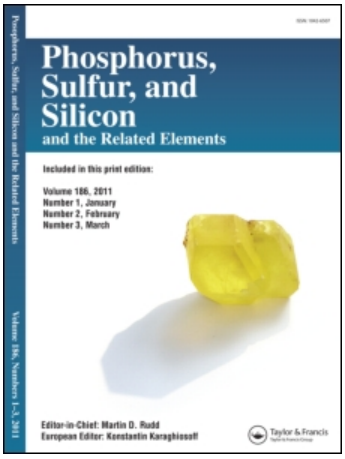

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

$H_2SO_4O_2$ AS AN EFFICIENT CATALYST FOR THE PREPARATION OF PHENYLHYDRAZONES AND 2,4-DINITROPHENYLHYDRAZONES UNDER SOLVENT-FREE CONDITIONS

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Online publication date: 12 August 2010

To cite this Article Kiasat, Ali Reza , Kazemi, Foad and Nourbakhsh, Kazem(2004) '$H_2SO_4O_2$ AS AN EFFICIENT CATALYST FOR THE PREPARATION OF PHENYLHYDRAZONES AND 2,4-DINITROPHENYLHYDRAZONES UNDER SOLVENT-FREE CONDITIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 3, 569 — 573
To link to this Article: DOI: 10.1080/10426500490422227
URL: http://dx.doi.org/10.1080/10426500490422227

Phosphorus, Sulfur, and Silicon, 179:569–573, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490422227

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H_2SO_4/SiO_2 AS AN EFFICIENT CATALYST FOR THE PREPARATION OF PHENYLHYDRAZONES AND 2,4-DINITROPHENYLHYDRAZONES UNDER SOLVENT-FREE CONDITIONS

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(Received September 9, 2003)

H_2SO_4 mixed with silica gel (1:1) by weight produces a white powder which is an effective catalyst for the conversion of carbonyl compounds to their corresponding phenylhydrazones and 2,4-dintrophenylhydrazones under solvent-free conditions.

Keywords: 2,4-Dinitrophenylhydrazone; carbonyl compound; phenylhydrazone; protection; silica gel; solvent free; sulfuric acid

Protection of carbonyl groups is often a necessary requirement in reactions involving substrates with multifunctional groups.[1] Derivatives of carbonyl compounds such as phenylhydrazone and 2,4-dintrophenylhydrazones not only are used for the characterization and purification of carbonyl compounds but also play an important role in the protection of carbonyl compounds.[2] Phenylhydrazones are largely oils or possess low melting points for many aliphatic aldehydes and ketones, but are generally crystalline for aromatic carbonyl compounds and also for cycloaliphatic and hetrocyclic aldehydes and ketones. 2,4-Dinitrophenylhydrazones are generally crystalline and are therefore eminently more suitable than phenylhydrazones for the detection, characterization, and protection of carbonyl compounds.[3]

The formation of these derivatives involves Brønsted as well as Lewis acid catalysis.[4] Although a protecting system consisting of phenylhydrazine or 2,4-diphenylhydrazine and acidic zeolite in methanol was recently reported[1] for the protection of carbonyl compounds,

Partial support of this work by Shahid Chamran Ahvaz University Research Council is gracefully acknowledged.

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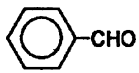
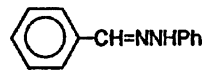
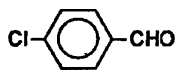
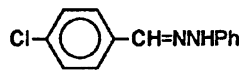
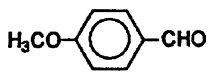
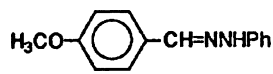
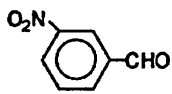
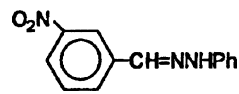
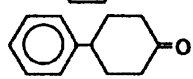
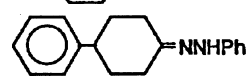
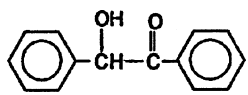
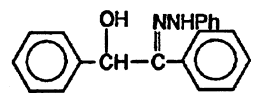
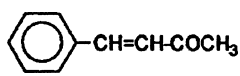
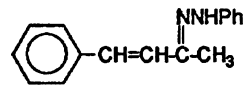
a literature survey reveals that no attention has been focused on the protection of carbonyl compound as phenylhydrazones or 2,4-dintrophenylhydrazones using inorganic solid supports under solvent-free conditions.

Recently considerable attention has been paid to solvent-free reactions.[5,6] These reactions are not only of interest from an environmental point of view, but in many cases also offer considerable synthetic advantages in terms of yield, selectivity, and simplicity of the reaction procedure.

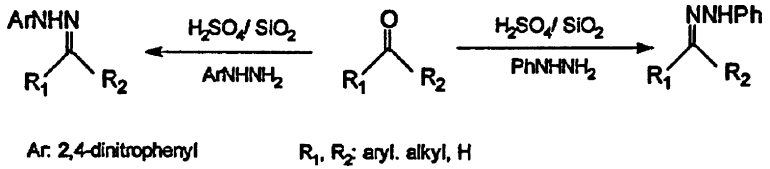
Sulfuric acid on silica gel (2.5:1) by weight has been used as a catalyst for the nitration of aromatic compounds.[7] Now, we report that a mixture of H_2SO_4 and SiO_2 in the ratio 1:1 (w/w) gives a white powder that can be used as efficient catalyst for conversion of carbonyl compounds to the corresponding phenylhydrazones and 2,4-dintrophenylhydrazones in the absence of solvent.

TABLE I SiO_2/H_2SO_4 Catalyzed Conversion of Carbonyl Compounds to Phenylhydrazone

Entry	Substrate	Product	Time (min)	Yield (%)
1			10	85
2			8	87
3			10	88
4			7	83
5			8	67
6			8	91
7			5	90

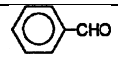
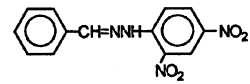
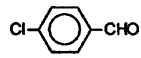
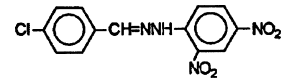
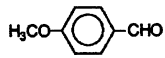
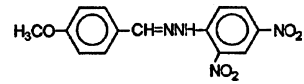
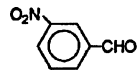
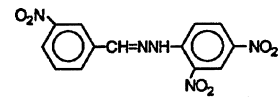
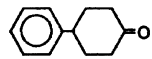
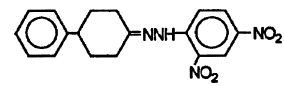
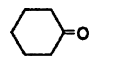
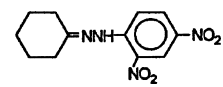
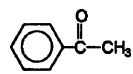
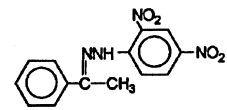
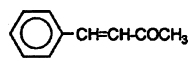
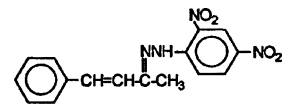
[a]Yields refer to pure isolated products.

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



H_2SO_4/SiO_2 was prepared by simply cogrinding silica gel with sulfuric acid in the ratio 1:1 (w/w) in an agate mortar. In this simple and efficient method the starting aldehydes and ketones were converted to

TABLE II SiO_2/H_2SO_4 Catalyzed Conversion of Carbonyl Compounds to 2.4-Dinitrophenyl Hydrazone[a,b]

Entry	Substrate	Product	Time (min)	Yield (%)
1			10	65
2			8	85
3			9	90
4			10	87
5			10	79
6			8	71
7			8	68
8			10	83

[a]Yields refer to pure isolated products.

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

the corresponding arylhydrazones in a mortar with grinding by a pestle in the presence of H_2SO_4/SiO_2 and arylhydrazine.

As shown in Tables I and II, various types of aldehydes and ketones were cleanly and rapidly condensed with phenylhydrazine and 2,4-dinitrophenylhydrazine under solvent free conditions, giving the corresponding phenylhydrazones and 2,4-dinitrophenylhydrazones in good to excellent isolated yields in the presence of H_2SO_4/SiO_2. The scope and generality of this process is illustrated with several examples and the results are summarized in Table I and II. The structure of all the products were settled from their analytical and spectral (IR, ^{1}H NMR) data and by direct comparison with authentic samples.

CONCLUSION

In summary, we have demonstrated an efficient, mild, and novel protection methodology of the carbonyl group using phenylhydrazine and 2,4-dinitrophenylhydrazine in the presence of silica gel and 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.

EXPERIMENTAL

General

All products are known compounds and are identified by comparison of their physical and spectral data with those of 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 Preparation of Phenylhydrazones and 2,4-Dinitrophenylhydrazones

H_2SO_4 (98%, 2 g) and SiO_2 (2 g) were thoroughly mixed together in a mortar to form an intimate mixture. A neat carbonyl compound (1 mmol) and phenylhydrazine or 2,4-dinitrophenylhydrazine (5 mmol) were added to this mixture. The reaction mixture was ground for the time specified in Table I and II. The progress of reaction was monitored by TLC using ether-CCl_4. On completion of the reaction, the reaction mixture was poured into ether (30 ml). The silica gel was filtered off

and the filtrate washed with water (30 ml). The organic layer was dried over anhydrous sodium sulfate and solvent evaporated under reduced pressure to give the product which was recrystallized from a suitable solvent to afford the TLC and ^{1}HNMR pure products in 65–91% isolated yields. (Caution: Phenylhydrazine and 2,4-dinitrophenylhydrazine are toxic and cancers suspect agent.

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