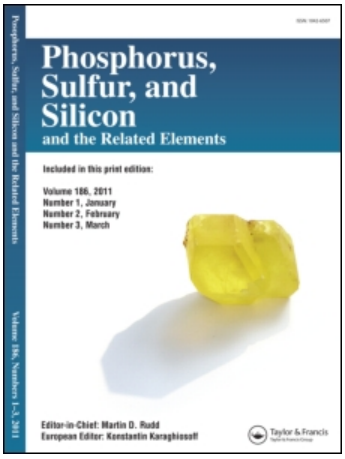

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A CONVENIENT ONE-POT METHOD OF CONVERTING ALCOHOLS INTO OXIMES

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The one-pot conversion of primary and secondary alcohols into oximes is reported using chromium trioxide supported on alumina and hydroxylamine hydrochloride under solvent free condition. This oxidation-oxime formation reaction has been applied to a range of aliphatic and benzylic alcohols.

Keywords: Alcohols; chromium trioxide; oximes; hydroxylamine hydrochloride; solvent free

In organic syntheses and reactions, increasing attention is being focused on solvent-free procedures,[1] which often lead to clean, eco-friendly, and highly efficient procedures involving simplified workup.[2]

The "ideal synthesis" of functionalized compounds requires the development of one-pot successive reactions from commercially available and cheap starting materials and/or catalysts.[3] Recently in a series of relevant papers Taylor and coworkers developed a number of synthetically useful tandem oxidation processes, such as conversion of primary alcohols to alkenes,[4] imines,[5] amines,[5] oxime ethers,[6] esters,[7] amides[7] and nitriles.[8] One of the main benefits of this methodology is the in situ formation and consumption of the intermediate aldehydes.

The remarkable ability of the alumina to promote the various reactions under solvent-free conditions[9] together with the importance of combinatorial chemistry as a preparative technique in organic synthesis[10] gave us impetus for testing the oxidation of primary and

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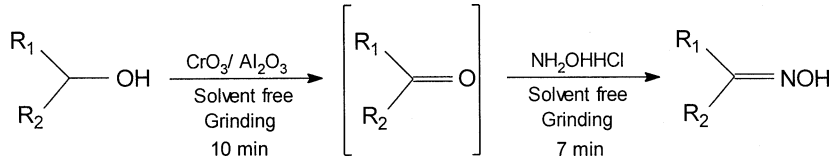


FIGURE 1

secondary alcohols followed by in situ protection of the resulting carbonyl compounds as oximes in an one-pot process using chromium trioxide supported on alumina and hydroxylamine hydrochloride under solvent-free conditions.

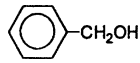
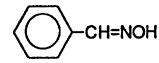
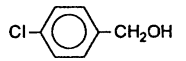
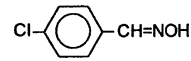
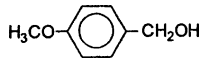
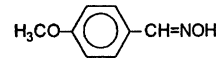
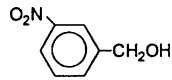
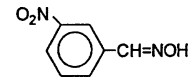
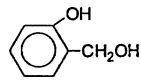
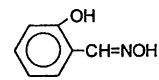
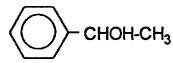
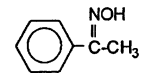
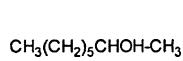
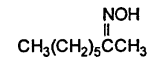
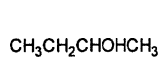
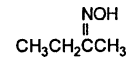
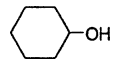
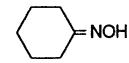
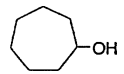
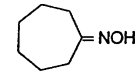
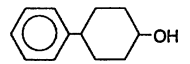
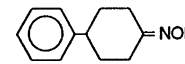
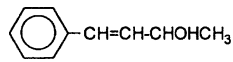
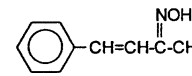
Chromium trioxide supported on alumina was prepared by simply cogrinding alumina with CrO_3 in the ratio 10:1 (w/w) in an agate mortar. In this simple and efficient method, when the starting alcohol and two molar equivalent of CrO_3/Al_2O_3 and a few drops of t-BuOH were mixed with grinding by a pestle, alcohol was consumed (TLC) within 10 min to furnish a 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 propose, the reaction mixture was ground with ten molar equivalent of hydroxylamine hydrochloride (7 min).

As reported in Table I, satisfactory results have been obtained in the oxidation-oxime formation reaction of a variety of primary and secondary alcohols with CrO_3/Al_2O_3 and NH_2OHHCl under solvent-free conditions. The tolerance of various functional groups under the present reaction conditions have been examined by reacting the substrates bearing phenolic hydroxy, ether, nitro, and olefinic double-bond groups. The structure of all the products was established from their analytical and spectral infrared (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 use of solvent-free conditions is favorable.

In conclusion, we have demonstrated a rapid and solvent-free method for one-pot conversion of alcohols to oximes. We believe that the present procedure provides easy, mild, efficient, versatile, and general methodology for the oxidation-oxime formation of different classes of alcohols.

TABLE I One-Pot Preparation of Oximes by Treatment of Alcohols with CrO_3/Al_2O_3 and NH_2OHHCl

Entry	Substrate	Product	Yield[a,b] (%)
1			80
2			89
3			80
4			87
5			68
6			75
7			81
8			79
9			71
10			90
11			83
12			91

[a]Yields refer to pure isolated products.

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

General Experimental Procedure for the Conversion of Alcohols to Oximes

A mortar was charged with Al_2O_3 (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. NH_2OHHCl (0.69 g, 10 mmol) was added to the mixture and ground for 7 min. 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 filtered to remove alumina and then mixed with water and extracted. The organic layer was dried over Na_2SO_4. The solvent was removed in vaccuo to give the product.

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