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Ultrasonic-assisted ruthenium-catalyzed oxidation of aromatic and heteroaromatic compounds

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Abstract

Ruthenium-catalyzed oxidation of aromatic and heteroaromatic compounds is reported. It was found that ultrasonic irradiation in a biphasic system consisting of substrate, CH_2Cl_2, H_2O, CH_3CN, $NaIO_4$ and catalytic amounts of $RuCl_3 \cdot nH_2O$, accelerates the oxidation reaction to afford the desired products in good yields.

Keywords: Ruthenium; Ultrasonic irradiation; Oxidation; Arenes

1. Introduction

Many organic transformations which involve organometallic ruthenium species as catalyst are known and well documented [1–3]. Ru^{III} salts are also well known to catalyze a variety of organic transformations, including aldol and Michael reactions [4–7], oxidation reactions of alkanes [8], oxidative cyanation of amines [9], and many others. We have recently reported the aldol and double-Michael addition reactions of indoles [10,11], using catalytic amounts of Ru^{III}, and the investigation of the chemistry of ruthenium continues to be one of the most active areas of organometallic chemistry. On the other hand, oxidation products of arenes are important because they serve as an intermediate in the preparation of other fused-ring molecules, which are of interest from both a theoretical and a practical point of view [12–16]. Direct oxidation of arenes is a simple and effective method, and much research has been carried out to develop practical methods which would be applicable to various arenes [17–19]. The usual oxidation of arenes requires a large excess of metal oxidant such as chromium (VI) oxide. Since the metal residues are environmentally undesirable and often cause problems during reaction and work-up, development of selective arene oxidations requiring only a catalytic amount of metal reagent in combination with an appropriate stoichiometric oxidant is a great challenge. Direct oxidation to diones has been reported in low yields by the oxidation with highly toxic osmium tetroxide [20]. From an economical point of view, sodium periodate ($NaIO_4$) is cheap and readily available, and RuO_4 species which are generated in situ are responsible for the oxidation in the reported methods [21–25]. Harris et al. recently reported a one-step synthesis of pyrene-4,5-diones and pyrene-4,5,9,10-tetraones using $RuCl_3$ and $NaIO_4$ as the oxidant [26]. We reinvestigated the same synthetic protocol on various arenes and heteroaromatic compounds, using ultrasonic irradiation to overcome the prolonged reaction times and the results were surprising, since previous works with ruthenium-catalyzed oxidations of arenes had resulted in either dicarboxylic acids, tetracarboxylic acids or diols [27–29].

2. Results and discussion

Typical results of the ultrasonic-assisted ruthenium-catalyzed oxidation of arenes are shown in Table 1. A mixture of naphthalene (1 mmol) and $NaIO_4$ (1 g, 4.68 mmol) in a biphasic system consisting of H_2O, CH_2Cl_2, CH_3CN (5, 4, 4 mL) and catalytic amounts of $RuCl_3 \cdot nH_2O$

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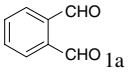
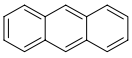
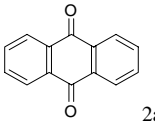
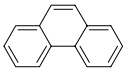
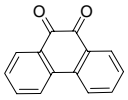
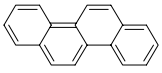
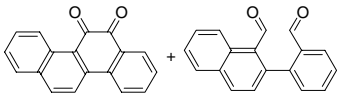
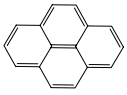
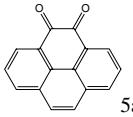
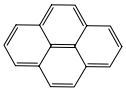
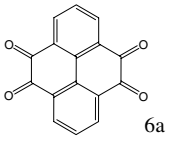
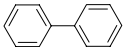
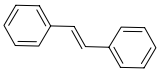
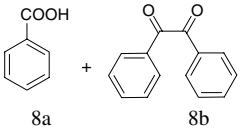
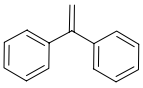
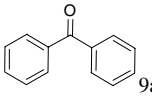
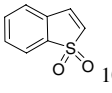
Table 1
Ultrasonic assisted ruthenium catalyzed oxidation of arenes and heteroaromatic compounds

Entry[a]	Substrate	Products	Yields[b] (%)			
			Irradiated	Time (h)	Non-irradiated	Time (h)
1		 1a	55[c]	2	50	12
2		 2a	85[c]	2	85	12
3		 3a	88[c]	2	85	12
4		 4a 4b	59, 15	2	60, 0	12
5		 5a	55	2	45[f]	12
6		 6a	40[d]	2.5	36[f]	12
7		 7a	82[c]	2	80	12
8		 8a 8b	95, 5[e]	2	95, 0	12
9		 9a	97[c]	1.5	95	12
10		 10a	98[c]	1.5	95	12

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