Communication

An Environmentally Benign System; A Simple and Effective Procedure for Dehydration of Oximes into Nitriles in Solvent Free Conditions

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In an environmentally benign solvent free system aldoximes are rapidly transformed into nitriles using trimethylsilylchloride under mild conditions.

Keywords: Nitriles; Oximes; Dehydration; Simple.

Nitrile compounds are organo-cyanides (R-CN) that occur naturally in plants and as intermediates in microbial metabolism.¹ Nitriles are also products of the petrochemical industry and are widely used as chemical solvents, recrystallizing agents, and chiral synthons. The conversion of aldehydes into the corresponding nitriles is a functional group transformation of significant practical importance, especially in the fine chemical industry.

The remarkable synthetic properties of the nitrile group have ensured long standing studies of their utilization in organic synthesis.² Several methods are available to accomplish the conversion of alkyl or aryl aldehydes to their corresponding nitriles under a variety of reaction conditions.³ Because of its role in synthetic chemistry, this reaction continues to receive attention from the chemists in search for newer methods. There are methods known for the conversion of aldehydes to nitriles in a one-pot procedure.⁴

Unfortunately, many of these one-pot conversions are limited to aromatic aldehydes which, generally, are transformed more readily to nitriles than the aliphatic aldehydes.

Recent methods which have been successfully applied to both the aliphatic and aromatic compounds include the use of expensive (2,4-dinitrophenyl hydroxylamine),⁵ (hydroxylamine *o*-sulfonic acid),⁶ hazardous (selenium dioxide)⁷ or corrosive (formic acid)⁸ reagents and tedious work-up procedures. The most widely used general method is based on the dehydration of aldoximes, and although numerous protocols already exist, new variants continue to

appear.⁹⁻¹³ A few methods are known which involve various transformations of other N-substituted azomethine derivatives of aldehydes, such as N,N-dialkylhydrazones,¹⁴⁻¹⁵ and imines with 1-amino-4,6-diphenyl-2-pyridone.¹⁶ Consequently there is a need for the development of protocols using readily available and safer reagents which lead to nitrile compounds. We now wish to report a facile conversion of aldoximes to their corresponding nitriles by trimethylsilylchloride in solvent free conditions. The reaction proceeds efficiently in moderate to high yield under mild conditions (Scheme I).

Scheme I

To study the effect of substitution, reactions were performed on different precursors as shown in Table 1, precursors with electron-withdrawing groups showed better yield in a shorter time. By paying attention to this evidence, the mechanism shown in (Scheme II) is proposed for the dehydration of oximes. We suggest that the chlorine ion released during the progress of the reaction acts as a base for separation of hydrogen at the next stage. Longer reaction times had no effect on the conversion of oximes.

In summary, in the present method -apart from the mild temperatures employed- the transformation has four important advantages: (i) no organic reagent or solvent is employed; (ii) the only by-products are relatively harmless; (iii) less toxic and hazardous chemicals can be used; and

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Entry	Aldoximes	Nitriles	Time (h)	Yield/%
1	Ме-С́Н	Me	5	80
2	MeO-CH	MeO	5	85
3	0 ₂ N-CH	O ₂ N-CN	2	96
4	N HC=NOH	N CN	3	73
5	СН=СН-СН=NOH	СН=СН-СМ	4	75
6	MeO MeO MeO	MeO MeO MeO	4	69
7	,́NOH	CN	5	91
8	CH ₃ (CH ₂) ₈ CH=NOH	CH ₃ (CH ₂) ₈ CN	5	70
9	CH ₃ (CH ₂) ₆ CH=NOH	CH ₃ (CH ₂) ₆ CN	5	75

Table 1. Conversion of aldoximes into nitriles

Scheme II



(iv) moderate to high yields are obtained (Table 1).

EXPERIMENTAL

Typical Experimental Procedure

A mixture of 1 mmol of aldoximes was added to 108 mg (1 mmol) of trimethylsilyl chloride heated for 5 h at 90

°C. Completion of reaction was followed by TLC (n-hexane/ethyl acetate, 2:1). After completion of the reaction, the mixture was diluted with chloroform and further purification was performed by flash chromatography. All compounds were known and their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Yields were obtained using GC analDehydration of Oximes into Nitriles

ysis.

Received August 8, 2007.

REFERENCES

- 1. Graham, D.; Pereira, R.; Barfield, D.; Cowan, D. *Enzyme Microb. Technol.* **2000**, *26*, 368-373.
- Sandler, S. R.; Karo, W. Nitriles (cyanides). In Organic Functional Group Preparations; Academic Press: San Diego, 1993; Vol. 12-I, Chapter 17.
- Larock, R. C. Comprehensive Organic Transformations, A Guide to Functional Group Preparations; VCH Publishers: New York, 1989.
- Karmarkar, S. N.; Kelkar, S. L.; Wadia, M. S. Synthesis. 1985, 25, 315-319.
- 5. Miller, M.; Loudon, G. J. Org. Chem. 1975, 40, 126-127.
- 6. Fizet, C.; Streith, J. Tetrahedron Lett. 1974, 3187-3190.
- 7. Sosnovsky, G.; Krogh, J. A.; Umhoefer, S. G. Synthesis. 1979, 722-724.
- 8. Olah, G. A.; Keumi, T. Synthesis. 1979, 112-113.

J. Chin. Chem. Soc., Vol. 55, No. 1, 2008 7

- Jose, B.; Sulatha, M. S.; Pillai, P. M.; Prathapan, S. Synth. Commun. 2000, 30, 1509-1514.
- Desai, D. G.; Swami, S. S.; Mahale, G. D. Synth. Commun. 2000, 30, 1623-1626.
- Sampath Kumar, H. M.; Subba Reddy, B. V.; Tirupathi Reddy, P.; Yadav, J. S. Synthesis 1999, 586-587.
- 12. Chaudhari, S. S.; Akamanchi, K. G. Synth. Commun. 1999, 29, 1741-1745.
- Wang, E.-Ch.; Lin, G.-J. Tetrahedron Lett. 1998, 39, 4047-4050.
- Smith, F. R.; Albright, J. A.; Waring, A. M. J. Org. Chem. 1966, 31, 4100-4102.
- 15. Mlochovski, J. Chem. Pap. 1998, 52, 45-51.
- Katritzky, A. R.; Molina-Buendia, P. J. Chem. Soc., Perkin Trans 1. 1979, 1957-1960.
- 17. Kukushkin, V. Y.; Pombeiro, A. J. L. *Coordin. Chem. Rev.* **1999**, *181*, 147.
- 18. O'Neil, M. J.; Smith, A.; Heckelman, P. E.; Obenchain Jr, J. R.; Gallipeau, J. A. R.; D'Arecca, M. A. *The Merck Index An Encyclopedia of Chemicals, Drugs, And Biologicals*; Merck Research Laboratories: USA, 2001.