Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

1,4-Bis(triphenylphosphonium)-2-butene Peroxodisulfate: An Efficient Reagent for Synthesis of β-Nitrato Alcohols

Rashid Badri [a] & Maryam Gorjizadeh [a]
[a] Department of Chemistry, College of Science , Chamran University , Ahvaz, Iran
Published online: 29 Oct 2009.

To cite this article: Rashid Badri & Maryam Gorjizadeh (2009) 1,4-Bis(triphenylphosphonium)-2-butene Peroxodisulfate: An Efficient Reagent for Synthesis of β-Nitrato Alcohols, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:23, 4239-4248, DOI: 10.1080/00397910902898593

To link to this article: http://dx.doi.org/10.1080/00397910902898593

Synthetic Communications®, 39: 4239–4248, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910902898593

Taylor & Francis
Taylor & Francis Group

1,4-Bis(triphenylphosphonium)-2-butene Peroxodisulfate: An Efficient Reagent for Synthesis of β-Nitrato Alcohols

Rashid Badri and Maryam Gorjizadeh
Department of Chemistry, College of Science, Chamran University, Ahvaz, Iran

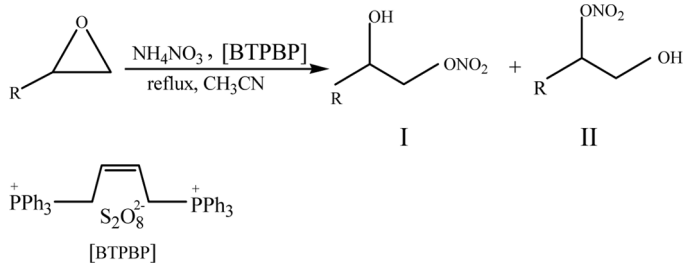
Abstract: A simple and efficient method for the ring opening of epoxides to β-hydroxy nitrates has been achieved in the presence of ammonium nitrate and 1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate.

Keywords: 1,4-Bis(triphenylphosphonium)-2-butene peroxodisulfate, epoxide, β-hydroxy nitrate, regioselectivity, ring opening

INTRODUCTION

Epoxides (oxiranes) are a useful class of precursors in organic synthesis. The epoxide ring can easily be cleaved by a variety of nucleophilic reagents, forming regio- and stereoselective ring-opened products, especially β-substituted alcohols.[1] However, there are few applications of the nitrate ion as the nucleophile for these reactions.[2] β-Hydroxy nitrates as functionalized alkyl nitrates, which are useful intermediates in organic synthesis,[3] have been prepared in low yields through the reaction of oxiranes with concentrated nitric acid[4] or by nitration of halohydrines with silver nitrates.[5] Recently, some methods for the synthesis of β-hydroxy nitrates based on the reaction of epoxides with tetranitromethane,[6] ceric ammonium nitrate (CAN),[7] nitric oxide (NO) in air,[8]

Received January 24, 2009.
Address correspondence to Rashid Badri, Chemistry Department, Faculty of Sciences, Shahid Chamran University, Ahvaz 61357-4-3169, Iran. E-mail: rashidbadri@yahoo.com



Scheme 1.

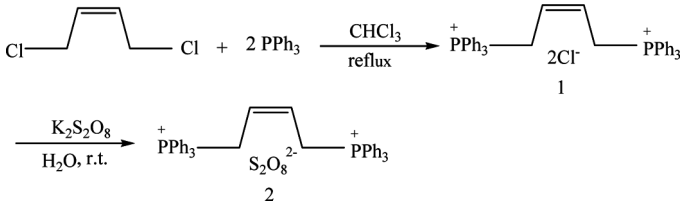
zirconyl nitrate,[9] and bismuth nitrate[2a] were reported. Unfortunately, some of these methods are not always fully satisfactory and suffer from disadvantages such as long reaction times, poor regioselectivity, using of expensive or sensitive reagents, and poor yields. Thus, a better method for ring opening of epoxides with nitrate ions is still required (Scheme 1).

Peroxodisulfate ion is an excellent and versatile oxidant, used mostly for the oxidation of compounds in aqueous solution.[10] In spite of the great convenience of using $K_2S_2O_8$, $Na_2S_2O_8$, or $(NH_4)_2S_2O_8$ and relatively high oxidation potential, many oxidation reactions by peroxodisulfate do not proceed at a convenient rate. This can be largely attributed to the rate-limiting homolysis, which has activation energy of approximately 30 Kcal/mol. Thus, certain limitations may be observed with these reagents. The decomposition of the peroxodisulfate ion requires strong mineral acids and heavy-metal ions[11] as catalysts, and also protic and polar solvents are needed, so the modification of $K_2S_2O_8$, $Na_2S_2O_8$, or $(NH_4)_2S_2O_8$ has received much attention recently.[12]

RESULTS AND DISCUSSION

In continuation of our studies on the application of peroxodisulfate in organic synthesis,[13] we report a mild and efficient method for the ring opening of oxiranes. Thus, 1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate was readily prepared by adding an aqueous solution of potassium peroxodisulfate to a solution of 1,4-bis(triphenylphosphonium)-2-butene dichloride in water. It is a very stable, white solid that can be stored for months without losing its activity. It is soluble in acetonitrile, methanol, dichloromethane, chloroform, and ethyl acetate and slightly soluble in CCl_4 and diethyl ether (Scheme 2).

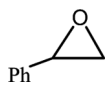
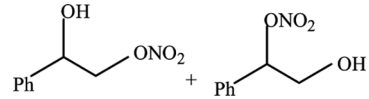
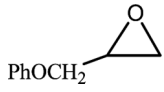
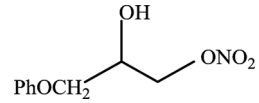
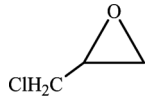
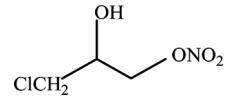
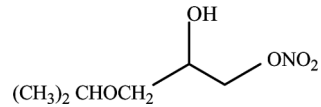
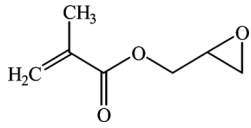
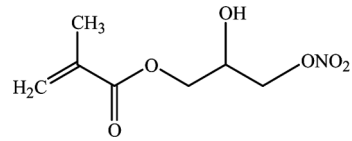
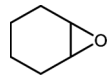
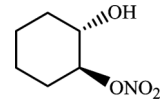
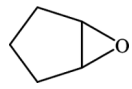
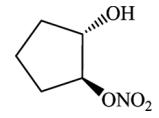
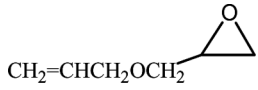
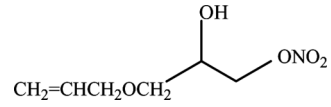
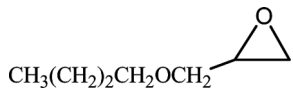
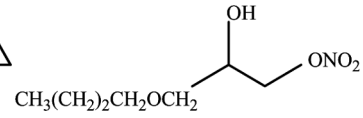
In our initial work, a variety of oxiranes were treated with appropriate amounts of 1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate



Scheme 2.

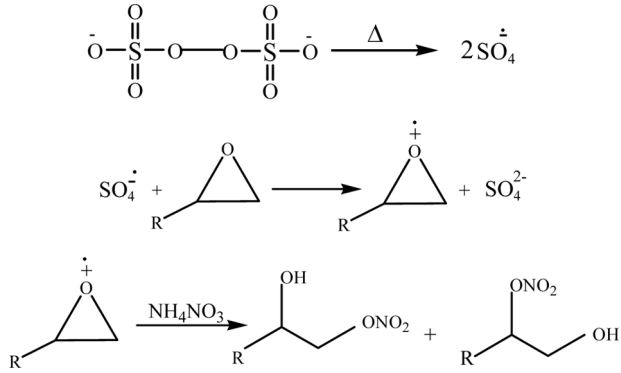
and NH_4NO_3 in three different conditions: (a) solid-state condition in the presence of silica gel as a surface activator, (b) microwave irradiation, and (c) reflux condition using acetonitrile as the most convenient solvent. The first two conditions, which were carried out with different amounts of substrates and microwave power, were not fruitful. With conventional reflux condition, the reaction with all used oxiranes in acetonitrile proceeded smoothly and selectively, and β-hydroxy nitrate in 80–92% yields were obtained. These results are summarized in Table 1. We conducted the same reactions with all epoxides listed in Table 1 at the same reaction conditions in the presence of $K_2S_2O_8$ as the oxidant and found that mixtures of possible hydroxyl nitrates and unidentified products were formed. The yields of isolated β-hydroxy nitrates were especially poor, and the reaction times were longer than in the case of oxidant **2**. Also, the saturated form of compound **2** was prepared either via hydrogenation of compound **1** followed by ($Cl^- \rightarrow S_2O_8^{2-}$) exchange or the reaction of 1,4-dichlorobutane with triphenylphosphine followed by anion exchange. Utilizing this saturated oxidant for the ring opening of epoxides caused long reaction times and smaller yields than unsaturated oxidant **2**. As mentioned, both procedures, using $K_2S_2O_8$ and the saturated form of oxidant **2**, were not attractive because of their very low solubility in reaction medium and the probable lack of fixed *cis* orientation of saturated oxidant compared to oxidant **2**. To determine the optimum condition for our procedure, the conversion of styrene oxide to the corresponding β-hydroxy nitrate in the presence of 1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate as an oxidant in acetonitrile was investigated. The optimum molar ratio of the oxidant to epoxide was found to be 0.6:1 mmol. When the nitrate ion was added to several unsymmetrical epoxides as shown in Scheme 1, formation of two isomeric products (I and II) was possible. Except for the reaction of styrene oxide (Table 1, entry 1), in which the ring opening occurred at the benzylic ring position and predominantly produced the primary alcohol, the reaction of the other unsymmetrical epoxides (Table 1, entries 2–5, 8, and 9) were highly regioselective. The products formed by cleavage at the unsubstitued ring

Table 1. Reaction of various epoxides with ammonium nitrate in the presence of 1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate as oxidant[a]

No.	Substrate	Product (s)	Time (h)	Yield (%)
1			1	80 (15:85)[b]
2			3	82
3			2	90
4			2.5	92
5			2	87
6			1	85
7			1.5	83
8			2.5	87
9			1.5	90

[a]Products were identified by comparison of their physical and spectral data with those of authentic samples.

[b]According to GC analysis.



Scheme 3.

position, and in each case only one isomer was obtained. Also in the case of cyclic epoxides (Table 1, entries 6 and 7), the reaction was completely antistereoselective, and only *trans* products were obtained. The coupling constant of the vicinal hydrogens is different in anti and syn products. The structures and configurations of the products were confirmed by comparison of their spectral values with those reported earlier.[9,2c] It is noteworthy that the reaction medium was almost neutral, so that some sensitive functional groups such as the carbon–carbon double bond remained intact (Table 1, entries 5 and 8). The possible mechanism of the oxidation reaction using the peroxodisulfate mechanism might be as follows: the sulfate anion radical gains an electron from epoxide and oxidizes the ring to a cation radical. This radical reacts with NH_4NO_3 to form the corresponding product (Scheme 3).

In conclusion, we have developed a novel and efficient protocol for the synthesis of β-nitrato alcohols with NH_4NO_3 using 1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate as oxidant. This method offers several advantages, including high conversions, short reaction times, and good isolated yields, which make it useful and attractive process for the ring opening of epoxides.

EXPERIMENTAL

All products were characterized by comparison of their physical data and infrared (IR), ^{1}H NMR, and ^{13}C NMR spectra with authentic samples. The IR spectra were recorded on a Bomem Fourier transform (FT)–IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were taken on a 400-MHz Broucker spectrometer. 1,4-Bis(triphenylphosphonium)-2-butene

peroxodisulfate was prepared, and other chemicals were purchased from the Merck Chemical Company in Darmstadt, Germany.

Preparation of 1,4-Bis(triphenylphosphonium)-2-butene Dichloride (1)

Triphenylphosphine (2.62 g, 10 mmol) was added to a solution of 1,4-dichlorobutene (0.63 g, 5 mmol) in $CHCl_3$ (10 mL) in a 50-mL, round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was refluxed for 2.5 h. The solution was cooled to room temperature, and then diethyl ether was added dropwise until an oily product was separated. The ether was removed by decantation, and acetone (40 mL) was added. Stirring the acetone solution for 40 min afforded a white precipitate, which was filtered, washed with acetone, and then dried. Yield 80%, mp 278–279°C. IR (KBr): $\upsilon = 3053$, 2755, 1613, 1575, 1478, 1437, 754, 693, 556 (cm^{-1}).^{13}C NMR ($CDCl_3$): $\delta = 20.7$, 120.8, 132.15, 134.2, 137.01, 140.17.^{1}H NMR ($CDCl_3$): $\delta = 5.7$ (dd, 4 H), 6.3 (m, 2 H), 7.79–8 (m, 30 H).

Preparation of 1,4-Bis(triphenylphosphonium)-2-butene Peroxodisulfate (2)

A solution of $K_2S_2O_8$ (0.54 g, 2 mmol) in H_2O (5 mL) was prepared in a 25-ml, round-bottomed flask with a magnetic stirrer. Compound **1** (1.298 g, 2 mmol) was added to this solution, and the reaction mixture was stirred at ambient temperature for 3 h. The resulting white precipitate was filtered, washed with distilled water (10 mL), and dried in vacuo. Yield 78%, mp 205–208°C. IR (KBr): $\upsilon = 3053$, 2750, 1623, 1585, 1472, 1437, 750, 724, 689, 556 (cm^{-1}).^{13}C NMR ($CDCl_3$): $\delta = 19.04$, 119.45, 130.05, 133.98, 136.91, 138.8.^{1}H NMR ($CDCl_3$): $\delta = 4.7$ (dd, 4 H), 5.8 (m, 2 H), 7.68–8 (m, 30 H).

General Procedure for the Preparation of β-Hydroxy Nitrate

1,4-Bis(triphenylphosphonium)-2-butene peroxodisulfate (0.6 mmol) was added in small portions to a solution of epoxide (1 mmol) and NH_4NO_3 (2 mmol) in CH_3CN/H_2O (5/1:30 mL) in a 50-mL, round-bottomed flask equipped with a condenser and a magnetic stirrer. The reaction mixture was refluxed for the appropriate time indicated in Table 1. The progress of the reaction was monitored by thin-layer chromatography (TLC). On completion of reaction, the reaction mixture was cooled to room temperature and filtered. The solvent was evaporated; water (20 mL) was added and extracted with diethyl ether (3×15 mL). The combined

organic layers were concentrated in vacuo; the resulting product was directly charged on a small silica-gel column and eluted with a mixture of ethyl acetate and n-hexane (1:4) to afford the pure product.

The IR, ^{1}H NMR, and ^{13}C NMR spectra data of the products are listed.

Selected Data

1-Hydroxy-2-phenylethyl Nitrate **1**

IR: 3365 (OH), 1632 (NO_2), 1455 (NO_2) (cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.9$ (br s, 1 H), 3.2 (d, 2 H), 5.52 (m, 1 H), 7.2–7.36 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 67.2$ (CH_2), 81.6 (CH), 127.2 ($2 \times$ CH), 128.4 ($2 \times$ CH), 131.1 (CH), 141.1 (C).

3-Phenoxy-2-hydroxypropyl Nitrate **2**

IR: 3389 (OH), 1630 (NO_2), 1452 (NO_2) (cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.68$ (br s, 1 H), 4.2 (d, 2 H), 4.5 (m, 1 H), 4.9 (d, 2 H), 6.7–7.26 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 71$ (CH_2), 73.2 (CH), 74.6 (CH_2), 115.2 ($2 \times$ CH), 122.7 ($2 \times$ CH), 131.7 (CH), 162.1 (C).

3-Chloro-2-hydroxypropyl Nitrate **3**

IR: 3400 (OH), 1640 (NO_2), 1435 (NO_2) (cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.35$ (br s, 1 H), 3.95 (d, 2 H), 4.88 (m, 1 H), 5.09 (d, 2 H).^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 49$ (CH_2), 75.2 (CH), 79.2 (CH_2).

2-Hydroxy-3-isopropoxypropyl Nitrate **4**

IR: 3382 (OH), 1632 (NO_2), 1467 (NO_2) (cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.3$ (d, 6 H), 3.15 (br s, 1 H), 3.85 (m, 1 H), 4.13 (m, 3 H), 4.86 (d, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22$ ($2 \times CH_3$), 71.2 (CH), 75.6 (CH), 76.1 (CH_2), 78.9 (CH_2).

3-Nitrato-2-hydroxypropyl Methacrylate **5**

IR: 3435 (OH), 1626 (NO_2), 1280 (NO_2) (cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.1$ (s, 3 H), 3.05 (br s, 1 H), 4.38 (m, 1 H), 4.5 (d, 2 H), 5.1 (d, 2 H), 5.7 (d, 1 H), 6.2 (d, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.5$ (CH_3), 69.2 (CH), 71.6 (CH_2), 77.5 (CH_2), 128.1 (CH_2), 134 (C), 168 (C).

2-Hydroxycyclohexyl Nitrate **6**

IR: 3365 (OH), 1633 (NO_2), 1439 (NO_2) (cm^{-1}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.3–1.5$ (m, 4 H), 1.95 (m, 2 H), 2.25 (m, 2 H), 2.55 (br s, 1 H), 4.18 (m, 1 H), 5.45 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 19.5 (CH_2), 20.2 (CH_2), 28.4 (CH_2), 33.8 (CH_2), 70.1 (CH), 78.3 (CH).

2-Hydroxycyclopentyl Nitrate **7**

IR: 3360 (OH), 1642 (NO_2), 1441 (NO_2) (cm^{-1}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.75$ (m, 2 H), 1.95–2.14 (m, 4 H), 2.45 (br s, 1 H), 4.28 (m, 1 H), 5.05 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.8$ (CH_2), 26.2 (CH_2), 31.3 (CH_2), 80.1 (CH), 81.3 (CH).

3-Allyloxy-2-hydroxypropyl Nitrate **8**

IR: 3454 (OH), 1631 (NO_2), 1377 (NO_2) (cm^{-1}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.09$ (br s, 1 H), 3.38 (d, 2 H), 3.85 (d, 2 H), 4.02 (m, 1 H), 4.56 (d, 2 H), 5.29–5.43 (m, 2 H), 5.96 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 69.2$ (CH), 74.6 (CH_2), 75.7 (CH_2), 75.9 (CH_2), 119.5 (CH_2), 140.5 (CH).

3-Butoxy-2-hydroxypropyl Nitrate **9**

IR: 3360 (OH), 1643 (NO_2), 1439 (NO_2) (cm^{-1}). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.95$ (t, 3 H), 1.41 (six, 2 H), 1.52 (pent, 2 H), 3.04 (br s, 1 H), 3.85 (t, 2 H), 4.03 (m, 2 H), 4.16 (m, 1 H), 4.33 (d, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.8$ (CH_3), 19.5 (CH_2), 31.9 (CH_2), 72.5 (CH_2), 72.9 (CH_2), 73.6 (CH), 74.1 (CH_2).

ACKNOWLEDGMENT

We thank Chamran University for financial support of this work.

REFERENCES

1. (a) Kiasat, A. R.; Badri, R.; Zargar, B.; Sayyahi, S. Poly(ethylene glycol) grafted onto Dowex resin: An efficient, recyclable, and mild polymer-supported phase-transfer catalyst for the regioselective azidolysis of epoxides in water. *J. Org. Chem.* **2008**, *73*, 8382–8385.

2. (a) Das, B.; Krishnaiah, M.; Venkateswarlu, K.; Reddy, V. S. Efficient regio- and stereoselective conversions of oxiranes and aziridines into (nitrooxy)-substituted alcohols and amines by using bismuth nitrate. *Helv. Chim. Acta* **2007**, *90*, 110–113; (b) Pinto, R. M. A.; Salvador, J. A. R.; Le Roux, C. Bismuth(III) salts–mediated regioselective ring opening of epoxides: An easy route to halohydrins and β-hydroxy nitrates. *Tetrahedron* **2007**, *63*, 9221–9228; (c) Fan, Y.; Shang, X.; Liu, Z.; Wu, L. Regio- and diastereoselective ring-opening reaction of epoxides with nitric oxide. *Synth. Commun.* **2006**, *36*, 3149–3152.
3. Boschan, R.; Merrow, R. T.; Van Dolah, R. W. The chemistry of nitrate esters. *Chem. Rev.* **1955**, *55*, 485–510.
4. Nichols, P. L.; Magnusson, A. B.; Ingham, J. D. Synthesis of nitric esters by the addition of nitric acid to the ethylene oxide ring. *J. Am. Chem. Soc.* **1953**, *75*, 4255–4258.
5. Marans, N. S.; Zelinski, R. P. 2-Nitratoethyl esters of acrylic, crotonic, and methacrylic acids. *J. Am. Chem. Soc.* **1950**, *72*, 5330–5331.
6. Volkova, Y. A.; Ivanova, O. A.; Budynina, E. M.; Averina, E. B.; Kuznetsova, T. S.; Zefirov, N. S. Tetranitromethane as an efficient reagent for the conversion of epoxides into β-hydroxy nitrates. *Tetrahedron Lett.* **2008**, *49*, 3935–3938.
7. Iranpoor, N.; Salehi, P. Ammonium nitrate: A mild and efficient reagent for conversion of epoxides to β-nitrato alcohols. *Tetrahedron* **1995**, *51*, 909–912.
8. Liu, Z.; Li, R.; Yang, D.; Wu, L. Ring opening of 2,3-epoxy phenyl ketones upon reaction with nitric oxide. *Tetrahedron Lett.* **2004**, *45*, 1565–1566.
9. Das, B.; Krishnaiah, M.; Venkateswarlu, K. Zirconyl nitrate–mediated regioselective ring opening of epoxides and aziridines: An easy synthesis of β-nitrato-alcohols and sulfonamides. *Tetrahedron Lett.* **2006**, *47*, 6027–6029.
10. House, D. A. Kinetics and mechanism of oxidations by peroxydisulfate. *Chem. Rev.* **1962**, *62*, 185–203.
11. Anderson, J. M. Silver(I)-catalyzed oxidative decarboxylation of acids by peroxydisulfate: Role of silver(II). *J. Am. Chem. Soc.* **1970**, *92*, 1651–1659.
12. (a) Hajipour, A. R.; Zahmatkesh, S.; Ruoho, A. E. Synthesis of methyltriphenylphosphonium peroxydisulfate as a mild selective reagent for the oxidation of alcohols. *Synth. Commun.* **2006**, *36*, 71–76; (b) Tajik, H.; Mohammadpoor-Baltork, I.; Albadi, J. Bromination of some aromatic compounds with potassium bromide in the presence of benzyltriphenylphosphonium-peroxodisulfate. *Synth. Commun.* **2007**, *37*, 323–328; (c) Tajbakhsh, M.; Lakouraj, M. M.; Fadavi, A. Allyltriphenylphosphonium peroxodisulfate $(CH_2{=}CHCH_2PPh_3)_2S_2O_8$: An efficient and convenient reagent for the oxidation of alcohols and silyl and THP-ethers under nonaqueous conditions. *Synth. Commun.* **2004**, *34*, 1173–1181; (d) Firouzabadi, H.; Salehi, P.; Mohammadpoor-Baltork, I. Tetrakis (pyridine) silver(II) peroxidisulfate, $[Ag(Py)_4]S_2O_8$, a reagent for the oxidative transformation. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2879; (e) Jung, J. C.; Choi, H. C.; Kim, Y. H. Direct facile tetrahyrofuranylation of alcohols through radical coupling with $(Bu_4N)_2S_2O_8$. *Tetrahedron Lett.* **1993**, *7*, 3581; (f) Mohammadpoor-Baltork, I.;

Hajipour, A. R.; Mohammadi, H. Benzytriphenylphosphonium peroxodisulfate ($PhCH_2PPh_3)_2S_2O_8$, a mild and inexpensive reagent for efficient oxidation of organic compounds under nonaqueous and aprotic conditions. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1649; (g) Mohammadpoor-Baltork, I.; Hajipour, A. R.; Aghajari, M. Selective and efficient oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers, etylene acetals, and ketals with n-butyltriphenylphosphonium peroxodisulfate $(BunPPh_3)_2S_2O_8$. *Synth. Commun.* **2002**, *32*, 1311–1317.

13. (a) Badri, R.; Soleymani, M. Selective oxidation of benzylic substrates to their corresponding carbonyl compounds with 3,6-bis(triphenylphosphonium)cyclohexene peroxodisulfate. *Synth. Commun.* **2003**, *33*, 1325–1332; (b) Badri, R.; Soleymani, M. 3,6-bis(triphenylphosphonium) cyclohexene peroxodisulfate as an efficient and mild oxidizing agent for conversion of alkylbenzenes to corresponding carbonyl compounds. *Synth. Commun.* **2002**, *32*, 2385–2389; (c) Badri, R.; Shalbaf, H.; Heidary, M. A. 3,6-Bis(triphenylphosphonium)cyclohexene peroxodisulfate: A highly efficient oxidant for the selective oxidation of benzylic alcohols. *Synth. Commun.* **2001**, *31*, 3473–3479.