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## Efficient Solar Photooxygenation with Supported Porphyrins as Catalysts

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Light can be used to mediate several chemical processes by changing the reactivity of molecules through their activation, thereby essentially corresponding to an electronic reorganization. This activation can be achieved with the aid of an intermediate molecule or even directly without the need for any additional reagents. According to the principles of sustainable chemistry, this latter option is the ideal choice.<sup>[1]</sup> The involvement of light-activated catalysts that can initiate a chemical reaction, thereby helping atom transfer or electron transfer, belongs to the field of photocatalysis.<sup>[2]</sup> Recent examples of these reactions that use solar irradiation include synthetic reactions<sup>[3]</sup> and clean degradation processes.<sup>[4]</sup> Otherwise, photochemical catalysis depends on the physical transfer of energy from excited molecules to ground-state molecules that afford excited states through their own reactivity.<sup>[2a]</sup> By using the relatively inexhaustible solar light, several photochemical processes can be performed.<sup>[5]</sup> Recent examples of photochemical synthetic processes that are promoted by sunlight include trans-to-cis double-bond isomerization<sup>[6]</sup> and the photo-Friedel–Crafts acylation of 1,4-naphthoquinones.<sup>[7]</sup> The photochemical oxidation reaction by singlet oxygen is an attractive process, not only because it provides access to useful derivatives, such as endoperoxides and allylic hydroperoxides, but also because it can be achieved by using molecular oxygen and solar radiation, thereby making it an example of a "green" process. This reaction requires the use of a soluble photosensitizer<sup>[8]</sup> or, better, a heterogenized form,<sup>[9]</sup> which improves the isolation procedures and is much closer to sustainable chemistry principles. Porphyrins are excellent photosensitizers and their covalent immobilization on polymeric matrices has been shown to give very active singlet-oxygen-generating materials.<sup>[10]</sup>

Porphyrins with halogen atoms in the *meso*-phenyl positions are better singlet-oxygen generators, mainly owing to the heavy-atom effect.<sup>[11]</sup> In the case of supported porphyrins, the type of support and the role of the spacer in photooxygenation reactions have been studied previously by ourselves.<sup>[12]</sup> Photosensitizer **Ps1** has been shown to be an active catalyst and, herein, two new supported photosensitizers with different spacer groups were prepared (**Ps2** and **Ps3**, Scheme 1). The linking of porphyrins to Merrifield polymers began with the



synthesis of a non-symmetric halogenated tetra-arylporphyrin (1) in a reaction sequence that did not involve any chromatographic purification steps. In fact, the chlorosulfonation reaction was performed directly on the mixture that was obtained from the condensation step. Owing to the different reactivities of the phenyl and 2,6-dichlorophenyl rings, a selective chlorosulfonation of the unsubstituted phenyl ring was achieved to give the reactive chlorosulfonylporphyrin derivative (2).<sup>[12]</sup> Subsequent condensation with aminated Merrifield polymers **Mp1–Mp3** gave photosensitizers **Ps1–Ps3**,<sup>[10e,12]</sup> with different spacers between the polymer backbone and the porphyrin macrocycle.

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The level of porphyrin incorporation into the polymer structure was calculated from elemental analysis of the supported photosensitizers, taking into account the nitrogen content of the Merrifield-modified polymers (**Mp1–Mp3**, Table 1).



Scheme 1. Reaction sequence that leads to photosensitizers Ps1-Ps3.

Selectivity<sup>[d]</sup> [%]

5 (16)

5 (39)

5 (29)

4 (84)

4 (61)

4 (71)

Table 1. Nitrogen content in the MpX and PsX polymers.									
Entry	Polymer	Nitrogen content [%]	Polymer	Nitrogen content [%]	Porphyrin incorporation $[mmol g^{-1}]$				
1 2 3	Mp1 Mp2 Mp3	1.34 1.18 3.45	Ps1 Ps2 Ps3	1.54 1.58 3.65	0.0357 0.0714 0.0365				

Entry

1

2

4

5

6

7

8

9

3<sup>[e]</sup>

PSX

PS1

PS1

PS1

version of  $\alpha$ -terpinene was achieved and NMR analysis of the reaction product showed that, besides ascaridol (4), which was the expected [4+2] cycloadduct, about 13% of *p*-cymene (5) was present (Scheme 2).

The usefulness of the photooxygenation system for  $\alpha$ -terpinene, citronellol, and linalool substrates was evaluated with all of the photosensitizers. After the completion of the reactions, the mixtures were filtered to isolate the catalyst, evaporated,

Yield<sup>[c]</sup> [%]

87

80

89

The order of porphyrin loading (mmol porphyrin per gram of polymer) was Ps2 (0.0714)> Ps1 (0.0365) > Ps3 (0.0357). Although being less reactive, the arylated diamine gave greater incorporation of the porphyrin macrocycle, thus suggesting that the polymer with the biphenyl spacer (Mp2) gave morefavorable conditions for the incorporation of porphyrin derivative 2. The polymers that were modified with a  $C_{12}$  chain or with a pentaethylene chain showed almost the same values for porphyrin incorporation.

For the solar experiments, we used a very simple apparatus that consisted of a two-necked

round-bottomed flask (250 mL) that was adapted with an ice condenser and a balloon that was filled with oxygen. The mixture was exposed to solar irradiation on the balcony of the Coimbra Chemistry Department (40°15'N08°27'W), with a solar fluence of 45-55 W cm<sup>-2</sup>, and was subjected to constant magnetic stirring (see the Supporting Information).

In the first experiment, the photooxidation of  $\alpha$ -terpinene (3, 75 mm), the photosensitizer (Ps1)-to-substrate ratio was 1:1000, and CHCl<sub>3</sub> was the solvent. After 1.5 h, complete con-



t [h]

3

4

5

Table 2. Solar photooxygenation reactions with supported photosensitizers Ps1-Ps3.<sup>[a]</sup>

 $n_{\rm PsX}/n_{\rm subs}^{[b]}$ 

1:10 000

1:30 000

1:30 000

Substrate

3

3

3

[c] Combined yield of the isolated products. [d] Relative amounts of the products, as determined by NMR spectroscopy of the reaction mixture. [e] Under a flow of air. [f] The same amount of compound 3 was used as in entry 1. [g] The remainder of the product was reagent 3.

> and the residues were analyzed by NMR spectroscopy (Table 2).

> With  $\alpha$ -terpinene, the supported photosensitizers Ps1-Ps3 showed very good efficiency, with complete conversion even at high molar ratios (1:60000; Table 2, entry 4). With this substrate, the amount of p-cymene increased with the reaction time, which showed that the oxygen-mediated oxidation reaction proceeded parallel to the photooxidation reaction, as confirmed by a blank experiment (Table 2, entry 14). In air (Table 2,

entry 3) the reaction is slower but, as expected, is more selective for ascaridole (4). With a substrate that is more difficult to oxidize, such as citronellol (6), the reaction is slower; however, complete conversion is achieved within 5 h with catalyst Ps2 at a 1:10000 catalyst-to-substrate molar ratio. This high activity is similar to a dendrimer porphyrin system,<sup>[13]</sup> but much more simple. The main interest in the photooxidation of citronellol is related to the production of rose oxide from the allylic alcohol that is derived from compound 7.<sup>[14]</sup> With this system, photooxi-



Scheme 2. Photooxidation of compounds 3, 6, and 9 with photosensitizers Ps1-Ps3.

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dation with compounds **Ps1–Ps3** gives hydroperoxides **7** and **8** in nearly equal amounts; this situation has also been observed with other photooxidation systems.<sup>[8b, 10b, 12a, 13, 15]</sup>

Linalool (9) is a monoterpene that contains one allylic-alcohol functionality and one trisubstituted double bond and it is found in many flavors and fragrances.<sup>[16]</sup> Photooxidation with a catalyst-to-substrate ratio of 1:10000 occurred efficiently (6– 8 h) and only at the more electron-rich double bond, thereby affording two regioisomeric hydroperoxides (**10** and **11**) in almost the same amounts. One reaction batch gave 1.0 g of the products with only 25 mg of the supported photosensitizer.

The possibility of catalyst recycling was analyzed for sensitizers **PS1** and **PS3** by using compound **3** as the substrate in a 1:30 000 catalyst-to-substrate ratio (Table 3).

Table 3. Catalyst-recycling experiments with photosensitizersPs1 andPs3 as the catalyst and compound 3 as the substrate. <sup>[a]</sup>								
Cycle number	PsX	<i>t</i> [h]	Yield <sup>[b]</sup> [%]	Selectivity <sup>[c]</sup> [%]				
1	Ps1	4	80	<b>4</b> (61)	<b>5</b> (39)			
2	Ps1	5	86	4 (53)	<b>5</b> (47)			
3	Ps1	8	83	4 (50)	<b>5</b> (50)			
1	Ps3	4	89	4 (67)	<b>5</b> (33)			
2	Ps3	4.5	91	4 (66)	<b>5</b> (34)			
3	Ps3	4	91	4 (73)	<b>5</b> (17)			
[a] CHCl <sub>3</sub> was used as the solvent, with a balloon that was filled with O <sub>2</sub> ; the substrate/catalyst ratio was 30000:1. [b] Combined yield of the isolated products. [c] Relative amounts of the products, as determined by NMR spectroscopy of the reaction mixture.								

The results of the recycling experiments show that catalyst **Ps3** is more active than catalyst **Ps1** and, more importantly, no apparent deactivation is observed after three consecutive runs. Moreover, the selectivity for ascaridole (4) is higher with this catalyst. With this catalytic system, at the end of the third cycle, 6 g of products can be obtained with 13 mg of the catalyst, which is an outstanding performance.

To attempt a further step forward, we moved towards "greener" conditions by replacing the solvent with EtOH because  $CHCl_3$  is not environmentally friendly,<sup>[17]</sup> although it provides a high lifetime for singlet oxygen.<sup>[18]</sup> The results of the photooxygenation reactions with **Ps3** in EtOH are presented in Table 4.

Unexpectedly, with EtOH as the solvent, the reaction proceeded faster than in CHCl<sub>3</sub> (Table 4, entry 1). The increase in the reaction rate was compared with unsupported porphyrin. The photooxygenation of  $\alpha$ -terpinene with a substrate-to-porphyrin ratio of 1:10000 was complete after 1.5 h and with 99% selectivity for the ascaridole product. This result confirms the high efficiency of this kind of supported catalyst. The increased catalyst efficiency with EtOH as the solvent was also clear at a **Ps3**/ $\alpha$ -terpinene (**3**) ratio of 1:30000 and was more evident in the case of the recycling experiments (Table 4, entry 3 and 4). In that particular case, 22 mg of the catalyst gave a total of 6 g of ascaridole after the three experiments (Table 4, en-

EtOH. <sup>[a]</sup>	. Solar phot	ooxygenation	reacti	ons with pho	otosensitiz	er <b>PS3</b> in	
Entry	Substrate	$n_{\rm Ps}/n_{\rm subs}$ <sup>[b]</sup>	t [h]	Yield <sup>[c]</sup> [%]	Selectivity <sup>[d]</sup> [%]		
1	3	1:10 000	1.5	94	4 (99)	<b>5</b> (1)	
2	3	1:30 000	2.5	92	<b>4</b> (99)	<b>5</b> (1)	
3 <sup>[e]</sup>	3	1:30 000	3	86	<b>4</b> (99)	<b>5</b> (1)	
4 <sup>[f]</sup>	3	1:30 000	3.5	89	<b>4</b> (99)	<b>5</b> (1)	
5	3	1:60 000	6	90	<b>4</b> (99)	<b>5</b> (1)	
6	6	1:10 000	7	99	<b>7</b> (49)	<b>8</b> (51)	
[a] EtOH was used as the solvent, with a balloon that was filled with $O_{2}$ .							

[b] Molar ratio of **Ps3** to the substrate. [c] Combined yield of the isolated products. [d] Relative amounts of the products, as determined by NMR spectroscopy of the reaction mixture. [e] First recycling experiment, second cycle. [f] Second recycling experiment, third cycle.

tries 2–4). At a ratio of 1:60000, only 6 h were needed to complete the reaction; this result corresponds to the formation of 3.2 g of product with 18 mg of the catalyst. With citronellol (6), the reaction occurred a little faster (7 h versus 8 h), but with the same diastereomeric preference as that observed in CHCl<sub>3</sub>.

The less-favorable lifetime of singlet oxygen in EtOH is known (12  $\mu$ s compared with 60  $\mu$ s in CHCl<sub>3</sub><sup>(18a)</sup>); thus, another favorable factor must be operating in this system. The similar solubility of oxygen in these two solvents<sup>(19)</sup> excludes the concentration factor. One possible explanation could be the photodecomposition of CHCl<sub>3</sub> catalyzed by the porphyrin,<sup>(20)</sup> which is likely to have two main consequences: 1) It quenches the excited porphyrin, thereby diminishing the amount that is involved in the singlet-oxygen formation and 2) the production of hydrochloric acid causes the formation of porphyrin dication, which is not so reactive.

In support of this theory, we detected the presence of the porphyrin dication during the reaction in CHCl3 and, thus, a small portion of solid sodium hydrogen carbonate was added. The polymer matrix influences the photooxygenation process by lowering the quantum yield of singlet oxygen.<sup>[10f]</sup> This fact points to another possible explanation of this solvent effect, which is related to the solvation process and the greater or smaller amount of solvent molecules that are present at the polymer surface where the oxidative process occurs. This solvation process has been implicated in the observed diastereoselectivities of ene reactions with supported catalysts<sup>[21]</sup> and may also be active in this case. However, the most important difference with the CHCl<sub>3</sub> system is that, with EtOH, almost no pcymene is formed. Taking into account that the source of pcymene is the oxygen oxidation of compound 3, with its corresponding reduction into water, the presence of acid is crucial for that reaction to occur. Again, this result points to the intervention of hydrochloric acid from the decomposition of CHCl<sub>3</sub> as being responsible for the difference in the observed reaction rate.

In conclusion, *meso*-phenyl-substituted porphyrins can be easily supported on aminated Merrified polymers through a selective chlorosulfonation reaction of the porphyrin macrocycle. These supported porphyrins act as efficient photosensitizers in

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singlet-oxygen oxidation reactions with solar radiation and molecular oxygen. Complete conversion of  $\alpha$ -terpinene (**3**) can be obtained with substrate-to-photosensitizer ratios as high as 60000:1. The major drawback of this process is the simultaneous oxidation of compound **3** into *p*-cymene. With citronellol (**6**) and linalool (**9**) as substrates, no diastereoselective oxygenation was observed. Replacing EtOH for CHCl<sub>3</sub> as the solvent gave a more convenient and "greener" system, with faster catalysis and negligible generation of *p*-cymene.

## **Experimental Section**

Photooxidation experiments were performed under direct sunlight at ambient temperature on a laboratory-built photoreactor (Figure S1 in the Supporting Information). A two-necked round-bottomed flask was charged with the substrate (5 mmol), the photosensitizer (supported porphyrin, to afford the desired molar ratio of sensitizer to substrate), sodium hydrogen carbonate (413 mg), and solvent (65 mL). The mixture was purged with O<sub>2</sub> for a few minutes, an ice condenser and an oxygen balloon inlet were added onto the reaction flask, and the apparatus was positioned at the center of an aluminum-plate reflector (see the Supporting Information). The mixture was stirred under an oxygen atmosphere during the irradiation. The reaction temperature remained between 31 and 34 °C. When the irradiation had finished, the reaction mixture was filtered to recover the sensitizer and the filtrate was evaporated to dryness and analyzed by NMR spectroscopy. The products were identified by comparison to literature data: Ascaridole (4),<sup>[12b]</sup> (**5**),<sup>[12b]</sup> *p*-cymene (E)-7-hydroperoxy-3,7-dimethyloct-5-en-1-ol (7),<sup>[10b]</sup> 6-hydroperoxy-3,7-dimethyloct-7-en-1-ol (8),<sup>[10b]</sup> 7-hydroperoxy-3,7-dimethyloct-1,5-dien-1-ol (10),<sup>[22]</sup> and (E)-6-hydroperoxy-3,7dimethyloct-1,7-dien-1-ol (11).[22]

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