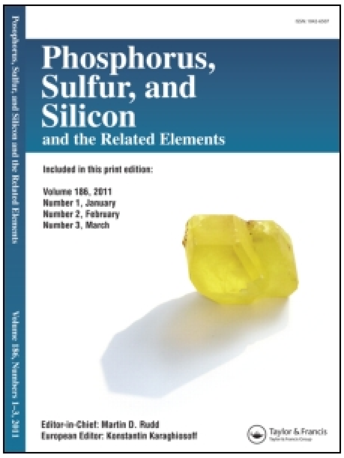

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OXIDATION OF ALCOHOLS WITH BENZYLTRIPHENYLPHOSPHONIUM PEROXYMONOSULFATE UNDER NON-AQUEOUS CONDITIONS

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Oxidation of allylic and benzylic alcohols with benzyltriphenylphosphonium peroxymonosulfate ($PhCH_2Ph_3P^+HSO_5^-$) **1** (BTPPMS) in refluxing acetonitrile is reported. The oxidation in the presence of a catalytic amount of bismuth chloride enhances the rate.

Keywords: : Alcohols; Benzyltriphenylphosphonium peroxymonosulfate; Bismuth chloride; Oxidation; Potassium peroxymonosulfate (Oxone®)

INTRODUCTION

Oxidation of organic compounds in the absence of a protic solvent is of importance. This subject has been under intensive investigation in recent years.[1–12] Along this line, we have introduced potentially oxidants in recent years.[13] In this paper, we wish to report benzyltriphenylphosphonium peroxymonosulfate **1** as a mild and novel oxidizing reagent for oxidation of allylic and benzylic alcohols under non-aqueous conditions. This reagent is readily prepared by the dropwise addition of an aqueous solution of oxone® ($2KHSO_5.KHSO_4.K2SO_4$), to an aqueous solution of benzyltriphenylphosphonium chloride in quantitative yield at room temperature.

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RESULTS AND DISCUSSION

The oxidation of alcohols with $PhCH_2Ph_3P^+HSO_5^-$ **1** (BTPPMS) proceeds under non-aqueous conditions. The effect of various solvents such as Et_2O, CH_2Cl_2, THF, $CHCl_3$ and CH_3CN on the oxidation of 3,4-dimethoxybenzyl alcohol with $PhCH_2Ph_3P^+HSO_5^-$ **1** were examined. TLC was used to monitor the rate of the oxidation. Only acetonitrile was a suitable solvent for this oxidation system (Table I).

TABLE I Oxidation of 3,4-Dimethoxybenzyl Alcohol with Reagent **1** in Different Refluxing Solvents [a,b]

Entry	*Solvent*	*Time (hr)*	*Yield (%)*
1	Et_2O	2	30
2	THF	2	40
3	CH_2Cl_2	2	60
4	$CHCl_3$	2	70
5	CH_3CN	2	100

a. Monitored by TLC analysis.
b. Oxidant/Alcohol (1:1).

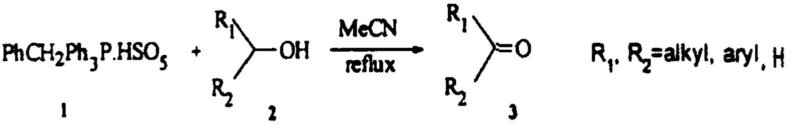
Oxidation of 3,4-dimethoxybenzyl alcohol to its corresponding aldehyde with reagent **1** in the presence of various Lewis acids such as $ZnCl_2$, $FeCl_3$, $BiCl_3$ and $AlCl_3$ were also examined in refluxing acetonitrile. Surprisingly, only $BiCl_3$ was shown to be effective catalyst for this purpose. (Table II). The reaction in the presence of $ZnCl_2$, $FeCl_3$, and $AlCl_3$ (0.5 mmol) proceeds with lower efficiency even with a higher molar ratio of the oxidant (1.5 mmol) in comparison with the amount of oxidant used in the presence of $BiCl_3$(0.4 mmol). This could be the effect of softness or less solubility of $BiCl_3$in comparison with the other Lewis acids which have been used in these experiments. Allylic and benzylic alcohols **2** are oxidized to the corresponding carbonyl compounds **3** in refluxing acetonitrile in the absence or presence of bismuth chloride in good to excellent yields; benzoin was converted to benzil in high yield (Scheme 1). In comparison to allylic and benzylic alcohols, oxidation of aliphatic alcohols with this reagent does not occur at all. Table III and IVshows the experimental results.

TABLE II Oxidation of 3,4-Dimethoxybenzyl Alcohol with Reagent 1 with Different Lewis Acids in Refluxing Acetonitrile [a,b]

Entry	*Lewis acid*	*Time (hr)*	*Yield (%)*
1	$ZnCl_2$	0.75	50
2	$FeCl_3$	0.75	60
3	$AlCl_3$	0.75	80
4	$BiCl_3$	0.75	100

a. Monitored by TLC analysis.
b. Oxidant/Alcohol/Lewis acid (1:1:0.4).

A noteworthy advantage of this reagent 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 α,β-unsaturated alcohols with **1**, only the OH group was selectively oxidized to the corresponding carbonyl compound; the double bonds remained intact (Table III). 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-phenylethyl alcohol and benzyl alcohol was treated with reagent **1** (1 mmol), only benzyl alcohol was selectively oxidized (Eq. 1). Treatment of benzyl alcohol with reagent **1** (1 mmol) in the presence of diphenylmethanol (1 mmol) led to exclusive oxidation of benzyl alcohol (Fq. 2). Interestingly, in the oxidation of alcohols the overoxidation of products to the corresponding carboxylic acids was not observed. When we treated benzyl alcohol (1 mmol) with reagent **1** in the presence of phenylmethyl sulfide (1 mmol), only the benzyl alcohol was selectively oxidized (Eq. 3).



SCHEME 1

This observation is in contrast to what is reported by us for 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane dichromate which decomposes upon standing in solution.[15] The stability of this reagent in comparison with 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane dichromate is the reflection of the presence of the phosphonium cation in the reagent, which is more stable than ammonium cation.

$$\mathrm{PhCH_2CH_2OH + PhCH_2OH} \xrightarrow[\substack{\text{MeCN, reflux} \\ \text{4.5 hr}}]{1} \underset{\text{(unchanged)}}{\mathrm{PhCH_2CH_2OH}} + \underset{(97\%)}{\mathrm{PhCHO}} \qquad \text{(Eq. 1)}$$

$$\mathrm{PhCH(OH)Ph + PhCH_2OH} \xrightarrow[\substack{\text{MeCN, reflux} \\ \text{4.5 hr}}]{1} \underset{\text{(unchanged)}}{\mathrm{PhCH(OH)Ph}} + \underset{(95\%)}{\mathrm{PhCHO}} \qquad \text{(Eq. 2)}$$

$$\mathrm{PhSMe + PhCH_2OH} \xrightarrow[\substack{\text{MeCN, reflux} \\ \text{4.5 hr}}]{1} \underset{\text{(unchanged)}}{\mathrm{PhSMe}} + \underset{(100\%)}{\mathrm{PhCHO}} \qquad \text{(Eq. 3)}$$

TABLE III Oxidation of Alcohols 2 with Reagent 1 to Carbonyl Compounds 3 in Refluxing Acetonitrile [a,b]

Compound	R_1	R_2	*Time(hr)*	*Yield*[c] *(%)*
2a	C_6H_5	H	4.5	90
2b	4-$NO_2C_6H_4$	H	5.0	78
2c	3,4-$(MeO)_2C_6H_3$	H	2	95
2d	4-PhC_6H_4	Me	2.2	99
2e	2-pyridyl	C_6H_5	4.0	90
2f	C_6H_5	Me	2	86
2g	4-$MeOC_6H_4$	H	4	80
2h	2-$MeOC_6H_4$	H	5	60
2i	C_6H_5	C_6H_5	5	93
2j	3-$MeOC_6H_4$	H	4	82
2k	4-ClC_6H_4	H	2.5	92
2l	2-ClC_6H_4	H	3	92
2m	C_6H_5	$C_6H_5CH_2$	4.5	90
2n	4-BrC_6H_4	Me	5.0	97
2o	4-ClC_6H_4	Me	2.5	89

Compound	R_1	R_2	*Time(hr)*	*Yield*[c] *(%)*
2p	C_6H_5	C_6H_5CO	4	85
2q	2,3-$(MeO)_2C_6H_3$	H	5.0	91
2r	$C_6H_5CH{=}CH$	C_6H_5	3.0	94
2s	$C_6H_5CH{=}CH$	Me	2.3	97
2t	4-$NO_2C_6H_4CH{=}CH$	H	2.0	98
2u	$C_6H_5CH{=}CH$	H	3.0	92
2v[d]	$C_6H_5(CH_2)_2$	H	6.0	nr
2w[d]	$C_6H_5(CH_2)_3$	H	6.0	nr

a. Confirmed by comparison with authentic samples (IR, TLC and NMR).1–13
b. Oxidant/Alcohol (1:1).
c. Yield of isolated pure product after chromatography or distillation.
d. Oxidant/Alcohol (2:1).

TABLE IV Oxidation of Alcohols **2** with Reagent **1** to Carbonyl Compounds **3** in Refluxing Acetonitrile in the Presence of Bismuth Chloride [a,b]

Compound	R_1	R_2	*Time(min)*	*Yield*[c] *(%)*
2a	C_6H_5	H	150	90
2b	4-$NO_2C_6H_4$	H	130	98
2c	3,4-$(MeO)_2C_6H_3$	H	45	96
2d	4-PhC_6H_4	Me	45	99
2e	2-pyridyl	C_6H_5	45	98
2f	C_6H_5	Me	60	90
2g	4-$MeOC_6H_4$	H	35	94
2h	2-$MeOC_6H_4$	H	30	95
2i	C_6H_5	C_6H_5	35	90
2j	3-$MeOC_6H_4$	H	90	92
2k	4-ClC_6H_4	H	45	94
2l	2-ClC_6H_4	H	45	96
2m	C_6H_5	$C_6H_5CH_2$	30	98
2n	4-BrC_6H_4	Me	30	95
2o	4-ClC_6H_4	Me	60	96
2p	C_6H_5	C_6H_5CO	30	90
2q	2,3-$(MeO)_2C_6H_3$	H	25	98
2r	$C_6H_5CH{=}CH$	C_6H_5	20	98
2s	$C_6H_5CH{=}CH$	Me	25	95

Compound	R_1	R_2	*Time(min)*	*Yield*[c] *(%)*
2t	$4\text{-}NO_2C_6H_4CH{=}CH$	H	45	95
2u	$C_6H_5CH{=}CH$	H	35	95
2v[d]	$C_6H_5(CH_2)_2$	H	180	nr
2w[d]	$C_6H_5(CH_2)_3$	H	180	nr

a. Confirmed by comparison with an authentic sample (IR, TLC and NMR).[1–13]
b. Oxidant/Alcohol/$BiCl_3$ (1:1:0.4).
c. Yield of isolated pure product after chromatography or distillation.
d. Oxidant/Alcohol/$BiCl_3$ (2:1:1).

In summary, we report here the preparation of benzyltriphenylphosphonium peroxymonosulfate 1as a mild, inexpensive and stable oxidizing reagent. This oxidizing reagent is easily prepared from commercially available starting materials and could 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 compound is an efficient and novel reagent for oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds under non-aqueous conditions in the absence or presence of $BiCl_3$.

EXPERIMENTAL

General

All yields refer to isolated products after purification by column chromatography or distillation in vacuum. Products were characterized by comparison with authentic samples (IR and ^{1}H-NMR spectrum, TLC, melting and boiling point).[1–13] All ^{1}H-NMR spectra were recorded at 90 MHz in CCl_4 and $CDCl_3$ relative to TMS (0.00 ppm) and IR spectra were recorded on Shimadzu 435 IR spectrophotometer. All reactions were carried out in acetonitrile under reflux conditions. The Research Institute of Petroleum Industry, Tehran, I.R. Iran performed elemental analysis.

Preparation of Benzyltriphenylphosphonium Peroxymonosulfate 1 (BTPPMS)

A solution of benzyltriphenylphosphonium chloride (19.0 g, 49 mmol) in 100 ml of water was prepared, then oxone® (30.06 g, 49 mmol) in water

(100 ml) was added dropwise to the above solution and stirred for 1 hour 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 decomposed at 144–146 °C to a dark-brown material. ^{1}H-NMR: δ 7.93–6.87 (m, 20 H), 4.7(d, J = 25.6 Hz, *CH2*-P). IR (KBr): 1298, 1269, 1098, 1060, 700, 658, 590 cm^{-1}. The white solid was then titrated three times using the following procedure.[14]: 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±0.6% by weight) of active oxidizing agent (HSO_5^-). Anal Calcd for $C_{25}H_{23}O_5PS$: C, 64.37; H 4.97; S, 6.87%. Found: 64.20; H, 5.20; S, 6.60%.

Oxidation of Alcohols 2 to the Corresponding Carbonyl Compounds 3 with Reagent 1 in Refluxing Acetonitrile

In a round-bottomed flask, the alcohol **2** (1 mmol) was added to the oxidant **1** (1 mmol, 0.47 g) in acetonitrile (5 ml). The reaction mixture was magnetically stirred under reflux conditions for the time specified in Table III. When, TLC showed the complete disappearance of the alcohol, the reaction mixture was cooled to room temperature, and the solid then filtered off and washed with CH_3CN (15 ml). Evaporation of the solvent gave the corresponding carbonyl compound **3**. The product was purified by column chromatography on silica gel using an appropriate eluent or distillation in vacuum.

Oxidation of Alcohols 2 to the Corresponding Carbonyl Compounds 3 with Reagent 1 in Refluxing Acetonitrile in the Presence of BiCl$_3$

In a round-bottomed flask, a solution of alcohol **2** (1 mmol) in CH_3CN (5 ml) was treated with $BnPh_3P^+HSO_5^-$(0.466 g, 1 mmol) and bismuth chloride (0.126 g, 0.4 mmol) and refluxed for 20–150 minutes. TLC (cyclohexane/EtOAc, 8:2) was used to monitor the reaction progress. The reaction mixture was cooled to room temperature, and the solid filtered off and washed with CH_3CN (15 ml). The filtrates were evaporated on a rotary evaporator and the resulting crude material was purified by column chromatography on silica gel with an appropriate eluent or distillation in vacuum to afford pure carbonyl compounds in 90–99% yields (Table IV).

Competitive Oxidation

Typical Procedure

Benzyl alcohol (1 mmol, 0.11 g) and diphenylmethanol (1 mmol, 0.19 g) were added to a solution of the oxidant **1** (1 mmol. 0.47 g) in acetonitrile (5 ml). The mixture was refluxed until TLC showed the complete disappearance of benzyl alcohol (4.5 hr). The other competitive reactions for Eqs. 1 and 2 were carried out under similar conditions.

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References

1. a) H. Firouzabadi, A. R. Sardarian and H. Badparva, *Bull. Chem. Soc. Jpn.*, **69**, 685 (**1996**);
   b) H. Firouzabadi, A. R. Sardarian, M. Nader and B. Vesal, *Tetrahedron*, **23**, 5001 (**1984**);
   c) H. Firouzabadi and I. M. Baltork, *Bull. Chem. Soc. Jpn.*, **65**, 1185 (**1992**);
   d) H. Firouzabadi and Z. Mostavipoor, *Bull. Chem. Soc. Jpn.*, **56**, 914 (**1983**);
   e) H. Firouzabadui and A. R. Sardarian, *Synth. Commun.*, **13**, 863 (**1983**).
2. A. Clericl and O. Pona, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1234.
3. W. E. Fristad and J. R. Peterson, *Tetrahedron Lett.*, **1983**, 4547.
4. P. T. Perumal, *Synth. Commun.*, **20**, 1353 (**1990**).
5. a) T. Itahara, R. Ebihara, Y. Fujii and M. Toda, *Chemistry Lett.*, **1986**, 1319;
   b) T. Itahara, Y. Fujii and M. Toda, *J. Org. Chem.*, **53**, 3421 (**1988**).
6. a) S. Yamasaki and Y. Yamasaki, *Bull. Chem. Soc. Jpn.*, **63**, 301 (**1990**);
   b) S. Yamasaki, Chemistry Lett., **1992**, 823;
   c) S. Yamasaki and Y. Yamasaki, *Chemistry Lett.*, **1990**, 571.
7. J. C. Juung, H. C. Choi and Y. H. Kim, *Tetrahedron Lett.*, **34**, 3581 (**1993**).
8. H. C. Choi and Y. H. Kim, *Synth Commun.*, **24**, 2307, (**1994**).
9. F. Chen, J. Yang, H. Zhang, C. Guan and J. Wan, *Synth. Commun.*, **25**, 3163 (**1995**).
10. H. C. Choi, K. Cho and Y. H. Kim, *Synlett*, **1995**, 207.
11. a) I. M. Baltork and Sh. Pourshirvani, *Synth. Commun.*, **26**, 1 (**1996**);
    b) I. M. Baltork and Sh. Pourshirvani, *Synthesis*, **1997**, 756;
    c) I. M. Baltork, M. M. Sadeghi, N. Mahmoodi and B. Kharamesh, *Indian J. Chem.*, **36B**, 438 (**1997**).
12. a) R. S. Varma and H. M. Meshram, *Tetrahedron Lett.*, **38**, 7973 (**1997**);
    b) R. S. Varma, R. K. Saini and R. Dahia, *Tetrahedron Lett.*, **38**, 7823 (**1997**);
    c) R. S. Varma, R. K. Saini and R. Dahia, *Tetrahedron Lett.*, **38**, 7823 (**1997**);
    d) R. S. Varma, R. K. Saini and H. M. Meshram, *Tetrahedron Lett.*, **38**, 6525 (**1997**).
13. a) I. M. Baltork, A. R. Hajipour and H. Mohammadi, *Bull. Chem. Soc. Jpn.*, **71**, 1649 (**1998**);

b) A. R. Hajipour and N. Mahboobkhah, *Synth. Common.*, **28**, 3143 (**1998**);
c) A. R. Hajipour and N. Mahboobkhah, *Indian J. Chem.*, **37B**, 285 (**1998**);
d) A. R. Hajipour and N. Mahboobkhah, *J. Chem. Research (S)*, **1998**, 122;
e) A.R. Hajipour and N. Mahboobkhah, *Indian J. Chem.*, **37B**, 1041 (**1998**);
f) A. R. Hajipour, I. M Baltork and G. Kianfar, *Bull. Chem. Soc. Jpn.*, **71**, 2655 (**1998**);
g) A. R. Hajipour, I. M Baltork and G. Kianfar,. *Indian J. Chem.*, **37B**, 607 (**1998**);
h) A. R. Hajipour and N. Mahboobkhah, *Org. Prep. Proced. Int.*, **31**, 112 (**1999**);
i) A. R. Hajipour, I. M Baltork and K. Niknam, *Org. Prep. Proced. Int.*, **31**, 335 (**1999**);
j) I. M. Baltork, A. R. Hajipour and R. Haddadi, *J. Chem. Research (S)*, **1999**, 102;
k) A. R. Hajipour, S. E. Mallakpour and Gh. Imanzadeh, *Chemistry Lett.*, **1999**, 99;
l) A. R. Hajipour, S. E. Mallakpour and H. Adibi, *Chemistry Lett.*, **2000**, 460.

14. B. M. Trost and R. Braslau, *J. Org. Chem.*, **53**, 532 (**1988**).
15. a) A. R. Hajipour, S. E. Mallakpour, I. M. Baltork and S. Khoee, *Chemistry Lett.*, **2000**, 120.
    b) A. R. Hajipour, S. E. Mallakpour and S. Khoee, *Synlett.*, **2000**, 740.