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### NaBrO<sub>3</sub>/NaHSO<sub>4</sub> · H<sub>2</sub>O as a Versatile Reagent System for the Oxidation of Benzylic Alcohols and Aldehydes

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## **NaBrO<sub>3</sub>/NaHSO<sub>4</sub> · H<sub>2</sub>O as a Versatile Reagent System for the Oxidation of Benzylic Alcohols and Aldehydes**

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**Abstract:** The oxidation of benzylic alcohols and aldehydes by NaBrO<sub>3</sub> is efficiently promoted in the presence of NaHSO<sub>4</sub> · H<sub>2</sub>O. All reactions were performed under mild and completely heterogeneous conditions in good to high yields.

**Keywords:** Alcohols, aldehydes, NaBrO<sub>3</sub>, NaHSO<sub>4</sub> · H<sub>2</sub>O, oxidation

Because of the important role of the oxidation reactions in functional group transformations, a huge number of methods and reagents have been reported for this purpose.<sup>[1–5]</sup>

Because of its capability in multielectron transfer, sodium bromate, a commercially available reagent, is thermodynamically considered to be a strong oxidant. However, a literature search shows that sodium bromate

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individually is not able to oxidize organic compounds, and it is usually used in aqueous media in the presence of coreactants such as  $\text{NH}_4\text{Cl}$ ,<sup>[6]</sup>  $\text{H}_2\text{SO}_4$ ,<sup>[7]</sup>  $\text{AlCl}_3$ ,<sup>[8]</sup>  $\text{HClO}_4$ ,<sup>[9]</sup>  $\text{KHSO}_4$ ,<sup>[10]</sup> and  $\text{CAN}$ .<sup>[11]</sup> Most of the reported methods suffer from disadvantages such as tedious workup, long reaction times, undesirable side reactions, and the need for an excess amount of the reagent.

In continuation of our ongoing research program on the application of hydrogen sulfate salts in functional group transformations,<sup>[12–15]</sup> we have found that the benzylic alcohols and aldehydes are efficiently oxidized using  $\text{NaBrO}_3$  in the presence of  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$  (Table 1, Scheme 1).

The oxidation of benzylic alcohols to their corresponding carbonyl compounds is achieved in refluxing n-hexane and under completely heterogeneous reaction conditions in good to high yields (Table 1, entries 1–10). Overoxidation of the products under this condition was not observed.

As shown in Table 1, when the reactions are carried out in refluxing  $\text{CH}_3\text{CN}$ , primary benzylic alcohols are converted to their corresponding carboxylic acids quantitatively (entries 11–21).

Also, this reagent system is capable of oxidizing benzylic aldehydes to corresponding acids in refluxing  $\text{CH}_3\text{CN}$ . All reactions were performed under completely heterogeneous reaction conditions in good to high yields (Table 1, entries 22–35).

It should be noted that the progress of the reaction strongly depends on the presence of  $\text{H}_2\text{O}$  in the structure of  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ ; the reaction in the presence of  $\text{NaHSO}_4$  does not proceed under the same reaction conditions (Table 1, entry 36).

To show the efficiency of the selected method, Table 2 compares some of the results with some of those reported in the literature.<sup>[5,16]</sup>

In conclusion, we have demonstrated an efficient method for the oxidation of benzylic alcohols and aldehydes using  $\text{NaBrO}_3$  in the presence of  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ . The ready availability and low cost of the reagents, good to high yields of the products, simple and convenient procedure, and heterogeneous nature of the reaction conditions are among the other advantages of the present method.

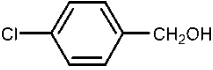
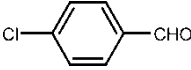
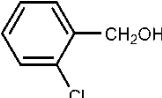

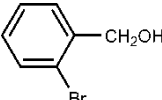
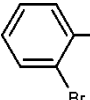
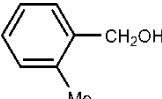

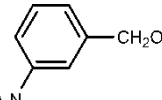
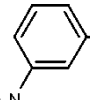
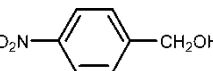
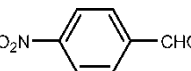
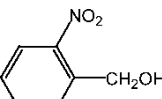

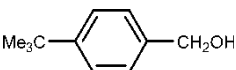
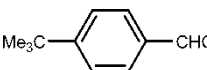
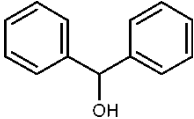
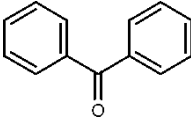
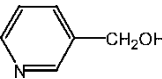

## EXPERIMENTAL

All of the products were characterized by comparison of their physical and spectral data with those of known samples. All yields refer to isolated products.

### General Procedure for the Oxidation of Benzylic Alcohols to Their Corresponding Aldehydes and Ketones

The substrate (1 mmol) was added to a suspension of  $\text{NaBrO}_3$  (0.47 g, 3 mmol) and  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$  (0.14 g, 1 mmol) in n-hexane (5 mL). The mixture was

**Table 1.** Oxidation of benzylic alcohols and aldehydes using NaBrO<sub>3</sub> in the presence of NaHSO<sub>4</sub> · H<sub>2</sub>O<sup>a</sup>

Entry	Substrate	Product	Solvent	Time (min)	Yield (%) <sup>b</sup>
1			n-hexane	2	90
2			n-hexane	10	95
3			n-hexane	3	90
4			n-hexane	17	70
5			n-hexane	18	70
6			n-hexane	60	70
7			n-hexane	65	60
8			n-hexane	10	80
9			n-hexane	7	90
10			n-hexane	10	80

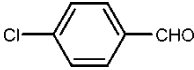
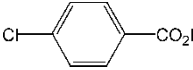
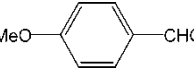
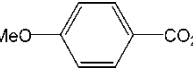
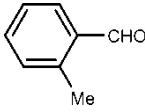
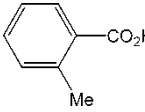
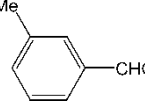
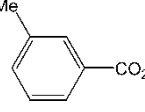
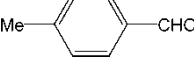
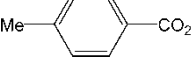
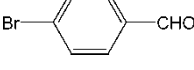
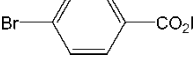
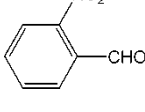
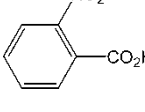
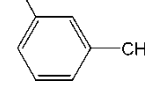
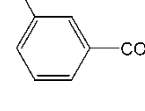
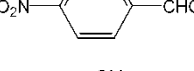
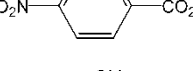
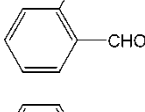
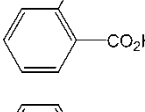


(continued)

Table 1. Continued

Entry	Substrate	Product	Solvent	Time (min)	Yield (%) <sup>b</sup>
11			CH <sub>3</sub> CN	20	90
12			CH <sub>3</sub> CN	20	80
13			CH <sub>3</sub> CN	20	95
14			CH <sub>3</sub> CN	20	95
15			CH <sub>3</sub> CN	30	90
16			CH <sub>3</sub> CN	30	80
17			CH <sub>3</sub> CN	30	80
18			CH <sub>3</sub> CN	35	70
19			CH <sub>3</sub> CN	35	70
20			CH <sub>3</sub> CN	45	80
21			CH <sub>3</sub> CN	10	95

(continued)

Table 1. Continued

Entry	Substrate	Product	Solvent	Time (min)	Yield (%) <sup>b</sup>
22			CH <sub>3</sub> CN	4	90
23			CH <sub>3</sub> CN	9	90
24			CH <sub>3</sub> CN	9	90
25			CH <sub>3</sub> CN	9	85
26			CH <sub>3</sub> CN	15	80
27			CH <sub>3</sub> CN	5	90
28			CH <sub>3</sub> CN	15	85
29			CH <sub>3</sub> CN	5	90
30			CH <sub>3</sub> CN	5	85
31			CH <sub>3</sub> CN	15	90
32			CH <sub>3</sub> CN	5	80

(continued)

Table 1. Continued

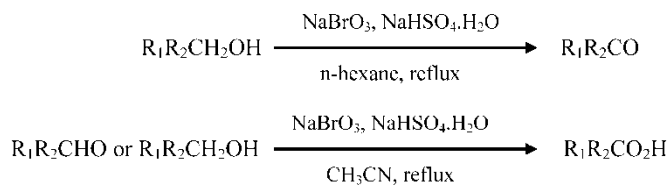
Entry	Substrate	Product	Solvent	Time (min)	Yield (%) <sup>b</sup>
33			CH <sub>3</sub> CN	5	60
34			CH <sub>3</sub> CN	15	70
35			CH <sub>3</sub> CN	15	70
36			CH <sub>3</sub> CN	20	0 <sup>c</sup>

<sup>a</sup>Isolated yields.

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

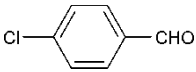
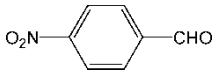
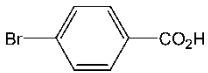
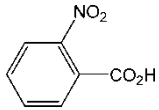
<sup>c</sup>Reaction was performed in the presence of NaHSO<sub>4</sub>, and the starting material was recovered at the end of the reaction.

refluxed for the appropriate time (Table 1). The progress of the reaction was monitored by thin-layer chromatography (TLC) (eluent: CCl<sub>4</sub>/Et<sub>2</sub>O, 6:1). After completion of the reaction, the mixture was cooled to room temperature and filtered. The solid material was washed with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solvent was evaporated, and the crude product was purified by chromatography on silica gel using an appropriate eluent. The pure products were obtained in good to high yields (Table 1).



Scheme 1.

**Table 2.** Comparison of some of the Results obtained by our method (1), with some of those reported with H<sub>3</sub>IO<sub>6</sub>/pyridinium chlorochromate (2),<sup>[16]</sup> and hydrogen peroxide in the presence of a cobalt(II) complex (3)<sup>[5]</sup>

Entry	Product	Yield, % (min)		
		(1)	(2)	(3)
1		90 (2)	89 (120)	—
2		70 (60)	71 (120)	—
3	PhCOPh	90 (7)	97 (120)	89 (180)
4		90 (5)	—	75 (420)
5		85 (15)	—	72 (540)

### General Procedure for the Oxidation of Benzylic Alcohols and Aldehydes to Their Corresponding Carboxylic Acids

To a solution of the substrate (1 mmol) in CH<sub>3</sub>CN (5 mL), NaBrO<sub>3</sub> (0.47 g, 3 mmol) and NaHSO<sub>4</sub> · H<sub>2</sub>O (0.144 g, 1 mmol) were added and refluxed for the appropriate time (Table 1). The progress of the reaction was monitored by TLC (eluent: CCl<sub>4</sub>/Et<sub>2</sub>O, 6:1). After completion of the reaction, the mixture was cooled to room temperature and filtered. The solid material was washed with CH<sub>3</sub>CN (10 mL). Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carboxylic acid in good to high yields (Table 1).

### ACKNOWLEDGMENT

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