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ORIGINAL ARTICLE

Polyvinylpolypyrrolidoniume tribromide (PVP-Br_3) as efficient and metal-free agent for the selective oxidation of alcohols, trimethylsilyl ethers and oximes under mild conditions

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Oxidation;
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Ketone

Abstract Polyvinylpolypyrrolidoniume tribromide (PVP-Br_3) was found to be a metal-free and highly efficient oxidizing polymer for the selective oxidation of a variety of benzylic alcohols, deprotection and selective oxidation of trimethylsilyl ethers and oximes to the corresponding aldehydes and ketones at room temperature in moderate to high yields. The main advantages of this procedure are selective oxidation, efficient, milder reaction conditions, shorter reaction times, and easier work-up.

1. Introduction

In the last few years, the supporting of homogenous reagent on the organic polymer has been a growing interest in organic reactions [1]. The advantages of this type of researches are easy product separation [2], ease of handling [3], inhibiting metal losing [4], lower environmental damages, and in many cases the possibility of recovering and reusing of the polymeric catalyst [5]. Furthermore, the heterogeneous supported reagents show lower toxicity than corresponding homogenous reagents [6]. Since many polymers as a basis for the homogeneous reagents have been reported, polyvinylpyrrolidone (PVP) is one of the polymers that are currently used. However, there are a few reports on the application of PVP as supporting reagent or catalyst [7–11]. Bromine has been known for a decade to be an efficient and moderate oxidizing agent for the oxidation of organic compounds, which gave no other oxidized side products [12–13]. Therefore, finding some methods for the synthesis of heterogeneous reagent is important. One of these reagents is polyvinylpolypyrrolidoniume tribromide (PVP-Br_3) [14–17].

The selective oxidation of primary and secondary alcohols into corresponding aldehydes and ketones is undoubtedly

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one of the most important and challenging transformations in organic chemistry both at the laboratory and industrial synthetic chemistry [18]. So far, many procedures and variety of reagents have been reported for the oxidation of alcohols to the carbonyl compounds [19–24].

On the other hand the protection of certain functional groups and the deprotection of the protected derivatives constitute important processes in synthetic organic chemistry of polyfunctional molecules, including the total synthesis of natural products [25]. Trimethylsilyl ethers and oxime compounds are useful protecting groups in organic syntheses and have been used as intermediates for the synthesis of multifunctional organic compounds. Therefore, many methods have been reported for the transformation of trimethylsilyl ethers and oximes into aldehydes and ketones [26–30].

However, some of these reported methods have significant drawbacks such as long reaction time, low yields of products, non-selectivity, harsh reaction conditions, difficult workup and use of environmentally toxic or expensive reagents.

2. Experimental

Chemicals were purchased from Fluka or Merck chemical companies. All products were known by physical properties and FT-IR data were compared with those of authentic samples.

2.1. Preparation of polyvinylpolypyrrolidoniume tribromide

In a 50 mL round-bottomed flask, 1 mL of HBr (47%) and 1.85 g of polyvinylpolypyrrolidoniume was stirred for 1 h, and then kept at 50 °C for 24 h to obtain dry polyvinylpolypyrrolidoniume bromide. In the next step, 1.2 mL of Br_2 was added to the resulting powder. This mixture was stirred for 2 h and an orange crystalline solid (polyvinylpolypyrrolidoniume tribromide) was quantitatively obtained (Scheme 2) [14].

2.2. General procedure for the oxidation of alcohols, deprotection and selective oxidation of trimethylsilyl ethers and oximes

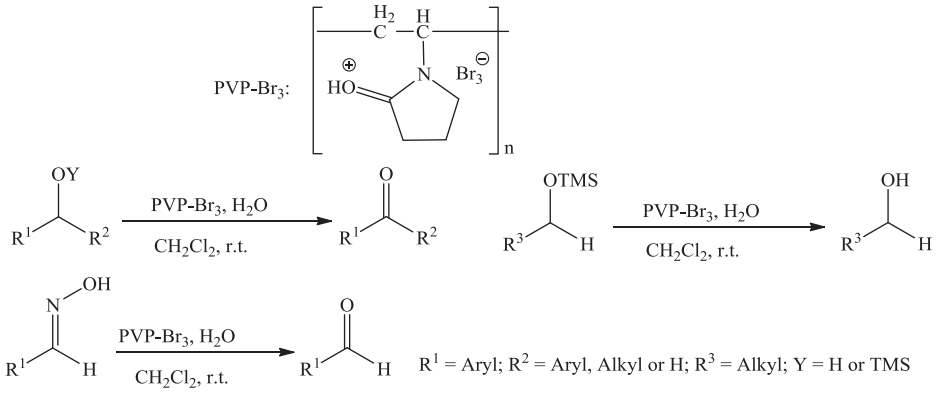
A mixture of the substrate (1 mmol), PVP-Br_3 (1.1–3 g) and H_2O (0.15 mL) was stirred in dichloromethane at room temperature for the appropriate reaction time (Scheme 1). The progress of the reaction was monitored by TLC. After completing the reaction the product was purified by filtering the reaction mixture through a short column of silica-gel (15 cm length, 1 cm diameter) using dichloromethane and acetone (95:5). The solvent was evaporated to afford pure products in good isolated yield (Table 3).

3. Results and discussion

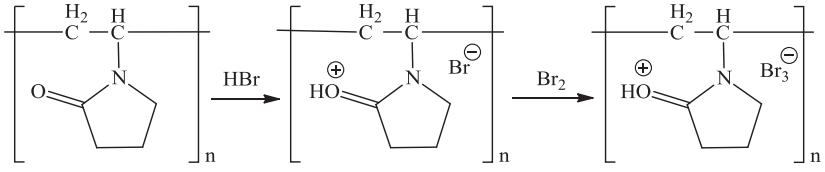
In continuation of our recent studies on the development of polymer-supported reagents, in the organic functional group transformations [31–33], we have decided to explore the application of a new and versatile reagent for the oxidation of organic compounds.

Therefore, herein we report the use of polyvinylpolypyrrolidoniume tribromide (PVP-Br_3) as an efficient and highly selective oxidizing polymer for the oxidation of alcohol, deprotection and selective oxidation of trimethylsilyl ether and oxime derivatives. The features of this oxidation reaction are outlined in (Scheme 1).

Polyvinylpolypyrrolidoniume tribromide is a safe, environmentally, stable and inexpensive source of bromine. This reagent was easily prepared via the combination of



Scheme 1 Oxidation of alcohols, trimethylsilyl ethers and oximes by PVP-Br_3.



Scheme 2 Preparation of polyvinylpolypyrrolidoniume tribromide (PVP-Br_3).