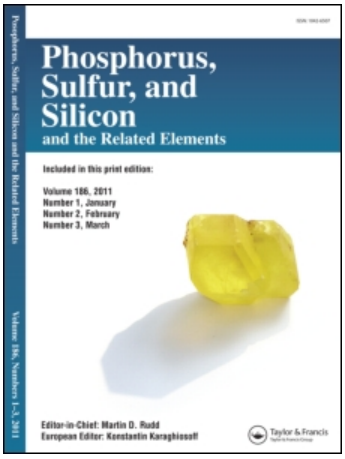

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A New, Mild, and Rapid Transformation of Acylals to Bisulfites in One-Pot Synthesis by Bismuth (III) Nitrate Pentahydrate

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A New, Mild, and Rapid Transformation of Acylals to Bisulfites in One-Pot Synthesis by Bismuth (III) Nitrate Pentahydrate

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Direct conversion of acylals to the corresponding bisulfites can be easily performed in the presence of bismuth (III) nitrate pentahydrate in ethanol at room temperature in good yields.

Keywords Acylals; bisulfites; $Bi(NO_3)_3.5H_2O$; direct transformation; mild conditions; one-pot synthesis

INTRODUCTION

Protection and deprotection of functional groups are common in multistep synthetic organic reactions.[1] Direct transformation of a protecting group of a carbonyl compound into another also is a useful conversion. Thus, the development of new methods for direct transformation in one-pot would be of significant utility. Among protecting groups for aldehydes, bisulfite addition products, which have been shown to be α-hydroxy alkanesulfonates, are useful due to their easy preparation, stability, and compatibility in neutal solutions. However, they are usually not stable under acidic or basic conditions.[2] Bisulfite addition products of aldehydes are highly crystalline and used not only for the isolation and characterization, but also for purification of carbonyl compounds.

The application of Bi (III) salts as catalysts in organic synthesis has been investigated extensively.[3] Very recently, we have reported some of their applications in organic transformations.[4]

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Thus, the conversion of acylals or 1,1-diacetates to bisulfite addition products of aldehydes in the presence of $Bi(NO_3)_3.5H_2O$ could be an important transformation in organic synthesis.

RESULTS AND DISCUSSION

The report on this transformation is absent in the literature and a practical method for its performance is desired. We wish to report a novel, convenient, and mild direct transformation of acylals to bisulfites with bismuth (III) nitrate pentahydrate at room temperature in one-pot and in short reaction times (Scheme 1).

$$ArCH(OAC)_2 \xrightarrow[aq.NaHSO_3(40\%),EtOH,rt]{Bi(NO_3)_3.5H_2O} ArCH(OH)SO_3Na$$

SCHEME 1

An efficient transformation of acylals of benzaldehyde having different substituent groups was performed in the presence of 0.5 molar ratio of $Bi(NO_3)_3.5H_2O$ and the results are shown in Table I. p-Methyl benzaldehyde,1,1-diacetate as a model compound converted to the bisulfite addition product of p-methyl benzaldehyde at room temperature in a 75% yield. However, under similar reaction conditions, transformation of p-chlorobenzaldehyde,1,1-diacetate into the corresponding bisulfite gave only 50% of the desired product.

TABLE I Direct Transformation of 1,1-Diacetates to Bisulfites With Sodium Bisulfite and $Bi(NO_3)_3.5H_2O$ as a Catalyst

Entry	Product	Time (min)	Yield(%)
1	4-CH_3—C_6H_4—CH(OH)SO_3Na	5	75
2	4-Cl—C_6H4—CH(OH)SO_3Na	60	40
3	2-AcO—C6H_4—CH(OH)SO_3Na	10	50
4	4-O2N—C_6H_4—CH(OH)SO_3Na	10	60
5	4-CH_3O—C_6H_4—CH(OH)SO_3Na	5	65
6	4-F—C_6H_4—CH(OH)SO_3Na	10	70
7	C_6H_5—CH(OH)SO_3Na	10	70
8	2,4-$(CH_3O)_2$—C_6H_3—CH(OH)SO_3Na	10	65
9	2-Br—C_6H_4—CH(OH)SO_3Na	15	75
10	4-Br—C_6H_4—CH(OH)SO_3Na	15	75
11	3-Cl—C_6H_4—CH(OH)SO_3Na	10	60
12	2,4-$(Cl)_2$—C_6H_3—CH(OH)SO_3Na	15	65
13	C_6H5—CH=CH—CH(OH)SO_3Na	10	70

In summary, we have developed a new method for the one-pot conversion of acylals to bisulfites in the presence of catalytic amounts of $Bi(NO_3)_3.5H_2O$. The advantages of this protocol, such as mild reaction conditions, short reaction times, and using relatively nontoxic, inexpensive, and commercially available catalyst, are worthy of mention and make this method an attractive and useful methodology.

EXPERIMENTAL

Products are known compounds and were characterized by comparison of their spectral data (^{1}H NMR, IR) with those reported in the literature. Monitoring of the reactions were accomplished by TLC on precoated silica gel 60 F_{254} sheets. All yields refer to isolated products.

General Procedure for the Transformation of 1,1-Diacetates to the Corresponding Bisulfites

To a solution of aryl acylal (1 mmol) in 1 mL of aqeous ethanol, 0.5 mmol of bismuth(III)nitrate pentahydrate was added and the solution stirred magnetically at room temperature until the acylal was deprotected and the corresponding aldehyde was regenerated (5–60 min). Then 40% aqueous sodium bisulfite solution was added to this solution and the reaction was completed in less than 1 min appearing with the white crystals. The crystals were filtered and washed with ethanol. The product was dissolved in distilled water at 0°C and the aqueous solution was filtered. Evaporation of water afforded the pure product in 50–75% yields.

REFERENCES AND NOTES

[1] T. Oriyama, M. Kimura, and G. Koga, *Bull. Chem. Soc. Jpn*., **67,** 885 (1994) and references cited in therein.
[2] (a) C. J. Cymerman ana D. P. G. Hamon, *J. Org. Chem.*, **30,** 4168 (1965): (b) P. R. Young, W. P. Jencks, *J. Am. Chem. Soc.*, **100,** 1228 (1978).
[3] Mohammadpor-Baltork, Aliyan, H.; A. R. Khosropour, *Tetrahedron*, **57,** 5851 (2001) and references cited therein.
[4] M. M. Khodaei, A. R. Khosropour, and K. Ghozati, *Tretrahedron Lett.*, **45,** 3525 (2004) and references cited therein.