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Benzyltriphenylphosphonium tribromide (BTPTB): A convenient and versatile catalyst 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

The hazardous nature of elemental bromine and difficulties encountered in its handling have led to the preparation of new active bromine reagents like organic tribromides [1]. These reagents are comparatively less hazardous, stable, solid, and environmentally benign reagents. These reagents can be synthesized very easily by oxidizing bromide to tribromide and then precipitating with phosphonium cation [2]. They are known to be convenient oxidizing and brominating agents [3-5]. In addition, they also used as efficient catalysts in organic Benzyltriphenylphosphonium synthesis [6-8]. tribromide is a yellow crystal with a melting point at 142.5-145°C [9]. It is known to be a convenient oxidizing [10,11] and brominating agent [12] and used as an efficient catalyst for organic synthesis [13]. It can be synthesized with four methods shown in Scheme 1 $[12^a, 9^b, 14^c, 10-11^d]$.

a)
$$Ph_{3}PCH_{2}Ph^{\oplus}Cl^{\ominus} + KBr_{3} \xrightarrow{H_{2}O} Ph_{3}PCH_{2}Ph^{\oplus}Br_{3}^{\ominus} + KCl$$

b) $Ph_{3}PCH_{2}Ph^{\oplus}Br^{\ominus} + Br_{2} \xrightarrow{CH_{2}Cl_{2}} Ph_{3}PCH_{2}Ph^{\oplus}Br_{3}^{\ominus}$
c) $Ph_{3}PCH_{2}Ph^{\oplus}Br^{\ominus} + 2NaBr \xrightarrow{Oxane} Ph_{3}PCH_{2}Ph^{\oplus}Br_{3}^{\ominus}$
d) $Ph_{3}PCH_{2}Ph^{\oplus}Br^{+} + Br_{2}(0.5M) \xrightarrow{EtOH} Ph_{3}PCH_{2}Ph^{\oplus}Br_{3}^{\ominus}$

Scheme 1

Abstracts

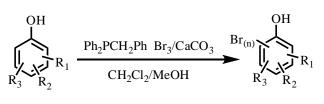
(A) Bromination, especially of aromatic substrates, is usually carried out by bromine solution [15], but benzyltriphenyl-phosphonium tribromide (BTATB) of phenols is preferable. Reactions with benzyltriphenyl-phosphonium tribromide in dichloromethane-methanol mixture (2:1)gave mono,di and tri brominated phenols at room temperature with high selectivity and good yields [12].

(B) A variety of carbonyl compounds have been successfully converted to the corresponding thioacetal derivatives in good to excellent yields on reaction of carbonyl compounds the with 1,3-propanedithiol, 1,2-ethanedithiole, and ethanethiol in the presence of catalytic amounts of benzyltriphenylphosphonium tribromide under solvent-free conditions and CH_2Cl_2 as solution [14, 16].

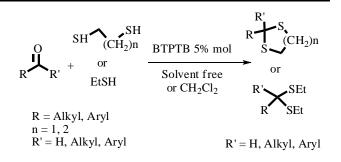
(C) A mild and efficient method for the conversion of alcohols to their corresponding methoxymethyl ethers and acetates using benzyltriphenylphosphonium tribromide (BTPTB) as the catalyst is investigated. All reactions were performed under completely heterogeneous reaction conditions in good to high yields [17].

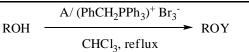
(**D**) Benzyltriphenylphosphonium tribromide can be used as an efficient catalyst for the conversion of alcohols to their corresponding trimethylsilyl ethers (TMS ethers) with hexamethyldisilazane (HMDS). Desilylation of TMS ethers is also catalyzed by BTPTB in MeOH at room temperature in high yields. BTPTB is also able to oxidize the TMS ethers to their corresponding carbonyl compounds in a mixture of MeOH: H₂O in good to high yields [11].

(E) Benzyltriphenylphosphonium tribromide (TBPTB) was found to catalyze the acetylation of different types of alcohols with acetic anhydride. All reactions were performed in refluxing $CHCl_3$ in good to high yields and in short reaction times [10].



$$R_1, R_2, R_3 = H \text{ or } Cl \text{ or } CH_3 \text{ or } NO_2$$





If
$$A = CH_2(OMe)_2$$
; $Y = CH_2OCH_3$
If $A = (CH_3CO)_2O$; $Y = COCH_3$

ROH
$$\xrightarrow{HMDS / BTPTB} ROTMS$$

CHCl₃, reflux $\xrightarrow{ROTMS} ROTMS$
ROTMS $\xrightarrow{BTPTB} ROH$
MeOH, r.t. $\xrightarrow{ROH} R^1R^2CH(OTMS) \xrightarrow{BTPTB} R^1R^2CO$
MeOH : H₂O
(2:1, v/v) / r.t.

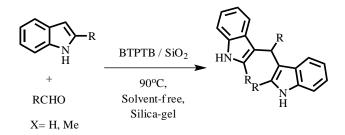
ROH
$$\longrightarrow$$
 ROAc
CHCl₃, reflux

(F) An efficient solvent-free procedure for the preparation of bis(indolyl)methanes via the condensation of indoles with aldehydes in the presence of catalytic amount of benzyltriphenylphosphonium tribromide is described.

The advantages of this method are generality, high yields, short reaction times, ease of product isolation, and ecologically friendly [13].

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