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Rose Bengal Immobilized on Wool as an Efficiently “Green” Sensitizer for Photooxygenation Reactions

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A new type of supported photosensitizer derived from renewable wool and Rose Bengal is described. The novel sensitizer could efficiently promote the photooxygenation of furan derivatives to the corresponding 5-hydroxy-2-(5*H*)-furanone in excellent yields, via singlet oxygen, using visible light as the energy source. The sensitizer could be easily recovered from the reaction mixture by a simple filtration. It is discovered that the recovered sensitizer can be reused four times.

Environmentally friendly synthesis of organic compounds is currently required for sustainable development. One way to develop green or sustainable organic synthesis is to utilize energy coming from nonrenewable sources like petroleum as little as possible. Another way is to develop processes with low E-factor[1] (weight of by-product per unit weight of desired product). Use of heterogeneous catalysts could result in waste minimization, simple and safe operation, and convenient work up. Thus, it is one important strategy to develop sustainable organic synthesis. Photocatalytic approaches are gaining increasing acceptance because light is used to trigger the reaction processes and, hence, allow the possibility to carry out oxidation in a more controllable manner than conventional thermal methods. The common approch involves dye-sensitized photoexcitation of ground-state triplet oxygen to produce excited-state singlet oxygen ($^{1}O_{2}$) using sensitizers such as Methylene Blue,[2] Rose Bengal,[3] porphyrins,[4] and fullerenes.[5] Highly reactive singlet oxygen ($^{1}O_{2}$) generated photochemically can be quenched either physically or by a chemical reaction. Furan and its derivatives are among the most reactive substrates for singlet oxygen leading to 5-hydroxy-2-(5*H*)-furanone[6] which is a key constituent of the potent analgesic and anti-inflammatory agent manoalide and many other natural and unnatural products of biomedical importance.[7] The most popular methods for preparing 5-hydroxy-2-(5*H*)-furanone compounds have been reported in many cases.[6,8] But one of the drawbacks of using a photosensitizer is that it needs to be removed from the reaction mixture once the oxidation is finished. The typical way to remove the sensitizer is chromatographic separation. And the sensitizer cannot be recycled. It is possible to attach a photosensitizer to a solid support, allowing it to be removed from the reaction mixture by means of simple filtration or centrifugation. One of the most employed photocatalysts of this type is Rose Bengal (RB) covalently linked to a series of polymers[9] or other supports.[10] However, to date, the utilization of the soluble sensitizer (Rose Bengal disodium salt) is preferred in synthesis of 5-hydroxy-2-(5*H*)-furanone. On the basis of our investigations of the photooxygenation of endocyclic enol ethers,[11] we recently became interested in the photooxgenation reaction using environmentally friendly solid sensitizer. We report herein a new type of Rose Bengal sensitizer supported by wool, which was prepared by a general dyeing procedure. It can promote the photochemical synthesis of 5-hydroxy-2-(5*H*)-furanone (butenolide, **2**) from furan derivatives (Figure 1) in excellent yields, by using solar light as a unique energy source and molecular oxygen as oxidant. This approach is undoubtedly environmentally friendly.

Figure 1. Synthesis of butenolide **2** from photooxygenation of furan derivatives.

Wool fabric was pretreated and dyed with Rose Bengal by a conventional dyeing method (see Supporting Information for detailed dyeing conditions).[14] The dye uptake (i.e., the Rose Bengal content in the solid wool sensitizer) was approximately 99%, which was calculated from the UV–vis spectra (see Supporting Information).[14] Then the dyed wool was subjected to the fastness test according to standard methods (see Supporting Information).[14] The washing and light fastness exhibit to be 3–4 grade. The results show that dyed wool exhibits good fastness properties.

In order to clarify the mechanism of adsorption of Rose Bengal to the wool fabrics, the adsorption behaviors were observed by SEM-EDX (S4800 Field-Emission Scanning Electron Microscope, Figure 2). Elemental analysis of the Rose Bengal which was absorbed in wool showed the presence of chlorine and iodine elements (Figure 2b). These images show that RB compound is bound to the surfaces of the wool.

We further analyzed the difference between the wool and RB–wool system by means of infrared spectroscopy (IR). IR spectroscopy of RB shows characteric absorption at 1334 cm^{-1} due to –Cl and 951 cm^{-1} due to –I, which was not observed in IR spectra of the wool. However, clear absorption at 1338 and 953 cm^{-1}could be observed for the RB–wool system (see Supporting Information).[14] This result indicated that the functional groups of –Cl and –I were present on the surface of wool.

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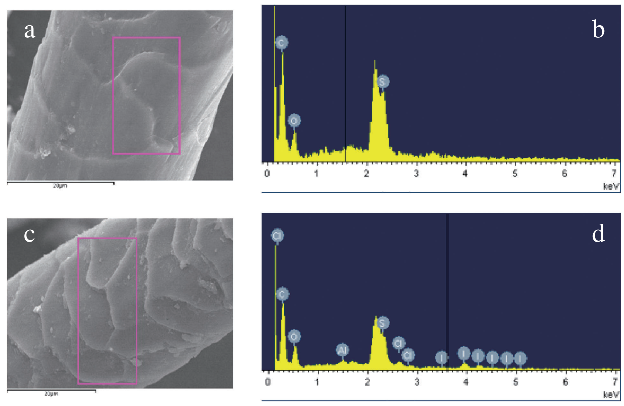

Figure 2. SEM-EDX spectras: a. SEM photograph of the surface of the wool, Bar indicates 20 µm. b. Results of elemental analysis in SEM-EDX of the surface of the wool [cursor in 1.557 (23 cts)], C carbon, O oxygen, S sulfur. c. SEM photograph of the surface of the RB–wool system, Bar indicates 20 µm. d. Results of elemental analysis in SEM-EDX of the surface of the RB–wool system [cursor in 3.592 (20 cts)], C carbon, O oxygen, S sulfur, Cl chlorine, I iodine.

As reported,[6] RB as a sensitizer could promote the photooxygenation of 2-furfural or other furan derivatives to 5-hydroxy-2-(5*H*)-furanone. We would like to explore wool-supported RB's activity of promoting photooxygenation of furan derivatives. The RB–wool system was washed repeatedly with CH_3CN until the final filtrate was colorless before use. The procedure is as follows: To a solution of 2-furfural (**1a**, 200 mg, 2.04 mmol) in CH_3CN (30 mL) was added RB–wool sensitizer (150 mg, 1% mol of substrate on the basis of RB). The resultant mixture contained in a Pyrex vessel was vigorously stirred at room temperature under O_2 and irradiated with a medium-pressure mercury lamp through a UV-cutoff filter. GC analysis indicated complete oxidation of **1a** after 10 h. Removal of the sensitizer by filtration of the reaction mixture and removal of the solvent under vacuum gave the crude product of **2** which could be further purified by flash chromatography to afford pure compound **2**[12] (145 mg, 71%). Absorption spectra of the filtered reaction solution after photolysis indicated that no RB is leached into the reaction solution.

Apart from the substrate **1a**, the photooxygenation reactions of **1b** was also studied. The reactions were carried out as described for the photooxygenation **1a**. **1b** could be smoothly converted into the expected products in decent yields (Table 1).

In each case, the products of the reaction using the wool–RB system were compared with those obtained by using Rose Bengal dye.[6a,6b,6d,6e]

Some solvents were screened. The results are summarized in Table 2. The reported yields and conversion were determined by GC analysis.

As shown in this table, this reaction is sensitive to solvent polarity which is consistent with the general rules of solvent effect on the photooxygenation.[13] $CHCl_3$ is the most preferable solvent, which leads to 81% conversion with a higher yield (Entry 2). Although a good yield was also obtained with acetone as solvent, the relatively low conversion was a problem (Entry 3).

Table 1. Photooxygenation of **1a** and **1b** sensitized by RB–wool system

Substrate	Reaction time/h	Yield/%
1a	10	71
1b	12	68

Table 2. Solvent effect for photooxygenation of 2-furfural (**1a**) with RB–wool system as the sensitizer

Entry	Solvent	Reaction time/h	Conv/%	Yield/%
1	MeCN	8	83	68
2	$CHCl_3$	8	81	72
3	Acetone	8	55	46
4	Benzene	8	40	22
5	Hexane	8	11	7

Table 3. Recycling of sensitizer in photooxygenation of **1a**

Cycle	Time/h	Yield/%	Degradation/%
1	8.5	67	19
2	9.5	54	43
3	10	50	75
4	11.5	49	96

The recyclability of the photosensitizer in the photooxygenation of 2-furfural (1a) was also investigated. The results for this study are summarized in Table 3.

For the photooxygenation of 2-furfural (**1a**), which required a longer reaction time, the RB–wool system could be repeatedly used a fourth time also. In the fifth run, no complete conversion was obtained due to the severe photobleaching of sensitizer. In fact, after 4 cycles of these reactions, the sensitizer was dissolved in 30 mL NaClO solution (3%). As shown by absorption spectroscopy of the solutions, about 96% of RB–wool sensitizer was photobleached for **1a**. These results indicated that the RB–wool system has a relatively higher photostability than RB and, therefore, serves as a better sensitizer for the photooxygenation reactions.

In summary, the utilization of RB–wool as an efficiently "green" sensitizer for photooxygenation of furan derivatives **1a** and **1b** to butenolides **2** in excellent yields has been demonstrated. The sensitizer was prepared by a general dyeing procedure. It could be recovered simply by filtration and reused four times. It represents a practical alternative to soluble RB for relatively high photostability, recyclability, sensitizing activity, and sustainable development. Further work is in progress to explore applications of RB–wool sensitizer in photooxygenation of other typical compounds in our laboratory.

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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