Tetrabutylammonium Hydrogen Sulfate

Compiled by Aditya Bhattacharyya

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Introduction

Tetrabutylammonium hydrogen sulfate (TBAHS, 1), is a stable, hygroscopic, white solid (mp 169–171 °C). It is widely used in various fields of chemistry as phase-transfer catalyst (PTC) and ion-pairing reagent as mobile phase additive in HPLC. It has been also used in a variety of organic transformations some of which include the syntheses of triarylpipridines, $N$-monosubstituted $\alpha$-keto amides, cyclic and acyclic $\beta$-disubstituted, $\alpha,\beta$-unsaturated ketones, $3$-alkylated indoles, benzopyran-annulated pyranol[2,3-c]pyrazoles, N1-alkylated 3,4-dihydropyrimidine-2(1H)-ones, 2-O-deacetylated glucosyl hydroxamates, 1,2,3-triazoles, 1,8-dioxooctahydroxanthene, $\beta$- and $\gamma$-amino ethers, morpholines and their higher homologues, etc.

Although TBAHS is commercially available and inexpensive, it can be prepared from tetrabutylammonium azide by treating it with potassium hydrogen sulfate and 10% aqueous sulfuric acid in aqueous medium (Scheme 1, eq. 1) or from tetrabutylammonium thiocyanate by treating it with relatively concentrated sulfuric acid (70%) at 75 °C (Scheme 1, eq. 2).

Scheme 1 Synthesis of tetrabutylammonium hydrogen sulfate (TBAHS, 1)

Abstracts

(A) Reddy et. al. reported a simple and efficient one-pot multicomponent condensation of various aromatic aldehydes and acetophenones in the presence of a catalytic amount of TBAHS and ammonium acetate (NH$_4$OAc) under solvent-free conditions to afford a variety of 2,4,6-triarylpipridines in good yields (65–75%).

(B) Liu, Xu and co-workers described an aerobic oxidation protocol for transforming a variety of aryl- and heteroarylacetamides to $N$-monosubstituted $\alpha$-keto amides in the presence of TBAHS and sodium bicarbonate under mild reaction conditions in moderate to high yields.

(C) Perumal and co-workers described an efficient TBAHS-catalyzed regioselective Michael addition of indoles to electron-deficient olefins viz. nitrostyrenes and chalcones in aqueous medium to afford a variety of Michael adducts in good to excellent yields. The resulting 3-alkylated indoles were found to be promising candidates against a wide range of Gram-positive and Gram-negative bacteria.
Very recently, we have reported the syntheses of haloalcohols in very high yields. In this case, TBAHS effectively controlled the partial racemization of the substrate which ensured the formation of the corresponding products with excellent enantio- and diastereoselectivity (ee up to >99%, de up to 99%)

Parmar et al. reported a TBAHS-mediated one-pot domino Knoevenagel–hetero-Diels–Alder reaction of substituted salicylaldehydes and 5-pyrazolones to synthesize a variety of benzyropyran-annulated pyran[2,3-c]pyrazoles in high yields and stereoselectivity.

Papot and co-workers observed that O-glycosylation of hydrazones to obtain substituted 4-benzoyl-1-(5-deoxy-1,2-D-xylofuranos-5-yl)-5-phenyl-1,2,3-triazoles in moderate to good yields.

Tripathi and co-workers reported a regioselective [3+2] cycloaddition of commercially available chalcones and 5-azido-5-deoxy-1,2,3-triazoles in moderate to good yields. Some of the synthesized N1-alkylated 3,4-dihydropyrimidine-2(1H)-ones were found to possess marginal calcium channel blocking activity.

Very recently, we have reported the syntheses of 3,4-dihydropyrimidine-2(1H)-ones in high yields under solvent-free conditions. Some of the synthesized N1-alkylated 3,4-dihydropyrimidine-2(1H)-ones were found to possess marginal calcium channel blocking activity.

References