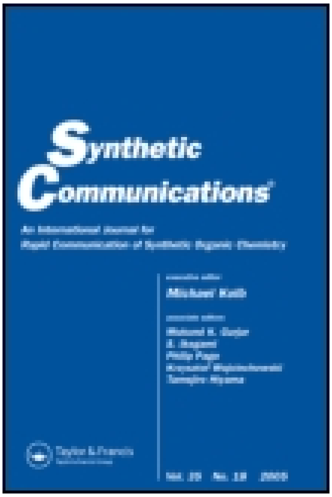


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

In Situ Alcohol Oxidation-Protection Reactions

A. R. Kiasat [a], F. Kazemi [a] & K. Nourbakhsh [a]
[a] Chemistry Department, College of Science, Shahid Chamran University, Ahvaz, Iran

To cite this article: A. R. Kiasat, F. Kazemi & K. Nourbakhsh (2005) In Situ Alcohol Oxidation-Protection Reactions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:11, 1555-1558, DOI: 10.1081/SCC-200058009

To link to this article: http://dx.doi.org/10.1081/SCC-200058009

Synthetic Communications®, 35: 1555–1558, 2005
Copyright © Taylor & Francis, Inc.
ISSN 0039-7911 print/1532-2432 online
DOI: 10.1081/SCC-200058009

In Situ Alcohol Oxidation-Protection Reactions

A. R. Kiasat, F. Kazemi, and K. Nourbakhsh
Chemistry Department, College of Science, Shahid Chamran University,
Ahvaz, Iran

Abstract: The one-pot conversion of primary and secondary alcohols into phenylhydrazones and 2,4-dintrophenylhydrazones is reported using chromium trioxide supported on silica gel and phenylhydrazines or 2,4-dintrophenylhydrazines under solvent-free conditions. This oxidation arylhydrazone formation reaction has been applied to a range of aliphatic and benzylic alcohols.

Keywords: Phenylhydrazone, oxidation, protection, chromium trioxide

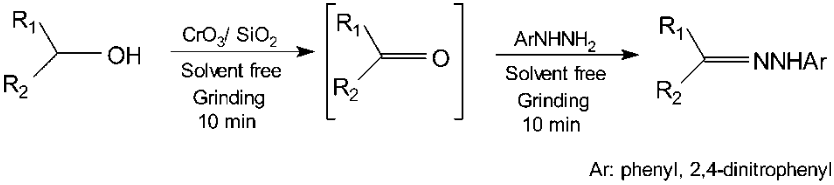
Multistep syntheses produce considerable amounts of waste, in part because of their complexity, but also because of a series of complex isolation procedures that must be carried out after each step. Thus, the combination of steps into a multistep, one-pot reaction sequence can be of great value, as long as overall yield and efficiency are not negatively influenced.[1] In a series of recent relevant papers, Taylor and coworkers developed a number of synthetically useful tandem oxidation processes such as conversion of primary alcohols to alkenes,[2] imines,[3] amines,[3] oxime ethers,[4] esters,[5] amides,[5] and nitriles.[6] One of the main benefits of this methodology is the in situ formation and consumption of the intermediate aldehydes.

Recently, studies of solvent-free organic reactions, especially with the reagents immobilized on porous solid supports, have had an important

Received in the UK November 10, 2004

Address correspondence to A. R. Kiasat, Chemistry Department, College of Science, Shahid Chamran University, Ahvaz 61357-4-3169, Iran. Fax: +98611 3337009; E-mail: kiasat_a@cua.ac.ir

effect.[7] The remarkable ability of silica gel to promote the various reactions under solvent-free conditions[8] together with the importance of combinatorial chemistry as a preparative technique[9] gave us the impetus to test the oxidation of primary and secondary alcohols followed by in situ protection of the resulting carbonyl compounds as arylhydrazones in a one-pot process using chromium trioxide supported on silica gel and arylhydrazine under solvent-free conditions.



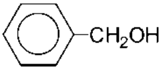
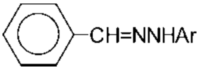
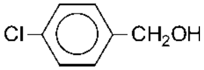
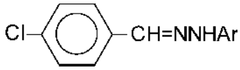
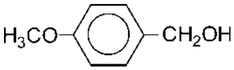
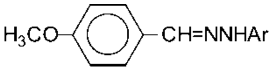
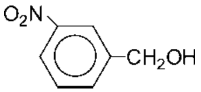
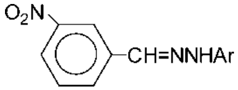
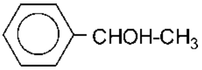
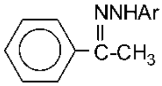
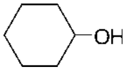
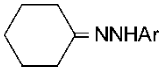
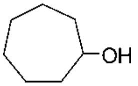
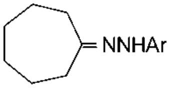
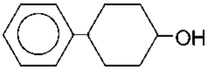
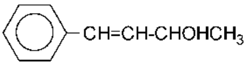
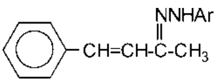
Chromium trioxide supported on silica gel was prepared by simply grinding silica gel with CrO_3 in the ratio 10:1 (w/w) in an agate mortar. In this simple and efficient method, when the starting alcohol and two molar equivalent of CrO_3/SiO_2 and a few drops of t-BuOH was mixed with grinding by a pestle, the alcohol was consumed (TLC) within 10 min to furnish carbonyl compound as the only product of the oxidation step. This reaction was followed by in situ trapping of the resulting carbonyl compound by an additional elimination reaction. For this purpose, the reaction mixture was ground with 5 molar equivalent of arylhydrazine (10 min).

As reported in Table 1, satisfactory results were obtained in the oxidation–arylhydrazone formation reaction of variety of primary and secondary alcohols with CrO_3/SiO_2 and arylhydrazine under solvent-free conditions. The structure of all the products were settled from their analytical and spectral (IR, ^1H NMR) data and by direct comparison with authentic samples.

This one-pot methodology avoids the need to isolate the intermediate carbonyl compounds, a particularly useful feature in the case of carbonyl compounds, which are volatile, toxic, or highly reactive. It can be emphasized that the reaction is clean, the workup is straightforward, and, from economical and environmental points of view, the use of solvent-free conditions is favorable.

We have demonstrated a rapid and solventless method for one-pot conversion of alcohols to arylhydrazone. We believe that the present procedure provides easy, mild, efficient, versatile, and general methodology for the oxidation–arylhydrazone formation of different classes of alcohols.

Table 1. One-pot preparation of arylhydrazone by treatment of alcohols with CrO_3/SiO_2 and phenylhydrazine or 2,4-dintrophenylhydrazine

Entry	Substrate	Product	Yield %[a,b] Ar: phenyl/2,4-dinitrophenyl
1			75/75
2			88/90
3			78/78
4			80/83
5			75/77
6			80/80
7			85/82
8			73/68
9			86/89

[a] Yields refer to pure isolated products.

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

EXPERIMENTAL

General Experimental Procedure for the Conversion of Alcohols to Arylhydrazone

A mortar was charged with SiO_2 (2 g) and CrO_3 (0.2 g, 2 mmol); the mixture was ground with a pestle for 1 min. Then, alcohols (1 mmol) and several drops of t-butanol were added to the mixture. The reaction mixture was ground for about 10 min. Phenylhydrazine or 2,4-dinitrophenylhydrazine (5 mmol) was added to the mixture and ground for 10 min. The progress of reaction was monitored by TLC using ether–CCl_4. On completion of reaction, the reaction mixture was mixed with ether. The mixture was filtered to remove silica gel and then mixed with water and extracted. The organic layer was dried over Na_2SO_4. The solvent was removed in vacuuo to give the product.

ACKNOWLEDGMENT

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

REFERENCES

1. Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.
2. Blackburn, L.; Pei, C.; Taylor, R. J. K. *Synlett* **2002**, 215.
3. Blackburn, L.; Taylor, R. J. K. *Org. Lett.* **2001**, *3*, 1637.
4. Kanno, H.; Taylor, R. J. K. *Synlett* **2002**, 1287.
5. Foot, J. S.; Kanno, H.; Giblin, G. M. P.; Taylor, R. J. K. *Synlett* **2002**, *8*, 1293.
6. McAllister, G. D.; Wilfred, C. D.; Taylor, R. J. K. *Synlett* **2002**, 1291.
7. Orita, A.; Katakami, M.; Yasui, Y.; Kurihara, A. J. O. *Green Chemistry* **2001**, 13.
8. Kotuki, H.; Shimanouchi, T.; Ohshima, R.; Fujiwara, S. *Tetrahedron* **1998**, *54*, 2709.
9. Baxendale, I. R.; Ley, S. V.; Sneddon, F. *Synlett* **2002**, *5*, 775.