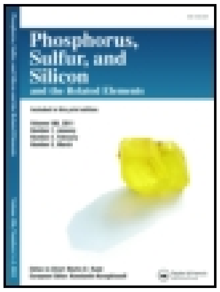


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

A CLEAN CONVERSION OF CARBONYL COMPOUNDS TO OXIMES USING SILICA GEL SUPPORTED HYDROXYLAMINE HYDROCHLORIDE

Ali Reza Kiasat [a] , Foad Kazemi [a] & Kazem Nourbakhsh [a]
[a] Shahid Chamran University, Ahvaz, Iran

To cite this article: Ali Reza Kiasat , Foad Kazemi & Kazem Nourbakhsh (2004): A CLEAN CONVERSION OF CARBONYL COMPOUNDS TO OXIMES USING SILICA GEL SUPPORTED HYDROXYLAMINE HYDROCHLORIDE, Phosphorus, Sulfur, and Silicon and the Related Elements, 179:6, 1193-1196

To link to this article: http://dx.doi.org/10.1080/10426500490459821

Phosphorus, Sulfur, and Silicon, 179:1193–1196, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490459821

A CLEAN CONVERSION OF CARBONYL COMPOUNDS TO OXIMES USING SILICA GEL SUPPORTED HYDROXYLAMINE HYDROCHLORIDE

Ali Reza Kiasat, Foad Kazemi, and Kazem Nourbakhsh
Shahid Chamran University, Ahvaz, Iran

(Received October 14, 2003; accepted October 16, 2003)

The efficient condensation of carbonyl compounds with hydroxylamine hydrochloride under solvent free conditions is described.

Keywords: Carbonyl compound; condensation; oxime; protection; silica gel; solvent free

Organic reactions on supported reagents recently have received considerable attention from synthetic chemists because of their high efficiency, environmentally benign conditions, and convenient work-up procedure.[1] In particular, silica gel has been shown to be the most useful inorganic solid for effecting a variety of functional group transformation.[1–3] The catalytic activity of silica gel is now recognized to be the results of water present in this reagent as a form of silicic acid, a so-called Brönsted acid.[3] One of the major advantages of using silica gel as a reagent is its weakly acidic character (pH 5.5–7.5).[3]

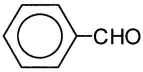
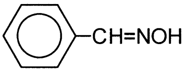
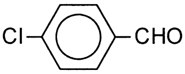
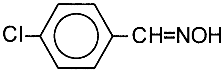
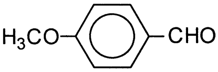
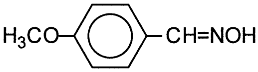
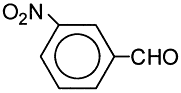
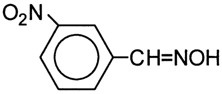
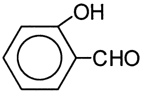
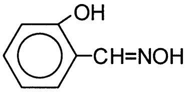
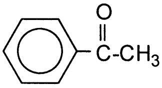
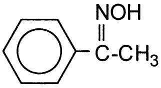
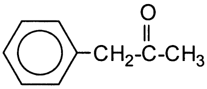
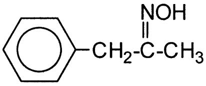
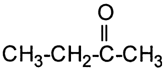
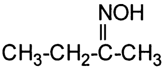
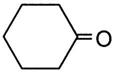
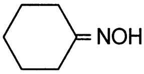
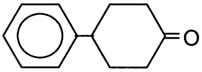
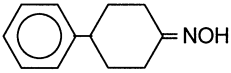
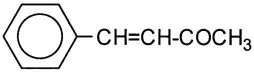
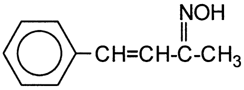
Protection of carbonyl compounds as oximes is of great interest to organic chemists, as they are readily prepared and highly stable compounds.[4] Oximes are employed as ketone and aldehyde functional group equivalent in synthesis, both because they provide convenient protection for the carbonyl group and because they are important synthetic intermediates.[5]

The addition of hydroxylamine hydrochloride to carbonyls to yield oximes is one of the best understood examples of a nonenzymatic addition-elimination reaction.[6] The process of this addition-elimination reaction usually was catalyzed by sulfuric acid that is highly corrosive

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

Address correspondence to Ali Reza Kiasat, Chemistry Department, College of Science, Shahid Chamran University, Ahvaz, Iran.

TABLE I Conversion of Carbonyl Compounds to Oximes Using SiO_2/NH_2OHHCl

Entry	Substrate	Product	Time (min)	Yield[a,b] (%)
1			9	78[c]
2			11	91
3			9	86
4			9	90
5			8	83
6			11	70
7			11	80
8	 $CH_3\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3$	 $CH_3\text{-}CH_2\text{-}\overset{\overset{\displaystyle NOH}{\|}}{C}\text{-}CH_3$	8	80[c]
9			9	74[c]
10			11	85
11			9	93

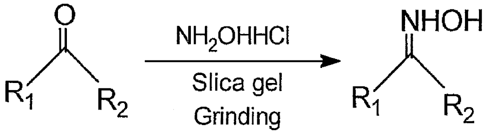
[a] Yields refer to pure isolated products.

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

[c] In the production isolation step, addition of water, and recrystallization steps were not performed.

and poses severe environmental hazards.[7] In 1988, a patent by Roffia et al.[8] outlined the preparation of the cyclohexanone oxime, as key intermediate for the preparation of nylon by liquid-phase ammoximation of cyclohexanone using ammonia hydrogen peroxide as the oxidizing agent and titanium silicite as the catalyst. But the economic attractiveness of this process, however, may be limited by the use of H_2O_2. Very recently Sharghi et al. have reported CaO,[4] $CuSO_4$,[9] and K_2CO_3[9] can be used as catalyst for the addition of hydroxylamine hydrochloride to carbonyl compounds in solvent free conditions at high temperature.

The remarkable ability of the silica gel to promote the various reactions together with the importance of protection reactions in organic synthesis gave us impetus for testing the oximation reaction of carbonyl compounds by hydroxylamine hydrochloride supported on silica gel. Our new approach reported herein involves the use of the cheap and commercially available silica gel as catalyst in the absence of solvent for mild and efficient conversion of carbonyl compounds to oximes.



Hydroxylamine hydrochloride supported on silica gel was prepared by simply cogrinding silica gel with NH_2OHHCl in the ratio 4:1 (w/w) in an agate mortar. In this simple and efficient method the starting carbonyl compounds were converted to the corresponding oximes in a mortar with grinding by a pestle in the presence of supported NH_2OHHCl on silica gel. It is proved that for rapid and clean conversion of carbonyl compounds to oximes, addition of small drops of t-BuOH in the reaction media is essential.

As reported in Table I satisfactory results have been obtained in the condensation of a variety of aldehydes and ketones with hydroxylamine hydrochloride under solvent free conditions in the presence of silica gel. 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.

CONCLUSION

In conclusion we have developed a rapid and solvent less method for protection of carbonyl compounds as their corresponding oximes. 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 Oximes

A mortar was charged with SiO_2 (2 g) and NH_2OHHCl (0.5 g, 7.2 mmol); the mixture was ground with a pestle of 1 min. A neat carbonyl compounds (1 mmol) and twelve drops of t-BuOH were added to this mixture. The reaction mixture was ground for the time specified in the Table I. The progress of reaction was monitored by TLC using ether-CCl_4. After the disappearance of starting material, the reaction mixture was mixed with ether. The mixture was filtrated to remove silica gel and then mixed with water and extracted. The solvent was removed in vaccuo to give the product which was recrystallized from a suitable solvent to afford the TLC and ^{1}HNMR pure products in 70–93% isolated yields.

REFERENCES

[1] H. J. Clark, *Catalysis of Organic Reactions by Supported in Organic Reagents* (VCH, New York, 1994).

[2] V. A. Basiuk, *Russ. Chem. Rev.*, **64,** 1003 (1995).

[3] H. Kotuki, T. Shimanouchi, R. Ohshima, and S. Fujiwara, *Tetrahedron*, **54,** 2709 (1998).

[4] H. Sharghi and M. Hosseini-Sarvari, *J. Chem. Res.*, 24 (2000).

[5] R. Ballini and M. Petrini, *J. Chem. Soc. Perkin Trans I*, 2563 (1988).

[6] W. P. Jencks, *J. Am. Chem. Soc.*, **81,** 475 (1959).

[7] T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis* (John Wiley & Sons, New York, 1991), 2nd ed.

[8] P. Roffia, N. Padovan, G. Leofanti, M. A. Mantagazza, G. Dealberti, and G. R. Tauszik., U. S. Pat. 4 794 198 (1988).

[9] H. Sharghi and M. Hosseini-Sarvari, *Synlett.*, **1,** 99 (2001).