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### Efficient Oxidation of Alcohols with $\text{KBrO}_3$ in the Presence of Silica Chloride and Wet $\text{SiO}_2$

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## EFFICIENT OXIDATION OF ALCOHOLS WITH $\text{KBrO}_3$ IN THE PRESENCE OF SILICA CHLORIDE AND WET $\text{SiO}_2$

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*Alcohols were oxidized to their corresponding carbonyl compounds with  $\text{KBrO}_3$  in the presence of silica chloride and wet  $\text{SiO}_2$ , in solution and under solvent free conditions.*

**Keywords:** Oxidation of alcohols; silica chloride; solution; solvent free conditions

The total syntheses of complex molecules demand new methods in different areas of organic chemistry. Therefore, the development of reagents is always rewarding to synthetic organic chemists.

Oxidation is one of the most important classes of reactions in synthetic organic chemistry and the development of new oxidizing agents and the modification of known reagents have been studied actively in recent years.<sup>3,4</sup>

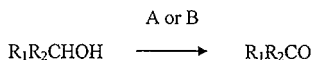
The most powerful oxidation state of bromine is (+5<sup>5</sup>). Bromates have been used for oxidation of a variety of inorganic compounds under aqueous conditions. However, a literature search shows that bromates have not found many applications as oxidizing agents in the field of organic synthesis. To the best of our knowledge only a few reports are available that deal with oxidation of organic compounds with bromate ion in either strong acidic or basic solution using sodium or potassium bromates.<sup>6–8</sup>

In connection with our ongoing research program directed toward the development of new oxidizing agents,<sup>9–12</sup> herein we report an efficient

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method for the oxidation of alcohols in solution and under solvent free conditions with  $\text{KBrO}_3$  in the presence of silica chloride and wet  $\text{SiO}_2$  (Scheme 1, Table I). Yields and reaction times are given in Table I. Overoxidation of the products using this method was not observed.



A:  $\text{KBrO}_3$ / Silica chloride/ wet  $\text{SiO}_2$ , Solvent Free, 80 °C.

B:  $\text{KBrO}_3$ / Silica chloride/ wet  $\text{SiO}_2$ , n-Hexane, reflux.

### SCHEME 1

As shown in Table I, there are appreciable differences between the results obtained in solution and those in solvent free conditions. Thus, by omitting the solvent, in addition to the ease of the work-up procedure, the reaction time was reduced and the need for solvent is avoided. This method is not suitable for the oxidation of allylic alcohols (Table I, entry 14).

It should be noted that oxidation did not proceed using  $\text{KBrO}_3$  or silica chloride or wet  $\text{SiO}_2$  alone even after prolonged heating.

In conclusion the ready availability and low cost of the reagents, the simple and clean work-up and the high product yields make this method a useful addition to the present methodologies for the oxidation of alcohols.

## EXPERIMENTAL

### Oxidation of 2-Bromobenzyl Alcohol Under Solvent-Free Conditions. A Typical Procedure

To a mixture of silica chloride (0.3 g), wet  $\text{SiO}_2$  [ $(\text{SiO}_2/\text{H}_2\text{O})$ : 50% w/w), 0.2 g] and  $\text{KBrO}_3$  (0.167 g, 1 mmol), was added 2-bromobenzyl alcohol (0.187 g, 1 mmol). The resultant mixture was heated in an oil bath (80°C) for 6 min. The progress of the reaction was monitored by TLC. The reaction mixture was triturated with  $\text{CH}_2\text{Cl}_2$  (10 mL) and then filtered. Anhydrous  $\text{MgSO}_4$  was added to the filtrate which was filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave 2-bromobenzaldehyde in 95% yield.

### Oxidation of 1-Phenylpropan-2-ol in n-Hexane. A Typical Procedure

In a round-bottomed flask (10 mL) equipped with a condenser and a magnetic stirrer a mixture of silica chloride (0.3 g), wet

**TABLE I** Oxidation of Alcohols to Their Corresponding Carbonyl Compounds in n-Hexane or Under Solvent-Free Conditions

Entry	Substrate	Product <sup>a</sup>	Solvent-free oxidation		Oxidation in solution	
			Time (min)	Yield (%) <sup>b</sup>	Time (min)	Yield (%) <sup>b</sup>
1	PhCH <sub>2</sub> OH	PhCHO	15	90	20	85
2	2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2-BrC <sub>6</sub> H <sub>4</sub> CHO	6	95	8	90
3	2-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2-ClC <sub>6</sub> H <sub>4</sub> CHO	5	85	15	86
4	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	4	90	20	90
5	4-(Me) <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	4-(Me) <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> CHO	8	92	65	85
6	PhCH(OH)Ph	PhC(OH)Ph	5	87	20	85
7	PhCH(OH)COPh	PhCOCOPh	10	85	110	86
8	PhCH(OH)CH <sub>2</sub> OH	PhCOCHO	20	82	180	80
9	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	PhCH <sub>2</sub> CH <sub>2</sub> CHO	25	92	150	80
10	PhCH <sub>2</sub> CH(OH)CH <sub>3</sub>	PhCH <sub>2</sub> COCH <sub>3</sub>	23	90	70	90
11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> OH	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CHO	5	85	10	90
12	cyclohexanol	cyclohexanone	5	90	15	86
13	4-methylcyclohexanol	4-methylcyclohexanone	10	86	15	85
14	PhCH=CHCH <sub>2</sub> OH	PhCH=CHCHO	10	— <sup>c</sup>	20	— <sup>c</sup>

<sup>a</sup>Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy.

<sup>b</sup>Isolated yield.

<sup>c</sup>Mixture of products.

$\text{SiO}_2[\text{SiO}_2/\text{H}_2\text{O}:50\% \text{ w/w}]$ , 0.2 g],  $\text{KBrO}_3$  (0.167 g, 1 mmol) and 1-phenylpropan-2-ol (0.136 g, 1 mmol) in hexane (5 ml) was prepared and refluxed for 70 min. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and the residue was washed with  $\text{CH}_2\text{Cl}_2$  (15 mL). Anhydrous  $\text{MgSO}_4$  was added to the filtrate and filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave phenylpropan-2-one in 90% yield.

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