

## **Silica Phosphoric Acid as an Efficient Heterogeneous Catalyst for Protection of Carbonyl Groups Under Solvent Free Conditions**

RASHID BADRI\*, ALI REZA KIASAT and MOSADEGH KESHAVARZ  
*Department of Chemistry, College of Science, Chamran University*  
*61357-4-3169 Ahvaz, Iran*  
*Fax: (98)(611)3337009; E-mail: rashidbadri@yahoo.com*

Aldehydes and ketones were protected by phenyl hydrazine and 2,4-dinitrophenylhydrazine in the presence of silica phosphoric acid in short time and high yields.

**Key Words:** Silica phosphoric acid, Solid state, Carbonyl groups, Protection, 2,4-Dinitrophenyl hydrazone, Phenyl hydrazone.

### **INTRODUCTION**

The derivatives of ammonia such as phenyl hydrazine and 2,4-dinitrophenyl hydrazine are well known protecting groups for carbonyl compounds and this protecting method is important in multi steps synthesis of organic, pharmacological and carbohydrate chemistry<sup>1,2</sup>. Application of solid acids, such as silica sulfuric and silica phosphoric acid, were found to have many useful advantages over traditional used of unsupported acids<sup>2,3</sup>. For example, Fry and Corker<sup>4</sup> reported the use of solid supported phosphoric acid as a catalyst in ketone rearranged material by passing the carbonyl compound over a bed of solid acid at elevated temperature. Kropp and co-workers<sup>5</sup> used a mixture of phosphoric acid and silica gel in solvent as a catalyst for cyclization of citronellal, dimerization of 1,3-dienes and Friedel-Crafts reaction. The solid acids are safe, easy to handle environmentally, benign and have low cost and straight forward work-up. They provide greater selectivity, enhanced reaction rates, clean products and manipulative simplicity<sup>6-8</sup>. Thus, silica phosphoric acid can be an excellent reagent for the replacement of sulfuric and phosphoric acids in organic reactions<sup>9-11</sup>.

### **EXPERIMENTAL**

Silica phosphoric acid was prepared according to the reported procedure<sup>12</sup>. Melting points were uncorrected. The IR spectra were recorded on Bomem FT-IR spectrometer. <sup>1</sup>H NMR spectra were taken on a 400 MHz

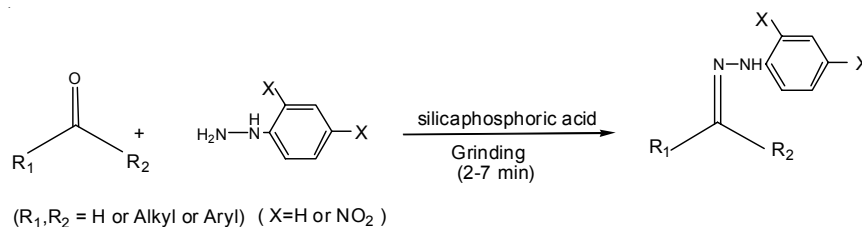
Bruker spectrometer. The purity determination of the products and reaction monitoring were accomplished by TLC on polygram SILG/UV 254 plates. Products were characterized by comparison of their physical data, IR and  $^1\text{H}$  NMR spectra with authentic samples.

**General procedure for protection of carbonyl groups:** Different carbonyl compounds (2 mmol), 2,4-dinitrophenyl hydrazine or phenyl hydrazine (2 mmol), silica phosphoric acid (0.4 g, 4 mmol  $\text{H}^+$ ) and silica gel (0.5 g) were mixed under grinding conditions at room temperature (2-7 min). After complete conversion of carbonyl to hydrazone as indicated by TLC, the mixture was washed with chloroform ( $2 \times 20$  mL) and then mixture was filtrated. Solvent of filtrate was removed by rotary and finally the solid residue was recrystallized in ethanol.

**Typical procedure for protection of cyclohexadione:** Cyclohexadione (0.112 g, 1 mmol), 2,4-dinitrophenyl hydrazine (0.206 g, 2 mmol), silica phosphoric acid (0.4 g, 4 mmol  $\text{H}^+$ ) and silica gel (0.5 g) were mixed under grinding conditions at room temperature. After complete conversion of carbonyl to hydrazone as indicated by TLC, mixture was washed with chloroform ( $2 \times 20$  mL) and then mixture was filtrated. Solvent of filtrate was removed by rotary and finally the solid residue was recrystallized in ethanol, yield 75 %.

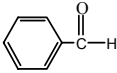
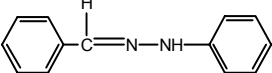
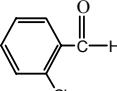
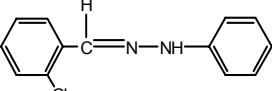
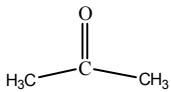
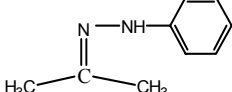
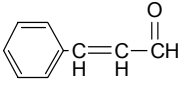
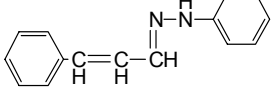
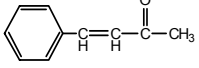
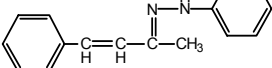
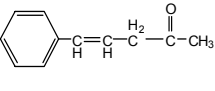
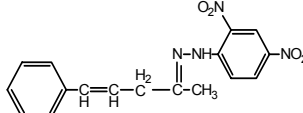
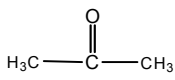
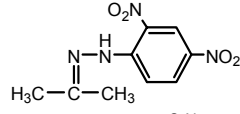
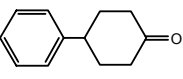
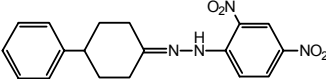
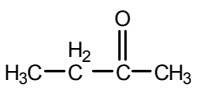
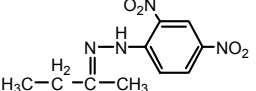
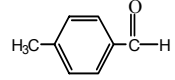
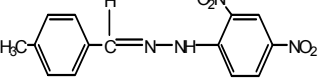
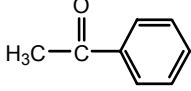
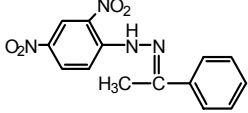
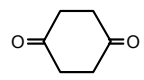
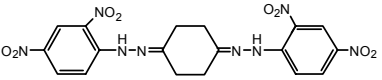
## RESULTS AND DISCUSSION

In this paper, we wish to report an extremely convenient method for the protection of carbonyl groups in the presence of silica phosphoric acid (SPA) as an efficient catalyst under solvent free conditions (**Scheme-I**). Preparation of silica phosphoric acid is a clean and simple reaction with straightforward work-up<sup>12</sup>. A variety of different types of aliphatic and aromatic ketones and aldehydes were subjected to reaction with phenylhydrazine and 2,4-dinitrophenyl hydrazine in the presence of silica phosphoric acid under grinding conditions. The reactions were completed within (2-7 min) and the corresponding hydrazones were obtained in the moderate to high yield (70-89%). The results of our studies are shown in Table-1.



**Scheme-I**

TABLE-1  
 PROTECTION OF CARBONYL COMPOUNDS AS 2,4-DINITROPHENYLHYDRAZONE AND PHENYLHYDRAZONE CATALYZED BY SILICA PHOSPHORIC ACID UNDER SOLVENT FREE CONDITIONS<sup>a,b</sup>

Carbonyl compound	Protecting group	Product	Time (min) / Yield (%)
	Phenyl hydrazine		4 (78)
	Phenyl hydrazine		5 (75)
	Phenyl hydrazine		3 (85)
	Phenyl hydrazine		2 (85)
	Phenyl hydrazine		2 (85)
	2,4-Dinitro phenyl hydrazine		2 (88)
	2,4-Dinitro phenyl hydrazine		2 (82)
	2,4-Dinitro phenyl hydrazine		7 (87)
	2,4-Dinitro phenyl hydrazine		3 (83)
	2,4-Dinitro phenyl hydrazine		2 (89)
	2,4-Dinitro phenyl hydrazine		4 (83)
	2,4-Dinitro phenyl hydrazine		4 (75)

<sup>a</sup>Yields refer to pure isolated products; <sup>b</sup>Products were characterized by comparison of their physical data, IR and NMR spectra with known samples.

As Table-1 indicates, nearly all carbonyl compounds have readily converted to their corresponding hydrazones at ambient temperature. Aliphatic ketones converted to their phenylhydrazones and 2,4-dinitrophenylhydrazones in good yields (Table-1). Aromatic and  $\alpha,\beta$ -unsaturated aldehydes and ketones produced corresponding hydrazones in moderate to high yields (Table-1). The acid sensitive  $\alpha,\beta$ -unsaturated substrates were efficiently gave hydrazones without the formation of any side products. Their carbon-carbon double bonds remained intact during the reaction course. Furfural and 2-formylpyridine failed to give hydrazones under the same reaction conditions. In conclusion, our procedure using silica phosphoric acid as a catalyst is of interest and provides another new convenient and facile method for protection of carbonyl groups under solid state conditions.

#### ACKNOWLEDGEMENT

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