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

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Electronic Supplementary Information

Table 1 Redox potentials of various components of oxidative cycle.

Compound	E^0 vs. SHE (V)	Reference
E_{cb} (ZnO)	– 0.42	1
TEMPO/TEMPO$^+$	0.64	2
Ag^+/Ag^0	0.80	3
$AR^{+\cdot}/AR$	0.79	4
E_{cb} (TiO_2)	– 0.50	5
$AR^*/AR^{+\cdot}$	–1.57	5

- The standard redox potential of for the excited state of Alizarin red ($AR^*/AR^{+\cdot}$) is lower than E_{cb}[1]of ZnO and E_{cb} of TiO_2 indicating that the excited state of the dye is capable of injecting electrons into the conduction band of the semiconductors.
- The standard redox potential of silver (I) (Ag^+/Ag^0) is higher than E_{cb} for the semiconductors indicating that the injected electrons can be trapped by silver (I).
- The standard redox potential of ($AR^{+\cdot}/AR$) is higher than the standard redox potential of TEMPO/TEMPO$^+$ indicating that the dye radical is capable of oxidising TEMPO.

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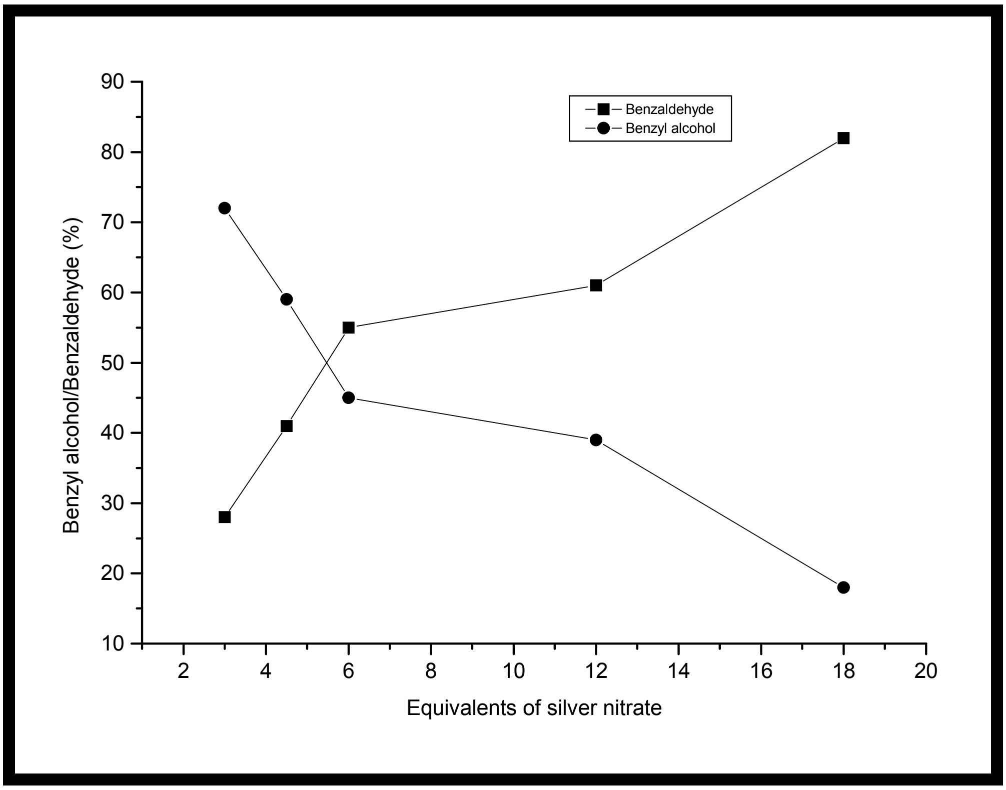
[1] cb = conduction band



Graph 1: Relationship between benzyl alcohol/benzaldehyde and equivalents of silver nitrate.

An increase in yield of benzaldehyde is observed as the quantity of silver nitrate increases until an optimum of 18 equivalents is reached.

Figure 1: The dye sensitised ZnO/$AgNO_3$/TEMPO system at the end of the reaction. The precipitated silver is evident on the sides of the reaction vessel.

Reaction conditions: Benzyl alcohol (0.1 mmol) TEMPO (1.5 mg), dye sensitised ZnO (20 mg) and silver nitrate (18 equivalents) in 1.5 ml H_2O under visible light irradiation for 2 hours.

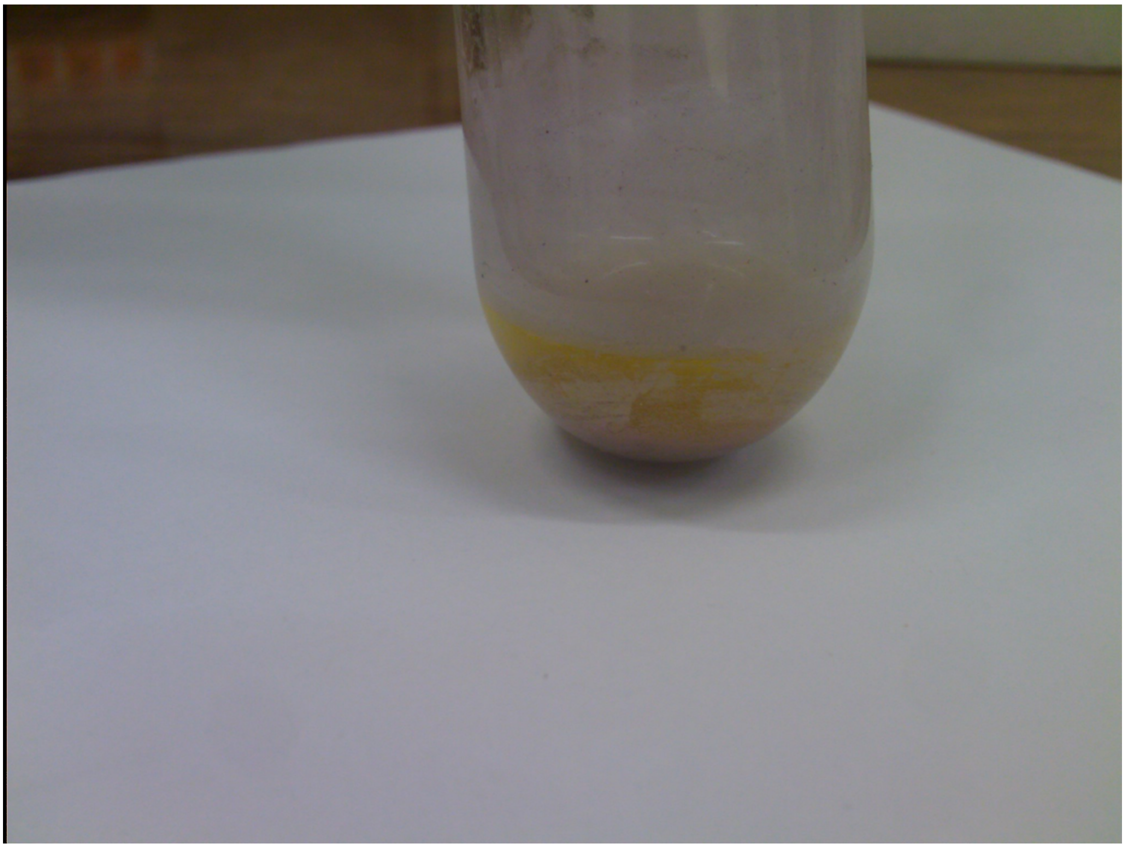


Figure 2: The dye sensitised $TiO_2/AgNO_3$/TEMPO at the end of the reaction. The dye sensitised TiO_2 is clearly evident at the bottom of the tube.

Reaction conditions: Benzyl alcohol (0.1 mmol) TEMPO (1.5 mg), dye sensitised TiO_2 (20 mg) and silver nitrate (18 equivalents) in 1.5 ml H_2O under visible light irradiation for 2 hours.

Figure 3: Comparison of ZnO (left) and dye sensitised ZnO (right). From the above pictures it was concluded that Alizarin red had successfully adsorbed onto ZnO.

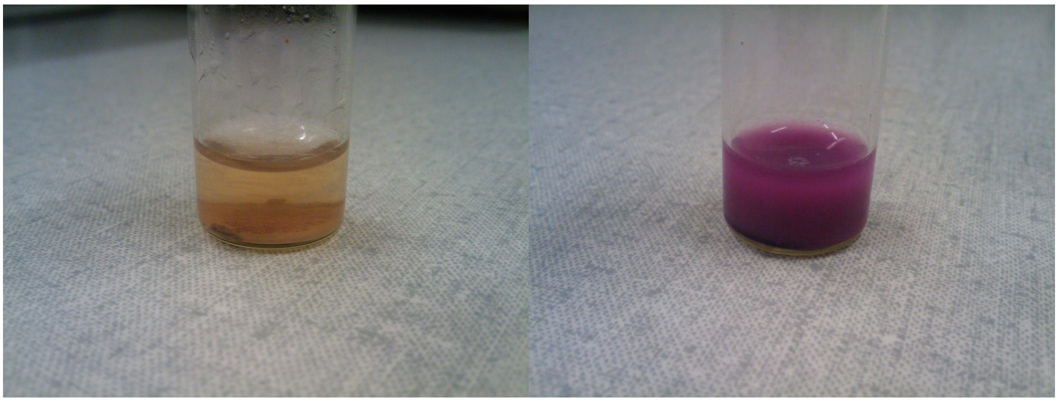


Figure 4: Comparison of reaction mixture in the presence of silver nitrate (left) and in the absence of silver nitrate (right). From the above pictures it was concluded that in the absence of silver nitrate the dye sensitised ZnO was unstable and that the dye detached from ZnO.

Reaction conditions: Silver nitrate (306 mg or 0 mg), TEMPO (1.5 mg), dye sensitised ZnO (20 mg) in 1.5 ml H_2O.

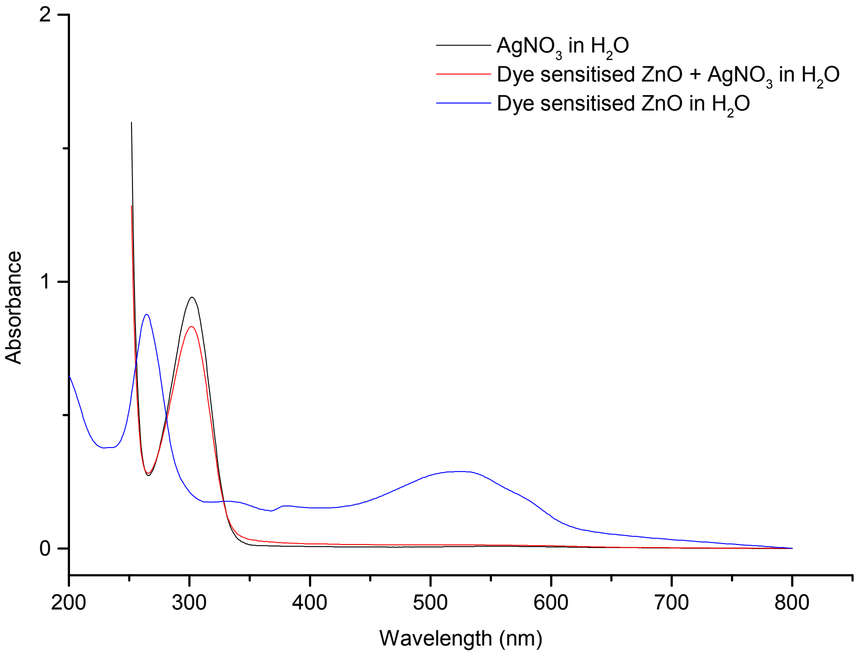


Figure 5: UV/Vis spectra of (a) AgNO$_3$ solution, (b) AgNO$_3$ + dye sensitised ZnO in H$_2$O and (c) Dye sensitised ZnO in H$_2$O.

General: ^{1}H and ^{13}C NMR spectra were obtained using a Bruker Avance 400 operating at either at 400 or 100 MHz using $CDCl_3$ as an internal standard. Data are expressed in parts per million relative to residual solvent. Coupling constants (*J*) were recorded in Hz. Chromatograms were obtained using Perkin Elmer Clarus 500 Gas Chromatograph. UV/Vis spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Reactions were irradiated using an OSRAM VIALOX 70 W lamp. Radial chromatography was performed on the Harrison Research Chromatatron (Model 7924T) with the solvent system delivered by gravity flow using a 1 mm layer of Merck silica gel.

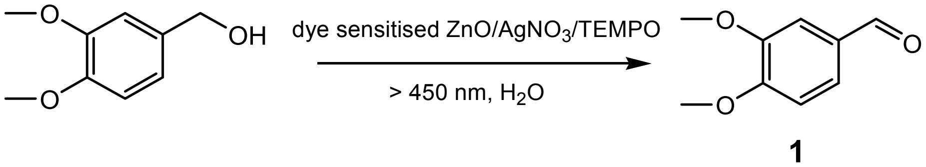
Procedure A: Oxidation of Alcohols on small scale

To a solution of $AgNO_3$ (1.8 mmol), TEMPO (1.5 mg) and dye sensitised ZnO (20 mg) in H_2O (1.5 ml) was added the appropriate alcohol (0.1 mmol). The mixture was irradiated under visible light (> 450 nm) for 2 hours. The mixture was diluted with ethyl acetate to dissolve any insoluble organic compounds and the resulting mixture was passed through a membrane, with a pore diameter of 2 μm, and analysed by gas chromatography. The structures were confirmed by comparison with authentic samples.

Procedure B: Oxidation of Alcohols on large scale

To a solution of $AgNO_3$ (9 mmol), TEMPO (10 mg) and dye sensitised ZnO (100 mg) in H_2O (10 ml) was added the appropriate alcohol (0.5 mmol). The mixture was irradiated under visible light (> 450 nm) for 10 hours. The resulting mixture was extracted with CH_2Cl_2 and the combined organic layers dried over anhydrous magnesium sulphate. The solution was filtered and subsequently concentrated under reduced pressure to produce a crude product which was purified using radial chromatography to afford pure product.

Characterisation of Isolated Aldehydes or Ketones



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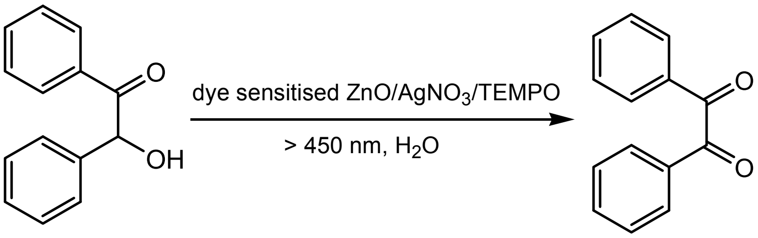
3,4-dimethoxybenzaldehyde (1). The title compound was prepared from 3,4-dimethoxybenzyl alcohol (0.50 mmol) according to Procedure B. The desired aldehyde **1** (0.0723g, 87%) was obtained after radial chromatography (1:1 PE:EtOAc) as a colourless oil. Spectra data identical to those previously reported.[6] ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.94 (s, 3H), 3.97 (s, 3H), 6.98 (d, J = 8.2 Hz, 1H), 7.41 (d, J = 1.8 Hz, 1H), 7.46 (dd, J_1 = 8.2 Hz, J_2 = 1.8Hz, 1H), 9.85 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 56.0, 56.2, 109.0, 110.4, 126.8, 130.2, 149.7, 154.5, 190.8.



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Benzil (2). The title compound was prepared from benzoin (0.50 mmol) according to Procedure B. The desired diketone **2** (0.0820 g, 78%) was obtained after radial chromatography (9:1 PE:EtOAc) as a yellow solid. Spectra data identical to those previously reported.[7] 1H NMR (400 MHz, CDCl$_3$) δ 7.50-7.54 (m, 4H), 7.64-7.68 (m, 2H), 7.97-7.99 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 129.0, 129.9, 133.0, 134.9, 194.5.

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