Practical Evaluation of Compact Fluorescent Lamps for Dye-Sensitized Photooxidation Reactions

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Abstract: Energy-efficient compact fluorescent lamps (CFL) have been evaluated as a light source for the sensitized generation of singlet oxygen used in the oxidation of 1,3-butadienes and furfural derivatives using a range of dyes including rose bengal, methylene blue, and tetraphenylporphyrin. An ambient temperature water jacket was sufficient to cool reaction mixtures due to the low heat output of lamps and the reaction rates using 110 W of CFL were slower but comparable to those obtained using a 500 W tungsten halogen lamp. The conditions were applied to the photooxidation of a series of furan aldehydes and 1,3-butadienes to give products in good yield in 4–96 hours.

Key words: peroxides, photooxidation, photochemistry, pericyclic reaction, oxygenations, sensitizer

Singlet-oxygen chemistry is of great interest due to its utility in synthesis. Applications include the [4+2] cycloaddition¹ and the Schenck–Ene reaction² generating useful endoperoxides and allylic hydroperoxides, respectively. The most common method for the production of singlet oxygen involves irradiating an air- or oxygen-saturated solution of substrate containing a photosensitizing dye.¹ The dye absorbs a photon of light and is excited to a singlet state (S_n) and then intersystem crossing gives rise to the triplet-state-excited dye. Transfer of energy from the triplet-excited-state dye to ground-state oxygen $({}^{3}\Delta O_{2})$ yields singlet-state oxygen $({}^{1}\Delta_{g}O_{2})$ or the excited state ${}^{1}\Sigma_{g}^{+}$ which relaxes to ${}^{1}\Delta_{g}O_{2}$.³ Oxygen saturation can improve the conversion of ${}^{3}\breve{\Delta}O_{2}$ to ${}^{1}\Delta_{g}O_{2}$ depending on the dye used and so reactions are usually performed with oxygen saturation.

The excitation of dyes used for the generation of singlet oxygen requires light with wavelength corresponding to the absorption bands of the dye.^{3b} For photooxidation reactions, reported light sources are most often tungsten halogen,⁴ xenon,⁵ or incandescent lamps.⁶ Tungsten halogen and incandescent lamps have emission maxima at 970 nm and 1050 nm, respectively.⁷ Both emit a range of light energies corresponding to black-body radiation of objects between 2750–3000 K, with the majority of light emitted in the near infrared region. The absorption bands for many of the dyes used for photooxidations are in the visible region of the spectrum between 500–700 nm and therefore

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much of the light is wasted as heat which needs to be removed by cooling of reaction mixtures. A typical multigram-scale photooxidation using rose bengal bis(triethylammonium) salt in CH_2Cl_2 can require 500– 1500 W of tungsten halogen lamps in close proximity to the reaction to achieve reaction times in the order of 5–8 hours.^{8,4b,4d} High light intensity can affect sensitizer lifetime,⁹ and the majority of the energy applied is heat so that cooling requirements can limit the practical scalability of photooxidations using these lamps.

In the consumer lighting market there has been a move to compact fluorescent lamps (CFL) from incandescent bulbs due to their energy efficiency as a source of lighting. CFL are inexpensive, readily available, and generate up to fivefold more visible light than incandescent bulbs for the equivalent energy input. Light is generated in a so-called tricolor CFL by the passage of current through mercury vapor with the light emitted consisting of visible and UV light.^{7,10} The UV light then strikes a rare earth phosphor coating on the inside of the bulb resulting in visible wavelength emission. To match the sensitivity of the human eye, red, green, and blue emitting materials are combined to generate white light, which has a series of maxima corresponding to the different phosphor emissions. Light emitted from a CFL measured using a diode array detector as well as the UV spectra of dyes used in this study are shown in Figure 1.



Figure 1 Normalized emission spectra for CFL and normalized absorption spectra for photosensitizing dyes (see also Table 1)

The application of energy-efficient light sources for chemical reactions is gaining momentum. CFL have previously been used for the photolysis of α -diazo Weinreb amides for the preparation of β -lactams via a Wolff rearrangement,¹¹ and CFL lights have been used to initiate polymerization reactions.¹² Seeberger has reported the use of LED lights for the production of singlet oxygen in a continuous-flow reactor system, however, only µmol/min quantities could be produced using this light source due to the low light intensity.¹³ To the best of our knowledge, CFL have not been reported for the generation of singlet oxygen.

Table 1 Absorption Maxima and Quantum Yields of the SensitisingDyes Used for Singlet Oxygen Generation

Sensitising dye	Solvent	$\lambda_{max} (nm)$	Quantum yield
rose bengal (RB)	МеОН	548	0.7614
tetraphenylporphyrin (TPP)	$\mathrm{CH}_2\mathrm{Cl}_2$	419, 514, 549	0.6315
eosin B (EB)	MeOH	514	0.4014
erythrosin (EN)	EtOH	532	0.6915
methylene blue (MB)	MeOH	653	0.5215

The absorption maxima and quantum yields for singletoxygen generation of common dyes used for photooxidation reactions are listed in Table 1. The major green emission band in CFL at 546 nm directly overlaps the Q-band absorption of TPP at 549 nm. The same emission band overlaps the absorptions of rose bengal at λ_{max} 548 nm and the shoulder of erythrosin at λ_{max} 532 nm. The red emission band in CFL at 620 nm overlaps the broad methylene blue absorption band at λ_{max} 653 nm. Due to these overlaps we hypothesized that CFL could be used with these sensitizers for singlet-oxygen generation.

Quantum yields,¹⁵ the lifetime of singlet oxygen,^{9,16} the dye spectra,¹⁷ and the rates of dye photobleaching reactions¹⁷ all show solvent dependence. As such, we considered that the evaluation of reaction outcomes would be the most appropriate method for examining the suitability of CFL for singlet-oxygen generation. Commercially available 55 W and 48 W CFL in reflective housings were used for photooxidation reactions in a 50 mm diameter jacketed Pyrex cylindrical flask cooled with water at 20 °C. The [4+2] addition of singlet oxygen to 1,4-diphenyl-1,3-butadiene (1) giving rise to 3,6-diphenyl-3,6-dihydro-1,2-dioxine (2) was used as a model reaction and the reactions followed by ¹H NMR (Scheme 1). A second substrate, 5-methylfurfural (3), suitable for use with alcohol-soluble dyes, was also used, and the reaction to give 5-methoxy-5-methyl-furan-2(5H)-one (4)¹⁸ followed by GC-MS. Reactions were sampled regularly to determine time to completion, and the results are summarized in Table 2.



Scheme 1 Photooxygenation of dienes

We found that CFL were an effective light source for the sensitizer TPP with the endoperoxide **2** formed in 93% conversion from butadiene following photolysis for 14 hours (Table 2, entry 1). Complete reaction was seen after 24 hours with no apparent decomposition of the product observable by ¹H NMR spectroscopy. The reaction rate obtained using a 500 W tungsten halogen globe was slightly higher than that of the 110 W CFL (Table 2, entries 1 and 5). Rose bengal disodium salt is insoluble in CH₂Cl₂ and so a mixture of MeOH–CH₂Cl₂ (2:1) was used for the reaction of **1** with only 34% conversion into

 Table 2
 Photooxidation of 1,3-Diphenylbutadiene and 5-Methylfurfural

Entry ^a	Diene	Dye	Solvent	Light source	Time (h)	Conv. (yield, %)
1	1	TPP	CH ₂ Cl ₂	CFL ^b	14	93
2	1	TPP	CH_2Cl_2	CFL	24	100 (72)
3	1	RB	MeOH	CFL	6	3
4	1	RB	MeOH/CH ₂ Cl ₂	CFL	24	34
5	1	TPP	CH_2Cl_2	TH	6	73
6 ^c	1	7	CH_2Cl_2	CFL ^b	26	86
7	1	MB	CH_2Cl_2	CFL	24	1
8	3	RB	MeOH	CFL	5	100
9	3	RB	MeOH	TH	4	100
10 ^d	3	RB	MeOH	CFL	3	100 (70)
11	3	TPP	MeOH-CH ₂ Cl ₂	CFL	23	65
12 ^d	3	EB	MeOH	CFL	5	89
13	3	EN	MeOH	CFL	24	100
14	3	MB	МеОН	CFL	5	100

^a Reactions were carried out using 2 g of substrate in 150 mL of solvent in a tubular reactor at 20 °C and 100 mg of sensitizing dye (Table 1) bubbled with oxygen. Reactions of **1** were followed by ¹H NMR spectroscopy, and **2** was isolated by crystallization. Reactions of **3** were followed by GC–MS, and **4** was isolated by reduced pressure distillation. CFL = 158 W CFL array, TH = 500 W tungsten halogen lamp.

^b Reaction performed with 4 g of substrate and 110 W lamps in 150 mL of solvent.

^c An additional portion of sensitizer (50 mg) was added at the 20 h mark (81% conversion).

 $^{^{\}rm d}$ Reaction performed using a rectangular cuboid reactor 300 mm \times 200 mm \times 3 mm using 110 W CFL.

the endoperoxide product 2 after 24 hours (Table 2, entry 4). Performing the reaction in methanol, a common solvent for rose bengal photooxidations gave only trace amounts of endoperoxide 2 due to the insolubility of the starting butadiene (Table 2, entry 3).

Methylene blue which is used in aqueous conditions for singlet-oxygen generation produced virtually no product from the reaction of **1** in CH_2Cl_2 after irradiation for 24 hours (Table 2, entry 7). This was surprising as CH_2Cl_2 has been used for methylene blue sensitized photooxidations in high yield^{1d} and the dye–CFL combination was suitable for the oxidation of **3** in methanol (Table 2, entry 14).

Lamberts and Neckers have reported a number of organicsoluble rose bengal derivatives that exhibit high quantum yields, and some of these derivatives such as the bis(triethylammonium)salt of rose bengal have found widespread use.¹⁴ We decided to investigate one of these derivatives with favorable quantum yield in conjunction with CFL and so rose bengal salt 7 ($\lambda_{max} = 561$ nm) was synthesized (Scheme 2). The alkylation of rose bengal disodium salt 5 with ethyl iodide and then treatment of the product 6 with triethylamine yielded material with spectroscopic properties matching those reported.¹¹ Irradiation of diene 1 sensitized with 7 using 110 W of CFL gave 86% conversion to product although an extended reaction time was required (Table 2, entry 6).



Scheme 2 Synthesis of sensitizer 7

The reaction of 5-methylfurfural (3) with singlet oxygen in methanol yielded furanone 4 as the sole product as judged by GC-MS and NMR spctroscopy (Table 2, entries 8-14). The reaction proceeds through a [4+2] cycloaddition to the furan giving an ozonide which decarbonylates presumably following hemiacetal formation on the side chain. Using 158 W of CFL as the light source and rose bengal as the sensitizer in methanol, complete transformation of the starting 5-methylfurfural (3) to the furanone 4 was seen in five hours (Table 2, entry 8). By comparison, irradiation with a 500 W tungsten halogen lamp took four hours for completion (Table 2, entry 9). No reaction was seen when the solution of dye and furfural was bubbled with nitrogen and stored in the dark confirming that singlet oxygen was the reactive species. Sampling the reaction every hour and analyzing by GC- MS showed that the rate of consumption of **3** was independent of the concentration of **3** until ca. 90% of **3** had been consumed.

Erythrosin has a lower quantum yield than rose bengal and a red-shifted absorption maxima. Using erythrosin B as the photosensitizer, rapid consumption of the starting furfural was observed with 50% consumption after 80 minutes, but the reaction slowed due to photobleaching of the dye. The reaction was incomplete after eight hours although 100% conversion to the product **4** was still seen after 24 hours (Table 2, entry 13).

The overnight reaction times for some of the substrates prompted us to examine alternative reaction conditions. The use of a cylindrical reaction vessel 40 mm $(I.D.) \times 130 \text{ mm}$ (length) gave a total reactor surface area of 160 cm² and due to the shape of the vessel, not all light impacted the reaction. An alternative reactor suitable for alcoholic solvents was constructed using 300 mm \times 200 mm glass plates spaced 3 mm apart, cooled with a water jacket, and sealed using cross-linked polydimethylsiloxane giving a rectangular cuboid reactor with a 1200 cm² surface area or ca. 800 cm² when partially filled. When placed close to the lamps, this reactor configuration resulted in greatly reduced stray light and shortened the time for the photooxidation of 5-methylfurfural sensititized with rose bengal from five hours to three hours using $2 \times 55W$ CFLs (Table 2, entry 10). Eosin also gave 89% conversion of 3 into 4 in five hours using this configuration.

A series of butadienes were prepared to demonstrate the scope of the reaction. The reaction of allyl triphenylphosphonium bromide with the appropriate substituted benzaldehyde in the presence of KO*t*-Bu gave 9-11 as E/Z mixtures¹⁹ while 8 and 12 were prepared from (*E*)-cinnamaldehyde using Wittig chemistry.²⁰

Photooxidation of **8–13** using CFL sensitized with rose bengal or TPP afforded endoperoxides on gram scale (Table 3). Extended reaction times were required for dienes **9** and **10**, and some polymerization of the diene was evident as insoluble material was present at the end of the reaction. In the case of cyclopentadiene **13**, the reaction progress was inferred by treating an aliquot of the reaction mixture with (R,R)-N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) and monitoring the appearance of epoxide **20** as the endoperoxide violently decomposes at room temperature when neat.

O'Shea and Foote have demonstrated that in the presence of singlet oxygen, the double bonds in (E,E)-, (E,Z)- and (Z,Z)-2,4-hexadiene rapidly isomerize.²¹ The recovered diene from the photooxidations of **9–11** were depleted in *E*-isomer indicating that isomerization is slower than [4+2] addition for these aryl-substituted dienes. The *E*-isomer would be expected to yield more 1,2-dioxine as it is able to adopt the required *s*-*cis* conformation and this may partly explain the lower yields of product that were obtained from **9–11** relative to (E)-1-phenyl-1,3-butadi-

ene (8). The mixture of (1E,3Z)- and (1E,3E)-1-phenyl-1,3-pentadiene (12) reacted completely and afforded the *cis*-peroxide containing 3% of the *trans*-isomer after isomerization of the butadiene. The ratio indicating fast isomerization of 12 agree with the findings of Motoshiya et al. obtained using a tungsten halogen lamp.²² Taken together, the results suggest that aryl-substituted butadienes should be synthesized in such a way that the aryl-substituted alkene has the geometry required for the addition of singlet oxygen as isomerization is slow. This study has demonstrated that inexpensive CFL are a suitable source of light for the singlet-oxygen-mediated [4+2] reaction sensitized by methylene blue, erythrosin, rose bengal, and TPP. Other energy-efficient light sources such as LED can be used to selectively generate a useable wavelength, however, there is significant cost associated with high wattage LED arrays. Long reaction times were required for some substrates, however, CFL are much cooler than tungsten halogen lamps and pose a much reduced risk of fire. It is envisaged that CFL could be used in conjunction with the dyes examined here to improve

Entry ^a	Starting material	Conditions ^b	Time	Solvent	Sensitizer	Product	Yield (% conv.) ^c
1		А	16	CH ₂ Cl ₂	TPP		72 (100), Lit: 30 ^{4b}
2	8 CI 9 22:78 <i>E</i> / <i>Z</i>	А	96	CH ₂ Cl ₂	TPP	15	26 (57), ^d Lit: 9 ^{8b}
3	10 51:49 <i>E/Z</i>	А	72	CH ₂ Cl ₂	TPP		20 (70) ^e
4		A	16	CH ₂ Cl ₂	TPP		28 (75) ^f
5	11 57:43 E/Z	A	24	CH ₂ Cl ₂	TPP	$10 \qquad \qquad$	61 (100) ^g
6	13	А	4	CH ₂ Cl ₂	TPP	$0 = \underbrace{H}_{20}$	(100) ^h
7	со С 14	В	6	MeOH	RB		78 (90)
8	J O H	В	4	EtOH	RB	Et0_0_0 22	57 (100) ^h

Table 3 Sensitized Photooxidations of Butadienes Using 110 W Compact Fluorescent Lamps

^a Reactions were performed on 2 g of starting material in 150 mL of solvent bubbled with oxygen.

^b Conditions A used a 40 mm (I.D.) \times 130 mm (length) cylindrical reactor. Conditions B used a rectangular cuboid reactor 300 mm \times 200 mm \times 3 mm.

^c Based on recovered diene.

^d 7:93 E/Z ratio in the recovered diene.

e 9:91 *E*/*Z* ratio in the recovered diene.

f 12:88 E/Z ratio in recovered diene.

g 1.4 g scale.

^h Measured using GC-MS.

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the safety and scalability of the many reactions involving singlet oxygen.

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