Recent Advances and Applications of tert-Butyl Nitrite (TBN) in Organic Synthesis

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Abstract: This mini-review will present the recent applications of tert-Butyl Nitrite (TBN) in organic synthesis. Due to its unique structural feature and wide application, TBN holds a prominent and great potential in organic synthesis. The applications of TBN in three areas viz. aerobic oxidation, annulation, and diazotization were reviewed recently; now, the current mini-review will describe the studies carried out to date in areas such as nitrification of alkanes, alkenes, alkynes, and aromatic compounds, nitrosylation and sequential nitrosylation reactions, using TBN as source of oxygen and nitrogen. The mechanisms of these transformations will be briefly described in this mini-review.

Keywords: Mechanism, nitration, nitrosylation, organic synthesis, source of nitrogen, source of oxygen, tert-butyl nitrite.

1. INTRODUCTION

The important and primary goals of green chemistry are the use of low risks of chemicals for the human health and environment, and performance of reactions and synthetic procedures at high-cost effectiveness and energy efficiency that can be achieved by redesigning the academic and industrial synthetic processes. Avoiding of waste generated in reactions, recycling catalysts and reagents, utilization of alternative energy sources, minimizing potential accidents, preparing the biodegradable or recyclable products, consuming sustainable raw materials, using of solvents and chemicals with lower toxicity are some strategies in green chemistry. Therefore, a green chemist will search for the greener procedures in the viewpoint of chemicals, catalysts, solvents, energy sources, and synthetic, separation and purification procedures which can be carried out instead of the conventional academic and industrial processes [1].

Recently, tert-Butyl Nitrite (TBN) is well known as a versatile compound in organic chemistry. The advantages of TBN are that it is a cheap and commercially available chemical, easy to handle, possesses good solvent solubility, and often it generates tert-butanol (t-BuOH) as a non-toxic by-product in the course of its reactions. TBN often act as a source of nitrogen, NO, nitrous acid or a radical initiator in the organic reactions. Although many reactions effectively proceeded by the solo utilization of TBN, combinations with palladium, N-hydroxypthalimide (NHPi), 2,2,6,6-tetramethyl-1-piperidinylxoy (TEMPO), 2-azaadamantane N-oxyl (AZADO), 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), 9-azabicyclo[3.3.1]nonagn-N-oxyl (ABNO), or ABNO/KPF6 catalysts were employed to important transformations such as the oxidation of alcohols, the oxidation of benzylic and allylic alcohols, the oxidative deprotection of benzyl-type ethers, as well as oxygenation of benzene. TBN was also utilized for the generation of aryl azides, and diazonium salts that are very important intermediates in organic synthesis. It can act as a powerful nitrogenating agent for terminal aryl alkenes and alkynes. TBN was employed for the multifunctionalization of alkenes, the nitration of olefins, the nitro-carbocyclization of activated alkenes and nitro-amination of alkenes. The direct nitrification and nitration of aryl boronic acids using TBN were reported. TBN has been extensively utilized for the efficient synthesis of nitrogen bearing heterocycles under mild conditions. Since the applications of TBN in three areas viz. aerobic oxidation, annulation, and diazotization were reviewed recently [2]; in this mini-review, we wish to focus on various transformations reported recently including nitrification of alkenes, alkene, alkynes, and aromatic compounds, nitrosylation and sequential nitrosylation reactions, using TBN as source of oxygen and nitrogen.

2. RECENT APPLICATIONS OF TBN IN ORGANIC TRANSFORMATIONS

2.1. Nitration of Alkane, Alkene, Alkyne, and Aromatic Compounds

Due to their wide application in pharmaceuticals [3, 4], dyes [5], and materials [6], nitroarenes are important inter-