

# SYNLETT Spotlight 265

## Phenyltrimethylammonium Tribromide: A Versatile Reagent in Organic Synthesis



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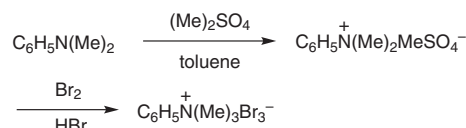
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

### 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.<sup>1</sup> 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 SbBr<sub>3</sub>,<sup>2</sup> for brominating the  $\alpha$ -position of carbonyl compounds,<sup>3–8</sup>  $\alpha'$ -bromination of  $\alpha,\beta$ -unsaturated ketones,<sup>9</sup> and for the addition of bromine to alkenes.<sup>10</sup> 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,<sup>11</sup> and synthesis of imi-

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

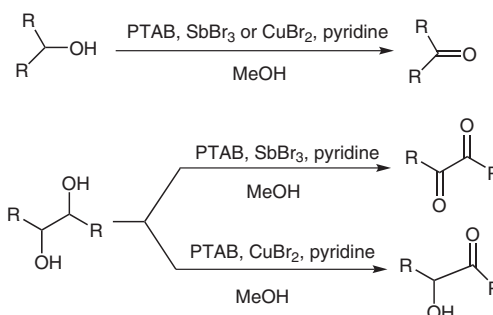
Phenyltrimethylammonium tribromide is commercially available now. It can be readily prepared from *N,N*-dimethylaniline and dimethyl sulfate, followed by treatment with 48% hydrobromic acid and bromine.<sup>1</sup>



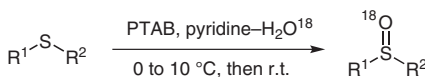
Scheme 1

### Abstracts

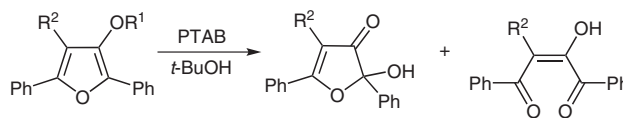
(A) *Oxidation of Secondary Alcohols to the Corresponding Carbonyl Compounds*: Sayama et al. showed that PTAB is an available and chemoselective reagent for the oxidation of secondary alcohols and substituted 1,2-diols to the corresponding ketones, 1,2-diketones and  $\alpha$ -ketols in the presence of catalytic amounts of SbBr<sub>3</sub> or CuBr<sub>2</sub> at room temperature.<sup>19</sup> 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.



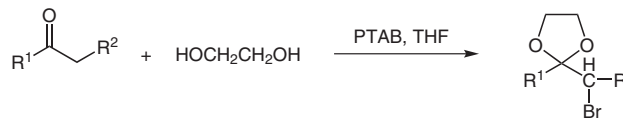
(B) *Selective Oxidation of Sulfides to Sulfoxides*: An efficient procedure for the selective oxidation of various sulfides to the corresponding sulfoxides in aqueous pyridine solution was achieved using PTAB as oxidant.<sup>20</sup> This method allowed <sup>18</sup>O-labelled sulfoxides to be prepared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



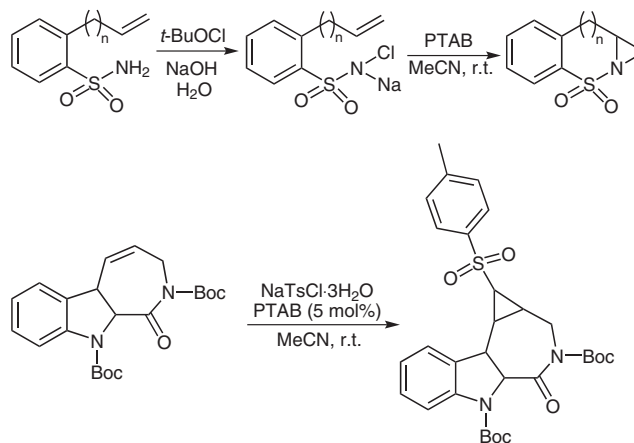
(C) *Oxidative Conversion of 3-Alkoxyfurans to 2-Hydroxy-3(2H)-furanones and 2-Hydroxy-2-butene-1,4-diones*: PATB can be applied for the oxidative ring opening of 3-alkoxy-2,5-diphenylfurans to 2-hydroxy-2-butene-1,4-dions in *t*-BuOH at room temperature. The transformation of 3-alkoxy-2,4,5-triphenylfurans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



(D) *One-Pot  $\alpha$ -Bromoacetalization of Carbonyl Compounds*: A convenient and practical method for the one-pot  $\alpha$ -bromoacetalization of carbonyl compound has been developed.<sup>22</sup> The reaction was performed in tetrahydrofuran–ethylene glycol (1:1) with 1–2 equivalents of PATB at room temperature to afford the corresponding  $\alpha$ -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  $\omega$ -unsaturated sulfonamides.<sup>23</sup> 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.<sup>24</sup>



(F) *Coupling Reaction of Carbon Dioxide and Epoxides*: A combination of SalenRu(PPh<sub>3</sub>)<sub>2</sub><sup>25</sup> or metal porphyrin<sup>26</sup> 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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