

## COMMUNICATIONS TO THE EDITOR

Oxidation of Alcohols by  $\text{Ca}(\text{OCl})_2\text{-Al}_2\text{O}_3$ 

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Since the discovery of the haloform reaction, the oxidation of various organic compounds by hypohalites has been extensively studied<sup>1</sup>. Oxidation of alcohols by hypohalites, however, has not attracted much attention mainly because several excellent transition metal oxidizing agents have been available for that purpose. Meyers first reported the oxidation of primary benzylic alcohols by potassium hypochlorite<sup>2</sup>. Sodium hypochlorite has also been used for the oxidation of secondary alcohols under phase-transfer catalysis condition<sup>3</sup> and in acetic acid solution<sup>4</sup>. Keehn has used calcium hypochlorite,  $\text{Ca}(\text{OCl})_2$ , for the oxidation of alcohols in acetic acid solution<sup>5</sup>. The condition employed by Keehn can not be applicable to the practical synthesis dealing with complex and labile organic compounds. Calcium hypochlorite has a great potential for the oxidation of organic compounds owing to its inexpensiveness, stability, and ready availability as a solid. Sodium hypochlorite, on the other hand, is available only as aqueous solution and the solution is relatively unstable. Keehn<sup>5</sup>, however, by using calcium hypochlorite in acetic acid solution, failed to show that calcium hypochlorite has advantages over sodium hypochlorite for the oxidation of alcohols. As continuation of our search<sup>6</sup> for the selective oxidizing agents for alcohols, we, therefore, investigated the oxidizing ability of calcium hypochlorite under the condition which was different from Keehn's condition<sup>5</sup> and would show the superiority of calcium hypochlorite over sodium hypochlorite.

In the present article, we report a solid mixture of calcium hypochlorite and basic alumina as an efficient and inexpensive oxidizing system for alcohols. In a typical oxidation, to a stirred solution of an alcohol (0.6 mmol) in benzene (10 ml) was added a grounded solid mixture of calcium hypochlorite<sup>7</sup> (0.68 g, 2.4 mmol) and basic alumina (0.68 g) at room temperature. The mixture was stirred further at room temperature. The reaction mixture was filtered and the solvent was evaporated to afford the crude product. The yield was determined by GLC. The experimental results are summarized in Table 1.

Benzylic alcohols were readily oxidized to the corresponding aldehydes or ketones in high yields. Oxidation of cinnamyl alcohol, however, produced cinnamaldehyde in 40% yield together with several unidentified by-products. Geraniol and crotyl alcohol were converted to the corresponding carboxylic acids in high yield. On the other hand, the oxidation of saturated primary alcohols and secondary alcohols by  $\text{Ca}(\text{OCl})_2\text{-Al}_2\text{O}_3$  was sluggish, though the secondary ones were substantially oxidized to ketones. When the mixture of

Table 1. Oxidation of Alcohols by  $\text{Ca}(\text{OCl})_2\text{-Al}_2\text{O}_3$ 

Alcohol	Time, h	Product	Yield, % <sup>a</sup>
benzyl alcohol	4	aldehyde	99
benzhydrol	3	ketone	100
<i>o</i> -chlorobenzyl alcohol	7	aldehyde	95
<i>p</i> -chlorobenzyl alcohol	6	aldehyde	96
cinnamyl alcohol	4	aldehyde	40
geraniol	2	carboxylic acid	90 <sup>b</sup>
crotyl alcohol	2	carboxylic acid	85 <sup>b</sup>
2-heptanol	12	ketone	5
4- <i>t</i> -butylcyclohexanol	7	ketone	20
cyclohexanol	8	ketone	15
1-dodecanol	10	aldehyde	5
benzyl alcohol	4	benzaldehyde	99
1-dodecanol		dodecanal	5
benzyl alcohol	5	benzaldehyde	90
4- <i>t</i> -butylcyclohexanol		4- <i>t</i> -butylcyclohexanone	18

<sup>a</sup> The yields were determined by GLC. <sup>b</sup> The yield is isolated one.

benzyl alcohol and 1-dodecanol was treated with  $\text{Ca}(\text{OCl})_2\text{-Al}_2\text{O}_3$ , benzyl alcohol was selectively oxidized to benzaldehyde. With the mixture of benzyl alcohol and 4-*t*-butylcyclohexanol, benzaldehyde and a substantial amount of 4-*t*-butylcyclohexanone were produced.

Although  $\text{Ca}(\text{OCl})_2\text{-Al}_2\text{O}_3$  system did not show remarkable selectivity for the oxidation of alcohols, the efficiency, the inexpensiveness, and the ready availability of  $\text{Ca}(\text{OCl})_2\text{-Al}_2\text{O}_3$  system indicate that this solid oxidizing agent would prove to be a useful alternative to other reagents in the oxidation of benzylic alcohols.

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7. Calcium hypochlorite (bleaching powder) was purchased from Oriental Chemical Industry Co., LTD. and used without further purification; available chlorine 50%.

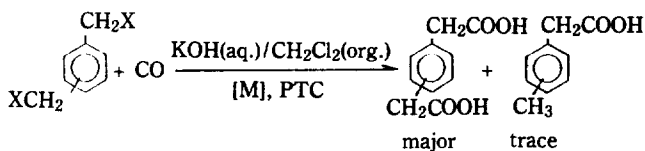
## Iron Carbonyl Complex Catalyzed Carbonylation of Xylylene Dihalides under Phase Transfer Catalyst (I)

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Recent investigations have demonstrated that the phase transfer catalysis is an exceedingly useful technique in organometallic chemistry<sup>1</sup>. One of the most useful phase transfer reactions is the carbonylation of organic halides to carboxylic acids by metal carbonyls such as cobalt carbonyl<sup>2,5</sup> and iron carbonyl<sup>6</sup>, and also by palladium complexes<sup>7</sup> at room temperature under an atmospheric pressure of carbon monoxide. The metal carbonyl complexes are the key intermediates generated, in these reactions, under the phase transfer conditions.

Various xylylene dihalides were reacted with carbon monoxide in the presence of phase transfer catalysts and metal carbonyls to give the corresponding carboxylic acids, phenylenediacetic acid in moderate yields with a trace amount of tolylacetic acid in a two-phase system, 2M-KOH (aq.)-CH<sub>2</sub>Cl<sub>2</sub>(org.) at -3°C to 7°C for 20 hrs. The reaction was depicted in Scheme and the results were listed in Table 1.



X; Br, Cl

M; Fe(CO)<sub>5</sub>, Co<sub>2</sub>(CO)<sub>8</sub>, Re<sub>2</sub>(CO)<sub>10</sub>

PTC; Crown ether or quaternary ammonium salt

### Scheme

Table 1 showed that iron pentacarbonyl in the presence of dibenzo-18-crown-6-ether as a phase transfer catalyst was the most efficient catalyst for the carbonylation of xylylene dibromide. Accordingly, in these conditions was the product obtained in moderate yield at 7°C (entry No. 2), but no carbonylation occurred at an elevated temperature, 80°C (entry No. 6). When a small amount of acetonitrile was added, the yield was slightly increased (entry No. 3).

On the other hand, the carbonylated products obtained from the *ortho*- and *meta*-xylylene dibromides were obtained

**Table 1. Products Obtained from the Carbonylation of Xylylene Dihalides by using Organometallic Phase Transfer Catalysis**

Entry No.	Substrate	Catalyst	PTC <sup>a</sup>	Reaction Temp.(°C)	Condition Time(hr)	Yield(%) <sup>b</sup>
1	<i>para</i> -	Fe(CO) <sub>5</sub>	DBCE	-3	20	38
2	<i>para</i> -	Fe(CO) <sub>5</sub>	DBCE	7	17	41
3 <sup>c</sup>	<i>para</i> -	Fe(CO) <sub>5</sub>	DBCE	7	17	46
4	<i>para</i> -	Fe(CO) <sub>5</sub>	DBCE	17	20	33
5	<i>para</i> -	Fe(CO) <sub>5</sub>	DBCE	30	30	27
6	<i>para</i> -	Fe(CO) <sub>5</sub>	DBCE	80	20	--
7	<i>para</i> -	Fe(CO) <sub>5</sub>	Aliq	7	20	--
8	<i>para</i> -	Fe(CO) <sub>5</sub>	BTMH	7	20	28
9	<i>meta</i> -	Fe(CO) <sub>5</sub>	DBCE	7	20	tr
10	<i>ortho</i> -	Fe(CO) <sub>5</sub>	DBCE	7	20	tr
11	<i>para</i> -	Co <sub>2</sub> (CO) <sub>8</sub>	DBCE	7	20	20
12	<i>para</i> -	Re <sub>2</sub> (CO) <sub>10</sub>	DBCE	7	20	20
13 <sup>d</sup>	<i>para</i> -	Fe(CO) <sub>5</sub>	DBCE	7	20	4

<sup>a</sup> PTC: DBCE; dibenzo-18-crown-6-ether, Aliq; tricaprylylmethylammonium chloride, BTMH; benzyltrimethylammonium hydroxide. <sup>b</sup> Isolated yields: Based on the amount of xylylene dihalide used. <sup>c</sup> Added small amount of acetonitrile. <sup>d</sup> When *p*-xylylene dichloride was used as a reactant, *p*-phenylenediacetic acid(4%) and *p*-tolylacetic acid(17%) were obtained.

in trace amounts under the similar conditions and intractable unknown materials were mainly formed. Dibenzo-18-crown-6-ether was more effective than the quaternary ammonium salts such as tricaprylylmethylammonium chloride (Aliquat 336) and benzyltrimethylammonium hydroxide (BTMH) (entry No. 7 and No. 8). Iron pentacarbonyl was more active than other metal carbonyl complexes such as rhenium carbonyl and cobalt carbonyl complexes (entries No. 11 and No. 12). Surprisingly, when *para*-xylylene dichloride was reacted with carbon monoxide under the same condition, *para*-tolylacetic acid was the major product (17%) and *para*-phenylene-