

## Benzyltriphenylphosphonium Peroxymonosulfate: As a Novel and Efficient Reagent for Oxidation of Alcohols under Solvent-Free Conditions

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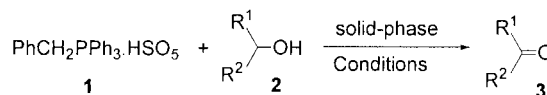
This paper describes the oxidation of alcohols under solvent-free conditions using benzyltriphenylphosphonium peroxymonosulfate, which has been prepared by mixing an aqueous solution of benzyltriphenylphosphonium chloride with oxone<sup>®</sup> at room temperature. This reagent is stable white powder, which may be stored for months without loss of its activity. This compound is readily soluble in organic solvents such as acetonitrile, chloroform, and dichloromethane and slightly soluble in carbon tetrachloride, ether, and hexane.

Oxidation of organic compounds in the absence of protic solvent is of importance. This subject has been under intensive investigation in recent years. Along this line, we have introduced potentially oxidants in recent years.<sup>1</sup>

Benzyltriphenylphosphonium peroxymonosulfate (**1**) has been prepared readily from an aqueous solution of oxone and benzyltriphenylphosphonium chloride in a quantitative yield at room temperature. This oxidizing agent is a white and stable solid compound, which could be stored for months without losing its activity. Heterogeneous reactions that are facilitated by supported reagents on various solid inorganic surfaces have received attention in recent years.<sup>2-6</sup> The advantage of these methods over conventional homogeneous reactions is that they provide greater selectivity enhanced reaction rates, cleaner products and manipulative simplicity. In continuation of our ongoing program to develop environmentally benign methods using solid supports,<sup>7</sup> here we wish to report the oxidation of alcohols with (**1**) in the presence of AlCl<sub>3</sub>. The oxidation of alcohols with (**1**) in the presence of AlCl<sub>3</sub> proceeds well under solid-phase conditions. Benzylic alcohols (**2**) are oxidized to the corresponding carbonyl compounds in high yields (Table 1); allylic alcohols have also been selectively oxidized to  $\alpha,\beta$ -unsaturated carbonyl compounds without cleavage of the carbon-carbon double bonds;  $\alpha$ -hydroxy ketone was converted to  $\alpha$ -diketone in excellent yield (Table 1). Because of the low reactivity of aliphatic alcohols only benzylic and allylic alcohols could be converted into the corresponding carbonyl compounds. The process in it entirely involves a simple mixing of benzyltriphenylphosphonium peroxymonosulfate (PhCH<sub>2</sub>PPh<sub>3</sub>·HSO<sub>5</sub>) (**1**) and alcohols (**2**) in the presence of AlCl<sub>3</sub> (1 molar ratio) in a mortar and grinding the mixture for the time specified in Table 1 at room temperature. The yields of the reactions are excellent (80-100%) and the reaction times are exceedingly short (5-20 min).

Oxidation of benzyl alcohol to its corresponding aldehyde with reagent (**1**) in the presence of various Lewis acids such as ZnCl<sub>2</sub>, FeCl<sub>3</sub>, BiCl<sub>3</sub> and AlCl<sub>3</sub> was examined under solid-state conditions. The rate of the reaction was monitored by TLC. Surprisingly, only AlCl<sub>3</sub> was recognized to be effective catalysis for this purpose. The reaction in the presence of ZnCl<sub>2</sub>,

FeCl<sub>3</sub>, and BiCl<sub>3</sub> (1 molar ratio) proceeds with lower efficiency even with higher molar ratio (2 molar ratio) of oxidant.



A noteworthy advantage of this reaction lies in its ability to selectively oxidize benzylic and allylic alcohols in the presence of other oxidizable functional groups such as double bonds. When we treated  $\alpha,\beta$ -unsaturated alcohols with (**1**), only the OH group was selectively oxidized to the corresponding carbonyl compounds; the double bonds remained intact (Table 1). In order to evaluate the selectivity of reagent (**1**), the competitive reactions shown in Eqs. 1-3 were carried out. When an equimolar amount of 2-phenethyl alcohol and benzyl alcohol was treated with 1.2 molar ratio of reagent (**1**) in the presence of AlCl<sub>3</sub> (1 molar ratio), only benzyl alcohol was selectively

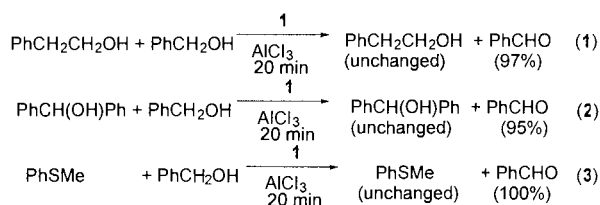
**Table 1.** Oxidation of alcohols (**2**) to carbonyl compounds (**3**) under solid-phase conditions<sup>a,b</sup>

R <sup>1</sup>	R <sup>2</sup>	Time /min	Yield /%	mp °C or bp °C/torr (lit. 1-3)
C <sub>6</sub> H <sub>5</sub>	H	10	90	179/760 (178)
4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	H	5	100	104 (104-105)
3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	5	100	82 (81-83)
4-PhC <sub>6</sub> H <sub>4</sub>	Me	5	99	117-119 (117)
2-pyridyl	C <sub>6</sub> H <sub>5</sub>	5	90	84/760 (83-85)
C <sub>6</sub> H <sub>5</sub>	Me	5	86	119/760 (118)
4-MeOC <sub>6</sub> H <sub>4</sub>	H	15	80	35-37 (35-37)
2-MeOC <sub>6</sub> H <sub>4</sub>	H	15	95	47 (47-49)
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	5	93	102/760 (101)
3-MeOC <sub>6</sub> H <sub>4</sub>	H	5	80	45 (45-47)
4-ClC <sub>6</sub> H <sub>4</sub>	H	5	92	196/760 (195)
2-ClC <sub>6</sub> H <sub>4</sub>	H	5	96	212/760 (212)
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	5	90	54 (54-55)
4-BrC <sub>6</sub> H <sub>4</sub>	Me	5	97	49-50 (49-51)
4-ClC <sub>6</sub> H <sub>4</sub>	Me	5	89	232/760 (232)
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CO	5	85	95 (94-96)
2,3-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	5	91	49-52 (49-53)
C <sub>6</sub> H <sub>5</sub> CH=CH	C <sub>6</sub> H <sub>5</sub>	5	94	54-57 (54-57)
C <sub>6</sub> H <sub>5</sub> CH=CH	Me	5	97	39 (39-40)
4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH=CH	H	5	98	138-142 (139)
C <sub>6</sub> H <sub>5</sub> CH=CH	H	5	92	127/760 (125)
C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub>	H	20	nr	-
C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>3</sub>	H	20	nr	-

<sup>a</sup>Confirmed by comparison with authentic sample (IR, TLC and NMR).

<sup>b</sup>Yield of isolated pure product after chromatography or distillation.

oxidized (Eq. 1). Treatment of benzyl alcohol with one mole ratio of reagent (1) in the presence of an equimolar amount of diphenylmethanol led to exclusive oxidation of benzyl alcohol (Eq. 2). Interestingly in the oxidation of alcohols the overoxidation of products to the corresponding carboxylic acids was not observed at all. When we treated one equimolar amount of benzyl alcohol with reagent (1) in the presence of an equimolar amount of phenylmethyl sulfide, only the benzyl alcohol was selectively oxidized (Eq. 3).



In summary, we report here the preparation of benzyltriphenylphosphonium peroxymonosulfate (1) as a mild, inexpensive and stable oxidizing agent. This oxidizing reagent is very easily prepared from commercially available starting materials and can be stored for months without losing its activity. The reagent is soluble in acetonitrile, chloroform and dichloromethane and slightly soluble in carbon tetrachloride, ether and hexane. This reagent is an efficient, rapid, mild and inexpensive reagent for oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds under solvent-free condition in the presence of  $\text{AlCl}_3$ . This method is superior to previously reported methods in terms of high yields, purity of products, facile work-up, cheaper reagent and short reaction time.

All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples (IR and  $^1\text{H-NMR}$  spectrum, thin layer chromatography, melting and boiling point). All  $^1\text{H-NMR}$  were recorded at 90 MHz in  $\text{CCl}_4$  relative to TMS (0.00 ppm) and IR spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectra of solid were carried out using KBr pellets. All reactions were carried out under solvent-free conditions. Elemental analysis was performed by the Research Institute of Petroleum Industry, Tehran, I.R. Iran.

A solution of benzyltriphenylphosphonium chloride (19.0 g, 49 mmol) in 100 ml of water was prepared, then oxone ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ , 30.06 g, 49 mmol) in water (100 mL) was added dropwise to the above solution and stirred for 1 h at room temperature. The resulting precipitate was filtered and washed with cooled distilled water (50 mL), and dried in a desiccator under vacuum over calcium chloride to afford a white powder (21.7 g, 95% yield), which was decomposed at 144-146 °C to a dark-brown material.  $^1\text{H NMR}$ :  $\delta$  7.90-6.85 (m, 20 H), 4.7 (d,  $J = 25.6$  Hz,  $\text{CH}_2\text{P}$ ). IR (KBr): 1298, 1269, 1098, 1060, 700, 658, 590  $\text{cm}^{-1}$ . The white solid was then titrated three times as following procedure:<sup>8</sup> To a 0.244 g sample was added 0.5 ml of glacial acetic acid and 1 mL of 10 % aqueous NaI. After dilution to 5 mL with THF, it was titrated with 5.20 mL of 0.1012 M solution of sodium sulfite to the yellow endpoint. The average of the three trials gave 99 % ( $24.24 \pm 0.6\%$  by weight) of active oxidizing agent ( $\text{HSO}_5^-$ ). Anal Calcd for

$\text{C}_{25}\text{H}_{23}\text{O}_5\text{PS}$ : C, 64.37; H 4.97; S, 6.87%. Found: 64.20; H, 5.20; S, 6.60%.

Oxidation of alcohols (2) with reagent (1) to the corresponding carbonyl compounds (3): A mixture of alcohol (2) (1 mmol), oxidizing agent (1) (1.2 mmol, 0.56 g) and  $\text{AlCl}_3$  (1 mmol, 0.13 g) in a mortar was ground for the time specified in Table 1. When TLC showed complete disappearance of alcohol, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . Evaporation of the solvent gave corresponding carbonyl compound (3). The product was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane as eluent (10:90).

Competitive oxidation: Typical procedure: A mixture of benzyl alcohol (1 mmol, 0.11 g), diphenylmethanol (1 mmol, 0.19 g), oxidizing agent (1) (1.2 mmol, 0.56 g) and  $\text{AlCl}_3$  (1 mmol, 0.13 g) in a mortar was ground. The mixture was ground until TLC showed complete disappearance of benzyl alcohol (20 min). The other competitive reactions for Eqs. 1-3 is the same as above.

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