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The Formation of 1,4-Quinones by Oxovanadium(IV)-Complexes Catalyzed Aerobic Oxygenation of Fused Aromatic Compounds

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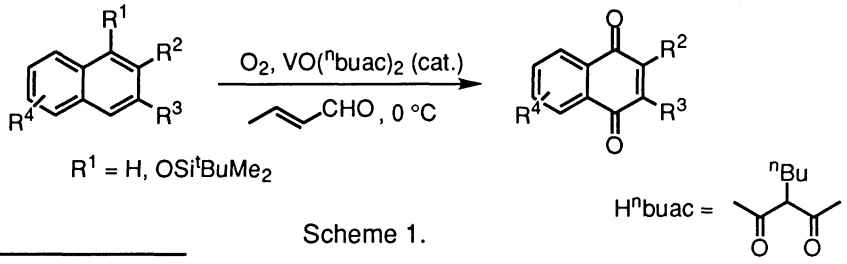
In the presence of a catalytic amount of oxovanadium(IV) complexes coordinated with 1,3-diketone ligands, fused aromatic compounds such as naphthalenes and naphthol derivatives are smoothly oxygenated into the corresponding 1,4-naphthoquinones by combined use of molecular oxygen and crotonaldehyde under an atmospheric pressure.

Quinones are useful compounds as not only synthetic intermediates but also as biologically active aromatic compounds. For example, 2-methyl-1,4-naphthoquinone, vitamin K3 and its derivatives have an antihemorrage activity,[1] and 5-hydroxy-1,4-naphthoquinone, juglone was reported to be an allelopathic agent.[2a, b] The direct oxygenation of arenes is a simple and effective reaction to form the corresponding quinones, and many researches have been carried out to develop practical procedures which would be applicable to various arenes. Since the oxidation of arenes requires rather strong oxidant such as chromium oxide[3a] or hydrogen peroxide,[3b] it has been difficult to control the undesirable side-reaction of substituents in arenes or the over-oxidation of initial products. On the other hand, anodic oxygenation of arenes is reported to afford the quinones in the presence of cerium salts.[3c] Further, phenols which are easily oxidized by Fremy's salt[4a] are known as precursors of quinones, and only phenolic compounds having appropriate substituents[2b, 4b] are avairable with molecular oxygen.

It was already reported from our laboratory that molecular oxygen, the most abundant oxidant was successfully utilized in oxygenations of various organic compounds such as olefinic compounds[5a] or cyclicketones[5b] by choosing suitable transition metal complex catalysts in the co-existence of aldehydes. Now, oxovanadium(IV) complexes are found to have specific catalytic activity toward aerobic oxygenation of fused aromatic compounds under similar conditions.[6] In this communication, we would like to describe the novel prepa-



Scheme 1.

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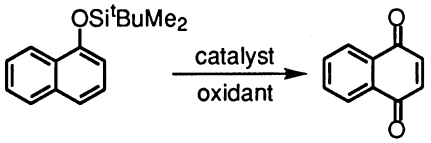
rative method for 1,4-naphthoquinones from the corresponding naphthalenes or naphthol derivatives by the combined use of molecular oxygen and crotonaldehyde catalyzed by oxovanadium(IV) complexes under an atmospheric pressure.

In the first place, the aerobic oxygenation of 1-(*tert*-butyldimethylsiloxy)naphthalene, 1-TBSO-naphthalene was examined by using various transition metal complex catalysts having 3-methyl-2,4-pentanedione, Hmac as a ligand together with a catalytic amount of peroxyacetic acid as an initiator[7] in the co-existence of crotonaldehyde.[8] As shown in Table 1, 1-TBSO-naphthalene was completely consumed only when oxovanadium(IV) complex was employed as catalyst and 1,4-naphthoquinone was obtained in 74% yield (Entry 1) while nickel(II) or cobalt(II) complex was not at all effective (Entries 2 and 3). It was confirmed that 1,4-naphthoquinone was not obtained regardless of the presence of oxovanadium(IV) complex catalyst when 2 equivalents of peroxyacetic acid, AcOOH were used as an oxidant under argon atmosphere (Entries 4 and 5). Based on these results, it is reasonable enough to assume that the active oxidant of the present reaction is not a simple peroxycarboxylic acid generated by autooxidation of an aldehyde.

Table 1. Reaction of 1-TBSO-naphthalene with Various Oxidant

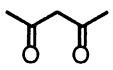
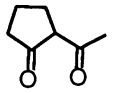
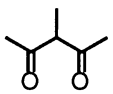
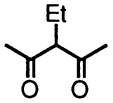
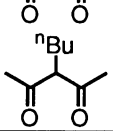


Entry	Reagents	Conversion /%[c]	Yield /%[c]
1[a]	O_2, $VO(mac)_2$ (cat.), RCHO	100	74
2[a]	O_2, $Ni(mac)_2$ (cat.), RCHO	2	trace
3[a]	O_2, $Co(mac)_2$ (cat.), RCHO	2	trace
4[b]	AcOOH, $VO(mac)_2$ (cat.)	7	trace
5[b]	AcOOH	2	trace

a) Reaction conditions; 1-TBSO-naphthalene 1.0 mmol, catalyst 0.30 mmol, crotonaldehyde 6.0 mmol, diethyl ketone 20 cm^3, AcOOH ca. 0.1mmol, 0 °C, 72 h, 1 atm O_2. b) AcOOH (2.0 mmol) was used. c) Determined by GC analysis.

In order to find a suitable ligand of the above catalyst, various bis(1,3-diketonato)oxovanadium(IV) complexes were prepared[9] and then the oxygenation reaction was carried out by using these complexes as catalysts at 0 °C. Oxovanadium(IV) complexes coordinated with electron donating type 1,3-diketone ligands were found to be

Table 2. Oxygenation of 1-TBSO-naphthalene Catalyzed by Bis(1,3-diketonato)oxovanadium(IV) Complexes

Entry[a]	Ligand (LH)		Eox / V vs Ag/Ag^+ [b]	Conversion /%[c]	Yield /%[c]
1		Hacac	1.00	2	trace
2			0.96	60	32
3		Hmac	0.86	100	74
4			0.86	100	76
5		H^{n}buac	0.86	100	78

a) Reaction conditions; 1-TBSO-naphthalene 1.0 mmol, V(IV)OL_2 0.30 mmol, crotonaldehyde 6.0 mmol, diethyl ketone 20 cm^3, AcOOH ca. 0.1mmol, 0 °C, 72 h, 1 atm O_2. b) Oxidation potential of VOL_2 complexes were measured in CH_3CN solution as described in reference 10. c) Determined by GC analysis.

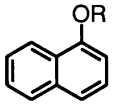
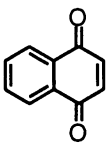
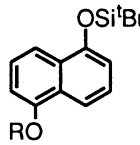
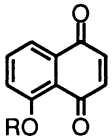
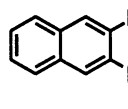
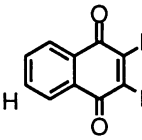
effective (Entries 2-5 in Table 2) whereas $VO(acac)_2$ catalyst did not work at all under the present reaction conditions (Entry 1). When bis(3-*n*-butyl-2,4-pentanedionato)oxovanadium(IV), $VO(^nbuac)_2$ was employed as a catalyst, 1,4-naphthoquinone was obtained in 78% yield (Entry 5). The measurement of oxidation potentials, E_{ox} (V vs. Ag/Ag^+) of these complexes indicated that oxovanadium(IV) complexes having lower E_{ox} values such as $VO(^nbuac)_2$ were suitable for the present oxygenation while $VO(acac)_2$ having higher E_{ox} value was not effective.

After optimization of the reaction conditions, 1,4-naphthoquinone was obtained from 1-TBSO-naphthalene in 86% yield[11] when methyl isobutyl ketone, MIBK was used as a solvent (Entry 1 in Table 3). Thus, the present procedure was successfully applied to various fused aromatic compounds; for example, 1-methoxynaphthalene afforded 1,4-naphthoquinone in 68% yield (Entry 2) and juglone ester of acetic acid and benzoic acid were obtained from 1-TBSO-5-acetoxylnaphthalene and 1-TBSO-5-benzoyloxynaphthalene in 79% and 62% yield, respectively (Entries 3 and 4). Alkyl naphthalenes such as 2,3-dimethylnaphthalene or 2-methylnaphthalene were converted into 2,3-dimethyl-1,4-naphthoquinone or 2-methyl-1,4-naphthoquinone, vitamin K_3 in 67% or 55% yield, respectively, without accompanying undesirable oxidation of methyl groups (Entries 5 and 6). Naphthalene was also oxygenated into 1,4-naphthoquinone in 34% yield though the conversion of naphthalene was not in satisfactory level (Entry 7).

The typical procedure was described as follows; to the stirred mixture of 1-(*tert*-butyldimethylsiloxy)-5-acetoxylnaphthalene 316 mg (1.0 mmol), $VO(^nbuac)_2$ 108 mg (0.30 mmol), crotonaldehyde 420 mg (6.0 mmol) in MIBK (20 cm^3), the solution of a catalytic amount of peroxyacetic acid in acetic acid was added at 0 °C, and stirring was continued under an atmospheric pressure of oxygen at 0 °C for 72 h. The reaction mixture was washed with aqueous potassium bicarbonate and dried over anhydrous sodium sulfate. After removal of solvent *in vacuo*, the mixture was purified by silica-gel chromatography to afford juglone ester of acetic acid 172 mg (79% yield).

Table 3. Synthesis of Various 1,4-Naphthoquinones

Fused Aromatic Compounds —O_2, $VO(^nbuac)_2$ (cat.), $CH_2{=}CHCHO$, MIBK, 0 °C→ 1,4-Quinones

Entry[a]	Substrate	Quinone	Yield /%
1	 R = Si^tBuMe_2		86[b]
2	R = CH_3		68[b]
3	 R = CH_3CO-		79[c]
4	R = PhCO-		62[c]
5	 R = R' = CH_3		67[b]
6	R = CH_3, R' = H		55[b]
7	R = R' = H		34[c, d]

a) Reaction conditions; substrate 1.0 mmol, $VO(^nbuac)_2$ 0.30 mmol, crotonaldehyde 6.0 mmol, MIBK 20 cm^3, AcOOH ca. 0.1mmol , 0 °C, 72 h, 1atm O_2. b) GC yield. c) Isolated yield. d) *p*-Tolualdehyde (6.0 mmol) was used.

It is noted that oxygenation of both naphthalenes and naphthol derivatives was successfully carried out by the combined use of molecular oxygen and crotonaldehyde under an atmospheric pressure and the corresponding 1,4-naphthoquinones was formed when oxovanadium(IV) complex having lower oxidation potential such as bis(3-*n*-

butyl-2,4-pentanedionato)oxovanadium(IV), $VO(^{n}buac)_2$ was employed as a catalyst.

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6) Vanadium(V) oxide was industrial catalyst for the oxidation of naphthalene into maleic anhydride or 1,4-naphthoquinone by molecular oxygen in vapor phase, M. S. Wainwright and T. W. Hoffman, *Can. J. Chem. Eng.*, **55**, 557 (1977); peroxyvanadium(V) complexes can introduce hydroxy group into benzene, H. Mimoun, *Isr. J. Chem.*, **23**, 451 (1983); M. Bonchio, V. Conte, F. Di Furia, and G. Modena, *J. Org. Chem.*, **54**, 4368 (1989).

7) Addition of peroxyacetic acid is not essential to carry out the present oxygenation, however, in the absence of peroxyacetic acid, the undesirable induction period (1day) was observed. When 1-TBSO-naphthalene was oxygenated by using $VO(mac)_2$ as a catalyst in the absence of peroxyacetic acid, 1,4-naphthoquinone was obtaied in 44% yield.

8) In cases of using aliphatic aldehydes such as isobutyraldehyde or isovaleraldehyde, consumption of 1-TBSO-naphthalene stopped half way under the present reaction conditions.

9) Oxovanadium(IV) complex,$VO(^{n}buac)_2$ was prepared as follows; to the stirred mixture of 3-*n*-butyl-2,4-pentanedione (0.20 mol) in methanol (200 cm^3), vanadyl sulfate (0.10 mol) in water (150 ml) was added under nitrogen atmosphere. After stirring for 10 min, aqueous sodium acetate (0.20 mol) was added over 10 min and stirring was continued for 1 h. Precipitated solid was filtered and washed with methanol and water. After drying at 90 °C *in vacuo*, $VO(^{n}buac)_2$ was obtained as grayish blue solid. Mp 144.2 - 145.0 °C. All the other oxovanadium(IV) complexes were prepared in a similar manner.

10) The oxidation potentials (E_{ox}) were measured in CH_3CN solution containing 0.1 mol/l tetrabutylammonium perchlorate and 0.001 mol/l V(IV)O complex in the cell equipped with a reference electrode (Ag/AgCl), a working electrode (Pt) and an auxiliary electrode (Pt); T. Takai, T. Yamada, and T.Muakiyama, *Chem. Lett.*, **1990**, 1657.

11) The formation of partially oxidized product such as 1-(*tert*-butyldimethylsiloxy)-4-crotonoyloxynaphthalene (4% yield), 1-crotonoyloxy-2,3-dimethylnaphthalene (16% yield), or 1-crotonoyloxy-2-methylnaphthalene (20% yield) was observed.

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