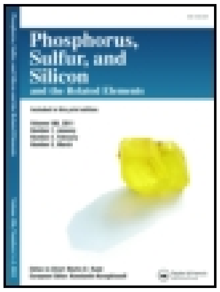

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A MILD METHOD FOR CONVERSION OF ALCOHOLS TO DIALKYL SULFITES BY USE OF $Na_2SO_3/SOCl_2$

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Alcohols are easily converted to their corresponding dialkyl sulfite under mild reaction conditions using $Na_2SO_3/SOCl_2$ in moderate to good isolated yields.

Keywords: Dialkyl sulfite; sodium sulfite; sulfurous acid diester; thionyl chloride

Sulfurous acid diesters, dialkyl sulfites, are of particular interest in preparative organic chemistry.[1] They serve as useful alkylating agent and react much faster than alkyl halides,[1] because the monoalkyl sulfite anion $(ROSO_2)^-$ is more effective as a leaving group than a halide ion. In 1986, a report by Kim et al.[2] 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 products.[1] Sulfites are similar to phosphites in transestrification[3] and isomerization[4] reactions.

Dialkyl sulfites are typically prepared by the reaction of thionyl chloride with alcohol in the presence of a base such as pyridine.[5] This method was improved by Ogata et al.[6] who used N,N′-thionyldiimidazol for the synthesis of diphenyl sulfite. A report of the synthesis of dialkyl sulfites by iodine or bromine in pyridine with liquid sulfur dioxide at 20°C also has appeared in the literature.[1] In 1966, a patent[7] described the preparation of dialkyl disulfites by heating the adduct of ethylene oxide and sulfur dioxide with primary alcohols in the presence of alkali

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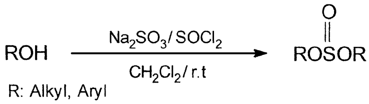
hydrides or a transition metal halide. Another method that applied for the synthesis of methyl alkyl sulfites consists of the reaction of diazomethane with alcoholic solutions of sulfur dioxide.[1] However, many of these methods met with some limitations, including low yields, laborious procedures, expensive or not readily accessible reagents, harsh reaction conditions, or tedious work-up. Consequently, it seems that there is still a great demand for a new and efficient method. In our development of new methods for functional group transformations,[8] we especially are interested in developing the application of modified forms of thionyl chloride in organic synthesis.[8f–h] In this line, very recently[8h] we have found that aldoximes undergo rapid dehydration using $Na_2SO_3/SOCl_2$ under mild reaction condition to afford the corresponding nitriles. Now we report conditions whereby various types of dialkyl sulfite can be synthesized conveniently from the corresponding alcohol under mild reaction conditions by sodium sulfite/thionyl chloride.



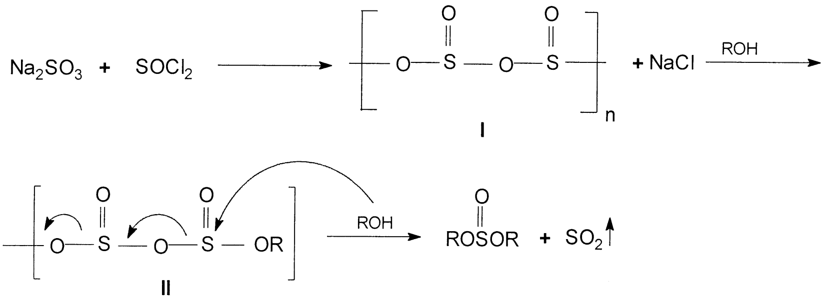
$$\mathrm{ROH} \xrightarrow[\mathrm{CH_2Cl_2/\,r.t}]{\mathrm{Na_2SO_3/\,SOCl_2}} \mathrm{RO}\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}\mathrm{OR}$$

R: Alkyl, Aryl

RESULTS AND DISCUSSION

The reagent easily was prepared by the reaction of thionyl chloride with stiochiometric amount of sodium sulfite at room temperature. Dialkyl sulfite was simply synthesized by adding the related alcohol to the reagent in CH_2Cl_2. For 1 mmol of alcohol, 1.5 eqiv. each of thionyl chloride and sodium sulfite were used. The plausible mechanism for this reaction is as follow: at first, (I) is probably formed; this kind of mechanism has been proposed in the reaction of thionyl chloride and polyvinylpyrrolidone,[8h] 1,4-diazabicyclo[2.2.2]octane,[14g] N-methyl-pyrolidone,[9] or N,N-dimethylformamide.[10] Representative alcohols were treated with (I) in CH_2Cl_2 at room temperature. The reaction proceeded probably via O-substituted alcohol (II), which forms dialkyl sulfite with the nucleophilic addition of a second alcohol followed by elimination of sulfur dioxide as shown in Scheme 1.

The effects of other solvents such as CCl_4, n-hexane, ether, and THF also were studied, but in comparison with CH_2Cl_2, the reaction times were longer and the yields were considerably lower. The procedure turned out to be general for a range of structurally diverse alcohols. As shown in Table I primary alcohols reacted faster than secondary

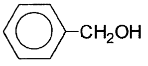
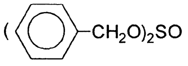
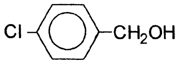
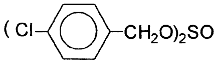
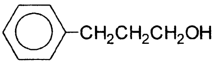
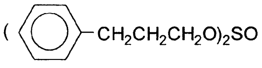
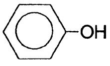
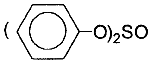


SCHEME 1

and tertiary alcohols and phenol. Most of the obtained product were purified by plate chromatography eluted with n-hexan and ether (4:1). The structure of all the products were confirmed by their analytical and spectral (IR, ^{1}H NMR) data.

Compared to some previously reported reagents with major or minor drawbacks, several noteworthy features of this system are apparent.

TABLE I Conversion of Alcohols to Dialkyl Sulfites Using Na_2SO_3/Thionyl Chloride[a]

Entry	Substrate	Product	Time (min)	Yield (%)[b,c]
1	CH_3OH	$(CH_3O)_2SO$	10	60
2	$CH_3(CH_2)_2CH_2OH$	$[CH_3(CH_2)_2CH_2O]_2SO$	15	80
3	$(CH_3)_2CHCH_2OH$	$[(CH_3)_2CHCH_2O]_2SO$	30	71
4	$(CH_3)_3COH$	$[(CH_3)_3CO]_2SO$	60	43
5	$CH_3(CH_2)_5CH_2OH$	$[CH_3(CH_2)_5CH_2O]_2SO$	10	82
6	$CH_3CH(CH_3)CH_2OH$	$[CH_3CH(CH_3)CH_2CH_2]_2SO$	5	80
7	$CH_3(CH_2)_5CHOHCH_3$	$[CH_3(CH_2)_5(CH_3)CHO]_2SO$	40	73
8			10	81
9			15	53
10			20	64
11			30	34

[a] Molar ratio of reagent to substrate was 1.5:1. The reaction performed at r.t.

[b] Yields refer to pure isolated products.

[c] Products were characterized by comparision of their physical data, IR, NMR spectra with known samples.

These are: availability of the reagent, operational simplicities, and use of inexpensive reagents.

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; it may be a suitable addition to methodologies already present in the literature.

EXPERIMENTAL

General

Progress of the reactions was followed by TLC using silica gel with fluorescent indicator coated on aluminum sheets. IR spectra were recorded on a Shimadzo 450 spectrophotometer. Sodium sulfite and thionyl chloride were purchased from Fluka Company. Alcohols were purchased from Fluka and Merck. Products were characterized by comparison of their physical data, IR, and ^{1}H 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 of Alcohols to Sulfite with $Na_2SO_3/SOCl_2$ in CH_2Cl_2

To a mixture of sodium sulfite (1.5 mmol, 0.189 g) and freshly distilled thionyl chloride (1.5 mmol, 0.179 g) was added a solution of alcohol (1 mmol) in dry CH_2Cl_2 (5 ml). The reaction mixture was stirred at room temperature for 5–60 min (Table I). The progress of the reaction was followed by TLC. The mixture was then filtered and the residue washed thoroughly with CH_2Cl_2 (5 ml). Evaporation of solvent under reduced pressure furnished the crude dialkyl sulfite which were purified by plate chromatography.

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