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Direct Oxygenation of Benzene and Its Analogues into Phenols Catalyzed by Oxovanadium(IV) Complex with Combined Use of Molecular Oxygen and Aldehyde

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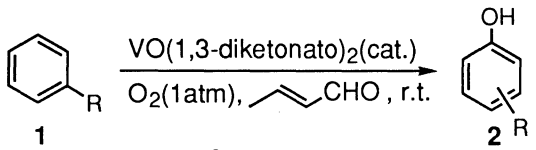
In the presence of a catalytic amount of oxovanadium(IV) complexes coordinated by 1,3-diketone-type ligands, benzene and its analogues are directly oxygenated into phenols by combined use of molecular oxygen and crotonaldehyde at room temperature.

Direct oxygenation of aromatics into their hydroxylated derivatives is one of the most challenging topics in organic synthesis and has also been expected in industrial chemistry as an alternative method to the cumene process.[1] As aromatic nucleus is resistant to oxidation under mild conditions because of its resonance stability, oxygenation requires highly reactive oxidant under severe conditions.[1] Several systems for the above oxygenation were reported by using peroxide combined with strong Lewis acid.[2] Transition metal-catalyzed oxygenation such as iron(II) / hydrogen peroxide (Fenton's reagent) has also been reported.[3] Stoichiometric oxygenation of aromatic compounds was achieved by vanadium(V) peroxo complex.[4] On the other hand, direct oxygenation of aromatic compounds with molecular oxygen was also performed *in vivo* by the promotion of several oxygenases which involve transition metal catalysts in liver microsomal cytochrome P-450 under mild conditions.[5] Aerobic oxygenation of aromatics were also demonstrated by using transition metal catalysts, but phenolic compounds were just detected or afforded in low yields.[6]

Recently, efficient and selective aerobic oxidation was reported for various organic compounds with molecular oxygen by combined use of appropriate reducing agents and transition metal complex catalysts under mild conditions from our laboratory. For example, in the presence of aldehydes, various olefins were effectively oxygenated into corresponding epoxides under an atmospheric pressure of molecular oxygen at room temperature catalyzed by nickel(II),[7a] iron(III),[7b] or manganese(III)[7c] complexes having 1,3-



1 2

Scheme 1.

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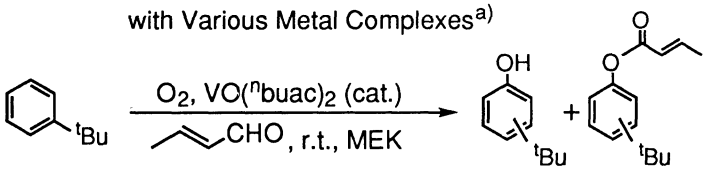
diketone-type ligands. Oxovanadium(IV) complex was effectively employed as a catalyst for oxygenation of fused aromatic compounds to give quinones by using molecular oxygen and crotonaldehyde as a reductant.[8]

In this communication, we would like to report direct oxygenation of benzene and its analogues into phenols catalyzed by oxovanadium(IV) complex with molecular oxygen in the coexistence of crotonaldehyde under mild conditions (Scheme 1).

Table 1. Aerobic Oxygenation of *tert*-Butylbenzene with Various Metal Complexes[a]



1a 2a 3a

Entry	Catalyst	Conv. /%[b]	Yield /%[b]
1	$VO(acac)_2$	42	17 [c]
2	$Ni(acac)_2$	6	0
3	$Mn(acac)_3$	6	0
4	$Co(acac)_2$	8	0
5	$Cu(acac)_2$	8	0
6	$Pd(acac)_2$	0	0

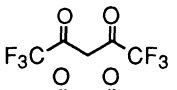
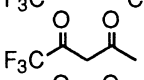
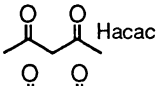
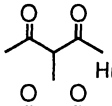
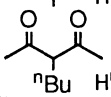
a) Reaction conditions; *tert*-butylbenzene 1.0 mmol, catalyst 0.1 mmol, crotonaldehyde 4.0 mmol, methylethylketone 4.0 cm^3, AcOOH ca. 0.05 mmol, r.t., 14 h, 1 atm O_2. b) Conversion of **1a** and total yield of **2a** and **3a** were determined by GC analysis based on *tert*-butylbenzene. c) Yield of **2a** and **3a** was 15% and 2%, respectively.

In the first place, aerobic oxygenation of *tert*-butylbenzene (**1a**) was tried using various acetylacetonato-metal complexes as catalysts according to the following procedure: to a stirred mixture of *tert*-butylbenzene 134 mg (1.0 mmol), metal complex catalyst 0.1 mmol, and crotonaldehyde 561 mg (8.0 mmol) in methylethylketone 4.0 cm^3 was added a catalytic amount of peracetic acid at room temperature,[9] and was kept stirring under an atmospheric pressure of molecular oxygen for 14 h. Then products were quantitatively analyzed by GLC.

When bis(2,4-pentanedionato)oxovanadium(IV) ($VO(acac)_2$)[10] was employed as a catalyst, the exothermic reaction started instantly, and the color of the solution rapidly changed from dark green to brown. After 14 h, the corresponding phenol derivatives, *tert*-butylphenol **2a** and *tert*-butylphenyl crotonate **3a** were obtained in 17% total yield (15% and 2% yield, respectively), based on *tert*-butylbenzene by GC analysis (Entry 1 in Table 1). On the other hand, no phenolic compound was detected at all when nickel(II),[7a] manganese(III),[7c] or cobalt(II)[11] was used as a catalyst which was effective in aerobic epoxidation of olefins (Entries 2-4). Copper(II) and palladium(II) were also ineffective in the above oxygenation reaction (Entries 5 and 6).

Of various 1,3-diketone-type ligands screened, oxovanadium(IV) complexes coordinated with 1,3-diketones having electron-donating substituent such as 3-n-butyl-2,4-pentanedione ($VO(^nbuac)_2$)[12] was found to be the most effective catalyst to afford phenolic compounds in 26% yield and 67% selectivity (Entry 5 in Table 2).[13]

Table 2. Oxygenation of *tert*-Butylbenzene Catalyzed by Bis(1,3-diketonato)oxovanadium(IV) Complexes[a]

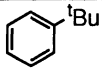
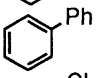
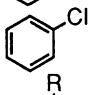
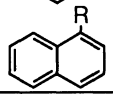
Entry	Ligand	Eox/V vs Ag/Ag^+[b]	Yield /%[c]	Selectivity /%[d]
1		1.40	17	40
2		1.30	19	48
3		1.00	21	50
4		0.86	22	55
5		0.86	26	67
6[e]			33	86

a) Reaction conditions; *tert*-butylbenzene 1.0 mmol, catalyst 0.1 mmol crotonaldehyde 8.0 mmol, acetone 4.0 cm^3, AcOOH ca. 0.05 mmol, r.t., 14 h, 1 atm O_2. b) Oxidation potential of VOL_2 was measured in CH_3CN as described in reference 8. c) Total yield of **2a** and **3a** was determined by GC analysis based on *tert*-butylbenzene. d) Total yield / Conversion x 100, determined by GC analysis. e) 0.5 mmol catalyst was used.

Phenolic compounds were obtained in 33% total yield (**2a**: 31%, *o/m/p* = 23/35/42, and **3a**: 2%) and 86% selectivity by increasing the amount of catalyst without accompanying any over-oxidation products (Entry 6).

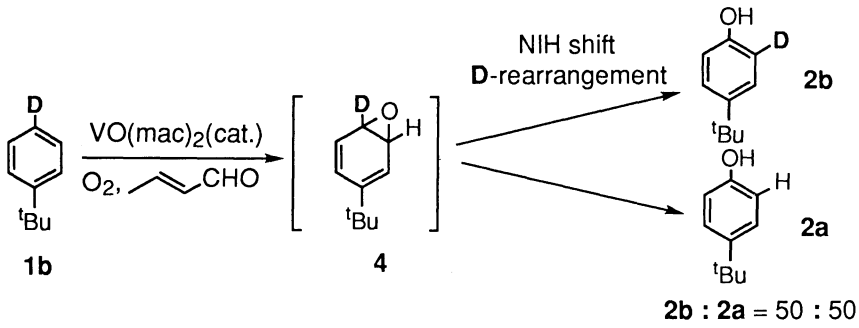
In the presence of a catalytic amount of VO(^{n}buac)$_2$, benzene, biphenyl and chlorobenzene were also oxygenated into phenol, phenylphenol and chlorophenol in 22%, 20% and 18% total yields, respectively (Entries 2-4 in Table 3). In contrast, 1,4-naphthoquinone was obtained without formation of phenolic compound **2** when 1-TBSO-naphthalene or naphthalene was oxygenated under the similar reaction conditions (Entries 5 and 6).[8]

Table 3. Oxygenation of Benzene and Its Analogues[a]

Entry	Substrate	Yield /%[b]	
		2 (*o/m/p*)	**3**
1[c]		31 (23/35/42)	2
2		21	1
3		18 (33/17/50)	2
4		17 (32/0/68)	1
5[d]	 R=OSi^{t}BuMe$_2$	0	4[e), f)]
6[d]	R=H	0	10[g)]

a) Reaction conditions; substrate 1.0 mmol, VO(^{n}buac)$_2$ 0.1 mmol crotonaldehyde 8.0 mmol, acetone 4.0 cm^3, AcOOH ca. 0.05 mmol, r.t., 14 h, 1 atm O_2. b) Yield of **2** and **3** was determined by GC analysis based on substrate. c) 0.5 mmol VO(^{n}buac)$_2$ was used. d) VO(^{n}buac)$_2$ 0.3 mmol crotonaldehyde 6.0 mmol, MIBK 20 cm^3, AcOOH ca. 0.1 mmol, 0 °C, 72h, 1 atm O_2. e) 1,4-Naphthoquinone was obtained in 86% yield. f) NIH shift was not observed. g)1,4-Naphthoquinone was obtained in 34% yield.

The above oxygenation was carried out using *tert*-butylbenzene-4-D[14] as a substrate in the presence of 10 mol% of VO(mac)$_2$ and 4.8 equiv. of crotonaldehyde in methylethylketone at 0 °C (Scheme 2). Based on GC analysis, *o*-, *m*-, and *p-tert*-butylphenols were obtained in 2%, 6% and 6% yield, respectively. The NIH shift[5] was observed in the present reaction; that is, *p*-phenolic compounds **2b** (2-deuterized) and **2a** were detected in the ratio of 50 to 50 on the basis of GC-MS analysis.[15] These results indicated that the present oxygenation would proceed *via* the corresponding arene oxide **4** to afford phenolic compounds **2b** (*via* D-rearrangement, NIH shift) and **2a**. Thus, it is reasonable to assume that the present oxygenation of aromatic compounds proceeded through epoxidation of aromatic double bond catalyzed by oxovanadium(IV) complexes.[16]



Scheme 2. NIH shift observed in the present oxygenation.

It is noted that, in the presence of 8 equiv. crotonaldehyde and a catalytic amount of oxovanadium(IV) complexes coordinated with 1,3-diketones having electron-donating substituents such as VO(^{n}buac)$_2$, direct oxygenations of benzene, *tert*-butylbenzene, biphenyl and chlorobenzene into the corresponding hydroxylated products were performed under an atmospheric pressure of molecular oxygen.

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9) Addition of peracetic acid (ca. 5 mol% against *tert*-butylbenzene, acetic acid solution 32 wt% Aldrich Co.) was not essential to proceed the present reaction, however, the induction period disappeared.

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12) Oxovanadium(IV) complexes were prepared by the reported procedure in Ref. 8.

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15) GC-MS analysis was conducted after methylation of **2a** and **2b** by MeI / K_2CO_3.

16) The NIH shift was not observed in the oxygenation of 1-TBSO-naphthalene-4-D into 1,4-naphthoquinone. Based on this result, it is reasonable enough to assume that the oxygenation of naphthalene derivatives into 1,4-naphthoquinones proceeds through the different reaction path from the present oxygenation including arene oxide as an intermediate.

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