



# Catalytic syntheses of 2-methyl-1,4-naphthoquinone in conventional solvents and supercritical carbon dioxide



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## HIGHLIGHTS

- Oxidation of 2-methylnaphthlene in acetic acid showed low selectivity.
- The gold catalyst allows an increase of the 2-methyl-1-naphthol conversion by 87%.
- The use of SC CO<sub>2</sub> results in increasing the 2-methyl-1-naphthol conversion by 10–15%.

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## ABSTRACT

This paper reports a comparison of commonly used methods of the 2-methyl-1,4-naphthoquinone syntheses and possible application of supercritical (SC) carbon dioxide (CO<sub>2</sub>) as a “green solvent” for this process. The 2-methyl-1,4-naphthoquinone syntheses were carried out by two main reaction routes using 2-methylnaphthalene or 2-methyl-1-naphthol as substrates in the presence or absence of catalysts in common solvents and the SC CO<sub>2</sub> media. The influence of SC CO<sub>2</sub> on the above reactions is discussed.

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## 1. Introduction

Menadione (2-methyl-1,4-naphthoquinone) is an important intermediate in the synthesis of vitamins K and at the same time menadione itself possesses the same activity as vitamin K [1]. Vitamins of the K group, or antihemorrhagic vitamins, are necessary for a normal fibrillation [2]. It is used in the cases of strong bleedings, hemorrhagic diathesis and in certain cases of a liver functions frustration [3]. The main methods of menadione synthesis is oxidation of 2-methylnaphthalene and 2-methyl-1-naphthol in different solvents by hydrogen peroxide, oxygen or other chemical oxidants [4–6], however the product yield does not exceed 50% due to formation of side products. Oxidation of 2-methylnaphthalene to menadione is a complex process (Fig. 1), because of the formation of a great number of side products. Commonly it is carried out in the acetic acid media by hydrogen peroxide, while usage of other solvents favors formation of side products and intermediates [7–10].

The other possible route of the menadione synthesis is oxidation of 2-methyl-1-naphthol (Fig. 2). This route is characterized

by selectivity close to 100% and by considerably higher oxidation rates [11]. However, 2-methyl-1-naphthol is more expensive compared to 2-methylnaphthalene therefore oxidation of 2-methylnaphthalene to menadione is preferred.

All routes of menadione syntheses include the use of toxic and aggressive organic solvents therefore their replacement by “green solvents”, for example, SC CO<sub>2</sub>, is an attractive way for pollution reduction. SC CO<sub>2</sub> is non-corrosive, non-toxic, non-flammable and relatively inert [12]. Carbon dioxide is easily separated from reactants and products. The SC regime for CO<sub>2</sub> is easily accessible, because its critical temperature is only 304 K [13,14]. Moreover, carbon dioxide can provide not only environmental advantages, but also chemical advantages [15].

Here we report a comparative study of the oxidation of 2-methylnaphthalene and 2-methyl-1-naphthol in commonly used solvents and in SC CO<sub>2</sub> over gold, platinum and palladium-containing catalysts formed in hypercrosslinked polystyrene along with conventional methods of oxidation. We investigated a variety of the reactions conditions and determined that the gold catalyst allows an increase of the 2-methyl-1-naphthol conversion by 20%. The use of SC CO<sub>2</sub> results in increasing the 2-methyl-1-naphthol conversion by 10–15%, while the reaction selectivity remains unchanged, revealing that SC CO<sub>2</sub> media does not influence the 2-methyl-1-naphthol oxidation mechanism. The use of SC CO<sub>2</sub> in

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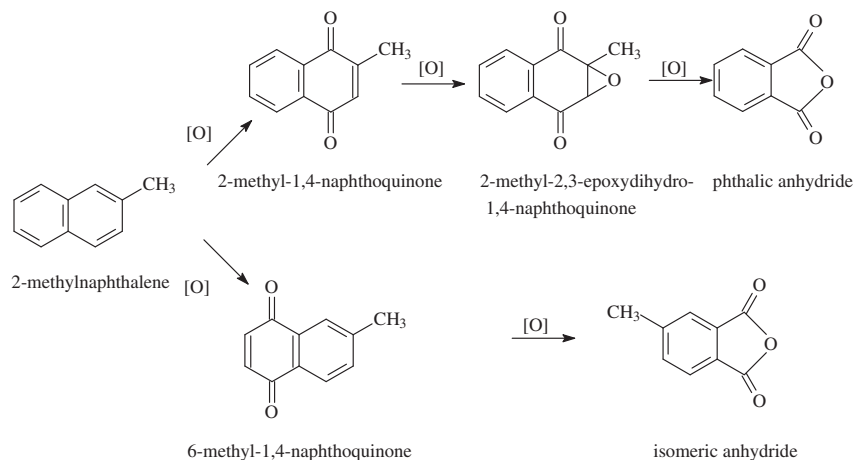


Fig. 1. Scheme of 2-methylnaphthalene oxidation.

2-methylnaphthalene results in the increase of the process selectivity while there is no influence on the reaction conversion. For comparison purposes the catalytic oxidation of 2-methylnaphthalene by potassium dichromate, chromic anhydride, potassium permanganate was carried out.

## 2. Materials and methods

### 2.1. Materials

Ethanol, tetrahydrofuran (THF), hydrogen peroxide and acetic acid were purchased from Aldrich and used as received. 2-Methylnaphthalene (98%), 2-methyl-1-naphthol (98%) and 2-methyl-1,4-naphthoquinone (98%) were purchased from Acros. Distilled water was purified with an Elsi-Aqua water purification system. Carbon dioxide, nitrogen, potassium permanganate, potassium dichromate, chromium oxide were purchased from a local supplier. HPS (a MN270 brand) was purchased from Puro-lite Inc. and used as received.

### 2.2. Synthesis of metal supported hypercrosslinked polystyrene

The 5% Pd/HPS catalyst was prepared as follows: 3 g of polymer was impregnated with 0.2493 g of PdCl<sub>2</sub> and 0.09 g of NaCl in 7.5 mL of complex solution THF/Methanol/Water 5/1/0.5 under stirring and dried at 70 °C. After that the catalyst was treated with 0.09 g of Na<sub>2</sub>CO<sub>3</sub> in 8.5 mL of H<sub>2</sub>O. Then it was dried again, washed to a pH of 7 and then dried.

The 5% Pt/HPS catalyst was prepared as follows: 3 g of polymer was impregnated with 0.3 g of H<sub>2</sub>PtCl<sub>6</sub> in 8.5 mL of THF and dried at 70 °C. Next the catalyst was treated with 1 g of Na<sub>2</sub>CO<sub>3</sub> in 12 mL of H<sub>2</sub>O. Then it was dried again, washed to a pH of 7 and then dried.

The 5%Au/HPS catalyst was prepared as follows: 3 g of polymer was impregnated with 0.25 g of HAuCl<sub>4</sub>·2H<sub>2</sub>O in 8.5 mL of THF under stirring and dried at 70 °C. Next the catalyst was treated with 0.5 g of Na<sub>2</sub>CO<sub>3</sub> in 12 mL of H<sub>2</sub>O. Then it was dried again, washed to a pH of 7 and then dried.

### 2.3. Oxidation methodology

The oxidation reaction was conducted batchwise in a PARR 4251 (Fig. 3) apparatus that permits independent control over such parameters as substrate concentrations, temperature, CO<sub>2</sub> pressure, and the stirring rate. And it is equipped with safety valves.

A solution of the substrate in the appropriate solvent (150 mL) prepared at a predetermined concentration was placed in the reac-

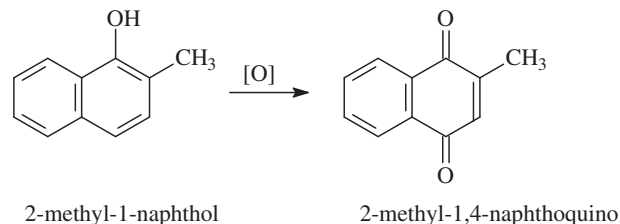


Fig. 2. Scheme of 2-methyl-1-naphthol oxidation.

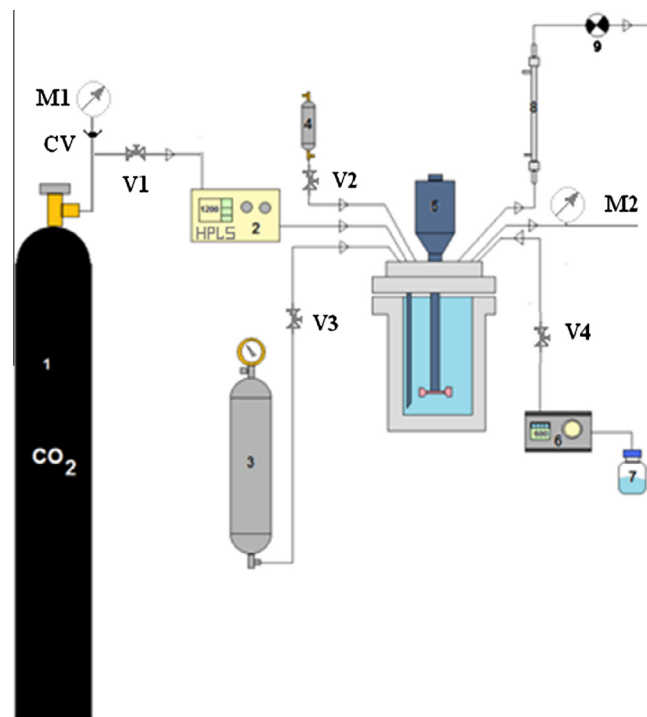


Fig. 3. Reaction setup for oxidation process: (1) carbon dioxide tank, (2) pump for carbon dioxide, (3) gas burette, (4) pipette for liquid, (5) high pressure reactor, (6) pump for reagents, (7) glass bottle for reagents, (8) cooler and (9) backpressure valve, V1–V4: high pressure valve, M1–M2: analogue manometer, CV: check valve.

tor. The rate of the CO<sub>2</sub> feed was controlled by a rotameter. The high stirring rates employed here ensured good mixing without

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