product dominated over oxidation (Table 4, entry 8). The loading of TEMPO was optimized to 4.38 mol% for the oxidation of 1-(4-methoxyphenyl)ethanol (Table 4, entry 4,). The oxidation was slower in solvents other than chloroform ($CHCl_3$) (Table 4, entries 6, 7).

Keeping eco-friendliness and recovery on priority, the use of polymer-supported TEMPO was necessary. Besides the availability of a wide variety of supported TEMPO reagents [37,38], we chose a

**Table 1**
Comparison of commercial *N*-chloro reagents with (NCBSI).[a]




1 1a

| Entry | Reagent | SM (%)[b] | Time | Yield (%)[c] |
|---|---|---|---|---|
| 1 | NCS | 100 | 12 h | NR[e] |
| 2 | NCSAC | 98 | 12 h | 2 |
| 3 | TCCA | 100 | 12 h | NR[e] |
| 4 | NCPI | 100 | 12 h | NR[e] |
| 5 | DCDMH | 94 | 12 h | 6 |
| 6 | NCBSI | 0 | 5 min. | 98[d] |

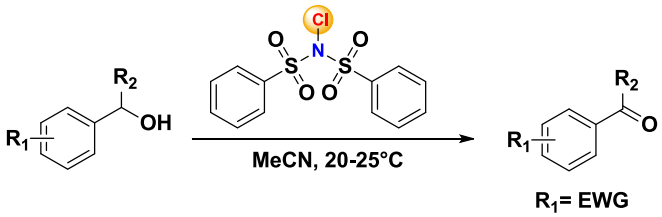
[a]Reaction condition: benzyl alcohol (3.6 mmol), oxidant (3.6 mmol) in 5 mL MeCN at 20–25 °C. [b]SM recovery by HPLC. [c]Yield by HPLC. [d]Isolated yield [e]NR-No reaction.

**Table 2**
Solvent optimization study.[a]

| Entry | Solvent | Time (min.) | Yield (%)[b] | Purity (%)[c] |
|---|---|---|---|---|
| 1 | MeCN | 5 | 98 | 99.8 |
| 2 | DCM | 10 | 95 | 99 |
| 3 | EDC | 10 | 96 | 99.2 |
| 4 | $CHCl_3$ | 15 | 95 | 99 |
| 5 | $CCl_4$ | 20 | 94 | 98 |
| 6 | DMF | 2 | 70 | 99 |

[a]Reaction condition: benzyl alcohol (3.6 mmol), NCBSI (3.6 mmol), 5 mL solvent, 20–25 °C. [b]Isolated Yield. [c]Purity by HPLC. EDC = Ethylene dichloride.

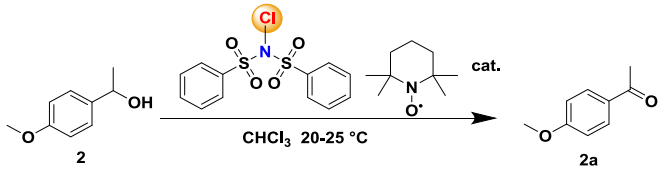
**Table 3**
Oxidation of electron-deficient primary and secondary alcohols [44].[a]




| Entry | $R_1$ | $R_2$ | Time (min) | Yield (%)[b] | Purity (%)[c] |
|---|---|---|---|---|---|
| 1 | H | H | 5 | 98 | 99.8 |
| 2 | 4-Cl | H | 5 | 99 | 99 |
| 3 | 3-Cl | H | 10 | 98 | 99 |
| 4 | 2-Cl | H | 15 | 98 | 99 |
| 5 | 4-Br | H | 5 | 98 | 99 |
| 6 | 3-Br | H | 15 | 98 | 99 |
| 7 | 2-Br | H | 20 | 99 | 99 |
| 8 | 4-F | H | 5 | 99 | 99 |
| 9 | 4-$NO_2$ | H | 10 | 98 | 99 |
| 10 | 4-$OHCH_2$ | H | 10[d] | 98 | 98 |
| 11 | H | $CH_3$ | 5 | 98 | 99 |
| 12 | 4-Br | $CH_3$ | 5 | 98 | 99 |
| 13 | 4-$NO_2$ | $CH_3$ | 5 | 98 | 99 |
| 14 | H | $C_6H_5$ | 5 | 99 | 99 |
| 15 | 4-Cl | $C_6H_5$ | 5 | 99 | 99 |
| 16 | 1-Napthyl | $CH_3$ | 5 | 99 | 99 |
| 17 | H | (OH)CH-$C_6H_5$ | 5 | 99 | 99 |
| 18 | 2-Methylpropan-1-ol | | 5 | 98[e] | 98 |
| 19 | Butan-2-ol | | 5 | 98[e] | 99 |
| 20 | (±)Cyclohexanol | | 5 | 98 | 99 |
| 21 | (±)Menthol | | 5 | 98 | 98 |
| 22 | (±)Borneol | | 5 | 98 | 98.9 |

[a]Reaction condition: Alcohol (3.6 mmol), NCBSI (3.6 mmol), 5 mL MeCN, 20–25 °C. [b]Isolated Yield. [c]Purity by GC, [d]NCBSI (7.2 mmol), [e]Solvent-free reaction, isolation by DCM extraction followed by atmospheric distillation, removal of traces under mild vacuum.

**Table 4**
Optimization of loading of TEMPO as catalyst.[a]

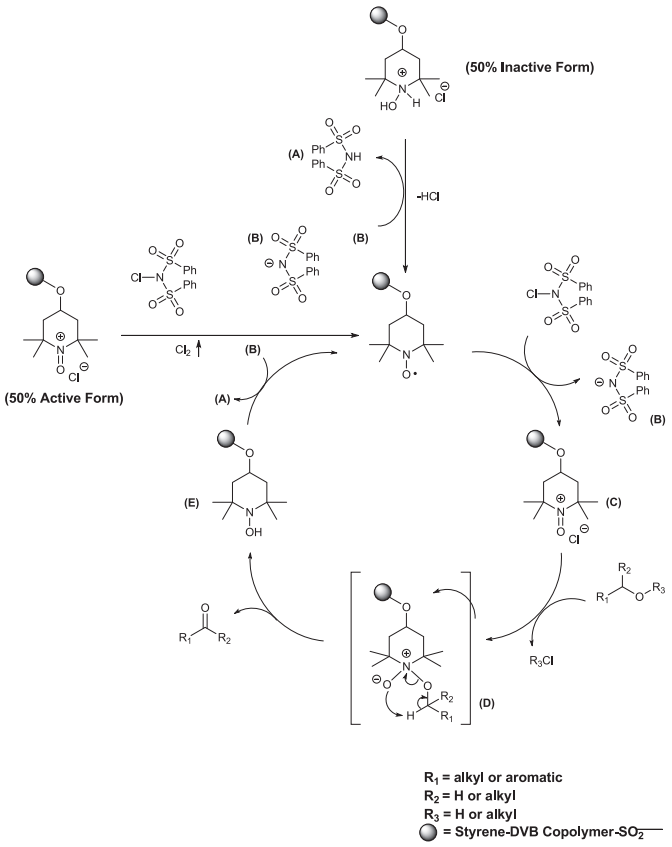



| Entry | TEMPO (mol%) | Solvent | Time (min.) | SM (%)[b] | Imp (%)[c] | 2a (%) | Yield (%)[d] |
|---|---|---|---|---|---|---|---|
| 1 | 1.49 | $CHCl_3$ | 15 | 13 | 87 | 0 | 0 |
| 2 | 2.44 | $CHCl_3$ | 15 | 30 | 12 | 58[e] | 58[e] |
| 3 | 3.40 | $CHCl_3$ | 10 | 0 | 8 | 92 | 85 |
| 4 | 4.38 | $CHCl_3$ | 10 | 0 | 0 | 99 | 98 |
| 6 | 4.38 | EDC | 20 | 0 | 0 | 99 | 98 |
| 7 | 4.38 | $CCl_4$ | 20 | 0 | 0 | 99 | 98 |
| 8 | 4.38 | MeCN | 5 | 10 | 89 | 0 | 0 |

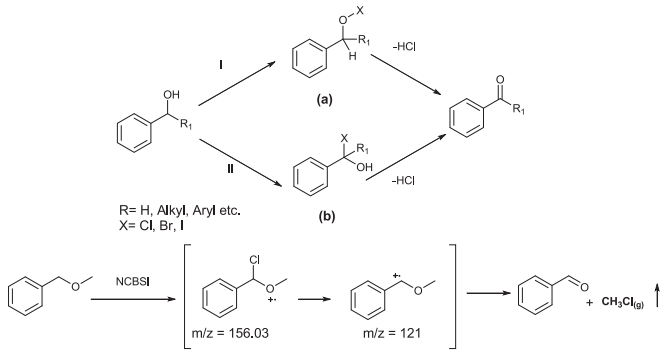
[a]Reaction condition: 1-(4-methoxyphenyl)ethanol (13.1 mmol), NCBSI (13.1 mmol), 10 mL $CHCl_3$, 20–25 °C. [b]SM by GC. [c]Mixture of chlorinated alcohol and ketone. [d]Isolated yield. [e]GC yield.

styrene–divinylbenzene copolymer bound sulfonic ester-linked TEMPO (PS-TEMPO) [39]. The label claim stated capacity of PS-TEMPO was 1 mmol/g in 50% active form. Thus, the optimized loading was calculated for PS-TEMPO (4.38 mol%) with an additional half equivalent NCBSI to completely activate it (Scheme 1) and the experiment was performed. To our surprise, 4.38 mol% PS-TEMPO loading resulted in 99% of the desired oxidation product with no chlorinated products. To study the scope of protocol, a wide variety of electron-rich aromatic, as well as heteroaromatic primary and secondary alcohols, were subjected (Table 5). The optimized condition was well suited for an array of electron-rich and α, β-unsaturated alcohols with high purity and yield of the product (Table 5, entries 1–3, 5, 7–9, 16–18). For oxidation of amino alcohols and *N*-heteroaromatic alcohols, the oxidation protocol needed triethylamine (TEA) as an acid scavenger as HCl as a side product (Table 5, entries 6, 10–12, 14, 15).

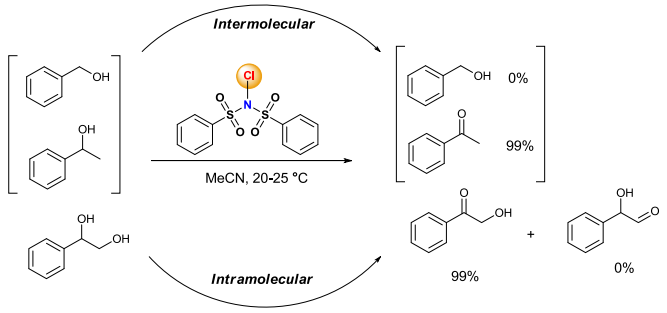
We may formulate the mechanism based on what has been documented in similar cases [40]. A plausible mechanism of PS-TEMPO/NCBSI for the oxidation of electron-rich alcohol was predicted where NCBSI reacts with the activated form of PS-TEMPO resin resulting in the liberation of chlorine gas, thus forming TEMPO radical (Scheme 1). The anion of NCBSI generated abstracts




**Scheme 1.** Plausible mechanism for PS-TEMPO-NCBSI oxidation.



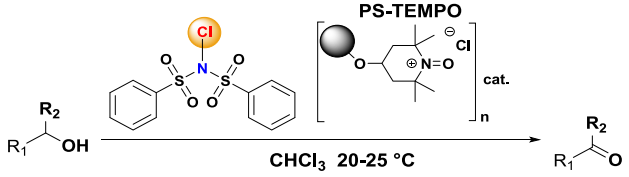

**Scheme 2.** Mechanistic pathway for oxidation of alcohols.




**Scheme 3.** Intermolecular and Intramolecular selectivity assessment of NCBSI.

a proton from the inactive form of PS-TEMPO resin followed by the elimination of HCl to form TEMPO radical. Thus, TEMPO radical is oxidized by NCBSI to *N*-oxoammonium ion (C) [40] and generates anion (B). The elimination of HCl or alkyl chloride during reaction *N*-oxoammonium ion (C) with the alcohols or ethers respectively lead to intermediate (D), which rapidly oxidizes the alcohol or ether to corresponding aldehyde or ketone with the formation of hydroxylamine intermediate (E) [40]. The anion (B) abstracts a proton from intermediate (E) to generate TEMPO radical to recycles for catalysis.

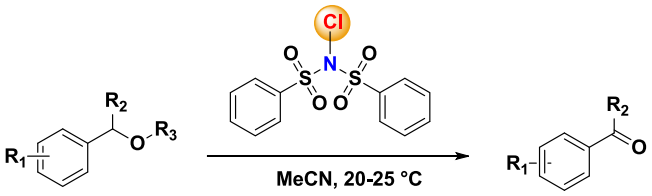
**Table 5**
Oxidation of electron-rich primary and secondary alcohols [45].[a]




| Entry | $R_1$ | $R_2$ | Time (min) | Yield (%)[b] | Purity (%)[c] |
|---|---|---|---|---|---|
| 1 | 4-$HOC_6H_4$ | H | 5 | 98 | 99 |
| 2 | 2-$HOC_6H_4$ | H | 5 | 98 | 99 |
| 3 | 4-$CH_3OC_6H_4$ | H | 5 | 99 | 99 |
| 4 | 4-$(CH_3)_2NC_6H_4$ | H | 5 | 98 | 98 |
| 5 | 2-Furyl | H | 15 | 96 | 98 |
| 6 | 2-Pyridinyl | H | 15 | 98[d] | 97 |
| 7 | 4-$HOC_6H_4$ | $CH_3$ | 10 | 99 | 98 |
| 8 | 3-$HOC_6H_4$ | $CH_3$ | 10 | 98 | 99 |
| 9 | 2,4-$(HO)_2C_6H_4$ | $CH_3$ | 5 | 98 | 98 |
| 10 | 2-$NH_2C_6H_4$ | $CH_3$ | 15 | 98[d] | 97 |
| 11 | 3-$NH_2C_6H_4$ | $CH_3$ | 15 | 97[d] | 97 |
| 12 | 4-$NH_2C_6H_4$ | $CH_3$ | 10 | 98[d] | 96 |
| 13 | 2-Thienyl | $CH_3$ | 10 | 98 | 98 |
| 14 | $C_6H_5$ | 2-Pyridinyl | 10 | 98[d] | 97 |
| 15 | $C_6H_5$ | 4-Pyridinyl | 10 | 98[d] | 98 |
| 16 | (*E*)-But-2-en-1-ol | | 10 | 97 | 98 |
| 17 | Cinnamyl alcohol | | 15 | 98 | 98 |
| 18 | Isophorol | | 15 | 98 | 97 |

[a]Reaction condition: Alcohol (13.1 mmol), NCBSI for activation (0.28 mmol), NCBSI for oxidation (13.1 mmol), PS-TEMPO (0.6 g, 4.38 mol%),10 mL $CHCl_3$, 20–25 °C, [b]Isolated Yield, [c]Purity by GC, [d]TEA (13.1 mmol) as acid scavenger.

**Table 6**
Oxidation of primary and secondary ethers.[a]




| Entry | $R_1$ | $R_2$ | $R_3$ | Time (min.) | Yield (%)[b] | Purity (%)[c] |
|---|---|---|---|---|---|---|
| 1 | H | H | $CH_3$ | 2 | 98.8 | 99.8 |
| 2 | H | H | $CH_2CH_3$ | 5 | 98.5 | 99.8 |
| 3 | H | H | *i*-$C_3H_7$ | 8 | 98 | 99.7 |
| 4 | H | H | *tert*-$C_4H_9$ | 3 | 98 | 99.6 |
| 5 | H | $CH_3$ | $CH_3$ | 2 | 98.9 | 99.8 |
| 6 | H | $CH_3$ | $CH_2CH_3$ | 2 | 98.8 | 99.8 |
| 7 | H | $CH_3$ | *i*-$C_3H_7$ | 10 | 98 | 99.7 |
| 8 | H | $CH_3$ | *tert*-$C_4H_9$ | 5 | 98 | 99.7 |

[a]Reaction condition: Ether (3.6 mmol), NCBSI (3.6 mmol), 5 mL MeCN, 20–25 °C. [b]Isolated Yield. [c]Purity by GC.

While referring to the literature [41,42] on mechanistic study on oxidation by *N*-halo reagent, two possible pathways are proposed *viz.* hypohalite (a) intermediate or halohydrin (b), both (a) and (b) intermediates converted to carbonyl by the elimination of hydrogen halide. Out of the two possible mechanisms, pathway *via* intermediate (b) has less energy compared to (a) [41] (Scheme 2). To investigate the pathway for the oxidation of electron-withdrawing substrates, the oxidation protocol was applied to benzyl methyl ether, where the probability of hypochlorite (a) was eliminated. The oxidation was performed in a sealed vial at −20 °C to avoid the escape of gaseous methyl chloride, the reaction mixture was allowed gradually to reach room temperature and analyzed by GCMS. We could not get the mass of methyl chloride, however, could determine *m*/*z* 156 and its fragment as *m*/*z* 121 (Fig. 1, supplementary information), and the reaction pathway *via* intermediate (b) was confirmed [43].

To get more unambiguous evidence, oxidation of dibenzyl ether was performed which resulted in the formation of an equimolar mixture of benzyl chloride and benzaldehyde, both products being detectable without a loss (supplementary information, Fig. 2). We also performed intramolecular [48] and intermolecular [49] selectivity of NCBSI. In the intermolecular reaction, no traces of benzaldehyde was observed, and similarly, secondary alcohol was oxidized selectively over the primary in intramolecular reaction with 1-phenyl ethane-1,2-diol. This confirmed the reagent was highly selective towards secondary alcohol in both the reactions (Scheme 3).

After learning during elucidation of the mechanism, that the ethers too easily oxidized to corresponding aldehydes and ketone, NCBSI was applied for the oxidation of ethers of benzyl alcohol and 1-phenyl ethanol with primary, secondary, and tertiary aliphatic alcohols. For alkyl benzyl ethers, the reaction was exothermic up to 38 °C with vigorous evolution of corresponding alkyl chloride (Table 6, entries 1–4) was observed. The reaction time increased with an increased alkyl chain. However, *tert*-butyl ether took a shorter reaction time (Table 6, entry 4). Similar observations were obtained for the oxidation of ethers of 1-phenyl ethanol (Table 6, entry 8).

For isopropyl ether, the reagent was selective towards the aromatic part compared to the alkyl part presumably due to the stability of benzylic carbocation for chlorination to form intermediate (b) (Scheme 2) (Table 6, entries 3 and 7).

To access the recyclability of *N*-(phenylsulfonyl) benzenesulfonamide, a precursor of NCBSI, benzyl alcohol, 1 was oxidized to benzaldehyde, 1a on a 10 g scale [46], and the *N*-(phenylsulfonyl) benzenesulfonamide was extracted from the product by washing with 5% $NaHCO_3$ and recovered from aqueous solution by acidification with concentrated hydrochloric acid [47] as a precipitate in 98% yield with 99.77% purity by HPLC and identified by HRMS.

In conclusion, we have first time identified and confirmed NCBSI as a mild, regioselective rapid oxidant for alcohols and ethers theoretically [33] as well as experimentally. The reagent was well suited for the oxidation of an array of alcohols and ethers without an additive. For electron-donating alcohols and ethers, the selectivity of oxidation over chlorination and yield was achieved by a combination of catalytic recoverable PS-TEMPO with NCBSI. The precursor of the NCBSI can be easily separated from the reaction mixture and recovered quantitatively for recycling to NCBSI.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

The authors are thankful to the Department of Science and Technology, India (WOS-A), Loba Chemie Pvt. Ltd. for supporting this work.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2021.153094.

## References

[1] C.K. Khatri, D.S. Rekunge, G.U. Chaturbhuj, New J. Chem. 40 (2016) 10412–10417.
[2] C.K. Khatri, V.S. Satalkar, G.U. Chaturbhuj, Tetrahedron Lett. 58 (2017) 694–698.
[3] D.S. Rekunge, C.K. Khatri, G.U. Chaturbhuj, Tetrahedron Lett. 58 (2017) 1240–1244.
[4] K.S. Indalkar, C.K. Khatri, G.U. Chaturbhuj, Tetrahedron Lett. 58 (2017) 2144–2148.
[5] A. Loudet, K. Burgess, Chem. Rev. 107 (2007) 4891–4932.
[6] J.R. Parikh, W. Doering, J. Am. Chem. Soc. 89 (1967) 5505–5507.
[7] K. Omura, D. Swern, Tetrahedron 34 (1978) 1651–1660.
[8] A.J. Mancuso, S. Huang, L.D. Swern, J. Org. Chem. 43 (1978) 2480–2482.
[9] E.J. Corey, C.U. Kim, J. Am. Chem. Soc. 94 (1972) 7586–7587.
[10] K.E. Harding, L.M. May, K.F. Dick, J. Org. Chem. 40 (1975) 1664–1665.
[11] C.R. Graves, B.S. Zeng, S.T. Nguyen, J. Am. Chem. Soc. 128 (2006) 12596–12597.

[12] S.D. Meyer, S.L. Schreiber, J. Org. Chem. 59 (1994) 7549–7552.
[13] K. Surendra, N.S. Krishnaveni, M.A. Reddy, Y.V. Nageswar, K.R. Rao, J. Org. Chem. 68 (2003) 2058–2059.
[14] I.E. Markó, P.R. Giles, M. Tsukazaki, I. Chellé-Regnaut, C.J. Urch, S.M. Brown, J. Am. Chem. Soc. 119 (1997) 12661–12662.
[15] B. Guan, D. Xing, G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang, Z. Shi, J. Am. Chem. Soc. 127 (2005) 18004–18005.
[16] T. Iwasawa, M. Tokunaga, Y. Obora, Y. Tsuji, J. Am. Chem. Soc. 126 (2004) 6554–6555.
[17] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247–283.
[18] K. Fujita, R. Tamura, Y. Tanaka, M. Yoshida, M. Onoda, R. Yamaguchi, ACS Catal. 7 (2017) 7226–7230.
[19] D. Sloboda-Rozner, P.L. Alsters, R. Neumann, A *J. Am. Chem. Soc.* 125 (2003) 5280–5281.
[20] J. Lee, J. Lee, C *Lett. Org. Chem.* 15 (2018) 895–898.
[21] C.B. Tripathi, S. Mukherjee, J. Org. Chem. 77 (2012) 1592–1598.
[22] S. Adimurthy, P.U. Patoliya, Synth. Commun. 37 (2007) 1571–1577.
[23] J.C. Lee, J.Y. Lee, J.M. Lee, Synth. Commun. 35 (2005) 1911–1914.
[24] T.R. Beebe, L. Boyd, S.B. Fonkeng, J. Horn, T.M. Mooney, M.J. Saderholm, M.V. Skidmore, J. Org. Chem. 60 (1995) 6602–6603.
[25] J.M. Khurana, B.M. Kandpal, Tetrahedron Lett. 44 (2003) 4909–4912.
[26] J. Einhorn, C. Einhorn, F. Ratajczak, J.L. Pierre, J. Org. Chem. 61 (1996) 7452–7454.
[27] T.R. Beebe, R.L. Adkins, C.C. Bogardus, B. Champney, P.S. Hii, P. Reinking, J. Shadday, W.D. Weatherford, M.W. Webb, S.W. Yates, J. Org. Chem. 48 (1983) 3126–3128.
[28] L. De Luca, G. Giacomelli, S. Masala, A. Porcheddu, J. Org. Chem. 68 (2003) 4999–5001.
[29] A.S. Mayhoub, A. Talukdar, M. Cushman, J. Org. Chem. 75 (2010) 3507–3510.
[30] K.N. Rankin, Q. Liu, J.H. Hendry, N. Yee, A. Noureldin, D.G. Lee, Tetrahedron Lett. 39 (1998) 1095–1098.
[31] A. Palav, B. Misal, A. Ernolla, V. Parab, P. Waske, D. Khandekar, V. Chaudhary, G. U. Chaturbhuj, Org. Process Res. Dev. 23 (2019) 244–251.
[32] N.N. Greenwood, A. Earnshaw, B. Heinemann, The Halogens: Fluorine, Chlorine, Bromine, Iodine and Astatine; In Chemistry of Elements, Second E, Eds. Oxford, 1997; pp 789–887.
[33] B. Misal, A. Palav, P. Ganwir, G.U. Chaturbhuj, Tetrahedron Lett. 63 (2021) 152689.
[34] P. Zhang, M. Li, X.S. Xue, C. Xu, Q. Zhao, Y. Liu, H. Wang, Y. Guo, L. Lu, Q.N. Shen, J. Org. Chem. 81 (2016) 7486–7509.
[35] T. Okada, Y. Asawa, M. Sugiyama, T. Kirihara, Y. Iwai, Kimura, Synlett 25 (2014) 596–598.
[36] W.F. Bailey, J.M. Bobbitt, K.B. Wiberg, J. Org. Chem. 72 (2007) 4504–4509.
[37] J. Luo, C. Pardin, W.D. Lubell, X.X. Zhu, Chem. Commun. 21 (2007) 2136–2138.
[38] G. Pozzi, M. Cavazzini, S. Quici, M. Benaglia, G. Dell'Anna, Org. Lett. 6 (2004) 441–443.
[39] PS TEMPO BIOTAGE https://www.biotage.com/product-page/biotage-ps-tempo.
[40] D.L. Luca, G. Giacomelli, S. Masala, A. Porchedu, J. Org. Chem. 68 (2003) 4999–5001.
[41] A. Berkessel, S. Das, D. Pekel, J.M. Neudörfl, Angew. Chemie Int. Ed. 53 (2014) 11660–11664.
[42] A.E. Nooy, E.J. De Besemer, A.C. Bekkum, H. Van, Synthesis (Stuttg). 10 (1996) 1153–1176.
[43] J.C. Fan, Z.C. Shang, J. Liang, X.H. Liu, Y. Liu, J. Phys. Org. Chem. 21 (2008) 945–953.
[44] General procedure for oxidation of electron-deficient alcohol and ether: In a 3 neck, 50.0 mL round-bottomed flask arranged with a nitrogen atmosphere, calcium chloride guard tube, and magnetic stirrer was charged with acetonitrile 5.0 mL followed by alcohol or ether (3.6 mmol). The reaction mixture was cooled to 20–25 °C and added NCBSI reagent (3.6 mmol) at once under a stream of nitrogen. After addition, the colour of the reaction changes to pale yellow and then colourless. The reaction was monitored by TLC and confirm with 2,4-DNPH spray. On completion of the reaction, the solvent was evaporated under reduced pressure. The residue was extracted in 5.0 mL DCM and washed with 1% sodium bicarbonate solution 5.0 mL, phase-separated, dried over anhyd. $Na_2SO_4$ and evaporated under reduced pressure to give the product as stated. The purity of the product was determined by G.C.
[45] General procedure for oxidation of electron-rich alcohol and ether: In a 3 neck, 50.0 mL round-bottomed flask arranged with a nitrogen balloon, calcium chloride guard tube, and magnetic stirrer was charged with chloroform 5.0 mL followed by PS-TEMPO, Biotage (0.6 g, 4.38 mol %). The reaction mixture was cooled to 20–25 °C and added NCBSI reagent portion I (0.29 mmol, 0.5 equiv. w. r. t PS-TEMPO) to activate the resin at once under a stream of nitrogen. The reaction mixture was stirred for 2 min. The colour change of resin was observed from yellow to dark red indicated the activation of resin. To the reaction mixture, alcohol or ether (13.1 mmol) was added followed by NCBSI reagent portion II (13.1 mmol). After addition, the colour of the resin changes from red to pale yellow which gives a preliminary indication of reaction completion. The reaction was monitored by TLC and confirm with 2,4-DNPH spray. On completion of the reaction, the TEMPO resin mixture was filtered and washed with chloroform. The filtrate was washed with 1% sodium bicarbonate solution, phase-separated, dried over anhyd. $Na_2SO_4$ and evaporated under reduced pressure to give the product. The purity of the product was determined by G.C.
[46] Gram scale procedure for oxidation of Benzyl alcohol: In a 4 neck, 250.0 mL round-bottomed flask arranged with a nitrogen blanketing, calcium chloride guard tube fitted on the double surface condenser and overhead stirrer was charged with acetonitrile 100.0 mL followed by benzyl alcohol (10.0 g, 92.48 mmol). The reaction mixture was cooled to 20–25 °C and added NCBSI reagent (30.6 g, 92.48 mmol) in 10 equal lots under the nitrogen atmosphere. After complete addition, the reaction was maintained until the colour of the reaction changes from pale yellow to colourless, over 10 min. The reaction was monitored by TLC and confirm with 2,4-DNPH spray. On completion of the reaction, the reaction mixture was transferred to a rotatory evaporation flask under a nitrogen stream and the solvent was evaporated under reduced pressure. The residue was extracted in 100.0 mL DCM and washed with 5% sodium bicarbonate solution 120.0 mL. The aqueous phase was separated and preserved. The solvent phase was dried over anhydrous $Na_2SO_4$, evaporated under reduced pressure to furnish 9.6 g of benzaldehyde as light yellow oil (98% yield, 99.5% purity by GC). b.p. 176–178 °C. $^1$H NMR ($CDCl_3$, 400 MHz) δ 10.00 (s, 1H), 7.86 (d, J = 6.9 Hz, 2H), 7.66 – 7.57 (m, 1H), 7.51 (t, J = 7.3 Hz, 2H).
[47] Recovery procedure of *N*-(phenylsulfonyl)benzenesulfonamide (reagent precursor): The aqueous phase from the above experiment was charged in a 250.0 mL 4 neck RBF fitted with an overhead stirrer and dropping funnel. Under stirring the reaction mixture was acidified with 10.0 mL 35% HCl. After the complete formation of white precipitate, the reaction mixture was cooled to 10–15 °C, maintained for 30 min, and filtered. The filter cake was washed with water and dried in an oven at 65 °C to afford 26.4 g of *N*-(phenylsulfonyl) benzenesulfonamide (98% yield, 99.77% purity by HPLC), confirmed by HRMS.
[48] Intramolecular selectivity experiment: In a 3 neck, 50.0 mL round-bottomed flask arranged with a nitrogen atmosphere, calcium chloride guard tube, and magnetic stirrer was charged with acetonitrile 10.0 mL followed by 1-phenyl ethane-1,2-diol (1.0 g, 7.2 mmol). The reaction mixture was cooled to 20–25 °C and added NCBSI reagent (2.4 g, 7.2 mmol) at once under a stream of nitrogen. The reaction was monitored by TLC and confirm with 2,4-DNPH spray. On completion of the reaction, the solvent was evaporated under reduced pressure. The residue was extracted in 10.0 mL DCM and washed with 1% sodium bicarbonate solution 10.0 mL, phase separated, dried over anhyd. $Na_2SO_4$ evaporated under reduced pressure to give 2-hydroxy-1-phenylethan-1-one, 0.96 g (98% yield, 99% purity) off-white crystalline powder. m.p. 85–87 °C, $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 7.3 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 4.86 (d, J = 4.6 Hz, 2H), 3.51 (t, J = 4.7 Hz, 1H); GCMS elemental calculated for C8H8O2: 136.05 found: 136.0 m/z.
[49] Intermolecular selectivity experiment: In a 3 neck, 50.0 mL round-bottomed flask arranged with a nitrogen atmosphere, calcium chloride guard tube, and magnetic stirrer was charged with acetonitrile 10.0 mL followed the addition of an equimolar mixture of benzyl alcohol (1.0 g, 9.2 mmol) and 1-phenyl ethanol (1.1 g, 9.2 mmol). The reaction mixture was cooled to 20–25 °C and added NCBSI reagent (3.0 g, 9.2 mmol) at once under a stream of nitrogen. The reaction was monitored by GC and confirm with 2, 4-DNPH spray. On completion of the reaction, the solvent was evaporated under reduced pressure. The residue was extracted in 10.0 mL DCM and washed with 1% sodium bicarbonate solution 10.0 mL, phase separated, dried over anhyd. $Na_2SO_4$ evaporated under reduced pressure to give an oil (1.98 g). The oil was analyzed by GC and compared with acetophenone and benzaldehyde standards. The crude oil was purified by column chromatography using silica gel 60–120 with 95:5 hexane: ethyl acetate to give 1.0 g acetophenone (98% yield, 99% purity) and 0.98 g unreacted benzyl alcohol.