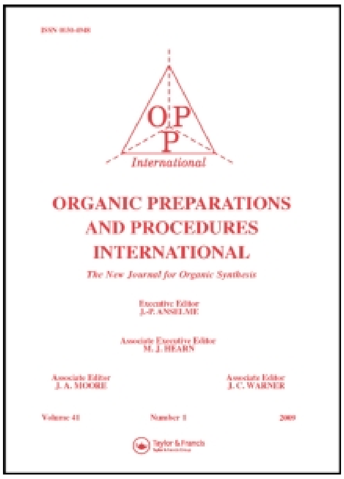

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A NEW METHOD FOR THE CONVERSION OF ALDOXIMES INTO NITRILES WITH ZEOLITES

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A NEW METHOD FOR THE CONVERSION OF ALDOXIMES INTO NITRILES WITH ZEOLITES[†]

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Recently we reported a convenient method for the synthesis of nitriles from the corresponding carboxamides using zeolite as catalyst.[1] The conversion of aldehydes into nitriles via aldoximes also represents an important reaction.[2] Several methods using a wide reagents have been reported[2] for the dehydration of aldoximes. Many of the reagents, however, are expensive and are consumed during the reaction and thus are not amenable to scale up, especially for industrial large scale continuous operations. We now report a facile and commercially feasible process for the conversion of aldoximes into nitriles using zeolite as a catalyst.

$$\underset{\mathbf{1}}{\mathrm{RCH{=}NOH}} \xrightarrow[350^{\circ}]{\mathrm{Cs\text{-}X\ Zeolite}} \underset{\mathbf{2}}{\mathrm{RC{\equiv}N}}$$

Zeolites have received much attention recently in a wide range of contexts, particularly in catalysis.[3] However, little attention has been given to the possibility of employing zeolites in the synthesis of nitriles. The HZSM-5 zeolite, which we reported for the dehydration of carboxamides,[1] was less effective in the conversion of aldoximes into nitriles because of its acidic nature. As the dehydration of aldoximes is base-catalyzed,[4] a basic zeolite is more suitable for the conversion.

The acid and base properites of zeolite can be easily modified by exchanging the cations involved in the zeolite.[5] Onaka et al.[6] applied various cation-exchanged zeolites to liquid phase organic reactions and showed the effectiveness of zeolite as acid and base. In the present work, cesium-exchanged X-type zeolite (Cs-X) was used for the dehydration of aldoximes. The commercially available zeolite Na-X, which is less basic than zeolite Cs-X, was less effective. The nitriles (2a-e) were obtained in almost quantitative yield when the aldoximes (1a-e) in benzene were passed over zeolite (Cs-X) catalyst column heated to 350° C. The results are summarized in the Table. The catalyst can be reused several times. The process permits a continuous operation and both (E)- and (Z)-isomers of oximes can be converted into nitriles [in most cases the oxime used is the mixture of (E)- and (Z)-isomers]. Thus the method is of general applicability and can be used for the conversion of aromatic, aliphatic and heterocyclic aldoximes.

TABLE. Dehydration of Aldoximes (1) to Nitriles (2)

Product[a]		Yield	bp.[°C]/torr or mp.[°C]	
	R	(%)	Found	Reported[7,8]
a	Phenyl	92	bp. 70/10	bp. 69/10
b	3,4-Dimethoxyphenyl	90	mp. 68[b]	67-68
c	n-Propyl	85	bp. 117	bp. 118
d	n-Nonyl	93	bp. 105/10	bp. 106/10
e	2-Furyl	95	bp. 147	bp. 146/738

a) All the nitriles were characterised by comparison of their mp./bp., tlc, IR and ^{1}H nmr data with those of authentic samples. b) Purified by crystallization from aqueous methanol.

EXPERIMENTAL SECTION

General Procedure.- A solution of benzaldoxime (5 g) in benzene (50 ml) was added dropwise to a corning tube (length 25 cm, dia. 3 cm) packed with porcelain beads, heated at 250° under a slow stream of nitrogen. The vapours of the oxime and benzene formed were allowed to pass through a silica column (length 35 cm, internal dia. 15 mm) packed with Cs X-type zeolite (prepared according to standard procedure[5]) in the form of pellets, kept in a cyclindrical furnace heated at 350°. The end of the column was connected to a coiled condenser fitted to a flask to collect the nitrile formed together with water and benzene vapour. The benzene solution was dried (Na_2SO_4) and evaporated under reduced pressure. The product was distilled in vacuo to give 3.9 g (97%) of benzonitrile, bp. 70°/10 mm.

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SIMPLE SYNTHESIS OF ALKYNES FROM 1,2-DIBROMOALKANES USING PTC CONDITIONS

Submitted by (09/21/87)

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Terminal alkynes are useful starting materials or intermediates in the synthesis of natural products.[1] One of the possible synthesis of terminal alkynes is the double elimination of hydrogen bromide from 1,2-dibromoalkanes (1). Although sodium amide[2] and potassium hydroxide[3,4] are used most often as bases, these reagents have some disadvantages. Potassium hydroxide, for example, promotes the migration of acetylenic bond to the center of the chain.[4]