

SYNLETT Spotlight 315

Triphenylphosphine Dibromide

Compiled by Garima



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

Garima was born in Allahabad, Uttar Pradesh, India. She obtained her B.Sc. (1999) and M.Sc. (2001) degrees in Organic Chemistry from the Allahabad University, Uttar Pradesh, India. After serving as a guest lecture in chemistry for five years (2003–2008) at the C.M.P. Degree College, Allahabad, she joined the research group of Prof. L. D. S. Yadav for her doctoral studies in April 2008 as a JRF of CSIR. Her research interests focus on the development of green synthetic routes to novel molecular structures for applications in functional materials.

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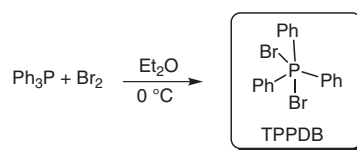
Dedicated to my honorable mentor Prof. L. D. S. Yadav

Introduction

Triphenylphosphine dibromide (TPPDB, PPh_3Br_2), originally synthesized by Horner and his co-workers,¹ has shown significant synthetic versatility over the course of the last decades in organic synthesis. It has been used extensively in various organic transformations, such as bromination of alcohols, phenols, and enols, cleavage of ethers and acetals to alkyl bromides, cyclization of β - and γ -amino alcohols to aziridines and azetidines, conversion of carboxylic acid derivatives into acyl bromides, bromination or dehydration of carboxamide groups and epoxide opening to vicinal dibromides.² Some of these resulting compounds have been reused in total syntheses of complex natural products during the final steps. Thus, the chemoselectivity and predictable reactivity of triphenylphosphine dibromide makes it a noteworthy and useful

reagent. It also finds application in the synthesis of ^{18}F -4-fluorobenzyltriphenylphosphonium bromide, a new class of positron-emitting lipophilic cations, acting as myocardial per fusion PET tracers.³

Triphenylphosphine dibromide is a colorless crystalline hygroscopic solid (mp 235 °C) that is readily prepared before use by addition of an equimolar amount of bromine to triphenylphosphine in anhydrous diethyl ether at 0 °C (Scheme 1).⁴ It is a molecular compound in the solid state, but ionises in dichloromethane to form $[\text{Ph}_3\text{PBr}]^+\text{Br}^-$.⁵

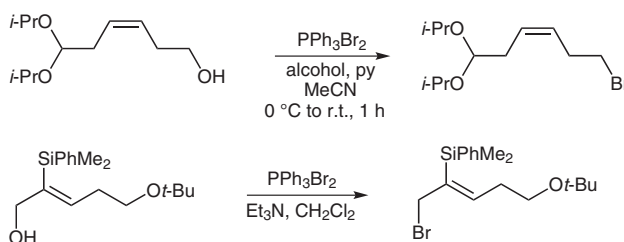


Scheme 1

Abstract

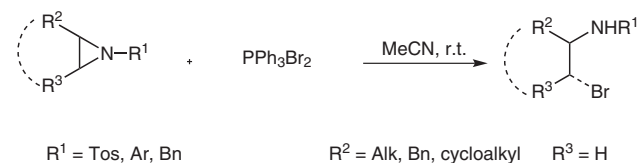
(A) Preparation of Alkyl, Allyl, and Aryl Bromides:

Horner and co-workers¹ demonstrated the application of triphenylphosphine dibromide for the conversion of alcohols and phenols into bromides. It has advantages over the other phosphorus-based reagents in effecting substitution without elimination or molecular rearrangement with inversion of the product configuration. It becomes the reagent of choice for the conversion of various types of alcohol-containing sensitive functionalities, such as *cis* double bonds and ketals, into the corresponding bromides.⁶



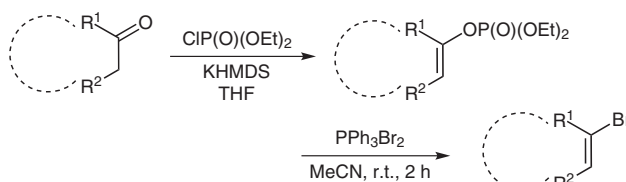
(B) Ring Opening of Aziridines:

Kumar and co-workers⁷ have reported the use of PPh_3Br_2 as highly efficient reagent for the ring opening of aziridines affording β -bromo amines. The method works effectively for both activated and non-activated aziridines in excellent yields within a short period of time.

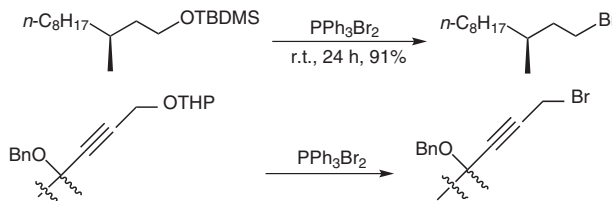


(C) *Synthesis of Vinyl Bromides:*

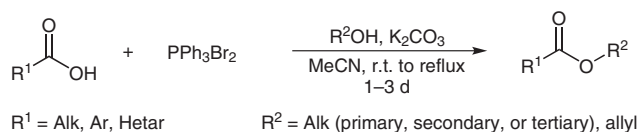
Kamei and co-workers⁸ have developed a new synthetic method for the preparation of vinyl bromides from acyclic and cyclic ketones.

(D) *Conversion of TBDMS and THP Ethers into Bromides:*

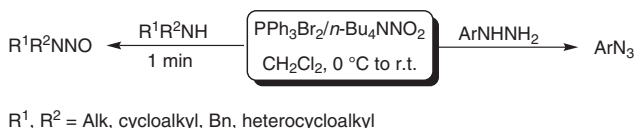
PPh_3Br_2 is a mild and highly effective reagent for the direct cleavage of TBDMS and THP ethers into bromides.⁹

(E) *Preparation of Esters:*

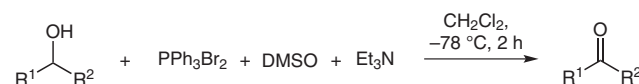
Salomé and Kohn¹⁰ have reported a one-pot, expedient protocol for the conversion of carboxylic acids into their esters using excess triphenylphosphine dibromide, base, and alcohol. The reaction gave the esterified product in moderate to high yields.

(F) *Preparation of N-Nitrosamines and Azides:*

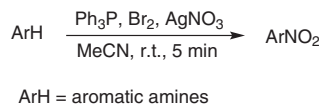
The PPh_3Br_2 in combination with $n\text{-Bu}_4\text{NNO}_2$ has been applied successfully for the preparation of *N*-nitrosamines and azides from the corresponding amines and hydrazine derivatives in excellent yields.¹¹

(G) *Oxidation of Alcohols:*

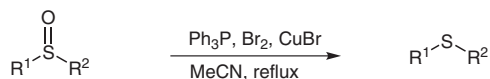
The use of PPh_3Br_2 in combination with DMSO is found to be a good alternative to the classical Swern oxidation. A variety of alcohols has been oxidized under mild conditions by the DMSO- PPh_3Br_2 complexes.¹²

(H) *Nitration of Aromatic Amines:*

The use of $\text{PPh}_3\text{Br}_2/\text{AgNO}_3$ provides a new reagent system for the novel and highly chemoselective nitration of aromatic amines under mild reaction conditions.¹³

(I) *Deoxygenation of Sulfoxides:*

The combination of $\text{Ph}_3\text{P}/\text{Br}_2/\text{CuBr}$ was found to be an effective promoter for the deoxygenation of sulfoxides and afforded the corresponding sulfides in excellent yields.¹⁴



References

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