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Formation of Dioxolane on the Surface of Silica-Sulphuric Acid in Dry Media—Chemoselective Protection of Aryl Aldehydes

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Formation of Dioxolane on the Surface of Silica–Sulphuric Acid in Dry Media—Chemoselective Protection of Aryl Aldehydes

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Abstract: Chemoselective protection of aryl aldehydes can be accomplished through the formation of dioxolane on the surface of silica–sulphuric acid under solvent-free conditions where aliphatic aldehydes, dialkyl ketones, aryl alkyl ketones, and diaryl ketones remain intact.

Keywords: acetal, chemoselectivity, solvent-free reaction, supported reagent

Protection of carbonyl groups is a very important organic transformation[1] in a synthetic sequence for the construction of complicated molecular architecture. Selective protection of one type of carbonyl functionality in the presence of other types is often a formidable task for a synthetic chemist, and numerous methods (especially through the formation of the corresponding dioxolanes[2]) have been reported in the literature. Many of them involve the use of costly and toxic chemicals, harshly acidic reaction conditions (causing various side reactions of sensitive moieties), and large amounts of organic solvents as reaction media most of which are highly toxic. Therefore, there is a need to develop a new methodology that would utilize relatively less toxic and readily available acidic reagents in milder conditions as well as

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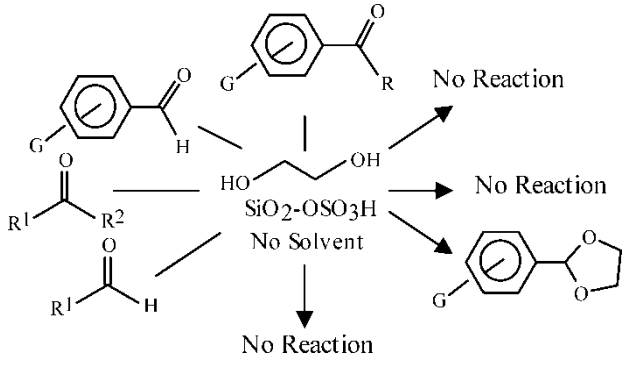
accomplish good chemoselectivity in the course of carbonyl protection in eco-friendly conditions. Silica–sulfuric acid[3a] has been recognized in recent times as a mild, heterogeneous, and ecofriendly acid catalyst to accomplish various important organic transformations.[3a–3g] As a part of our continuous effort[4] to develop a new methodology for important and selective organic reactions, we report herein a mild, cost-effective, chemoselective, and eco-friendly protocol for the protection of aryl aldehydes through the formation of the dioxolanes on the surface of silica–sulfuric acid under solvent-free conditions (Scheme 1). The detailed results are furnished in Table 1.

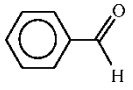
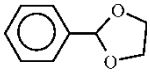
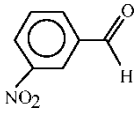
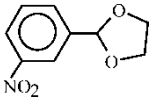
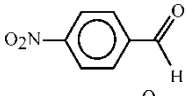
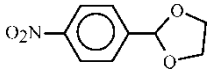
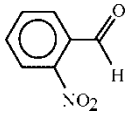
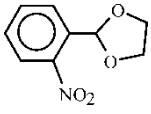
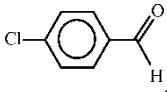
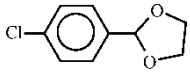
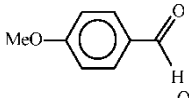
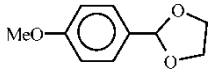
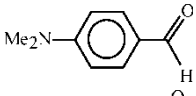
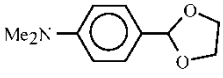
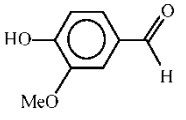
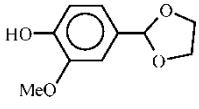
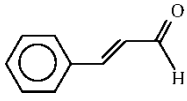
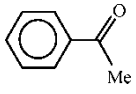
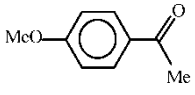
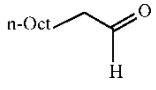
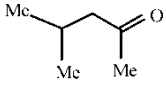
As shown in Table 1, several aryl aldehydes bearing electron-withdrawing (entries 2 – and in Table 1) and electron-donating substituents (entries 6–8 in Table 1) at various locations smoothly underwent acetalization in the presence of 1.5 mol equivalents of ethane-1,2-diol on the surface of silica–sulfuric acid under solvent-free conditions. Interestingly, vinylogous aryl aldehyde (entry 9 in Table 1), aliphatic aldehyde (entry 12 in Table 1), dialkyl ketone (entry 13 in Table 1), and aryl alkyl ketones (entries 10 and 11 in Table 1) remained completely unaffected under the present reaction condition. Diaryl ketones have also been reluctant to produce any ketal in this condition. It is very important to note that the substrates not producing any dioxolane in the previously mentioned protocol were recovered totally unchanged without any side reaction. Therefore, the aforementioned protocol can be used to protect aryl aldehydes with high chemoselectivity in the presence of alkyl aldehydes, vinylogous aryl aldehydes, dialkyl ketones, aryl alkyl ketones, and diaryl ketones. This protocol completely eliminates the use of toxic and harsh reagents and organic solvents in the reaction medium. Therefore, it can be considered a relatively greener process in comparison to most of the existing methods. Silica–sulphuric acid can be recycled after product isolation with little variation of yield.

In conclusion, a novel, mild, cost-effective, and highly chemoselective protocol has been developed in dry media on the surface of silica–sulfuric



Scheme 1.

Table 1. Selective formation of dioxolane from aryl aldehydes and 1,2-ethanediol on the surface of silica–sulphuric acid under solvent-free conditions

Entry	Substrate	Product	Time (min)	Yield (%)
1			60	61
2			45	70
3			45	71
4			45	70
5			30	68
6			90	64
7			120	62
8			120	60
9		No reaction	720	—
10		No reaction	720	—
11		No reaction	720	—
12		No reaction	720	—
13		No reaction	720	—

acid for chemoselective protection of aryl aldehydes in the presence of other types of oxo- and formyl functionalities.

EXPERIMENTAL

General Procedure for Acetalization of Aldehydes on the Surface of Silica–Sulfuric Acid

Silica–sulfuric acid[3g] (1 g) was added slowly with stirring to a mixture of the appropriate aldehyde (2 mmol) and freshly distilled ethylene glycol (3 mmol) at room temperature, and the entire mass was thoroughly mixed to obtain an easy-flowing powder. After completion of reaction (monitored with thin-layer chromatography [TLC] on silica gel) the reaction mixture was eluded with ether or ethyl acetate (10 mL). The organic extract was washed with saturated aqueous bicarbonate solution (2×10 mL) and dried over anhydrous sodium sulfate, and the solvent was evaporated to furnish the product in pure form.

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