

Novel Deprotection Method of Aryl Aldehyde Bisulfite Adducts with Recoverable [BPy]FeCl₄ as a New Ionic Liquid Catalyst

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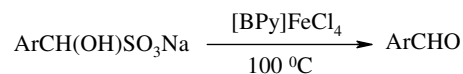
The aryl aldehyde bisulfite adducts were deprotected to the parent aldehydes in n-butylpyridinium tetrachloroferrate as a catalyst and solvent with excellent yields and high chemoselectivity.

Keywords: Aldehyde, Bisulfite, Ionic liquid, Chemoselective

INTRODUCTION

Protection and deprotection of carbonyl functional groups in poly functional molecules constitute important processes in the field of synthetic chemistry [1]. Thus, a number of protecting groups have been introduced and variety methods made available for their deprotection [2]. Aldehyde bisulfite derivatives are frequently used as protected aldehydes due to their stabilities and ease of preparation. Because of their highly crystalline form, they are extensively used for purification of the parent carbonyl compounds [3]. Regeneration of the corresponding aldehydes under mild conditions is of great interest to organic chemists. Despite their wide range of synthetic applications, little attention has been paid to the cleavage of the aryl aldehyde bisulfite adducts and only a few reports are available [4-6]. However, there are several disadvantages with these methodologies such as lower yields and using toxic solvents. Consequently, the development of mild and efficient methods is desirable.

Over the last decades, the use of ionic liquids (ILs) has become popular and many reactions have been reported to occur in these media with good to excellent performance [7].



Scheme 1

ILs are currently used for a variety of different applications such as solvent media for homogeneous catalysis [8], extraction processes [9], oligomerization and polymerization catalysts [10]. These ionic systems are salts that have melting points at or below ambient temperature. Very low vapor pressure, easy recoverability, and high thermal stability are some advantages of these media [7]. We now report an excellent, mild, inexpensive and selective method for the deprotection of aryl aldehyde bisulfite addition products to their aldehydes using n-butylpyridinium tetrachloroferrate ([BPy]FeCl₄) as a recoverable reaction media without any additional catalyst at 100 °C (Scheme 1).

EXPERIMENTAL

All yields refer to isolated products. Most of the products are known compounds and were characterized by comparison of their spectral data (¹H NMR, ¹³C NMR, IR) with those

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reported in the literature. Monitoring of the reactions was accomplished by TLC.

General Procedure for Deprotection of Aryl Aldehyde Bisulfite Adducts with [BPy]FeCl₄

To a stirred solution of the IL (0.25 ml) at room temperature, aryl aldehyde bisulfite (1 mmol) was added. The mixture was then stirred at 100 °C for the appropriate time shown in Table 1. After completion of the reaction as indicated by TLC, the product was extracted with Et₂O (3 x 10 ml) and the organic layer dried (MgSO₄). Evaporation of the

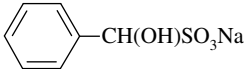
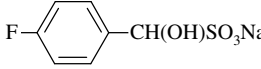
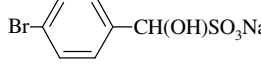
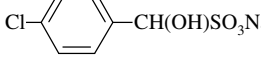
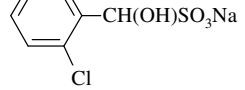
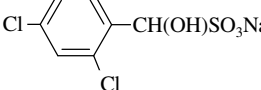
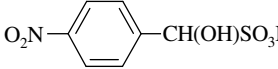
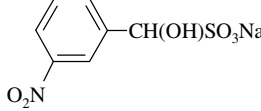
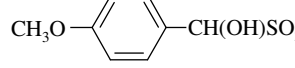
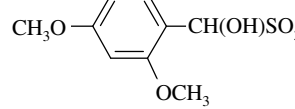
solvent under low pressure affords the pure aldehyde.

RESULTS AND DISCUSSION

When different classes of aryl aldehyde bisulfites carrying activated or deactivated groups were treated in the presence of [BPy]FeCl₄, complete deprotection was achieved. The results are summarized in Table 1. To the best of our knowledge, this is the first report of the regeneration of these aldehydes from their bisulfite addition products using an IL catalyst.

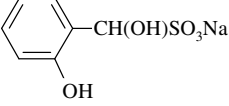
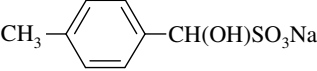
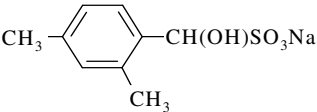
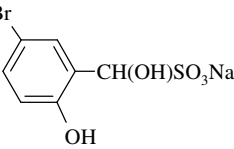
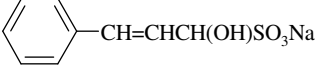
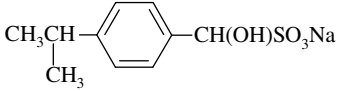
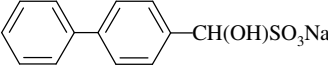
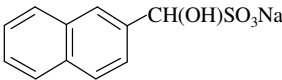
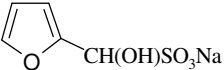
Both the reaction conditions and work up procedure are

Table 1. Conversion of Aryl Aldehyde Bisulfites to the Aldehydes^a in [BPy]FeCl₄

Entry	Substrate	Time (min)	Yield (%) ^b
1		5	90
2		5	92
3		4	91
4		4	94
5		5	90
6		5	97
7		5	91
8		5	87
9		5	89
10		4	89

Novel Deprotection Method of Aryl Aldehyde Bisulfite Adducts

Table 1. Continued

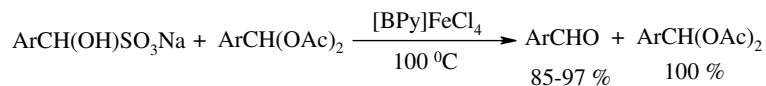
11		3	91
12		5	90
13		5	92
14		5	90
15		5	87
16		5	89
17		6	89
18		5	85
19		4	90

^aAll products were known and identified by comparison of their physical and spectral data with those of authentic samples. ^bIsolated yields.

simple and convenient. Another advantage of this method is the recyclability of this media. Since [BPy]FeCl₄ is weakly soluble in Et₂O, it was separated by washing with Et₂O and dried at 80 °C under reduced pressure and reused in three more runs without any loss of activity. In order to evaluate the intermolecular chemoselectivity of this method, the competitive reactions were carried out and we found that acylals (geminal diacetates), another protecting form of aldehydes, were stable in these reaction conditions (Scheme 2).

CONCLUSION

In conclusion, we have developed a simple and convenient protocol for the deprotection of bisulfite addition products in the presence of [BPy]FeCl₄. This method offers several advantages including recoverability of the catalyst media, very short reaction times, high yields and cleaner reactions, all of which make it one of the most efficient procedures for this conversion.



Scheme 2

ACKNOWLEDGMENT

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