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Silica sulfuric acid mediated protection of carbonyl groups as 2,4-dinitrophenylhydrazone

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Abstract

Silica sulfuric acid is employed as solid acid catalyst for the clean and less hazardous protection of carbonyl compounds as 2,4-dinitrophenylhydrazone under solvent-free conditions.

Keywords: Protection; Silica sulfuric acid; 2,4-Dinitrophenylhydrazone; Carbonyl compound; Solvent-free.

1. Introduction

In several chemical important processes a large excess of sulfuric acid is required and therefore at the end of these processes, a large amount of “spent acid” is obtained. The separation of the products from the spent acid is often a difficult and energy consuming process that habitually implies a basic aqueous work-up. Moreover, sulfuric acid is corrosive and is dangerous to transport and handle. Consequently, any reduction in the amount of sulfuric acid needed and/or any simplification in handling procedures would be highly convenient in terms of risk reduction, economic advantages and environment protection [1, 2].

Arylhydrazones [3] are a most popular and promising protecting groups of carbonyl functions in synthetic organic chemistry, and various types of arylhydrazones have been developed so far. 2,4-Dinitrophenylhydrazone is one of the most common and useful derivative for that protection, because of its ease of formation, relative ease of removal and highly its crystallity. They are also extensively used for the isolation, characterization, and purification of carbonyl compounds.

Protection of carbonyl compounds as 2,4-dinitrophenylhydrazone is commonly catalyzed by sulfuric acid [4]. In 1999, a report by Lalitha et al. outlined the protection of carbonyl compounds as 2,4-dinitrophenylhydrazone in the presence of activated acidic zeolite in hexane/methanol as solvent and under reflux conditions [5]. Recently we have reported H_2SO_4/SiO_2 is an effective catalyst for the conversion of carbonyl compounds to their corresponding 2,4-dinitrophenylhydrazone under solvent-free conditions [6].

In addition, application of basic alumina as a catalyst for protection of carbonyl compounds under solvent-free conditions was reported [7]. These transformations have some outstanding green-chemical features. From the viewpoint of green chemistry, a solvent-free reaction is very significant and attractive in synthetic organic chemistry [8]. However, sulfuric acid used in this

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protection reaction is highly corrosive, and it poses severe environmental hazards. In addition, it is not efficient satisfactory, especially when acid-sensitive functional groups are present elsewhere in the molecule.

These days, silica sulfuric acid as an inexpensive reagent which can be easily prepared has been frequently used in synthetic organic laboratories [2]. It enjoy advantages over conventional liquid acid catalysts by giving good and higher yields, easier separation of products, reusability, milder reaction conditions, *etc.* These facts motivated us to use of this inorganic acidic resin as a sulfuric acid function immobilized on the surface of silica gel via covalent bonding for the preparation of 2,4-dinitrophenylhydrazone. Recently, we reported an efficient protection of carbonyl compounds as 2,4-dintrophenylhydrazones using Dowex [9] as a strongly acidic cationic exchange resin or silica sulfuric acid [10] in ethanol at room temperature. Herein, we wish to report a mild and convenient method for fast and efficient conversion by silica sulfuric acid as solid acid catalyst under solvent-free condition.

2. Experimental

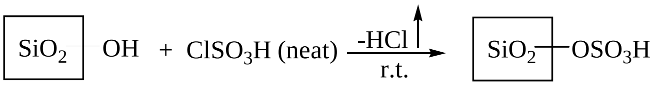
Silica sulfuric acid was prepared according to the previously reported procedure [2]. All products are known compounds and are identified by comparison of their physical and spectral data with those of authentic samples [11]. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

2.1. General procedure

Silica sulfuric acid (0.4 g), SiO_2 (0.6 g) and 2,4-dinitrophenylhydrazine (1.1 mmol) were thoroughly mixed together in a mortar to form an intimate mixture. A neat carbonyl compound (1 mmol) and little drops of t-BuOH were added to this mixture. The reaction mixture was ground for the time specified in the Table 1. The progress of reaction was monitored by TLC using ether-CCl_4. On completion of reaction, the reaction mixture was poured into $CHCl_3$ (20 mL). The solid was filtered off and the solvent evaporated under reduced pressure to give the product which was recrystallized from a suitable solvent and afford the TLC and ^{1}HNMR pure products in 71-94% isolated yields.

3. Results and discussion

Silica sulfuric acid was easily prepared by reaction of silica gel with chlorosulfonic acid. The reaction is very clean and not requiring any work-up procedure because the evolved HCl gas can be removed from the reaction vessel immediately (Scheme 1).

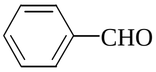
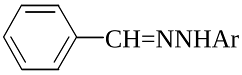
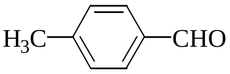
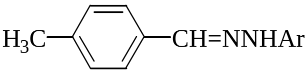
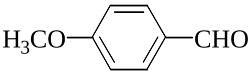
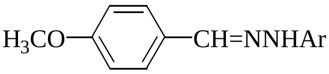
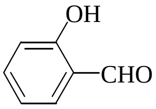
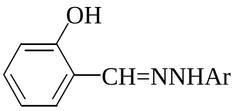
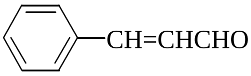
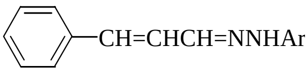
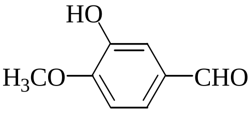
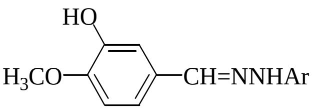
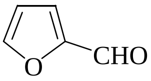
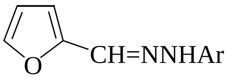
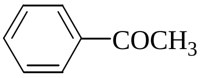
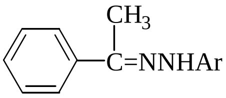
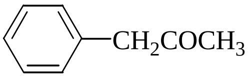
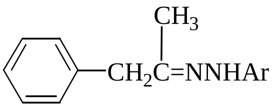
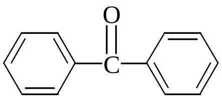
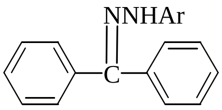
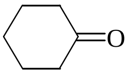
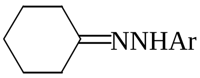
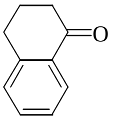
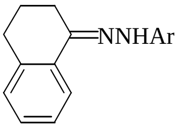
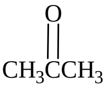
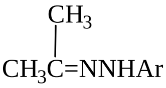


Scheme 1

In this simple and efficient method the starting carbonyl compounds were converted to the corresponding 2,4-dinitrophenylhydrazones in a mortar with grinding by a pestle in the presence of silica gel, silica sulfuric acid and 2,4-dinitrophenylhydrazine (Scheme 2). It is proved that for rapid and clean conversion of carbonyl compounds to 2,4-dinitrophenylhydrazone, addition of little drops of t-BuOH in the reaction media is essential.

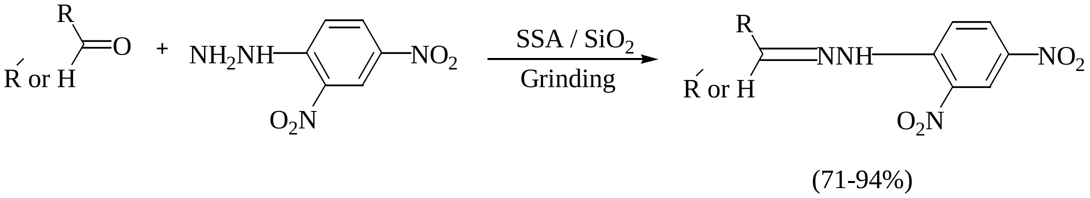
Satisfactory results have been obtained in the condensation of variety of aromatic and aliphatic aldehydes and ketones with 2,4-dinitrophenylhydrazine under solvent-free conditions in the presence of silica gel and silica sulfuric acid. Acid sensitive substrate like furfural and cinnamaldehyde are also protected as 2,4-dinitrophenylhydrazone in very good yield without the formation of any side products. It can be emphasized that the reaction is clean, the work-up is straightforward and, from economical and environmental points of view, use of solvent-free conditions is favorable.

Table 1
SiO_2/Silica sulfuric acid catalyzed conversion of carbonyl compounds to 2,4-dinitrophenylhydrazones.[a,b]

Entry	**Substrate**	**Product**	**Time (min)**	**Yield[c] (%)**
1			2	90
2			2	88
3			3	87
4			2	83
5			2	80
6			4	85
7			2	94
8	CH_3CHO	$CH_3CH{=}NNHAr$	2	94
9			3	93
10			2	80
11			3	83
12			2	84
13			3	85
14	 $CH_3\overset{\overset{O}{\Vert}}{C}CH_3$	 $CH_3\overset{\overset{CH_3}{\vert}}{C}{=}NNHAr$	2	71

[a] Products were characterized by comparison of their physical data, IR, NMR spectra with known samples.
[b] Ar = 2,4-dinitrophenyl.
[c] Isolated yields.

In summary, we have demonstrated an efficient, mild and novel protection methodology of carbonyl groups using of 2,4-dinitrophenylhydrazine in the presence of silica gel and silica sulfuric acid under solvent-free conditions. We believe that the present procedure provides an easy, mild, efficient, versatile and general methodology for the protection of different classes of carbonyl compounds, and we feel that it may be a suitable addition to methodologies already present in the literature.



Scheme 2

Acknowledgements

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