

## Catalytic Oxidation of Naphthalene on Palladium in Cooperation with Copper(I)/(II) Redox Couple

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Catalytic oxidation of naphthalene in moist acetic acid solutions has been studied. The catalyst used was a silica-supported palladium which works in cooperation with the  $\text{Cu}^+/\text{Cu}^{2+}$  redox couple. Products were 1-naphthol, 1,4-naphthoquinone and (*E*)-2-formylcinnamaldehyde with a total yield of more than 78% in which naphthoquinone shared 40%. Reaction mechanism has been discussed in comparison with that of benzene.

Among many unit processes of organic synthesis, aromatic hydroxylation reaction is one of the most difficult reactions. In recent years, we have developed a new catalytic oxidation process which works efficiently under ambient conditions and proceeds in a single batch reactor without any cumbersome treatment.<sup>1,2)</sup> Our attention to date was, however, limited to the reaction of benzene. Since the process is expected to be applied to many aromatics other than benzene, the reaction of naphthalene has been studied tentatively. A similar study regarding the reaction of benzoic acid will appear separately.<sup>3)</sup>

### Experimental

**Catalyst.** For preparing catalysts, a mixture of metal salts ( $\text{CuSO}_4$  and/or  $\text{PdCl}_2$ ) and powdery silica (Merck, No. 9385, 230—400 mesh) dispersed in water was first exposed to ultrasonic wave for 90 min to homogenize the mixture. This process is necessary for achieving a high catalytic activity.<sup>2)</sup> The mixture was then heated to dryness on a steam bath with gentle agitation. Two catalysts of different composition were prepared in this manner. They are shown as Catalyst A (1000  $\text{CuSO}_4$ —50  $\text{PdCl}_2$ ) and B (100  $\text{PdCl}_2$ ), respectively, where numbers in the parentheses indicate  $\mu\text{mol}$  of respective metal salt per gram of silica support. In case of Catalyst B that contains no copper salt, a preliminary activation (reduction of  $\text{Pd}^{2+}$  to  $\text{Pd}^0$ ) of the catalyst with hydrogen was done separately in benzene.

**Reaction.** All reactions were carried out at 25 °C under the atmospheric pressure. When catalyst A was used, the catalyst (1 g) and a mixture (20  $\text{cm}^3$ ) of benzene with a solvent given in Tables 1 and 2 were placed into an Erlenmeyer flask (100  $\text{cm}^3$  in volume). After replacing air in the flask with hydrogen, the flask was shaken (30 mm stroke, 140 cycle/min) or stirred magnetically for 2 h to activate the catalyst. Upon this treatment the catalyst color gets black indicating that  $\text{Pd}^{2+}$  is reduced to its metallic state.  $\text{Cu}^{2+}$  ion is also believed to be reduced to its lower valence states, at least partly. Control of the stirring rate (800 rpm) is required for attaining reproducible results. Hydrogen was then replaced by air or pure oxygen to begin the oxidation reaction.

For reactions in acetic acid, copper(II) acetate (1 mmol) and naphthalene were dissolved into the solution (25  $\text{cm}^3$ ). Reaction was performed by using Catalyst B (1 g) that contains Pd

species alone and by introducing hydrogen and oxygen into the reactor flask either alternately or simultaneously.

The reaction mixture was filtered to remove the catalyst, and the solvent was removed using a rotary evaporator. Hexane was added to the residue and copper acetate was filtered off. The filtrate was concentrated, and (*E*)-2-formylcinnamaldehyde was isolated by thin-layer chromatography on silica gel: MS  $m/z$  131 ( $\text{M}^+ - 29$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ =6.67 (1H, dd,  $J$ =16.1, 7.8 Hz), 7.6—8.0 (4H, m), 8.58 (1H, d,  $J$ =16.1 Hz), 9.81 (1H, d,  $J$ =7.8 Hz), 10.23 (1H, s);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$ =128.0, 130.7, 132.3, 133.6, 133.9, 134.6, 135.4, 149.2, 192.7, 193.7.

**Product Analysis.** Product analysis was made by use of a high-performance liquid chromatograph equipped with a Merck Hibar column (Lichrosorb RP-18, 10×250 mm). Eluent used was a mixture of acetonitrile and a phosphate buffer solution of pH 3.5, of which the mixing ratio was varied depending on the nature of compounds to be analyzed.

### Results and Discussion

**1. Examination of Catalyst and Solvent.** We have already demonstrated that Catalyst A shows excellent activity for producing phenol even in benzene itself.<sup>2)</sup> We thus tried to use this catalyst for the oxidation of naphthalene. In contrast to benzene, however, naphthalene is solid at room temperature and thus needs some appropriate solvents.

We have first studied the effect of several organic solvents given in Table 1 in the reaction of benzene. The reaction was performed by using Catalyst A (1 g) in a mixture (20  $\text{cm}^3$ ) of benzene with a given solvent at several different ratio. After shaking the mixture under hydrogen for 2 h, the oxidation reaction was started and continued for 1 h by introducing air to the reactor flask. Yields of phenol are listed in Table 1. As is expected, the presence of any of the solvent hinders the oxidation of benzene appreciably. However, the hindering effect is minor in cyclohexane and this prompted us to study the oxidation of naphthalene in this solvent. Unfortunately, however, the reactivity of naphthalene in cyclohexane was unexpectedly low and produced only 0.5  $\mu\text{mol}$  of 1-naphthol.

As has been reported in a previous paper,<sup>2)</sup> the catalyst containing copper acetate was not effective when it

Table 1. Yield of Phenol ( $\mu\text{mol}$ ) in the Oxidation of Benzene in Several Solvents

Exp.	Solvent	Volume fraction of organic solvent/%			
		80	50	20	0
1	Cyclohexane	10.5	19.3	22.0	
2	Ethyl acetate	6.9	12.5	12.2	
3	Propylene carbonate	1.1	5.1	14.7	25.9 $\pm$ 4.3 <sup>a)</sup>
4	Acetic acid	3.2	3.8	6.8	
5	95% Acetic acid	2.4	3.6	—	

Catalyst: A (1 g), Solution volume: 20 cm<sup>3</sup>, Gas feeding: H<sub>2</sub> (2 h) followed by Air (1 h).

a) Mean value of ten measurements using catalysts from five different lots. Rather a big deviation is due to the use of different lots of catalyst. Values for a given solvent were determined using a single lot of catalyst and the error was less than a few %.

Table 2. Oxidation of Benzene in Acetic Acid

Exp.	Solvent component / v/v			Product yield/ $\mu\text{mol}$				Formal potential <sup>f)</sup> (Cu <sup>+</sup> /Cu <sup>2+</sup> ) /mV vs. SCE
	AN <sup>a)</sup>	H <sub>2</sub> O	AcOH <sup>b)</sup>	PhOH <sup>c)</sup>	HQ <sup>d)</sup>	BQ <sup>e)</sup>	Total	
1	0	0	100	4.3	0.2	1.0	5.5	—
2	0	6.5	93.5	5.7	0.4	1.2	7.3	—
3	6.5	0	93.5	4.0	4.0	3.9	11.9	625
4	6.5	6.5	87	14.8	14.0	4.8	33.6	560

Catalyst: B (1 g), Solution: Solvent (20 cm<sup>3</sup>)+Benzene (5 cm<sup>3</sup>)+Cu(OAc)<sub>2</sub>(40 mM), Gas feeding: H<sub>2</sub> (15 min) followed by Air (2 h).

a) Acetonitrile, b) acetic acid, c) phenol, d) hydroquinone, e) *p*-benzoquinone. f) Formal potential was measured in a Cu(OAc)<sub>2</sub>(1.3 mM) solution containing NaClO<sub>4</sub> (100 mM).

Table 3. Oxidation of Naphthalene in Acetic Acid

Exp.	Concn of naph./M	Product yield/ $\mu\text{mol}$				Turnover frequency <sup>k)</sup> /cycle h <sup>-1</sup>
		1-NaphOH <sup>h)</sup>	1,4-NaphQ <sup>i)</sup>	Dialdehyde <sup>j)</sup>	Total	
1 <sup>a)</sup>	0.1	2.5	5.9	2.8	11.2	0.056
2 <sup>a)</sup>	0.3	4.7	10.3	4.8	19.8	0.099
3 <sup>a)</sup>	0.5	4.8	10.4	4.7	19.9	0.100
4 <sup>b)</sup>	0.3	6.7	21.7	7.7	36.1	0.181
5 <sup>c)</sup>	0.3	21.3	50.0	18.8	90.1	0.451
6 <sup>d)</sup>	0.3	25.3	62.5	25.0	112.8	0.564
7 <sup>d,f)</sup>	0.3	25.5	72.3	22.5	120.3	0.602
8 <sup>e,g)</sup>	0.1	63.3(12.0)	209.8(39.9)	139.5(26.5)	412.6(78.4)	0.206

Catalyst: B (1 g), Solution: Cu(OAc)<sub>2</sub> (40 mM) was dissolved in AcOH (25 cm<sup>3</sup>) containing both AN and H<sub>2</sub>O at 4% in volume.

a) H<sub>2</sub> (15 min) followed by air (2 h), b) H<sub>2</sub> (15 min) followed by O<sub>2</sub> (2 h), c) H<sub>2</sub> (15 min) followed by O<sub>2</sub> (15 min), cycle repeated 4 times, d) simultaneous (7.5 cm<sup>3</sup> min<sup>-1</sup> for both H<sub>2</sub> and O<sub>2</sub>, 2h), e) simultaneous (7.5 cm<sup>3</sup> min<sup>-1</sup> for both H<sub>2</sub> and O<sub>2</sub>, 20 h), f) CH<sub>3</sub>COONa (50 mM) was added. g) Values in the parentheses indicate selectivity (%) based on the amount of naphthalene consumed, h) 1-naphthol, i) 1,4-naphthoquinone, j) (*E*)-2-formylcinnamaldehyde. k) Based on Pd.

was used in neat benzene. However, the catalyst became effective when a small amount of acetic acid was added to benzene. Accordingly, we next studied the reaction in acetic acid using Catalyst B that contains Pd species alone. In this case, copper(II) acetate was dissolved in the solution phase. The use of neat acetic acid resulted, however, in a poor product yield (Table 2, exp. 1). This can be attributed to the slow redox rates of the Cu(I)/Cu(II) couple in acetic acid. It is known that hydrated Cu(I) ions are oxidized readily to Cu(II)

ions with dioxygen<sup>4-7)</sup> and also that they can be stabilized with acetonitrile (AN).<sup>4,8)</sup> We hence added both AN and water as the cosolvents. As is seen in Table 2, the presence of both the two cosolvents increased markedly the oxidation efficiency (exp. 4). Electrochemical measurements also proved that the presence of water favors the oxidation of Cu(I) to Cu(II) while AN favors the reverse reaction. The effect of water and AN is counteracting and the use of 4–7% in volume ratio for both the cosolvents seems to be optimal.

It is worth noting that under the conditions in experiment 4, nearly equal amounts of hydroquinone and phenol are produced. This is in accordance with our previous observations. In the reaction in aqueous  $\text{CuSO}_4$  solutions, phenol was formed as the main product at pH 1 while hydroquinone dominated at pH 3.5.<sup>7)</sup> Even in the reaction in neat benzene under a pressurized oxygen atmosphere, the use of the Pd-Cu composite catalyst resulted in a predominant formation of *p*-benzoquinone.<sup>2)</sup> The present result is consistent with those and the presence of copper acetate favors the formation of hydroquinone.

**2. Reaction of Naphthalene.** Basic knowledges obtained for the oxidation of benzene were applied to the reaction of naphthalene by using 1 g of Catalyst B in a solution (25 cm<sup>3</sup>) of 40 mM  $\text{Cu}(\text{OAc})_2$  (1 M=1 mol dm<sup>-3</sup>) in acetic acid containing water and acetonitrile (4.0% for each). Results obtained are shown in Table 3. In experiments 1–7, the reaction was continued for 2 h. Products obtained are 1-naphthol, 1,4-naphthoquinone and (*E*)-2-formylcinnamaldehyde (which will be abbreviated as dialdehyde hereafter). A trace amount of 2-naphthol was detected among some other minor products.

The first three experiments, in which hydrogen was first supplied to the reactor for 15 min and then air followed for 2 h, indicate that the concentration of naphthalene has no remarkable effect on the yield (exps. 1–3). Replacement of air by pure oxygen results in the increase in the yield of naphthoquinone and thus total products (exp. 4).

In experiment 5, the supply of hydrogen and oxygen was alternated every 15 min and the cycle was repeated 4 times (total oxygen feeding: 1 h). The frequent alternation of gas feeding results in a marked increase of the product yield indicating that 1 h of oxidation time is unnecessarily long. The selectivity of each product remains almost unchanged. Experiment 6 was conducted under the conditions of simultaneous gas feeding i.e., both hydrogen and oxygen were supplied with an equal feed rate (7.5 cm<sup>3</sup> min<sup>-1</sup>). In comparison with the foregoing (exps. 4 and 5), the total yield increased still more by keeping the product distribution unchanged. A deliberate addition of sodium acetate increases the product yield and so that the turnover frequency (exp. 7).

In order to determine the material balance, a prolonged experiment was carried out (exp. 8), and the total selectivity with regard to the sum of the three products was found to be 78.4% and naphthoquinone shared 39.9% in it. The rest 21.4% was left undetermined. The prolonged reaction time (exp. 8) seems to increase the relative yield of dialdehyde.

Under the condition of alternate gas feeding, the product accumulation during the oxidation of naphthalene was studied. A typical example is shown in Fig. 1. It is interesting that the yield of naphthol first increases but after a short period of time it decreases gradually

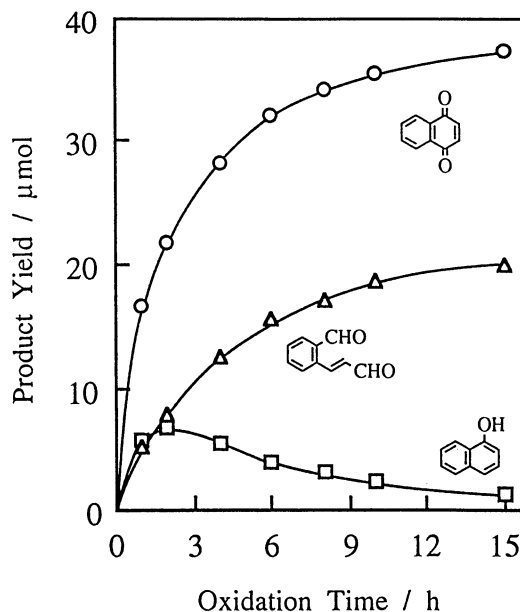


Fig. 1. Accumulation of the products during oxidation of naphthalene in acetic acid. Catalyst: B (1 g). Solution: 0.3 M Naphthalene and 40 mM  $\text{Cu}(\text{OAc})_2$  in AcOH (25 cm<sup>3</sup>) containing both AN and H<sub>2</sub>O at 6.5% in volume. Gas feeding: H<sub>2</sub> (15 min) followed by O<sub>2</sub>.

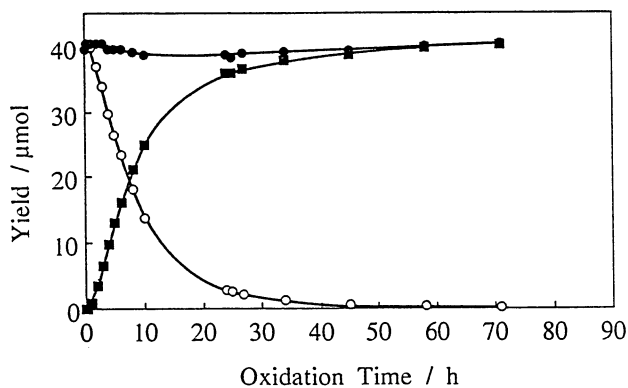


Fig. 2. Aerial oxidation of 1-naphthol to 1,4-naphthoquinone in the presence of Pd-catalyst and copper salt. Catalyst: B (1 g). Solution: 2 mM 1-Naphthol and 10 mM  $\text{Cu}(\text{OAc})_2$  in AcOH (20 cm<sup>3</sup>) containing both AN and H<sub>2</sub>O at 6.5% in volume. Gas feeding: H<sub>2</sub> (15 min) followed by O<sub>2</sub>. ○: 1-Naphthol, ■: 1,4-Naphthoquinone, ●: Total sum.

while other two products increases monotonously. Undoubtedly, this suggests that 1-naphthol is converted secondarily to some other product(s). In order to confirm what the final product was, the reaction of 1-naphthol was studied separately under similar reaction conditions as in Fig. 1. Further details are indicated in the caption of Fig. 2. As this figure indicates, 1-naphthol is converted quantitatively to 1,4-naphthoquinone. Fig. 3 shows results of another experiment in which Pd catalyst was not used but naphthol was

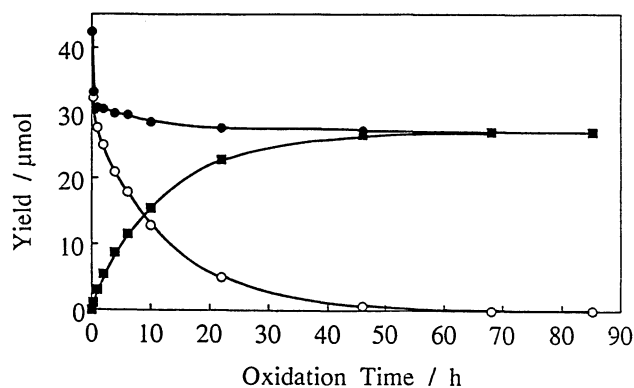


Fig. 3. Aerial oxidation of 1-naphthol in the absence of Pd-catalyst.

Solution: 2 mM 1-Naphthol and 10 mM  $\text{Cu}(\text{OAc})_2$  in  $\text{AcOH}$  ( $20 \text{ cm}^3$ ) containing both AN and  $\text{H}_2\text{O}$  at 6.5% in volume. The solution was kept under  $\text{O}_2$  atmosphere with use of neither Pd-catalyst nor  $\text{Cu}^+$  salt. ○: 1-Naphthol, ■: 1,4-Naphthoquinone, ●: Total sum.

simply dissolved in an acetic acid solution containing copper(II) acetate. In this case too, 1-naphthol was oxidized under the oxygen atmosphere to give 1,4-naphthoquinone although 35% of starting material was missed from detection by some unknown reason. In any case, it is clear that the primary product, 1-naphthol, is converted to the corresponding quinone under the conditions of the present experiments.

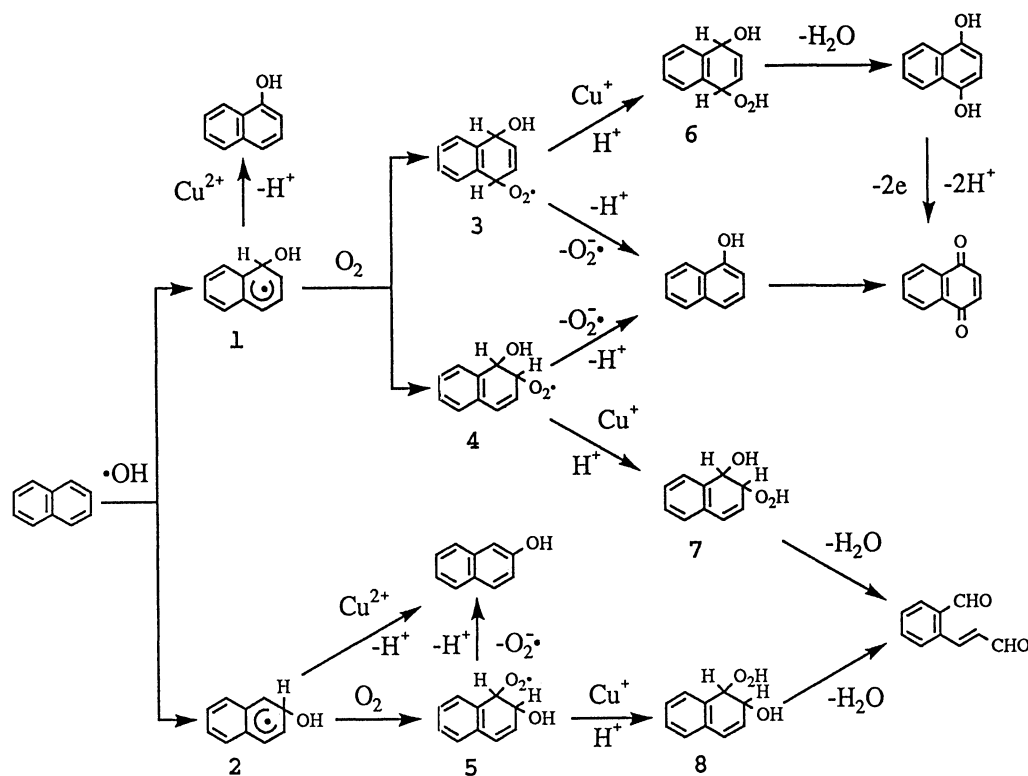
### 3. Reaction Mechanism.

We have already demon-

strated in the aqueous phase reactions that  $\text{Cu}(\text{I})$  ions activate dioxygen to produce hydrogen peroxide.<sup>5-7)</sup> Hydrogen peroxide is then reduced with  $\text{Cu}(\text{I})$  ions to water via transient formation of hydroxyl radical. Of course, there still remain several uncertainties regarding detailed points. For instance, transient formation of a copper-oxygen complex was suggested by Zuberbuehler<sup>9)</sup> and it might be involved in the reaction sequence. These, however, do not affect the following discussion. According to our view, the basic mechanism in the oxidation of benzene involves the formation of hydroxyl radical as the reactive species as described in our previous papers<sup>5-7)</sup> as well as the work of several authors.<sup>10,11)</sup> The recent publication of Okunowski<sup>12)</sup> is in consistent with our view, particularly.

The primary intermediate is hydroxycyclohexadienyl radical, an adduct of hydroxyl radical to benzene. Under the oxygen atmosphere, the cyclohexadienyl radical readily transforms to its peroxy radicals by adding dioxygen.<sup>13)</sup> The peroxy radicals are converted, depending upon the conditions of the surroundings, to either phenol or hydroquinone. We have also demonstrated that copper ions have an ability of converting efficiently a peroxy intermediate, 4-hydroxy-2,5-cyclohexadienylperoxy radical, to hydroquinone via, presumably, the corresponding hydroperoxy intermediate.<sup>5-7)</sup> These mechanisms may also be applied to the reaction of other aromatic compounds regardless of reaction media.

Generally speaking, addition of hydroxyl radical to



Scheme 1.

naphthalene has a possibility of occurring at either 1- or 2-position of the ring (see, Scheme 1). Considering the electrophilic nature of the reaction, however, one may conclude the preference for the 1-position, since the electron density is 0.362 at 1-position while it is 0.138 at 2-position.<sup>14)</sup> The relative ratio of the 1- and 2-isomers will indicate the relative rate of forming 1- and 2-hydroxylated cyclohexadienyl radicals (radicals **1** and **2**, respectively), to which dioxygen adds to give peroxy radicals (radicals **3**, **4**, and **5**). It should be noted that 1-naphthol is derived from either radical **3** or **4** by eliminating HO<sub>2</sub> radical (Dorfman's path<sup>10)</sup>). Experimental results shown in Table 3 agree with this expectation and 1-naphthol is produced as the dominant product while 2-naphthol is minor. By analogy of the reaction of benzene,<sup>5-7)</sup> direct formation of naphthols from the cyclohexadienyl radicals through the oxidative elimination of proton can be ruled out when sufficient amount of oxygen is present in the reaction medium, where radical **3** or **4** prevails.

We have shown that 1,4-naphthoquinone is certainly produced from 1-naphthol. However, this route seems to be of secondary importance in the reaction, because 1,4-naphthoquinone is produced and increases steadily from the initial stage of oxidation (see Fig. 1). The main route to lead to 1,4-naphthoquinone is believed to pass through radical **3**.

Dialdehyde may be produced through the formation of either peroxy radical **4** or **5** derived from radical **1** or **2**, respectively. Of these, the route via radical **5** and thus hydroperoxide **8** is ruled out since radical **2** is believed to have a minor contribution. Hydroperoxide **7** derived from **4** will result in a carbon-carbon bond cleavage upon elimination of water because of the steric hindrance between hydroxyl and hydroperoxyl groups. In the oxidation of benzene, a trace amount of 2,4-hexadienedial was found in the products. In contrast, naphthalene produces dialdehyde as the second main product following to the main product, 1,4-naphthoquinone. This is due to increased stability resulted from the conjugation of an unsaturated bond in peroxy radical **4** with a fused benzenoid system. As a result, contribution of the Dorfman's path<sup>10)</sup> decreases and the amount of dialdehyde increases appreciably.

1,4-Naphthoquinone is formed not only by the com-

peting reaction but also by oxidation of 1-naphthol, particularly, after the latter compound has been accumulated. As a result, the selectivity of naphthoquinone becomes more than 52% (Table 3, exp. 8). In addition, an appreciable formation of the dialdehyde from naphthalene contrasts to the negligible production of 2,4-hexadienedial from benzene. This is attributed to the difference in relative stability of oxygenated cyclohexadienyl radicals derived from benzene and naphthalene.

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