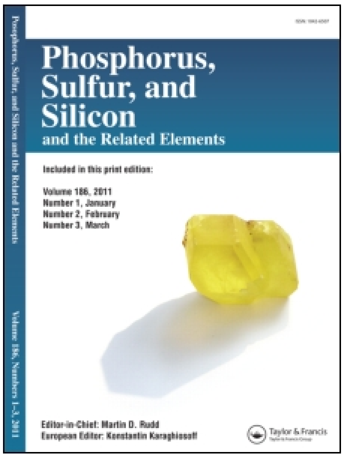

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BISMUTH (III) NITRATE SUPPORTED ONTO SILICA GEL, A NEW CATALYST FOR ACETYLATION OF ALCOHOLS AND PHENOLS UNDER MICROWAVE IRRADIATION

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Bismuth (III) nitrate supported onto silica gel is found to be efficient catalyst for acetylation of alcohols, phenols and naphthals in the presence of acetic anhydride under microwave irradiation in solventless system.

Keywords: Acetylation; alcohols; bismuth (III) nitrate; microwave irradiation; solventless system

INTRODUCTION

Esters have potential in industry because of their use in fragrance, flavors, surfactants, plasticizers, and as solvents.[1] The protections of hydroxyl groups of alcohols and phenols by the formation of esters is of parmount importance in organic chemistry.[2] In general, acetylation takes place by reaction of alcohols and phenols with acid anhydride in the presence 4-(dimethylamino)pyridine (DMAP),[3] 4-pyrrolidinopyridine (PPY),[4] tributyl phosphine,[5] cobalt(II) chloride,[6] or trimethyl silyl trifluoromethane sulfonate.[7] Scandium trifluoromethane sulfonate,[8] $Sc(NTF)_3$,[9] silica gel-supported $Ce(SO^4)_3$ and $NaHSO_4$,[10] vanadyl(IV) acetate,[11] triphenylphosphine and carbon tetraboromide,[12] and bismuth(III) salts[13] are other reagents for this purpose. In addition to the above catalysts, tertiary amines such as triethylamine and pyridine,[14] toluene-p-sulfonic acid,[15] zinc chloride,[16] montmorillonite K-10, KSF,[17]

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HZSM-360 zeolite,[18] and sulfuric acid adsorbed on silicagel[19] are also known for the acetylation of alcohols and phenols. All of these methods have their own merits and drawbacks. Pyridine and its derivatieves have an unpleasant and irritant odor, and they are not easy to remove. Tributyl phosphine is highly flammable and expensive. Some of the above catalysts suffer from inherent disadvantages such as high cost, poor regioselectivity, and affording the elimination of by-product in the case of tert alcohols. Due to the importance of esters, introduction of new methods and catalysts are still in demand.

In recent years, the organic reactions on solid supports have gained popularity because of their selectivity and associated ease of manipulation. Since only the polar reactants adsorbed on the surface of various mineral supports absorb microwaves (MW), a variety of reagents supported on such surfaces can be utilized for the enhancement of organic reaction using a simple microwave oven. Microwave-enhanced chemical reactions, especially under solvent-free conditions, have several advantages over the conventional reactions in view of the rapid reaction rates attained and higher yields of pure products obtained.[20]

Bismuth compounds are attractive candidates for use in green chemistry, and the application of bismuth (III) compounds in organic reaction transformation has been recently reviewed.[21]

In continuation of our ongoing program on MW-assisted solvent-free reactions[22] and our interest in using bismuth (III) nitrate,[23] the less toxic of heavy metals, herein we wish to report a facile acetylation protocol that utilizes bismuth (III) nitrate impregnated onto silica gel under microwave irradiation.

The reactions were simply conducted by mixing of neat substances with bismuth (III) nitrate supported onto silica gel and acetic anhydride in an open container. The mixture is placed in a household microwave oven in solid state. The progress of the reaction was monitored by thin layer chromatography (TLC). As shown in Table I. Primary, secondary, and benzylic alcohols are acetylated in excellent yields under this condition. 2-Hydroxy benzyl alcohol gave a poor yield. However, when 2 moles ratio of bismuth (III) nitrate was used, it was converted to the corresponding diacetate efficiently (Table I, entry 6). Tertiary alcohols such as t-butyl alcohol were not converted to acetate in the above reaction condition.

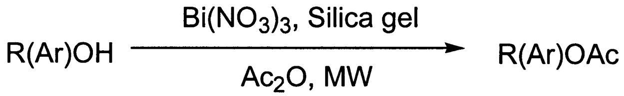
In order to extend the scope of this reaction, phenol was also acetylated in excellent yields. It is also noteworthy to mention that in this reaction bismuth (III) nitrate did not show the disadvantage of giving nitrate side products observed in the reaction of aromatic compounds with this catalyst.[24]

TABLE I Acylation of Alcohols and Phenols with Ac_2O, Catalyzed by $Bi(NO_3)_3$/Silica Gel under Microwave Irradiation in Solventless System

Entry	Substrate	Reaction time (min)	Products	Yield (%)
1	n-Amylalcohol	2	n-Amylacetate	85
2	2-Octanol	4	2-Octyl acetate	79
3	Cyclohexanol	3	Cyclohexyl acetate	87
4	Cinnamyl alcohol	3	Cinnamyl acetate	98
5	Benzyl alcohol	2	Benzyl acetate	85
6	2-Hydroxybenzyl alcohol	2	2-Acetoxybenzyl acetate	80
7	Benzoin	3	Benzoin acetate	75
8	Phenol	2	Phenol acetate	83
9	Naphthol	1	Naphthyl acetate	80

Yields refer to isolated product.

In summary, an efficient, rapid, and high-yielding method for the acetylation of alcohols, phenols, and naphthols has been developed. Mild condition and easy workup procedure are two other advantages of this method. We believe this methodology will find application in organic synthesis.



SCHEME 1

EXPERIMENTAL

All products were characterized by comparison of their physical and spectral data with those of authentic samples. Bismuth (III) nitrate was purchased and used as received. Yields refer to isolated products, although we did not observe any accident using bismuth (III) nitrate in microwave oven, using of microwave in an efficient hood is highly recommended.

Acetylation of alcohols and phenols with Ac_2O, catalyzed by $Bi(NO_3)_3$, supported onto silica gel under microwave irradiation.

General Procedure

An appropriate alcohol or phenol (1 mmol) and acetic anhydride (2 equiv. For each hydroxy group of alcohol) were mixed thoroughly in a beaker using a spatula. To this mixture bismuth (III) nitrate (0.25 mmol for each hydroxy group) supported onto silica gel (2 equiv. weight of $Bi(NO_3)_3$) was added and mixed thoroughly. The beaker was placed in a microwave oven for the indicated time (Table I). The progress of the reaction was monitored by TLC, using EtOAc:Et_2O (1:3) as eluents. Upon completion of the reaction, CH_2Cl_2 (10 ml) was added to the residue. The mixture was filtered off, and a solution of $NaHCO_3$ (5%) was added to the filtrate. The organic layer was separated, dried, and evaporated to dryness under reduced pressure to afford the corresponding acetate (Table I).

REFERENCES

[1] W. Rumenschneider, Ester, organic, in *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A9 (VCH, Germany, 1997), p. 565.

[2] T. W. Grien and P. G. M. Wutz, *Protective Groups in Organic Synthesis*, Vol. II (Wiley, New York, 1991).

[3] G. Hofle, V. Steglich, and H. Varhruggen, *Angew. Chem. Int. Ed. Engl.*, **17,** 56 (1978).

[4] E. F. V. Seriven, *Chem. Soc. Rev.*, **12,** 1291 (1983).

[5] a) E. Velgs and S. T. Diver, *J. Am. Chem. Soc.*, **115,** 3358 (1993); b) E. Velgs, N. S. Bemdt, L. M. Cown, S. T. Diver, M. Mingras, S. Lim, P. A. Oliver, and M. J. Peterson, *J. Org. Chem.*, **58,** 7286 (1993).

[6] a) S. Ahmad and J. Iqlal, *J. Chem. Soc. Chem. Commun.*, 114, 1987; b) J. Iqlal and K. Srivastava, *J. Org. Chem*, **57,** 2001 (1992).

[7] P. A. Procopiou, S. P. D. Baugh, S. S. Flack, and G. G. A. Inglis, *J. Chem. Soc. Chem. Commun.*, 2625 (1996).

[8] a) K. Ishihara, M. Kubota, H. Kuvhara, and H. Yamamoto, *J. Org. Chem.*, **117,** 4413 (1995); b) K. Ishihara, M. Kubota, H. Kuvhara, and H. Yamamoto, *J. Org. Chem.*, **61,** 4560 (1996); c) I. Shima and T. Mukavyarn, *Chem. Lett.*, 677 (1997).

[9] K. Ishihara, M. Kubota, and H. Yamamoto, *Synlett*, 265 (1996).

[10] T. Nishiguchi and H. Taya, *J. Chem. Soc. Trans.*, **1,** 172 (1990).

[11] B. M. Choudary, M. L. Kantam, V. Neeraja, T. Bandyopo, and P. N. Reddy, *J. Molecular Catalysis*, **140,** 25 (1999).

[12] H. H. Isahiro, M. Kimie, S. Hitoshi, S. Toshio, and A. Masayoshi, *Tetrahedron*, **54,** 5845 (1998).

[13] I. Mohammad Poor Boltark, H. Aliyan, and A. K. Khosropour, *Tetrahedron*, **57,** 5851 (2001).

[14] a) R. I. Zhdanov and S. M. Zhenolarova, *Synthesis*, 222 (1975); b) D. Harton, *Org. Synth. Collective*, **5,** 1 (1973).

[15] A. C. Cope and E. C. Herick, *Org. Synth. Collective*, **4,** 304 (1963).

[16] R. H. Baker and F. G. Bardwell, *Org. Synth. Collective*, **3,** 141 (1955).

[17] A. Yiao, T. Snili, and T. H. Ding, *Chem. Commun.*, 1389 (1997).

[18] R. Ballini, G. Basic, and S. Carloxi, *Tetrahedron Lett.*, **39,** 6049 (1998).

[19] M. A. Bigdeli, N. Nahid, and M. M. Heravi, *Sran. J. Chem. Chem. Eng.*, **19,** 37 (2000).

[20] K. S. Varma and R. Dahiya, *Tetrahedron Lett.*, **39,** 1307 (1998) and references cited therein.

[21] N. M. Leonard, L. C. Wieland, and R. S. Mohan, *Tetrahedron*, **58,** 8373 (2002).

[22] a) M. M. Heravi, D. Ajami, and M. Ghassemzadeh, *Synthesis*, **3,** 393 (1999); b) D. Ajami, M. Ghassemzadeh, and M. M. Mojtahedi, *Tetrahedron Lett.*, **40,** 561 (1999); c) M. M. Heravi, D. Ajami, K. Aghapoor, and M. Ghassemzadeh, *Chem. Commun.*, 833 (1999).

[23] a) Sh. Khaleghi, M. M. Heravi, and L. Fotouhi, *Phosphorus, Sulfur, and Silicon*, **178,** 155 (2003); b) M. Tajbakhsh, M. M. Heravi, A. Hoseini, and A. Shahrezaiee, *Phosphorus, Sulfur, and Silicon*, **178,** 773 (2003); c) M. M. Heravi, S. Yazdanpanah, H. A. Oskooiee, and M. M. Mojtahedi, *J. Chem. Res.*, **2,** 129 (2004).

[24] S. Susanta and B. K. Bimal, *Tetrahedron Lett.*, **41,** 8017 (2000).