Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron

Tetrahedron 62 (2006) 1467–1473

Photooxygenations of 1-naphthols: an environmentally friendly access to 1,4-naphthoquinones

Oliver Suchard,[a] Ronan Kane,[b] Bernard J. Roe,[b] Elmar Zimmermann,[c] Christian Jung,[d] Prashant A. Waske,[a] Jochen Mattay[a,*] and Michael Oelgemöller[b,*]

[a]*Organische Chemie I, Fakultät für Chemie, Universität Bielefeld, Postfach 10 01 31, D-33501 Bielefeld, Germany*
[b]*School of Chemical Sciences and National Institute for Cellular Biotechnology, Dublin City University, Glasnevin, Dublin 9, Ireland*
[c]*Institut für Organische Chemie, Universität zu Köln, Greinstr. 4, D-50939 Köln, Germany*
[d]*Deutsches Zentrum für Luft- und Raumfahrt e.V. (DLR), Solarforschung, Linder Höhe, D-51147 Köln, Germany*

Received 9 September 2005; revised 26 October 2005; accepted 10 November 2005

Abstract—Dye sensitized photooxygenations of 1-naphthols were investigated with soluble and solid-supported sensitizers and moderate to excellent yields of the corresponding 1,4-naphthoquinones were achieved in relatively short irradiation times. The mild and environmentally friendly reaction conditions made this application particularly attractive for 'Green Photochemistry'. Consequently, the photooxygenation of 1,5-dihydroxynaphthalene was studied with non-concentrated and moderately concentrated sunlight and 5-hydroxy-1,4-naphthoquinone (Juglone) was obtained in yields up to 71%.

1. Introduction

Naphthoquinone derivatives based on 5-hydroxy-1,4-naphthoquinone (Juglone, **1**) represent an important class of natural products.[1] Additionally, Juglone serves as a valuable building block for the synthesis of biologically active quinonoid compounds (Chart 1),[2] and was thus selected by us as starting material for our ongoing photoacylation study.[3] Most commonly, Juglone is synthesized from the cheap and commercially available 1,5-dihydroxynaphthalene by oxidation, but many of these thermal pathways suffer from severe disadvantages concerning yield, selectivity, sustainability, scale-up or reproducibility, respectively.[4] Dye sensitized photooxygenations can serve as a versatile alternative and various examples involving 1-naphthols have been reported in the literature.[5–7]

Due to the favorable absorption of most dyes within the visible spectrum, photooxygenation reactions have been subjected to concentrated sunlight and served as model systems for environmentally friendly and benign 'Green Photochemistry'.[8–10] Recently, we have briefly reported on solar photooxygenations to Juglone using novel holographic mirror elements.[8b] In this publication, we would like to present a comprehensive study on solar and artificial light induced photooxygenations of 1-naphthols and 1,5-dihydroxynaphthalene in particular.

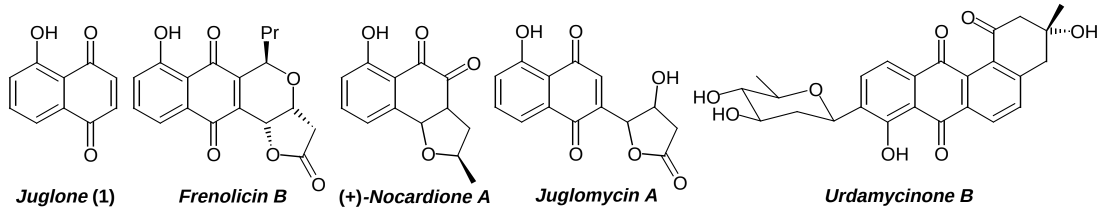


Chart 1. Quinonoid natural products synthesized from Juglone **1** (for more examples see Ref. 2).

Keywords: Quinones; Photochemistry; Photooxygenations; Green chemistry.

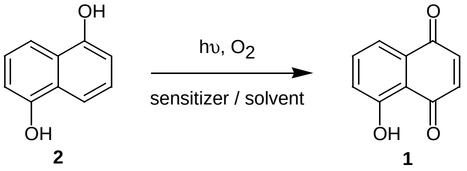
* Corresponding authors. Tel.: +49 521 106 2072; fax: +49 521 106 6417 (J.M.); tel.: +353 1 700 5312; fax: +353 1 700 5503 (M.O.); e-mail addresses: mattay@uni-bielefeld.de; michael.oelgemoeller@dcu.ie

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.11.021

2. Results and discussion

2.1. Experiments with artificial light

To find suitable reaction conditions for the solar chemical campaign, we have launched a detailed laboratory study with artificial light and selected the photooxygenation of 1,5-dihydroxynaphthalene **2** to Juglone **1** as model system (Scheme 1). A major disadvantage of the literature procedures was the usage of the hazardous solvents dichloromethane, acetonitrile or methanol, respectively,[5] which needed to be replaced for a solar 'outdoor' application. In order to simplify the work-up procedure, we furthermore examined the usage of solid-supported sensitizers, in particular Sensitox® (rose bengal on Merryfield resin; RB_{MF})[11] and methylene blue on ion exchange resin (MB_{IE}).[12] Both materials can be easily removed by filtration and are, in principal, reusable.



Scheme 1. Photooxygenation of 1,5-dihydroxynaphthalene **2**.

Following a standardized procedure, a 0.01 M solution of 1,5-dihydroxynaphthalene **2** was irradiated with a 150 W medium-pressure mercury lamp in the presence of a sensitizer while a gentle stream of oxygen was passed through the solution (Table 1). The progress of the reaction was followed by GC or TLC analysis. After 5 h, Juglone was isolated via column chromatography using chloroform as eluent or, more conveniently, via continuous extraction with *n*-hexane in a Soxhlet extractor.

Table 1. Experimental data for the photooxygenations of **2** with artificial light (150 W medium-pressure mercury lamp)

Entry	Sens.[a]	Solvent	Time (h)	**1** (%)
1	MB	MeOH	5	51
2	RB	MeOH	5	34
3	MB_{IE}	MeOH	5	43
4	RB_{MF}	MeOH	5	32
5	—[b]	MeOH	5	2
6	MB	EtOH	5	54
7	RB	EtOH	5	37
8	MB_{IE}	EtOH	5	47
9	RB_{MF}	EtOH	5	32
10	—[b]	EtOH	5	2
11	MB	*i*-PrOH	5	58
12	RB	*i*-PrOH	5	38
13	MB_{IE}	*i*-PrOH	5	46
14	RB_{MF}	*i*-PrOH	5	33
15	—[b]	*i*-PrOH	5	2
16	MB	Acetone	5	48
17	RB	Acetone	5	71
18	MB_{IE}	Acetone	5	41
19	RB_{MF}	Acetone	5	68
20	—[b]	Acetone	5	8
21	MB	CH_2Cl_2/MeOH[c]	5	51
22	RB	CH_2Cl_2/MeOH[c]	5	34
23	MB_{IE}	CH_2Cl_2/MeOH[c]	5	43
24	RB_{MF}	CH_2Cl_2/MeOH[c]	5	28
25	—[b]	CH_2Cl_2/MeOH[c]	5	3

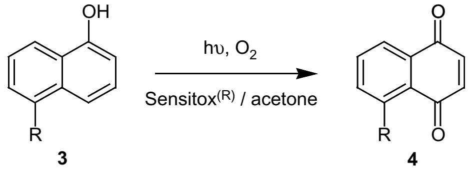
[a] Sensitizers: methylene blue (MB), rose bengal (RB), methylene blue on ion exchange resin (MB_{IE}), rose bengal on Merryfield resin (Sensitox®, RB_{MF}).
[b] Without sensitizer.
[c] CH_2Cl_2/MeOH (9:1).

In methanol, methylene blue was found to be the most effective sensitizer and the desired **1** was isolated in a reasonable yield of 51%. As would be expected for heterogeneous conditions, the yields for the solid-supported sensitizers were slightly lower with 43% (MB_{IE}) and 32% (RB_{MF}), respectively. With Sensitox®, the characteristic orange color of Juglone became clearly visible after a relatively short irradiation time. After 5 h, TLC analysis showed no sign of sensitizer leaching. In contrast to the literature,[12] significant leaching was, however, observed for methylene blue on ion exchange resin as noticeable from the green color of the final reaction mixture. Similar preferences and yields were obtained when ethanol was used as solvent. Likewise, the photooxygenation proceeded satisfactory in isopropanol and **2** was isolated in yields of 33–58%. The best Juglone yields of 71 and 68% were obtained using acetone as solvent and rose bengal or Sensitox® as sensitizer (entries 17 and 19), respectively. In comparison to the irradiations in alcohols, methylene blue gave a somewhat lower yield of 48%. Due to the limited solubility of the diol **2** in pure dichloromethane, photosensitized oxygenations were conducted alternatively in a 9:1 mixture with methanol, and Juglone was formed in yields of 28–51%. Surprisingly, the product yields did not improve as would be expected from the longer $^1O_2$ lifetime in this solvent mixture.[13] Enhanced photobleaching of the dye and photodecomposition of **1** due to the rather harsh radiation emitted from the medium-pressure mercury lamp,[5b] in combination with the formation of acid from the halogenated solvent, might explain this unexpected drop.

In the absence of sensitizer, **1** was formed in only small amounts of 2–3% in all alcoholic solvents and in the dichloromethane/methanol mixture. Solely the irradiation of **2** in pure acetone furnished Juglone in a significant yield of 8% (entry 20),[14] and we tentatively postulate a type-I photooxidation for its formation as known for phenols.[5d]

A scale-up of the photooxygenation to **1** was furthermore examined in acetone with Sensitox®, and the concentration of **2** was stepwise increased in 0.01 mol/l intervals. Up to a concentration of **2** of 0.05 mol/l, complete conversions were achieved within 5 h and **1** was isolated in yields of 65–70%. At higher concentrations, prolonged irradiation times up to 10 h were required but **1** was still isolated in good yields of 63–68%. At a diol concentration of 0.1 mol/l, the reaction was stopped after 10 h. At this stage, GC analysis showed a conversion of ca. 80%. After work-up, Juglone was obtained in 55% yield (69% based on conversion).

The photooxygenation protocol was additionally applied to 1-naphthol **3a**, 1-acetoxy-5-hydroxynaphthalene **3b** and 5-acetamido-1-hydroxynaphthalene **3c** (Scheme 2; Table 2), respectively. 1-Naphthol **3a** readily gave 53% of 1,4-naphthoquinone **4a** when irradiated with a medium-pressure mercury lamp in acetone and in the presence of Sensitox®. In line with the literature,[15b] irradiation of **3b** under identical conditions furnished Juglone **1** in 68% yield. Obviously, the acetate-group is cleaved during the course of the reaction. In contrast, the related amide-linked compound **3c** readily gave the corresponding quinone **4c** in a good yield of 61%.[15a]



Scheme 2. Photooxygenations of **3**.

Table 2. Experimental data for the photooxygenations of **3** with artificial light (150 W medium-pressure mercury lamp)

Entry	R	Sens.[a]	Solvent	Time (h)	**4** (%)
1	H (**3a**)	RB_{MF}	Acetone	5	53 (**4a**)
2	OAc (**3b**)	RB_{MF}	Acetone	5	68 (**1**)
3	NHAc (**3c**)	RB_{MF}	Acetone	5	61 (**4c**)

[a] Sensitizer: rose bengal on Merryfield resin (Sensitox®, RB_{MF}).

Due to the absorption of Juglone within the emission spectra of the medium-pressure mercury lamp,[16] we have conducted a series of experiments using a pair of 500 W halogen lamps (Table 3). Since solution purging with pure oxygen is furthermore problematic for industrial applications, we have examined its replacement with compressed air. Almost all experiments were run in non-hazardous isopropanol. Irradiations with pure oxygen readily furnished Juglone in yields of 25–70% after 5 h. Since the given set-up did not allow an even distribution of the solid-supported sensitizers within the reaction mixture, the experiments involving Sensitox® and methylene blue on ion exchanger resin (MB_{IE}) showed significantly lower conversions and yields. With compressed air, prolonged irradiation times of 10 h were required but the desired **1** was still obtained in fair to high yields of 21–71%. For laboratory purposes, we have furthermore modified the conditions reported by Cossy and Belotti for photooxygenations of 8-hydroxyquinolines.[7b] Irradiation in a 9:1 mixture of dichloromethane and methanol for 2 h and in the presence of TTP as sensitizer yielded **1** in an excellent yield of 88% (entry 5). The yield was somewhat lower with 78% when air was used as oxygen source (entry 10). Noteworthy, this procedure represents the so far best synthetic pathway to Juglone.[4]

Table 3. Experimental data for the photooxygenations of **2** with artificial light (2×500 W halogen lamps)

Entry	Sens.[a]	Solvent	Gas	Time (h)	**1** (%)
1	MB	*i*-PrOH	O_2	5	69
2	RB	*i*-PrOH	O_2	5	70
3	MB_{IE}	*i*-PrOH	O_2	5	34
4	RB_{MF}	*i*-PrOH	O_2	5	25
5	TPP[b]	$CH_2Cl_2/MeOH$[c]	O_2	2	88
6	MB	*i*-PrOH	Air	10	71
7	RB	*i*-PrOH	Air	10	55
8	MB_{IE}	*i*-PrOH	Air	10	45
9	RB_{MF}	*i*-PrOH	Air	10	21
10	TPP[b]	$CH_2Cl_2/MeOH$[c]	Air	3	78

[a] Sensitizers: methylene blue (MB), rose bengal (RB), methylene blue on ion exchange resin (MB_{IE}), rose bengal on Merryfield resin (Sensitox®, RB_{MF}), tetraphenylporphine (TPP).

[b] TPP insoluble in *i*-PrOH.

[c] $CH_2Cl_2/MeOH$ (9:1).

2.2. Solar chemical experiments

In July and August 2005, we have conducted a series of solar chemical experiments at Dublin City University (latitude 53°23′N, 6°15′W, 50 m above sea level). Due to the volatility and flammability of the solvent acetone, we have selected the less hazardous isopropanol for our campaign. Following this strategy, various solutions of **2** were exposed in a Schlenck-flask equipped with a cold finger and a reflux condenser to direct sunlight while the solution was purged with a gentle stream of air. All experiments went smoothly and gave satisfactory results in reasonable periods of time without any noticeable side-products (Table 4). The first run (**I**) was performed with soluble rose bengal under ideal solar conditions and Juglone was isolated in a moderate yield of 39% after 3.5 h of illumination. A somewhat lower yield of 30% of **1** was obtained when the reaction was repeated for 6.5 h during a partly sunny period (**II**). With soluble methylene blue as sensitizer (**III**), Juglone became available in 44% yield after 5.5 h of partly sunny weather. Likewise, Sensitox® was tested as a heterogeneous sensitizer (**IV**). Within ½ h, the orange color of **1** became clearly visible and further intensified with progressing illumination. Due to the limited distribution of the solid sensitizer within the reaction mixture, **1** was obtained in just 19% yield after 6.5 h of perfect weather conditions. Noteworthy, all reactions described above could have been driven easily to high conversions with longer illumination times. Thus, the preliminary results obtained clearly indicate that the solar photosensitized oxygenation of 1,5-dihydroxynaphthalene opens a promising and environmentally friendly pathway to Juglone.

Table 4. Experimental data for the solar photooxygenation reactions of **2** with non-concentrated sunlight

	Experiment			
	I	**II**	**III**	**IV**
Date	12.07.2005	13.07.2005	25.07.2005	08.08.2005
Scale				
2 (g)	0.56	0.56	0.56	0.56
Sens. (g)[a]	0.05 (RB)	0.05 (RB)	0.05 (MB)	0.4 (RB_{MF})
Solvent	*i*-PrOH	*i*-PrOH	*i*-PrOH	*i*-PrOH
V (ml)	350	350	350	350
Time				
IST[b]	14:15–17:45	11:45–18:15	10:45–16:15	10:15–16:45
Total (h)	3.5	6.5	5.5	6.5
Weather	Sunny	Partly sunny	Partly sunny	Sunny
Yield **1** (%)	39	30	44	19

[a] Sensitizers: rose bengal (RB), methylene blue (MB), rose bengal on Merryfield resin (Sensitox®, RB_{MF}).

[b] Irish summer time.

Further solar chemical experiments were performed with moderately concentrated sunlight at the solar chemical facility of the German Aerospace Center (DLR) close to Cologne/Germany (latitude 50°51′N, 7°07′E, 70 m above sea level).[17] A parabolic trough collector designed for laboratory-scale (<500 ml) applications and equipped with an aluminum mirror (aperture: 41×36 cm) was selected (Fig. 1).[18] The reactor offers a geometric concentration factor of about 18 suns, but its efficiency is reduced in practice due to optical losses. Tracking of the sun is performed manually for the elevation and the azimuth every 15 min. The reaction mixture is pumped through the jacket of a Liebig condenser (diameter: 2.4 cm), which is placed in the focal line of the concentrator. Cooling water is passed through the inner tube of the condenser. Oxygen is added via a simple Y-connector, which limited its homogeneous distribution within the absorber tube.

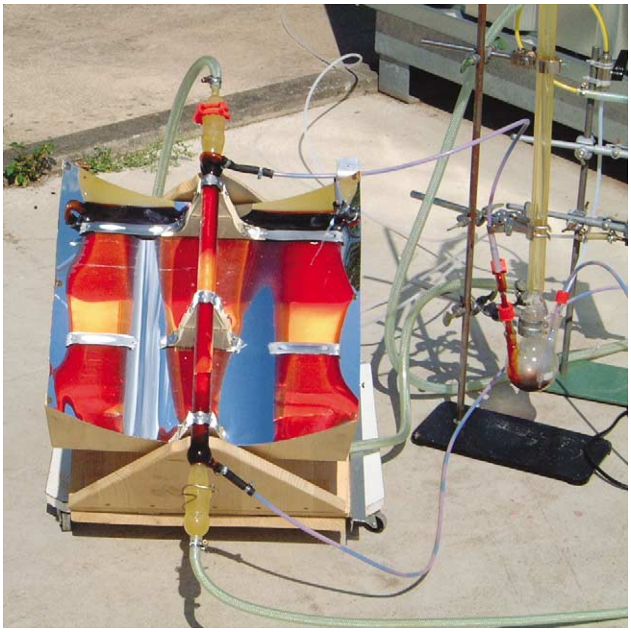


Figure 1. Laboratory-scale parabolic trough reactor during the solar photooxygenation of 1,5-dihydroxynaphthalene **2** (the red color of the sensitizer rose bengal can be clearly seen).

In August and September 2003, three laboratory-scale experiments were conducted, and the progress of each reaction was followed by GC analysis versus tetradecane as internal standard. Due to its favorable solar sensitization efficiency and overall stability,[8d] rose bengal was chosen as sensitizer. The experimental details and results from the solar chemical studies are summarized in Table 5.

Table 5. Experimental data for the solar photooxygenation reactions of **2** with moderately concentrated sunlight

	Experiment		
	V	**VI**	**VII**
Date	15.08.2003	09.09.2003	11.09.2003
Scale			
2 (g)	0.5	1.0	1.0
Rose bengal (g)	0.05	0.01	0.1
Solvent	*i*-PrOH	*i*-PrOH	MeOH
V (ml)	100	100	100
Time			
CEST[a]	14:20–16:50	13:45–17:15	10:15–14:45
Total (h)	2.5	3.5	4.5[b]
Effective (h)[c]	⅔	2.5	—
Weather	Sunny	Mostly sunny	Partly sunny
Photons (mol)[d]			
Total	0.26	0.21	0.16
Effective[e]	0.07	0.16	—
Conversion (%)[f]	>95	88	86
Yield **1** (%)	71 (75)[g]	69 (78)[g]	46 (54)[g]

[a] Central European summer time.
[b] Stopped due to rainfall.
[c] Time until conversion reaches an almost constant value.
[d] Estimated amount of photons collected between 500–600 nm.[18]
[e] Estimated amount of photons (500–600 nm) for effective illumination time.
[f] Conversion of **2** as determined by GC analysis (vs tetradecane).
[g] Yield based on conversion of **2**.

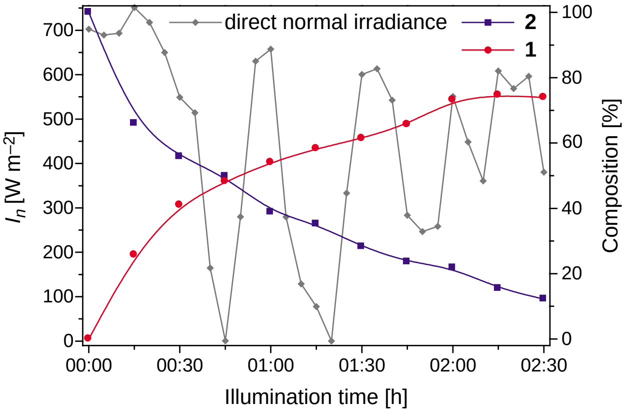


Figure 2. Direct normal irradiance (I_n) and product composition versus illumination time for the photooxygenation of 1,5-dihydroxynaphthalene **2** (Experiment VI).

The first run (**V**) was performed during a sunny period with 0.5 g of diol **2** and 0.05 g of rose bengal in 100 ml of isopropanol. The starting material was readily consumed and already after 40 min, GC analysis revealed complete conversion (>95%). During that time the reactor collected 0.07 mol of photons in the important absorption range of rose bengal between 500–600 nm.[19] After work-up, the desired product **1** was obtained in 71% yield. For the second experiment (**VI**) under mostly sunny conditions, the amount of diol **2** was doubled to 1.0 g and after 2.5 h, GC analysis showed a constant value for Juglone **1** of 74% (Fig. 2). The collector received 0.16 mol of photons in the range of 500–600 nm,[19] slightly more than double the amount as during the first experiment. After a total illumination period of 3.5 h, Juglone was obtained in a good yield of 69% (78% based on conversion). For the final experiment (**VII**), the solvent was replaced by methanol. Due to the less favorable weather, the illumination time needed to be extended. After 4.5 h of partly sunny conditions, the reaction was stopped at 86% conversion due to beginning rainfall. At this stage the reactor had collected 0.16 mol of photons between 500–600 nm.[19] After work-up, Juglone was isolated in a moderate yield of 46% (54% based on conversion).

3. Conclusion

In conclusion, photooxygenations of 1-naphthols to the corresponding 1,4-naphthoquinones can serve as a useful and environmentally friendly alternative to existing thermal processes. The solar chemical reaction of the cheap and commercially available 1,5-dihydroxynaphthalene can be easily performed with non-concentrated or concentrated sunlight, and yields the valuable intermediate Juglone. Thus, a realization of Giacomo Ciamician's spectacular vision of 'the photochemistry of the future' (presented at the International Congress of Applied Chemistry in New York in 1912)[20] seems feasible.

4. Experimental

4.1. General methods

Melting points were measured on a Büchi B-540 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 and 100 MHz, respectively) using the solvent residual peak as internal standard. Chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. MS spectra were recorded on a Finnigan MAT 8230 (EI) spectrometer. IR spectra were recorded as KBr discs on a Perkin-Elmer 298 infrared spectrophotometer, UV/vis spectra on a Perkin-Elmer Lambda 7 spectrophotometer using *n*-hexane (Janssen Chimica, spectrophotometric grade) as solvent. For combustion analysis a Heraeus CHN-O-Rapid Elemental Analyzer was used. GC analysis was performed on a Shimadzu GC-14A or a Hewlett-Packard GC 5890 Series II. A Hanau TQ-150 medium-pressure mercury lamp (150 W) or Armley 500 W halogen lamps (2×500 W) and immersion well reactors ($\lambda > 280$ nm) were used for irradiation experiments. TLC was carried out on Merck Kieselgel 60 F_{254}, column chromatography on silica gel (Macherey and Nagel) 230–240 mesh using chloroform or a 19:1 mixture of chloroform and methanol. 1,5-Dihydroxynaphthalene **2** was purified according to a modified procedure of Johnson and co-workers.[21] 1-Acetoxy-5-hydroxynaphthalene **3b** was synthesized as reported by Becher et al.,[22] 5-acetamido-1-hydroxynaphthalene **3c** via a method described by Jindal and co-workers.[23] Sensitox® was prepared with chloromethylated styrene–divinylbenzene copolymer (50–100 mesh, 1% cross-linked) according to Schapp et al.,[11] methylene blue on ion exchange resin (Lewatit SC 104 or MonoPlus SP 112) according to Williams and co-workers.[12] Solvents and reagents were commercially available and were used without further purification.

4.2. Irradiation and illumination experiments

4.2.1. Irradiations with artificial light. General procedure (medium-pressure mercury lamp). The naphthol (1.5 mmol) was dissolved in 150 ml of solvent. The sensitizer was added (MB: 10 mg; RB: 20 mg; MB_{IE}: 400 mg; RB_{MF}: 100 mg) and the solution was irradiated with a Hanau TQ-150 medium-pressure mercury lamp (150 W) for 5 h at room temperature while purging with a gentle stream of oxygen. Evaporated solvent was frequently refilled. The progress of the reaction was monitored by TLC or GC analysis. The reaction mixture was filtrated, the solvent removed in vacuum, and the residue was purified by column chromatography on silica or by extraction in a Soxhlet extractor with *n*-hexane. Experimental details are given in Tables 1 and 2.

4.2.1.1. 5-Hydroxy-1,4-naphthoquinone (Juglone, 1). Isolated by Soxhlet extraction with *n*-hexane. Orange solid, mp: 152 °C (lit.:[5a] 151–154 °C). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.94$ (s, 2H), 7.27 (dd, 1H, $J = 2.2$, 7.5 Hz), 7.60–7.65 (m, 2H), 11.90 ppm (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 114.0$, 118.1, 123.5, 130.8, 135.5, 137.6, 138.6, 160.6, 183.2, 189.3 ppm. MS (EI, 70 eV): $m/z = 174$ (M^+, 100%), 146, 118, 90, 63, 39. IR (KBr): $\nu =$ 3400, 3058, 1662, 1641, 1590, 1448, 1289, 1225, 1151, 1098, 1081, 863, 827, 762, 703 cm^{-1}. UV/vis (*n*-hexane): $\lambda_{max} = 247.8$, 318.0, 427.8 nm. Anal. Calcd for $C_{10}H_6O_3$: C 68.97, H 3.47. Found: C 68.25, H 3.70.

4.2.1.2. 1,4-Naphthoquinone (4a). Isolated by column chromatography using chloroform as eluent. Yellow-brownish solid, mp: 128 °C (lit.:[24] 128.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.96$ (s, 2H), 7.74 (m, 2H), 8.06 ppm (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 126.5, 132.0, 134.1, 138.8, 185.2 ppm. MS (EI, 70 eV): $m/z = 158$ (M^+, 100%), 130, 102, 76, 62, 50, 40. IR (KBr): $\nu = 1660$, 1587, 1331, 1302, 1146, 1115, 1059, 863, 771 cm^{-1}. UV/vis (*n*-hexane): $\lambda_{max} = 240.2$, 245.3, 328.3 nm. Anal. Calcd for $C_{10}H_6O_2$: C 75.94, H 3.82. Found: C 75.55, H 3.91.

4.2.1.3. 5-Acetamido-1,4-naphthoquinone (4c). Isolated by column chromatography using chloroform as eluent. Yellow solid, mp: 170 °C (lit.:[14a] 172 °C). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.29$ (s, 3H), 6.90 (d, 1H, $J = 10$ Hz), 6.94 (d, 1H, $J = 10$ Hz), 7.72 (dd, 1H, $J =$ 8.4 Hz), 7.81 (dd, 1H, $J = 1.2$, 8.4 Hz), 9.07 (dd, 1H, $J = 1.2$, 8.4 Hz), 11.85 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 25.8$, 116.1, 122.1, 126.2, 132.3, 135.9, 138.1, 140.1, 141.5, 170.1, 184.7, 189.3 ppm. MS (EI, 70 eV): $m/z = 215$ (M^+), 173 (100%), 145, 117, 101, 91, 63, 43. IR (KBr): $\nu =$ 3477, 3211, 1707, 1666, 1646, 1609, 1580, 1496, 1408, 1302, 1264, 1159, 833, 766, 723 cm^{-1}. Anal. Calcd for $C_{12}H_9N_1O_3$: C 66.97, H 4.22, N 6.51. Found: C 66.51, H 4.39, N 6.70.

4.2.2. General procedure (halogen lamps). Five hundred and forty milligrams (3.5 mmol) of 1,5-dihydroxynaphthalene **2** were dissolved in 350 ml of solvent. The sensitizer was added (MB: 50 mg; RB: 50 mg; MB_{IE}: 400 mg; RB_{MF}: 400 mg; TPP: 20 mg) and the solution was irradiated (2×500 W halogen lamps) in a Schlenck-flask equipped with a cold finger and a reflux condenser for 2–10 h at room temperature while purging with a gentle stream of oxygen or air. Evaporated solvent was frequently refilled. The progress of the reaction was monitored by TLC analysis. The reaction mixture was filtrated the solvent removed in vacuum, and the residue was purified by column chromatography (SiO_2, $CHCl_3$) or by extraction in a Soxhlet extractor with *n*-hexane. Experimental details are given in Table 3.

4.2.3. Illuminations with sunlight. General procedure (non-concentrated sunlight). Five hundred and forty milligrams (3.5 mmol) of 1,5-dihydroxynaphthalene **2** were dissolved in 350 ml of isopropanol. The sensitizer was added (RB: 50 mg; MB: 50 mg; RB_{MF}: 400 mg) and the solution was exposed to direct sunlight in a Schlenck-flask equipped with a cold finger and a reflux condenser for 3.5–6.5 h while purging with a gentle stream of air. Evaporated isopropanol was frequently refilled and the progress of the reaction was monitored by TLC analysis. The reaction mixture was filtrated, the solvent removed in vacuum, and the residue was purified by column chromatography (SiO_2, $CHCl_3$) or by extraction in a Soxhlet extractor with *n*-hexane. Experimental details are given in Table 4.

4.2.4. General procedure (concentrated sunlight). 1,5-Dihydroxynaphthalene **2** was dissolved in 100 ml of solvent. Rose bengal was added and the solution was exposed to moderately concentrated sunlight in a parabolic trough reactor for 2.5–4.5 h while purging with a gentle stream of oxygen. The progress of each reaction was monitored by GC analysis versus tetradecane as internal standard. The solvent was removed in vacuum, and the residue was purified by column chromatography (SiO_2, $CHCl_3/MeOH=19:1$). Experimental details are given in Table 5.

Acknowledgements

This research project was financially supported by the Arbeitsgemeinschaft Solar Nordrhein-Westfalen (Themenfeld 3: Solare Chemie und Solare Materialuntersuchungen) and Dublin City University (Research Alliance Fund). The authors would like to thank Prof. Axel G. Griesbeck for valuable discussions and Damien McGuirk for technical assistance.

References and notes

1. (a) Thomson, R. H. *Naturally Occurring Quinones IV*; Blackie: London, 1997. (b) Thomson, R. H. *Naturally Occurring Quinones III. Recent Advances*; Chapman and Hall: London, 1988. (c) Bérdy, J.; Aszalos, A.; Bostian, N.; McNitt, K. L.; CRC Handbook of Antibiotic Compounds. Quinone and Similar Antibiotics; CRC: Boca Raton, 1980; Vol. 3. (d) Thomson, R. H. *Naturally Occurring Quinones* 2nd ed.; Academic: New York, 1971. (e) *Biochemistry of Quinones*; Morton, R. A., Ed.; Academic: New York, 1965.
2. For *rac*-frenolicin B, see: (a) Contant, P.; Haess, M.; Riegl, J.; Scalone, M.; Visnick, M. *Synthesis* **1999**, 821. For (+)-nocardione A, see: (b) Clive, D. L. J.; Fletcher, S. P. *Chem. Commun.* **2003**, 2464. (c) Clive, D. L. J.; Fletcher, S. P. *J. Org. Chem.* **2004**, *69*, 3282. For *rac*-juglomycin A, see: (d) Kraus, G. A.; Liu, P. *Synth. Commun.* **1996**, *26*, 4501. For urdamycinone B, see: (e) Matsuo, G.; Miki, Y.; Nakata, M.; Matsumura, S.; Toshima, K. *Chem. Commun.* **1996**, 225. (f) Matsuo, G.; Miki, Y.; Nakata, M.; Matsumura, S.; Toshima, K. *J. Org. Chem.* **1999**, *64*, 7101. For aloesaponarin I, see: (g) Bingham, S. J.; Tyman, J. H. P. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3637. For (+)-rubiginone B_2, see: (h) Motoyoshiya, J.; Masue, Y.; Iwayama, G.; Yoshioka, S.; Nishii, Y.; Aoyama, H. *Synthesis* **2004**, 2099. For angucyclines in general, see: (i) Carreño, M. C.; Urbano, A. *Synlett* **2005**, 1.
3. (a) Oelgemöller, M.; Schiel, C.; Fröhlich, R.; Mattay, J. *Eur. J. Org. Chem.* **2002**, 2465. (b) Schiel, C.; Oelgemöller, M.; Mattay, J. *Synthesis* **2001**, 1275. (c) Schiel, C.; Oelgemöller, M.; Mattay, J. *J. Inf. Rec.* **1998**, *24*, 257.
4. For overviews on thermal preparations of Juglone, see: (a) Wakamatsu, T.; Nishi, T.; Ohnuma, T.; Ban, Y. *Synth. Commun.* **1984**, *14*, 1167. (b) Crouse, D. J.; Wheeler, M. M.; Goemann, M.; Tobin, P. S.; Basu, S. K.; Wheeler, D. M. S. *J. Org. Chem.* **1981**, *46*, 1814. (c) Grundmann, C. *Synthesis* **1977**, 644.
5. (a) Wurm, G.; Geres, U. *Arch. Pharm. (Weinheim)* **1985**, *318*, 931. (b) Durchstein, H.-J.; Wurm, G. *Arch. Pharm. (Weinheim)* **1984**, *317*, 809. (c) Wurm, G.; Geres, U.; Schmidt, H. *Dtsch. Apoth. Ztg.* **1980**, *120*, 2045. (d) Griffiths, J.; Chu, K.-Y.; Hawkins, C. *J. Chem. Soc., Chem. Commun.* **1976**, 676.
6. (a) Takaguchi, Y.; Yanagimoto, Y.; Fujima, S.; Tsuboi, S. *Chem. Lett.* **2005**, *33*, 1142. (b) Jensen, A. W.; Daniels, C. *J. Org. Chem.* **2003**, *68*, 207. (c) Chawla, H. M.; Kaul, K.; Kaul, M. *Indian J. Chem., Sect. B* **1993**, *32*, 733.
7. (a) Amarasekara, A. S. *Synth. Commun.* **1999**, *29*, 3063. (b) Cossy, J.; Belotti, D. *Tetrahedron Lett.* **2001**, *42*, 4329.
8. (a) Oelgemöller, M.; Jung, C.; Ortner, J.; Mattay, J.; Schiel, C.; Zimmermann, E. *The Spectrum* **2005**, *18*, 28. (b) Oelgemöller, M.; Jung, C.; Ortner, J.; Mattay, J.; Zimmermann, E. *Green Chem.* **2005**, *7*, 35. (c) Pohlmann, B.; Scharf, H.-D.; Jarolimek, U.; Mauermann, P. *Sol. Energy* **1997**, *61*, 159. (d) Esser, P.; Pohlmann, B.; Scharf, H.-D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2009. (e) Oelgemöller, M.; Jung, C.; Ortner, J.; Mattay, J.; Schiel, C.; Zimmermann, E. Proceedings of the 2004 International Solar Energy Conference, Portland, OR, USA, July 11–14, 2004; ASME, 2004; ISEC2004-65021.
9. For general overviews on 'Green Photochemistry', see: (a) Albini, A.; Fagnoni, M. *Green Chem.* **2004**, *6*, 1. (b) Mattay, J. *Chem. unserer Zeit* **2002**, *36*, 98. (c) Albini, A.; Fagnoni, M.; Mella, M. *Pure Appl. Chem.* **2000**, *72*, 1321. (d) Funken, K.-H. *Sol. Energy Mater.* **1991**, *24*, 370.
10. For other examples of the 'Green Photochemistry' concept, see: (a) Doohan, R. A.; Geragthy, N. W. A. *Green Chem.* **2005**, *7*, 91. (b) Schiel, C.; Oelgemöller, M.; Ortner, J.; Mattay, J. *Green Chem.* **2001**, *3*, 224. (c) Heinemann, C.; Xing, X.; Warzecha, K.-D.; Ritterskamp, P.; Görner, H.; Demuth, M. *Pure Appl. Chem.* **1998**, *70*, 2167. (d) Covell, C.; Gilbert, A.; Richter, C. *J. Chem. Res. (S)* **1998**, 316.
11. (a) Blossey, E. C.; Neckers, D. C.; Thayer, A. L.; Schapp, A. P. *J. Am. Chem. Soc.* **1973**, *95*, 5820. (b) Schapp, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 3741. (c) Paczkowska, B.; Paczkowski, J.; Neckers, D. C. *Macromolecules* **1986**, *19*, 863.
12. Williams, J. R.; Orton, G.; Unger, L. R. *Tetrahedron Lett.* **1973**, 4603.
13. (a) Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065. (b) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244. (c) For an extensive database on $^1O_2$ lifetimes in various solvents, see the Radiation Chemistry Data Center: http://allen.rad.nd.edu/compilations/SingOx/table1/t1.htm.
14. Much higher yields were obtained in acetone when quartz vessels were used and this phenomenon is currently investigated. Suchard, O.; Waske, P. A.; Mattay, J.; Oelgemöller M. Unpublished results.
15. (a) Möhrle, H.; Folttmann, H. *Z. Naturforsch.* **1987**, *42b*, 1578. (b) Möhrle, H.; Folttmann, H. *Arch. Pharm. (Weinheim)* **1988**, *321*, 167.
16. Singh, I.; Ogata, R. T.; Moore, R. E.; Chang, C. W.; Scheuer, P. J. *Tetrahedron* **1968**, *24*, 6053.
17. Funken, K.-H.; Becker, M. *Ren. Energy* **2001**, *24*, 469.

18. For overviews on different reactor types, see: (a) Malato, S.; Blanco, J.; Vidal, A.; Richter, C. *Appl. Catal. B: Environ.* **2002**, *37*, 1. (b) Funken, K.-H.; Ortner, J. *Z. Phys. Chem.* **1999**, *213*, 99.
19. Calculated using: Walsch, T.; Riffelmann, K.-J. *SEDES for Windows*, DLR, V. 2.5, 1997.
20. Ciamician, G. *Science* **1912**, *36*, 385.
21. Johnson, W. S.; Gutsche, C. D.; Banerjee, D. K. *J. Am. Chem. Soc.* **1951**, *73*, 5464.
22. Becher, J.; Matthews, O. A.; Nielsen, M. B.; Raymo, F. M.; Stoddart, J. F. *Synlett* **1999**, 330.
23. Jindal, D. P.; Coumar, M. S.; Bruni, G.; Massarelli, P. *Arzneim.-Forsch.* **2002**, *52*, 654.
24. Fieser, L. F.; Peters, M. A. *J. Am. Chem. Soc.* **1931**, *53*, 4080.