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**SHORT COMMUNICATION**

# FACILE, MILD AND SELECTIVE SILICA SULFURIC ACID CATALYZED OXIDATION OF BENZYLALCOHOLS TO BENZALDEHYDE DERIVATIVES BY POTASSIUM PEROXODISULFATE

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**ABSTRACT**. An efficient, facile, and mild oxidation of a variety of primary benzylic alcohols to the corresponding aldehydes with potassium peroxodisulfate in the presence of a catalytic amount of sodium chloride and silica sulfuric acid (SSA) in acetonitrile as solvent is reported. It is a renowned fact that potassium peroxodisulfate acts as a powerful oxidizing agent and the control of conditions is difficult. For this purpose, SSA as a mild, efficient and reusable solid acid catalyst was used to afford the carbonyl compounds in excellent yields and short time. The structure of all of the resulting products was confirmed by FT-IR spectroscopy.

**KEY WORDS**: Potassium peroxodisulfate, Silica sulfuric acid, Benzylic alcohol, Oxidizing agent

## INTRODUCTION

The oxidation of benzylic alcohols to carbonyl compounds is a fundamental transformation in synthetic organic chemistry. Many methods using a variety of reagents have been reported over the years, most notably the Oppenhauer and Swern oxidations and reactions utilizing high valent metal compounds such as manganese dioxide, ammonium perruthenates and pyridinium chlorochromate. However, the majority of known methods generally suffer from one or more disadvantages such as difficulty in manipulation, long reaction times, and utilization of toxic reagents [1-3]. Therefore, it is still attractive to develop a new efficient oxidant with properties of high stability, low toxicity, ready availability and high selectivity for the benzylic oxidations and overcome typical problems that occur during oxidation and accept wide rang of alcohols with improved selectivity. In addition, the oxidation of alkylarene compounds and benzylic alcohols to their corresponding carbonyl compounds is of significant importance in synthetic organic chemistry for basic research and industrial manufacturing, because of the complexities in natural product structures. The international annual production of carbonyl compounds is over $1\times10^7$ tons and the largest part of these compounds are produced from the oxidation of alkylarenes and alcohols [4-8].

Peroxodisulfate ion is an excellent and versatile oxidant; used mostly for the oxidation of synthetic and natural organic and inorganic compounds in aqueous solution and it has also been employed as an initiator for the polymerization of vinyl monomers [9-17]. In spite of the great convenience of using $S_2O_8^{2-}$, many oxidations by peroxodisulfate do not proceed at a convenient rate. This can be largely attributed to the rate-limiting homolysis ($S_2O_8^{2-} \rightarrow 2\ SO_4^{-}$), which has the activation energy of approximately 30 kcal/mol.

Thus certain limitations may be observed with this reagent. The decomposition of the peroxodisulfate ion requires strong mineral acids and heavy metal ions as catalysts [18]. For this purpose, silica sulfuric acid (SSA), as a mild, inexpensive, efficient, reusable, environmentally

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*Corresponding author. E-mail: mkmohamadi@yahoo.com safe and solid heterogeneous acid catalyst or promoter, could be used. SSA have frequently been used for many organic transformations because of its low cost, ease of preparation, catalyst recycling, ease of handling and easy separation from reactants and products [19-24]. SSA can enhance the reactivity and selectivity of many types of reaction, such as oxidation [25], carbon-carbon bond formation for example aldol and Knovenagel condensation [26, 27], Friedel-Crafts alkylation [28], Beckmann rearrangement [29], cycloaddition [30], aromatization [31] protection [32] and deprotection [33]. It is easily prepared by treatment of silica gel with chlorosulfonic acid at room temperature [34]. It must be noted that the preparation method is simple, clean, and without work-up procedure, because hydrogen chloride gas is evolved from the reaction vessel immediately. In this paper we wish to report a simple, mild, convenient and selective procedure for the oxidation of benzylic alcohols to their corresponding aldehyde compounds with peroxodisulfate in the presence of sodium chloride (NaCl) and SSA. This method is shown to be of considerable utility for the oxidation of benzylic alcohols at benzylic position.

## EXPERIMENTAL

*General*. Chemicals were purchased from Merck Co. (Darmstadt, Germany) and were used without further purification. Solvents were dried over BaO and then were distilled under reduced pressure. FT-IR spectra were recorded on Perkin Elmer Spectrum Rx 1 spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers ($cm^{-1}$). Band intensities are assigned as weak (w), medium (m), strong (s) and broad (br). Purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV254 plates. All yields refer to isolated products.

*Preparation of SSA*. SSA was prepared by the reaction of chlorosulfonic acid with silica gel [35].

*General procedure for peroxodisulfate oxidation of benzylic alcohols*. To a solution of alcohol (1 mmol) in $CH_3CN$ (8 mL) in a 50 mL round-bottomed flask-equipped with a condenser and a magnetic stirrer was added potassium peroxodisulfate (1 mmol) (0.27 g), NaCl (1 mmol = 0.06 g NaCl) and SSA (0.07 g) in three portions. The reaction mixture was stirred magnetically under reflux condition for the appropriate time indicated in Table 1. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and the solid was washed with ether (5-15 mL). The filtrates were evaporated and the residue was purified on a silica-gel plate with appropriate eluent. Pure carbonyl compounds were obtained in 72-96% yields (Table 1).

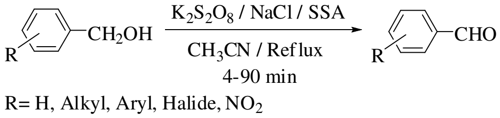
*Characterization of products*. The structure of all products was confirmed by FT-IR spectroscopy. All of these carbonyl compounds exhibiting absorption at 1660-1750 $cm^{-1}$ range are commonly attributed to the stretching vibration of carbonyl groups. They also exhibiting absorption at 2850-2750 $cm^{-1}$ range are commonly attributed to the aldehyde C-H. The absorption band with near medium intensity with absorption band of carbonyl group is a good testimony for existence of aldehyde. FT-IR data for all of the resulting aldehydes are listed in Table 1.

Table 1. FT-IR spectral data for some of synthesized compounds.

| Product | Spectral data |
|---|---|
| PhCHO | FT-IR (KBr, cm$^{-1}$): 3080 (m, br), 2850 (m), 2735 (m), 1702 (s), 1580 (m), 1455 (s), 1288 (s), 1200 (s), 1017 (w), 826 (s), 743 (s), 685 (s), 614 (m). |
| *p*-$CH_3OC_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 2935 (m, br), 2865 (m), 2724 (m), 1705 (s), 1604 (s), 1506 (s), 1455 (w), 1268 (s), 1204 (m), 1155 (s), 1124 (m), 846 (s). |
| *m*-$CH_3OC_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 3084 (m, br), 2912 (m, br), 2825 (m), 2716 (w), 1736 (s), 1603 (s), 1487 (m, br), 1276 (s), 1171 (m), 1037 (m), 780 (m), 727 (m). |
| *p*-$Me_3CC_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 2965 (m, br), 2865 (m), 2732 (w) , 2672 (m), 2552 (m), 2285 (w), 1660 (s), 1610 (s), 1570 (m), 1423 (s), 1289 (s), 1188 (s), 1015 (m), 942 (m, br), 856 (m), 779 (m), 708 (m). |
| *o*-$NO_2C_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 3106 (m, br), 2872 (m, br), 2755 (m), 1701 (s), 1604 (m), 1564 (w), 1527 (s), 1455 (w),1392 (w), 1343 (s), 1196 (s), 864 (m), 783 (m). |
| *m*-$NO_2C_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 3068 (m, br), 2878 (m), 2720 (m), 1706 (s), 1616 (s), 1535 (w), 1352 (w), 1203 (s), 1077 (m), 933 (m), 811 (s), 729 (s). |
| *p*-$NO_2C_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 3107 (m, br), 2849 (m), 2778 (m) ,1710 (s), 1606 (s), 1540 (s), 1325 (m), 1198 (s), 1104 (m), 1008 (m), 850 (s), 816 (s), 739 (s). |
| *o*-$BrC_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 3063 (m, br), 2859 (m, br), 2752 (m), 1702 (s), 1591 (s), 1449 (m), 1396 (m), 1265 (s), 1168 (w), 1033 (m), 963 (w), 822 (s), 766 (m). |
| *p*-$BrC_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 3015 (m, br, 2859 (m, br), 2763 (w), 1690 (s), 1588 (s), 1479 (m), 1384 (m), 1205 (s), 1065 (s), 1248 (m), 835 (m), 810 (m). |
| *o*-$ClC_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 3071 (m, br), 2862 (s),2744 (m), 1754 (m), 1675 (s), 1592 (s), 1460 (m), 1268 (w), 1200 (s), 1052 (s), 956 (w), 1077 (w), 824 (s), 765 (s), 715 (s). |
| *m*-$IC_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 2922 (m, br), 2857 (m) ,2715 (w) ,1699 (s), 1567 (m), 1467 (w), 1432 (w), 1378 (s), 1295 (w),1058 (w), 997 (m), 945 (m), 781 (s). |
| *p*-$C_6H_5C_6H_4CHO$ | FT-IR (KBr, cm$^{-1}$): 2972 (m, br), 2871 (m, br), 2748 (w), 1700 (s), 1604 (s), 1566 (w), 1459 (w), 1214 (m), 1176 (w), 828 (w), 767 (s), 709 (m). |

## RESULTS AND DISCUSSION

As development of our studies on the oxidation reaction with peroxodisulfate, we wish to report a simple and efficient method for the mild and selective oxidation of a series of benzylic alcohols to their corresponding aldehydes as shown in Scheme 1. In spite of the great convenience of using $K_2S_2O_8$ and relatively high oxidation potential, oxidation by peroxodisulfate generally does not proceed at a convenient rate. Thus certain limitations may be observed with this reagent. Hence, SSA was used as catalyst which could carry out the oxidation reaction. Thermal conditions should be adjusted for using of inorganic salts, because these compounds decompose at high temperature. Consequently, the temperature was controlled during the oxidation reaction. The solubility of the oxidant was investigated in several solvents such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF), acetonitrile ($CH_3CN$), carbontetrachloride ($CCl_4$), dichloromethane ($CH_2Cl_2$), chloroform ($CHCl_3$), diethyl ether and acetone. The experimental results showed that $CH_3CN$ was the best choice for this purpose. At first, *p*-methoxybenzyl alcohol was selected as a typical compound and reacted in the presence of oxidant, NaCl and SSA. In order to find the optimum time of reaction and the best solvent, the effect of solvent and reaction time on the yields of the products was studied (Scheme 1).



Scheme 1

Table 2. The effect of solvent on the typical oxidation time and product yield of *p*-methoxybenzyl in the presence of $K_2S_2O_8$/NaCl/SSA.

| Solvent | Time (min) | Yield (%) | Solvent | Time (min) | Yield (%) |
|---|---|---|---|---|---|
| DMSO | 20 | 57 | $CH_2Cl_2$ | 60 | 30 |
| DMF | 38 | 40 | $CHCl_3$ | 80 | 50 |
| $CH_3CN$ | 15 | 95 | $Et_2O$ | 60 | 38 |
| $CCl_4$ | 80 | 30 | Aceton | 35 | 45 |

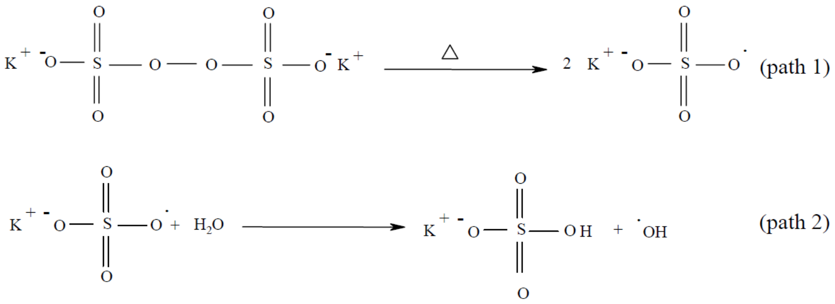
Table 2 shows that the optimum result was obtained after 15 min in $CH_3CN$. In other solvents, reaction gave low yields. The carbonyl compounds prepared in this solvent at a special time and their yields are listed in Table 3.

Table 3. SSA/NaCl-catalyzed oxidation of benzylic alcohols with $K_2S_2O_8$ in refluxing $CH_3CN$.

| Entry | Substrate | Time (min) | Yield (%)a | Product b |
|---|---|---|---|---|
| 1 | $PhCH_2OH$ | 5 | 85 | PhCHO |
| 2 | *p*-$CH_3OC_6H_4CH_2OH$ | 4 | 96 | *p*-$CH_3OC_6H_4CHO$ |
| 3 | *m*-$CH_3OC_6H_4CH_2OH$ | 7 | 90 | *m*-$CH_3OC_6H_4CHO$ |
| 4 | *p*-$Me_3CC_6H_4CH_2OH$ | 7 | 83 | *p*-$Me_3CC_6H_4CHO$ |
| 5 | *o*-$NO_2C_6H_4CH_2OH$ | 90 | 74 | *o*-$NO_2C_6H_4CHO$ |
| 6 | *m*-$NO_2C_6H_4CH_2OH$ | 45 | 86 | *m*-$NO_2C_6H_4CHO$ |
| 7 | *p*-$NO_2C_6H_4CH_2OH$ | 60 | 72 | *p*-$NO_2C_6H_4CHO$ |
| 8 | *o*-$BrC_6H_4CH_2OH$ | 7 | 85 | *o*-$BrC_6H_4CHO$ |
| 9 | *p*-$BrC_6H_4CH_2OH$ | 9 | 86 | *p*-$BrC_6H_4CHO$ |
| 10 | *o*-$ClC_6H_4CH_2OH$ | 6 | 82 | *o*-$ClC_6H_4CHO$ |
| 11 | *m*-$IC_6H_4CH_2OH$ | 16 | 95 | *m*-$IC_6H_4CHO$ |
| 12 | *p*-$C_6H_5C_6H_4CH_2OH$ | 50 | 93 | *p*-$C_6H_5C_6H_4CHO$ |

[a]Yields refer to isolated yields. [b]Products were characterized by comparison of their physical and spectra data with authentic samples.

As shown in Table 3, various types of benzylic alcohols were reacted efficiently with $K_2S_2O_8$ to afford corresponding aldehydes in good to excellent yields (entries 1-12). Further oxidation of aldehydes to their carboxylic acids and also fragmentation products were not observed in this method. In order to show the better chemo selectivity of the described method, an equimolar mixture of benzyl, allyl and alkyl alcohols was treated with this reagent in refluxing $CH_3CN$ for 3 h. We found that *p*-methoxybenzyl alcohol was oxidized selectively in the presence of alkyl alcohols. This selectivity is of vital importance in modern synthetic methodologies. The mechanism of reaction was been seemed to be the hydrogen attraction of hydroxyl group in the bezylic alcohol by the $K^+$ $SO_4OH^-$ (produced in path 2) (Scheme 2) that followed with radically attack of hydroxyl radical group to the α-H and then formation of keto group. The rule of NaCl was seemed to be for the increase of reaction ionic power and then better developing the oxidation reaction procedure.



Scheme 2

The noteworthy advantages of this reagent lie in its reusability. Thus Table 4 demonstrates the reusability of the oxidant after 4 replicate oxidations of *p*-methoxy benzyl alcohol to *p*-methoxy benzaldehyde. The oxidant was recovered by stirring of the white solid, which obtained after oxidation of alcohols, with $K_2S_2O_8$ for 2 h.

Table 4. Reusability of oxidant[a].

| Experimental | Yield (%) |
|---|---|
| 1st | 96 |
| 2nd | 93 |
| 3rd | 95 |

[a] All reactions are carried out under similar conditions.

## CONCLUSIONS

In this work, a series of benzyl aldehyde compound were synthesized via mild oxidation of benzylic alcohols with potassium peroxodisulfate as an oxidant in the presence of NaCl and SSA as heterogeneous catalyst. It is evident from the results presented in Table 2 that this procedure for oxidation of benzylic alkohols was a mild, convenient, and versatile method and is broadly applicable for the conversion of benzyl alcohol compounds into their aldehyde derivatives. The said conditions have many advantages such as: i) short time of oxidation, ii) high selectivity of oxidant in the presence of NaCl/SSA, iii) mild condition, iv) stability of oxidant and v) easy preparation of oxidant.

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