SYNLETT
Spotlight 310

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Benzyltriphenylphosphonium Peroxymonosulfate

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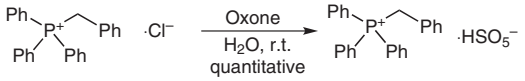
Dedicated to my parents and honorable mentor Prof. C. Venkata Rao.

Introduction

Benzyltriphenylphosphonium peroxymonosulfate (**1**, BTPPMS) is a mild, efficient, stable, and cheap reagent which displays its versatility in organic synthesis. It is a white solid and generally stored at room temperature. It is quite soluble in dichloromethane, chloroform, acetone, and acetonitrile but insoluble in non-polar solvents, such as carbon tetrachloride, *n*-hexane, and diethyl ether. It has been used for the oxidation of alcohols to aldehydes and ketones under aprotic solvent condition,[1] oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers under non-aqueous conditions,[2] and selective oxidation of sulfides and thiols to the corresponding sulfoxides and disulfides under solvent-free conditions.[3] It was also found to be useful for the dethioacetalization of 1,3-dithiolanes and 1,3-dithianes to the corresponding carbonyl compounds in the presence of bismuth chloride under aprotic conditions[4] and conversion of oximes and semicarbazones to carbonyl compounds using microwave irradiation to afford the carbonyl compounds.[5] Because of the mild conditions as well as the high yields, this reagent has wide acceptance in the area of synthetic chemistry.

Preparation

BTPPMS can be easily prepared[6] from commercially available reagents. To a solution of benzyltriphenylphosphonium chloride in water a solution of Oxone® in water was added dropwise. After stirring for 1 h at room temperature, the resulting precipitate was filtered, washed with cooled distilled water and dried in a desiccator to afford a white powder which decomposed at 144–146 °C. The white solid was then titrated three times[7] to yield 99% of the active oxidizing agent (HSO_5).



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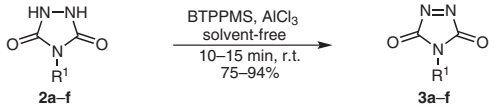
Scheme 1

Abstracts

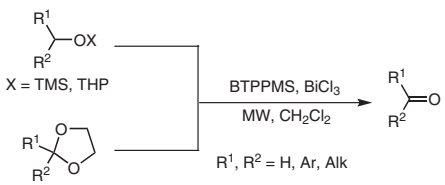
(A) *Oxidation of Urazoles to Triazolinediones*:
A convenient practical method for the oxidation of urazoles **2a–f** to their corresponding triazolinediones **3a–f** in high yields (75–94%) and exceedingly short reaction times (10–15 min) has been developed.[8] The process involves the mixing of BTPPMS and urazoles **2a–f** in the presence of $AlCl_3$ in a mortar to afford corresponding triazolinediones **3a–f** in high yields under solvent-free conditions.



2a–f **3a–f**

R^1 = Ph, Cy, *n*-Bu, 4-ClC_6H_4, 4-$O_2NC_6H_4$, 4-$Cl^-NH_3^+C_6H_4$

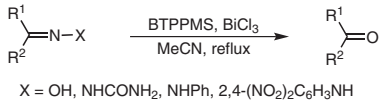
(B) *Oxidative Deprotection*:
BTPPMS and a catalytic amount of bismuth chloride (0.4 molar ratio) can be applied to the oxidative deprotection of primary and secondary trimethylsilyl ethers as well as tetrahydropyranyl ethers to their corresponding carbonyl compounds. Further, ethylene acetals can be transformed to the corresponding carbonyl compounds in high yields under microwave irradiation.[6b]



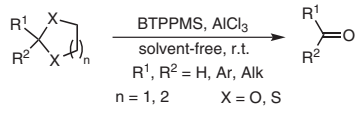
R^1, R^2 = H, Ar, Alk

SYNLETT 2010, No. 6, pp 0989–0990
Advanced online publication: 10.03.2010
DOI: 10.1055/s-0029-1219570; Art ID: V31609ST

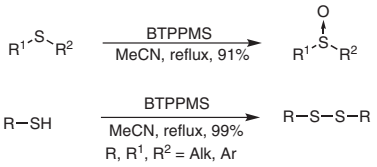
(C) *Deoximation of Oximes*:
The conversion of oximes, phenylhydrazones, 2,4-dinitrophenylhydrazones and semicarbazones to the corresponding carbonyl compounds can be performed using BTPPMS in the presence of a catalytic amount of $BiCl_3$.[6c]



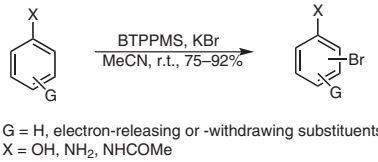
(D) *Deprotection of Acetals and Thioacetals*:
A variety of acetals and thioacetals are deprotected to the corresponding parent carbonyl compounds under solvent-free conditions[9] using BTPPMS in the presence of aluminum chloride in high yields.



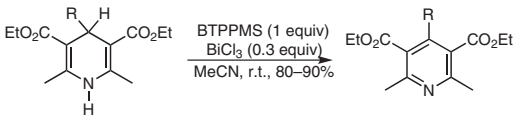
(E) *Selective Oxidation of Sulphides and Thiols*:
An efficient procedure for the selective oxidation of various aromatic and aliphatic sulphides and thiols to their corresponding sulfoxides and disulfides under non-aqueous and aprotic conditions without catalyst has been developed by Hajipour et al.[10]



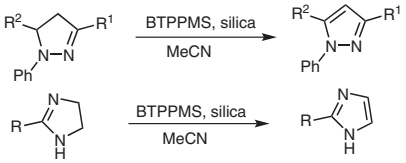
(F) *Regioselective Oxidative Bromination of Electron-Rich Aromatic Rings*:
The regioselective oxidative bromination of electron-rich aromatic rings has been studied using potassium bromide as a bromine source in the presence of BTPPMS as oxidant under nearly neutral reaction conditions.[11] In most cases monobrominated derivatives have been obtained regioselectively in good to high yields without the aid of strong acids.



(G) *Oxidative Aromatization of 4-Alkyl- or Aryl- and Heterocyclic-Substituted Derivatives*:
A convenient and efficient protocol for the oxidative aromatization of 4-alkyl-, aryl-, and heterocyclic-substituted derivatives of Hantzsch 1,4-dihydropyridines to the corresponding pyridine derivatives has been studied using BTPPMS in the presence of $BiCl_3$ under nearly neutral reaction conditions.[12]



(H) *Metal-Free Oxidative Dehydrogenation of Imidazolines and Pyrazolines*:
Oxidative dehydrogenation of 1,3,5-trisubstituted pyrazolines and 2-substituted imidazolines to their corresponding pyrazoles and imidazoles is carried out effectively by treatment with BTPPMS.[13]



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