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Chromium(VI) oxide-catalyzed oxidation of arenes with periodic acid

Shigekazu Yamazaki*

Toyama Industrial Technology Center, 150 Futagami, Takaoka, Toyama 933-0981, Japan

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Abstract—Chromium(VI) oxide was found to catalyze the oxidation of arenes such as naphthalenes and anthrathene to the corresponding quinones with periodic acid as the terminal oxidant in acetonitrile. 2-Methylnaphthalene was oxidized smoothly to 2-methyl-1,4-naphthoquinone (vitamin K_3) by the catalytic system in high yield and regioselectivity.

Quinones are useful compounds as synthetic intermediates and biologically active compounds. The preparation of quinones by 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.[1] 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.

Recently the Merck researchers reported a novel CrO_3-catalyzed oxidation of primary and secondary alcohols to carboxylic acids and ketones with H_5IO_6 as the terminal oxidant.[2] We also reported that CrO_3/H_5IO_6 acts as an efficient catalytic system for the benzylic oxidation of toluenes, alkylbenzenes and cyclic benzylethers to the corresponding benzoic acids, ketones and lactones.[3] We now report a new preparation method of quinones by CrO_3 catalyzed oxidation of arenes with H_5IO_6 as the terminal oxidant.

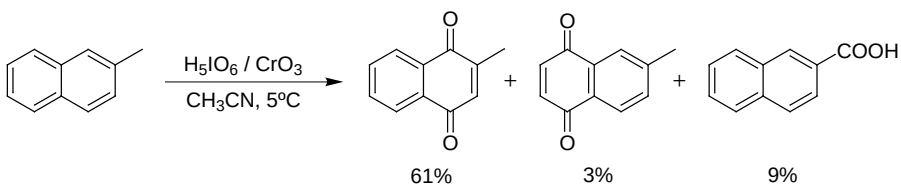
First, the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone (vitamin K_3, menadione) was examined. Vitamin K_3, which displays antihemorrhagic activity, is an important compound as a supplement in animal feed and a synthetic intermediate of vitamin K. Vitamin K_3 is produced on an industrial scale by stoichiometric oxidation of 2-methylnaphthalene with chromium(VI) oxide in sulfuric acid.[4] Other stoichiometric[5–9] and catalytic[10–19] methods for

Table 1. Oxidation of 2-methylnaphthalene with CrO_3/H_5IO_6[a]

Entry	CrO_3 (mol%)	H_5IO_6 (equiv.)	Conv. (%)	Yield (%)[b]
1	10	3.0	82	52
2	10	4.0	97	62
3	10	4.2	99	64
4	10	5.0	99	61
5	5	4.2	95	55
6	20	4.2	>99	57

[a] Reaction in acetonitrile at 5°C for 1 h.

[b] Total yield of 2-methyl-1,4-naphthoquinone and 2-methyl-5,8-naphthoquinone.



* Fax: +81-766-21-2402; e-mail: s-yamazk@itc.pref.toyama.jp

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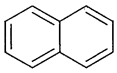
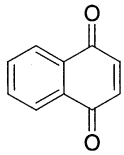
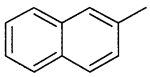
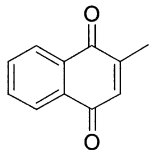
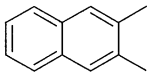
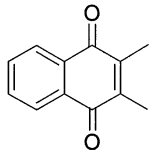
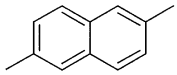
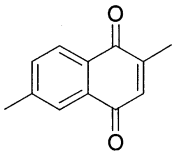
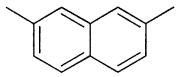
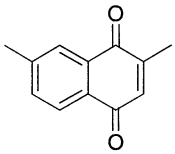
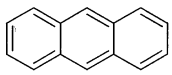
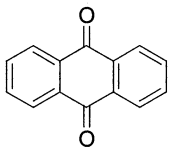
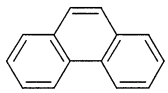
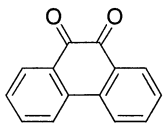
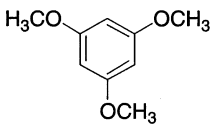
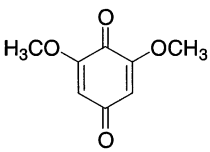
Table 2. Oxidation of arenes with CrO_3/H_5IO_6[a]

Entry	Substrate	Product	Yield %
1			44[b]
2			61[c]
3			66[d]
4			70
5			79
6			85
7			85[e]
8			90[f]

[a]Reaction in acetonitrile at 5°C for 1h. Substrate/CrO_3/H_5IO_6=1/0.1/4.2. [b]Convn 88%.
[c]2-Methyl-5,8-naphthoquinone and 2-naphthoic acid were also isolated in 3% and 9% yields.
[d]2,3-Dimethyl-5,8-naphthoquinone was also isolated in 3% yield. [e]Convn 95%.
[f]Substrate/CrO_3/H_5IO_6=1/0.03/5.

oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone have been reported. However, these methods have disadvantages and limitations, and new oxidation methods are still desired.

The influence of the amount of catalyst and oxidant on the oxidation of 2-methylnaphthalene was examined. The results are summarized in Table 1. 2-Methylnaphthalene was oxidized smoothly at 5°C in acetonitrile in the presence of 10 mol% of CrO_3 and 4.2 equiv. H_5IO_6 to 2-methyl-1,4-naphthoquinone in 61% yield along with a small amount of 2-methyl-5,8-naphthoquinone (3%) and 2-naphthoic acid (9%) (entry 3). The use of 4.0–4.2 equiv. H_5IO_6 maximized the yield of the

quinones (entries 2 and 3). The use of a smaller amount of oxidant resulted in the recovery of a considerable amount of 2-methylnaphthalene (entry 1). The use of a larger amount of oxidant did not increase the yield of the quinones (entry 4). The use of 10 mol% of catalyst afforded maximum yield of the quinones among a variant amount of catalyst examined (entries 3 and 5–6).

Concerning the regioselectivity of the aromatic ring oxidation, 1,4-naphthoquinone/5,8-naphthoquinone molar ratio was 95:5. This regioselectivity is higher than that of reported catalytic procedures such as H_2O_2/methyltrioxorhenium (total quinone yield 52%, 1,4-quinone/5,8-quinone ratio 89:11)[10] and $KHSO_5$/Mn-porphyrins (total quinone yield 86%, 1,4-quinone/5,8-quinone ratio 53:47).[12] Recently, the Barkanova group reported the selective formation of 2-methyl-1,4-naphthoquinone (65% yield) without any 2-methyl-5,8-naphthoquinone by AcOOH/Mn-tetraazaporphines.[11]

Additional examples, which show the scope of this catalytic oxidation, are given in Table 2. Naphthalene was oxidized to 1,4-naphthoquinone in 44% yield (entry 1). 2,3-Dimethylnaphthalene was oxidized to 2,3-dimethyl-1,4-naphthoquinone in 66 % yield along with 3% of 2,3-dimethyl-5,8-naphthoquinone (entry 3). 2,6-Dimethylnaphthalene and 2,7-dimethylnaphthalene gave corresponding 1,4-naphthoquinones in 70 and 79% yields, respectively (entries 4 and 5). Anthracene and phenanthrene were oxidized by this catalytic system to the corresponding quinones, anthraquinones and phenanthrenequinones in 85% (entries 6 and 7). 1,3,5-Trimethoxybenzene was oxidized to 2,6-dimethoxy-1,4-benzoquinone in 90% yield with 3 mol% catalyst (entry 8).

The procedure for the oxidation of 2-methylnaphthalene is as follows; H_5IO_6 (3.37 g, 14.8 mmol) was dissolved in acetonitrile (65 mL) with vigorous stirring, and then CrO_3 (35.2 mg, 0.352 mmol) was dissolved to the solution. The resulted solution was cooled to 5°C. 2-Methylnaphthalene (0.500 g, 3.52 mmol) dissolved in 5 mL acetonitrile was added all at once to the above solution with stirring. A white precipitate formed immediately with exothermic reaction. After 1 h stirring at 5°C, the supernatant liquid of the reaction mixture was decanted to a flask, and the solvent was removed by evaporation. The residues after decantation and evaporation were dissolved in H_2O and CH_2Cl_2, combined and then extracted with CH_2Cl_2 (10 mL×2). The collected organic extracts were washed with aqueous NaOH solution. 2-Naphthoic acid (55 mg, 9%) was obtained from acidified aqueous solution by CH_2Cl_2 extraction. The organic layer was washed with brine, and then dried over anhydrous $MgSO_4$. The solvent was distilled off under reduced pressure. The raw product obtained was recrystallized from ethanol to afford 298 mg of 2-methyl-1,4-naphthoquinone as yellow crystals. The residue of recrystallization was separated by silica gel column chromatography (CH_2Cl_2:hexane = 1.5:1) to give 2-methyl-1,4-naphthoquinone (71 mg, total yield 369 mg, 61%) and 2-methyl-5,8-naphthoquinone (18 mg, 3%).

In summary, CrO_3 has been found to be an efficient catalyst for oxidation of arenes with H_5IO_6 as the terminal oxidant in acetonitrile. 2-Methylnaphthalene was oxidized to 2-methyl-1,4-naphthoquinone in high yield and regioselectivity by this catalytic system. The use of easily accessible commercial reagents, the simple operation, rapid reaction rate at low temperature and formation of product in high yield and selectivity make this method advantageous to existing procedures.

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