Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 270 (2007) 68–75
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Selective oxidation of naphthalene derivatives with ruthenium catalysts using hydrogen peroxide as terminal oxidant

Feng Shi [a], Man Kin Tse [a,b], Matthias Beller [a,b,*]

[a] *Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany*
[b] *University of Rostock, Center for Life Science Automation (CELISCA), Friedrich-Barnewitz-Str. 8, D-18119 Rostock-Warnemünde, Germany*

Received 15 December 2006; accepted 15 December 2006
Available online 19 January 2007

Abstract

The selective oxidation of naphthalene and its derivatives to give naphthoquinones has been investigated in detail. The reaction can be carried out effectively in the presence of a catalytic amount of Ru complexes (0.2 mol%) and phase transfer catalysts (PTC) using H_2O_2 as the terminal oxidant and water as the solvent. The effect of different ruthenium complexes, phase transfer catalysts, and the concentration of hydrogen peroxide were studied. Compared to previous procedures for this type of reactions, acidic solvents and high concentration of hydrogen peroxide are not necessary, which makes the reaction more environmentally friendly.

Keywords: Arene; Selective oxidation; Hydrogen peroxide; Ruthenium; Green chemistry

1. Introduction

Menadione (Vitamin K_3) and its derivatives received significant attention in their synthesis in the last decades [1,2]. The traditional well-known method for the production of Vitamin K_3 usually used stoichiometric quantities of chromium trioxide in sulfuric acid to oxidize 2-methylnapthalene in 38–60% yield [3–6]. Alternative procedures using stoichiometric amounts of Mn(III) or Ce(IV) have also been described [7,8]. However, all these methods caused serious environmental problems due to the resulting heavy metal waste. In light of the improved ecological issues, various catalytic methods were reported, in which vanadium, chromium, molybdenum/tungsten, rhenium, palladium and cerium, phthalocyanine and porphyrin complexes, zeolites or inorganic acid were used in different catalytic systems with O_2, H_2O_2 or percarboxylic acid as the terminal oxidant [9–22].

However, all known procedures require the use of acidic solvents, such as acetic acid, or the necessity to employ inorganic acidic catalysts, which also causes environmental pollution, equipment corrosion problem and even the *in situ* generation of potential explosive materials in this system [22]. Thus, the development of selective oxidations of 2-methylnaphthalene and its derivatives under neutral conditions is highly desired. Here, we describe a full account of our work towards this goal.

2. Experiment

2.1. Materials and methods

Ruthenium complexes, **1**–**4**, were prepared according to previously reported methods (Fig. 1) [23,24]. H_2O_2 (29–31%) was purchased from Merck. Naphthalene derivatives and phase transfer catalysts, **5**–**18**, were of analytical purity and used without further purification (Fig. 2).

2.2. General procedure for the ruthenium-catalyzed 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 (0.144 g) 2-methylnaphthalene (**18**), 0.002 mmol **4** (1.0 mg), 0.025 mmol (7.9 mg) tributylbenzylammonium chloride, 0.5 ml H_2O, and 7 mmol (~0.7 ml) 30 wt% H_2O_2 were added respectively. The

* Corresponding author at: Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany.
Tel.: +49 381 1281 0; fax: +49 381 1281 5000.
E-mail address: matthias.beller@catalysis.de (M. Beller).

1381-1169/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.12.047

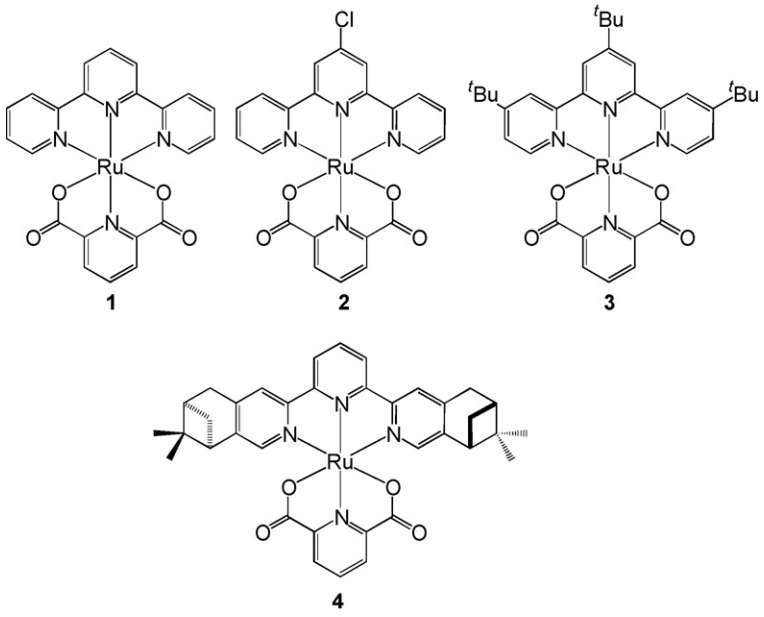


Fig. 1. Ruthenium(terpyridine)(pyridine-2,6-dicarboxylate) **1**–**4**.

reaction was vigorously stirred (750*t* (min)) at the appropriate temperature for 1 h.

2.3. Analysis

After the reaction, the mixture was cooled to room temperature, and extracted by CH_2Cl_2 (3× 20 ml). The solvent was removed under reduced pressure and the naphthoquinones were isolated by flash column chromatography (silica gel 60, 70–230 mesh, hexane:EtOAc = 8:2 (v/v)). A mixture of **19** and **20** (0.11 g, 64%) was obtained, which was characterized by ^{1}H NMR, ^{13}C NMR, GC-FID (HP6890N with FID detector, column HP5 30 m × 0.250 mm × 0.25 μm), GC–MS (HP6890N with MSD5973, column HP5MS 30 m × 0.250 mm × 0.25 μm), and compared with the authentic sample of **19**. The ratio between **19** and **20** was ∼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 between **19** and **20** was determined by the integral ratio of the corresponding methyl groups (δ 2.17–2.20, d and δ 2.49, s).

19: ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ 2.17–2.20 (3 H, d, J = 1.5 Hz), 6.80–6.85 (1 H, q, J = 1.5 Hz), 7.66–7.72 (2 H, m), 8.03–8.06 (1 H, m), 8.07–8.11 (1 H, m); GC–MS: t_R = 12.20 min (40 °C, 2 min; 15 °C/min; 280 °C, 12 min), m/z (relative intensity): 172 (M^+, 100), 116 (33), 115 (43), 104 (39), 76 (27).

20: ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ 2.49 (3 H, s), 6.93 (2 H, s), 7.52–7.57 (1 H, m), 7.84–7.87 (1 , m), 7.94–7.99 (1 , d, J = 7.9 Hz); GC–MS: t_R = 12.43 min (40 °C, 2 min; 15 °C/min;

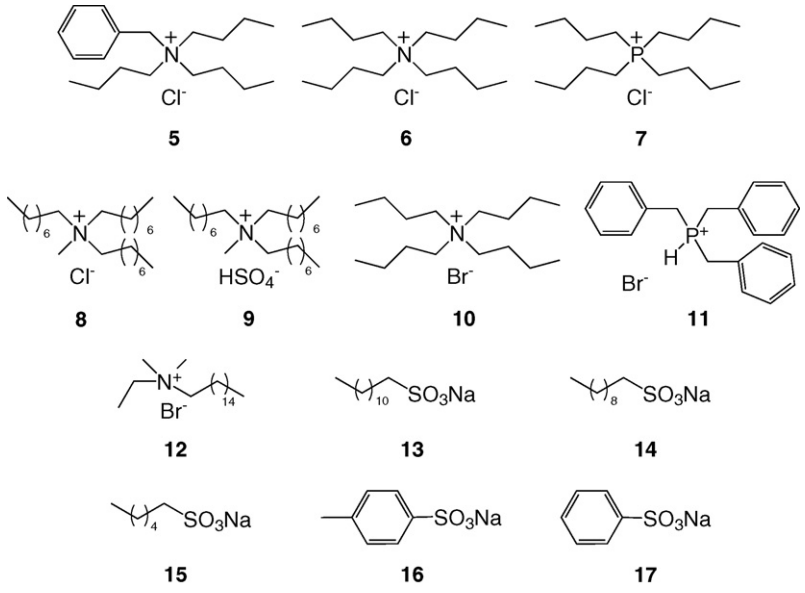
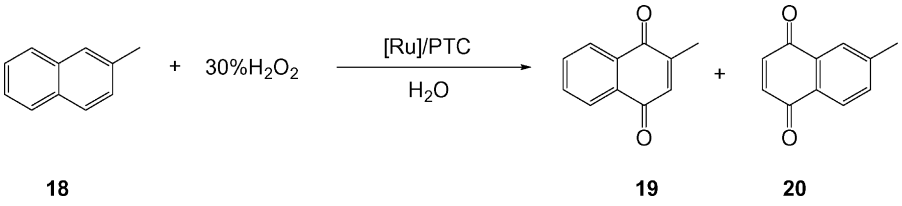


Fig. 2. Phase transfer catalysts.



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

280 °C, 12 min), *m/z* (relative intensity): 172 (M^+, 100), 118 (32), 115 (37), 89 (23).

All the other products are known compounds [12,25–34] and are characterized by GC-FID, GC–MS and NMR.

3. Results and discussion

3.1. Selective oxidation of 2-methyl naphthalene with different ruthenium complexes

Based on our experience in the synthesis of ruthenium(II) complexes with tridentate nitrogen and oxygen ligands and their applications in olefin epoxidations and alcohol oxidations [24,35–41], we became interested in the utility of these complexes in arene oxidations. Clearly, with respect to chemoselectivity the latter reactions are more challenging than olefin or alcohol oxidations. In exploratory experiments, 2-methylnaphthalene was oxidized with hydrogen peroxide (2.3 equiv.) in the presence of different Ru catalysts (Scheme 1).

Among the four ruthenium complexes employed, **1** and **2** were more hydrophilic than **3** and **4**. In fact, the catalytic activity increased with the decreasing of the hydrophilicity (Table 1). In aqueous media, more lipophilic **3** and **4** act not only as oxidation catalysts, but also simultaneously as phase transfer catalysts for the substrate 2-methylnaphthalene. However, with respect to the selectivity and yield of the desired product **19**, catalysts **1** and **4** gave the best results. The yields were 51% and 53%, respectively (Table 1, entries 1 and 4). There is no significant influence of the catalyst on the ratio of quinones **19** and **20**, which is in between 2.5:1 and 2.9:1.

3.2. Preliminary optimization of the reaction conditions

Next, the proto-typical reaction was tested with 0.2 mol% of the easily available catalyst **1** in the presence of various amounts of hydrogen peroxide. Interestingly, the yields of **19** and **20** were almost the same, 49–51%, when the ratio of 2-methylnaphthylene to hydrogen peroxide was changed from 1:3.6 to 1:10 (Table 2, entries 1–3). Apparently, the increased amount of hydrogen peroxide is mainly decomposed. The initial results suggested that the lipophilicity of ruthenium catalysts **1**–**4** is important. Hence, the addition of a phase transfer catalyst may be advantageous. Indeed, the addition of PTC **5** improved the yield of **19** and **20** slightly (Table 2, entries 4–7). However, at higher concentration of **5** only unproductive over-oxidation reactions were enhanced, leading to higher conversion with similar yield of **19** and **20**.

To our delight the combination of an increased amount of 30% H_2O_2 and the presence of PTC **5** led to a higher yield and chemoselectivity. The best result was obtained when 0.2 mol% Ru complex **1**, 2.5 mol% PTC **5** was used and 7 equiv. of hydrogen peroxide were employed (Table 2, entry 9). Further variation of the concentration of **1** gave no improvement.

3.3. Effects of phase transfer catalysts

Applying the optimized reaction conditions (0.2 mol% **1** and 2.5 mol% PTC), different kinds of PTC were tested in this reaction. Among the chloride containing cationic phase transfer catalysts **5**–**8**, phenyltributylammonium chloride was more effective. Here, the conversion was 88% and 64% isolated yield was obtained (Table 3, entries 1–4). Other anions such as HSO_4^- and Br^- with various tetraalkylammonium ions **9**–**12** resulted in similar yields (41–60%) (Table 3, entries 5–8).

Next, we tested various anionic phase transfer catalysts. To our surprise, the PTC **13** led to an extraordinarily high catalyst activity (Table 4, entry 1). Even with less hydrogen peroxide (3.6 equiv.) and at lower temperature (room temperature), 99% conversion was obtained with similar isolated yield (56%) (Table 4, entries 1 and 2). Due to the special catalytic property

Table 1
Selective oxidation of 2-methylnaphthalene with different Ru-complexes

Entry	Catalyst	mol%	**18**: H_2O_2	T (°C)	t (h)	Conversion[a] (%)	Yield[b] (%)	Selectivity[c] (%)	**19:20**[d]
1	**1**	0.2	1:7.0	40	1	67	51	77	2.8:1
2	**2**	0.2	1:7.0	40	1	65	32	50	2.7:1
3	**3**	0.2	1:7.0	40	1	91	26	29	2.9:1
4	**4**	0.2	1:7.0	40	1	88	53	61	2.5:1

For the procedure, see experiment.
[a] The calculation of conversion was based on recovered **18** after reaction.
[b] Isolated yield of **19** and **20**.
[c] Selectivity = yield/conversion.
[d] The ratio between **19** and **20** was determined by GC-FID and NMR.

Table 2
The effect of Ru catalyst loading, PTC loading and amount of H_2O_2

Entry	**1** (mol%)	PTC **5** (mol%)	**18**: H_2O_2	T (°C)	t (h)	Conversion[a] (%)	Yield[b] (%)	Selectivity[c] (%)	**19:20**[d]
1	0.2	0	1:3.6	40	1	58	50	86	2.9:1
2	0.2	0	1:7.0	40	1	67	51	77	3.1:1
3	0.2	0	1:10	40	1	65	49	75	2.9:1
4	0.2	2.5	1:3.6	40	1	70	54	77	3.2:1
5	0.2	5.0	1:3.6	40	1	80	53	67	3.1:1
6	0.2	7.5	1:3.6	40	1	87	54	62	3.3:1
7	0.2	10	1:3.6	40	1	94	55	59	3.4:1
8	0.1	2.5	1:7.0	40	1	90	53	59	3.0:1
9	**0.2**	**2.5**	**1:7.0**	**40**	**1**	**88**	**64**	**73**	**3.0:1**
10	0.4	2.5	1:7.0	40	1	84	50	60	3.0:1

For the procedure, see experiment.
[a] The calculation of conversion was based on recovered **18** after reaction.
[b] Isolated yield of **19** and **20**.
[c] Selectivity = yield/conversion.
[d] The ratio between **19** and **20** was determined by GC-FID and NMR.

Table 3
Selective oxidation of 2-methylnaphthalene in the presence of different phase transfer catalysts.

Entry	**1** (mol%)	PTC	mol%	**18**: H_2O_2	T (°C)	t (h)	Conversion[a] (%)	Yield[b] (%)	Selectivity[c] (%)	**19:20**[d]
1	**0.2**	**5**	**2.5**	**1:7.0**	**40**	**1**	**88**	**64**	**73**	**3.0:1**
2	0.2	**6**	2.5	1:7.0	40	1	76	41	53	2.8:1
3	0.2	**7**	2.5	1:7.0	40	1	80	50	57	2.8:1
4	0.2	**8**	2.5	1:7.0	40	1	87	56	64	2.9:1
5	0.2	**9**	2.5	1:7.0	40	1	90	60	64	2.8:1
6	0.2	**10**	2.5	1:7.0	40	1	97	52	54	3.0:1
7	0.2	**11**	2.5	1:7.0	40	1	73	56	77	2.9:1
8	0.2	**12**	2.5	1:7.0	40	1	58	41	71	2.9:1

For the procedure, see experiment.
[a] The calculation of conversion was based on recovered **18** after reaction.
[b] Isolated yield of **19** and **20**.
[c] Selectivity = yield/conversion.
[d] The ratio between **19** and **20** was determined by GC-FID and NMR.

Table 4
Investigation of the reaction conditions with anionic PTCs

Entry	**1** (mol%)	PTC	mol%	**18**:H_2O_2	T (°C)	t (h)	Conversion[a] (%)	Yield[b] (%)	Selectivity[c] (%)	**19:20**[d]
1	0.2	**13**	2.5	1:7.0	40	1	99	41	42	2.9:1
1	0.2	**13**	2.5	1:3.6	40	1	99	56	56	2.8:1
2	0.2	**13**	2	1:3.6	40	0.17	100	47	47	2.8:1
3	0.2	**13**	1.25	1:7.0	40	0.17	100	44	44	3.2:1
4	0.2	**13**	1	1:3.6	80	0.17	99	47	47	3.3:1
5	0.2	**13**	1	1:3.6	40	0.17	93	47	51	2.8:1
6	0.2	**13**	1	1:3.6	rt	0.17	85	51	60	2.6:1
7	0.2	**13**	1	1:7.0	rt	0.17	99	50	50	2.8:1
8	**0.2**	**13**	**1**	**1:3.6**	**rt**	**0.33**	**99**	**56**	**56**	**2.8:1**
9	0.2	**13**	1	1:3.6	rt[e]	0.50	99	44	44	2.4:1
10	0.2	**13**	1	1:3.6	0	0.5	42	20	48	2.2:1
11	0.2	**13**	1	1:3.6	rt	0.33	99	56	56	2.8:1
12	0.2	**14**	1	1:3.6	rt	0.33	58	37	64	2.7:1
13	0.2	**15**	1	1:3.6	rt	0.33	38	17	48	2.9:1
14	0.2	**16**	1	1:3.6	rt	0.33	40	18	45	2.5:1
15	0.2	**17**	1	1:3.6	rt	0.33	32	20	62	2.3:1

For the procedure, see experiment.
[a] The calculation of conversion was based on recovered **18** after reaction.
[b] Isolated yield of **19** and **20**.
[c] Selectivity = yield/conversion.
[d] The ratio between **19** and **20** was determined by GC-FID and NMR.
[e] The reaction was performed in a water bath at rt.

Table 5
Selective oxidation of naphthalene derivatives

Entry	Substrate	Method[a]	Substrate: H_2O_2	T (°C)	t (h)	Conversion[b] (%)	Yield[c] (%)	Selectivity[d] (%)	Product[e]
1	**21**	A	1:7	40	1	95	39	40	**37**
2	**21**	B	1:7	rt	1	96	59	61	**37**
3	**22**	A	1:7	40	1	35	22	61	**38:39** = 2.7:1
4	**22**	B	1:7	rt	1	73	25	34	**38:39** = 2.7:1
5	**23**	A	1:7	40	15	55	55	100	**40**
6	**23**	B	1:10	40	21	83	64	77	**40**
7	**24**	A	1:7	40	15	55	50	90	**41:42** = 2.3:1
8	**24**	B	1:3.6	rt	14	94	48	51	**41:42** = 2.4:1
9	**25**	A	1:7	40	1	22	6	28	**43**
10	**25**	B	1:7	rt	1	99	26	26	**43**
11	**26**	A	1:7	40	1	100	26	26	**19**
12	**26**	B	1:3.6	rt	1	100	10	10	**19**
13	**27**	A	1:7	40	4	68	6	9	**48**
14	**27**	B	1:7	rt	4	88	12	9	**48**

For the procedure, see experiment.
[a] A = 0.2 mol% **1** + 2.5 mol% **5**, B = 0.2 mol% **1** + 1 mol%.
[b] The calculation of conversion was based on recovered starting material after reaction.
[c] Isolated yield of the products listed in the table.
[d] Selectivity = yield/conversion.
[e] The ratio between **38** and **39**, **41** and **42** were determined by GC-FID.

exhibited by **13**, the reaction conditions were further optimized. The amounts of PTC **13**, 1–2.5 mol%, the ratio of **18** to hydrogen peroxide, 1:3.6–1:7, and the reaction temperature, 0–80 °C, were studied more closely (Table 4, entries 1–11). It is noteworthy that this system is so active that only 0.2 mol% **1** and 1 mol% **13** catalyzed the oxidation of 2-methylnaphthylene to the corresponding naphtoquinones in 20 min at rt with >99% conversion and 56% isolated yield. To the best of our knowledge the resulting turnover frequency (1200 h^{-1} at rt) is the highest reported so far for this type of arene oxidation. Different anionic PTCs with various alkyl sulfate groups were further tested, but no better results were obtained (Table 4, entries 12–15).

3.4. Selective oxidation of naphthalene derivatives

In order to study the scope and limitation of the oxidation of aromatic rings in the presence of our convenient catalyst system, two reactions protocols (0.2 mol% **1** + 2.5 mol% **5** = catalyst system A and 0.2 mol% **1** + 1 mol% **13** = catalyst system B) were further employed for naphthalene and its

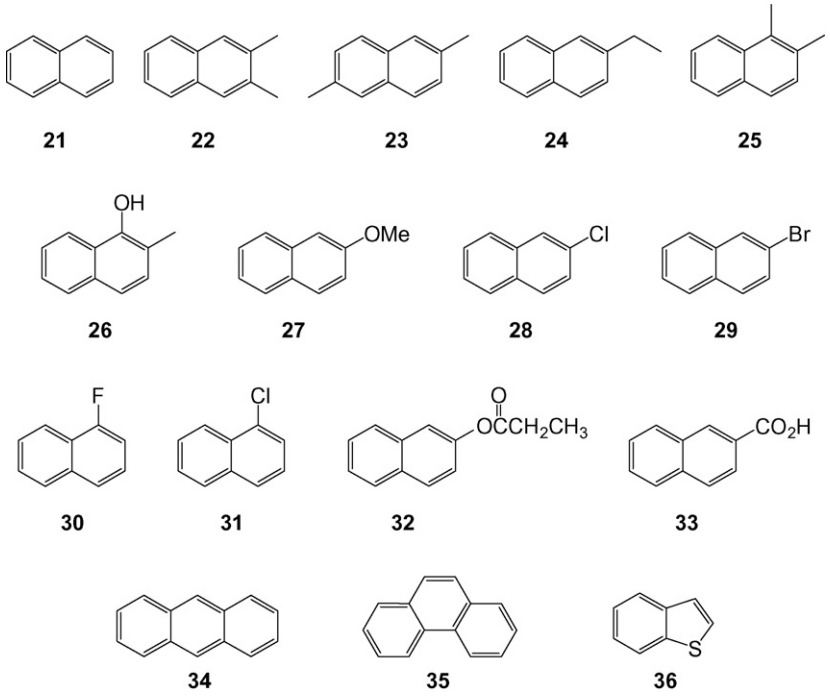


Fig. 3. Structures of arene substrates.

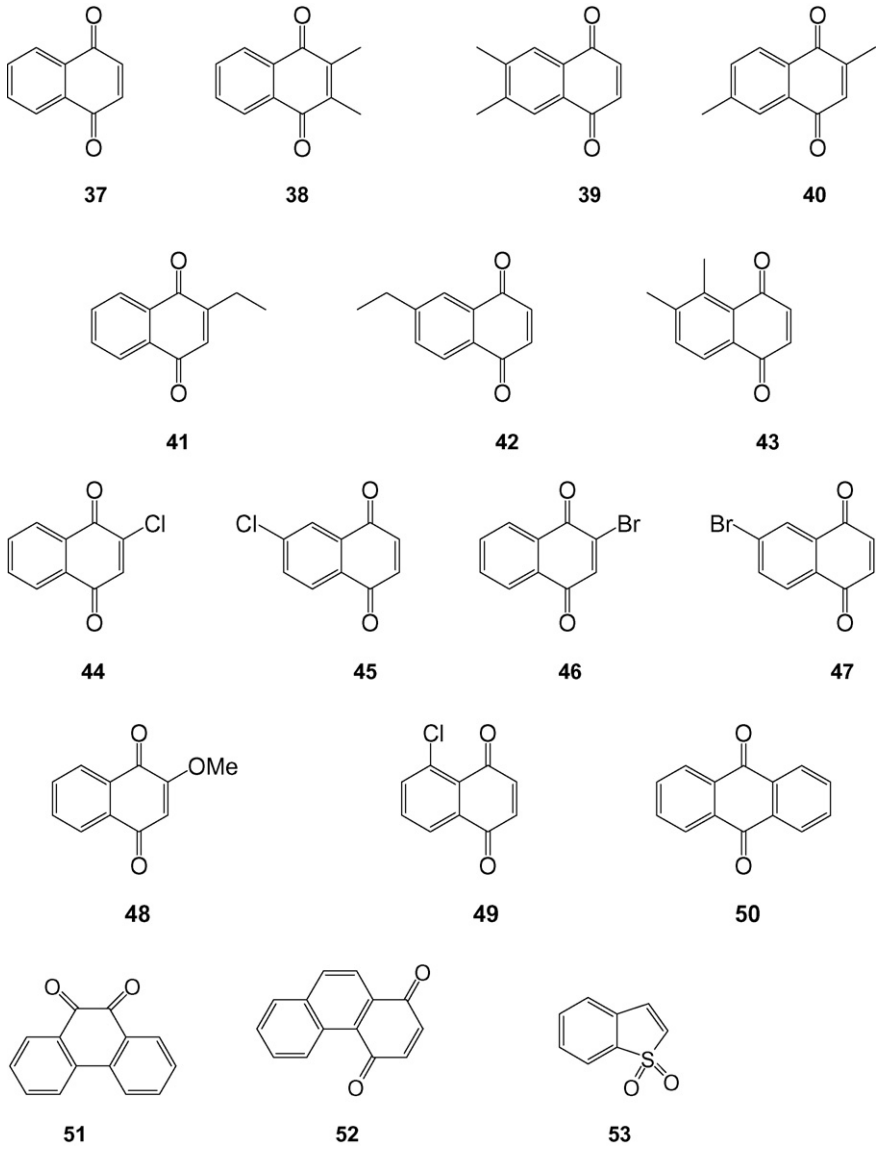


Fig. 4. Structures of quinone products.

derivatives (Table 5). Notably, both naphthalenes with electron-rich **21**–**27**, and electron-poor substituents **28**–**33** were used (Figs. 3 and 4).

Applying catalyst systems A and B for the selective oxidation of naphthalene (**21**) gave the desired naphthoquinone (**37**) in 39–59% isolated yield (Table 5, entries 1–2). It is important to note that methyltrioxorhenium (MTO), a previous state-of-the-art catalyst for this type of oxidation, gave only 11% yield for this substrate [12,13]. The industrially important 2,6-dimethylnaphthalene (**23**) and 2-ethylnaphthalene (**24**) led to similar results as 2-methylnaphthalene with isolated yields of 64% and 50% of the corresponding naphthoquinones, respectively (Table 5, entries 5–8). However, for 1,2-dimethylnaphthalene (**25**) and 2,3-dimethylnaphthalene (**22**), only 6–26% isolated yield was obtained for the corresponding quinone (Table 5, entries 3–4, 9–10). Full conversions but only low yields (up to 26%) were observed with 2-methyl-1-hydroxynaphthalene (**26**) or 2-methoxynaphthalene (**27**) as substrates (Table 5, entries 11–14). In general, 2-methyl-1-hydroxnaphthalene is considered to be the key intermediate to yield menadione (**2**) [12,13,22]. These results clearly demonstrate that A and B behave differently compared to previously reported catalytic systems [12,13,22]. Apparently, the oxidation mechanism is under the neutral conditions 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 (**28**) and 2-bromonaphthalene (**29**) were carried out effectively (54% and 60% yield, respectively, Table 6, entries 1–4). Unexpectedly, 1-fluoronaphthalene (**30**) and 1-chloronaphthalene (**31**) gave interesting results. While the oxidation 1-fluoronaphthalene (**30**) proceeds for this type of reaction with good selectivity (40–50% yield) (Table 6, entries 5–6), 1-chloronaphthalene led to a relative complex mixture of products (28–31% yield of the corresponding chloro-naphthochinones) (Table 6, entries 7 and 8). Two of the

Table 6
Selective oxidation of polyaromatics and heterocycles

Entry	Substrate	Method[a]	Substrate: H_2O_2	T (°C)	t (h)	Conversion[b] (%)	Yield[c] (%)	Selectivity[d] (%)	Product[e]
1	**28**	A	1:3.6	40	15	83	58	83	**44:45** = 3:5
2	**28**	B	1:7	rt	14	53	53	100	**44:45** = 3:5
3	**29**	A	1:7	40	18	61	38	63	**46:47** = 3:2
4	**29**	B	1:7	rt	0.5	96	51	53	**46:47** = 3:2
5	**30**	A	1:7	40	1	99	50	50	**37**
6	**30**	B	1:7	rt	0.5	99	40	40	**37**
7	**31**	A	1:7	40	1	73	28	100	**37**:**49** = 1:6
8	**31**	B	1:7	rt	0.5	99	31	32	**37**:**49** = 1:4
9	**32**	A	1:7	40	1	99	16	16	**37**
10	**32**	B	1:7	rt	0.5	100	8	8	**37**
11	**33**	A	1:7	40	18	0	0	0	–
12	**33**	B	1:7	40	18	0	0	0	–
13	**34**	A	1:7	70	1	24	12	50	**50**
14	**34**	B	1:7	70	1	25	8	32	**50**
15	**35**	A	1:7	40	15	83	35	40	**51**:**52** = 3.0:1
16	**35**	B	1:7	40	15	90	54	60	**51**:**52** = 2.7:1
17	**36**	A	1:7	rt	14	100	100	100	**53**
18	**36**	B	1:3.6	40	15	96	93	95	**53**

For the procedure, see experiment.
[a] A = 0.2 mol% **1** + 2.5 mol% **5**, B = 0.2 mol% **1** + 1 mol%.
[b] The calculation of conversion was based on recovered starting material after reaction.
[c] Isolated yield of the products listed in the table.
[d] Selectivity = yield/conversion.
[e] The amounts of isolated products listed in table compared with the starting material converted; e. the ratio between **44** and **45**, **46** and **47, 37** and **49**, **52** and **53** were determined by GC-FID.

side-products were identified by GC–MS as **37** and **49**. Presumably, nucleophilic aromatic substitution and direct aromatic oxidation occurred simultaneously for 1-chloronaphthalene in the initial steps and the former dominated in the case of 1-fluoronaphthalene in the first step followed by subsequent oxidations. For 1-naphthyl propionate (**32**), only naphthoquinone (**37**) was obtained in low yield (Table 6, entries 9 and 10). This result further supports that nucleophilic aromatic substitution at the 1-position of naphthalene is one of the possible reaction pathways. No reaction occurred for naphthalene-2-carboxylic acid (**33**) (Table 6, entries 11 and 12).

Finally, we extended the oxidation protocol to the reaction of polyaromatics and heterocycles **34**–**36**. For substrate **34**, **51** was obtained in only 8–12% yield (Table 6, entries 13–14). 9,10-Anthraquinone (**51**) and 1,4-anthraquinone (**52**) were obtained in a ratio of about 3:1, if **35** was oxidized in the catalytic system (Table 6, entries 15 and 16). Not surprisingly, employing MTO as catalyst for this reaction, no quinone was observed at all and only the over-oxidized product of 2,2′-biphenyldicarboxylic acid could be isolated [12,13]. Lastly, benzothiophene (**36**) was oxidized efficiently with our system to **54** in nearly 100% yield, in which the sulfur atom was oxidized to the corresponding sulfone (Table 6, entries 17 and 18).

4. Conclusions

In summary, an easy to use Ru-PTC catalyst system for the selective oxidation of naphthalene and its derivatives was successfully developed with hydrogen peroxide (30 wt%) as the terminal oxidant and water as the solvent. Moderate to good results are obtained for different kinds of naphthalene derivatives. Compared to previous protocols for this type of reaction, small amount of catalyst (0.2 mol%) and neutral solvent were employed.

Acknowledgements

This work has been supported by the State of Mecklenburg-Western Pommerania, the Deutsche Forschungsgemeinschaft (SPP 1118 and Leibniz prize), and the Federal Ministry of Education and Research (BMBF). Dr. Feng Shi thanks the Alexander-von-Humboldt-Stiftung for an AvH-Fellowship.

References

[1] J. Rodriguez, E. Quinoa, R. Riguera, B.M. Peters, L.M. Abrell, P. Crews, Tetrahedron 48 (1992) 6667.
[2] L.F. Fieser, M. Tushler, W.L. Sampson, J. Biol. Chem. 137 (1941) 659.
[3] S. Chocron, M. Michman, Appl. Catal. 62 (1990) 119.
[4] M. Juaristi, J.M. Aiypurua, B. Lecea, C. Palomo, Can. J. Chem. 62 (1984) 2941.
[5] R.A. Sheldon, J.K. Kochi, Metal-catalyzed Oxidation of Organic Compounds, Academic Press, New York, 1981.
[6] R.A. Sheldon, Top. Curr. Chem. 164 (1993) 21.
[7] R.P. Kreh, R.M. Spotnitz, J.T. Lundquist, J. Org. Chem. 54 (1989) 1526.
[8] M. Periasamy, M.V. Bhatt, Tetrahedron Lett. 19 (1978) 4561.
[9] T. Takai, E. Hata, T. Mukaiyama, Chem. Lett. (1994) 885.
[10] S. Yamazaki, Tetrahedron Lett. 42 (2001) 3355.
[11] R. Neumann, M. de LaVega, J. Mol. Catal. 84 (1993) 93.
[12] W.A. Herrmann, J.D.G. Correia, R.W. Fischer, J. Mol. Catal. 138 (1999) 115.
[13] W. Adam, W.A. Herrmann, J. Lin, C.R. Sahamöller, R.W. Fischer, J.D.G. Correia, Angew. Chem. Int. Ed. Eng. 33 (1994) 2475.
[14] S. Yamaguchi, M. Inoue, S. Enomoto, Chem. Lett. (1985) 827.
[15] J. Skaryewski, Tetrahedron 40 (1984) 4997.

[16] A.B. Sorokin, S. Mangematin, C. Pergrale, J. Mol. Catal. 182–183 (2002) 267.
[17] A.B. Sorokin, A. Tuel, Catal. Today 57 (2000) 45.
[18] A.B. Sorokin, A. Tuel, New J. Chem. 23 (1999) 473.
[19] S.V. Barkanova, V.M. Derkacheva, O.V. Dolotova, V.D. Li, V.M. Negrimovsky, O.L. Kaliya, E.A. Luk'yanets, Tetrahedron Lett. 3 (1996) 1637.
[20] R. Song, A. Sorokin, J. Bernadou, B. Meunier, J. Org. Chem. 62 (1997) 673.
[21] O.A. Anunyiata, L.B. Pierella, A.R. Beltramone, J. Mol. Catal. 149 (1999) 255.
[22] A. Bohle, A. Schubert, Y. Sun, W.R. Thiel, Adv. Synth. Catal. 348 (2006) 1011.
[23] H. Nishiyama, T. Shimada, H. Itoh, H. Sugiyama, Y. Motoyama, Chem. Commun. (1997) 1863.
[24] M.K. Tse, M. Klawonn, S. Bhor, C. Döbler, G. Anilkumar, M. Beller, Org. Lett. 7 (2005) 987.
[25] M. Catir, H. Kilic, Synth. Lett. 12 (2004) 2151.
[26] F. Weygand, H. Weber, E. Maekawa, Chem. Ber. 90 (1957) 1879.
[27] W.A. Herrmann, C. Galamba, D. Joao, R.W. Fischer, W. Adam, J. Lin, C.R. Saha-Moeller, M. Shimizu, Eur. Pat. Appl. EP665209 (1995).
[28] G.H. Jones, M.C. Venuti, J.M. Young, D.V.K. Murthy, B.E. Loe, R.A. Simpson, A.H. Berks, D.A. Spires, P.J. Maloney, J. Med. Chem. 29 (1986) 1504.
[29] S. Shi, T.J. Thomas, B.V. Yang, L. Liu, J. Org. Chem. 60 (1995) 1285.
[30] T.V. Nguyen, N. De Kimpe, Tetrahedron 59 (2003) 5941.
[31] H. Ishii, T. Hanaoka, T. Asaka, Y. Harada, N. Ikeda, Tetrahedron 32 (1976) 2693.
[32] S. Ghammamy, S.A.S. Sajadi, J. Serb. Chem. Soc. 70 (2005) 1243.
[33] G.A. Kraus, A. Melekhov, J. Org. Chem. 64 (1999) 1720.
[34] J. Zhang, C. Che, Chem. Eur. J. 11 (2005) 3899.
[35] M. Klawonn, M.K. Tse, S. Bhor, C. Döbler, M. Beller, J. Mol. Catal. 218 (2004) 13.
[36] M.K. Tse, C. Döbler, S. Bhor, M. Klawonn, W. Mägerlein, H. Hugl, M. Beller, Angew. Chem. Int. Ed. 43 (2004) 5255.
[37] S. Bhor, G. Anilkumar, M.K. Tse, M. Klawonn, C. Döbler, B. Bitterlich, A. Grotevendt, M. Beller, Org. Lett. 7 (2005) 3393.
[38] G. Anilkumar, S. Bhor, M.K. Tse, M. Klawonn, B. Bitterlich, Tetrahedron Asymm. 16 (2005) 3536.
[39] M.K. Tse, S. Bhor, M. Klawonn, C. Döbler, W. Mägerlein, H. Hugl, A. Spannenberg, M. Beller, Chem. Eur. J. 12 (2006) 1855.
[40] M.K. Tse, S. Bhor, M. Klawonn, C. Döbler, W. Mägerlein, H. Hugl, H.-J. Jiao, M. Beller, Chem. Eur. J. 12 (2006) 1875.
[41] M.K. Tse, H.-J. Jiao, G. Anilkumar, B. Bitterlich, F.G. Gelalcha, M. Beller, J. Organomet. Chem. 691 (2006) 4419.