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A Novel and Highly Efficient Method for the Direct Conversion of Aryl Aldehyde Bisulfite Adducts to their Aryl Trimethylsilyl Ethers in a One-Pot Manner Catalyzed by Montmorillonite K-10

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A new, convenient, and chemoselective method has been developed for the one-pot conversion of aryl aldehyde bisulfite adducts to the corresponding trimethylsilyl ethers.

Keywords bisulfites; montmorillonite K-10; direct conversion; sodium borohydride; trimethylsilyl ethers

INTRODUCTION

Protection and deprotection of functional groups are important in multistep organic synthesis. Direct transformation between protecting groups is also of great importance due to their efficiency and convenience.[2] The interconversion of a protecting group of the hydroxy or the carbonyl function into another has been investigated. However, direct conversion of a protecting group of the carbonyl function into the protected form of the hydroxy group has not been reported.

Aryl bisulfite adducts are used frequently as protecting forms of aldehydes under basic conditions, and due to their highly crystalline forms, they are extensively utilized for the purification of these carbonyl compounds.[3] On the other hand, silyl ethers as a protecting form of hydroxyl groups have been extensively utilized in organic synthesis.[4] They show (a) resistance to oxidation, (b) good thermal stability, (c) low viscosity, and (d) are easily recoverable

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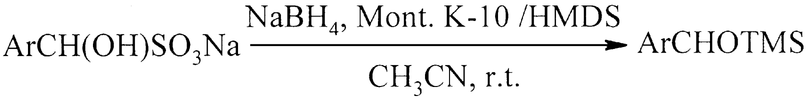
from the parent compounds.[4b] As a result, a variety of methods have been examined for their formation, but all of them are limited to the utilization of alcohols or phenol as a precursor.[5] Therefore, the introduction of new methods for the synthesis of these compounds with other substrates is important in multistep organic synthesis.

Among the reducing agents, sodium borohydride is the most frequently used in the reduction process. It is a mild, inexpensive, and invaluable reagent with applications in a wide range of functional groups.[6] In addition, the extensive application of heterogeneous catalysis in synthetic chemistry can help to achieve new reactions to lower the waste product. Recently, more attention has been focused on montmorillonite K-10 due to its strong catalytic activity as a Brønsted acid as a heterogeneous catalyst in fine organic synthesis.[7] Although montmorillonite K-10 has been extensively used as a catalyst in organic synthesis, a literature search clearly shows that there has been no investigation into the reduction–protection procedure in the presence of this clay. Thus, we decided to study the one-pot transformation of the bisulfite addition product of aldehydes into silyl ethers-protected alcohol by montmorillonite K-10.

RESULTS AND DISCUSSION

As shown in Table I, a series of aryl aldehyde bisulfide adducts reacted with sodium borohydride and hexamethyldisilazine (HMDS) in acetonitrile to afford the corresponding TMS-ethers in the presence of montmorillonite K-10 at room temperature in high to excellent yields at short reaction times (Scheme 1).

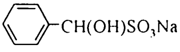
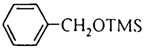
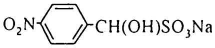
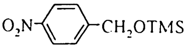
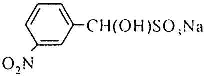
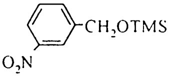
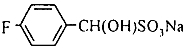
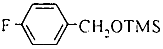
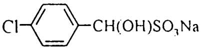
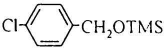
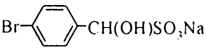
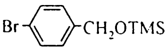
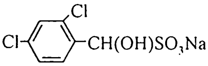
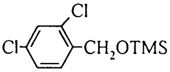
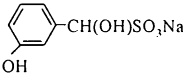
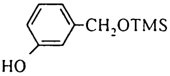
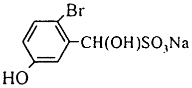
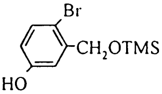
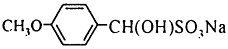
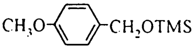
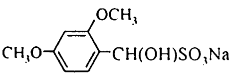
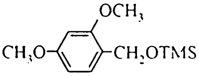
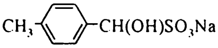
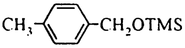
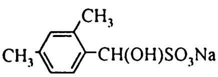
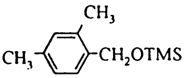
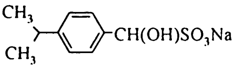
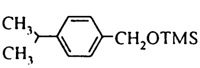
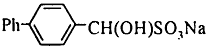
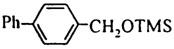
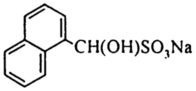
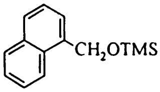
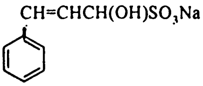
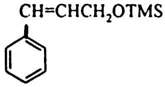


$$\mathrm{ArCH(OH)SO_3Na} \xrightarrow[\mathrm{CH_3CN,\ r.t.}]{\mathrm{NaBH_4,\ Mont.\ K\text{-}10\ /HMDS}} \mathrm{ArCHOTMS}$$

SCHEME 1

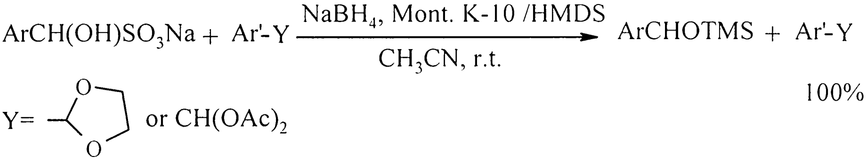
The presence of electron-donating and electron-withdrawing groups on the aromatic ring of the bisulfites, irrespective of their positions in the ring, did not make any obvious difference in the rate of the reaction. Only in nitro aromatic bisulfites (Entries 2, 3), due to the deactivation of the benzylic carbon, reaction times were prolonged. The reaction conditions were mild enough not to induce any isomerization for conjugated aldehyde bisulfites (Entry 17), or to damage moieties such as methoxy

TABLE I One-Pot Conversion of Aryl Bisulfite Adducts to the Corresponding Trimethylsilyl Ethes Catalyzed by Montmorillonite K-10

Entry	Aryl bisulfite	Product	Time (min)	Yield (%)
1			12	98
2			90	87
3			40	90
4			13	96
5			8	97
6			8	94
7			12	90
8			8	95
9			56	90
10			13	91
11			18	97
12			12	95
13			10	90
14			8	98
15			35	82
16			32	93
17			33	80

(Entries 10, 11), which often undergo cleavage in strongly acidic reaction media. Side product formation was not observed in these reactions.

It worth noting that hydroxyl groups in the aromatic ring remain intact under similar conditions (Entries 8, 9). In order to evaluate the selectivity of the present method, competition reactions were carried out for the conversion of aryl bisulfite adducts in the presence of the cyclic acetals or 1,1-diacetates (acylals) as other protecting aldehyde forms (Scheme 2).



SCHEME 2

When a 1:1 mixture of these protecting forms was allowed to react with $NaBH_4$ and HMDS in the presence of montmorillonite K-10 (50 mg in lieu of 1 mmol of substrate) for about 60 minutes at room temperature, TLC analysis of the reaction mixture indicated complete conversion of aryl bisulfite to its TMS-ether, while the acetal or acylal was still intact.

In conclusion, we demonstrated a novel and highly efficient procedure for the one-pot conversion of aryl aldehyde bisulfite adducts to their TMS-ethers. The mild experimental conditions, short reaction times, high yields and excellent chemoselectivity in addition to the utilization of an inexpensive and nontoxic catalyst, represent the notable feature of this procedure.

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 was accomplished by TLC on precoated silica gel 60 F_{254} sheets. All yields refer to isolated products.

General Procedure for the Transformation of Bisulfites to Trimethylsilyl Ethers

To a stirred mixture of aryl aldehyde bisulfite adducts (1 mmol) and sodium borohydride (1 mmol) in CH_3CN (2 mL), HMDS (1.5 mmol) and montmorillonite K-10 (50 mg) were added at 25°C. The mixture was stirred at room temperature for the appropriate time according to

Table I. The end of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and washed with Et_2O (3 × 5 mL). The filtrate was dried with Na_2SO_4 and evaporation of the organic solvent gave the crude product, which was purified by plate or column chromatography on silica gel to afford the pure TMS-ethers in 80–98% yields.

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