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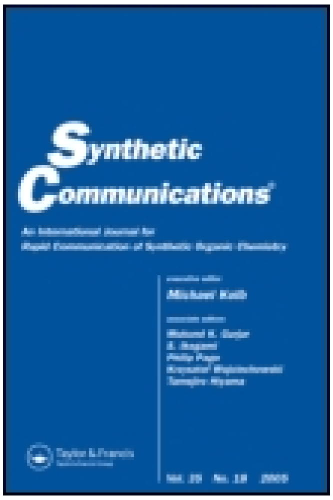

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

3,6-BIS(TRIPHENYLPHOSPHONIUM)-CYCLOHEXENE PEROXODISULFATE: A HIGHLY EFFICIENT OXIDANT FOR THE SELECTIVE OXIDATION OF BENZYLIC ALCOHOLS

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Published online: 22 Aug 2006.

To cite this article: R. Badri , H. Shalbaf & M. A. Heidary (2001) 3,6-BIS(TRIPHENYLPHOSPHONIUM)-CYCLOHEXENE PEROXODISULFATE: A HIGHLY EFFICIENT OXIDANT FOR THE SELECTIVE OXIDATION OF BENZYLIC ALCOHOLS, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:22, 3473-3479, DOI: 10.1081/SCC-100106207

To link to this article: http://dx.doi.org/10.1081/SCC-100106207

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SYNTHETIC COMMUNICATIONS, 31(22), 3473–3479 (2001)

3,6-*BIS*(TRIPHENYLPHOSPHONIUM)-CYCLOHEXENE PEROXODISULFATE: A HIGHLY EFFICIENT OXIDANT FOR THE SELECTIVE OXIDATION OF BENZYLIC ALCOHOLS

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ABSTRACT

The synthesis of 3,6-*bis*(triphenylphosphonium)cyclohexene peroxodisulfate and its application for the selective oxidation of benzylic alcohols is reported.

Peroxodisulfate is a well-known strong oxidizing agent for a variety of organic compounds. Some reported successful examples of oxidation with this oxidant are: oxidation decarboxylation of acids,[1] aromatic hydroxylation,[2–4] oxidation of carbon-nitrogen double bonds,[5,6] oxidation of alkyl benzenes,[7] alkenes,[8–10] amines[11] and alcohols.[12–15] Although the standard redox potential of peroxodisulfate ion is high (about 2.01 V in aqueous solution), its reaction at ambient temperature is considerably slow and therefore, as reported, is accelerated in the presence of Ag(I),[16,17] Cu(I)[17]

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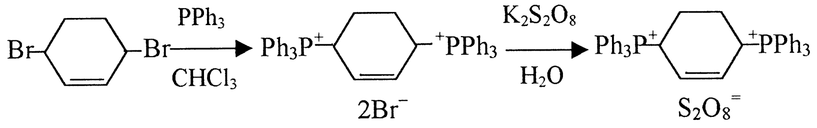
and Ni(II)[18] under reflux condition. In the case of alcohols, the oxidation reaction carried out at acidic condition and is accompanied by fragmentation.[13] Therefore, introduction of a new Peroxodisulfate oxidizing agent which works under neutral and aprotic condition for the selective oxidation of alcohols is an important process in organic synthesis.

In this paper we wish to report the synthesis of new Peroxodisulfate reagent and its application in selective oxidation of benzylic alcohols in neutral solution and in the absence of the metal ions as catalysts. Thus, 3,6-dibromocyclohexene[19] **I** was stirred with triphenylphosphine in refluxing $CHCl_3$ for 2 h to produce, upon cooling and treatment first with Et_2O and then with acetone, 3,6-*bis*(triphenylphosphonium)-cyclohexene dibromide **2** as a white solid in 80.5% yield. Stirring a mixture of **2** and $K_2S_2O_8$ in H_2O at ambient temperature for 3 h, afforded after filtration and washing with H_2O and drying, 3,6-*bis*(triphenylphosphonium)cyclohexene peroxodisulfate **3** in 78% yield (Scheme 1). Structures of **2** and **3** were confirmed by elemental analysis, IR and ^{1}H NMR. Compound **3** is a white solid which is stable for long periods without losing its activity.



1 **2** **3**

Scheme 1.

As shown in Table 1, primary and secondary benzylic alcohols are oxidized to their corresponding aldehydes and ketones in high yields (entries 1–12). Further oxidation of aldehydes to their carboxylic acids and also fragmentation products were not observed in this method. It is noteworthy that under the same reaction conditions, primary and secondary saturated and allylic alcohols were resistant toward oxidation and the corresponding carbonyl compounds were obtained in non or poor yields. It is also important to note, since the reaction medium was almost neutral, some sensitive functionalities such as carbon-carbon double bond remained intact (entries 11, 12, Scheme 2).

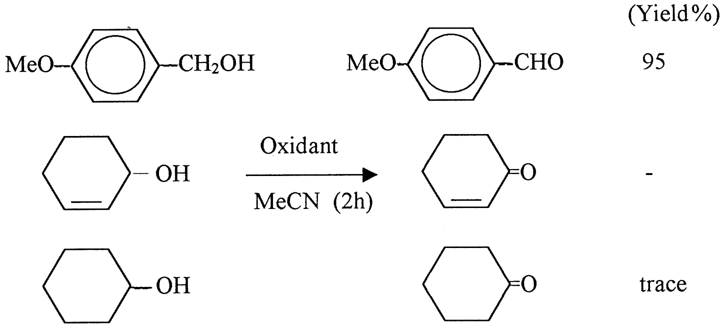
In order to show the better chemoselectivity of the described method an equimolar mixture of benzyl, allyl and alkyl alcohols was treated with this reagent in refluxing MeCN for 2 h. We found that *p*-methoxybenzyl alcohol is oxidized selectively in the presence of allyl and alkyl alcohols (Scheme 2). This selectivity is of vital importance in modern synthetic methodologies.

The effect of various solvents such as DMSO, DMF, MeCN, CCl_4, $CHCl_3$ and CH_2Cl_2 were also investigated. The experimental results show that MeCN is the best choice for this purpose (Table 2).

Table 1. Oxidation of Alcohols with BTPCP in Refluxing MeCN

Entry	Substrate	t (min)	Yield (%)[a]	Product[b]
1	$PhCH_2OH$	9	92	PhCHO
2	p-$ClPhCH_2OH$	11	93	p-ClPhCHO
3	O-NO_2PhCH_2OH	20	57	O-NO_2PhCHO
4	P-NO_2PhCH_2OH	15	86	P-NO_2PhCHO
5	P-$MeOPhCH_2OH$	7	95	p-MeOPhCHO
6	PhCHOHMe	8	94	PhCOMe
7	PhCHOHPh	7	95	PhCOPh
8	$PhCHOH(CH_2)_2CO_2Me$	15	87	$PhCO(CH_2)_2CO_2Me$
9	p-$MePhCH_2OH$	8	94	p-MePhCHO
10	p-$MeOPhCHOH(CH_2)_2CO_2Me$	14	96	p-$MeOPhCO(CH_2)_2CO_2Me$
11	$PhCHOHCH{=}CHCH_2OH$	10	89	$PhCOCH{=}CHCH_2OH$
12	$PhCHOH(CH_2)_2CO_2(CH_2)_2OH$	11	89	$PHCO(CH_2)_2CO_2(CH_2)_2OH$

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



Scheme 2.

Table 2. Data for the p-MeOPhCH$_2$OH Oxidation with BTPCP in Various Solvents

Entry	Solvent	t. (min)	Yield (%)*
1	DMSO	9	88
2	DMF	13	80
3	MeCN	7	95
4	CCl_4	20	40
5	$CHCl_3$	15	70
6	CH_2Cl_2	20	50

*GLC yields

Table 3. Reusability of Oxidant*

Experimental	Yield (%)
1st	95
2nd	92
3rd	89

*All reactions are carried out under similar conditions.

The noteworthy advantages of this reagent lies in its reusability. Thus Table 3 demonstrates the reusability of the oxidant after **3** 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 $K_2S_2O_8$ in H_2O for 3 h.

In conclusion, 3,6-*bis*(triphenylphosphonium)cyclohexene peroxodisulfate is a stable, mild, efficient, easily prepared and reusable reagent for the selective oxidation of benzylic alcohol.

EXPERIMENTAL

General: ^{1}H NMR was recorded on a Bruker advance DPX-250 MHz NMR spectrometer in $CDCl_3$. The IR spectra were recorded on a Shimadzu 470 Spectrophotometer (4000–400 cm^{-1} region). GLC analysis was performed with a Gas Chromatography 6A Shimadzu with a flame ionization detector and Carbowax 20 M/Chromosorb-*W*60–80-mesh column. The C, H, S, analysis were performed by the microanalytical service of research institute of petroleum industry (N.I.O.C). Melting points were measured on a mettler FP5 apparatus. TLC accomplished the purity of the substrates and reactions monitored on silica gel plates. All yields refer to isolated products.

Preparation of 3,6-*bis*(Triphenylphosphonium)-cyclohexene Dibromide (2)

To a solution of 3,6-dibromocyclohexene **I** (2.4 g, 10 mmol) in $CHCl_3$ (10 ml) in a 50 ml round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was added triphenylphosphine (5.24 g, 20 mmol). The reaction mixture was refluxed for 2 h. The solution was cooled to room temperature and then Et_2O was added drop wise with stirring 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 that was filtered, washed with acetone and then dried. Yield (80.5%), m.p. = 276–7°C.

IR (KBr): 3053, 2755, 1613, 1575, 1475, 1446, 1108, 750, 723, 692, 537 (cm^{-1}). ^1H NMR (250 MHz), δ_H ($CDCl_3$): 2.37–2.85 (m, 4H), 5.78 (d, 2H), 6.47 (m, 2H), 7.12–7.96 (m, 30H).

Anal. (Calc. C% 65.98; H% 5.01; found C% 66.02; H% 4.95).

Preparation of 3,6-*bis*(Triphenylphosphonium)-cyclohexene Peroxodisulfate (3)

In a 25 ml round-bottomed flask with a magnetic stirrer a solution of $K_2S_2O_8$ (0.135 g, 2 mmol) in H_2O (5 ml) was prepared. Compound **2** (3.82 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%) m.p. = 177–8°C.

IR (KBr): 3050, 1625, 1576, 1478, 1437, 1258, 1108, 1059, 754, 724, 693, 556, 525 (cm^{-1}).

^1H NMR (250 MHz), δ (d_6-DMSO): 2.46 (m, 4H), 5.12 (d, 2H), 6.10 (m, 2H), 7.91 (m, 30 H). ^{13}C NMR (250 MHz), δ (d_6-DMSO): 22.51(t), 31.05(dd), 117.58, 130.80(d), 131.00, 134.95, 135.52.

Anal. (Calc. C% 63.31; H% 4.81; S% 8.05; found C% 63.29; H% 4.82; S% 8.52).

General Procedure for Oxidation of Alcohols

To a solution of alcohol (1 mmol) in solvent CH_3CN (5 ml) in a 50 ml round-bottomed flask-equipped with a condenser and a magnetic stirrer was added 3,6-*bis*(triphenylphosphonium)cyclohexene peroxodisulfate (1 mmol) 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 or GLC. The reaction mixture was filtered and the solid was washed with ether (3 × 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 57–96% yields (Table 1).

ACKNOWLEDGMENT

We were thankful to Shahid Chamran University for the partial support of this work.

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Received in the UK June 19, 2000

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