Bestmann–Ohira Reagent: A Versatile Reagent in Organic Synthesis

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Dedicated to Professor S. L. Patil

Introduction

Bestmann–Ohira reagent [(1-diazo-2-oxopropyl)phosphonate] can be prepared by the reaction of dimethyl-2-oxopropylphosphonate, TosN₃, NaH, t-BuOK or Et₃N in benzene and THF. An alternative is the preparation using polymer-supported sulfonyl azide and t-BuOK in methylenchloride. The Bestmann–Ohira reagent is widely used in the conversion of primary alcohols, aldehydes, ketones, and amides into alkynes. Recently, it was employed in the synthesis of pyrazoles as well as 1,3-oxazoles.

Abstracts

(A) The use of the Bestmann–Ohira reagent is an alternative to the Fritsch–Buttenberg–Wiechell-type rearrangement and the Corey–Fuchs procedure that allows the addition of the reagent to an aldehyde under mild reaction conditions, thus avoiding the use of a strong base under low-temperature conditions. The reaction works with alkyl and aryl as well as hindered aldehydes. In case of α,β-unsaturated aldehydes the main products were isolated as homopropargylic methyl ethers. The reaction can be easily performed under one-pot conditions.

(B) Hamilton D. Dickson and co-workers reported that esters and amides undergo reduction to the corresponding aldehydes using DIBAL-H followed by in situ conversion into terminal alkynes utilizing the Bestmann–Ohira reagent in good to excellent yields. Additionally, chiral nonracemic substrates undergo this transformation with complete preservation of stereochemical integrity.

(C) E. Quesada et al. described the direct conversion of activated primary alcohols into terminal alkynes through a sequential one-pot, two-step process involving oxidation with manganese dioxide and then treatment with the Bestmann–Ohira reagent. This transformation proceeds efficiently (59–99% yield) under mild reaction conditions with a range of benzylic, heterocyclic, and propargylic alcohols.
(D) 1,3-Dipolar cycloaddition of the anion of diethyl 1-diazomethylphosphonate, generated in situ from Bestmann–Ohira reagent, with conjugated nitroalkenes provided regioisomerically pure phosphonylpyrazoles in moderate to good yield. These pyrazoles are formed in one pot via spontaneous elimination of the nitro group.5

(E) D. Gong et al. prepared a series of 4-phosphoryl-substituted 1,3-oxazoles conveniently by reaction of Bestmann–Ohira reagent and aromatic nitriles in the presence of a catalytic amount of rhodium(II) acetate.6

(F) Oxidation of epoxy alcohol by Dess–Martin periodinane gave an aldehyde which was subsequently treated with the Ohira reagent to give an epoxy alkyne in 93% yield.7

(G) Barrett and co-workers prepared ROMPgel-supported ethyl 1-diazo-2-oxopropylphosphonate and employed this reagent in the conversion of a variety of aldehydes into terminal alkynes.8 The use of polymer-supported Ohira reagent led to high product yield.

(H) The cycloaddition of diethyl 1-diazomethylphosphonate with benzylidine alkylamines afford (1-alkyl-5-phenyl-4,5-dihydro-1H-[1,2,3]triazol-4-yl)-phosphonic acid diethyl ester.9

(I) Gilbert et al. described the base-promoted reaction of dimethyl (diazomethyl)phosphonate with aldehydes and aryl ketones at low temperature. The alkynes are obtained in modest to excellent yields.10

(J) The Bestmann–Ohira reagent itself was used for the preparation of enol ethers or alkynes from carbonyl compounds in the presence of excess potassium carbonate and methanol.11

References