Asian Journal of Chemistry Vol. 18, No. 2 (2006), 969–972

Protection of Carbonyl Groups as 2,4-Dinitro-phenylhydrazone Catalyzed by Silica Sulfuric Acid

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The protection of aldehydes and ketones as 2,4-dinitrophenylhydrazone is studied using silica sulfuric acid as solid acid catalyst. The reaction is clean and work-up is very simple. The use of this solid acid catalyst allows replacing the usual soluble inorganic acid, contributing to waste reduction.

Key Words: Carbonyl groups, 2,4-Dinitro-phenylhydrazone.

INTRODUCTION

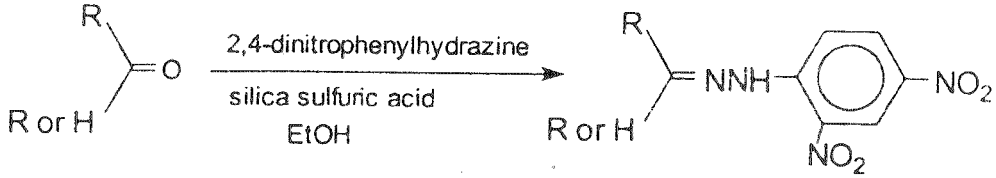
During the multistep synthesis of natural products, the efficiency of the synthetic protocol employed often depends largely on protection and deprotection of functional groups involved. To this end, protecting groups have been playing a crucial role during the synthesis of complex natural products[1]. Among the various protecting groups used for carbonyl function in aldehydes and ketones, 2,4-dinitrophenylhydrazone is the most common group in view of its easy introduction and high stability. It is also extensively used for the isolation, characterization and purification of carbonyl compounds[2].

The addition of 2,4-dinitrophenylhydrazine to carbonyls to yield 2,4-dinitrophenylhydrazone is one of the best understood examples of a nonenzymatic addition-elimination reaction. The process of this addition-elimination reaction was usually catalyzed by sulfuric acid that is highly corrosive and it poses severe environmental hazards[1]. In 1999, a report by Lalitha *et al.*[3] 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.

Recently we have reported sulfuric acid mixed with silica gel as an effective catalyst for the conversion of carbonyl compounds to their corresponding 2,4-dinitrophenylhydrazone under solvent free conditions[4]. These transformations have some outstanding green-chemical features. However, sulfuric acid used in this protection reaction is highly corrosive; it poses severe environmental hazards. In addition, it is not efficient satisfactorily, especially when acid-sensitive functional groups are present elsewhere in the molecule.

Heterogeneous reactions that are facilitated by supported reagents on various solid inorganic surfaces have received attention in recent years[5]. The advantage of these methods over conventional homogenous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products and manipulative simplicity. In continuation of our ongoing program to develop environmentally benign methods using solid supports[4, 6, 7], we report the application of silica sulfuric acid as solid acid catalyst for protection of aldehydes and ketones as 2,4-dinitrophenylhydrazone.

It was believed that the silica sulfuric acid with high and adjustable acidity can overcome this problem. It enjoys advantages over conventional liquid acid catalysts by giving good and higher yields, easier separation of products, reusability, milder reaction conditions, etc. Therefore, the authors were interested in using 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.



68-90%

EXPERIMENTAL

Silica sulfuric acid was prepared according to the previously reported procedure[8]. All products are known compounds and are identified by comparison of their physical and spectral data with those of authentic samples[9]. 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 protection of carbonyl compounds as 2,4-dinitrophenylhydrazones: Protection was carried out mixing the carbonyl compound (1 mmol), 2,4-dinitrophenylhydrazine (1.5 mmol), silica sulfuric acid (1 g) and ethanol (20 mL). The suspension was stirred at room temperature for 5 min. The solvent was evaporated under reduced pressure and to the obtained residue, $CHCl_3$ (20 mL) was added. 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 ^1H NMR pure products in 68–90% isolated yields.

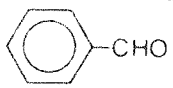
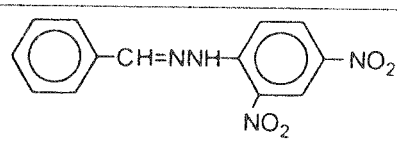
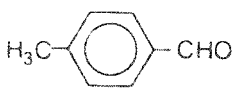
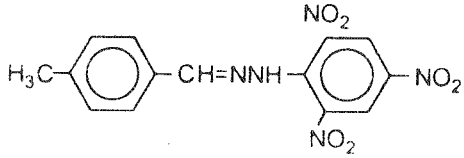
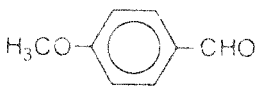
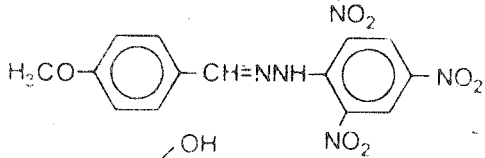
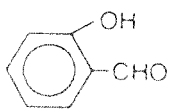
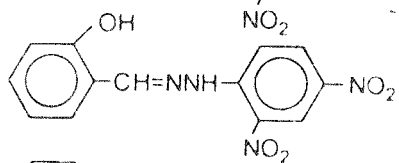
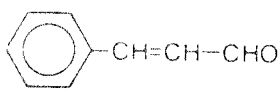
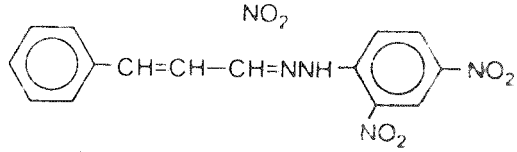
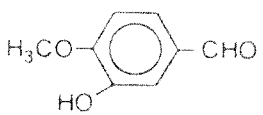
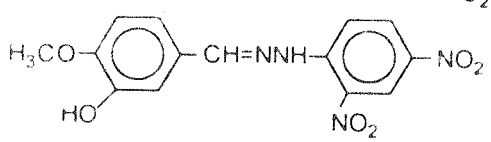
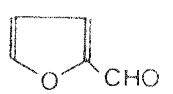
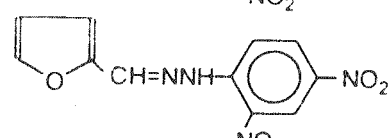
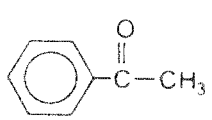
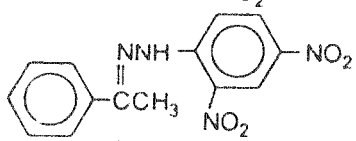
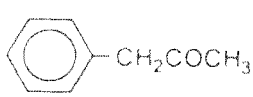
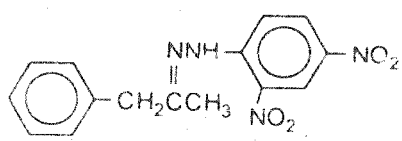
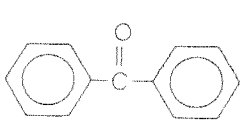
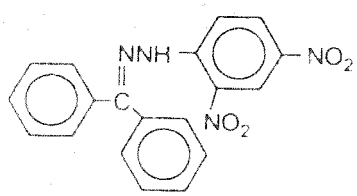
(*Caution: 2,4-Dinitrophenylhydrazine is toxic and cancer suspect agent.*)

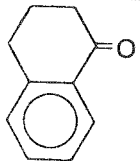
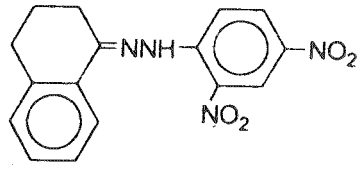
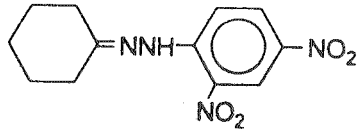
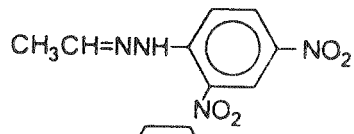
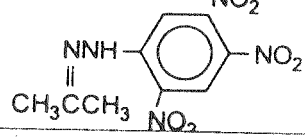
RESULTS AND DISCUSSION

Silica sulfuric acid is easily prepared by neat addition of chlorosulfonic acid with silica gel. It is interesting to note that the reaction is easy and clean without any work-up procedure, because HCl gas is evolved from the reaction vessel immediately. The reaction of benzaldehyde with 2,4-dinitrophenylhydrazine in the presence of silica sulfuric acid in ethanol gave benzaldehyde 2,4-dinitrophenylhydrazone in 87% isolated yield. Similarly, several aromatic, aliphatic, α, β-unsaturated and heterocyclic aldehydes and ketones were efficiently converted into the corresponding 2,4-dinitrophenylhydrazone in the presence of silica sulfuric acid (Table-1). The cyclic ketones like cyclohexanone and α-tetralone reacted with 2,4-dinitrophenylhydrazine to give the corresponding 2,4-dinitrophenylhydrazone in high yields. The tolerance of various functional groups under the present reaction conditions has been examined by reacting the substrates bearing OMe, OH, olefinic group and the reaction conditions are compatible with these functional groups. Acid sensitive substrates like furfural and cinnamaldehyde are also protected in good yield without the formation of any side products. It can be emphasized that the reaction is clean and the work-up is straightforward.

In summary, an efficient, mild and novel protection methodology of carbonyl group using 2,4-dinitrophenylhydrazine in the presence of silica sulfuric acid in ethanol has been demonstrated. The authors believe that the present procedure provides an easy, mild, efficient, versatile and general methodoiogy for the protection of different classes of carbonyl compounds, and they feel that it may be a suitable addition to methodologies already present in literature.

TABLE-1
PROTECTION OF CARBONYL COMPOUNDS AS 2,4-DINITROPHENYLHYDRAZONE CATALYZED BY SILICA SULFURIC ACID IN ETHANOL[a, b]

Substrate	Product	Yield (%)
		87
		87
		73
		80
		83
		68
		85
		90
		73
		83

Substrate	Product	Yield (%)
		83
		72
CH_3CHO		72
CH_3COCH_3		80

(a) Yields refer to pure isolated products. (b) Products were characterized by comparison of their physical data, IR, NMR spectra with known samples.

ACKNOWLEDGEMENT

The authors acknowledge the partial support of this work by Shahid Chamran Ahvaz University Research Council.

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(*Received*: 16 March 2005; *Accepted*: 12 December 2005) AJC-4516