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Convenient photooxidation of alcohols using dye sensitised zinc oxide in combination with silver nitrate and TEMPO†

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A novel photooxidative system using dye sensitised zinc oxide in combination with silver nitrate and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) in an aqueous solution is described. Under visible light irradiation the selective oxidation of alcohols to their corresponding aldehydes and ketones was effected in good to excellent yields.

Photocatalysis, by semiconductor metal oxides, has been identified as a promising route for organic chemistry in the 21st century.¹ Of the semiconductors available, TiO₂ (the most studied semiconductor) and ZnO have emerged as the semiconductors of choice due to their low cost, stability under irradiation and environmental friendliness.² From a synthetic chemistry point of view, the most appealing aspect of semiconductor mediated photocatalysis is their ability to oxidise alcohols to their carbonyl derivatives.³

As part of our interest in tandem coupling reactions,⁴ we aimed to carry out a photocatalysed tandem oxidation coupling reaction which involves the oxidation of an alcohol to its aldehyde, followed by a trapping of the generated aldehyde by an appropriate nucleophile without the isolation of the intermediate aldehyde. While the TiO₂ mediated alcohol oxidation has been well documented the photocatalytic procedure is unselective, due to the high oxidative potential of the holes created in the valence band,⁵ resulting in a variety of products in addition to the desired carbonyl compound.⁶ Thus, before embarking on a photocatalysed tandem coupling reaction, the photooxidative procedure needed to be refined. Recently, Zhao *et al.*^{7a} and Nagata *et al.*^{7b} have demonstrated the light activated oxidation of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) to the oxoammonium salt (TEMPO⁺) which selectively oxidises alcohols to their carbonyl compounds. However, due to the small scale (300 μmol–0.1 mmol) and long reaction times (18–24 h) these procedures are unlikely to find application in traditional organic synthesis.

Herein, we report an improved strategy for the oxidation of alcohols to aldehydes using a dye sensitised metal oxide/silver/TEMPO system in an aqueous solution. The semiconductor

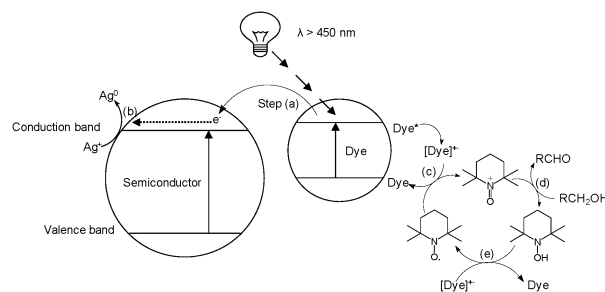


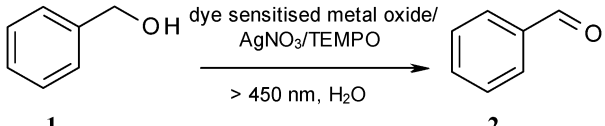
Fig. 1

was sensitised with alizarin red to allow the system to be activated by visible light irradiation. Under the above conditions, the dye and not the semiconductor will be activated preventing the formation of strongly oxidising hydroxyl radicals.

Upon visible light irradiation, the activated dye transfers an electron into the conduction band of the semiconductor (see Fig. 1, step a). The injected electron is readily consumed by silver(i) which is reduced to metallic silver (Fig. 1, step b). The activated dye returns to its ground state oxidising TEMPO from its radical form into the oxoammonium salt (the active oxidising species of TEMPO) (Fig. 1, step c). The oxoammonium salt oxidises the alcohol to its carbonyl derivative (Fig. 1, step d), forming the hydroxylamine which can regenerate the TEMPO radical *via* oxidation by the dye radical (Fig. 1, step e) (see ESI† for table of standard redox potentials).

In an effort to validate the proposed mechanism, we attempted a test reaction which involved mixing a portion of dye sensitised TiO₂ or ZnO, silver nitrate, TEMPO and benzyl alcohol in water under visible light irradiation. The reactions were conducted on the 0.1 mmol scale to aid comparison with the previously mentioned photooxidative systems.⁷ Preliminary investigations revealed that the quantity of silver nitrate was vital for the photooxidative system to proceed (see ESI† for details) with 18 equivalents shown to be optimum. While the quantity of silver nitrate may be deemed to be excessive, there are a number of beneficial effects relating to the use of silver(i) as a sacrificial electron acceptor. Firstly, dye sensitised photocatalysts are unstable in aqueous solution as the dye can easily detach from the photocatalyst.⁸ Concentrated silver solutions are known to stabilise dye sensitised photocatalysts preventing the detachment of the dye.⁹ Secondly, the superior electron accepting ability of silver(i) would drive the photooxidative

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Table 1 Oxidation of benzyl alcohol using a dye sensitised metal oxide/AgNO₃/TEMPO system


Entry	Metal oxide	Time/h	Yield ^a (%)
1	TiO ₂	1	3
2	ZnO	1	54
3	TiO ₂	2	8
4	ZnO	2	82
5 ^b	—	2	16
6 ^c	ZnO	2	12
7 ^d	ZnO	—	nd ^f
8 ^e	ZnO	—	nd ^f

^a GC yield. ^b Absence of Zinc oxide. ^c Absence of TEMPO. ^d Absence of AgNO₃. ^e CH₃CN as solvent. ^f Not determined as the dye sensitised ZnO was unstable under these conditions, see ESI.

system resulting in shorter reaction times and higher yields (*vide infra*). Additionally, methods are available to recover the precipitated silver¹⁰ which would allow for the reuse of the photocatalyst.

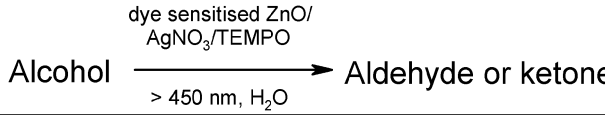
Using the conditions as highlighted above, we aimed to probe the contribution of each of the additives to the photo-oxidative procedure (Table 1). As can be seen, pleasing yields were produced in the presence of dye sensitised ZnO while the reaction using dye sensitised TiO₂ produced only trace amounts of the product. This result is somewhat surprising as TiO₂ is expected to display similar behaviour to ZnO.¹¹



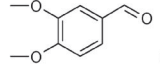

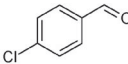

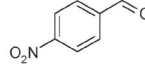



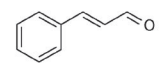





On analysis of the reaction vessel at the completion of the reaction, the ZnO system shows a high degree of metallic silver while the TiO₂ system shows only minute quantities of silver (see ESI†). This implies that electrons are not being efficiently injected into the conduction band of TiO₂. One possible explanation is the strong back electron transfer (BET) on the TiO₂/Alizarin system¹² which decreases the quantity of electrons injected into the conduction band. Further detailed studies are underway to probe the mechanism of these systems.

In the absence of dye sensitised ZnO or TEMPO a dramatic decrease in yield was observed (Table 1, entries 5 and 6). The formation of benzaldehyde in the absence of dye sensitised ZnO suggests that other mechanisms may be occurring but the highest yield of 82% is only obtained in the presence of all the additives indicating that the proposed mechanism is the major route for product formation. This observation is in agreement with other research in the development of complex oxidative systems.^{7a} The results of this study highlight the importance and distinct contribution of each of the additives to the oxidative system. The turnover number (TON) was calculated and found to be less than 100, indicating that this is a photoreaction rather than a photocatalytic reaction. In the absence of silver nitrate, the dye sensitised ZnO was unstable and as expected the dye readily detached from ZnO (Table 1, entry 7) (see ESI†). Similar results were observed when water was replaced with acetonitrile as a solvent (Table 1, entry 8). With this optimised procedure in hand, we attempted to explore the scope of the oxidation system on a series of alcohols (Table 2).

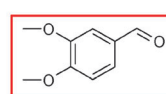
The present oxidative system was particularly effective on benzylic alcohols with good to excellent yields being obtained (Table 2, entries 3–8). This point is even more impressive considering certain alcohols are solids at room temperature and display limited solubility in water (Table 2, entries 5–7). The effect of substitution resulted in an increase in yield with the lowest increase observed for the 4-chloro derivative (82% for benzyl alcohol vs. 89% for 4-chlorobenzyl alcohol). The dimethoxy, 4-nitro, 4-methyl derivatives as well as cinnamyl alcohol showed almost quantitative conversion to the aldehyde. In all cases, the obtained yields are superior to those previously reported. Hence, the high yields obtained make the tandem coupling reaction on benzylic alcohols a highly attractive and viable procedure. The dye sensitised ZnO/AgNO₃/TEMPO system was, however, less prolific on an unactivated alcohol (Table 2, entry 9) due to oxoammonium salt's limitation on these substrates.¹³ More encouraging was the performance of the system on a secondary benzylic alcohol (Table 2, entry 10) which produced the desired ketone in a satisfactory yield of 67% after 2 hours of irradiation. To the best of our knowledge, this is the first report of a photocatalysed oxoammonium salt oxidation on a secondary benzylic alcohol.

To illustrate the potential utility of this system, we attempted two scale-up reactions. Firstly, we chose to oxidise 3,4-dimethoxybenzyl alcohol as the reaction on the smaller scale gave quantitative yields. Secondly, we chose to attempt the oxidation of benzoin to benzil as benzoin is an important starting material for tandem

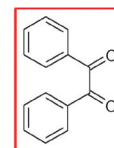
Table 2 Oxidation of alcohols using a ZnO/AgNO₃/TEMPO system^a


Alcohol	Aldehyde or ketone	Yield (%)
		3 82%
		4 >99%
		5 89%
		6 97%
		7 98%
		8 >99%
		9 12%
		10 67%

^aReaction conditions: alcohol (0.1 mmol), dye sensitised Zinc oxide (20 mg), TEMPO (1.5 mg) and AgNO₃ (18 equiv.) in 1.5 ml H₂O under visible light irradiation for 2 hours. ^b GC yield.



4 87%



11 78%

^aReaction conditions: alcohol (0.5 mmol), dye sensitised Zinc oxide (100 mg), TEMPO (10 mg) and AgNO₃ (18 equiv.) in 10 ml H₂O under visible light irradiation for 10 hours. ^b Isolated yield.

coupling reactions.¹⁴ The oxidation of 3,4-dimethoxybenzyl alcohol resulted in the formation of the desired aldehyde in an isolated yield of 87%, highlighting the 'scale up' applicability of this procedure. The oxidation of benzoin to benzil also proceeded smoothly with the desired ketone isolated in a yield of 78% despite the hindered nature of the alcohol.

In conclusion, we have shown that the combination of dye sensitised ZnO in combination with AgNO₃ and TEMPO in water under visible light irradiation leads to selective oxidation of alcohols to aldehydes and ketones in good to excellent yields. The system is appealing due to the high yields, short reaction times together with mild reaction conditions. The photooxidative system was also scaled up with great success further highlighting its efficacy. Further studies are underway to expand the scope of the methodology and extend the application of the oxidative system to tandem coupling reactions.

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