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Original Research Article

Mild and selective oxidation of sulfur compounds by *p*-xylylenebis (tri-phenyl-phosphonium tribromide) as green and reusable reagent

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ABSTRACT

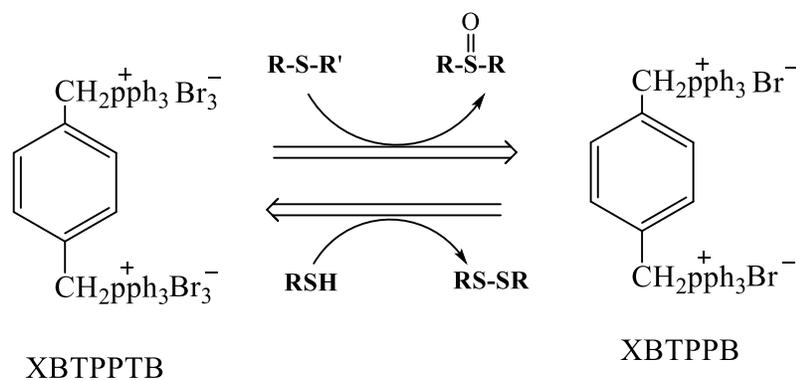
p-Xylylene bis(triphenylphosphonium tribromide) (XBTPPTB) could be used for selective oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides as an effective and green reagent, under nonaqueous and aprotic conditions without catalyst. This reagent can be recovered and reused several times. Also it is readily prepared and could be stored for months without losing its potency. To study the effect of solvent, oxidation of benzenethiol was performed in different solvents. Acetonitrile is the best solvent due to the relatively good solubility of the catalyst and starting materials. To study the effect of solvent, oxidation of methyl phenyl sulfide was performed in different solvents. Acetonitrile is the best solvent due to the relatively good solubility of the catalyst and starting materials. The effect of catalyst amount was investigated and the optimum ratio of reactant to oxidant (1:0.5) is found to be ideal for complete conversion of sulfides and thiols to the corresponded *products*

Keywords: Sulfide; Sulfoxide; Selective oxidation; *p*-Xylylenebis(triphenylphosphonium tribromide).

Introduction

The oxidation coupling of thiols to disulfides is an essential reaction in the synthesis of natural products, and further oxidation to disulfide S-oxides (thiosulfonates), 1,1-dioxides (thiosulfonates), and sulfonic acids is possible. Weak S-S bonds in these compounds impart high reactivity [1] and in natural products, these moieties and related cyclic analogues are associated with interesting biological activity [2]. Several methods based on oxidative S-S coupling have already been reported [3-11]. Some of these methods suffer from disadvantages such as long reaction times, limited availability of oxidant, toxicity of reagents and isolation of products. Therefore, the introduction of readily available, safe and stable reagents for oxidation of thiols to disulfides is still a necessity. On the other hand, the oxidation of sulfides to sulfoxides is the most straightforward synthetic route to the latter, and numerous reagents and oxidative procedures are available for this transformation. However, many of them cause over oxidation to the corresponding sulfones. Therefore, control of the reaction conditions, that is, time, temperature and the relative amount of oxidants, plays an important role in avoiding the formation of oxidation side products, but this is often hard to achieve and therefore there is still considerable interest in the development of selective oxidants for this transformation [12-14].

As part of our current studies on the synthesis of organic compounds [15-17], we have reported *p*-xylylenebis(triphenylphosphonium tribromide) [18] XBTPPTB as a mild, inexpensive, and efficient oxidizing reagent for oxidation of sulfides **1** and thiols **3** to their corresponding sulfoxides **2** and disulfides **4** under nonaqueous conditions (Scheme 1).



Scheme 1: The selective oxidation of sulfides and thiols by XBTPPTB

XBTPPTB a mild, efficient, stable, and cheap reagent, is a yellow powder that is quite soluble in chloroform and acetonitrile and insoluble in nonpolar solvents such as carbon tetrachloride, *n*-hexane, and diethyl ether. This reagent is readily prepared and could be stored for months without losing its potency. This new method has the following advantages: (a) XBTPPTB is an efficient and inexpensive reagent for the oxidation of thiols and sulfides to the corresponding disulfides and sulfoxides at room temperature. (b) XBTPPTB is a reusable and safe oxidant (c) unlike Br₂, it is easy to transport and selective oxidation is also observed with this reagent (d) The yields of products are very good.

Material and Methods

Equipment and Materials

¹H NMR spectra were measured on Bruker Avance DRX 500 MHz spectrometers, using deuterated chloroform (CDCl₃) as solvent. Melting points were determined on Electro Thermal 9100. Materials were purchased from Fluka and Merck companies. All the products were characterized by ¹H NMR, IR, TLC, melting and boiling points by comparison with authentic samples.

Preparation of *p*-Xylylenebis(triphenylphosphonium tribromide)

A solution of 20.7g *p*-xylylenebis(triphenylphosphonium bromide) (24.2 mmol) in 40 mL of acetic acid was prepared, then Br₂ (2.5 ml, 48.4 mmol) in *n*-hexane (20 ml) was added dropwise to the above solution and stirred for 30 min at room temperature.

The resulting orange solid was collected by filtration, washed with diethyl ether, and dried under vacuum to give 26.8 g XBTPPTB. Mp 148–150 °C; ¹HMR: δ 7.90–6.85 (m, 40 H), δ 4.7 (d, 4 H, CH₂P). The content of active oxidizing agent (Br⁻³) was determined by the titrimetric method [19]. Anal. calcd. for C₄₄H₃₈P₂Br₆: C, 47.69; H, 3.46; Found: C, 47.82; H, 3.73.

General Procedure for Oxidation of sulfur compounds with XBTPPTB

To a solution of thiol or sulfide (1 mmol) in acetonitrile (5 mL), XBTPPTB (0.5 mmol) was added. The reaction mixture was refluxed for the appropriate time (Tables 1, 2). The progress of the reaction was monitored by TLC (eluent: *n*-hexane/ethyl acetate: 5/1). After disappearance of

the starting material, the mixture was filtered through a sintered glass funnel and the solid residue was washed with acetonitrile (10 mL). Evaporation of the filtrates gave products. All of the products were known compounds and characterized by comparing melting point and ^1H NMR spectra with those reported in the literature.

Results and discussion

p-Xylylene bis (triphenylphosphoniumtribromide) is easily prepared from *p*-xylylene, triphenylphosphonium dibromide and bromine and used for oxidation of thiols and sulfides to disulfides and sulfoxides as a green reagent. The effect of catalyst amount was investigated using 1/0.25, 1/0.5 and 1/1 molar ratios of XBTPPTB in the conversion of methyl phenyl sulfide. The results revealed that a 0.5 /1 molar ratio was optimum and a higher amount of catalyst did not have any effect on the completion of the reaction. The optimum ratio of sulfide to oxidant (1:0.5) is found to be ideal for complete conversion of sulfides **1** to sulfoxides **2** while the reaction remains incomplete with lesser ratio of substrate and oxidant, for example 1:1 and 1:1.2. By using this oxidation system, a wide variety of alkyl aryl and dialkyl sulfides **1** were oxygenated to their corresponding sulfoxides **2** in high yields within mild reaction periods (Table 1).

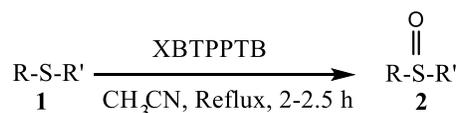


Table 1. Oxidation of sulfides with XBTPPTB.

Entry	R	R'	Time(h)	Yield ^a	Mp($^{\circ}\text{C}$) ^{Ref}
1	<i>p</i> -Methyl benzyl	Phenyl	2	90	95-97 [20a]
2	Phenyl	Benzyl	2.5	88	123-125 [20b]
3	Benzyl	Benzyl	2	90	134-136 [20c]
4	Phenyl	Me	2	92	30-32 [20d]

^a Yield of isolated pure products

In this method, oxidation of a sulfide is achieved by stirring a mixture of a sulfide and the reagent under reflux condition. The reaction time is usually between 2 and 2.5 h. The sulfoxides are isolated by filtering the reaction mixture and washing the filter cake with appropriate solvent. Evaporation of filtrate under vacuum often produces pure sulfoxide without any purification. All the reactions occurred with complete selectivity for sulfoxide formation, no overoxidation

Conclusion

In this paper, we have described a facile, mild and selective synthesis of disulfides and sulfoxides using XBTPPTB as a stable, safe and non-toxic oxidant. The several advantages of this method, including high yields of products, inexpensive, simple procedure, the easy and clean work-up, and unlike previous oxygenation methods, this one requires neither an aldehyde nor a transition metal complex, make this reaction convenient and efficient.

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