

## The Effect of Metal Ions on the Hydroxylation of Fluorobenzene and Toluene by Peroxydisulfate

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The hydroxylation of fluorobenzene and toluene and the attempted hydroxylation of anisole, nitrobenzene, and benzonitrile by  $\text{SO}_4^{\cdot-}$  has been investigated. Fluorobenzene forms almost exclusively phenol and *p*-fluorophenol and toluene forms *o*- and *p*-cresol, bibenzyl, benzyl alcohol, and benzaldehyde. The proportions of these products depend on oxidizing metal salts and pH. The phenol isomer distribution is consistent with a nucleophilic attack by  $\text{H}_2\text{O}$  at the  $\alpha$  and para positions of the radical cation. SCF-MO calculations (INDO) of the radical cations show the highest positive charge at the  $\alpha$  and para positions. The results show that in the homolytic hydroxylation of fluorobenzene and toluene a reversible acid-catalyzed dehydration will lead to an isomerization of the initially formed hydroxycyclohexadienyl radicals. The absence of hydroxylation of nitrobenzene, benzonitrile, and anisole is probably due to the smaller positive charges at the ring carbons of the radical cations of these aromatics as compared to toluene and fluorobenzene radical cation.

In the homolytic hydroxylation of aromatic compounds usually only a small fraction of the OH radicals are converted to phenols. It has been recognized for some time that in the hydroxylation of benzene in the presence of oxidizing agents, like oxygen<sup>2</sup> or metal salts,<sup>3</sup> the yield of phenol increases considerably. In recent work on the hydroxylation of nitrobenzene,<sup>4</sup> toluene,<sup>5</sup> benzonitrile,<sup>6</sup> anisole,<sup>6</sup> and fluorobenzene<sup>6</sup> in the presence of metal salts we have observed a quantitative conversion of OH radicals to phenols. The isomer distribution of the phenols however, varied in some cases quite dramatically depending on the metal salt. It seems that the initially formed hydroxycyclohexadienyl radicals undergo isomerization during the course of the reaction. Several mechanisms for this isomerization have been discussed.<sup>6</sup> Walling and Camaioni<sup>7</sup> have recently presented evidence that the well-known dehydration of the hydroxymethyl-cyclohexadienyl radicals is reversible, and proceeds via the toluene radical cation. We have suggested<sup>6</sup> that this reversible dehydration may in some cases be responsible for the change in isomer distribution in the presence of different metal salts. To test this hypothesis we have now investigated the hydroxylation and attempted hydroxylation of a number of aromatic compounds with peroxydisulfate and metal salts.

### Results

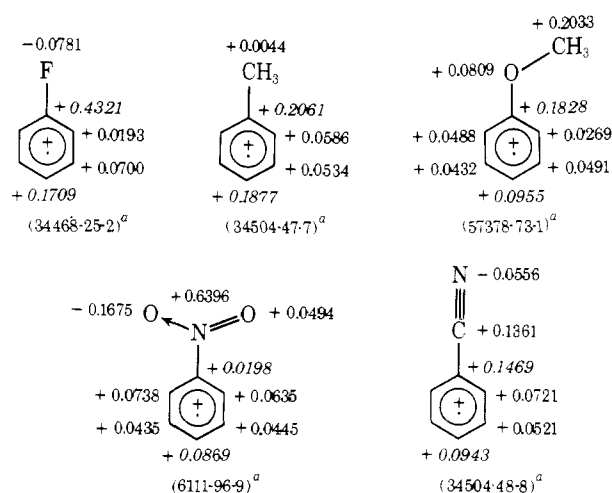
**Fluorobenzene.** The results of the hydroxylation of fluorobenzene are summarized in Table I. Under identical conditions as those shown in expt 2, no hydroxylation was observed with anisole, nitrobenzene, and benzonitrile. The products are mainly phenol and *p*-fluorophenol, whose proportions depend on the oxidizing metal salts and the pH. With  $\text{Cu}^{2+}$  as oxidizing agent we observe with decreasing pH an increase in the ratio of phenol to *p*-fluorophenol (expt 7-9). This change in product distribution with decreasing pH was, however, not observed if  $\text{K}_3\text{Fe}(\text{CN})_6$  was the oxidizing agent (expt 2, 3, 4). At constant pH the ratio of phenol to *p*-fluorophenol increases in the series  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  (expt 3, 8, 6).

**Toluene.** The results in Table II again show a considerable variation in product distribution, depending on oxidizing metal salts. With  $\text{K}_3\text{Fe}(\text{CN})_6$  we observe exclusively cresols, whereas with  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  large amounts of benzaldehyde, benzyl alcohol, and bibenzyl are also formed in addition to cresols. Analogous to the hydroxylation of fluorobenzene (Table I) the cresol isomer distribution depends on the oxidizing metal salt. With  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  we obtain much more *o*-cresol and less *p*-cresol than with  $\text{Fe}(\text{CN})_6^{3-}$ . Interesting is the comparison between  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  at the same pH (expt 6 and 9). With  $\text{Fe}^{3+}$  we obtain large amounts of bibenzyl,

whereas with  $\text{Cu}^{2+}$  we obtain only traces of bibenzyl, but instead more benzaldehyde and benzyl alcohol.

**SCF-MO Calculations.** The results are shown in Chart I. The calculations were carried out in the INDO approxi-

Chart I. Positive Charge Distributions of Some Aromatic Radical Cations (INDO Calculations)



<sup>a</sup> Registry no.

mation.<sup>8</sup> The following bond distances and bond angles were used:  $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}$ , 1.40 Å;  $\text{C}_{\text{ar}}-\text{H}$ , 1.085 Å;  $\text{C}_{\text{ar}}-\text{N}$ , 1.46 Å;  $\text{N}=\text{O}$ , 1.10 Å;  $\text{N}\rightarrow\text{O}$ , 1.18 Å;  $\text{C}_{\text{ar}}-\text{CN}$ , 1.419 Å;  $\text{C}\equiv\text{N}$ , 1.15 Å;  $\text{C}_{\text{ar}}-\text{CH}_3$ , 1.52 Å;  $\text{C}_{\text{ar}}-\text{O}$ , 1.36 Å;  $\text{O}-\text{CH}_3$ , 1.35 Å;  $\text{C}_{\text{ar}}-\text{F}$ , 1.30 Å;  $\text{C}_{\text{ali}}-\text{H}$ , 1.09 Å; tetrahedral angles 109.5°, all other angles 120°.

### Discussion

The mechanism of reaction of  $\text{SO}_4^{\cdot-}$  with aromatics has been discussed by a number of investigators. Norman et al.<sup>9,10</sup> have proposed addition of  $\text{SO}_4^{\cdot-}$  to the aromatic ring, whereas a number of other investigators<sup>11-13</sup> have proposed the formation of a radical cation. Recently Schulte-Frohlinde and co-workers<sup>14</sup> have clearly shown that radical cations are formed in the reaction of  $\text{SO}_4^{\cdot-}$  with methoxylated benzenes. The formation of radical cations is further supported by recent work of Neta et al.<sup>15</sup> These authors determined the rate constants of the reaction of  $\text{SO}_4^{\cdot-}$  with a number of aromatics, and have shown that these rate constants follow a Hammett relationship with a  $\rho$  value greater than 2. A comparison of this  $\rho$  value with the one obtained from the reaction with OH (0.5) and  $e_{\text{aq}}^-$  (3.8) suggests that the reaction involves an electron transfer and does not take place via addition like OH.

The mechanism of the hydroxylation is shown in Scheme

Table I. Hydroxylation of Fluorobenzene with Peroxydisulfate in Presence of Metal Salts<sup>a</sup>

Expt no.	Conditions <sup>b</sup>	Fluoroben- zene consumed mol/l.	Total phenols produced, mol/l. × 10 <sup>4</sup>	Fluorophenols and phenol, %			
				Ortho	Meta	Para	Phenol
1	K <sub>4</sub> Fe(CN) <sub>6</sub>	5 h	6.5 × 10 <sup>-4</sup>	4.7	Trace	60.2	35.1
2	K <sub>4</sub> Fe(CN) <sub>6</sub> + K <sub>3</sub> Fe(CN) <sub>6</sub>	pH 6.3	2 h	N.D. <sup>c</sup>	4.5	Trace	62.4
3	K <sub>4</sub> Fe(CN) <sub>6</sub> + K <sub>3</sub> Fe(CN) <sub>6</sub>	pH 2.8 <sup>d</sup>	24 h	N.D. <sup>c</sup>	5.8	Trace	61.2
4	K <sub>4</sub> Fe(CN) <sub>6</sub> + K <sub>3</sub> Fe(CN) <sub>6</sub>	pH 1.6 <sup>d</sup>	1 h	N.D. <sup>c</sup>	6.0	Trace	65.0
5	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>		5 h	N.D. <sup>c</sup>	6.29	Trace	11.8
6	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + Fe(NH <sub>4</sub> )(SO <sub>4</sub> ) <sub>2</sub>	pH 2.8	15 min	2.5 × 10 <sup>-3</sup>	6.20	Trace	13.5
7	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + CuSO <sub>4</sub>	pH 4.2	15 min	2.5 × 10 <sup>-3</sup>	7.97	Trace	38.9
8	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + CuSO <sub>4</sub>	pH 2.8 <sup>d</sup>	15 min	N.D. <sup>c</sup>	7.46	Trace	31.2
9	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + CuSO <sub>4</sub>	pH 1.8 <sup>d</sup>	15 min	N.D. <sup>c</sup>	7.88	Trace	2.0

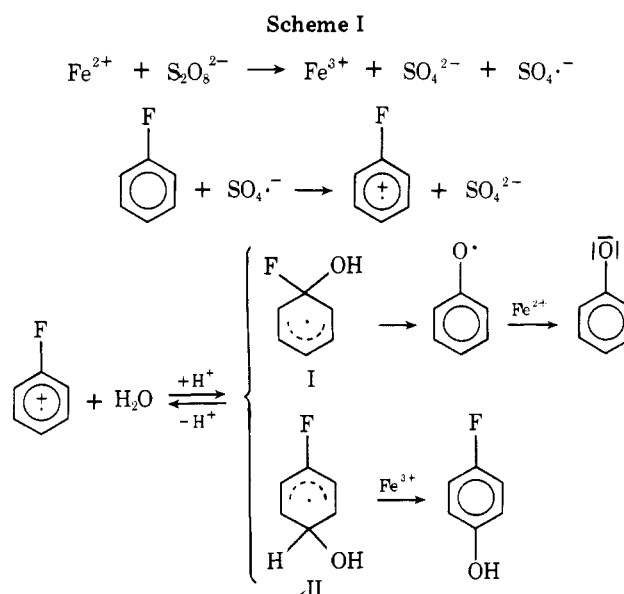
<sup>a</sup> In all experiments the concentration of fluorobenzene and peroxydisulfate was 5 × 10<sup>-3</sup> M. <sup>b</sup> Concentration of all metal salts was 5 × 10<sup>-3</sup> M. <sup>c</sup> N.D. = not determined. <sup>d</sup> In these experiments the pH was adjusted with H<sub>2</sub>SO<sub>4</sub>.

Table II. Hydroxylation of Toluene with Peroxydisulfate in Presence of Metal Salts<sup>a</sup>

Expt no.	Conditions <sup>b</sup>	Toluene con- sumed, mol/l. × 10 <sup>3</sup>	Products, mol/l. × 10 <sup>5</sup>						% Cresol				
			Ph- CHO	Ph- CH <sub>2</sub> OH	Ph- CH <sub>2</sub> ) <sub>2</sub>	<i>o</i> - Cresol	<i>m</i> - Cresol	<i>p</i> - Cresol	Ortho	Meta	Para		
1	K <sub>4</sub> Fe(CN) <sub>6</sub> + K <sub>3</sub> Fe(CN) <sub>6</sub>	pH 5.8	1 h	1.1			7.3	0.5	9.8	41.5	2.8	55.7	
2	K <sub>4</sub> Fe(CN) <sub>6</sub> + K <sub>3</sub> Fe(CN) <sub>6</sub>	pH 5.8	2.5 h	1.3			17.0	1.2	23.2	41.1	2.9	56.0	
3	K <sub>4</sub> Fe(CN) <sub>6</sub> + K <sub>3</sub> Fe(CN) <sub>6</sub>	pH 5.8	5 h	1.7			24.3	1.7	33.4	40.9	2.9	56.2	
4	K <sub>4</sub> Fe(CN) <sub>6</sub> + K <sub>3</sub> Fe(CN) <sub>6</sub>	pH 2.6 <sup>c</sup>	24 h	2.3			29.2	3.1	40.7	40.0	4.2	55.8	
5	K <sub>4</sub> Fe(CN) <sub>6</sub> + K <sub>3</sub> Fe(CN) <sub>6</sub>	pH 1.7 <sup>c</sup>	24 h	1.1			12.7	1.1	14.6	44.7	3.9	51.4	
6	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + Fe(NH <sub>4</sub> )(SO <sub>4</sub> ) <sub>2</sub>	pH 2.5	115 min	2.3	2.8	14.6	38.0	9.3	0.4	6.7	56.7	2.4	40.9
7	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + Fe(NH <sub>4</sub> )(SO <sub>4</sub> ) <sub>2</sub>	pH 2.5	1 h	2.3	2.8	16.9	39.0	8.5	0.3	5.3	60.3	2.1	37.6
8	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + CuSO <sub>4</sub>	pH 4.1	15 min	2.4	13.0	62.5	Trace	51.0	2.7	27.0	63.2	3.4	33.4
9	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + CuSO <sub>4</sub>	pH 2.4 <sup>c</sup>	15 min	2.8	17.6	76.5	Trace	29.4	1.6	14.3	64.9	3.5	31.6

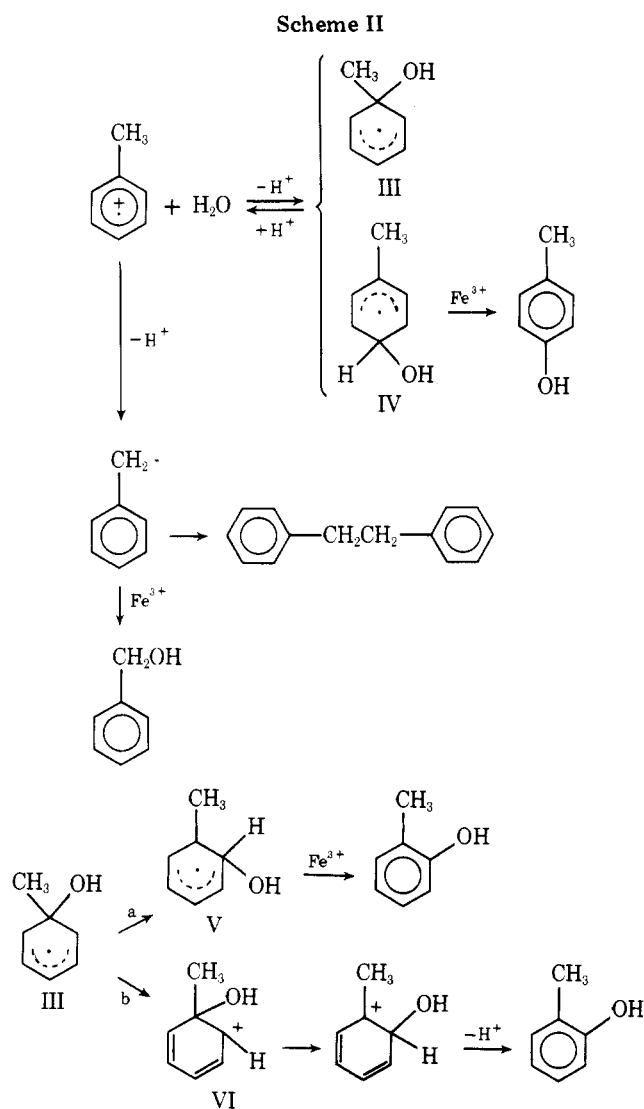
<sup>a</sup> In all experiments the concentration of toluene and peroxydisulfate was 5 × 10<sup>-3</sup> M. <sup>b</sup> All metal salts were at a concentration of 5 × 10<sup>-3</sup> M. <sup>c</sup> In these experiments the pH was adjusted with H<sub>2</sub>SO<sub>4</sub>.

I for the reaction with fluorobenzene. The fluorobenzene radical cation undergoes nucleophilic attack by water to give 1-fluoro-1-hydroxycyclohexadienyl radical (I) and 1-fluoro-4-hydroxycyclohexadienyl radical (II). These radicals are converted by metal salts to phenol and *p*-fluorophenol, respectively. The results in Table I show that almost exclusively phenol and *p*-fluorophenol are formed. The small amount of *o*-fluorophenol and the trace amounts of *m*-fluorophenol show that only an insignificant amount of ortho or meta hydroxyl radical adduct is formed, since previous results have shown that all isomeric hydroxyfluorocyclohexadienyl radicals are quantitatively oxidized by K<sub>3</sub>Fe(CN)<sub>6</sub> to the corresponding fluorophenols (43% ortho, 21% meta, 36% para). The preferred formation of I and II is to be expected on the basis of the charge distribution in the fluorobenzene radical cation. Results of SCF-MO calculations (INDO) of a number of radical cations are shown in Chart I. In the fluorobenzene radical cation the biggest positive charges are at the  $\alpha$  and para positions, and nucleophilic attack by water is expected to take place at these positions. We have pointed out<sup>6</sup> that in absence of oxidizing agents, because of the reversibility of the dehy-



dration, all hydroxyfluorocyclohexadienyl radicals will eventually give phenol. In the radiation induced hydroxylation of fluorobenzene at low pH in absence of metal salts we indeed obtained an almost quantitative conversion of OH radicals to phenol. We have further shown<sup>6</sup> that the rate constants for oxidation of the cyclohexadienyl radicals decrease in the sequence  $\text{Fe}(\text{CN})_6 > \text{Cu}^{2+} > \text{Fe}^{3+}$ . This sequence can also be deduced from our results in Table I. The ratio of phenol to *p*-fluorophenol increases in this series. The ratio also increases with decreasing pH (expt 17–19) consistent with our mechanism outlined in Scheme I, and in agreement with results on the radiation induced hydroxylations.<sup>6</sup> We can conclude that the hydroxyl radical adducts to fluorobenzene can isomerize to the  $\alpha$  and para adducts via a reversible dehydration involving the fluorobenzene radical cation.

The reaction of  $\text{SO}_4^{\cdot-}$  with toluene has been studied in absence of oxidizing metal salts,<sup>16,17</sup> and only products arising from side chain attack have been observed. Walling and Camaioni<sup>7</sup> recently reported that in the presence of oxidizing metal salts mostly cresols were formed. The hydroxylation of toluene with  $\text{SO}_4^{\cdot-}$  in the presence of  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{Fe}^{3+}$ , and  $\text{Cu}^{2+}$  gives almost exclusively *o*- and *p*-cresol (Table II). The charge distribution of the toluene radical cation again shows the highest positive charges at the  $\alpha$  and para positions, and we expect to obtain radicals III and IV as shown in Scheme II.



all isomeric hydroxymethylcyclohexadienyl radicals quantitatively to cresols<sup>5</sup> (50% *ortho*, 24% *meta*, 26% *para*).

The acid-catalyzed dehydration of hydroxymethylcyclohexadienyl radicals is well established. We therefore conclude that in the hydroxylation of toluene with hydroxyl radicals, the intermediate *m*-hydroxyl radical adduct can isomerize to the  $\alpha$  and *para* adduct via a reversible dehydration, consistent with previous results.<sup>5,6</sup>

The  $\alpha$  hydroxyl radical adduct (III) does not have the same reaction pathway available as the corresponding adduct to fluorobenzene (I). *o*-Cresol can be produced by rearrangement of III either before or after the oxidation step (pathways a or b). Eberhardt and Yoshida<sup>18</sup> have shown by SCF-MO calculations that the intermediate (V) is of lower energy than III, so rearrangement appears energetically possible. However, the present data do not allow us to distinguish between these two pathways. The absence of either of these two pathways for the intermediate 1-fluoro-1-hydroxycyclohexadienyl radical is consistent with the short lifetime of this intermediate as observed by pulse radiolysis.<sup>19</sup>

The ratio *o*-:*p*-cresol, as well as the ratio of cresols to benzyl radical derived products, depends on the oxidizing metal salt. Owing to the reversibility of the hydration, the slower the rate of oxidation of the cyclohexadienyl radicals the more bibenzyl and benzyl alcohol do we expect in agreement with experiment. We again obtain the sequence  $\text{Fe}(\text{CN})_6^{3-} > \text{Cu}^{2+} > \text{Fe}^{3+}$  for the rate of oxidation. The ratio *o*-:*p*-cresol is higher with  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  than with  $\text{Fe}(\text{CN})_6^{3-}$ . A faster rate of dehydration from IV compared to III is consistent with this result. The highest percentage of *p*-cresol is obtained with the most effective oxidizing agent, the ferricyanide ion. Comparing the experiments with  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  we can see that the rate of oxidation of benzyl radical is much faster with  $\text{Cu}^{2+}$  than with  $\text{Fe}^{3+}$  (Table II, expt 6 and 9).

**Attempted Hydroxylation of Anisole, Nitrobenzene, and Benzonitrile.** No phenols were obtained in the reaction of  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ , and  $\text{K}_3\text{Fe}(\text{CN})_6$  with anisole, nitrobenzene, and benzonitrile under the same conditions as expt 2, Table I. Since the hydroxymethoxy, hydroxynitro, and hydroxycyanocyclohexadienyl radicals are oxidized by  $\text{K}_3\text{Fe}(\text{CN})_6$  to substituted phenols,<sup>4,6</sup> we conclude that in the reaction of these aromatics with  $\text{SO}_4^{\cdot-}$  none of the above intermediates are formed. According to our mechanism (Scheme I) the formation of hydroxycyclohexadienyl radicals involves two steps, either of which may not take place. Recent work of Neta et al.<sup>15</sup> has shown that  $\text{SO}_4^{\cdot-}$  reacts with nitrobenzene and benzonitrile but at much slower rates ( $k = 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively) than with anisole ( $k = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). We may therefore conclude that in these cases the radical cations do not become hydrated to the hydroxycyclohexadienyl radicals. Since in the hydroxylation of anisole by OH radicals the acid-catalyzed dehydration is well established,<sup>20</sup> this dehydration must be irreversible consistent with the  $\text{H}_2^{18}\text{O}$  exchange experiments of Shevchuck and Vysotskaya,<sup>21</sup> and also in agreement with recent results of O'Neill et al.<sup>14</sup> A possible explanation for this behavior may be obtained from a consideration of the positive charge distribution of the radical cations of anisole, nitrobenzene, and benzonitrile (Chart I). The highest positive charges at the  $\alpha$  and *para* positions are smaller than those in the fluorobenzene and toluene radical cations. Nucleophilic attack by water at the ring positions does not take place because of the lower nucleophilicity of these radical cations.

### Experimental Section

**Materials.** All experiments were carried out using water which was doubly distilled from an all-glass still. Then it was further distilled over alkaline permanganate and acidic dichromate, and one final distillation was performed. The aromatic components were reagent grade quality, and were distilled prior to use. All metal salts were of

reagent grade quality. Aqueous solutions containing the metal salts were deoxygenated by bubbling argon through 1 l. of the solution for 1 h. The saturation was enhanced by frequent shaking. The aromatic compound was added and the solution was shaken to enhance the saturation. Then  $\text{Na}_2\text{S}_2\text{O}_8$  was added at once and the solution was shaken and left to react for different times. All solutions were homogeneous and the reactions were carried out at room temperature. The solutions were extracted once with 200 ml of ether and four times with 100 ml of ether. The ether extracts were dried over  $\text{Na}_2\text{SO}_4$ , concentrated to 10 ml, and analyzed by vapor phase chromatography. The analytical procedure has been described in detail in previous publications.<sup>4-6</sup>

**Registry No.**—Toluene, 108-88-3; peroxydisulfate, 15092-81-6; fluorobenzene, 462-06-6; anisole, 100-66-3; nitrobenzene, 98-95-3; benzonitrile, 100-47-0;  $\text{K}_4\text{Fe}(\text{CN})_6$ , 13943-58-3;  $\text{K}_3\text{Fe}(\text{CN})_6$ , 13746-66-2;  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ , 10045-89-3;  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$ , 10138-04-2;  $\text{CuSO}_4$ , 10124-44-4.

### References and Notes

- (1) This paper was prepared in connection with work under Contract E-(40-1)-1833 with the U.S. Energy Research and Development Administration (ERDA). ERDA retains a nonexclusive, royalty-free license in and to any copyright covering this paper, with the right to authorize others to reproduce all or any part of the copyrighted paper.
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## Studies on Selective Preparation of Aromatic Compounds. 12. Selective Reductive Dehalogenation of Some Halophenols with Zinc Powder in Basic and Acidic Media<sup>1</sup>

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The reductive dehalogenation of 2,4,6-trihalophenols (**1a-c**), *m*-alkylhalophenols (**7a-c** and **8c**), and *o*-alkylhalophenols (**15a-e**) were carried out with zinc powder in basic and acidic media under various conditions. 2-Bromo-6-chloro- (**3a**), 2,4-dichloro- (**3b**), 2-chloro- (**4a**), 2,6-dichloro-3-methyl- (**10b**), 2-bromo-6-chloro-3-*tert*-butyl- (**10c**), 6-bromo-3-*tert*-butyl- (**11c**), 2-chloro-3-*tert*-butyl- (**12c**), 6-bromo-2-*tert*-butyl- (**17a**), and 6-chloro-2-*tert*-butylphenol (**17b**) were selectively prepared by reduction with zinc powder in basic medium such as 10% sodium hydroxide solution. The reductive dehalogenation of halophenols with zinc powder in acidic media such as 10% HCl aqueous-EtOH and Zn-AcOH was also discussed in this paper.

It has been previously reported that *tert*-butyl,<sup>2-5</sup> chloro,<sup>6,7</sup> and bromo groups<sup>6-8</sup> could serve as positional protective groups for the preparation of some phenolic compounds. In the previous paper,<sup>1</sup> 2-bromo- and 2,4-dibromophenol were prepared in good yields by the selective reductive debromination of 2,4,6-tribromophenol with zinc powder in 10% sodium hydroxide and 10% hydrochloric acid-ethanol solution, respectively.

This paper presents additional applications of the selective

reductive dehalogenation of halophenols with zinc powder in basic or acidic media.

### Results and Discussion

The reductive dehalogenations of 2,4-dibromo-6-chloro- (**1a**), 4-bromo-2,6-dichloro- (**1b**), and 2,4,6-trichlorophenol (**1c**) were carried out under various conditions as summarized in Table I. Possible reductions products are **2**, **3**, **4**, **5**, and **6**.

Unlike 2,4,6-tribromophenol,<sup>9</sup> the treatment of **1a** with zinc

Scheme I

