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Dehydration of Aldoximes to Nitriles Using a Polymeric Reagent†

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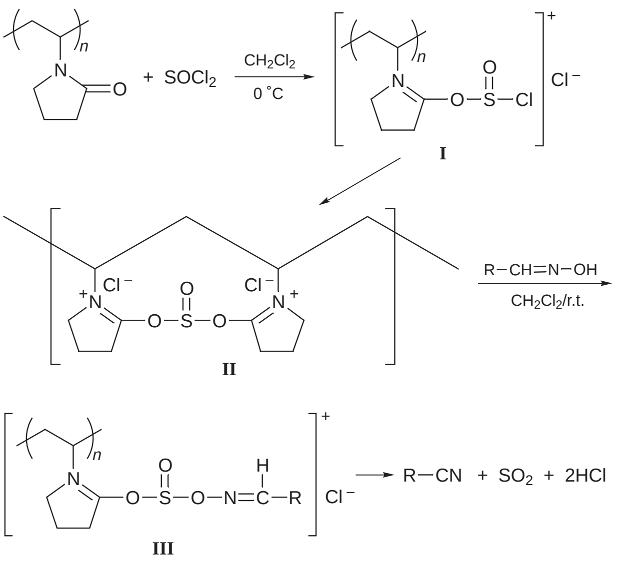
Aldoximes undergo rapid dehydration with polyvinylpyrrolidone–thionyl chloride complex under mild reaction conditions to afford nitriles in high yields

The conversion of aldoximes into nitriles is an important functional group transformation in organic synthesis.[1] Development of efficient, mild and reliable reagents for this propose has been an objective of synthetic chemists and over the years a large number of such reagents have been reported, e.g. Sulfuryl chloride fluoride,[2] chlorosulfonyl isocyanate,[3] diphosphorus tetraiodide,[4] 1,1′-dicarbonylbisimidazole,[5] chlorothionoformate,[6] trimethylamine–sulfur dioxide complex,[7] phosphonitrilic chloride,[8] titanium chloride–pyridine,[9] dialkyl hydrogenphosphonate,[10] ortho ester–acid catalyst,[11] polymer supported triphenylphosphine–carbon tetrachloride,[12] *N*-trifluoroacetylimidazole,[13] 2-methylthio-4,6-diphenyl-pyrylium tetrafluoroborate–triethylamine,[14] 1-chlorosulfinyl-4-dimethylaminopyridinium chloride,[15] carbon disulfide–phase transfer catalyst,[16], CsX–zeolite,[17], montmorillonite-KSF,[18], 1,1′-carbonyldibenzotriazole,[19] envirocat EPZG,[20] sulfuric acid–silica gel,[21] *N,N*′-sulfinylbisimidazole[22] and di-2-pyridyl sulfite.[23] Each method using the above reagents encounters at least one of the following drawbacks: (1) long reaction times, (2) unsatisfactory yields, (3) harsh reaction conditions, (4) expensive or not readily available reagents, (5) inconvenient preparation of reagents, (6) need for addition of an acid or a base, (7) need of a phase transfer catalyst, (8) high reaction temperature, (9) tedious work-up procedures, or (10) limited adaptability both to aryl and alkyl substituted aldoximes. Considering these facts, there is still a need for new reagents for this conversion. In connection with our interest in using polyvinylpyrrolidone–thionyl chloride complex as a mild polymeric reagent in functional group transformation,[24] we describe in this article a new approach to easy and efficient one pot conversion of aldoximes into the corresponding nitriles by this polymeric reagent.

Results and discussion

The polymeric reagent was easily prepared in essentially quantitative yield as a white solid by the reaction of thionyl chloride with two equivalents of polyvinylpyrrolidone in dichloromethane at 0 °C. At first, polyvinylpyrrolidone-thionyl chloride complex **I** is probably formed, which is then converted into **II** by reaction with additional pyrrolidone units; this kind of mechanism has been proposed in the reaction of thionyl chloride and *N*-methylpyrrolidone[25] or *N,N*-dimethylformamide.[26] Since this white solid polymeric reagent was sensitive to moisture it was used directly in its crude form suspended in dichloromethane. The reaction of a stoichiometric amount of polymeric reagent **II** and different aldoximes at room temperature was complete in 15 min to afford the corresponding nitriles probably *via* **III**.



Scheme 1

The procedure is general for various structurally different aldoximes. Aromatic, alicyclic, olefinic as well as heterocyclic aldoximes with electron-withdrawing or donating groups were easily and efficiently dehydrated and afforded high yields of nitriles within a short time (Table 1).

Compared to some previously reported reagents with major or minor drawbacks, several noteworthy features of this reagent are apparent: easy work-up procedure, availability of the reagent, operational simplicity, use of inexpensive reagent, and high yields of products in considerably short reaction times. It is also worthy of note that attempts to perform the dehydration reaction with thionyl chloride alone were not successful due to its very high reactivity and the mixture of unidentified products obtained.

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, and we feel that it may be a suitable addition to the currently available methodologies.

Experimental

Polyvinylpyrrolidone (K30) and thionyl chloride were purchased from Fluka. Aldoximes were purchased from Fluka or prepared in our ad laboratory from the corresponding aldehydes according to the reported procedures.[30] Products were characterized by comparison of their physical data, IR and ^{1}H NMR spectra with those of known samples. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/ UV 254 plates.

General Procedure for the Synthesis of Nitriles Using the Polymeric Reagent.—To a stirred solution of polyvinylpyrrolidone (0.45 g, 4 mmol) in anhydrous dichloromethane (15 ml) at 0 °C under a dry nitrogen atmosphere was slowly added freshly distilled thionyl chloride (0.25 g, 2.1 mmol) to give a white precipitate. The reaction mixture was maintained at room temperature for about 5 min to

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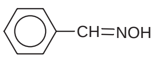
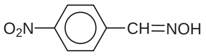
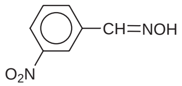
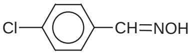
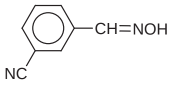
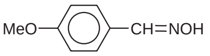
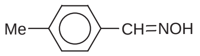
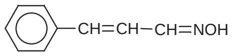
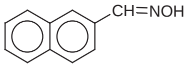
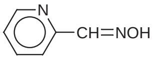
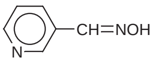
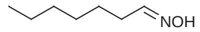
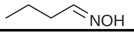
† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Conversion of aldoximes into their corresponding nitriles using the polymeric reagent

Entry	Substrate	Isolated yield[a] of nitriles(%)
1		86
2		94
3		91
4		93
5		84
6		95
7		95
8		95
9		92
10		93
11		95
12		90
13		88

[a] Reactions are completed within about 15 min. Yields refer to isolated yields. Products were characterized by comparison of their physical data, IR, NMR spectra with those of known samples.[27–29]

effect complete reaction. Aldoxime (2 mmol) was then slowly added and stirred for about 15 min at room temperature. The progress of the reaction was followed by TLC ($CH_2Cl_2-CCl_4$). On its completion the mixture was filtered and washed with CH_2Cl_2. The pure product was obtained by either of the following procedures: (A) the combined filtrates were chromatographed on a short column of silica gel with $CH_2Cl_2-CCl_4$ as eluent, or (B) poured into water and extracted with CH_2Cl_2, with subsequent washing of organic layers with water. In both cases the organic phase was dried over anhydrous sodium sulfate and solvent evaporation under reduced pressure afforded the TLC and ^{1}H NMR pure products in 84–95% isolated yields.

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References

1 K. Friedrich and K. Waaensfels, *The Chemistry of Cyano Group*, ed. Z. Rappoport, Wiley-Interscience, New York, 1970; D. T. Mowry, *Chem. Rev.*, 1948, **42**, 250.
2 G. A. Olah, S. C. Narang and A. Garcia-Luna, *Synthesis*, 1980, 659.
3 G. A. Olah, Y. D. Vankar and A. Garcia-Luna, *Synthesis*, 1979, 227.
4 H. Suzuki, T. Fuchita, A. Iwasa and T. Mishina, *Synthesis*, 1978, 905.
5 H. G. Foley and D. R. Dalton, *J. Chem. Soc., Chem. Commun.*, 1973, 628.
6 D. L. Clive, *J. Chem. Soc., Chem. Commun.*, 1970, 1014.
7 G. A. Olah and Y. D. Vanker, *Synthesis*, 1978, 702.
8 G. Rosini, G. Baccolini and S. Cacchi, *J. Org. Chem.*, 1973, **38**, 1060.
9 W. Lehnert, *Tetrahedron Lett.*, 1971, **6**, 559.
10 A. S. Surgie, *J. Org. Chem.*, 1969, **34**, 2805.
11 M. Rogic, J. F. Van Paooen, K. P. Klein and T. P. Demmin, *J. Org. Chem.*, 1974, **39**, 3424.
12 C. R. Harrison, P. Hodge and W. J. Rogers, *Synthesis*, 1977, 41.
13 T. Keumi, T. Yamamoto, T. Saga and H. Kitajima, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1579.
14 P. Molina, M. Alajarin and M. J. Vilaplana, *Synthesis*, 1982, 1016.
15 A. Arrieta and C. Palomo, *Synthesis*, 1983, 472.
16 M. Shinozaki, M. Imaizumi and M. Tajima, *Chem. Lett.*, 1983, 929.
17 M. Narayana Rao, P. Kumar and K. Garyaki, *Org. Prep. Proced Int.*, 1989, **21**, 230.
18 H. M. Meshram, *Synthesis*, 1992, 943.
19 A. R. Katritzky, G. F. Zhang and W. G. Fan, *Org. Prep. Proced Int.*, 1993, **25**, 315.
20 A. R. Bandger, S. R. Jagtap and S. B. Ghodeshwar, *Synth. Commun.*, 1995, **25**, 2993.
21 H. M. S. Kumar, P. K. Mohanty and M. S.Kumar, *Synth. Commun.*, 1997, **27**, 1327.
22. Y. H. Kim and J. M. Shin, *Tetrahedron Lett.*, 1985, **26**, 3821.
23 S. Kim and K. Y. Yi, *Tetrahedron Lett.*, 1986, **27**, 1925.
24 A. R. Kiasat, Ph.D. Thesis, Shiraz University, Shiraz, Iran, 1998.
25 F. Hiashi and T. Nishi, *J. Polym. Sci., Part A, Polym. Chem.*, 1986, **24**, 701.
26 M. S. Newman and P. K. Sujeeth, *J. Org. Chem.*, 1978, **43**, 4367.
27 A. Saednya, *Synthesis*, 1983, 748.
28 K. Mai and G. Patil, *Synthesis*, 1986, 1037.
29 *Fluka Handbook of Fine Chemicals*, 1993–1994.
30 A. I. Vogel, *A Text Book of Practical Organic Chemistry*, 4th edn., Elbs and Longman, 1978.