Bromodimethylsulphonium Bromide (BDMS): A Versatile Reagent in Organic Synthesis

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Dedicated to my mentor Prof. Abu T. Khan

Introduction

Bromodimethylsulphonium bromide (BDMS) (Figure 1) is a light orange solid compound, which has been used extensively in various organic transformations. It can easily be prepared from molecular bromine and dimethylsulfide. It can also be generated in situ from the reaction of dimethylsulfoxide and aqueous HBr. BDMS can be considered a convenient storage for the bromonium ion, just as hypobromite, N-bromosuccinimide or bromoazide. After Meerwein’s discovery of bromodimethylsulphonium bromide in 1965, it has gained considerable interest in current organic chemistry due to its easy handling and low cost, its easy access and varied application both as catalyst, as well as an effective reagent.

Abstracts

(A) Preparation of alkyl bromides from corresponding alcohols:
Furukawa et. al first demonstrated the application of this reagent for the conversion of alcohols to bromides in high yield. The reaction proceeds via an inversion, i.e. an optically active alcohol gives the corresponding bromide with inversion of configuration.

(B) Conversion of epoxides and enamines to α-haloketones:
Epoxides upon treatment with halodimethylsulphonium halides (chloride/bromide) in the presence of triethyl amine give α-halo ketones in high yields. The reaction proceeds well with alkeno oxides and cycloalkene oxides of small ring sizes. Epoxides with medium and large ring sizes undergo transannular rearrangements, giving mixtures of products. Similarly, enamines react with BDMS to give α-bromoketones.
(C) Electrophilic addition to olefins:
Chow et al. showed that bromodimethylsulfonium bromide reacts with various alkenes and provides corresponding addition products. The resultant sulfonium bromides on treatment with aqueous potassium carbonate give dehydrobrominated products.\(^\text{13}\)


(G) Electrophilic aromatic bromination by in situ generated BDMS:
Majetich et al. showed that BDMS, generated in situ by treating DMSO with aqueous HBr, is a milder and more selective reagent for electrophilic aromatic bromination than elemental bromine.\(^\text{15}\)

Indole alkaloids can also be brominated using the same reagent.\(^\text{16}\)

References


