

Silica Gel/Thionyl Chloride: An Efficient Reagent for the Conversion of Alcohols to Symmetrical Dialkyl Sulfites

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Silica gel/thionyl chloride is used as an efficient reagent for symmetrical dialkyl sulfite preparations from their corresponding alcohols under mild reaction conditions. The isolated yields are good to excellent and sterically hindered alcohols have been successfully converted to dialkyl sulfites.

Key Words: Silica Gel, Reagent, Alcohols, Dialkyl sulfite.

INTRODUCTION

The application of solid adsorbents such as alumina and silica gel as solid supports in organic synthesis affords a new procedure for selective reactions¹ involving oxidation, alkylation, condensation, acetylation and monomethyl esterification^{1, 2}. The significant potential of adsorbents is due to the milder reaction conditions and simpler work-up required and the selective organic transformations.

Sulfurous acid diesters and dialkyl sulfites are of particular interest in preparative organic chemistry³. They serve as useful alkylating agents and react much faster than alkyl halides³, since the monoalkyl sulfite anion $(\text{ROSO}_2)^-$ is more effective as a leaving group than a halide ion. Kim *et al.*⁴ outlined the application of di-2-pyridyl sulfite as a useful reagent for the preparation of N-sulfinylamines, nitriles, isocyanides and carbodiimides. The elimination processes of dialkyl sulfites occur upon heating and produce olefines, ethers or other oxygenated products³. Sulfites are similar to phosphites in transesterification⁵ and isomerization⁶ reactions.

Symmetrical dialkyl sulfites are typically prepared by the reaction of thionyl chloride with two molecules of an alcohol in pyridine⁷. An alternative route is the reaction of iodine or bromine in pyridine with liquid sulfur dioxide at 20°C, which gives good-to-high yields of sulfite¹. A report of the synthesis of symmetrical dialkyl sulfite by heating the adduct of ethylene oxide and sulfur dioxide with primary alcohols in the presence of alkali hydrides or a transition metal halide has also appeared in literature⁸. Unfortunately, these methods involve some disadvantages, such as low yields, laborious procedures, expensive or not readily accessible reagents, harsh reaction conditions or tedious work-up. Conse-

quently, it seems that there is still need for development of newer methods, which proceed under mild and economically appropriate conditions.

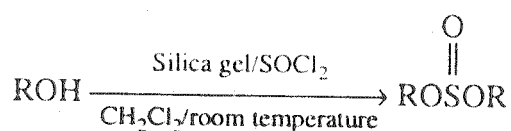
EXPERIMENTAL

Alcohols were purchased from Fluka and Merck. Product were characterized by comparison of their physical data, IR and ^1H NMR spectra with authentic samples. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

General procedure for the conversion or preparation of symmetrical dialkyl sulfite from silica gel/ SOCl_2 in CH_2Cl_2 : Silica gel (0.5 g) was mixed with freshly distilled thionyl chloride (0.7 mmol, 0.083 g) in a 25 mL round bottomed flask at room temperature. To the resulting powder, a solution of alcohol (1 mmol) in anhydrous CH_2Cl_2 (5 mL) was slowly added and stirred at room temperature for 7–75 min. The progress of the reaction was followed by TLC until no starting material could be detected. The mixture was shaken with CH_2Cl_2 (5 mL) and filtered. The residue was washed with CH_2Cl_2 and the solvent evaporated under reduced pressure (60–97% yield).

RESULTS AND DISCUSSION

In continuation of our research for development of functional group transformation⁹, recently, we found that silica gel could easily promote the oxidation of alcohols with cobalt nitrate hexahydrate, in which the silica gel acts not only as the reaction medium but also as an activator⁹. Now we wish to report conditions whereby various types of dialkyl sulfites can be conveniently synthesized from the corresponding alcohol under mild reaction conditions by silica gel/thionyl chloride.

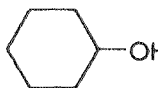
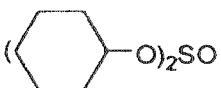
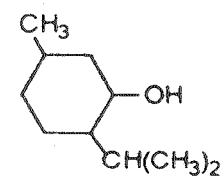
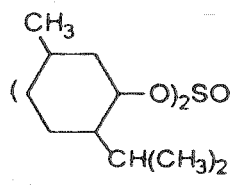
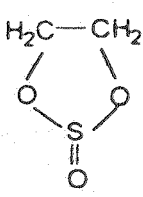


Symmetrical dialkyl sulfite was simply synthesized by adding the related alcohol to silica gel in CH_2Cl_2 . For 1 mmol of alcohol, 0.7 mmol of thionyl chloride and 0.5 g of silica gel were used. The effect of other solvents such as CCl_4 , *n*-hexane, ether and THF were also studied, but in comparison to CH_2Cl_2 the reaction times were longer and the yields were considerably lower. As shown in Table-1, a variety of alcohols could conveniently be converted into the corresponding symmetrical dialkyl sulfites at room temperature within 7–75 min and in good to excellent isolated yields. Even the sterically hindered menthol has been successfully converted to dialkyl sulfites in excellent yield. The structures of all the products were settled from their analytical and spectral (IR, ^1H NMR) data.

It is worthy to note that attempts at conversion of benzyl alcohols to the corresponding sulfites were not successful and produced excellent yields of

benzyl chlorides and no dialkyl sulfite was detected. To show the dramatic effect of silica gel in this reaction, under the same experimental conditions several alcohols were reacted with SOCl_2 in the absence of silica gel. The reactions were not completed and only produced moderate yields of alkyl chlorides and no dialkyl sulfite was detected. Increasing the mole ratio of SOCl_2 to alcohol to 1 : 1, only caused the completion of the reaction and produced only alkyl chloride.

TABLE-I
CONVERSION OF ALCOHOLS TO DIALKYL SULFITES USING SILICA
GEL/THIONYL CHLORIDE^a

Entry	Substrate	Product	Time(min)	Yield % ^{b,c}
1	CH_3OH	$(\text{CH}_3\text{O})_2\text{SO}$	75	86
2	$\text{CH}_3\text{CH}_2\text{OH}$	$(\text{CH}_3\text{CH}_2\text{O})_2\text{SO}$	30	89
3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_2\text{SO}$	15	91
4	$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$	$[\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{O}]_2\text{SO}$	7	93
5	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	$[(\text{CH}_3)_2\text{CHCH}_2\text{O}]_2\text{SO}$	35	92
6	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$	$[\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{O}]_2\text{SO}$	12	93
7	$\text{CH}_3\text{CH}(\text{CH}_3)\text{OH}$	$[\text{CH}_3\text{CH}(\text{CH}_3)\text{O}]_2\text{SO}$	15	90
8	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$	$[\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_2\text{SO}$	20	95
9			60	84
10			75	96
11	$(\text{CH}_3)_3\text{COH}$	$[(\text{CH}_3)_3\text{CO}]_2\text{SO}$	45	60
12	$\text{HOCH}_2\text{CH}_2\text{OH}$		12	90

(a) Molar ratio of reagent to substrate was 0.7 : 1 and performed at room temperature. (b) Yields refer to pure isolated products. (c) Products were characterized by comparison of their physical data, IR, NMR spectra with known samples.

Cyclic sulfites and sulfates like epoxides have played a significant role in organic synthesis¹. As shown in Table-1, ethylene sulfite as a cyclic sulfite was easily synthesized by the reaction of ethylene glycol with silica gel/thionyl chloride in excellent yield.

It is noteworthy that, unlike SOCl_2 in the presence of pyridine method, the major drawback of formation of alkyl chloride and chlorosulfite byproducts is not observed under the reaction conditions.

Compared to some previously reported reagents with major or minor drawbacks, several noteworthy features of this system are apparent. These are: availability of the reagents, operational simplicities and use of inexpensive reagents.

In conclusion, we believe that the present procedure provides an easy, mild and efficient methodology for the preparation of dialkyl sulfites from different classes of alcohols and we feel that it may be a suitable addition to the methodologies already present in literature.

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