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Catalytic Oxidation of Hydroquinones and Naphthalenediols to 1,4-Quinones with H_2O_2 in the Presence of Chromium(VI) Oxide-Bistributyltin Oxide and an Application to Vitamin K_1 Synthesis

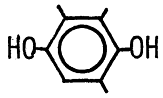
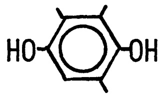
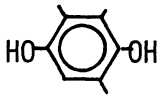
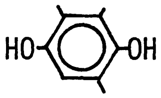
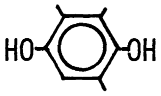
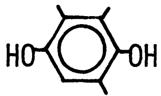
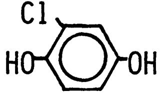
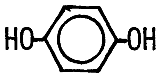
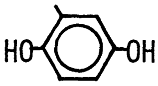
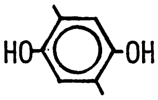
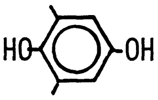
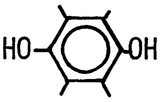
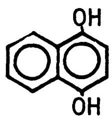
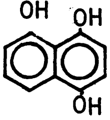
Masami INOUE,* Toshitaka URAGAKI, and Saburo ENOMOTO
Faculty of Pharmaceutical Sciences, Toyama Medical and
Pharmaceutical University, Sugitani,
Toyama 930-01

The oxidation of hydroquinones and naphthalenediols to 1,4-quinones was carried out in the presence of a chromium(VI) compound formed from chromium(VI) oxide and bistributyltin oxide with 30% aqueous H_2O_2 in benzene-isopropyl ether at 50 °C. The catalyst was fixed on charcoal and used for the oxidation of dihydrovitamin K_1 to vitamin K_1 in ethyl alcohol.

Chromium(VI) oxide is conveniently used for the oxidation of hydroquinones,[1] though the use in practical scale takes cost compared with the catalytic oxidation. Hydrogen peroxide is an alternative versatile oxidation agent. However, catalysts for this purpose have not yet been reported. Authors found that a chromium(VI) compound formed from chromium(VI) oxide and bistributyltin oxide is a mild oxidation catalyst to give benzoquinones and naphthoquinones from corresponding hydroquinones with 30% H_2O_2. The catalyst was supported on charcoal and applied on the oxidation of dihydrovitamin K_1 to vitamin K_1. The oxidation was efficiently carried out again using the recovered catalyst after the separation by filtration.

The catalyst was prepared in a manner similar to molybdenum(VI) or tungsten(VI) catalysts[2] by the addition of bistributyltin oxide(2 g, 3.3 mmol) to an excess amount of the aqueous solution of chromium(VI) oxide(0.4 g, 4.0 mmol) in H_2O(10 ml) by stirring vigorously. An orange fine solid was separated out; 95% yield based on bistributyltin oxide; mp 74 °C. The elemental analysis of the chromium (VI) compound was reasonable for $(Bu_3SnO)_2CrO_2$; Found: C, 41.11; H, 7.82. Calcd for $C_{24}H_{54}O_4CrSn_2$: C, 41.41; H, 7.76%. Results for the oxidation of hydroquinones with H_2O_2 in the presence of various chromium compounds are shown in Table 1. The oxidation of trimethylhydroquinone did not take place in the absence of the catalyst. Chromium(VI) oxide itself decomposed H_2O_2 vigorously. Although bistributyltin oxide catalyzed the oxidation of trimethylhydroquinone to give trimethylbenzoquinone, the activity was low. In Cr(III) acetylacetonate or $CrCl_3$, both the activity and the selectivity to the quinone were lower. However, in the presence of our catalyst, the oxidation took place to give quinones selectively in good yields with 30% H_2O_2 in a benzene-isopropyl ether(1 : 2) solvent at 50 °C; benzene dissolved the catalyst while isopropyl ether was an appropriate solvent for the substrates. The oxidation took place between two phases of

Table 1. Oxidation of hydroquinones and naphthalenediols with H_2O_2 in the presence of various chromium catalysts

Entry	Substrate	Catalyst	Time/h	Conv./%	Yield/%
1		None	3	3	3
2		CrO_3	-	-	- a)
3		$(Bu_3Sn)_2O$	4	13	2
4		Cr(III)acac	0.5	10	5
5		$CrCl_3$	0.5	45	30
6		Cr-Sn[b)]	0.5	98	98
7		Cr-Sn	20	25	23
8		Cr-Sn	20	52	52
9		Cr-Sn	20	74	74
10		Cr-Sn	4	94	94
11		Cr-Sn	2	100	91
12		Cr-Sn	0.5	100	100
13		Cr-Sn	3	98	90
14		Cr-Sn	1.5	100	100

Substrate(1.5 mmol), 30% H_2O_2(6.0 mmol), catalyst(1.5×10^{-2} mmol), and solvent (benzene-isopropyl ether, 1 : 2)(15 ml) were used. Reaction was carried out at 50 °C. a) H_2O_2 was decomposed vigorously. b) $(Bu_3SnO)_2CrO_2$.

a benzene-isopropyl ether layer and aqueous H_2O_2. The progress of the oxidation was traced by high-performance liquid chromatography(HPLC) (M & S pack, C-18, 4.6 mm x 150 mm column, Gilson Co. Model 302) using $MeOH-H_2O$(100 : 50) as the eluent(flow rate, 0.5 ml min^{-1}; detector, UV at 285 nm). After the reaction, the quinones were separated by frash-chromatography with kieselgel 60(Merck Co.) and CH_2Cl_2 as the eluent.

The rate of oxidation differed according to the substituents on the hydroquinones, e. g., 2-chloro-hydroquinone reached 23% yield after 20 h while tetramethylhydroquinone was oxidized completely after half an hour at 50 °C. With increase in the number of the methyl groups bound on hydroquinone increased the yield. Hydroquinone took 20 h to reach 52% yield. On the other hand, dimethylhydroquinone was oxidized from 2 to 4 h at 50 °C. Naphthalenediols also gave naphthoquinones almost quantitatively. Since no color change was observed during the reaction, the oxidation seems to occur by way of peroxo-type3) chromium compound keeping a chromium(VI) state.

Vitamin K_1, an antihaemorrhage drug, has been produced hitherto by the oxidation of dihydrovitamin K_1 with silver oxide.4) Recently, nickel peroxide,5) manganic (VI) oxide,6) dimethylsulfoxide,7) or dioxygen in alkaline solution,8) have been claimed for this oxidation.

$(Bu_3SnO)_2CrO_2$(70 mg) was dissolved in ethyl alcohol(10 ml) and adsorbed on charcoal(palm-type, DC 5200, Dia Catalyst CO.)(1.0 g). The catalyst was separated by filtration and used for the oxidation of dihydrovitamin K_1 to vitamin K_1 with 30% H_2O_2 in ethyl alcohol under an Ar atmosphere at 40 °C. Results are shown in Table 2. The oxidation took place to give vitamin K_1 in good yield without oxidizing the double bond of the side chain. After the reaction, the catalyst was recovered by filtration and used repeatedly.

The solvent was evaporated and the products were extracted with ether. The evaporation of ether gave a pale yellow oil. The spectra of the oily products in isooctane were identical to those of vitamin K_1 which are shown in Japanese pharmacopoeia XI.

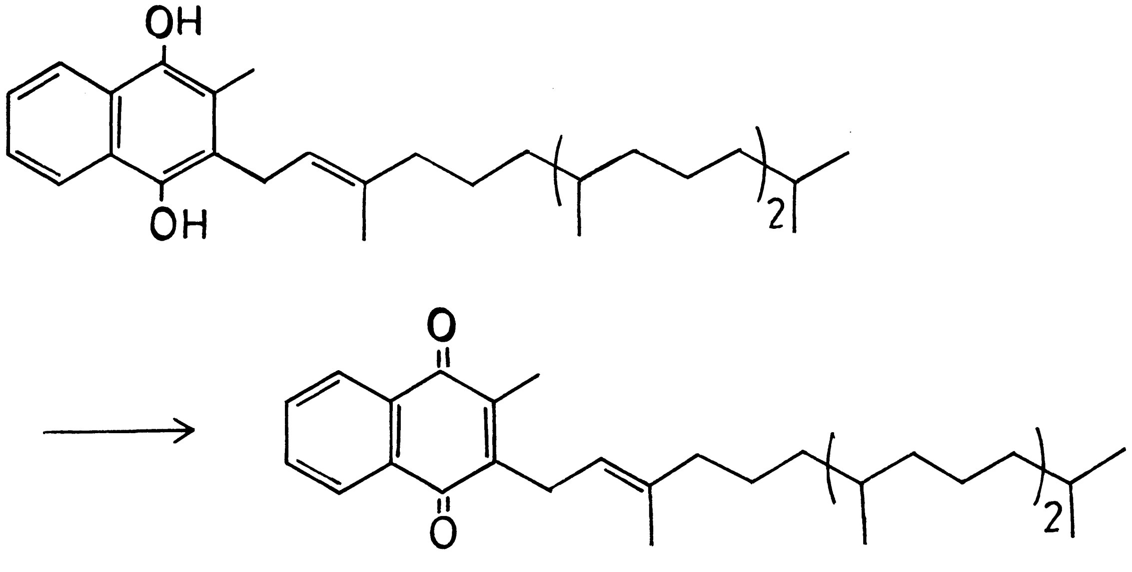


Table 2. Oxidation of dihydrovitamin K_1 to vitamin K_1 with H_2O_2 in the presence of a $(Bu_3SnO)_2CrO_2$ on charcoal catalyst at 40 °C

Entry	Catalyst	Conversion %	Time min	Yield %
1	Cr-Sn[a)]	100	15	81
2	Charcoal(1 g)	47	90	40
3	Cr-Sn(Charcoal 1 g)	100	90	97
4	Recovered cata. of entry 3	100	90	95
5	Recovered cata. of entry 4	99	90	95

Dihydrovitamin K_1(2.0 mmol), 30% H_2O_2(3.0 mmol), $(Bu_3SnO)_2CrO_2$(0.1 mmol) on charcoal(1 g), and ethyl alcohol(15 ml) were used. a) $(Bu_3SnO)_2CrO_2$.

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