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Spotlight 403

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

Tetrabutylammonium Hydrogen Sulfate

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Aditya Bhattacharyya was born in West Bengal, India in 1986. He graduated in Chemistry from the University of Calcutta in 2006 and received his M.Sc. in 2008 from Bengal Engineering and Science University, Shibpur. Presently, he is working towards his Ph.D. under the supervision of Prof. Manas K. Ghorai in organic chemistry at the Indian Institute of Technology, Kanpur. His research interests focus on the development of novel synthetic methodologies for heterocyclic compounds via $S_n2$-type ring opening of small ring aza-heterocycles with various nucleophiles.

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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 triarylpuridines,\(^1\) N-monosubstituted $\alpha$-keto amides,\(^2\) cyclic and acyclic $\beta$-disubstituted, $\alpha,\beta$-unsaturated ketones,\(^3\) 3-alkylated indoles,\(^4\) benzopyran-annulated pyrao[2,3-c]pyrazoles,\(^5\) N1-alkylated 3,4-dihydropyrimidine-2(1H)-ones,\(^6\) 2-O-deacetylated glucosyl hydroxamates,\(^7\) 1,2,3-triazoles,\(^8\) 1,8-dioxooctahydroxanthenes,\(^9\) $\beta$- and $\gamma$-amino ethers, morpholines and their higher homologues,\(^10\) etc.

Abstracts

(A) Reddy et al.\(^1\) 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-triarylpyridines in good yields (65–75%).

(B) Liu, Xu and co-workers\(^2\) 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\(^4\) 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.

Although TBAHS is commercially available and inexpensive, it can be prepared from tetrabutylammonium azide\(^11\) by treating it with potassium hydrogen sulfate and 10% aqueous sulfuric acid in aqueous medium (Scheme 1, eq. 1) or from tetrabutylammonium thiocyanate\(^12\) 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)

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(D) Parmar et al.\(^1\) reported a TBAHS-mediated one-pot domino Knoevenagel–hetero-Diels–Alder reaction of substituted salicylaldehydes and 5-pyrazolones to synthesize a variety of benzopyran-annulated pyrano[2,3-c]pyrazoles in high yields and stereoselectivity.

(E) Singh et al.\(^6\) observed that O-glycosylation of haloalcohols in very high yields. In this case, TBAHS effectively catalyzed S\(^\text{N2}\)-type ring opening of activated aziridines and azetidines with alcohols and diastereospecificity (ee up to >99%, de up to 99%).

(F) Papot and co-workers\(^7\) observed that O-glycosylation of hydroxamic acids can be performed using TBAHS as catalyst. For a representative example acetobromoglucose was converted into the corresponding 2-O-deacetylated glucosyl hydroxamate with complete β-selectivity in moderate yield.

(G) Tripathi and co-workers\(^8\) reported a regioselective [3+2] cycloaddition of commercially available chalcones and 5-azido-5-deoxy-1,2-O-isopropylidene-α-D-xylofuranose in the presence of TBAHS to obtain substituted 4-benzoyl-1-(5-deoxy-1,2-O-isopropylidene-α-D-xylofuranos-5-yl)-5-phenyl-1H-1,2,3-triazoles in moderate to good yields.

(H) Very recently, we have reported\(^10\) the syntheses of β- and γ-aminoo ethers, morpholines, and their higher homologues via Lewis acid catalyzed TBAHS-mediated highly regioselective S\(_2\)2-type ring opening of activated aziridines and azetidines with alcohols and 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%).

References