

SHORT
COMMUNICATIONS

Solvent-Free DABCO-Catalyzed One-Pot Conversion of Tetrahydropyranyl Ethers into Acetates by the Action of Bismuth(III) Nitrate under Microwave Irradiation*

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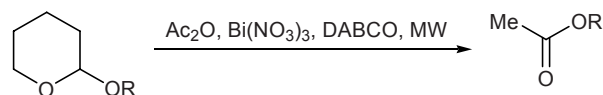
Acetylation of alcohols is an important transformation frequently used in organic synthesis [1]. Selective protection of functional groups and their subsequent deprotection are common processes in multistep organic syntheses, and conversion of one functional group into another is useful in day-to-day synthetic practice. Among protecting groups for alcohols, tetrahydropyranyl (THP) ethers are used most frequently due to their easy formation, reasonable stability, and compatibility with various reaction conditions [1, 2]. Although several methods have been reported for deprotection of THP ethers [2], as well as for the transformation of alcohols into acetates [3], procedures for direct conversion of THP ethers into acetates are few in number, and they suffer from serious disadvantages. These procedures make use of the following reagents: $\text{FeCl}_3/\text{Ac}_2\text{O}$ [4], AcCl/AcOH [5], $\text{Ti}/\text{Ac}_2\text{O}$ [6], bismuth salts [7], $\text{Cu}(\text{OTf})_2/\text{Ac}_2\text{O}$ [8], and ZrCl_4 [9]. In the recent years, microwave irradiation has become popular in organic synthesis due to acceleration of a wide variety of transformations [10]. Examples of microwave-assisted synthesis utilizing supported reagents under solvent-free conditions have been reported very recently; here, a combination of the convenience of supported reagents and the gain in reaction rate produced by microwaves gave excellent results in the preparation of various organic compounds [11]. The utility of bismuth compounds in organic transformations has been extensively studied [12].

In continuation of our studies on catalytic reactions [13, 14] and the use of bismuth compounds in organic transformations [15] we now report that 1,4-diazabicyclo[2.2.2]octane (DABCO) is an effective co-cata-

lyst in the direct conversion of THP ethers into the corresponding acetates in the presence of bismuth(III) nitrate under microwave irradiation without a solvent.

Development of clean and efficient catalytic procedures is important from both economic and environmental points of view. Our experience in performing catalytic transformations of THP ethers [16] under ecologically friendly conditions [13–15] prompted us to elaborate a direct and fast one-pot procedure for the transformation of THP ethers into acetates. We recently described a mild and efficient method for the conversion of alcohols and phenols into the corresponding tetrahydropyranyl ethers [16]. For direct deprotection and acetylation, tetrahydropyranyl ether derived from benzyl alcohol was applied onto silica gel, bismuth(III) nitrate and acetic anhydride were added, and the mixture was thoroughly stirred and placed in microwave oven. The reaction gave benzaldehyde as the major product and benzyl acetate as minor one. When benzyl alcohol was used instead of its THP ether, benzaldehyde was formed in quantitative yield. These findings indicated that oxidative deprotection of THP ether must be minimized to ensure direct one-pot transformation of benzyl THP ether into benzyl acetate. In other words, the oxidative ability of bismuth(III) nitrate should be suppressed.

It is known that bismuth(III) nitrate readily forms complexes with amines [17] and that such complex formation should reduce the oxidative power of $\text{Bi}(\text{NO}_3)_3$ [18]. For this purpose, we used a catalytic



* The text was submitted by the authors in English.

amount of DABCO in the above reaction. A large number of structurally different THP ethers were subjected to deprotection–acetylation with acetic anhydride in the presence of DABCO and bismuth(III) nitrate under microwave irradiation. Below are listed the R group in the substrate, reaction time (min), yield (%), isolated product, and boiling point, °C: PhCH₂, 4, 86, 213 (212 [19]); 4-MeC₆H₄CH₂, 4, 89, 176–178 (174–178) [20]; Ph₂CH, 3, 79, 127–128 (128–129 [20]); cyclohexyl, 3, 82, 173 (172 [19]); C₅H₁₁, 4, 91, 148 (145 [19]); oct-2-yl, 4, 84, 196 (193 [19]); prop-2-yn-1-yl, 3, 88, 124 (125 [19]); PhCH=CHCH₂, 2, 88, 143 (144 [19]); Ph, 3, 85, 195–196 (194 [19]); 4-NO₂C₆H₄, 3, 75, 153–155 (150 [19]), 4-MeOC₆H₄, 3, 88, 123–124 (122 [19]); Me₂CCMe₂, 3, 77, 242 (240 [19]).

All isolated compounds were identified by comparing their physical properties and spectral parameters with those of authentic samples. As follows from the obtained data, both primary and secondary benzylic and allylic THP ethers, as well as unsaturated THP ethers are smoothly converted into the corresponding acetates in a short time. The proposed procedure is equally efficient for substrates containing double and triple bonds (cinnamyl and prop-2-yn-1-yl THP ethers gave the corresponding acetates in 88 and 85% yield, respectively) and phenol ethers. Furthermore, pinacol diether was also converted into the corresponding diacetate, and no pinacol rearrangement was observed.

The reaction mechanism and the role of DABCO in the described transformation remain so far unclear.

We can conclude that the proposed procedure for the direct one-pot transformation of tetrahydropyranyl ethers into acetates is simple, efficient, and general. It requires no solvent and utilizes accessible, inexpensive, and nontoxic reagents and ensures high yields in short reaction time. We believe that this procedure will become a useful tool in organic synthesis.

Typical procedure for the transformation of tetrahydropyranyl ethers into the corresponding acetates. A mixture of 0.5 mmol of THP ether [16], 0.5 mmol of bismuth(III) nitrate pentahydrate, 0.1 mmol of DABCO, and silica gel was thoroughly stirred and ground in a mortar. The mixture was transferred to a glass beaker, 2 mmol of acetic anhydride was added, the mixture was thoroughly stirred with a spatula, and the beaker was placed into a microwave oven and irradiated for a time indicated above. The progress of the reaction was monitored by TLC. The product was extracted into methylene chloride, the extract was washed with 10% aqueous sodium hydrox-

ide and water, dried over MgSO₄, and evaporated to dryness, and the residue was purified by column chromatography.

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