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VIP

Selective Iron-Catalyzed Oxidation of Phenols and Arenes with Hydrogen Peroxide: Synthesis of Vitamin E Intermediates and Vitamin K_3

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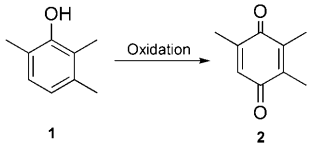
The selective oxidation of arenes to quinones constitutes an important biological process and is of significant interest to the chemical industry.[1] Various quinone derivatives are currently produced on ton-scale as fine chemicals and they are common constituents of biologically relevant molecules, for example, vitamin K_1 (phylloquinone).[2] Notably, quinones serve as electron acceptors in electron transport chains in photosynthesis and aerobic respiration.[3]

Among the industrially relevant quinones, 2,3,5-trimethyl-*p*-benzoquinone **2** (TMBQ) represents one of the intermediates for the synthesis of vitamin E (α-tocopherol),[4] which is used extensively as antioxidant in food, medical treatments, and cosmetics.[5] While in nature, quinones are produced by oxidation of aromatic amines, polyhydric phenols, and polynuclear hydrocarbons or enzymatic oxidation of polyphenols,[6] the key step in the synthesis of vitamin E is the conversion of 2,3,6-trimethylphenol **1** (TMP) to **2** (Scheme 1).



Scheme 1. Oxidation of TMP **1** to its corresponding quinone TMBQ **2**.

To date several protocols have been established for the direct oxidation of TMP to TMBQ,[7] though few of them are of industrial relevance. Notably, Schuster et al. reported that Salcomin (a salencobalt(II) complex) catalyzed the oxidation of TMP to the corresponding quinone in 80–95% yield.[8] A process developed by Shimizu et al. is based on the smooth oxidation of TMP with hydrogen peroxide in an organic solvent. Here, the reaction proceeds in the presence of a special heteropolyacid catalyst with yields of 70–85%.[9]

However, the most common procedure in industry makes use of a copper chloride mediated oxidation of TMP with molecular oxygen resulting in high yield.[10] Unfortunately, stoichiometric amounts of copper are applied in this reaction. This results in large amounts of copper waste and product contamination. Thus, the development of more environmentally friendly procedures for the oxidation of TMP is still of actual interest.

Based on our recent work in ruthenium-catalyzed oxidation of arenes to the corresponding quinones,[11] we asked ourselves whether iron complexes might be also suitable for this task. Evidently, iron is an ideal candidate for catalysis, because of its abundant availability and its relative non-toxicity compared to precious metals.[12,13,14] In addition, iron is involved in manifold biological systems as fundamental key element. Based on the development of iron-catalyzed epoxidations,[15] we applied a three component catalyst system consisting of $FeCl_3 \cdot 6H_2O$, pyridine-2,6-dicarboxylic acid (H_2pydic), and different benzylamines for the oxidation of TMP with hydrogen peroxide. At this point it should be noted, that next to air, H_2O_2 is the most "green", and waste-avoiding oxidant.[16]

In preliminary tests we discovered that TMP is indeed smoothly oxidized in the presence of different iron catalysts. Best results are obtained in *t*-amyl alcohol as solvent with 7.5 mol% catalyst ($FeCl_3 \cdot 6H_2O$/H_2Pydic/amine = 1/1/2.2) and 4 equivalents of H_2O_2 (30%) at 0°C. Notably, the co-ligand (amine) controlled the chemoselectivity to a major extent. In Table 1 the influence of the added co-ligands on the model reaction is summarized in more detail. In all cases high conversion is obtained (≥90%) independent of the amine co-ligand. However, without any amine added only low conversion is achieved. While aliphatic amines gave low selectivities (25%), the addition of benzylamine led to 73% selectivity (Table 1, entries 1–3). Similar to benzylamine, *o*-, *m*-, and *p*-chloro-substituted as well as *p*-hy-

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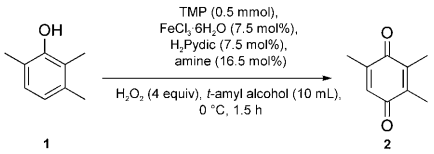
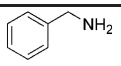
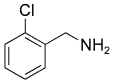
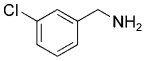
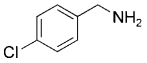
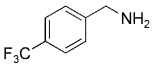
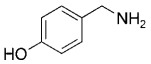
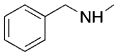
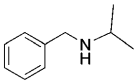
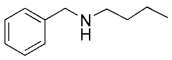
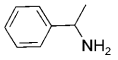
Table 1. Iron-catalyzed oxidation of TMP (**1**) using different amines.[a]



1 2

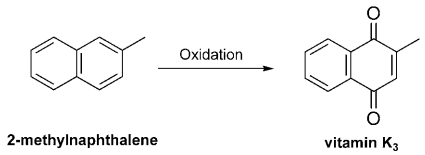
	Amine	Conv. [%][b]	Yield [%][b]	Select. [%][b,c]
1		>99	73	73
2		>99	25	25
3		97	24	25
4		>99	73	73
5		>99	68	68
6		>99	66	66
7		>99	77	77
8		90	55	62
9		98	57	58
10		99	66	66
11		>99	79	79
12		>99	73	73

[a] See Experimental Section (catalytic system **A**). [b] Conversion and yield were determined by GC analysis after 1.5 h using dodecane (0.44 mmol) as the internal standard. [c] Selectivity refers to the chemoselectivity of TMBQ from TMP.

droxy- and *p*-trifluoromethyl-substituted benzylamines gave comparable chemoselectivities from 62–77% (Table 1, entries 4–8). Interestingly, *N*-methylbenzylamine provided only moderate selectivity (Table 1, entry 9); however, the combination of $FeCl_3{\cdot}6H_2O/H_2Pydic/n$-butylbenzylamine (catalyst system **A**) provided the best chemoselectivity (79%) (Table 1, entry 11).

Next, we tested the optimized catalyst system **A** in the oxidation of more challenging non-activated arenes. Here, as an industrially important benchmark system the reaction of 2-methylnaphthalene to vitamin K_3 was investigated (Scheme 2).[11,17]

Under the conditions of system **A** only moderate selectivity was obtained for 2-methylnaphthalene (36%). To improve the selective oxidation for this substrate, we re-optimized the catalytic system. To our delight it was possible to reduce the catalyst loading to 2.5 mol% Fe and the amount of oxidant to 3.5 equivalents and still smooth oxidation is



Scheme 2. Oxidation of 2-methylnaphthalene to vitamin K_3.

observed when working at room temperature instead of 0°C. Best results were obtained in the presence of $FeCl_3{\cdot}6H_2O/H_2Pydic/benzylamine = 1/1/2.2$ (catalyst system **B**), when a second loading of the catalyst and H_2O_2 was added after 30 min (1.25 mol% and 1.8 equiv, respectively).

It is evident that the chemoselectivity for the oxidation of 2,3,6-trimethylbenzol (TMB) to TMBQ is lower compared to the oxidation of TMP, which is an intermediate in the former reaction. A similar trend is observed for other arenes and the corresponding phenols. For example, *p*-, *m*-xylenol, and 1-naphthol are oxidized to the corresponding quinones in moderate to good selectivities (54–81%; Table 2, entries 3–5).

While *p*- and *m*-xylene showed no reactivity at all, in the case of naphthalene only low conversion (<40%) was observed. 2-Methyl-1-naphthol (Table 2, entry 6) and 2-methylnaphthalene (Table 2, entry 8) gave the desired quinones, both in 55% yield. However, in the latter oxidation two regioisomers **3** and **4** in a 4:1 ratio are formed, which is similar to other metal-catalyzed oxidations.[17] To our delight 1,2,4,5-tetramethylbenzene was oxidized to duroquinone in high yield (75%) (Table 2, entry 7).

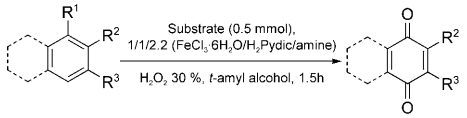
For the oxidation of alkylated naphthalene derivatives we found that catalytic system **B** gave better results (vide supra). For example, oxidation of 2-methylnaphthalene (Table 2, entry 8) showed a 10% increase in selectivity to the corresponding quinone in the presence of catalytic system **B**. The same trend is observed with 2,3- and 2,6-dimethylnaphthalene (Table 2, entries 9-10). Here, the corresponding quinones are obtained in 61–63% yield. Although some side-products could be identified the majority of the decomposition-products were not detectable (by GC, GC/MS, NMR spectroscopy).

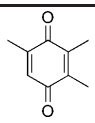
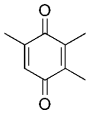
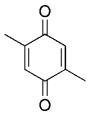
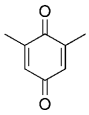
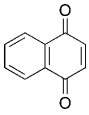
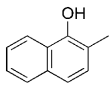
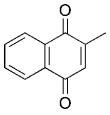
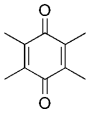
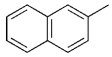
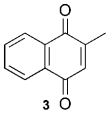
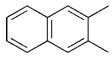
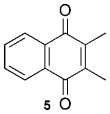
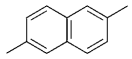
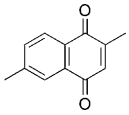
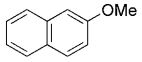
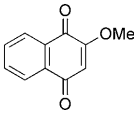
In summary, the first iron-catalyzed oxidation of phenols and arenes to 1,4-quinones has been developed. This selective oxidation reaction takes place under mild conditions (room temperature, alcoholic solvents) with H_2O_2 as the terminal oxidant. Applying the inexpensive and practical catalyst system consisting of iron trichloride hexahydrate, pyridine-2,6-dicarboxylic acid, and benzylamine derivatives industrially important oxidations of TMP and 2-methylnaphthalene took place in 79% and 55% yield, respectively.

Experimental Section

General: All reagents are commercially available. 2,3-Dimethylnaphthoquinone, 2,6-dimethylnaphthoquinone, and 2,3,5-trimethylbenzoquinone were prepared according to literature methods.[18]

Table 2. Selective oxidation of arenes to the corresponding quinones under optimized conditions.[a]



	Substrate	Major product	Cat.	Conv. [%][b]	Select. [%][b,c]
1			**A**	>99	79 (77)[d]
2			**A**	69	38
3			**A**	>99	81
4			**A**	>99	54
5			**A**	>99	78
6			**A**	>99	55
7			**A**	88	75
8		 3	**B**[f]	>99	55[e]
9		 5	**B**	>99	61[g]
10			**B**	>99	63
11			**B**	>99	24

[a] See Experimental Section. [b] Conversion and yield were determined by GC analysis after 1.5 h, using dodecane (0.44 mmol) as the internal standard. [c] Selectivity refers to the chemoselectivity of quinone from arene. [d] Isolated yield. [e] 2-Methyl-1,4-naphthoquinone **3**: 44% yield, 6-methyl-1,4-naphthoquinone **4**: 11% yield. [f] Catalytic system **A**: selectivity: 36%, **3**:**4** ≈3:1. [g] 2,3-Dimethyl-1,4-naphthoquinone **5**: 52% yield; 6,7-dimethyl-1,4-naphthoquinone **6**: 9% yield.

Catalyst system A: In a 25 mL flask, the catalyst ($FeCl_3 \cdot 6H_2O/H_2Pydic$/*n*-butylbenzylamine, 1/1/2.2; 7.5 mol%) in *t*-amyl alcohol (9 mL) was stirred at RT for 10 min in an ultrasonic bath. Substrate (0.5 mmol) and dodecane (GC internal standard, 100 μL) were added to the reaction mixture at 0°C. A solution of 30% H_2O_2 (4 equiv) in *t*-amyl alcohol (796 μL) was added over a period of 1 h by a syringe pump. 30 min after the addition, aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion.

Catalytic system B: In a 25 mL flask, the catalyst ($FeCl_3 \cdot 6H_2O/H_2Pydic$/benzylamine, 1/1/2.2; 3.75 mol%) in *t*-amyl alcohol (13.5 mL) was stirred at RT for 10 min in an ultrasonic bath. Substrate (0.5 mmol) and dodecane (GC internal standard, 100 μL) were added to the reaction mixture (9 mL) at RT. A solution of 30% H_2O_2 (3.5 equiv) in *t*-amyl alcohol (818 μL) was added directly. After 30 min the remaining catalyst solution and H_2O_2 (1.8 equiv) in *t*-amyl alcohol (409 μL) were added. 1 h after the last addition, aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion.

2,3,5-Trimethyl-1,4-benzoquinone (Table 2, entry 1): General procedure (catalyst system **A**) was employed. The reaction solution was concentrated in vacuo. The residue was diluted in ether, filtered over silica and concentrated in vacuo to give TMBQ (58 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 23°C, TMS): δ = 6,54 (q, ^3J (H,H) = 1.6 Hz, 1H; CH), 2.03–1.99 ppm (m, ^3J (H,H), 9H; 3×CH_3); ^{13}C NMR (75 MHz, 23°C, $CDCl_3$): δ = 187.95 (CO), 187.58 (CO), 145.37 (C), 140.94 (C), 140.77 (C), 133.09 (CH), 15.95 (CH_3), 12.41 (CH_3), 12.10 ppm (CH_3).

Acknowledgements

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Keywords: hydrogen peroxide · iron · oxidation · quinones · vitamins

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