Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 888

www.rsc.org/greenchem

COMMUNICATION

Photooxygenations in a bubble column reactor†

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Received 11th November 2011, Accepted 10th January 2012
DOI: 10.1039/c2gc16439f

A novel column reactor was constructed and successfully applied to dye-sensitized photooxygenation reactions in aqueous alcohol solutions. The air flow pattern within the narrow glass column could be controlled *via* the size of the air inlet capillary. Using a 500 μm capillary, a slug flow pattern was realized which allowed for superior mass transfer and light transparency within a thin solvent layer. These features subsequently gave higher conversion rates and isolated yields.

Synthetic organic photochemistry uses light as an efficient and clean energy source that can be controlled with a 'flick of a switch'.[1] It has thus emerged as a powerful synthesis method[2] and is furthermore regarded a prototype of a green chemical technology.[3] Dye-sensitized photooxygenation reactions are particularly interesting since they avoid the need of strong and hazardous oxidants.[4] Over recent years, we have investigated green photooxygenations using concentrated and direct sunlight,[5] microemulsions as alternative reaction media[6] and biopolymeric sensitizer supports.[7] We have also developed novel reactor concepts, for example excimer[8] or microflow systems.[9] During our ongoing study on microflow photochemistry,[10] we became interested in the construction of a simple and reliable batch reactor for small-scale photooxygenation reactions. Schlenk flasks in combinations with halogen lamps, as previously used,[5a–c] had unfavorable light penetration properties or generated large amounts of heat that facilitated thermal decomposition reactions. While microflow falling film reactors[11] and air-sparged hydrocyclone floatation reactors[12] have been described, these systems were found not practical for the current study. A simple glass column reactor was thus constructed (Fig. 1). The reactor consisted of a single Pyrex glass tube (length: 1.5 m; outer-∅: 6 mm; inner-∅: 4.5 mm) centered between two domestic fluorescent lamps (2 × 60 W; distance from glass tube: 1.5 cm). A HPLC connector and a shut-off valve were attached to the bottom of the glass tube and were secured with a short piece of polytetrafluoroethylene (PTFE) tubing (enlargement in Fig. 1b). A domestic air pump and a flow meter were connected to the valve. At its centre, the HPLC connector held a narrow PTFE capillary, through which air was injected into the solution. Due to buoyancy, the air bubbles rose, inducing a circulating motion in the liquid column. The size of the capillary allowed for the generation of various bubble sizes and consequently flow pattern. In addition, as the air rose through the solution, oxygen dissolved from the bubbles into the reaction liquid. The reactor thus represents a batch system with a rising air flow. The reactor tube was filled with the reaction mixture through the top with the help of a burette funnel or, more conveniently, using a HPLC pump.

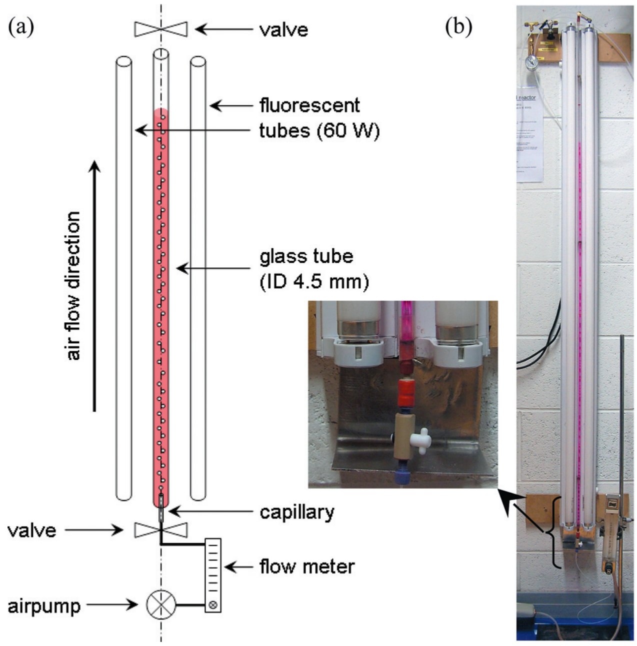

Fig. 1 Glass column reactor: (a) general design and (b) actual reactor (gas feeding head shown as enlargement).

To evaluate this new reactor system, the photooxygenation of 1,5-dihydroxynaphthalene **1** using rose bengal (RB) as sensitizer was selected as a model transformation (Scheme 1).[13] The photoproduct, 5-hydroxy-1,4-naphthoquinone (juglone) **2**, is an important natural product[14] and serves as a valuable building block in organic synthesis.[15]

Initially, a solvent study was conducted using a standard solution (10 mL) of **1** (10 mM) and rose bengal (0.49 mM).[16] A 100 μm capillary was applied as an air inlet. At an air flow rate

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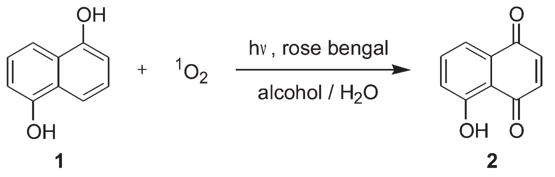
† Dedicated to Prof. Jochen Mattay (University of Bielefeld, Germany) on the occasion of his 65th birthday.



Scheme 1 Photooxygenation of 1,5-dihydroxynaphthalene **1**.

Table 1 Solvent study (**1**: 10 mM; RB: 0.49 mM)

	Solvent	Time (h)	Conversion[a] (%)
1	*i*-PrOH	0.5	37
2	*i*-PrOH	1	52
3	*i*-PrOH	3	100
4	*i*-PrOH–H_2O (9 : 1)	0.5	55
5	*i*-PrOH–H_2O (9 : 1)	1.5	82
6	*i*-PrOH–H_2O (9 : 1)	2	91
7	*i*-PrOH–H_2O (9 : 1)	2.5	100
8	*t*-AmOH–H_2O (9 : 1)	2	91
9	EtOH–H_2O (9 : 1)	2	88
10	MeOH–H_2O (9 : 1)	2	75

[a] Determined by ^{1}H-NMR spectroscopic analysis of the crude product (±2%).

of 7–10 cm^3 min^{-1}, an almost evenly distributed bubble flow (bubble-∅: 100–150 μm) was achieved. Laboratory-scale photooxygenations are most commonly performed in halogenated solvents. For this study, different alcohols were utilized as more environmentally benign alternatives (Table 1).[17] Isolation of **2** was not attempted due to the small reaction scales of 100 μmol of **1**. However, the photooxygenation to **2** is known to proceed smoothly.[5] Stability tests performed with pure **2** under the irradiation conditions also gave high recovery rates of >80%. As demonstrated for isopropanol, the addition of 10 vol% of water gave higher conversions, presumably due to the improved transparency of the reaction mixture. As an example, a conversion of **1** of 55% was achieved after 30 minutes of irradiation in aqueous isopropanol (entry 4). In contrast, the reaction in pure isopropanol reached a similar value of 52% only after a prolonged irradiation time of 1 hour (entry 2). Small undissolved particles within the initial reaction mixture may have caused light scattering and reflection. In both cases, complete conversions were observed after 2.5 and 3 hours of irradiation (entries 7 and 3), respectively, which was more than twice as efficient if compared to reactions performed in conventional Schlenk flasks.[5b,c] The photooxygenation proceeded faster in aqueous isopropyl and *tert*-amyl alcohol than in ethanol or methanol, which is supported by the prolonged life time of singlet oxygen in these solvents (*t*-BuOH [shown for comparison]: 31 μs; *i*-PrOH: 22 μs; EtOH: 9.7–15.3 μs; MeOH: 9.5–10.4 μs).[1,18]

Due to the heterogeneous (gas/liquid) nature of the reaction protocol, the influence of both bubble size and distribution, and consequently of the flow pattern,‡[19] on the reaction efficiency was investigated (Fig. 2). For this purpose air was delivered to the solution through a capillary with different inner diameters. The narrowest capillary (inner-∅: 50 μm) provided an almost even bubble flow with bubbles of approximately 50–100 μm in diameter. In contrast, the widest capillary (inner-∅: 500 μm) furnished large bubbles in bullet shape with a diameter similar to that of the glass tube. In order to avoid uncontrolled merging of individual bubbles, the flow rate was increased to 20 cm^3 min^{-1}. Following this strategy, a stable and evenly distributed slug flow pattern was achieved. At a constant flow rate, the average size of the air bubbles depended on the solvent and thus its physicochemical properties.[20]

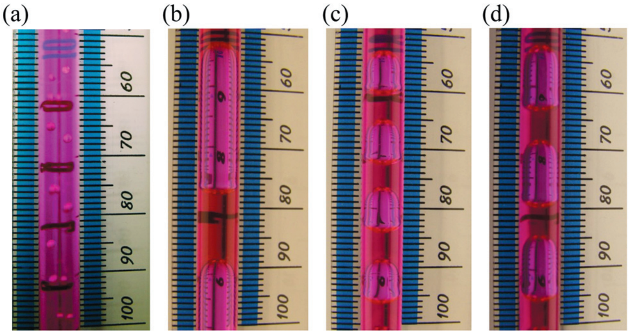


Fig. 2 Images of the flow pattern formed inside the glass tube in different solvents (taken at a height of approximately 30 cm): (a) bubble flow in isopropanol–water (100 μm capillary); (b) slug flow in methanol–water (500 μm capillary); (c) slug flow in isopropanol–water (500 μm capillary); (d) slug flow in *tert*-amyl alcohol–water (500 μm capillary).

Table 2 Flow pattern study (**1**: 10 mM; RB: 0.49 mM)

	Solvent[a]	Time (h)	Air flow (cm^3 min^{-1})	ID (μm) [flow pattern[19]]	Conv.[b] (%)
1	*i*-PrOH–H_2O	3	10	50 [bubble]	49
2	*i*-PrOH–H_2O	1.5	10	100 [bubble]	82
3	*i*-PrOH–H_2O	3	10	100 [bubble]	100
4	*i*-PrOH–H_2O	1	20	500 [slug]	91/91[c]
5	*t*-AmOH–H_2O	1	20	500 [slug]	100

[a] Alcohol : H_2O (9 : 1). [b] Determined by ^{1}H-NMR spectroscopic analysis of the crude product (±2%). [c] Repetition gave same conversion values.

The air flow pattern had a significant influence on the photooxygenation reaction (Table 2). Bubble flow conditions required prolonged irradiation times in order to reach high conversions of **1** (entries 1–3). In contrast, high to complete conversion values were achieved after just 1 hour under slug flow conditions (entries 4 and 5). In addition, the reaction in aqueous isopropanol showed an excellent reproducibility and a conversion of 91% was achieved in duplicates (entry 4).

The sensitizer and its concentration were subsequently examined under slug flow conditions (capillary: 500 μm; air flow: 20 cm^3 min^{-1}) using aqueous *tert*-amyl alcohol as a solvent. The concentration of rose bengal was halved and methylene blue was investigated as an alternative sensitizer (Table 3). A reduction in the rose bengal concentration had almost no impact on the conversions and juglone **2** was formed in similar amounts of 83 and 87% after just 30 minutes of irradiation (entries 1 and 2). In contrast, the reaction with methylene blue as sensitizer gave a much lower value of 56% under identical conditions (entry 3). This reduced performance can be explained by the poor solubility of methylene blue in *tert*-amyl alcohol in combination with its lower quantum yield for singlet oxygen formation (MB: $\Phi = 0.52$; RB: $\Phi = 0.68$).[21] Previous studies have shown that

Table 3 Sensitizer study (**1**: 10 mM)

	Solvent[a]	Time (h)	Sensitizer (mmol L^{-1})	Conv.[b] (%)
1	*t*-AmOH–H_2O	0.5	Rose bengal (0.25)	83
2	*t*-AmOH–H_2O	0.5	Rose bengal (0.49)	87
3	*t*-AmOH–H_2O	0.5	Methylene blue (0.25)	56
4	*t*-AmOH–H_2O	0.5	None	8

[a] Alcohol : H_2O (9 : 1). [b] Determined by ^1H-NMR spectroscopic analysis of the crude product (±2%).

Table 4 Flow rate and irradiation time study (**1**: 10 mM; RB: 0.49 mM)

	Solvent[a]	Time (h)	Air flow (cm^3 min^{-1})	Conversion[b] (%)
1	*t*-AmOH–H_2O	0.17	90	47
2	*t*-AmOH–H_2O	0.25	90	64
3	*t*-AmOH–H_2O	0.5	90	89
4	*t*-AmOH–H_2O	1	90	100/100[c]
5	*t*-AmOH–H_2O	0.17	20	46
6	*t*-AmOH–H_2O	0.5	20	87
7	*t*-AmOH–H_2O	1	20	100/100[c]
8	*t*-AmOH–H_2O	1	10	100/100[c]

[a] Alcohol : H_2O (9 : 1). [b] Determined by ^1H-NMR spectroscopic analysis of the crude product (±2%). [c] Repetition gave same conversion values.

Table 5 Simplified reactor comparison (**1**: 10 mM; RB: 0.49 mM; 1 hour)

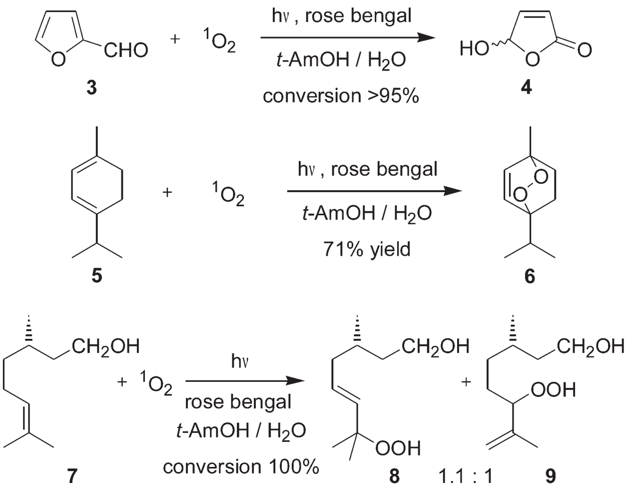
		Conversion of **1**[b]/yield of **2** (%)	
	Solvent[a]	Column reactor	Schlenk
1	*i*-PrOH–H_2O (9 : 1)	91/54	56/39
2	*t*-AmOH–H_2O (9 : 1)	100/70	70/64

[a] Alcohol : H_2O (9 : 1). [b] Determined by ^1H-NMR spectroscopic analysis of the crude product (±2%).

1,5-dihydroxynaphthalene **1** can self-sensitize the photooxidation to **2**.[13,22] Irradiation in the absence of any sensitizer, however, resulted in a low conversion to **2** of just 8% (entry 4).

The influence of the irradiation time and the air flow rate was furthermore investigated in aqueous *tert*-amyl alcohol with rose bengal as sensitizer and a 500 µm aeration capillary under slug flow conditions (Table 4). As would be expected, the amount of juglone **2** formed steadily improved with increasing residence time (entries 1–4). More than half of **1**, *i.e.* 64%, was converted after just 15 minutes and complete conversion to **2** was achieved after 1 hour. In contrast, the air flow rate had no influence on the reaction efficiency. As an example, irradiations for 30 minutes at air flows of 20 and 90 cm^3 min^{-1} gave almost identical conversion values of 87 and 89% (entries 6 and 3), respectively. The irradiations for 1 hour (entries 4, 7 and 8) were repeated twice and gave excellent reproducibilities, *i.e.* complete conversions.

The excellent reproducibility of the reaction justified the isolation of the photoproduct **2** by combining three reaction mixtures obtained under identical conditions. The conversions and yields were compared to reactions conducted in Schlenk flasks and using a Rayonet chamber reactor equipped with 16 visible lamps (Table 5). Using an irradiation time of 1 hour and an air flow rate of 20 cm^3 min^{-1}, the reaction performed in the column reactor in aqueous isopropanol showed a conversion of 91% and gave an isolated yield of **2** of 54%. In contrast, the reaction in the conventional Schlenk flask produced a conversion of 56% and gave an isolated yield of **2** of 39%. Irradiation in aqueous *tert*-amyl alcohol under slug flow conditions in the column reactor furnished complete conversion and gave a higher isolated yield of 70% instead. With the Schlenk setup, the conversion was 70% and **2** was isolated in a yield of 64%. While the reactors differed in scales and lamp power, the results still offer a valid comparison. The current column reactor prototype does not allow for any scale-up, but this may be easily achieved by using parallel glass tubes (numbering up) in the future.



Scheme 2 Additional photooxygenations studied.

The optimized irradiation conditions in the column reactor were subsequently transferred to other photooxygenation reactions (Scheme 2). The transformation of furfural **3** gave 5-hydroxyfuranone **4** in a conversion of >95% without any pseudo-ester.[23] Likewise, the [4 + 2]-cycloaddition of α-terpinene **5** gave ascaridole **6** in a yield of 71%.§[24] No trace of the commonly observed by-product *p*-cymene was detected in the crude product. The Schenck-*ene*-reaction of citronellol **7** is an important key-step in the industrial synthesis of the fragrance rose oxide.[4f,25] In the slug flow column reactor, complete conversion of **7** to a 1.1 : 1 mixture of the regioisomeric hydroperoxides **8** and **9** (the latter in a 1 : 1 mixture of diastereoisomers) was achieved within 1 hour. These examples clearly show the general suitability of the column reactor for preparative photooxygenations. Irradiations under conventional conditions in a Schlenk flask required prolonged reaction times of up to 5 hours to achieve complete conversions.

The different performances between reactions conducted in slug flow and bubble flow was striking. The slug flow pattern results in the formation of a thin liquid film (<0.5 mm) along the side of the air bubbles (Fig. 3). Consequently, the specific surface area of the liquid phase is increased significantly which subsequently results in an improved mass transfer within the thin solvent layer. A similar dependency on the flow pattern has been recently reported by Lévesque and Seeberger for photooxygenations in a microcapillary under continuous flow conditions.[26] At

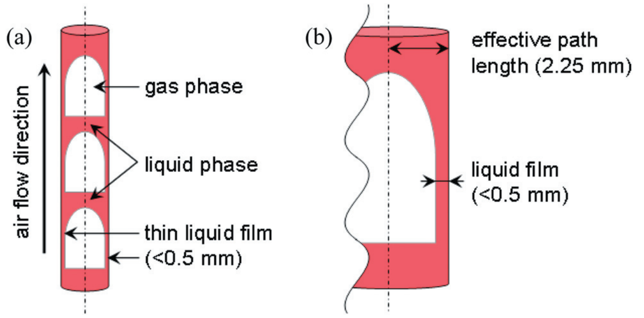


Fig. 3 (a) Representation of vertical slug flow pattern; (b) important dimensions.

the same time, the thin film allowed for a superior light penetration.¶

The emission spectra of the chosen fluorescent tubes showed a reasonable overlap with the main absorption band of rose bengal (Fig. 4a). Based on the absorption of the sensitizer the penetration profile of light was calculated at 546 nm and compared to the path length of the film and the glass tube (Fig. 4b). Due to the arrangement of the lamps at both sides of the glass tube (inner-∅: 4.5 mm) its effective path length was reduced to 2.25 mm. As would be expected, the thin liquid film (<0.5 mm) allowed for complete transmission of light at the given standard concentration of rose bengal (0.49 mM).

The light from the chosen fluorescent lamps (total optical power of 120 W) covered the entire surface of the glass tube of 211.95 cm^2. This design feature of the reactor setup thus provided a maximized irradiated area to volume ratio of 2119.5 $\mathrm{m}^2\ \mathrm{m}^{-3}$ and a lamp power per irradiated area of 0.57 W cm^{-2}. The efficiency of the reactor was furthermore evaluated using space–time–yield (STY) calculations. STYs are depending on the reactor geometry and were determined using eqn (1).[9a,27]

$$\mathrm{STY} = n_{\mathrm{R}}/(V_{\mathrm{R}} \times t) \tag{1}$$

n_{R} = yield of **2**, V_{R} = reactor volume and t = irradiation time.

For the preparative irradiation performed in aqueous *tert*-amyl alcohol, a STY of 0.12 mmol $\mathrm{L}^{-1}\ \mathrm{min}^{-1}$ was achieved. The reaction in aqueous isopropanol furnished a somewhat lower STY of 0.09 mmol $\mathrm{L}^{-1}\ \mathrm{min}^{-1}$ which resulted from the poorer isolated yield of **2**. Isopropanol likely promoted photodegradation of **2** *via* hydrogen-abstraction, which subsequently reduced its yield.[28] This degradation process is prevented or significantly reduced in *tert*-amyl alcohol.

In order to compare the energy efficiency of the bubble column reactor to conventional lamps, the energy consumption per hour of operation was measured using a commercially available domestic electricity meter (Nikkai power, N67FU).[5a,29] A common 500 W halogen lamp consumed the by far largest amount of electrical power with 0.432 kW h (1555.2 kJ). The Rayonet reactor gave a lower value of 0.149 kW h (536.4 kJ). Due to the significant generation of heat by the lamp(s) both setups additionally required water cooling. The water consumption was subsequently determined to be 1–4 L min^{-1}. In contrast, the fluorescent lamps in the column reactor consumed 0.055 kW h (198 kJ) each. The reactor also did not require any cooling. The air pump used for all setups consumed just 0.001 kW h (or 3.6 kJ) of additional energy.

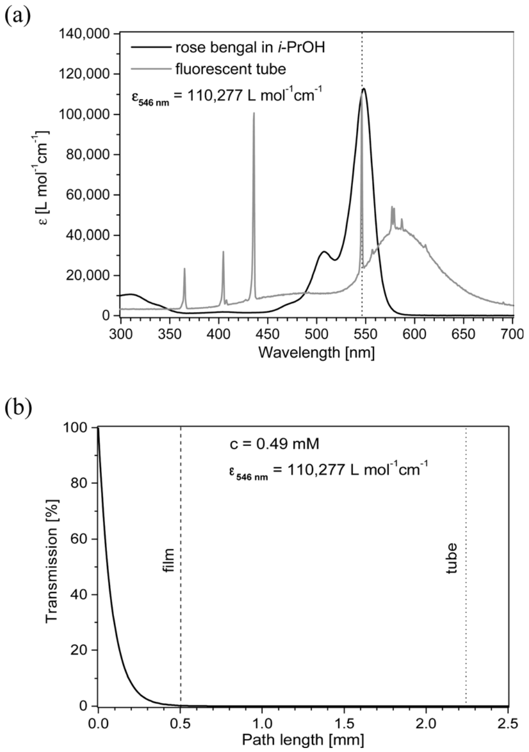


Fig. 4 (a) UV-spectrum of rose bengal (in *i*-PrOH) *vs.* emission spectrum of the fluorescent tubes; (b) light-penetration profile for a 0.49 mM solution of rose bengal at 546 nm. The vertical lines represent the maximum path length of the film (---) and the effective path length of the reactor tube (···).

In conclusion, we have developed an efficient and reliable column reactor for photooxygenation reactions. An air slug flow pattern was easily achieved using an appropriate capillary for aerating. Superior conversions and yields were realized due to the formation of a thin liquid film which allowed for an enlarged surface area, improved mass transfer and superior light penetration. The reactions were performed under 'green' conditions in aqueous alcohols using air as a safe oxidant. The simple setup also allowed for a reduction in energy consumption and a complete avoidance of cooling water.

Acknowledgements

This work was financially supported by Science Foundation Ireland (SFI, 07/RFP/CHEF817), the Environmental Protection Agency (EPA, 2008-ET-MS-2-S2) and the Department of Environment, Heritage and Local Government (DEHLG, 2008-S-ET-2). C.L. thanks the Deutsche Forschungsgemeinschaft (DFG) for a research fellowship (GZ: LI2112/1-1).

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‡ The flow patterns follow the definitions of Chen and coworkers.[19]

§ A significant amount of unreacted α-terpinene **5** is removed during evaporation of the reaction mixture. Thus, the conversion of **5** to **6** can not be determined by NMR analysis of the crude product.

¶ As noticeable from Fig. 2, the overall surface area of the air bubbles in the bubble flow is unlikely to reach that of the slug flow.

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16 *Typical irradiation procedure*: A mixture of 1,5-dihydroxynaphthalene (16 mg; 100 μmol) and rose bengal (5 mg; 5 μmol) in 10 mL of alcohol–H_2O (9 : 1) was sonicated for 30 minutes. The clear reaction mixture was filled into the glass reactor column (filling height: approx. 60 cm) and was subsequently irradiated by two fluorescent tubes (OSRAM L58W/535 T8 Tube; 2 × 60 W). A stream of air was injected continuously *via* a capillary tube, which raised the solution level to approx. 1.45 m. After a set irradiation time, the reaction mixture was collected and evaporated to dryness. The conversion was determined by NMR analysis in acetone-d_6. For isolation purposes, three batches obtained under identical irradiation conditions were combined and **2** was isolated by column chromatography (SiO_2, $CHCl_3$). Analogue reactions were performed in Schlenk flasks (50 mL) using a Rayonet chamber reactor (Southern New England Ultraviolet Company; RPR-200) equipped with 16 visible lamps (Philips TL 8W/33-640; 16 × 8 W). *Selected physical and spectral data for 5-hydroxy-1,4-naphthoquinone (**2**)*: orange needles: mp 152 °C (Lit.: 151–154 °C[11f]). ^1H NMR (400 MHz, acetone-d_6): $\delta = 7.04$ (d, 1H, $^3J = 10.4$ Hz, H_{quin}), 7.08 (d, 1H, $^3J = 10.4$ Hz, H_{quin}), 7.33 (dd, 1H, $^3J = 8.4$, $^4J = 1.2$ Hz, H_{arom}), 7.58 (dd, 1H, $^3J = 7.6$, $^4J = 1.2$ Hz, H_{arom}), 7.78 (dd, 1H, $^3J = 8.4$, 7.6 Hz, H_{arom}), 11.92 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 114.0$, 118.1, 123.5, 130.8, 135.5, 137.6, 160.6, 183.2, 189.3 ppm. IR (KBr): $\nu = 3400$, 3058, 1662, 1641, 1590, 1448, 1289, 1225, 1151, 1098, 1081, 863, 827, 762, 703cm^{-1}. MS (EI, 70 eV): $m/z = 174$ [M^+], 146, 118, 90, 63, 39. Anal. Calcd for $C_{10}H_6O_3$: C 68.97, H 3.47. Found: C 68.25, H 3.70.

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