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### A VERSATILE METHOD FOR THE CONVERSION OF ALDOXIMES TO NITRILES USING SILICA GEL/THIONYL CHLORIDE

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## A VERSATILE METHOD FOR THE CONVERSION OF ALDOXIMES TO NITRILES USING SILICA GEL/THIONYL CHLORIDE

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*A simple convenient procedure for dehydration of aldoximes has been developed using silica gel/thionyl chloride in heterogeneous conditions. The method has been found to be effective for a wide range of aromatic oximes.*

**Keywords:** Aldoxime; nitrile; silica gel; thionyl chloride

The development of new methods for the synthesis of nitriles is important in organic synthesis because nitriles are useful as intermediates for the preparation of amines and other functional group moieties.<sup>1–3</sup> They usually are prepared by nucleophilic substitution with the cyanide anion or by regenerating the cyano group via oxidation, rearrangement, or elimination.<sup>2</sup> The most efficient route reported so far is based on the dehydration of aldoximes into the corresponding nitriles. The classical methods<sup>4–7</sup> of dehydration include trifluoroacetic anhydride, chlorosulphonyl isocyanate, diphosphorous tetraiodide, selenium dioxide, 4,6-diphenyl-2-methylthiopyrylium tetrafluoroborate, copper(II) acetate, and the triphenylphosphine/ $\text{CCl}_4$ . Unfortunately, most of these methods are deficient in some respects, such as long reaction times, unsatisfactory yields, harsh reaction conditions, expensive or not readily available reagents, inconvenient preparation of reagents, need for addition of an acid or a base, high reaction temperature, and tedious work-up procedure. Considering these facts, there is still a need for new reagents for this conversion.

The application of solid adsorbents such as alumina and silica gel as solid supports in organic synthesis affords a new procedure

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for functional group transformation.<sup>8,9</sup> Recently it was demonstrated that heterogeneous reaction systems have many advantages such as simple experimental procedures, mild reaction conditions, and minimization of chemical wastes as compared to their liquid phase counterparts.<sup>8</sup>

Consequently, we decided to seek a heterogeneous system for the dehydration of aldoximes. In continuation of our studies on the applications of modified form of thionyl chloride in organic synthesis,<sup>7,10,11</sup> we found that various types of nitriles can be synthesized conveniently from the corresponding aldoximes under mild nonaqueous reaction conditions by silica gel/thionyl chloride in  $\text{CH}_2\text{Cl}_2$ .

The heterogeneous reagent was prepared easily by the reaction of 3 mmol of thionyl chloride with 1 g of silica gel at room temperature. The feasibility of this reagent as dehydrating agent was first examined using benzaldoxime as a model substrate. Thus, the solution of benzaldoxime (1 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  was slowly added to 1.5 equiv. of silica gel/ $\text{SOCl}_2$  at room temperature. The progress of the reaction was monitored by TLC. After 5 min dehydration of benzaldoxime was complete and afforded benzonitrile in almost quantitative yield.

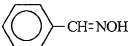

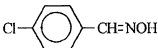
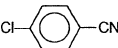
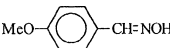
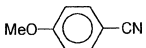
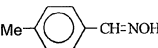
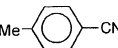
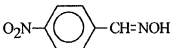

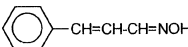
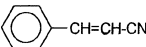
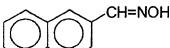
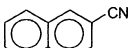
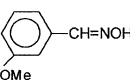

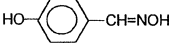

It is worthy to note that attempts to perform the dehydration with thionyl chloride alone were not successful due to its very high reactivity and mixtures of unidentified products were obtained.

The effects of other solvents such as  $\text{CCl}_4$ , n-hexane, ether, and THF also were studied, but in comparison with  $\text{CH}_2\text{Cl}_2$  the reaction times were longer and the yields were considerably lower. The scope and generality of this process is illustrated with several examples and the results are summarized in Table I. The procedure turned out to be general for a range of structurally diverse aromatic aldoximes. Aromatic aldoximes with electron-withdrawing or electron-donating groups were cleanly, easily, and efficiently dehydrated and afforded excellent isolated yields of nitriles within a short reaction time. They were of high purity as determined by TLC and  $^1\text{H}$  NMR spectroscopy.

All reactions were performed under mild and heterogeneous condition at room temperature in anhydrous  $\text{CH}_2\text{Cl}_2$ . As shown in Table I functional groups such as  $\text{OCH}_3$  (entry 3), OH (entry 9),  $\text{NO}_2$  (entry 5), and olefinic groups (entry 6) remain unaltered under this reaction condition.

Compared to some previously reported reagents with major or minor drawbacks, several noteworthy features of this reagent are apparent. These are: the easy work-up procedure, availability of the reagent, operational simplicities, and use of inexpensive reagent.

**TABLE I** Dehydration of Aldoximes to Their Corresponding Nitriles Using Silica Gel/SOCl<sub>2</sub><sup>a</sup>

Entry	Substrate	Product	Time (min)	Yield (%) <sup>b,c</sup>
1			5	98
2			5	90
3			35	95
4			5	92
5			23	90
6			5	92
7			23	95
8			15	90
9			7	98

<sup>a</sup>Molar ratio of substrate to reagent was 1:1.5.<sup>b</sup>Yields refer to isolated yields.<sup>c</sup>Products were characterized by comparison of their physical data, IR, NMR spectra with known samples.

In conclusion, the present one-pot procedure for dehydration of aldoximes provides an easy, mild, efficient, versatile, and general methodology for the preparation of nitriles from different classes of aldoximes; it may be a suitable addition to methodologies already present in the literature.

## EXPERIMENTAL

### General

Aldoximes were purchased from Fluka and Merck or were prepared in our laboratory from the corresponding aldehydes according to known procedures.<sup>12</sup> Products were characterized by comparison of their physical data, IR, and <sup>1</sup>H NMR spectra with authentic samples.<sup>13–15</sup> 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 Conversion of Aldoximes to Nitriles with Silica Gel/ $\text{SOCl}_2$ in $\text{CH}_2\text{Cl}_2$**

Silica gel (0.5 g) was mixed with the freshly distilled thionyl chloride (1.5 mmol, 0.179 g) in a 25 ml round bottomed flask at room temperature. To the resulting powder, a solution of aldoxime (1 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (5 ml) was slowly added and stirred at  $0^\circ\text{C}$  for 5–35 min. The progress of the reaction was followed by TLC until no starting material could be detected. The mixture was shaken with  $\text{CH}_2\text{Cl}_2$  (5 ml) and filtered. The residue was washed with  $\text{CH}_2\text{Cl}_2$  and the solvent evaporated under reduced pressure to afford the TLC and  $^1\text{H}$ NMR pure products in 87–98% isolated yields.

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