SYNLETT Spotlight 353

N-Benzyl-DABCO Tribromide

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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

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Introduction

Organic ammonium tribromides are of high molecular weight, stable, crystalline solids, and capable to release a stoichiometric amount of bromine (where small quantities of bromine are necessary for microscale reactions). N-Benzyl-DABCO tribromide (NBDTB) is an efficient, stable, and cheap solid reagent, which is quite soluble in methanol, dichloromethane, and dimethylsulfoxide, but insoluble in most nonpolar or less polar solvents, such as n-hexane and diethyl ether.² N-Benzyl-DABCO tribromide can be readily prepared from DABCO and benzyl bromide, followed by treatment with liquid bromine.³

Scheme 1

Abstract

(A) Oxidative Cyclization of Thiobenzanilides to Benzothiazoles: Moghaddam and Boeini showed that NBDTB is an efficient oxidative reagent for the synthesis of 2-arylbenzothiazoles with different substituents on the two aromatic rings.4 These oxidative cyclizations were carried out in short reaction times and in high yields.

(B) Deprotection of Dithioacetals:

N-Benzyl-DABCO tribromide is a mild and highly effective reagent for the deprotection of dithioacetals in dichloromethane-methanol at room temperature. The reaction can be performed cleanly, in a short time, and in high yield.5

(C) Oxidative Coupling of Benzyl Cyanides:

The NBDTB has been applied successfully for the preparation of α,α -dicyanostilbenes from the corresponding benzyl cyanides in the presence of K₂CO₃ in excellent yields.⁶

$$C \equiv N \qquad \underbrace{\begin{array}{c} Ph & Br_3 \\ \hline DMSO, K_2CO_3, 1-3 h, r.t. \\ 57-90\% \end{array}}_{Ph} R \qquad N \qquad N \qquad \qquad N$$

1332 SPOTLIGHT

(D) Regioselective Bromination of Aromatic Amines and Phenols: Moghaddam and Zargarani have reported the use of NBDTB as highly efficient reagent for the mono-bromination of phenols and substituted anilines at room temperature with good yields. The mild reaction conditions, rapid conversion, excellent yield, and high regioselectivity are the impressive advantages of the present protocol.²

$$\label{eq:R} \begin{split} R &= \text{OH}, \, \text{NMe}_2, \, \text{NH}_2, \, \text{OMe} \\ G &= \text{H}, \, \text{electron-releasing or -withdrawing substituent} \end{split}$$

(E) Green Protocol towards 3,5-Disubstituted 1,2,4-Thiadiazoles: Boeini reported a new and mild method for the synthesis of thiadiazoles from thiobenzamides using NBDTB in water at room temperature. The reaction occurs cleanly in aqueous media without the formation of any tarry materials.³

References

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