

1,4-bis(triphenyl phosphonium)butane peroxodisulfate: conversion of alkyl benzenes to carbonyl compounds

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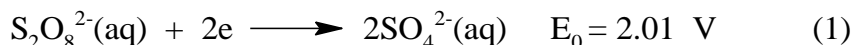
Abstract-1,4-bis(triphenyl phosphonium)butane peroxodisulfate(BTPPBPS) were synthesized by treating 1,4-bis(triphenyl phosphonium)butane dibromide and potassium peroxydisulfate in aqueous solution. This was used mild and efficient reagent for oxidation of alkyl benzenes to their corresponding carbonyl compounds in very good to high yields.

Keywords: 1,4-bis(triphenyl phosphonium)butane - alkyl benzenes - carbonyl compounds

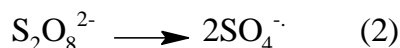
Introduction

The oxidation of organic substrates in aprotic solvents, under mild and neutral conditions, was important in modern organic synthesis. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success. [1]

The oxidation of alkyl benzenes to the corresponding carbonyl compounds is one of the most important and frequently used synthetic procedures, and the development of such a procedure is still desirable in academic as well as in industrial research. The readily available peroxydisulfate ion, $S_2O_8^{2-}$, is an excellent and versatile oxidant for a variety of organic and inorganic compounds [1-3]. Peroxodisulfate radical anion $SO_4^{\cdot-}$, is one of the most important and strong one-electron oxidant in organic synthesis [4-11]. Despite the relatively high oxidation potential for the half-reaction (eq 1), many oxidations by peroxydisulfate do not proceed at a convenient rate at ambient temperatures.



The latter can be largely attributed to the rate-limiting homolysis given by (eq 2) [1,12], which has an activation energy of approximately 30 kcal/mole.



The decomposition of the peroxydisulfate ion, however, is accelerated by strong mineral acids as well as by trace-metal ions [1,2].

These reagents suffer from either one or more of the following disadvantages such as availability of the reagent, cumbersome work-up procedure, high cost of the reagent, over oxidation or oxidation of other functional groups. As a result, there is still a need for the development of general, efficient, and new reagents to synthesize carbonyl compounds from the corresponding arenes under mild reaction conditions.

Herein, we have reported the synthesis and application of 1,4-bis(triphenyl phosphonium)butane

peroxodisulfate(BTPPBDS) as an efficient and selective oxidant in nonaqueous medium. Therefore, use of a mild, efficient, unexpensive, simple, convenient and selective method for the oxidation of alkylbenzenes to their corresponding carbonyl compounds with (BTPPBDS) under neutral conditions and in the absence of metal catalysts.

Experimental Section

Material and methods:

Arenes , dialkyl halid, PPh_3 , $\text{K}_2\text{S}_2\text{O}_8$ (Merck, P.A.) were used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. ^1H and ^{13}C , (for product) were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H and ^{13}C NMR spectra were referenced to external SiMe_4 and ^{19}F NMR spectra to external CFCl_3 . The relative concentrations of carbon, hydrogen and nitrogen were obtained from the microanalytical laboratories, Department of Chemistry, OIRC, Tehran. Melting points were measured on an Electrothermal 9100 melting point apparatus.

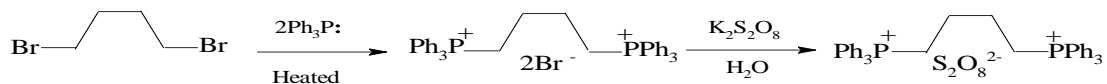
General procedure:

To a solution of arenes (1mmol) were dissolved in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (5:1,10 ml) in a 50 ml round-bottomed flask equipped with a condenser and a magnetic stirrer . oxidant (2 mmol) in small portions over (7-60) min was added under reflux condition. The progress of the reaction was monitored by TLC (eluent; $\text{CCl}_4/\text{Et}_2\text{O}$ (6:1)). After completion of the reaction, the mixture was filtered and the solvent was evaporated. The resulted crude product was purified on a silica-gel (20×20cm) plate with appropriate solvent (Hexan / EtOAC). Pure carbonyl compounds were obtained in 57-96% yields. (table 1)

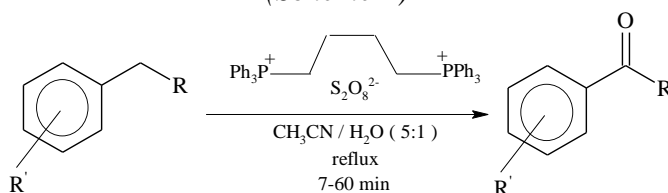
Results and discussion

BTPPBPS was an easily prepared reagent, which was used for oxidation of alcohols recently. [20] The oxidative formation of carbonyl compounds with this reagent was investigated in CH₃CN/H₂O. As shown in table 1, a series of appropriate arenes were reacted with 2 molar equivalent of the reagent to afford the corresponding carbonyl group in excellent yields

Use of a mild, efficient, unexpensive, simple, convenient and selective method for the oxidation of alkylbenzenes to their corresponding carbonyl compounds with (BTPPBPS) under neutral conditions and in the absence of metal catalysts. This reagent was easily prepared in two steps reaction. Thus treatment of two moles of triphenylphosphine with one mole of 1,4-dibromo butane at 200-250 °C afforded, after filtration and purification and ion exchanges 1,4-bis(triphenyl phosphonium)butane peroxodisulfate in (57-96%) yield (Scheme 1 and 2).



(Scheme 1)



R = H, Alkyl, Alkenyl, Aryl

R' = H, OH, Cl, Br, OMe, NO₂, CH₃

(Scheme 2)

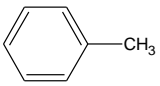
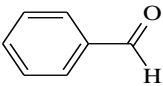
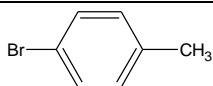
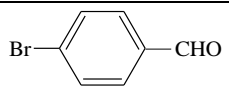
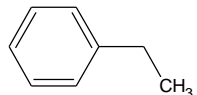
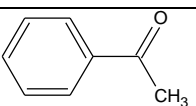
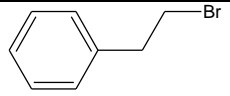
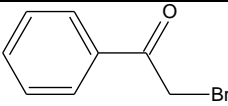
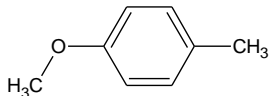
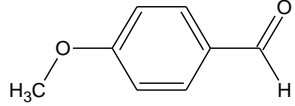
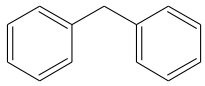
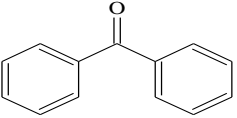
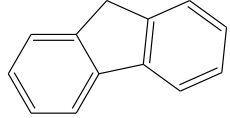
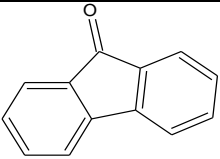
The procedure developed for oxidation of alkylbenzenes consists of simply addition of BTPPBPS in small portions to a refluxing solution of alkylbenzenes in aqueous acetonitrile. The results obtained are summarized in Table 1.

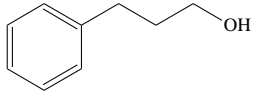
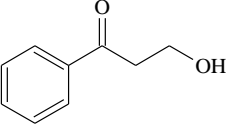
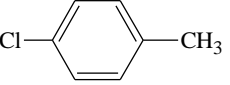
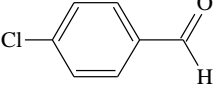
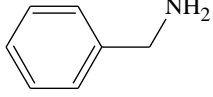
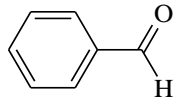
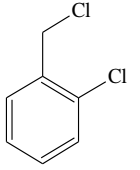
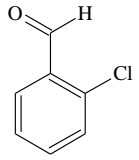
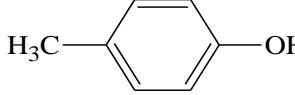
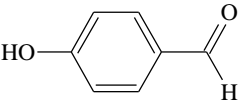
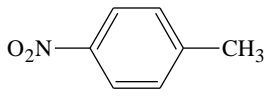
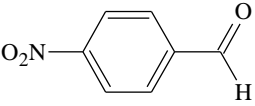
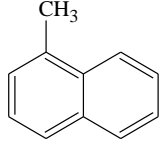
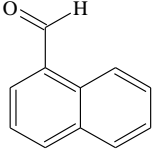
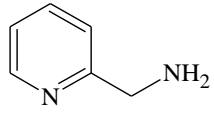
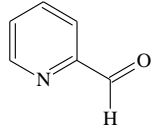
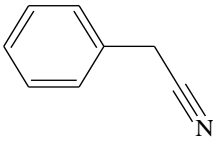
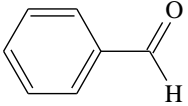
Because of the stability and solubility of BTPPBPS, reactions could be performed at

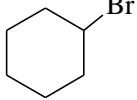
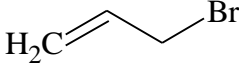
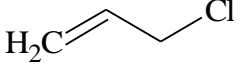

reflux condition and the separation of the products was facile. The mechanism for the present oxidation is still unclear. However we assumed that the mechanism of oxidation was similar to that of other similar oxidants. In addition, this oxidant and the oxidation conditions could be used for the synthesis of highly functionalized molecules.

It has been found also that this reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, and especially in the short reaction times required and in higher product yields. [4-11]

Table1. oxidation of alkylbenzenes to carbonyl compounds by BTPPBDS

Entry	Substrate	product	Time (min)	Yield (%)
1			8	95
2			12	93
3			9	94
4			10	85
5			7	96
6			10	87
7			10	92

8			10	70
9			10	88
10			15	90
11			12	91
12			10	90
13			35	57
14			14	86
15			60	75
16			10	90

17		-	120	-
18		-	120	-
19		-	120	-
20		-	120	-

Acknowledgments

We gratefully acknowledge the support of this work by Islamic Azad University Science and Research Branch , Ahvaz Branch, Iran.

Keywords

1,4-bis(triphenyl phosphonium)butane peroxodisulfate(BTPPBPS), alkyl benzenes, potassium peroxydisulfate, carbonyl compound

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11. The problem is complicated by the ready induced decomposition of peroxydisulfate and the chain character of many of these reactions.