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A tunable synthesis of either benzaldehyde or benzoic acid through blue-violet LED irradiation using TBATB

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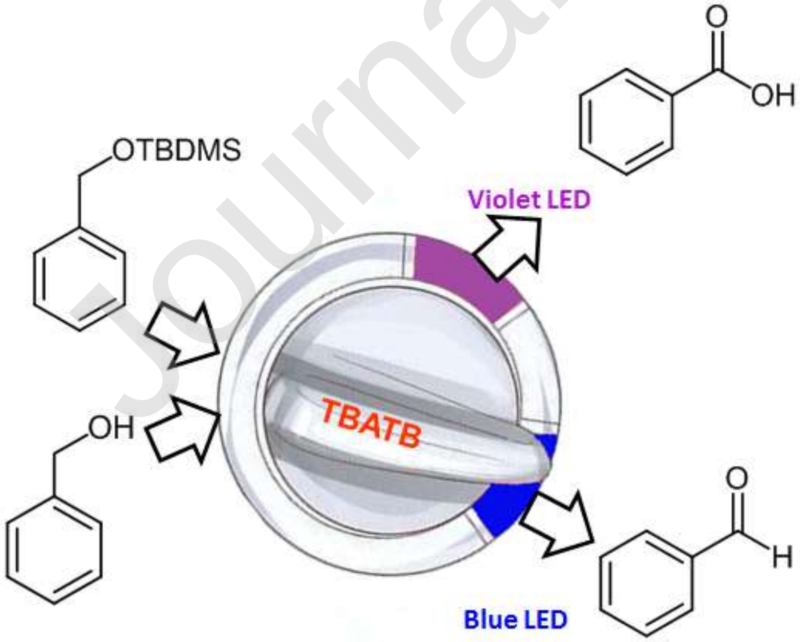
Graphical abstract



Highlights

- TBATB an efficient metal-free and homogeneous visible light active photocatalyst for selective aerobic oxidation
- Selective aerobic photooxidation of benzyl alcohols and benzyl tert-butyldimethylsilyl ethers to benzaldehydes in high yield under blue LED irradiation
- Selective aerobic oxidation of benzyl alcohols to the corresponding benzoic acids under irradiation of violet LED (400 nm) in the presence of TBATB
- Visible light-controlled selectivity to products in aerobic photooxidation

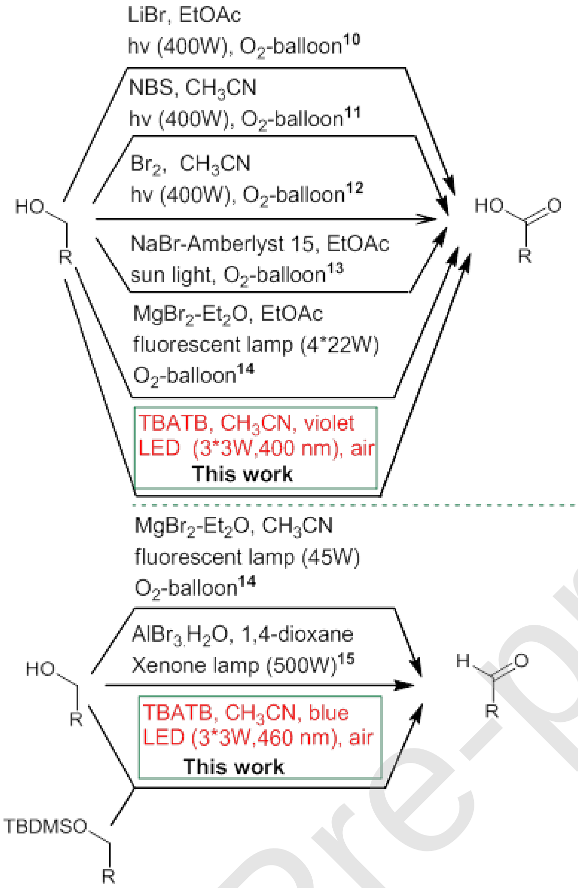
Abstract: In this paper, a highly efficient, metal-free, and homogeneous method for the selective aerobic photooxidation of alcohols and photooxidative-desilylation of tert-butyldimethylsilyl ethers (TBDMS) in the presence of tetrabutylammonium tribromide (TBATB) under irradiation of visible light was reported. The light source: blue (460 nm) and violet (400 nm) LED, can control selective oxidation to aldehyde or carboxylic acid.

Keywords: "tetrabutylamonium tribromide", "visible light photocatalyst", "tunable synthesis", "oxidative-desilylation", "metal-free", "benzyl alcohol".

1. Introduction

Oxidation of benzyl alcohols and oxidative-desilylation of benzyl silyl ethers are very important reactions in organic synthesis because related oxidation products such as benzaldehydes and benzoic acids are versatile intermediates which can serve as starting materials and precursors in a wide range of areas from industrial chemistry to biological and pharmaceutical applications [1-5] . On the other hand, controlled oxidation of benzyl alcohol to benzaldehyde, while avoiding over-oxidation to benzoic acid, is highly important as considerable research efforts have been devoted to the selective oxidation of benzyl alcohol to benzaldehyde [6-8].

Several aerobic photocatalytic systems have been reported to support oxidation reactions [9-13]. Some of these strategies were shown in scheme 1. Aerobic photooxidation reactions have provided a clean, short, and direct route in organic synthesis. Photocatalysts of bromo sources have shown high potential for aerobic photooxidation of alcohols under mild conditions. Itoh et al. used lithium bromide [14], N-bromosuccinimide [15], hydrobromic acid or bromine [16] for the aerobic photooxidation of alcohols to the corresponding carboxylic acids under UV irradiation by a high-pressure mercury lamp.



Scheme 1 Strategies to carboxylic acid and aldehyde from alcohol

They believed that the bromine was generated from bromo sources under UV irradiation. Because of harmful suppressing effects on human beings health, they used solar radiation in the oxidation of alcohols with a combination of NaBr and ion-exchange resins Amberlyst 15. The combination of sodium bromide and Amberlyst 15 resulted in the highest yield of carboxylic acids [17]. they also found that the aerobic photooxidation of a trace amount of the alcohols (0.3 mmol) to the corresponding carboxylic acids can carry out in the presence of a catalytic amount of $MgBr_2$-Et_2O under irradiation of visible lights from fluorescent lamps [18]. Lei et al. reported aerobic photooxidation of benzylic alcohols (0.1 mmol) to the corresponding benzaldehydes over a catalytic amount of $AlBr_3.6H_2O$ under visible light irradiation from a high-pressure xenon lamp [19]. Ananthakrishnan et al. reported aerobic photooxidation of benzyl alcohols (1 mmol) to the corresponding benzaldehydes in the presence of a catalytic amount of bromodimethylsulfonium bromide under visible light irradiation. They proposed that the bromo radicals help to the production of benzylic radicals [20]. Evans et al. reported direct oxidation of primary tert-butyldimethylsilyl ethers to the corresponding carboxylic acids with jones reagent [21]. To our knowledge, there seems to be no report on the oxidative-desilylation of benzyl tert-butyldimethylsilyl ethers by light.

TBATB, as a stable solid source of bromine, is a considerable reagent due to mildness, easy to handle and safety in comparison to elemental bromine. It is an efficient environmentally benign brominating agent [22-26] which has been used in some reactions such as cleavage of dithioacetals [27], pyranylation-depyranylation of alcohols [28], diacylation of aldehydes [29], preparation of a wide variety of flavones and aurones [30], direct condensation of various alcohols and carboxylic acids [31], etc. Although oxidation of alcohols, diols, and also cleavage of silyl ethers with TBATB has been reported by a few research groups [32-34], to our knowledge, selective aerobic photooxidation of benzyl alcohols and photooxidative-desilylation of benzyl tert-butyldimethylsilyl ethers with a catalytic amount of TBATB has not been investigated previously.

In this work, we found that benzyl alcohols and tert-butyldimethylsilyl ethers were selectively oxidized into the corresponding benzaldehydes in high yield in the presence of catalytic amount of TBATB at room temperature under blue LED irradiation and air atmosphere.

2. Experimental

2.1 Materials and methods

Tetrabutylammonium tribromide (TBATB) was (Acros, 123970250). The other chemicals and solvents purchased from Merck and Sigma-Aldrich. The reagents were applied without further purification. Oxidation products were detected by gas chromatography (GC) using a VARIAN CP3800 model. Identification of products was performed by 1H NMR and 13C NMR spectroscopies (Bruker 400MHz AVANCE III spectrometer) in $CDCl_3$. Chemical shifts (δ) were reported in ppm from TMS using the residual solvent resonance ($CDCl_3$: 77.1 ppm for ^{13}C NMR and 7.3 ppm for ^{1}H NMR). The blue (460 nm), violet (400 nm), and green (520 nm) LED lamps (Epistar 3W 20-30LM 700mAh) were applied in photooxidation reactions .The progress of the photocatalytic oxidation reactions was monitored by TLC on silica gel plates.

2.2 General experimental procedure for the Photocatalytic Oxidation of Alcohol:

In a 50 ml Pyrex round-bottom flask, a mixture of alcohol (1 mmol), TBATB (10-20 mg, 0.02-0.04 mmol) in 10 ml of CH_3CN was exposed to blue or violet light LED irradiation at room temperature under an air atmosphere with stirring. The progress of the photocatalytic oxidation reaction was monitored by TLC on silica gel plates. The reaction mixture externally irradiated until the alcohol was completely consumed.

2.3 General experimental procedure for the photooxidative-desilylation of tert-butyldimethylsilyl ether:

In a 50 ml Pyrex round-bottom flask, 10 ml of CH_3CN was taken. Then TBATB (20 mg, 0.04 mmol) and tert-butyldimethylsilyl ether (1 mmol) which has been produced by using a very widely used procedure[35] were added. The solution was exposed to the blue LED irradiation at room temperature under an air atmosphere with stirring. The irradiation was continued until the complete photooxidative-desilylation of tert-butyldimethylsilyl ether in the reaction mixture.

3. Results and Discussion

First, aerobic photooxidation of benzyl alcohol with TBATB was carried out in acetonitrile under irradiation of blue LEDs (3*3W) as model reaction. Aerobic photooxidation of 1 mmol benzyl alcohol in the presence of 0.01 mmol TBATB during 5, 15, and 20 h was examined. Increasing the reaction time from 5 to 20 h did not offer significant advantages on the conversion of benzyl alcohol (Table 1, entries 1-3). Increasing the amount of TBATB from 0.01 to 0.02 mmol led to a significant increase in the conversion of benzyl alcohol (Table 1, entry 4). Increasing the amount of TBATB from 0.02 to 0.03 and 0.04 mmol resulted in a decrease in benzaldehyde formation from 98% to 92% and 85%, respectively, due to the over-oxidation of benzyl alcohol to benzoic acid (Table 1, entries 4-6). Therefore, 0.02 mmol of TBATB and 5 h were chosen as optimized amount of catalyst and time, respectively (Table 1, entry 4).

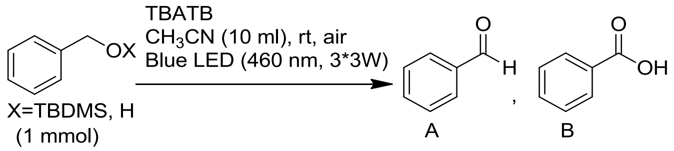
In the following, the effect of irradiation of LED with various wavelengths on the photooxidation conversion of benzyl alcohol and the product yield was investigated. Photocatalytic aerobic oxidation over 0.02 mmol TBATB under green LED lamps resulted in low conversions 7% during 5 h, (Table 1, entry 7). Photocatalytic aerobic oxidation of benzyl alcohol over 0.02 mmol of TBATB under violet LED irradiation resulted in both complete conversion (100%) and good yield (87%) to benzaldehyde in 5 h (Table 1, entry 8). Therefore, the photocatalytic activity of the TBATB is strictly affected by the wavelength of the light. TBATB exhibited lower activity under green light irradiation and higher activity under violet light irradiation. With increasing the amount of TBATB to

0.04 mmol, 100% conversion to benzoic acid was obtained under irradiation of violet LED in 8 h (Table 1, entry 9).

The photocatalytic behavior of the oxidation of benzyl alcohol was confirmed by the fact that the negligible conversion of benzyl alcohol was observed when the reaction was performed in the absence of TBATB or LED irradiation (Table 1, entries 10-11). The non-thermal and aerobic properties of the oxidation of benzyl alcohol was considered through the formation of benzaldehyde in low yields of 2% and 7%, respectively, when the reaction was carried out under an argon atmosphere and under reflux condition without LED irradiation (Table 1, entries 12-13). Therefore, the LED irradiation, TBATB, and air have a crucial role in the photooxidation transformation of benzyl alcohol.

Subsequently, for the purpose of comparison, the same photooxidation reaction was also studied with Br_2 (Table 1, entries 14-18). Complete conversion of benzyl alcohol to benzaldehyde (85%) and benzoic acid (15%) was observed in photooxidation of benzyl alcohol in the presence of Br_2 (Table 1, entry 14). It can be concluded that TBATB is more selective than elemental bromine. Also, the probability of the formation of bromine from $MgBr_2$, $AlBr_3$, TBAB (tetrabutylammonium bromide), and NBS as bromide sources was examined. The result revealed that bromine radical generated from bromine in TBATB, NBS and Br_2 is an active species in photooxidation of benzyl alcohol, while the other bromide sources such as TBAB, $AlBr_3$ and $MgBr_2$ shown lack or low ability to perform oxidation of benzyl alcohol (Table 1, entries 16-18).

Table 1 Aerobic photooxidation of benzyl alcohol and photooxidative-desilylation of benzyl tert-butyldimethylsilyl ether using TBATB



entry	TBATB (mmol)	time (h)	A (%)[y]	B (%)[y]	conversion (%)[y]
1	0.01	5	31	0	31
2	0.01	15	32	0	32
3	0.01	20	35	0	35
4	0.02	5	98	0	98
5	0.03	3	92	8	100
6	0.04	3	85	15	100
7[a]	0.02	5	7	0	7
8[b]	0.02	5	87	13	100
9[b]	0.04	8	0	100	100
10[c]	0	24	2	0	2
11[d]	0.02	24	2	0	2
12[e]	0.02	24	2	0	2
13[f]	0.02	24	7	0	7
14	Br_2[g]	5	85	15	100
15	NBS[g]	5	89	6	95
16	TBAB[h]	5	0	0	0
17	$AlBr_3$[g]	5	18	0	18
18	$MgBr_2$[g]	5	13	0	13
19[i]	0.02	9	13	4	17
20[i]	0.02	12	45	55	100
21[i]	0.04	5	88	12	100
22[i]	0.04	9	83	17	100

Photooxidation [a] under irradiation of green LED lamps (520 nm, 3*3W), [b] violet LED lamps (400 nm, 3*3W), [c] in the absence of TBATB, [d] in the absence of LED lamps irradiation (dark room), [e] under argon atmosphere, [f] under reflux condition, [g] 0.02 mmol, [h] 0.04 mmol, [i] photooxidative-desilylation of 1 mmol of benzyl tert-butyldimethylsilyl ether. [y] GC yield.

Next, direct aerobic photooxidative-desilylation of 1 mmol benzyl tert-butyldimethylsilyl ether to benzaldehyde was carried out in the presence of TBATB in CH_3CN under blue LED irradiation (Table 1, entries 19-22). In the presence of 0.02 mmol of TBATB, the conversion of benzyl tert-butyldimethylsilyl ether was 17% in 9 h (Table 1, entry 19). Increasing the time of reaction from 9 to 12 h encouraged oxidation of benzyl tert-butyldimethylsilyl ether and production of benzoic acid (Table 1, entry 20). Increasing the amount of TBATB from 0.02 to 0.04 mmol led to the complete conversion of benzyl tert-butyldimethylsilyl ether and production of 88% benzaldehyde in 5 h (Table 1, entry 21). Also, increasing the reaction time to 9 h led to the more over-oxidation of benzyl alcohol to benzoic acid (Table 1, entry 22). Therefore, 0.04 mmol of TBATB and 5 h reaction time were selected as the optimized condition for photooxidative- desilylation of benzyl tert-butyldimethylsilyl ether (Table 1, entry 22).

Subsequently, the effect of solvent on the photocatalytic aerobic oxidation of benzyl alcohol was investigated in the optimized reaction condition (0.02 mmol TBATB, 10 ml CH_3CN, blue LED irradiation and 5 h). The results were shown in Figure 1.

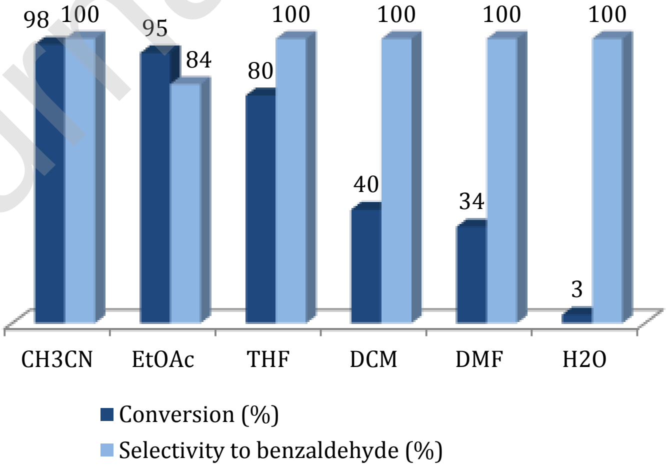
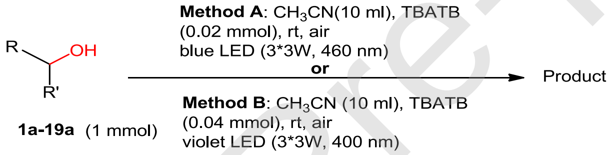


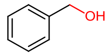
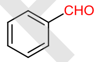
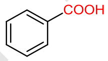
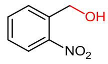
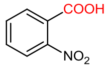
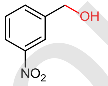
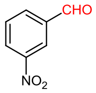
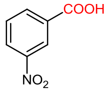
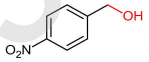
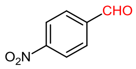
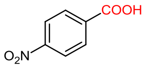
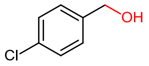
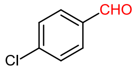
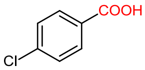
Figure 1 Photooxidation of 1 mmol benzyl alcohol in various solvents using 0.02 mmol TBATB in 5 h under blue LED irradiation

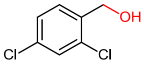
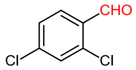
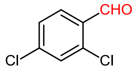
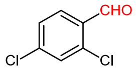
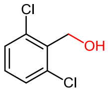
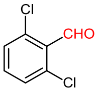
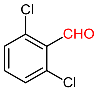
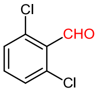
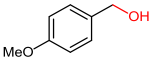
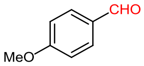
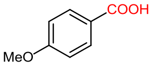
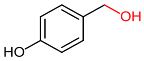
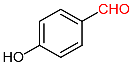
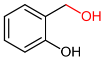
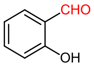
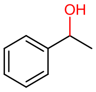
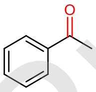
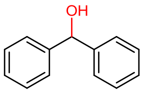
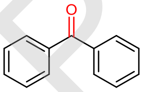
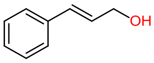
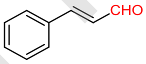
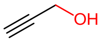
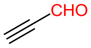
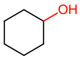
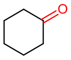
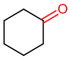
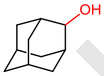
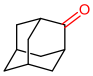
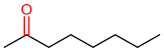
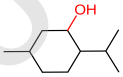
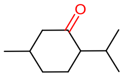
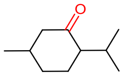
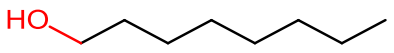
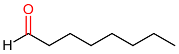
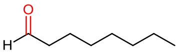
Among CH_3CN, EtOAc, THF, DCM, DMF, and H_2O, the lowest conversion (3%) was observed when using H_2O indicating a non-radical and non-catalytic mechanism for the conversion of benzyl alcohol into the benzaldehyde [36]. CH_3CN, as a common solvent for oxidation purposes [37], provided the highest conversion (98%) of benzyl alcohol to benzaldehyde.

Our investigation was extended to the photooxidation of substituted benzyl alcohols, allylic, and aliphatic alcohols (**1a-19a**) (Table 2).

Table 2 Photooxidation of various alcohols



entry	substrate	method	time (h)	product	conversion (%)	GC yield (%)	isolated yield (%)
1a		A	5		98	98	96
		B	8		100	100	98
2a		A	7		98	98	96
		B	15		100	98	95
3a		A	10		90	90	87
		B	24		100	100	98
4a		A	3		100	100	97
		B	8		100	100	98
5a		A	3		100	100	97
		B	6		100	100	95

6a		A	5		90	90	88
		A	6		100	100	97
		B	24		100	72	70
7a		A	10		82	82	79
		B	6		72	72	70
		B	24		82	82	78
8a		A	2		100	100	96
		B	10		100	90	86
9a		A	10		5	5	2
10a		A	10		0	0	0
11a		B	24		100	100	99
12a		A	5		100	100	83
13a		A	10		30	30	24
14a		A	24		2	2	1
15a		A	24		10	10	5
		B	72		70	70	63
16a		B	24		10	10	6
17a		B	72		100	100	95
18a		A	14		5	5	4
		B	72		55	55	48
19a		A	20		0	0	0
		B	72		65	65	59

Both the electron donating (–OCH_3) and withdrawing (–Cl, –NO_2) groups at the para position of benzyl alcohol ring enhanced its photocatalytic reactivity: In **4a** and **5a**, nitro and chloro as electron-withdrawing groups at the para position of benzyl alcohol ring exhibited an accelerating influence on the photooxidation reaction, 100% conversions and 100% selectivities to the corresponding benzaldehydes could be obtained after 3 h. Also, methoxy as an electron-donating group at the para position of benzyl alcohol ring showed an accelerating effect on the photooxidation reaction. Photooxidation of 4-methoxybenzyl alcohol (**8a**) led to complete conversion and production of 4-methoxybenzaldehyde after 2 h. Compared to p-nitrobenzyl alcohol (**4a**), the o-nitro (**2a**) and m-nitro (**3a**) benzyl alcohols exhibited low activity in this reaction but with increasing reaction times, the high conversions could be obtained. Therefore, the photocatalytic reactivity of substituted benzyl alcohols can be affected by the position of the substituents on the aromatic ring of benzyl alcohol. Also, compared to 2,4-dichlorobenzyl alcohol (**6a**), the 2,6-dichlorobenzyl alcohol (**7a**) required to long reaction time (10 h) to reach high conversion. It may be caused by the steric hindrance of chloro substitutions near the active site. Photooxidation of **9a** and **10a** resulted in a very low and no conversions, respectively. It seems that reactions between the phenolic compounds and bromine led to inactivation of bromine. Photooxidation of cinnamyl alcohol (**13a**) as allylic alcohol resulted in the production of only 30% cinnamaldehyde after 10 h. It seems that TBATB acts as a brominating agent in the presence of carbon–carbon double bond of cinnamyl alcohol.

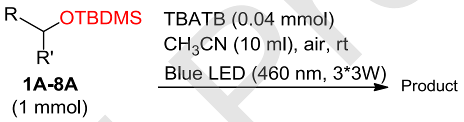
The scope of photooxidation reaction with TBATB was also expended to aliphatic alcohols (**14a-19a**). Compared to benzyl alcohols, aliphatic alcohols showed low activity in this reaction. **15a** and **18a** were oxidized into the corresponding ketones in 10% and 5% conversions, respectively, after 24 and 14 h under method A. Also, in **19a**, no conversion of 1-octanole to the corresponding aldehyde and acid observed after 20 h. With increasing the reaction time to 72 h, the conversion of **15a**, **18a** and **19a** increased to 70, 55 and 65%, respectively under method B.

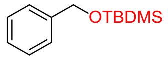
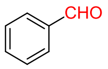
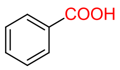
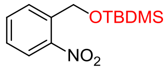
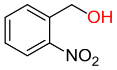
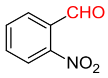
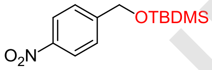
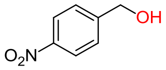
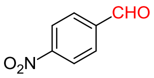
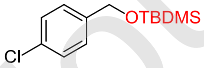
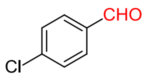
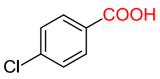
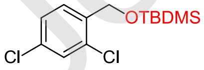
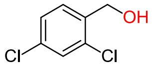
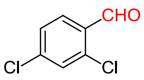
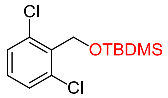
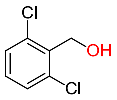
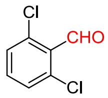
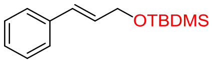
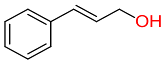
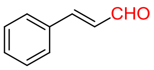
To produce carboxylic acids through over-oxidation of alcohols, three violet LED lamps and 0.04 mmol TBATB (method B) were used instead of three blue LED lamps and 0.02 mmol TBATB (method A). Obtained results were shown in Table 2. In general, benzylic and secondary alcohols converted into the corresponding carboxylic acids and ketones, respectively, in high yield under irradiation of violet LED; however, in **6a** and **7a**, corresponding benzaldehydes were the main oxidation product due to the steric hindrance of chloro substitutions (in these cases, low over-oxidation to carboxylic acids was observed).

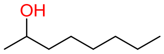
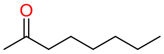
Also, the aliphatic alcohols (**16a-17a**) exhibited a lower activity than benzyl alcohols to undergo photooxidation.

Subsequently, our study was extended to the photooxidative-desilylation of several tert-butyldimethylsilyl ethers (**1A-8A**) over 0.04 mmol of TBATB under blue LED irradiation (Table 3). High conversion and yield for the photooxidative-desilylation of 4-nitro (**3A**) and 4-chloro (**4A**) benzyl tert-butyldimethylsilyl ethers were obtained. In **2A**, the nitro group at the ortho position of benzyl tert-butyldimethylsilyl ether showed a decelerating effect on the photooxidation reaction, 38% conversion was obtained after 20 h.

Table 3 Photooxidative-desilylation of various tert- butyldimethylsilyl ethers



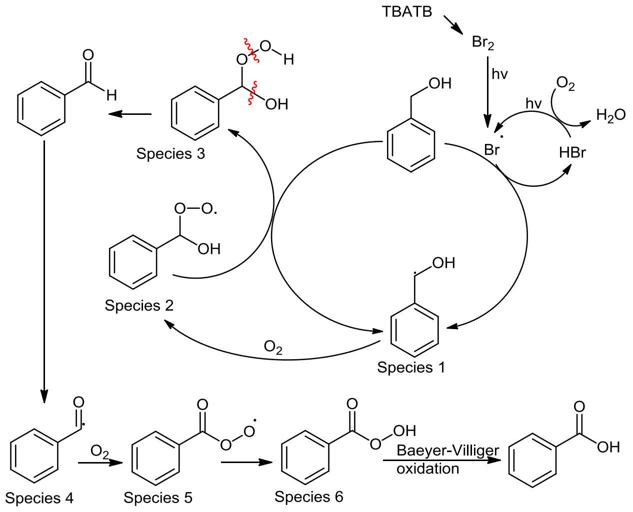
entry	substrate	time (h)	conversion	product	isolated yield (%)	product	isolated yield (%)
1A		5	100		85		10
2A		20	38		12		23
3A		6	100		0		98
4A		5	100		93		2
5A		8	100		0		96
6A		15	80		70		4
7A		20	15		0		10

8A		20	88		80		5

In **6A**, due to the steric hindrance of chloro substitutions, low oxidation to the corresponding benzaldehyde was observed (2,6-dichlorobenzyl alcohol was the main oxidation product). Secondary and allylic tert-butyldimethylsilyl ethers were found to be less reactive than other benzylic tert-butyldimethylsilyl ethers examined. 2-Octyl tert-butyldimethylsilyl ether (**8A**) as a secondary tert-butyldimethylsilyl ether exhibited low activity in photooxidative-desilylation to the corresponding aldehyde. (2-octanol was the main oxidation product after 20 h). Also, cinnamyl tert-butyldimethylsilyl ether (**7A**) as an allylic tert-butyldimethylsilyl ether afforded the cinnamaldehyde in low yield (10%) after 20 h. It should be noted that oxidation of **1A** resulted in no oxidation products in the absence of TBATB, and only 4% benzyl alcohol in the absence of LED lamps (dark room) after 24 h. Therefore TBATB and LED lights play crucial role in photooxidative-desilylation of tert-butyldimethylsilyl ethers.

Finally, based on the obtained results and previous literature, a probable mechanism was proposed for the present aerobic photooxidation of benzyl alcohol by TBATB in Scheme 2. The yellow coloration of the solution containing TBATB suggests that initially Br_2 is formed from TBATB. Also, immediately color fading of this solution after the introduction of phenolic compounds which resulted in a very low and no conversion in the photooxidation reaction (Table 2, **9a** and **10a**) verify this suggestion.

Benzyl alcohol can react with a bromo radical, generated via photodissociation of bromine to afford benzylic radical (**species 1**) and HBr, which subsequently can be converted into the bromo radical upon aerobic photooxidation [18]. Then the benzylic radical can trap O_2 to afford the peroxy radical (**species 2**), which abstracts hydrogen to afford hydroperoxide (**species 3**) [14, 15, 17, 19, 20, 38]. **Species 3**converts into benzaldehyde with the selective C–O bond cleavage [19]. The aldehyde C-H bond in benzaldehyde can be cleaved by free radicals [39] (such as peroxy radicals which can be produced during the photocatalytic oxidation reaction), therefore **species 4** can be generated. The abstraction of molecular oxygen by **species 4** leads to the formation of radical **species 5**, which subsequently transforms to perbenzoic acid (**species 6**) via hydrogen abstraction [39]. Finally, perbenzoic acid converts into benzoic acid by non-radical Baeyer–Villiger-type oxidation [39].



Scheme 2 Possible reaction pathway

3. Conclusion

In this work, we report an efficient metal-free visible light active photocatalytic system that can be used to convert benzyl alcohols and benzyl silyl ethers into their corresponding carbonyl compounds in high yield under mild conditions, using a catalytic amount of TBATB (0.02-0.04 mmol) as photocatalyst, air and blue (460 nm) or violet LED (400 nm) as light sources. We found the oxidation products selectivity can be affected and controlled by changing the irradiation wavelengths in this photocatalytic system.

Utilizing the air as a green oxidant, LED as visible light source, and TBATB as a metal-free photocatalyst provided an advantage approach over protocols that needed toxic and expensive metal catalysts, corrosive oxidant, elevated reaction temperature, and time-consuming intermediate separation.

Conflict of Interest and Authorship Conformation Form

Please check the following as appropriate:

- ○ All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.
- ○ This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.
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