

SHORT
COMMUNICATIONS

Bismuth(III) Nitrate-Catalyzed Solvent-Free Acetylation of Alcohols and Phenols with Acetic Anhydride*

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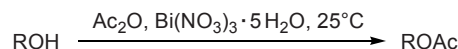
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Development of efficient and mild procedures for the protection of hydroxy group in alcohols and phenols is very important for synthetic organic chemistry. One of the most common methods for the protection of these compounds is their conversion into *O*-acetyl derivatives. Protection of hydroxy group is often necessary in the course of various transformations in multistep syntheses, especially in the preparation of polyfunctional compounds, such as nucleosides, carbohydrates, steroids, and other natural products [1].

A number of procedures for the preparation of acetyl derivatives have been reported, including those implying the use of homogeneous and heterogeneous reagents, e.g., ZnCl₂ [2], CoCl₂ [3], K-10 montmorillonite and KSF₄ [4], Mg(ClO₄)₂ [5], etc. While searching for new methods of transformation of functional groups, we were especially interested in using various neutral or almost neutral catalysts and used bismuth(III) salts in various syntheses [6–10]. In the recent years, bismuth(III) nitrate efficiently catalyzed synthesis of coumarins [11], oxidation of dihydropyrimidinones [12], microwave-assisted deoximation [13], chemoselective synthesis of acylals [14], and oxidation of benzoin [15], thiols, and disulfides [16].

In the present communication we report on the use of Bi(NO₃)₃·5H₂O to catalyze mild and effective acetylation of alcohols and phenols with acetic anhydride at room temperature under solvent-free conditions. The corresponding acetates were thus obtained in high yield. Listed below are the R group in the substrate, reaction time (h), and yield (%), according to the GLC data): PhCH₂, 12, 98; CH₂=CHCH₂, 12, 92; Me₂CHCH₂CH₂, 12, 96; Bu, 12, 91; *s*-Bu, 12, 95; *i*-Pr,

12, 93; CH≡CHCH₂, 12, 97; cyclohexyl, 12, 93; 2-methylcyclohexyl, 12, 91.5; *t*-Bu, 12, 88; PhCH=CHCH₂, 12, 93; C₅H₁₁, 12, 87; Me, 12, 91; 4-BrC₆H₄, 2.3, 86; Ph, 2.3, 93; 4-O₂NC₆H₄, 2.0, 85; 2-naphthyl, 3.0, 94.



Advantages of the proposed procedure include the use of 1 to 1.5 equiv of acetic anhydride and a catalytic amount of bismuth(III) nitrate, mild solvent-free conditions, and high yield. All reagents were commercial products which were not subjected to additional purification.

Typical procedure for the acetylation of alcohols and phenols with acetic anhydride in the presence of bismuth(III) nitrate. A mixture of 0.504 ml (5 mmol) of benzyl alcohol, 0.7 ml (7.5 mmol) of acetic anhydride, and 0.05 g (0.1 mmol) of Bi(NO₃)₃·5H₂O was stirred at room temperature until the reaction was complete according to the TLC data. The mixture was treated with 15 ml of 10% aqueous sodium hydrogen carbonate and extracted with diethyl ether (3×20 ml). The extracts were combined, dried over Na₂SO₄, and evaporated, and the product was identified by comparing its spectral parameters with those of an authentic sample.

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