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Catalyst-free aerobic photooxidation of sensitive benzylic alcohols with chemoselectivity controlled using DMSO as the solvent†

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The drawbacks commonly observed in synthetic methods for alcohol oxidation often stem from the utilization of complex, toxic, hazardous, or waste-producing oxidants. When sensitive or complex substrates bearing several functional groups are to be transformed, the selectivity of oxidation becomes another significant challenge. Herein, a chemoselective and operationally simple catalyst-free and additive-free method is presented for the aerial oxidation of 1-phenylpropargyl and 1-phenylallyl alcohols to their corresponding ketones, requiring only a solvent and visible light irradiation. The crucial role of dimethylsulfoxide (DMSO) as the solvent lies in achieving high chemoselectivity. Singlet oxygen, whose formation is photosensitized by the substrate and the product, is captured by DMSO, thereby preventing the undesired over-oxidation that occurs in other solvents. The application of DMSO to protect the substrate against singlet oxygen represents a novel approach that is potentially applicable to other aerobic photocatalytic processes.

Introduction

Most syntheses of valuable organic compounds, such as pharmaceuticals, dyes and agrochemicals, involve an alcohol oxidation reaction to form their corresponding aldehyde or ketone derivative.[1] This transformation has been routinely achieved using stoichiometric agents based on high-valent metals, for example, chromium(VI) compounds or MnO_2;[2] alternatively hypervalent iodine reagents,[3] activated dimethyl sulfoxide (DMSO)[4] and organic peroxides have been used.[5,6] Unfortunately, these stoichiometric procedures always produce a lot of waste and many of the reagents involved in these reactions are highly toxic.

Molecular oxygen is considered a green oxidant producing only water as the by-product.[7] However, oxidation with oxygen requires either the substrate or oxygen to be activated (Scheme 1A), which is traditionally achieved using transition metal-containing homogeneous or heterogeneous catalysts,[1b,8] although some metal-free or biocatalytic procedures have also been developed.[6a,9,10] Recent progress in oxidation reactions with oxygen has been made within photoredox catalysis using light and a photoexcited catalyst.[11] In particular, methods using organic dyes[12,13] seem to be promising from an environmental point of view, although they still suffer from the low stability of the photocatalyst and/or, with a few exceptions, the need for an additive. Thus, an oxidation reaction with oxygen, which does not require both a catalyst and an additive, could be considered as an optimal process. However, such methods for alcohol oxidation are rare and require high temperature and pressure conditions or a strong light source.[14] Harsh conditions similar to those for excitation with light cause another problem not mentioned yet – low chemoselectivity, which is manifested by the production of undesired by-products. Thus, the discovery of a green method without the need for additives utilizing mild conditions, which would also be suitable for sensitive substrates, remains an unsolved problem.

1-Phenyl propargyl alcohols **1** contain a triple bond and an activated benzylic position, which are prone to undesired side- or over-oxidation reactions.[15] On the other hand, they are considered as difficult to oxidize substrates.[16] In addition to their importance in organic synthesis,[15] alcohols **1** are suitable representatives of sensitive substrates. Some procedures have been reported in the literature that can transform benzylic alcohols bearing multiple bonds to their corresponding ketone derivatives (Scheme 1B). However, most of them use stoichiometric amounts of Cr(VI) or other metal-based reagents.[17]

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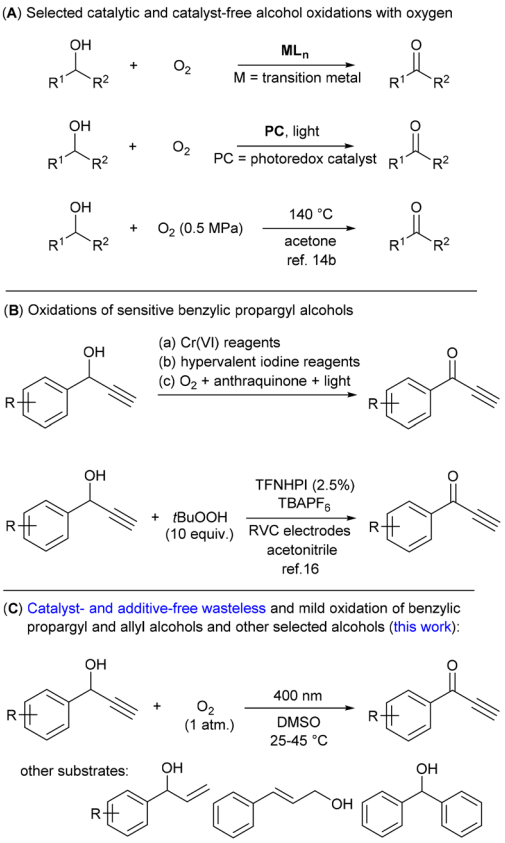


Scheme 1 Oxidation of alcohols to ketones with molecular oxygen and overview of oxidations of sensitive 1-phenylpropargyl alcohols.

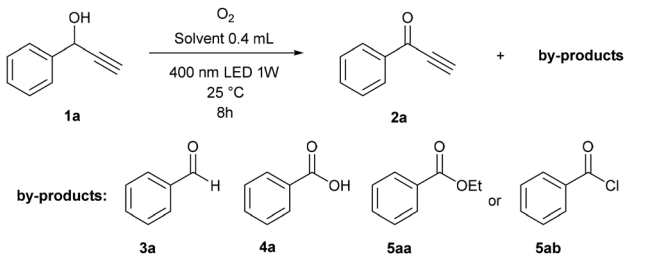
Alternatively, oxidation reactions using hypervalent iodine reagents[18] or photocatalytic procedures with 2-bromoanthraquinone[19] have been shown in a limited number of examples. Very recently, the most effective and general procedure based on *N*-hydroxy-tetrafluorophtalimide (TFNHPI) as an electrochemical mediator and *tert*-butylhydroperoxide as a stoichiometric oxidizing agent has been developed.[16] Herein, we report the catalyst- and additive-free chemoselective photooxidation of alcohols **1** to ketones **2** using oxygen performed at room temperature (Scheme 1C). The operational simplicity and lack of waste generation characterize this method, which requires only irradiation by visible light and the use of DMSO as the solvent. The choice of solvent was crucial to achieve the desired chemoselectivity; DMSO exhibits an important protective role against singlet oxygen processes, described in this paper for the first time.

Results and discussion

Development and optimization of the reaction

With the aim of developing the selective oxidation of sensitive 1-phenylpropargyl alcohols **1** to give the corresponding ketones **2** using photoredox catalysis (see ESI S4† for preliminary experiments), we observed that the remarkable oxidation

Table 1 Optimizing conditions of propargyl alcohol photooxidation[a,b]



Entry	Solvent	Condition alternation	Yield[c] [%] 1a	2a	3a	4a
1	DMSO	No	4	90	2	4
2	DMF	No	42	0	0	58
3	EtOH	No	7	6	2	40[e]
4	Acetonitrile	No	0	62	0	38
5	Dioxane	No	2	3	47	48
6	$CHCl_3$	No	0	0	0	47[f]
7	Acetone	No	0	7	1	90
8	Toluene	No	8	16	17	43
9	DMSO	45 °C	2	91	3	4
10	DMSO	0 °C	38	55	3	4
11	DMSO	450 nm	64	34	1	0
12	DMSO	385 nm	45	48	3	4
13	DMSO	Sunlight[d]	25	65	10	0
14	DMSO	Air	90	9	1	0
15	DMSO	Ar	100	0	0	0
16	DMSO	Under darkness	100	0	0	0

[a] Selected data; for further experiments, see ESI S5.† [b] Conditions: **1a** (0.1 mmol), solvent (0.4 mL), 400 nm LED 1 W, oxygen (balloon), 25 °C, 8 h. [c] Determined by GC-MS. [d] 20 hours. [e] 22% of **5aa**. [f] 52% of **5ab**.

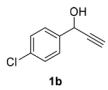
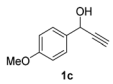
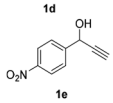
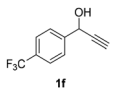
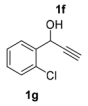
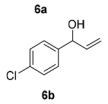
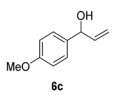
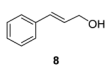
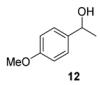
of model substrate **1a** also occurred in the absence of a catalyst when irradiated with 400 nm light (Table 1). Interestingly, the reaction in dimethyl sulfoxide (DMSO) took place and gave ketone **2** in an excellent yield with high chemoselectivity (entry 1), while those performed in other solvents formed several undesired by-products (entries 2–8). Benzoic acid (**4a**) was the main product formed in *N*,*N*-dimethylformamide (DMF), ethanol, dioxane and toluene, and also appeared in high amounts in acetonitrile. In dioxane, ethanol and chloroform, significant amounts of benzaldehyde (**3a**), ethyl benzoate (**5aa**) or benzoylchloride (**5ab**) were also observed, respectively. For the reaction in DMSO, we investigated the effect of temperature (entries 9 and 10) and wavelength (entries 11 and 12), but the original conditions, *i.e.* 25 °C and 400 nm appeared to be the best. We successfully demonstrated the use of sunlight by performing the reaction at a window, which achieved a good yield, albeit a longer reaction time was necessary (entry 13). Under air instead of oxygen, the system was less efficient (entry 14). Control experiments showed that oxidation does not occur in the absence of oxygen or light (entries 15 and 16).

Substrate scope investigation

Having in hand such a photooxidation method that requires only a solvent (DMSO), visible light (400 nm) and oxygen, we

were interested in its limitations regarding the substrate structure (Table 2). We found that in addition to the unsubstituted derivative **1a** (entries 1 and 2), the method can be used for *para*-substituted 1-phenylpropargyl alcohols containing electron-withdrawing (**1b**) or electron-donating (**1c** and **1d**) groups (entries 3–8). Substrates **1e** and **1f** containing strongly electron-withdrawing nitro- and trifluoromethyl groups gave their corresponding ketone products in a lower yield, which were not enhanced by an elevated temperature (45 °C) or prolonging the reaction time (entries 9–14). A very low yield of the ketone product was observed with the *ortho*-substituted derivative **1g** (entries 15 and 16), which corresponds to its low ability to absorb 400 nm light (see ESI S3† and discussion below). In contrast, the *meta*-substituted derivative **1h** with an absorbing well in the 400 nm region (similar to *para*-derivative **1b**) gave a significant amount of ketone after irradiation (entries 17 and 18).

Table 2 Effect of the benzylic alcohol structure on its photooxidation[a,b]

Entry	Substrate	Temperature [°C]	Time [h]	Yield[c] [%]
1	 **1a**	25	8	90
2		45	8	91
3	 **1b**	25	8	89
4		45	8	39
5	 **1c**	25	8	93
6		45	8	79
7	 **1d**	25	8	85
8		45	8	86
9	 **1e**	25	8	14
10		25	16	4
11		45	8	12
12	 **1f**	25	8	27
13		25	16	28
14		45	8	32
15	 **1g**	25	8	2
16		45	8	5
17	 **1h**	25	8	49
18		45	8	19
19	 **6a**	25	8	47
20		45	8	42
21	 **6b**	25	8	44
22		45	8	26
23	 **6c**	25	8	70
24		45	8	16
25	 **8**	25	8	75
26		45	8	64
27	 **10**	25	8	45[d]
28		45	8	72[d]
29	 **12**	25	8	17[d]
30		45	8	41[d]

[a] Selected data; for further experiments, see the ESI.† [b] Conditions: **1a** (0.1 mmol), DMSO (0.4 mL), 400 nm LED 1 W, oxygen (balloon), 8 h. [c] Determined by GC-MS. [d] Determined by ^{1}H NMR.

Our method can also be applied to 1-phenylallyl alcohols **6** (entries 19–24), although they are less reactive in oxidation to ketones **7**, which are, on the other hand, more susceptible to over-oxidation to their benzoic acid derivatives, as especially evident at 45 °C. This tendency was demonstrated by the decreased yield of ketone **7** (see ESI S5† for reactions performed under different conditions). On the other hand, cinnamyl alcohol **8** (entries 25 and 26) was sufficiently oxidized to aldehyde **9** with high yield and selectivity. Diphenylmethanol (**10**) and 1-(4-methoxyphenyl)ethanol (**12**), which are representatives of 1,1-diaryl- and 1-arylalkanols, were also effectively oxidized at higher temperatures (entries 27–30).

In selected cases, we demonstrated the effectiveness of our method on a preparative scale giving the corresponding ketones in good to high isolated yields (Fig. 1). Preparative experiments occurred mainly at 40 °C because the reaction mixture was heated upon irradiation by the LED. For compounds **1b**, **1c** and **8**, the mixtures were cooled to 25 °C to maintain the chemoselectivity of the reaction. The reaction times were optimized to achieve the highest conversions to carbonyl compounds (see data in Fig. 1). Thus, with the exception of **1c**, some alcohol remained unreacted in the mixture. Moreover, a minor amount of the corresponding benzaldehyde or benzoic acid was present in the crude reaction mixtures after preparative experiments with **1a–d** and **8** (see ESI S3†). Decreased isolated yields of ketones as compared with conver-

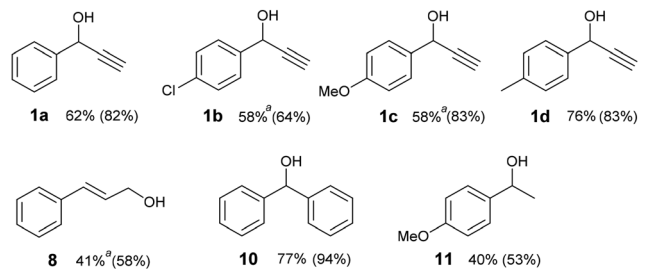


Fig. 1 Isolated yields of catalyst-free photooxidation on a 1 mmol scale. Conversions to ketones analysed by ^{1}H NMR are given in parentheses. Conditions: alcohol (1 mmol), DMSO (4 mL), 400 nm LED 1 W, oxygen (balloon), 40 °C, 8–10 hours, see ESI S5† for details. [a]Cooling to 25 °C.

sions were caused by purification with column chromatography.

The essence of the ease of oxidization upon LED irradiation under oxygen was based on the ability of the respective substrates to absorb visible light at the concentration used in the photooxidation reactions. 1-Phenyl propargyl alcohol **1a** exhibits a broad absorption band at around 260 nm and does not absorb 400 nm light at "analytical" concentrations. However, a highly concentrated 0.25 M solution of **1a** in DMSO (the concentration of **1a** in the reaction mixture) and acetonitrile display some absorption at around 400 nm, which is probably caused by the aggregation of **1a** (see Fig. 2A and ESI S3†). A similar situation was observed with other substrates, giving a remarkable yield of the ketone product. On the other hand, an *ortho*-substituted derivative **1g** exhibited a relatively small absorption around 400 nm even at high concentrations (see ESI S3†), which is probably the reason why only a small amount of ketone **2g** (together with starting material) was found in the reaction mixture after the oxidation reaction. Interestingly, alcohol **1a** exhibits fluorescence in the visible light region (see ESI S8†). Thus, we measured the excitation spectra of **1a** in DMSO showing a clear band at around 400 nm (see Fig. 2B).

Mechanistic investigations

In our mechanistic investigations, we focused on explaining the overall reaction scheme and origin of the high chemoselectivity observed in the oxidation reactions performed in DMSO. For detailed studies, we selected acetonitrile as a solvent representative, allowing the undesired over-oxidation reaction.

First, we monitored the concentrations of the starting alcohol **1a**, ketone **2a** and over-oxidation products **3** and **4** under photooxidation conditions over 24 h (Fig. 3).

The reaction courses in both DMSO and acetonitrile correspond to a sequence of consecutive reactions: alcohol **1a** was oxidized to ketone **2a**, which was further oxidized to carboxylic acid. In both solvents, ketone **2a** oxidation likely occurred *via* aldehyde **3a**, which was detected in small concentrations most of the time. Overall, the oxidation is slower in DMSO. However, the most significant difference can be found in the rate of the transformation from **2a** to **4a**, which was much

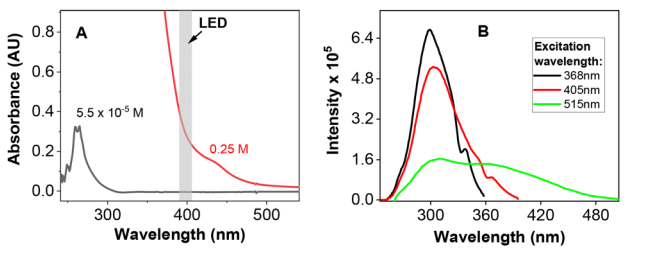


Fig. 2 (A) Absorption spectra of **1a** at a low concentration (5×10^{-5} mol L^{-1}, black) and at the concentration of photocatalytic experiments (0.25 mol L^{-1}, red) in DMSO. Dominant LED emission is highlighted in grey. (B) Excitation spectra of **1a** in DMSO.

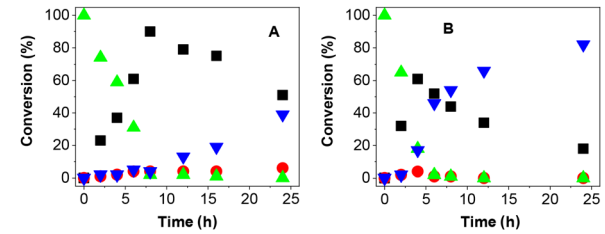


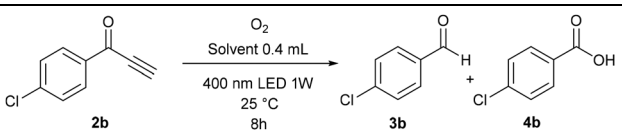
Fig. 3 Reaction course of **1a** photooxidation under standard conditions in (A) DMSO and (B) acetonitrile. Symbols mean conversion of **1a** (▲), **2a** (■), **3a** (●) and **4a** (▼).

faster in acetonitrile. Moreover, carboxylic acid **4a** was formed immediately in acetonitrile after **2a** appeared, even in small concentrations. Thus, the direct oxidation of alcohol **1a** to form **4a** in acetonitrile cannot be excluded.

Analogous conclusions can be drawn from independent experiments on the oxidation of ketone **2b** (Table 3). In DMSO, only small amounts of the over-oxidation products were observed after 8 h of irradiation (entries 1–3). On the other hand, all of ketone **2b** was consumed in acetonitrile and quantitatively converted into benzoic acid **4b**, even after 3 h (entries 4 and 5). Interestingly, a faster reaction was observed in deuterated acetonitrile when compared to non-deuterated acetonitrile (entries 6 and 7), which indicates the participation of singlet oxygen (see the mechanistic studies below).

The photophysical and spectral properties of **1a** and **2a** were studied using steady state and transient absorption spectroscopy in acetonitrile (Fig. 4). After irradiation, both **1a** and **2a** enter short-lived singlet excited states, followed by fast intersystem crossing (ISC) to the triplet T_1 state (Fig. 4A and B), which was found to be quenched by oxygen: the lifetimes of T_1 for **1a** and **2a** were found to be 1.4 μs and 19.6 μs under argon and 115 ns and 0.4 μs under an air atmosphere, respectively, measured by transient absorption spectroscopy (Fig. 4C

Table 3 Effect of the solvent on the photooxidation of ketone **2b** to aldehyde **3b** or acid **4b**[a]



Entry	Solvent	Condition alternation	Conversion[b] [%] 2b	3b	4b
1	DMSO	—	69	6	25
2	DMSO	Under darkness	92	4	0
3	DMSO	Ar	100[c]	0	0
4	Acetonitrile	—	0	0	100
5	Acetonitrile	3 h	2	0	98
6	Acetonitrile	1 h	77	2	21
7	Acetonitrile-d_3	1 h	67	1	32

[a] Conditions: **2a** (0.1 mmol), solvent (0.4 mL), 400 nm LED 1 W, oxygen (balloon), 25 °C, 8 h. [b] Determined by GC-MS. [c] Determined by ^{1}H NMR.

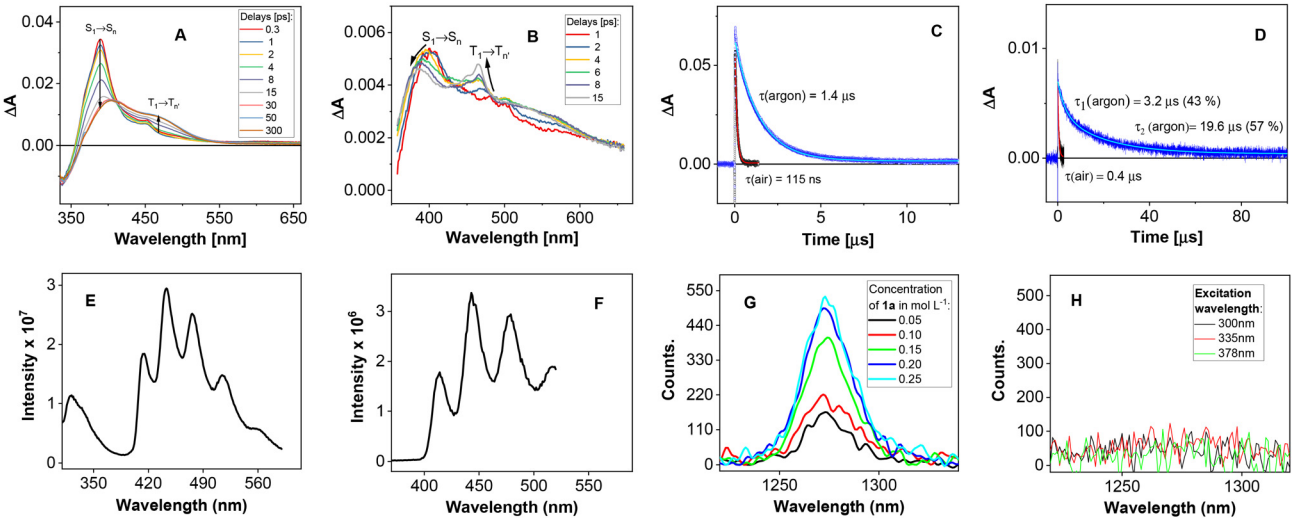


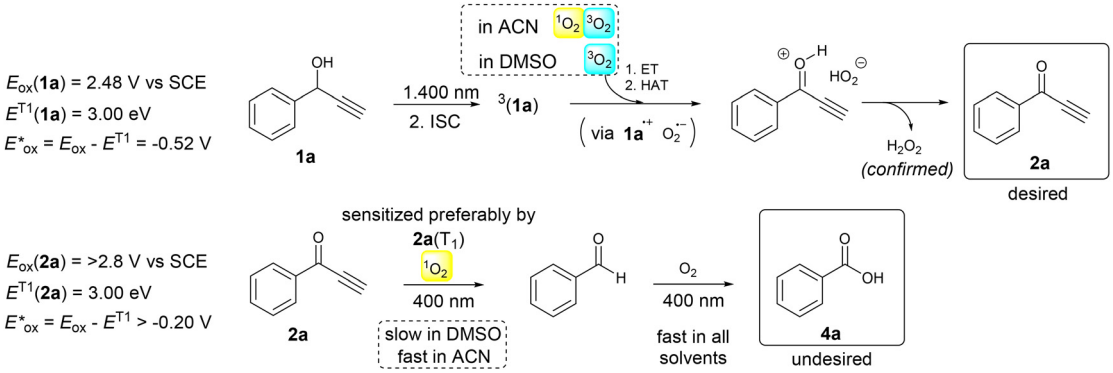
Fig. 4 Time resolved absorption data for (A) **1a** and (B) **2a** in acetonitrile demonstrating formation of a triplet state. T_1 kinetic traces for (C) **1a** and (D) **2a** in acetonitrile under argon (blue) and air (black). Phosphorescence spectra of (E) **1a** (λ_{ext} = 300 nm) and (F) **2a** (λ_{ext} = 263 nm) at 77 K in acetonitrile. The emission spectra of singlet oxygen in the presence of **1a** (G) in acetonitrile (different concentrations) and (H) in DMSO (different excitation wavelengths).

and D). Both compounds show phosphorescence spectra (Fig. 4E and F), which are measurable even at room temperature. Taking into account the concentration of oxygen in acetonitrile under normal pressure (2.42×10^{-3} mol L^{-1}, 1 atm. air),[20] the rate constants of **1a** ($k_q^{T1} = 3.15 \times 10^9$ L mol^{-1} s^{-1}) and **2a** ($k_q^{T1} = 1.0 \times 10^9$ L mol^{-1} s^{-1}) T_1 state quenching by oxygen were determined. The energy transfer mechanism was confirmed as k_q^{T1}/k_{diff}, which was close to 1/9.[21] We also found that the quantum yield of singlet oxygen formation sensitized by **1a** or **2a** was 0.17 and 0.31, respectively (see ESI S8†). Thus, singlet oxygen seems to be, in addition to molecular oxygen, the stoichiometric oxidation agent in oxidative processes in acetonitrile. In DMSO, similar data were found for the excited **1a** and **2a** states as in acetonitrile (see ESI S8†). On the other hand, a significant difference was found in the production of singlet oxygen, which was barely detected after **1a** or **2a** was irradiated in DMSO (*cf.* Fig. 4G and H for **1a** as an example).

The phosphorescence spectra obtained for both **1a** and **2a** have allowed us to estimate the triplet state energies and, in combination with the ground state oxidation potentials, the excited state oxidation potentials characterizing the ease of oxidation of both compounds in their excited T_1 states (see Scheme 2). When comparing the data obtained for E_{ox}^{T1}(**1a**) = −0.52 V *vs.* SCE and E_{ox}^{T1}(**2a**) = −0.20 V *vs.* SCE with the oxygen species reduction potentials [$E(^3O_2/O_2^{\bullet-})$ = −0.43 V *vs.* SCE; $E(^1O_2/O_2^{\bullet-})$ = +0.56 V *vs.* SCE],[22] it can be concluded that while oxidation of **1a** can occur with both molecular oxygen and singlet oxygen, **2a** was probably oxidized by only singlet oxygen.

Looking for a difference between DMSO and acetonitrile to elucidate the potential origin of the DMSO-based chemoselectivity of the photooxidation reactions, one should keep in mind the lower oxygen solubility in DMSO (2.2×10^{-3} mol L^{-1}, 1 atm. O_2) compared to acetonitrile (9.1×10^{-3} mol L^{-1}, 1 atm. O_2).[23] We were also interested in the singlet oxygen lifetime in both solvents. While singlet oxygen in acetonitrile has been well studied, the data for DMSO have rarely been reported. The singlet oxygen lifetime is also significantly influenced by solvent deuteration, as demonstrated by the values observed for acetonitrile (81 μs) and acetonitrile-d_3 (1613 μs).[24] We were surprised to observe only a slight effect of deuteration on the singlet oxygen lifetimes in DMSO (8.4 μs) and DMSO-d_6 (9.7 μs) (see ESI S9†). This can be attributed to the fact that DMSO and DMSO-d_6 readily react with singlet oxygen to form the corresponding sulfone.[25] Thus, the singlet oxygen lifetime was controlled by consumption due to sulfoxide oxidation rather than physical quenching in DMSO.

The findings described above enabled us to propose the overall reaction mechanism as well as explain the unique chemoselectivity observed during the photooxidation of **1a** in DMSO (Scheme 2). Initially, alcohol **1a** in a triplet excited state undergoes a photoinduced electron transfer primary with molecular oxygen in DMSO. In solvents like acetonitrile, characterized by longer singlet oxygen lifetimes, electron exchange with singlet oxygen is also expected. After hydrogen atom and proton transfer, ketone **2a** is formed along with hydrogen peroxide, whose amount corresponds to that calculated theoretically and confirmed using independent experiments (see ESI S6†). The oxidation of ketone **2a** needs singlet oxygen as photoinduced electron transfer with molecular oxygen is not thermodynamically feasible. Alternatively, [2 + 2] cycloaddition of singlet oxygen to a multiple bond can occur to form a dioxetane species,[26] which undergoes C–C bond fragmentation to benzaldehyde or benzoic acid. This photooxidative cleavage is favoured in acetonitrile and represents an inter-



Scheme 2 Proposed mechanism of **1a** photooxidation with oxygen under catalyst- and additive-free conditions. In DMSO, ground state oxygen ($^3O_2$) is involved in photooxidation of alcohol **1a** to ketone **2a**, while in acetonitrile, singlet oxygen ($^1O_2$) can be involved. In acetonitrile, the first step oxidation is followed by fast oxidation of **2a** with singlet oxygen. The second process is inhibited in DMSO. Thermodynamic parameters based on cyclic voltammetry and phosphorescence measurements are given. For oxidation potential measurements, see ESI S7.†

esting reaction which usually needs transition metal catalysis or peroxides.[27]

In DMSO, singlet oxygen was rapidly consumed by solvent oxidation to dimethylsulfone, which was found in significant amounts in all the reaction mixtures upon photooxidation using ^{1}H NMR spectroscopy and mass spectrometry (see ESI S6†). Therefore, the undesired oxidation of ketone **2a** was very slow in DMSO, allowing its isolation after an appropriate time in high yield. In contrast, singlet oxygen in acetonitrile is relatively long-lived, which supports the over-oxidation reactions. Thus, ketone **2a** was, in fact, "protected" against oxidation by DMSO. Additionally, the overall low concentration of oxygen in DMSO can also contribute to chemoselectivity, slowing down the oxidative processes.

Conclusions

A novel, operationally simple chemoselective oxidation methodology for sensitive benzylic propargyl alcohols and allyl alcohols has been presented. This method has been shown to be also useful for other sensitive substrates, such as diphenylmethanol and 1-phenylethanol. The method is catalyst-free and additive-free requiring only solvent and visible light irradiation (400 nm), thus significantly distinguishing itself from all other methodologies published to date for similar sensitive substrates. In general, it is also unique among the few catalyst- and additive-free procedures reported for alcohol oxidation, functioning at room temperature or a slightly elevated temperature with a relatively weak light source (1 W LED). Previous methodologies have typically required high temperature and pressure along with a strong light source (45 W LED).[14]

An original and unique source of chemoselectivity in oxidation reactions using molecular oxygen has been presented in this work, based on the use of DMSO as the solvent. Due to its ability to react with singlet oxygen, DMSO in fact "protects" the substrate from undesired over-oxidation. This novel concept might find application in other oxidative processes suffering from poor selectivity due to singlet oxygen. Regarding green chemistry, our procedure fulfills several criteria: (i) atom economy as it uses oxygen as the sole oxidant, (ii) selectivity, leading to the production of a single product, and (iii) low energy consumption, using a weak light source (1 W LED) at room temperature and under atmospheric pressure conditions. The relatively low amount of a non-toxic solvent (400 μL for 1 mmol) used in the reaction represents another advantage.

Author contributions

R. C., I. W. and M. S. wrote the paper with input from all of the authors. I. W. performed synthesis of all the used compounds and conducted all photochemical reactions. J. C. performed all mass spectroscopy analyses. N. V. together with M. S. collected the stationary spectroscopy and singlet oxygen data. G. B. performed all other time-resolved spectroscopic experiments. Experimental spectroscopy data were analysed by M. S. together with G. B. The project was conceived by R. C., I. W., and M. S.

Conflicts of interest

There are no conflicts to declare.

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