

SYNLETT Spotlight 265

Phenyltrimethylammonium Tribromide: A Versatile Reagent in Organic Synthesis



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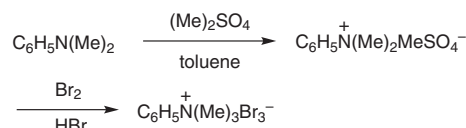
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Introduction

Phenyltrimethylammonium tribromide (PTAB) is known to be a convenient oxidizing and brominating agent. It is an orange crystal and easy to handle, with a melting point at 113–115 °C.¹ It has been used for the oxidative transformation of *trans*-stilbene oxide to 2-phenyl-1,3-dioxane in the presence of various of 1,3-diols and a catalytic amount of SbBr₃,² for brominating the α -position of carbonyl compounds,^{3–8} α' -bromination of α,β -unsaturated ketones,⁹ and for the addition of bromine to alkenes.¹⁰ It was also found to be useful for the chemoselective conversion of 3-alkoxyfurans to 2-alkoxy-3(2*H*)-furanones, oxidative ring-opening of 3-alkoxy-2,5-diphenylfurans to *cis*-2-alkoxy-2-butene-1,4-diones,¹¹ and synthesis of imi-

dazoles,¹² 3-bromo-2-styrylchromones,¹³ nitro dibromophenols,¹⁴ pyridazines,¹⁵ phytoalexin cyclobrassinin,¹⁶ *p*-bromodienone calixarene derivatives,¹⁷ and 2-arylthiazino[5,6-*b*]indoles.¹⁸

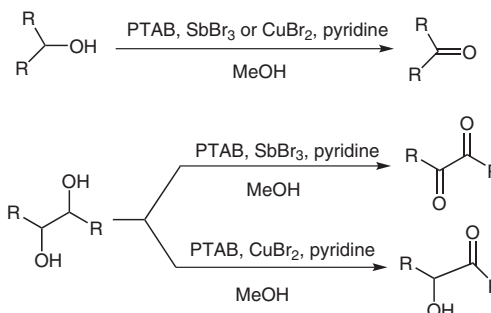
Phenyltrimethylammonium tribromide is commercially available now. It can be readily prepared from *N,N*-dimethylaniline and dimethyl sulfate, followed by treatment with 48% hydrobromic acid and bromine.¹



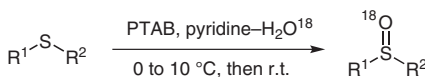
Scheme 1

Abstracts

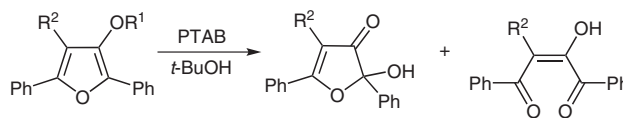
(A) *Oxidation of Secondary Alcohols to the Corresponding Carbonyl Compounds*: Sayama et al. showed that PTAB is an available and chemoselective reagent for the oxidation of secondary alcohols and substituted 1,2-diols to the corresponding ketones, 1,2-diketones and α -ketols in the presence of catalytic amounts of SbBr₃ or CuBr₂ at room temperature.¹⁹ The oxidative cleavage of the glycol C–C bond for 1,2-diols was not found. Furthermore, aliphatic primary alcohols were not affected under the same oxidative conditions.



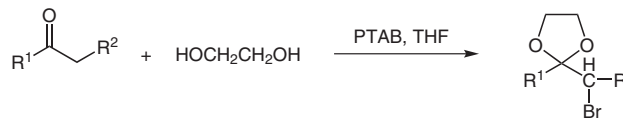
(B) *Selective Oxidation of Sulfides to Sulfoxides*: An efficient procedure for the selective oxidation of various sulfides to the corresponding sulfoxides in aqueous pyridine solution was achieved using PTAB as oxidant.²⁰ This method allowed ¹⁸O-labelled sulfoxides to be prepared without loss of isotope enrichment of the used ¹⁸O-water.



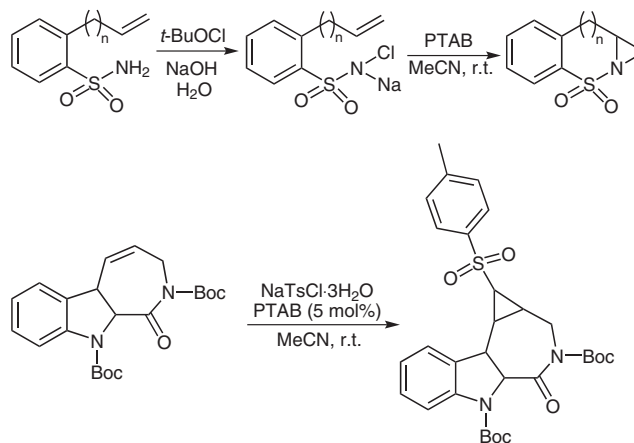
(C) *Oxidative Conversion of 3-Alkoxyfurans to 2-Hydroxy-3(2H)-furanones and 2-Hydroxy-2-butene-1,4-diones*: PATB can be applied for the oxidative ring opening of 3-alkoxy-2,5-diphenylfurans to 2-hydroxy-2-butene-1,4-dions in *t*-BuOH at room temperature. The transformation of 3-alkoxy-2,4,5-triphenylfurans to 2-hydroxy-2,4,5-triphenyl-3-(2H)-furanone was also accomplished with PATB in *t*-BuOH under the same reaction conditions.²¹



(D) *One-Pot α -Bromoacetalization of Carbonyl Compounds*: A convenient and practical method for the one-pot α -bromoacetalization of carbonyl compound has been developed.²² The reaction was performed in tetrahydrofuran–ethylene glycol (1:1) with 1–2 equivalents of PATB at room temperature to afford the corresponding α -bromoacetals in good to excellent yields.



(E) *Aziridination of Alkenes*: Dauban and co-workers showed that PATB can catalyze the intramolecular aziridination of *N*-chloramine salts of ω -unsaturated sulfonamides.²³ The aziridination of the alkene can also be carried out employing an understoichiometric amount of chloramines-T trihydrate in the presence of 5 mol% PATB.²⁴



(F) *Coupling Reaction of Carbon Dioxide and Epoxides*: A combination of SalenRu(PPh₃)₂²⁵ or metal porphyrin²⁶ with PATB has been used as novel and high efficient catalysts for the coupling reaction of carbon dioxide and epoxides to yield the corresponding cyclic carbonates.



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