Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Microwave Activation in Organic Synthesis: Natural Indian Clay, EPIC^R EPZG^R and EPZ10^R as Novel Heterogenous Catalysts for Rapid Synthesis of Nitriles from Aldoximes in Absence of Solvent

B. P. Bandgar [a] , V. S. Sadavarte [a] & K. R. Sabu [b]

[a] Organic Chemistry Research Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, 431 606, India

[b] Clay and Minerals Division, RRL, Trivandrum, India

Published online: 17 Sep 2007.

To cite this article: B. P. Bandgar , V. S. Sadavarte & K. R. Sabu (1999): Microwave Activation in Organic Synthesis: Natural Indian Clay, EPIC^R EPZG^R and EPZ10^R as Novel Heterogenous Catalysts for Rapid Synthesis of Nitriles from Aldoximes in Absence of Solvent, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:19, 3409-3413

To link to this article: http://dx.doi.org/10.1080/00397919908085968

SYNTHETIC COMMUNICATIONS, 29(19), 3409-3413 (1999)

MICROWAVE ACTIVATION IN ORGANIC SYNTHESIS : NATURAL INDIAN CLAY, EPIC^R EPZG^R AND EPZ10^R AS NOVEL HETEROGENOUS CATALYSTS FOR RAPID SYNTHESIS OF NITRILES FROM ALDOXIMES IN ABSENCE OF SOLVENT

B. P. Bandgar*[a], V. S. Sadavarte[a] and K. R. Sabu[b]

a. Organic Chemistry Research Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431 606, India.
b. Clay and Minerals Division, RRL, Trivandrum, India.

ABSTRACT : The Conversion of aldoximes into nitriles was carried out in the absence of solvent under microwave irradiation using environmentally-friendly catalysts like natural kaolinitic clay, EPIC^R EPZG^R and EPZ10^R. Acceleration of reaction rate, simple work-up and formation of clean products are salient features of this method.

The conversion of aldoximes into nitriles represents an important reaction[2]. For dehydration of aldoximes to nitriles various reagents have been used[3]. However, many of these methods are defficient in some respect. The reagents are expensive or not readily available or work-up is tedious. The preparation of reagents like triethylamine-sulfur dioxide[4] and sulfuryl chloride fluoride is incovenient

*To whom correspondence should be addressed.

(at- 70 °C)[5]. Dehydration of aldoximes with zeolites requires high temperature (350 °C)[6] whereas Envirocat EPZG® requires very long reaction time (12-24 h)[3]. The reagents like phosgene[7], diphosgene[8] and triphosgene[9] are hazardous to use. Therefore, there is still a need for simple, rapid, convenient and generally applicable method for this conversion.

In recent years there has been a considerable growth in interest in the catalysis of organic reactions by inorganic reagents supported on high surface area inorganic materials[10]. Envirocats® a new family of solid supported reagents are a significant breakthrough in environmentally friendly chemistry[11]. These solid supported reagents are non-toxic powders which can be filtered off from the process and may be reused. There is no aqueous effluent and HCl emission is very limited. Envirocats EPZG® and EPZ10® are solid supported catalysts which have Bronsted and Lewis acid characteristics whereas EPIC® is solid supported strong Bronsted acid.

Clays also have many advantages such as ease of handling, non-corrosiveness, low cost and regeneration. Due to their Bronsted and Lewis acidities, clays both in their natural and ion exchanged forms, function as efficient catalysts for various organic transformations[12]. We wish to report herein application of Indian natural kaolinitic clay and envirocats such as EPZG®, EPZ10® and EPIC® as catalysts for the conversion of aldoximes into nitriles under microwave irradiation.

Scheme

The results are presented in table 1. Various substituted aromatic aldoximes are converted into corresponding nitriles in the absence of solvent under microwave irradiation by using natural clay, EPZG®, EPZ10® and EPIC® as catalysts.

Table : Conversion of aldoximes into nitriles under microwave irradiation

Entry	Aromatic acid	Catalyst	Product	Reaction Time(min.)	Yield (%)	MP/BP* °C
1.	2,4-Dichloro benzaldehyde oxime	EPZ10	2,4-Dichloro benzonitrile	06	68	58-60
2.	2,4-Dichloro benzaldehyde oxime	EPIC	2,4-Dichloro benzonitrile	07	74	58-60
3.	2,4-Dichloro benzaldehyde oxime	EPZG	2,4-Dichloro benzonitrile	13	52	58-60
4.	2,4-Dichloro benzaldehyde oxime	Natural Clay	2,4 Dichloro benzonitrile	02	86	58-60
5.	3,4,5-Trimethoxy benzaldehyde oxime	EPZ10	3,4,5-Trimethoxy benzonitrile	02	82	92-94
6.	3,4,5-Trimethoxy benzaldehyde oxime	EPIC	3,4,5-Trimethoxy benzonitrile	11	87	92-94
7.	3,4,5-Trimethoxy benzaldehyde oxime	EPZG	3,4,5-Trimethoxy benzonitrile	12	87	92-94
8.	3,4,5-Trimethoxy benzaldehyde oxime	Natural Clay	3,4,5-Trimethoxy benzonitrile	03	95	92-94
9.	4-Chloro benzaldehyde oxime	EPZ10	4-Chloro benzonitrile	08	93	91-93
10.	4-Chloro benzaldehyde oxime	Natural Clay	4-Chloro benzonitrile	11	78	91-93
11.	2,4-Dimethoxy benzaldehyde oxime	EPZ10	2,4-Dimethoxy benzonitrile	02	73	93-94
12.	2,4-Dimethoxy benzaldehyde oxime	Natural Clay	2,4-Dimethoxy benzonitrile	03	95	93-94
13.	4-N,N-dimethylamino benzaldehyde oxime	EPZ10	4-N,Ndimethylamino benzonitrile	05	74	72-75
14.	4-N,N-dimethylamino benzaldehyde oxime	Natural Clay	4-N,Ndimethylamino benzonitrile	05	71	72-75
15.	Furfuraldehyde oxime	EPZ10	Furfurylnitrile	08	70	146-148*
16.	Furfuraldehyde oxime	Natural Clay	Furfurylnitrile	10	75	146-148*
17.	Salicylaldehyde oxime	EPZ10	2-hydroxy benzonitrile	06	86	92-95
18.	Salicylaldehyde oxime	Natural Clay	2-hydroxy benzonitrile	05	71	92-95
19.	3-Nitro benzaldehyde oxime	Natural Clay	3-Nitro-benzonitrile	02	91	116-117
20.	4-Nitro benzaldehyde	Natural Clay	4-Nitro benzonitrile	12	90	147-149
21.	Vaniline oxime	EPZ10	3-OMe, 4-OH benzonitrile	12	65	85-87

Acceleration of reaction rate, simple work-up, recyclability of the catalysts and formation of clean products under solvent-free conditions are salient features of this method.

Experimental

Envirocats EPZG[R], EPZ10[R], EPIC[R] were procured from Contract Chemicals, England and used as obtained. The natural kaolinitic clay was obtained from the Paolappakara mine of Quilon Distric Kerala, India and after processing supplied by Dr. Lalithambika, RRL, Trivandrum. Commercial microwave oven (Kelvinator, T-37) was used for microwave irradiation. All products were characterized by their physical constants and spectral characteristics (IR and ^{1}H NMR).

General procedure for the conversion of aldoximes into nitriles :

Aldoxime (1 mmol) and catalyst (50 mg) were thoroughly mixed in a morter. Then this reaction mixture was placed in microwave oven and irradiated at 760 W (100% power) for a period specified in the table. Reaction was monitored by TLC. After completion of the reaction, product was extracted with ether or chloroform (3 x 10ml). Removal of the solvent under reduced pressure gave product in almost pure form.

Acknowledgement :

BPB thanks UGC, New Delhi for financial assistance (Project no. W-14 / 600) and Dr. Latithambika, RRL, Trivandrum for the supply of natural kaolinitic clay. We also thanks Contract Chemicals, England for the generous gift of Envirocats.

References :

R : Registered trade mark of Contract Chemicals, England

1. Solid Supported Reagents and Reactions part 26, for part 25 see Bandgar, B. P. and Sadavarte, V. S. *Synth. Commun.* (Communicated)
2. Friedrich, K. and Wallenfels, K. " The Chemistry of the Cyano Group" Rappoport, Z. Edn., Interscience, New York, 1970, pp. 92-93
3. Bandgar, B. P.; Jagtab, S. R.; Ghodeshwar, S. B. and Wadgaonkar, P. P. *Synth. Commun.* **1995**, *25,* 2993 and references cited therein.
4. Olah G. A. and Vankar Y. D. *Synthesis* **1978**, 702
5. Olah, G. A.; Narang, S. C. and Garcia-Luna A. *Synthesis* **1980**, 659
6. Narayanrao, M.; Kumar, P. and Garyali, K. *Org. Prep. Proced. Int.* **1989**, *21,* 230
7. Babad, H. and Zeiler, A. G. *Chemical Review* **1973**, *73,* 75.
8. (a) Mai, K. and Patil, G. *Synthesis* **1986**, 1037
   (b) Skorma, G. and Ugi, I. Angew. *Chem. Int. Ed. Eng.* **1977**, *16,* 259
9. Sabu, D. P. *Ind. J. Chem.* **1993**, *32B,* 385
10. Laszlo, P. "Preparative Chemistry Using Supported Reagents" Academic Press, Inc., London **1987**
11. Contract Chemicals, England "Envirocats - Supported Reagents; Product In formation" **1993**
12. Ponde, D.; Borate, H. B.; Sudlai, A.; Ravindranathan, T. and Deshpande, V. H. *Tetrahedron. Lett.* **1996**, *37,* 4605

accepted 02-11-99