

One-step synthesis of substituted isobenzofuran-1(3*H*)-ones and isobenzofuran-1,3-diones from indane derivatives in subcritical media

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Abstract Molecular oxygen is one of the most attractive oxidants in organic synthesis because it is highly soluble in subcritical water. In this study, indane derivatives were oxidized to the corresponding isobenzofuran-1(3*H*)-one with molecular oxygen and isobenzofuran-1,3-dione with a mixture of molecular oxygen and H₂O₂ in subcritical water. This paper describes a simple, economic, environmentally benign, and general procedure that can be used for the synthesis of substituted isobenzofuran-1(3*H*)-ones and isobenzofuran-1,3-diones in only one step and without catalyst.

Keywords Oxidation · Subcritical water · Isobenzofuran-1,3-dione · Isobenzofuran-1(3*H*)-one

Introduction

Subcritical water is liquid water under pressure at temperatures between the usual boiling point (100 °C) and the critical temperature (374 °C) (Fig. 1) [1, 2]. Many of the anomalous properties of water are due to very strong hydrogen bonding. Above the subcritical temperature range, the extensive hydrogen bonds break down, changing the properties more than usually expected by increasing the temperature alone [2]. Water effectively becomes less polar and behaves more like an organic solvent such as methanol or ethanol and the water itself can act as a solvent, reagent, and catalyst in industrial and analytical applications, including extraction, chemical

reactions, and cleaning [1]. The present work describes an environmentally benign procedure for the synthesis of isobenzofuran-1(3*H*)-ones and isobenzofuran-1,3-diones (Scheme 1), employing molecular oxygen as an oxidant in subcritical water as a reaction medium.

Results and discussion

In this study, indane derivatives were oxidized without catalyst in subcritical water under oxygen pressure. Indane derivatives were surprisingly transformed into isobenzofuran-1(3*H*)-one (**1**). A plausible reaction mechanism based on classical reactions is presented in Scheme 2. First, oxygen probably attacks the α -carbon atom to form a hydroperoxide, which is readily decomposed to a carbonyl group via the well-known Kornblum–DeLaMare reaction [3–6]. The diketone can be attacked by hydrogen peroxide formed during this reaction to form a lactone via the Baeyer–Villiger reaction. Removal of 1 mol carbon monoxide results in the formation of **1**.

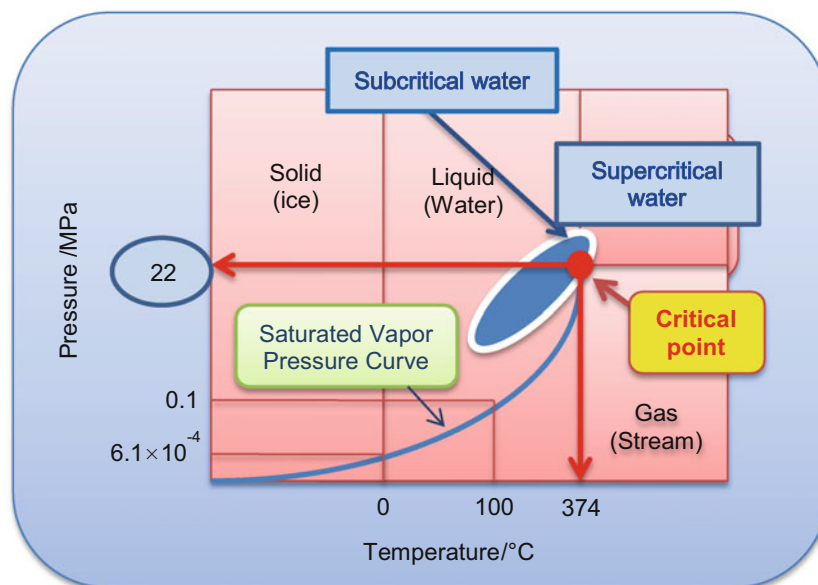
In the first part of this study, the experiments were performed only with molecular oxygen in subcritical water. In these experiments, 2,3-dihydro-1*H*-inden-1-one (**3**) and 1,2-dibromo-2,3-dihydro-1*H*-indene (**4**) were oxidized to isobenzofuran-1(3*H*)-ones [7] (**1**) in high yields within approximately 5 h. Unexpectedly, 2-bromo-2,3-dihydro-1*H*-inden-1-one (**5**) also gave isobenzofuran-1(3*H*)-one [7] (**1**) in poor yield within 8 h (Scheme 3).

2-Methyl-2,3-dihydro-1*H*-inden-1-one (**6**), 3-methyl-2,3-dihydro-1*H*-inden-1-one (**7**), and 2,2-dibromo-1*H*-indene-1,3(2*H*)-dione (**8**) did not react with molecular oxygen in subcritical water (Scheme 4). 1,1,2,3-Tetrabromo-1*H*-indene (**9**) gave 2,2-dibromo-1*H*-indene-1,3(2*H*)-dione (**10**) [8, 9] in 90 % yield (Scheme 5).

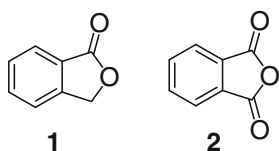
Dedicated to prof. Dr. Metin Balci on the occasion of 65th birthday.

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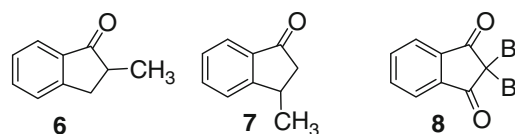
Fig. 1 Phase diagram for a pure substance; the regions of supercritical and subcritical water are marked [1]



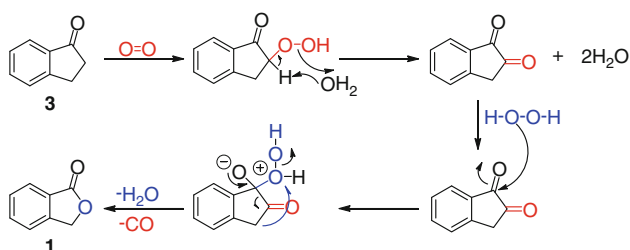
Scheme 1



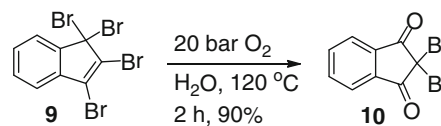
Scheme 4



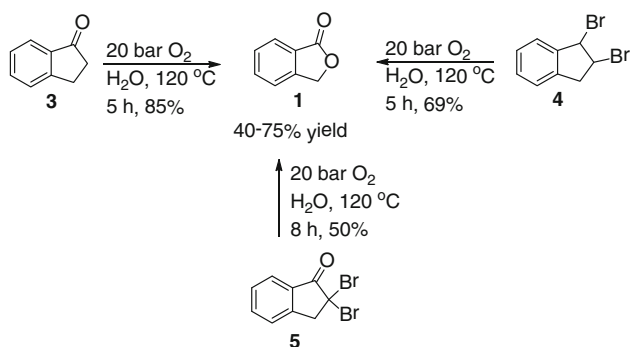
Scheme 2



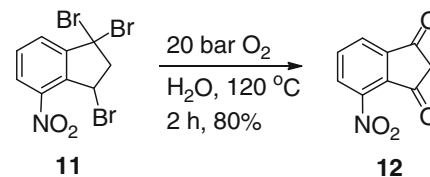
Scheme 5



Scheme 3

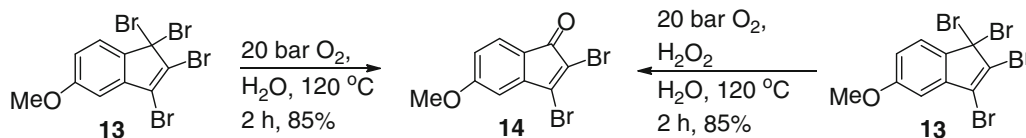


Scheme 6

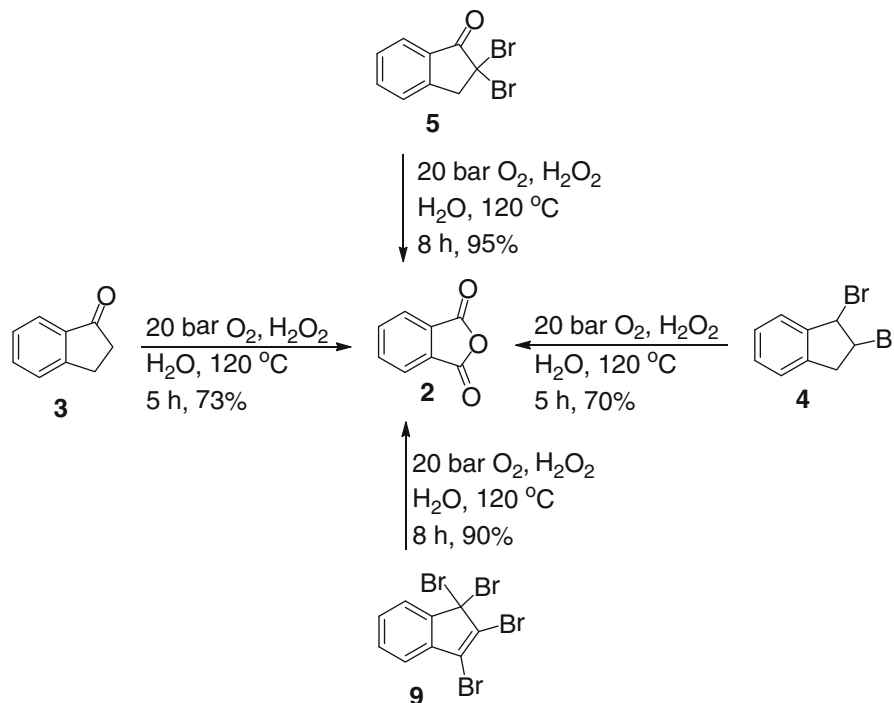


1,1,3-Tribromo-4-nitro-2,3-dihydro-1H-indene (**11**) was oxidized to 4-nitro-1H-indene-1,3(2H)-dione [**7**] (**12**) in 70 % yield (Scheme 6). 1,1,2,3-Tetrabromo-5-methoxy-1H-indene (**13**) was converted to 2,3-dibromo-5-methoxy-1H-inden-1-one (**14**) [10] with both molecular oxygen (at 2 MPa) and a mixture of molecular oxygen (at 2 MPa) and 30 % H₂O₂ in subcritical water (Scheme 7).

Scheme 7



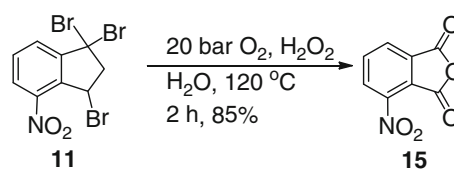
Scheme 8



In the second part of this study, the experiments were performed with both molecular oxygen (at 2 MPa) and 30 % H_2O_2 in subcritical water. 2,3-Dihydro-1*H*-inden-1-one (**3**), 1,2-dibromo-2,3-dihydro-1*H*-indene (**4**), 2,2-dibromo-2,3-dihydro-1*H*-inden-1-one (**5**), and 1,1,2,3-tetrabromo-1*H*-indene (**9**) were oxidized to isobenzofuran-1,3-dione [**7**] (**2**) (Scheme 8). 1,1,3-Tribromo-4-nitro-2,3-dihydro-1*H*-indene (**11**) was similarly oxidized to the corresponding isobenzofuran-1,3-dione (**15**) (Scheme 9).

The structures of all products obtained in the synthesis of substituted isobenzofuran-1(3*H*)-one and isobenzofuran-1,3-dione from substituted indane derivatives were identified by ^1H and ^{13}C NMR analyses. The amount of oxygen was regulated by the oxygen pressure, and the amount of dissolved oxygen in water (2.4 mmol at 2 MPa and 120 °C) was determined according to Henry's law [11]. All oxidation reactions were performed with one equivalent of substrate and 2.4 equivalents of oxygen in 50 cm^3 of water. Furthermore, it was observed that a greater increase in oxygen pressure led to decomposition of the starting materials to afford uncharacterized tars.

Scheme 9



Conclusions

This paper describes the synthesis of substituted isobenzofuran-1(3*H*)-ones and isobenzofuran-1,3-diones from indane derivatives in subcritical water in the absence of an organic solvent and metal salts/complexes; this method is indeed very green chemistry. Indane derivatives were oxidized without catalyst in a single step via the well-known Kornblum–DeLaMare reaction [3–6] in subcritical water under oxygen pressure. Substituted isobenzofuran-1(3*H*)-ones and isobenzofuran-1,3-diones are important molecules

in many areas. The syntheses in subcritical water media outlined here have potentially abundant applications, and it is hoped that this paper will motivate such efforts.

Experimental

All chemical reagents were commercially available. The substrates were purified (distilled or crystallized) before application in the reaction. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Infrared spectra were obtained as films on NaCl plates for liquid and KBr pellets for solids on a Win First[®] Satellite infrared recording spectrophotometer. All column chromatography was performed on silica gel (60-mesh, Merck).

General procedure for oxidation reactions with O_2

Oxidation reactions were carried out at 120 °C in a 150-cm³ stainless steel reactor. A Teflon vessel was inserted into the reactor and the oxidation occurred without contact with the stainless steel reactor surface in order to avoid the catalytic effect of steel and corrosion. The oxidation was performed by adding 50 cm³ of water and 1 mmol of substrate to a high pressure reaction vessel under nitrogen. The vessel was pressurized with 2 MPa (2.4 mmol) oxygen and placed in a tube furnace preheated to 120 °C. The internal operating pressure of this vessel is 4 MPa at its maximum operating conditions. After the reaction was completed, the mixture was cooled to room temperature and filtered, and the residue was washed with CHCl_3 (3 × 40 cm³). After drying over MgSO_4 , the solvents were evaporated in vacuo and the products were purified by column chromatography on silica gel (60-mesh, Merck with 50-cm glass column, eluent $\text{CCl}_4/\text{Et}_2\text{O}$). The products were characterized by ^1H and ^{13}C NMR, GC/MS, and IR spectroscopy.

General procedure for oxidation reactions with both O_2 and H_2O_2

The oxidation reactions were carried out at 120 °C in a 150-cm³ stainless steel reactor. The reaction conditions

were the same as those described above. Only 3 cm³ 30 % H_2O_2 with 47 cm³ H_2O was put into the reaction medium.

Isobenzofuran-1(3H)-one (**1**) [7]

Yield 50–85 %; colorless crystals; m.p.: 69–71 °C.

Isobenzofuran-1,3-dione (**2**) [7]

Yield 70–95 %; colorless crystals; m.p.: 129–131 °C.

2,2-Dibromo-1H-indene-1,3(2H)-dione (**10**) [8, 9]

Yield 90 %; colorless crystals; m.p.: 183–185 °C.

4-Nitro-1H-indene-1,3(2H)-dione (**12**) [7]

Yield 70 %; colorless crystals; m.p.: 127–129 °C.

2,3-Dibromo-5-methoxy-1H-inden-1-one (**14**) [10]

Yield 85 %; yellow crystals; m.p.: 151–152 °C.

4-Nitroisobenzofuran-1,3-dione (**15**) [7]

Yield 85 %; colorless crystals; m.p.: 158–161 °C.

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