



Dioxygenation of styrenes with molecular oxygen in water

Shuang-Qi Tang, An-Ping Wang, Martine Schmitt, Frédéric Bihel*

Laboratoire d'Innovation thérapeutique, UMR 7200, CNRS, Université de Strasbourg, Faculté de Pharmacie, 74 route du Rhin, BP 60024, 67401 Illkirch, France

ARTICLE INFO

Article history:

Received 14 December 2017

Revised 23 February 2018

Accepted 2 March 2018

Available online 3 March 2018

Keywords:

Alkene

Oxidation

N-hydroxyphthalimide

Triton X-100

Water

ABSTRACT

Employing Triton X-100 as a surfactant, the *tert*-butyl hydroperoxide-mediated dioxygenation of styrene with molecular oxygen and *N*-hydroxyphthalimide was achieved in water at room temperature, providing the corresponding dioxygenated products in 9–93% yield. This facile method is eco-friendly, feasible on gram scale, and applicable to a wide range of styrene derivatives with a variety of functional groups.

© 2018 Elsevier Ltd. All rights reserved.

The environmental impact of the chemical industry is a major issue; approximately 80% of the chemical waste from a reaction mixture corresponds to organic solvents.¹ One of the main research fields is the development of alternatives to organic solvents, with expected outputs in terms of health, safety and environmental impacts. Solvent-free alternatives represent the best solution, however, most organic reactions require a medium to enable matter and heat transfer. Ionic liquids, supercritical media and other non-conventional media have been described as efficient alternatives to conventional organic solvents, but the use of water appears to be one of the best solutions in terms of safety and environmental impact.² Unfortunately, most organic reactants have poor solubility in water, leading to low yields and poor reaction rate. The development of organic synthesis in aqueous medium using surfactants represents an efficient ecofriendly strategy.³ Indeed, due to their amphiphilic nature, surfactants in water undergo spontaneous self-assembly into micelles, which act as nanoreactors, and their hydrophobic cores play the role of reaction vessels in which organic transformations involving water-insoluble reagents can occur. By using versatile nonionic surfactants, such as TPGS-750-M, a set of chemical transformations has been developed under micellar conditions, including nucleophilic substitution,⁴ oxidation,⁵ reduction,^{6,7} olefin metathesis,⁸ and Pd-catalyzed cross-coupling,⁹ as well as solution phase peptide synthesis in water.¹⁰ Recently, our group developed an efficient and versatile method for the Buchwald-Hartwig cross-coupling reaction and the Ullmann-type amination reaction in water with the assistance of

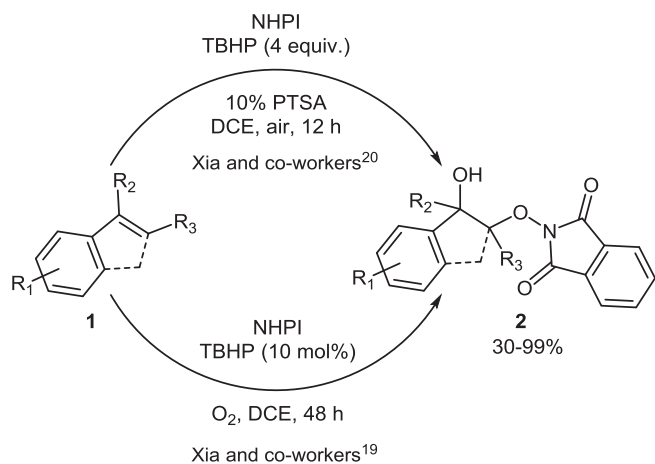
the non-ionic surfactant TPGS-750-M.^{11–14} The adoption of surfactants in these reactions resulted in significant benefits across the entire synthetic route, not just from an environment standpoint, but also from an economic and productivity perspective.¹⁵

1,2-Dioxygenated structures are present in many biologically active molecules.^{16–18} In view of the importance of such structures, Xia and co-workers have developed efficient radical methods for styrene 1,2-dioxygenation using *N*-hydroxyphthalimide (NHPI, Scheme 1).^{19,20} Although these methods furnished **2** in good to excellent yields, optimal yields were obtained in dichloroethane (DCE), a chlorinated organic solvent which is a known human carcinogen and highly hazardous for the environment. Accordingly, the development of an “*in water*” method is desirable to avoid the use of such a toxic solvent. Inspired by the work of Xia and co-workers, and in continuation of our efforts in the development of reactions in water,^{19,20} we considered whether it was possible to perform the radical dioxygenation of styrene with NHPI under micellar conditions in water. Herein, we disclose the radical dioxygenation of styrene derivatives in an aqueous solution including Triton X-100-based micelles.

Following Xia and co-workers conditions which were published in 2015,²⁰ we initiated our studies with styrene **1a** as a model substrate for the synthesis of 2-(2-hydroxy-2-phenylethoxy)-2,3-dihydro-1*H*-isoindoline-1,3-dione **2a** using commercially available NHPI, catalytic PTSA, and excess TBHP under air in an aqueous solution of TPGS-750-M (2 wt%) at room temperature (Table 1, entries 1 and 2). The reaction without surfactant was carried out in parallel as a control. Disappointedly, unsatisfactory yields were obtained (5% without surfactant and 9% in the TPGS-750-M solution), which prompted us to run subsequent reactions under O₂

* Corresponding author.

E-mail address: fbihel@unistra.fr (F. Bihel).



Scheme 1. Reported methods from Xia and co-workers.

with different types of surfactants (Table 1, entries 3–9). To our delight, the reaction proceeded well in the aqueous solution of Triton X-100 (2 wt%) and produced **2a** in 87% yield. Other surfactants did not produce better yields (58% TPGS-750-M, 73% Brij 30, 83% TPGS-1000, 14% SPGS-550-M, 57% Tween-80, 15% SDS). Interestingly, when the structures of these surfactants were compared (ESI, Fig. S1), it was noticeable that all the surfactants bearing one terminal hydroxyl group (Brij 30, TPGS-1000, Triton X-100) were favorable to the reaction except for Tween 80. In contrast with most of the reactions reported so far, surfactants bearing terminal ether groups such as TPGS-750-M or SPGS-550-M, appeared less efficient. Lipshutz and co-workers proposed that the size of the micelle may have an impact on the reaction.^{3–10} According to Lipshutz and co-workers, with a diameter of about 50 nm, micelles formed by TPGS-750-M are suitable for micellar chemistry.^{5,9} In

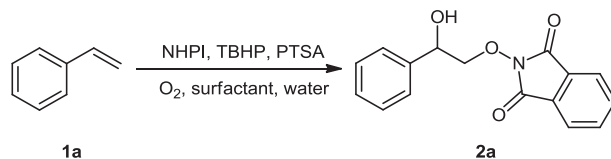
contrast, TPGS-1000 and Triton X-100 lead to micelles with a small diameter of 15 nm and 10 nm, respectively, while micelles resulting from Brij-30 have a diameter of 110 nm (ESI, Table S1).^{5,9,21,22} In this work, the good yields obtained with TPGS-1000, Triton X-100 and Brij-30 indicate that micelle diameter does not significantly influence the reaction. The common point of these three nonionic surfactants is the presence of a hydroxyl group at the terminus of the PEG moiety. Further work will be necessary to explain the role of this hydroxyl group in this reaction under micellar conditions. Triton X-100 and TPGS-1000 are both stable and biodegradable surfactants,²³ but since triton X-100 is much cheaper than TPGS-1000, it was preferred for the following reactions in water.

When the concentration of Triton X-100 was increased from 2 wt% to 5 wt% or decreased to 1 wt% (Table 1, entries 10 and 11), the yields decreased to 51% and 73%, respectively, suggesting the dependence of the reaction on the concentration of Triton X-100. Surprisingly, the absence of the PTSA catalyst did not have a significant impact on the reaction and produced **2a** in 88% yield (Table 1, entry 12). On another hand, decreasing **1a** or TBHP to 2 equivalents led to a significant decrease in yield (55% and 51%, respectively, Table 1, entries 13 and 14).

In an effort to accelerate the reaction, the temperature was raised to 50 °C (Table 1, entry 15), resulting in an exacerbation of side reactions and producing **2a** in only 62% yield. Several other catalyst/oxidant combinations also have been reported in the alkene 1,2-dioxygenation with NHPI.^{20,24–28} Herein, we tested several used combinations TBAI/TBHP, CuBr₂/DTBP, CuCl, Cu(OAc)₂/TBHP, FeCl₃ and PhI(OAc)₂. However, except for TBAI/TBHP which led to trace amounts of **2a**, most did not give the desired product.

To examine the scope of the established method, various styrene derivatives were investigated as substrates to react with NHPI under the optimized conditions (Table 1, entry 12). As shown in Scheme 2, the electronic properties and positions of the sub-

Table 1
Optimization of the reaction conditions.^a



Entry	1a (equiv.)	TBHP (equiv.)	PTSA (mol%)	Surfactant (% w/w in H ₂ O)	Yield (%) ^c
1 ^b	3	4	10	–	5
2 ^b	3	4	10	TPGS-750-M (2)	9
3	3	4	10	TPGS-750-M (2)	58
4	3	4	10	Brij 30 (2)	73
5	3	4	10	TPGS-1000 (2)	83
6	3	4	10	Triton X-100 (2)	87
7	3	4	10	SPGS-550-M (2)	14
8	3	4	10	Tween 80 (2)	57
9	3	4	10	SDS (2)	15
10	3	4	10	Triton X-100 (5)	51
11	3	4	10	Triton X-100 (1)	73
12	3	4	–	Triton X-100 (2)	88
13	2	4	–	Triton X-100 (2)	55
14	3	2	–	Triton X-100 (2)	51
15 ^d	3	4	–	Triton X-100 (2)	62

^a Reactions were carried out in a vial on a bioshaker (1800 rpm) using NHPI (0.122 mmol, 1 equiv.), styrene (**1a**), PTSA, TBHP, and the surfactant in water (2 mL) under an O₂ balloon at r.t. for 19 h, unless otherwise noted.

^b Reaction performed under air.

^c Yield of **2a** based on NHPI was determined by HPLC/UV using caffeine as an internal standard.

^d Reaction performed at 50 °C for 9 h.

Download English Version:

<https://daneshyari.com/en/article/7829664>

Download Persian Version:

<https://daneshyari.com/article/7829664>

[Daneshyari.com](https://daneshyari.com)