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# Microwave-Induced Conversion of Aldoximes to Nitriles by DBU

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# MICROWAVE - INDUCED CONVERSION OF ALDOXIMES TO NITRILES BY DBU

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**Abstract:** Aldoximes (**1**) can be rapidly converted into corresponding nitriles (**2**) in good yields with a novel reagent DBU under microwave irradiation.

The conversion of aldoximes into nitriles is a useful transformation[1] and a topic of current interest to organic chemists. As a result, a number of reagents have been emerged for this purpose such as selenium dioxide-chloroform,[2] triethylamine-sulfurdioxide,[3] sulphuryl chloride fluoride,[4] montmorillonite KSF,[5] envirocat EPZG[6] etc. However many of these methods are deficient in some respect. For eg, the preparation of triethylamine-sulfurdioxide and sulphuryl chloride fluoride is inconvenient (at -70$^0$C). Dehydration with montmorillonite KSF, zeolites[7] and envirocat EPZG may require high temperatures or longer reaction times. Therefore, there is a still great demand for a new and efficient catalyst.

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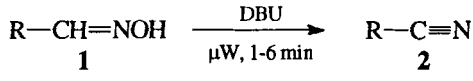
DBU is a novel reagent and it has been extensively applied to organic transformations including eliminations,[8] isomerizations,[9] esterifications,[10] amidations,[11] condensations,[12] and halogenations.[13] However it has been widely used for dehydrohalogenations but not utilised for the dehydrations directly. Herein we wish to report for the first time the novel utility of DBU as an efficient reagent for the conversion of aldoximes (**1**) to nitriles (**2**) under microwave irradiation(Scheme-I). The reactions were very fast and completed in 1-6 minutes.

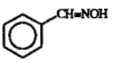
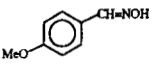
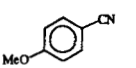
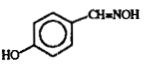
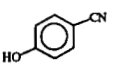
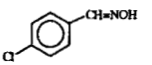
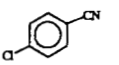
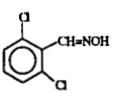
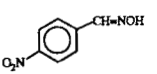
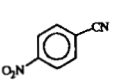
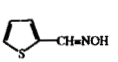
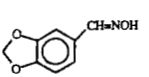
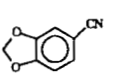
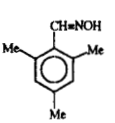
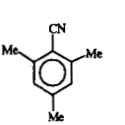
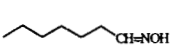
**Scheme I**




Under similar conditions the dehydration of aliphatic aldoximes to nitriles did not take place. It is also worth mentioning that the dehydration of aromatic and hetrocyclic aldoximes was carried out with DBU in refluxing carbon tetrachloride, methanol etc. by conventional heating instead of microwave, the starting aldoximes were recovered back without any formation of nitriles. This clearly indicates the advantage of doing the above reaction under microwave irridation rather than by conventional heating.

In conclusion, the dehydration of aldoximes to nitriles was achieved effectively by DBU under microwave irradiation in dry media. This is the first report of the dehydration by DBU directly. Generally, dehydration by DBU will be carried out via mesylations, acetylations etc. The dehydration is achieved in solvent free condition (dry media). So, it is also environmentally benign protocol. The conversion is very fast under microwave irridation reducing longer reaction times when compared to other conventional methods.

**Table I : Microwave-induced preparation of nitriles by DBU.**

| Entry | Aldoxime | Nitrile | Time (minutes) | Yield(a) (%) | mp or bp(°C)/torr Found/Reported[14] |
|---|---|---|---|---|---|
| 1. |  |  | 2 | 92 | 191/190.7 |
| 2. |  |  | 6 | 66 | 60-62/61-62 |
| 3. |  |  | 3.5 | 82 | 110-112/110-113 |
| 4. |  |  | 1.5 | 85 | 93-94/91-92[2] |
| 5. |  |  | 2 | 83 | 143-145/144-145 |
| 6. |  |  | 1 | 90 | 146-147/146-147[2] |
| 7. |  |  | 2 | 88 | 192/191-192 |
| 8. |  |  | 4.5 | 73 | 94-95/95 |
| 9. |  |  | 5 | 62 | 51-52/50-52 |
| 10. |  | No reaction | 6 | - | - |
| 11. |  | No reaction | 5 | - | - |

a) Yields refer to pure isolated products.
b) Products were characterised by comparision of their melting points, IR and 'H NMR spectra with authentic samples.

## EXPERIMENTAL

Melting points were determined by Buchi 510 apparatus and are uncorrected. Boiling points also are uncorrected. Mass spectra were recorded on VG-Micromass 70-70H mass spectrometer at 70eV and IR spectra recorded on Perkin Elmer 683 spctrometer. Proton NMR spectra were recorded on Gemini 200 spectrometer. Microwave irradiations were carried out with BPL BMO 700T commercial microwave oven, operating at a frequency of 2450 MHz. The aldoximes were prepared according to the literature procedure.[15]

**General procedure: Dehydration of aldoximes (1) to nitriles (2):** A mixture of aldoxime (1 mmol) and a catalytic amount of DBU (0.25 mmol), was taken in a pyrex test tube inserted in a neutral alumina bath and irradiated in a microwave oven at around 600 watts for 1-6 minutes. The residue on purification by column chromatography on silica gel gave the corresponding nitrile in 62-92% yield.



### References


1. Friedrich. K. and Wallenfels, K. "The Chemistry of the cyano Group" Rappoport, Z. Ed., Interscience, New York, 1970, PP.92-93.
2. Sosnovsky, G. and Krogh, *J.A.Synthesis* **1978**, 703.
3. Olah, G.A., Vankar, Y.D. *Synthesis* **1978**, 702.
4. Olah, G.A., Narang, S.C. and Garcia - Luna, A. *Synthesis* **1980**, 659.
5. Meshram, H.M. *Synthesis* **1992**, 943.
6. B.P.Bandgar, S.R.Jagtap, S.B. Ghodeshwar and P.P. Wadgaonkar, *Synth.commun.*, **1995**, 25(19), 2993-2998.
7. Narayan Rao, M.; Kumar, P. and Garyali, K., *Org. Prep. Proceed. Int.*, **1989**, *21*, 230.
8. Otter, B.A., Taube, A, Fox, J.J., *J.Org.Chem.* **1971**, 36, 1251.
9. Jpn. Patent. 56 055 345, **1981** (CA **1981**, 95, **1866** 53e).
10. Ono, N., Yamada, T., Saito, T., Tanaka, K., Kaji, A. *Bull. Chem. Soc. Japan* **1978**, 51, 2401.
11. Cabre J. Palomo, A.L. *Synth.Commun.* **1984**, 413.
12. Yamanaka, H., Yokoyama, M., Sakamoto, T., Shiraishi, T., Mataichi, S., Mizugati, M., *Heterocycles* **1983**, 20, 1541.
13. Koppel, G.A., Kinnick, M.D., Nummy, L.J. *J. Am. Chem. Soc.*, **1977**, 99, 822.
14. (a) CRC Hand Book of Data on Organic Compounds: CRC Press, BOCa Raton, Florida, 1988. (b) Hand Book of Tables for Organic Compounds identification, 3rd ed., Chemical Rubber Company, Cleveland, Ohio, 1978. (c) Dictionary of Organic Compounds.
15. For preparation see Vogel, A.I. A Text book of practical organic chemistry, 4th Ed., ELBS and Longmann, 1978.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