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A Novel and Convenient Process for the Selective Oxidation of Naphthalenes with Hydrogen Peroxide

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Abstract: A practical ruthenium phase-transfer catalyst (Ru-PTC) system for the oxidation of naphthalene derivatives has been developed. Substituted 1,4-quinones are obtained in good selectivity and yield in water without the addition of any organic solvent and acid. By applying the optimized conditions the feed additive menadione (vitamin K_3) is obtained from 2-methylnaphthalene with 64% yield and 73% selectivity.

Keywords: arenes; hydrogen peroxide; oxidation; ruthenium

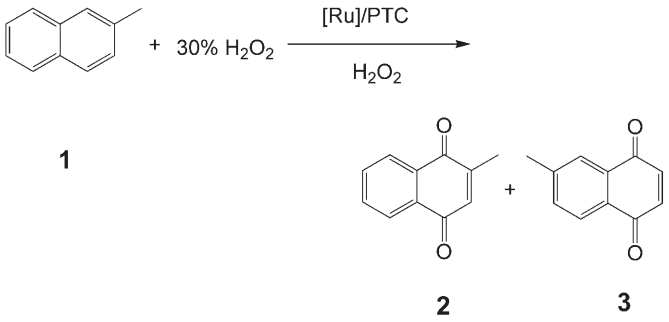
The development and implementation of chemical processes which reduce or eliminate the use and generation of waste and hazardous substances is an important goal for current organic synthesis.[1] This is especially true for oxidation chemistry because in traditional oxidation processes large amounts of toxic and volatile organic solvents, corrosive inorganic acids and metals oxidants, etc., were extensively used. Developing green selective oxidation processes is still a challenging task in catalysis. By comparing different oxidation methods it is apparent that the choice of the respective oxidant determines to a large extent the practicability and efficiency of the respective reaction. In addition to molecular oxygen, hydrogen peroxide, H_2O_2, is the most "green", and waste-avoiding oxidant.[1] It can oxidize organic compounds with an atom efficiency of 47% and generates theoretically only water as co-product. Due to its properties H_2O_2 is particularly useful for liquid-phase oxidations for the synthesis of fine chemicals, pharmaceuticals, and electronic materials.[2] Recently, we became interested in the development of novel catalysts for catalytic epoxidations using hydrogen peroxide.[3] Herein, we report for the first time our results on the ruthenium-catalyzed oxidation of arenes in the presence of phase-transfer agents.

The selective oxidation of arenes offers an efficient access to substituted 1,4-quinones. Among the various products 2-methyl-1,4-naphthoquinone (so-called menadione or vitamin K_3) is a useful supplement for vitamins K_1 and K_2 in animal feed.[4] Menadione is usually prepared from 2-methylnaphthalene *via* oxidation and various protocols were developed. As an example the well-known chromium-mediated oxidation carried out with stoichiometric quantities of chromium trioxide in sulfuric acid has been reported to give 38 to 60% yield of menadione.[5] Alternative procedures using stoichiometric amounts of Mn(III) or Ce(IV) have also been described.[6] Obviously these processes do not meet the standard of today's environmental requirements, e.g., 18 kg of chromium-containing waste is produced per kg of product.[7] In the last decade more environmentally benign routes using catalytic quantities of metal salts were established. In these processes, vanadium,[8] chromium,[9] molybdenum/tungsten,[10] rhenium,[11] palladium,[12] cerium,[13] phthalocyanine,[14] porphyrin complexes[15] or zeolites,[16] were used as the catalysts and O_2, H_2O_2 or a percarboxylic acid were applied as the oxidant. The best result till now for the selective oxidation of 2-methylnaphthalene was achieved in glacial acetic acid as solvent, sulfuric acid as catalyst and acetic anhydride as the dehydration reagent in about 80% yield.[17]

A drawback of all known oxidation protocols is the use of acidic solvents, i.e., acetic acid, or the necessity to add inorganic acid catalysts, which causes environmental pollution and more seriously corrosion problems on a larger scale. In general, a high concentration of hydrogen peroxide (50–83%) is needed in order to get acceptable yields of menadione.[11] This may lead to explosive mixtures and causes severe safety problems.[17] Thus, the development of selective oxidations of 2-methylnaphthalene and its derivatives which work under neutral conditions with easy to use hydrogen peroxide (30% aqueous solution) is still an important and challenging goal.

Based on our experience in the synthesis of ruthenium(II) complexes with tridentate nitrogen ligands

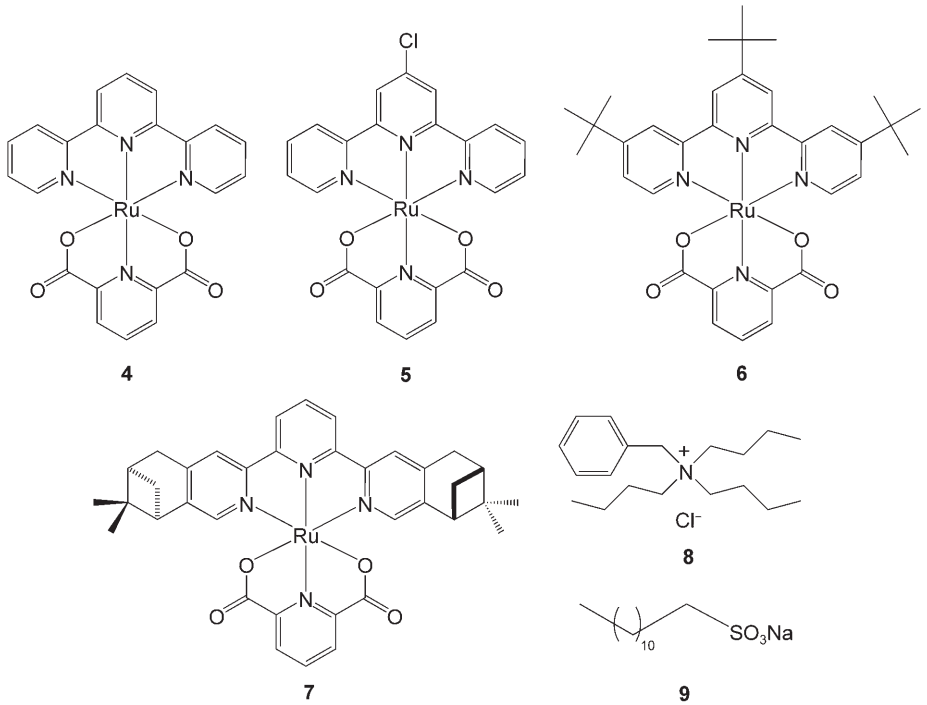
and their application in oxidation catalysis,[3] we became interested in demonstrating the utility of such complexes in arene oxidations. In exploratory experiments, the reaction of 2-methylnaphthalene with hydrogen peroxide (2.3 equivs.) in the presence of different Ru catalysts was examined (Scheme 1).



Scheme 1. Synthesis of 2-methyl-1,4-naphthoquinone (menadione).

In general, 0.2 mol% of a ruthenium complex catalyzed the reaction at room temperature to 40 °C for 1 h in the absence of any organic solvent. Owing to solubility problems the reactions were performed with or without a catalytic amount of phase-transfer agents. Among the various Ru complexes, Ru(II)(terpyridine)(2,6-pyridinedicarboxylate) (**4**) showed significant activity. Thus, we prepared complexes **4**–**7** (Scheme 2) and studied their behaviour for the synthesis of menadione (**2**) (Table 1). To our delight all prepared Ru complexes catalyze the oxidation to give the corresponding 1,4-naphthoquinones (Table 1, entries 1–4).[3c,18] Apart from the desired menadione (**2**) also the regioisomeric product **3** is formed in a minor amount. There is no significant influence of the catalyst on the ratio of quinones **2** and **3**, which is in between 2.5:1 and 2.9:1. Depending on the catalyst, conversions of 65–91% and isolated yields of 26–53% are obtained. In addition benzoic acids are formed as side-products in minor amounts.

The easily available catalyst **4** was next investigated in more detail. Applying only a slight excess of hydrogen peroxide (1.2 equivs.) the best chemoselectivity (86%) is observed (Table 1, entry 5). It is noteworthy that the starting material can be recovered and reused for this oxidation protocol. Increasing the catalyst concentration resulted in an increase of the unproductive decomposition of hydrogen peroxide. Hence, an excess of hydrogen peroxide has to be used in order to get comparable yields (Table 1, entries 11 and 12). The addition of 1–2.5 mol% of phase-transfer catalysts **8** and **9** resulted in a significant improvement of the catalyst activity (Table 1, entries 6, 8, 10, 13). For example, 2-methylnaphthalene was completely consumed in 20 min in the presence of only 0.2 mol% of Ru catalyst **4** and 1 mol% of sodium dodecyl sulfate to give naphthoquinones **2** and **3** in 56% isolated yield [catalyst turnover frequency (TOF) = 840 h^{-1}]. Interestingly, both cationic and anionic



Scheme 2. Ruthenium catalysts and phase-transfer catalysts used for the synthesis of menadione (**2**).

Table 1. Selective oxidation of 2-methylnaphthalene with different ruthenium catalysts.[a]

Entry	Cat. [mol%]	PTC [mol%]	T [°C]	**1**/H_2O_2	Conversion[b] [%]	Yield[c] [%]	Selectivity [%]	Ratio of **2:3**[d]
1	**4** (0.2)	-	40	1:7	67	51	77	2.8:1
2	**5** (0.2)	-	40	1:7	65	32	50	2.7:1
3	**6** (0.2)	-	40	1:7	91	26	29	2.9:1
4	**7** (0.2)	-	40	1:7	88	53	61	2.5:1
5	**4** (0.2)	-	40	1:3.6	58	50	86	2.9:1
6	**4** (0.2)	**8** (2.5)	40	1:3.6	70	54	77	3.2:1
7	**4** (0.2)	-	40	1:7	67	51	77	3.1:1
8	**4** (0.2)	**8** (2.5)	40	1:7	88	64	73	3.0:1
9	**4** (0.2)	-	40	1:10	65	49	75	2.9:1
10	**4** (0.2)	**8** (2.5)	40	1:10	97	52	54	3.0:1
11	**4** (0.5)	-	40	1:7	73	56	77	2.9:1
12	**4** (1.0)	-	40	1:10	58	41	71	2.9:1
13	**4** (0.2)	**9** (1)	r.t.	1:3.6	99	56	56	2.8:1

[a] 1 mmol of starting material, 0.5 mL of H_2O.
[b] Conversion was determined by GC.
[c] Isolated yield of quinones **2** and **3**.
[d] The ratio between products **2** and **3** was determined by GC and ^{1}H NMR.

phase-transfer catalysts showed a similar rate increase.

To demonstrate the usefulness of our novel protocol the most effective catalyst systems, 0.2 mol% **4**+2.5 mol% **8** (catalyst system **A**), and 0.2 mol% **4**+1 mol% **9** (catalyst system **B**) were further employed in the oxidation of electron-rich and electron-poor naphthalenes (Table 2). For this comparative study, naph-

Table 2. Selective oxidation of different naphthalene derivatives.[a]

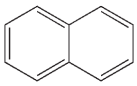
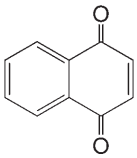
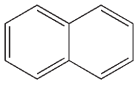
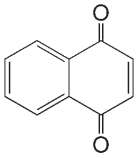
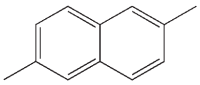
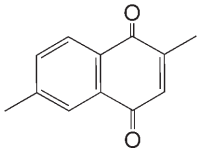
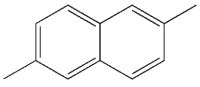
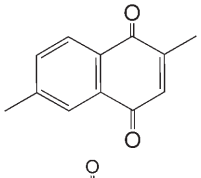
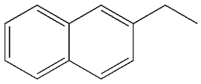
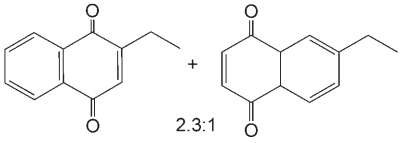
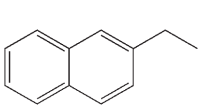
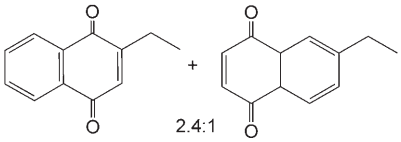
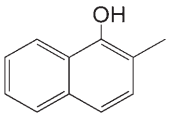
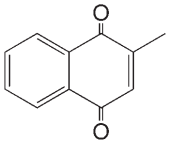
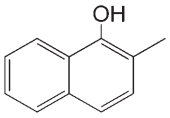
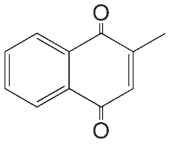
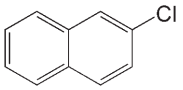
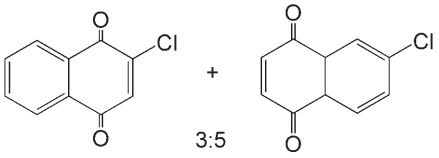
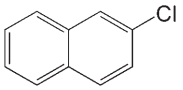
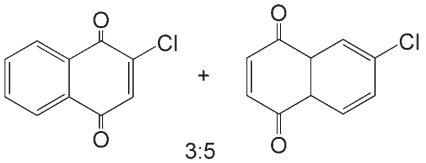
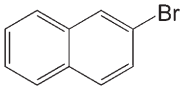
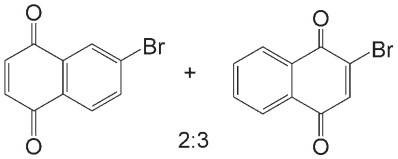
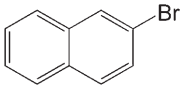
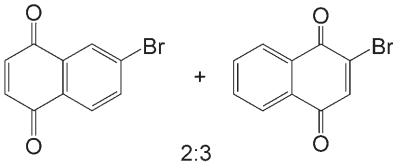
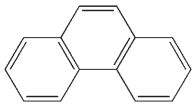
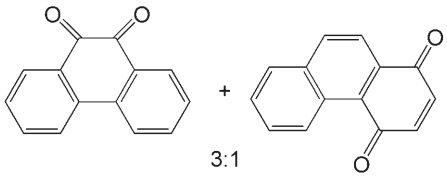
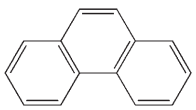
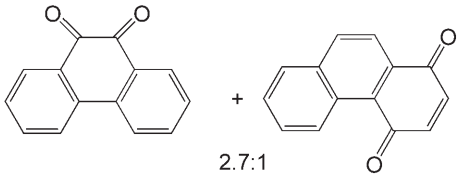
Entry	Substrate	Product[b]	Cat.	t [h]	Conversion [%]	Yield [%][c]	Selectivity [%]
1			**A**	1	95	39	40
2[d]			**B**	1	96	59	61
3			**A**	15	55	55	99
4[e]			**B**	21	83	64	77
5		 2.3:1	**A**	15	55	50	90

Table 2. (Continued)

Entry	Substrate	Product[b]	Cat.	*t* [h]	Conversion [%]	Yield [%][c]	Selectivity [%]
6[d,f]		 2.4:1	**B**	14	94	48	51
7			**A**	1	100	26	26
8[d,f]			**B**	1	100	10	10
9[f]		 3:5	**A**	15	83	58	83
10[d]		 3:5	**B**	14	53	53	99
11		 2:3	**A**	18	61	38	63
12[d]		 2:3	**B**	0.5	96	51	53
13		 3:1	**A**	15	83	35	40
14		 2.7:1	**B**	15	90	54	60

[a] 1 mmol of starting material, catalyst **A** or **B**, 0.5 mL of H_2O, 7 mmol (*ca.* 0.7 mL) of 30 wt% H_2O_2, 40 °C. **A** = 0.2 mol% of **4** + 2.5 mol% of **8**; **B** = 0.2 mol% of **4** + 1 mol% of **9**.
[b] The ratio between the products was determined by GC and ^{1}H NMR.
[c] Isolated yield.
[d] Performed at room temperature.
[e] **1**:H_2O_2 = 1:10.
[f] **1**:H_2O_2 = 1:3.6.

thalene, 2-ethylnaphthalene, 2,6-dimethylnaphthalene, 2-methyl-1-hydroxynaphthalene, 2-chloronaphthalene, 2-bromonaphthalene, and anthracene were chosen as representative substrates.

Applying catalyst system **B** naphthalene furnished the desired naphthoquinone in 59% isolated yield (Table 2, entry 2). Noteworthy, methyltrioxorhenium (MTO), a previous state-of-the-art catalyst for this type of oxidation, gave only 11% yield for this substrate.[11] The industrially important 2,6-dimethylnaphthalene and 2-ethylnaphthalene led to similar results compared to 2-methylnaphthalene. Here, the isolated yields of the corresponding naphthoquinones were 64% and 50%, respectively (Table 2, entries 3–6). Full conversions but only low yields (up to 26%) were obtained with 2-methyl-1-hydroxynaphthalene as substrate (Table 2, entries 7 and 8). These results demonstrate that **A** and **B** behave differently compared to previously reported catalysts. In general, 2-methyl-1-hydroxnaphthalene is considered to be the key intermediate to yield menadione **2**.[11,17] Apparently, the oxidation mechanism is unlike to those processes in acidic solvents or in the presence of acid catalysts.

In addition to alkyl-substituted naphthalenes, the selective oxidation of 2-chloronaphthalene and 2-bromonaphthalene could be carried out effectively (54% and 60% yield, respectively). In the presence of other catalysts often such electron-poor naphthalenes gave only low yields of quinones. Finally, we investigated the oxidation of anthracene. Here a mixture of 73% of 9,10-anthraquinone and 27% of 1,4-anthraquinone is obtained. Again using MTO as catalyst no quinone was observed and only 2,2'-biphenyldicarboxylic acid was isolated.[11]

In summary, we have developed an easy to use Ru-PTC catalyst system for the selective oxidation of naphthalene derivatives. Good results are obtained for alkyl-substituted naphthalenes and electron-poor naphthalenes. The process needs only a small amount of catalyst (0.2 mol%) and proceeds with water as the solvent. Compared to previous protocols for this type of reaction, there is no need for acidic solvents and high concentrations of hydrogen peroxide, which makes the reaction more environmentally friendly.

Experimental Section

Reagents and Methods

Ruthenium complexes were prepared according to previously reported methods.[3c,18] H_2O_2 (29–31%) was purchased from Merck. Naphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 2-ethylnaphthalene, 2-chloronaphthalene, 2-bromonaphthalene, tributylbenzyl ammonium chloride and sodium dodecyl sulfate were of analytical purity and used without further purification.

General Procedure for Ruthenium-Catalyzed Selective Oxidation of Naphthalene Derivatives

All reactions were carried out in an oil bath (40 °C) or directly in air (23–26 °C). To a glass reactor (40 mL), 1 mmol (0.1442 g) of 2-methylnaphthalene, 0.002 mmol of **4** (1.0 mg), 0.025 mmol (7.9 mg) of tributylbenzylammonium chloride, 0.5 mL of H_2O and 7 mmol (*ca.* 0.7 mL) of 30 wt% H_2O_2 were added, respectively. The reaction mixture was vigorously stirred (750 t/min) at 40 °C for 1 hour. Then, the mixture was cooled to room temperature, and extracted with CH_2Cl_2 (20 mL × 3). The solvent was removed in vacuum and the naphthoquinones are isolated by column chromatography (silica gel 60, 70–230 mesh, hexane: EtOAc = 8:2, v/v). A mixture of **2** and **3** (0.11 g, 64%) was obtained, which were characterized by ^{1}H NMR, GC-FID (HP6890N with FID detector, column HP5 MS 30 m × 0.250 mm × 0.25 μm) and GC-MS (HP6890N with MSD5973, column HP5 MS 30 m × 0.250 mm × 0.25 μm) and compared with the authentic sample of **2**. The ratio of **2** and **3** was *ca.* 3:1. It was determined by ^{1}H NMR and GC-FID (the same ratios were obtained from both methods). Using ^{1}H NMR spectroscopy the ratio of **2** and **3** was determined by the integral of the methyl group signals (δ = 2.17–2.20, d and δ = 2.49, s).

Product **2**: ^{1}H NMR(400.1 MHz, $CDCl_3$): δ = 2.17–2.20 (3H, d, J = 1.5 Hz), 6.80–6.85 (1H, q, J = 1.5 Hz), 7.66–7.72 (m, 2H), 8.03–8.06 (m, 1H), 8.07–8.11 (m, 1H); GC-MS (relative intensity): m/z = 172 (M^+, 100), 116 (33), 115 (43), 104 (39), 76 (27).

Product **3**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.49 (3H, s), 6.93 (s, 2H), 7.52–7.57 (1H, m), 7.84–7.87 (1H, m), 7.94–7.99 (1H, d, J = 7.9 Hz); GC-MS (relative intensity): m/z = 172 (M^+, 100), 118 (32), 115 (37), 89 (23).

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