

SYNLETT Spotlight 176

Tetra-*n*-Butylammonium Tribromide

Compiled by Valdemar B. C. Figueira



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

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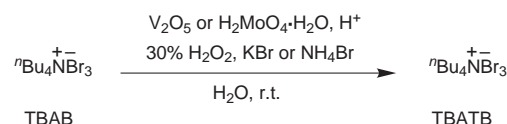
Introduction

Tetra-*n*-butylammonium tribromide (TBATB) is one of the most widely used organic ammonium tribromides (OATB's) for bromination^{1–3} of several organic substrates.

Because it is a stable crystalline solid, easy to handle and maintains the desired reaction stoichiometry it is looked at as a substitute of Br₂. It can also be considered as a 'greener' brominating agent⁴ as well as an in situ generator of anhydrous HBr.

Other types of reactions like acylation, oxidation and protection/deprotection of several functional groups can be performed with TBATB in catalytic amounts and under solvent-free conditions.

Preparation

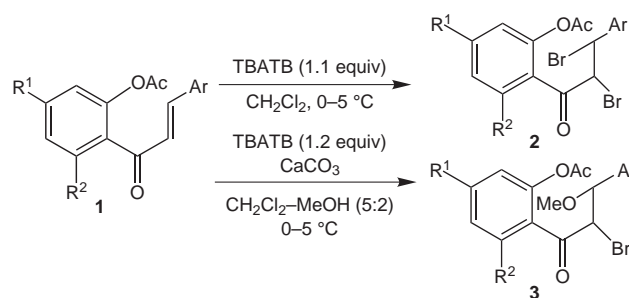


Properties

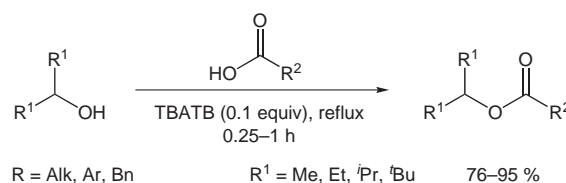
Yellow-orange crystalline ionic solid, mp 75 °C (acetonitrile). IR bands at 170 and 190 cm⁻¹. Monoclinic space group C2/c structure determined by X-ray.

Abstracts

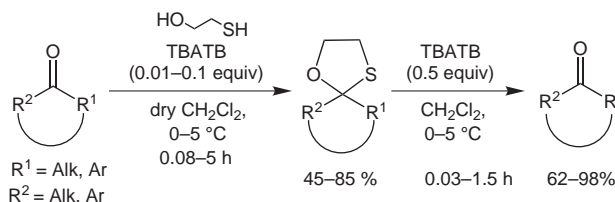
(A) Preparation of a wide variety of flavones and aurones starting from 2'-acetoxychalcones **1** in high yields (36–55% and 65–85%, respectively) was accomplished in two steps, being the first selective bromination with TBATB (70–80% for **2** and 75–85% for **3**).⁵



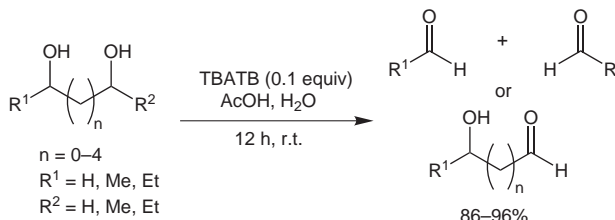
(B) Direct condensation of various alcohols and carboxylic acids was efficiently achieved with a catalytic amount of TBATB under solvent-free conditions at reflux. Chemoselectivity for primary alcohols was observed when secondary and phenolic alcohols were also present.⁶



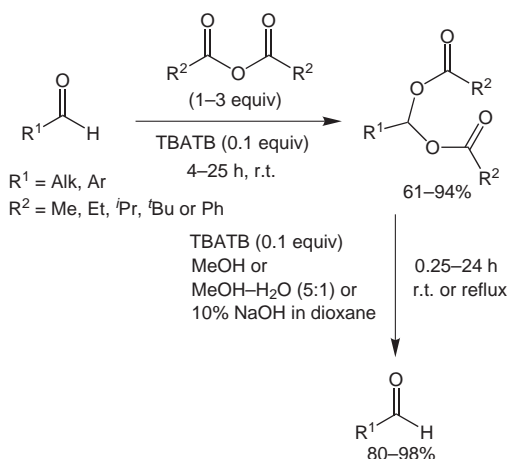
(C) Selective protection of various carbonyl compounds to the corresponding 1,3-oxathiolanes was performed with catalytic amount of TBATB. Chemoselective deprotection of synthesized 1,3-oxathiolanes to the parent carbonyl compounds was also obtained with TBATB. No bromination on α -keto position, aromatic ring, allylic position or double bond was observed.⁷



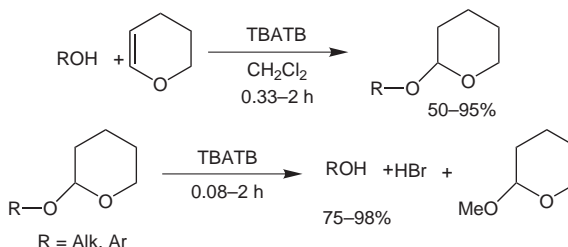
(D) Gosain and Sharma described the kinetics and mechanism for oxidation of vicinal and non-vicinal diols to the corresponding aldehydes and hydroxycarbonyl compounds, respectively. Excellent yields were obtained.⁸



(E) Solvent-free, chemoselective diacylation of aldehydes was accomplished using a catalytic amount of TBATB, without side reaction yielding brominated products. Chemoselective cleavage of diacylates was also reported with TBATB when the reaction was performed in different conditions.⁹



(F) TBATB promotes tetrahydropyranylation and detetrahydropyranylation of primary, secondary and tertiary alcohols when present in 10 mol%. Mild reaction conditions make both reactions compatible with other acid-sensitive groups such as OTs, nitro and Boc, among others.¹⁰



References

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